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# Investigation of anthropogenic greenhouse gas emissions generated through the production of Portland cement and a comparison of mitigation strategies

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# INVESTIGATION OF ANTHROPOGENIC GREENHOUSE GAS EMISSIONS GENERATED THROUGH THE PRODUCTION OF PORTLAND CEMENT AND A COMPARISON OF MITIGATION STRATEGIES

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A Project

Presented to the

Faculty of

California State University,

San Bernardino

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in

Environmental Science

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by

Sheri Marie Haggard

March 2009

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# ABSTRACT

Studies have shown that more than 5% of the world's total anthropogenic carbon dioxide emissions may be attributed to the production of cement *(1)*. Recent concerns surrounding the topic of global climate change have led to a number of controversial studies on an array of climate changing causes and effects. This research investigates the projected anthropogenic $CO_2$ emissions generated through the production of Portland cement at three manufacturing facilities in southern California. Research consisted of projecting annual greenhouse gas emission inventories for three case studies pursuant to Assembly Bill 32, The Global Warming Solutions Act of 2006, which requires mandatory reporting of large producers of greenhouse gas emissions in California. The three case studies provide insight on the emissions generated in Portland cement manufacturing, as well as, offer comparisons of $CO_2$ mitigation strategies such as alternative fuel use and technological advancements in manufacturing. The projected emission inventories revealed that the primary contributors to $CO_2$ emissions during Portland cement production are those associated with the calcination process and the combustion of fossil fuels in the kilns. Alternative fuel use and advancements in manufacturing equipment appeared to be the more effective methods of reducing the amount of $CO_2$ generated per metric ton of cementitious product, since calcination cannot be altered to produce traditional Portland cement.

# ACKNOWLEDGMENTS

I would like to express my sincere gratitude to the members of my graduate committee, Dr. James A. Noblet and Dr. Brett J. Stanley, for their knowledgeable guidance, and especially Ms. Darlene Bray, for her inspiration both as a woman of industry and an environmental manager. I also would like to acknowledge Mr. Gregory Knapp for the opportunities he presented me with as an intern, and for sparking my interest in the environmental field, specifically the topic that led to this graduate research project.

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# CHAPTER ONE

# INTRODUCTION AND BACKGROUND

## Introduction

Throughout history, the basic concoction of "cement" has remained a choice material in construction. From the ancient pyramids of Egypt, to the mighty towers of the Brooklyn Bridge, to the monumental Hoover Dam, to the relic aqueducts of Rome-- these architectural wonders share a common infrastructural thread whose strength and longevity justify its continued use today. A thread of liquid stone, cement can be molded and mixed to form an array of versatile uses such as mortar, stucco, grout, and concrete. The cement industry is the backbone of the nation's construction industry.

Portland cement is the most common type of cement utilized, accounting for nearly 90% of all cement produced in the United States (*2*). Patented in 1824, by British stone Mason, Joseph Aspdin, the formula of Portland cement remains relatively unchanged: a calcium silicate cement made with a combination of calcium, silicon, aluminum, and iron that yields a reliable, versatile building media (*3*). Portland cement manufacturing requires a process known as calcination, in which, primarily, calcium carbonate ($CaCO_3$) is decomposed by intense heat to form lime (CaO), and liberates carbon dioxide ($CO_2$) as a by-product (*4*). The manufacturing process also requires the combustion of considerable amounts of fossil fuels to provide the energy necessary for these calcining reactions to occur, often reaching temperatures in excess of 1400°C (*5,6*).

In recent years, the controversial topic of climate change has led to a global awareness of anthropogenic contributions, such as greenhouse gases, $CO_2$ in particular. As a consequence, the cement industry has been under close examination for its contributions, since it is estimated to conduce as high as 5% of the total global anthropogenic $CO_2$ emissions (*1*). Studies suggests that about half of the $CO_2$ emissions generated from cement production originate from the calcination of limestone, and the other half from the combustion of fuels (7).

The passing of California's Assembly Bill 32: The Global Warming Solutions Act of 2006 (AB 32), was the first national legislation governing anthropogenically produced greenhouse gas emissions. The regulation requires a three-step process for reduction in California's greenhouse gas emissions, ultimately reducing emissions 80% by 2050 (*8,9*).

The California Air Resources Board finalized a 1990 baseline in which the 2050 goal is aimed for, with a subsequent mandatory reporting regulation adopted into state law in December of 2007. The rule requires mandatory greenhouse gas emission reporting from California's largest sources, including the cement industry (*8,9,10*).

This research focuses on the two major sources of greenhouse gases in cement manufacturing: 1) emissions associated with the calcination process, and 2) emissions from the combustion of fossil fuels. An extensive investigation into the manufacturing process and chemistry of Portland cement is also presented to provide a clearer understanding of the generation of these emission sources. This research also entails annual projected greenhouse gas inventories, pursuant to the mandatory reporting requirements of AB 32, for three Portland cement facilities operating in southern California. The three case studies provide insight on the emissions generated in Portland cement manufacturing, as well as, offer comparisons of $CO_2$ mitigation strategies including alternative fuel use, technological advancements in manufacturing, and sequestration innovations. It should be noted that this research is limited by its use of projected data obtained from permits to operate in each of the facilities' Title V permits. The projected emissions are calculated using publically available information and are presented as an approximation to actual totals.

## Portland Cement Manufacturing Process

The manufacturing process of Portland cement, quite bluntly, starts with a rock. Not just any rock, but one whose formation is dependent upon very specific physio-chemical and climatic precursors on a geological time scale that may take over 600 million years to generate *(11)*. Limestone deposits represent 10% of the earth's surface with 4,500 million tons mined annually *(12)*. Of the 4.5 billon tons extracted, nearly a third of the limestone is used in cement manufacturing *(12)*. Since limestone is a bulk component for the cement process, most cement operations are strategically placed near these deposits. These limestone deposits can be quarried for cement production upon receiving the appropriate mining rights and operating permits through state and local environmental agencies. The deposit, deemed a quarry, is then the front most line in the cement manufacturing process.

After surveying the chemical aspects of the deposit, the limestone material within the quarry is blasted and harvested according to the specific stoichiometric traits needed in order to maintain quality product throughout the manufacturing line (*3*). One might compare the quarry operation to a full-scale display of a child's sandbox; equipped with busy Tonka trucks and dirt-scooping loaders. These haul trucks; however, are far from the toys of childhood, and may have a loading capacity capable of transporting 100 tons of material at a time (*13*). Other equipment common to the quarry operation may include drills, ammunition rigs, bulldozers, water trucks, and graders; with some operations running around the clock (*13*). At any one time, the quarry may be a careful ballet of massive heavy-equipment, drilling, blasting, and transporting rocks, the key component of Portland cement, limestone, where it can then continue its journey through the manufacturing process.

The next area in the manufacturing process involves a series of crushing machinery, the purpose of which is to reduce the size of the monstrous boulders of limestone material received from the quarry, as well as any other additive material, if need be (*14*). Typically, the haul trucks introduce limestone material to this system in a maximum caliper of 1 to 2 m *(15)*. The crushing portion of the manufacturing process reduces the limestone and any other additive material, to progressively smaller sizes ranging from 80 mm to less than 30 mm *(14)*. The reduced size is dependent upon the cement facility's specific crushing system and manufacturing line.

"Crushing is effected by compression, shear, impact, and attrition - singly or in combination" *(15)*. It is common for a cement manufacturing facility to employ both primary and secondary crushing systems, while some even operate tertiary contributions. Most crushing systems are conducted in open circuit and, generally, are equipped with screens to bypass any fine material directly down product lines *(14)*. The primary crusher of the circuit receives the largest-sized material, typically what come straight from quarry operations *(14)*. The material is usually dumped directly from the quarry haul trucks into a hopper which feeds the primary crusher *(14)*. There is an array of crusher types that may be designated for primary crushing. The most common primary crushers utilized in cement manufacturing are toggle jaw crushers and gyratory crushers *(15)*. Jaw crushers can either be single or double toggled, and are gravity-fed, compression machines, that are decreasing in use due to their capacity limitation and operational problems (*15*).

More commonly favored for primary crushing, are the gyratory-type crushers, which exploit a mortar and pestle design approach. Gyratory crushers are similar to jaw crushers in that they are gravity-fed and crush via compression; however, the compression of the gyratory-type is continual and constant despite the location of the material in the crushing cavity, yielding a smooth, relatively consistent flow of crushed material (*15*). Modified gyratory crushers are sometimes also used in the secondary crushing portion of the system because the design proves to be quite efficient (*14*).

The secondary portion of the crushing circuit receives the crushed output from the primary, which is now significantly reduced in size. Material exiting a primary gyratory crusher, for example, may have a reduction ratio of 5:1 (*14*). The material must further be pulverized in a secondary crushing unit, and sometimes, even in a tertiary crushing unit, in order to prepare the material for the stacking/reclaim system (*3*).

Secondary/tertiary crusher types can be classified in two general designs: roll crushers and impact crushers. Roll crushers consist of either a single or double rotor that crushes material as it rolls, either in the surrounding shell, for a single-roll crusher, or within the pinch point between opposing rotors, in a double-roll crusher (*15*). Impact crushers, as the name implies, operate primarily on impact in which high-speed, free-falling material is subjected to stationary, impacting hammers that are attached to a rotor in various design patterns (*15*). Exiting pulverized material is separated by screens and grates to ensure that the appropriately sized material is forwarded down the process line (*3*).

Material is forwarded along the crushing system through a series of belt conveyors, and ultimately, the large limestone boulders which entered the primary end of the crushing system emerge as small crushed portions about 50 mm in size (*14*). The crushed limestone and all other additive materials, such as sand, clay, and iron, are stacked in designated storage piles or storage domes in the stacker/reclaim portion of the cement facility (*14*). Figure 1 on the next page illustrates the quarry and crushing systems discussed thus far.

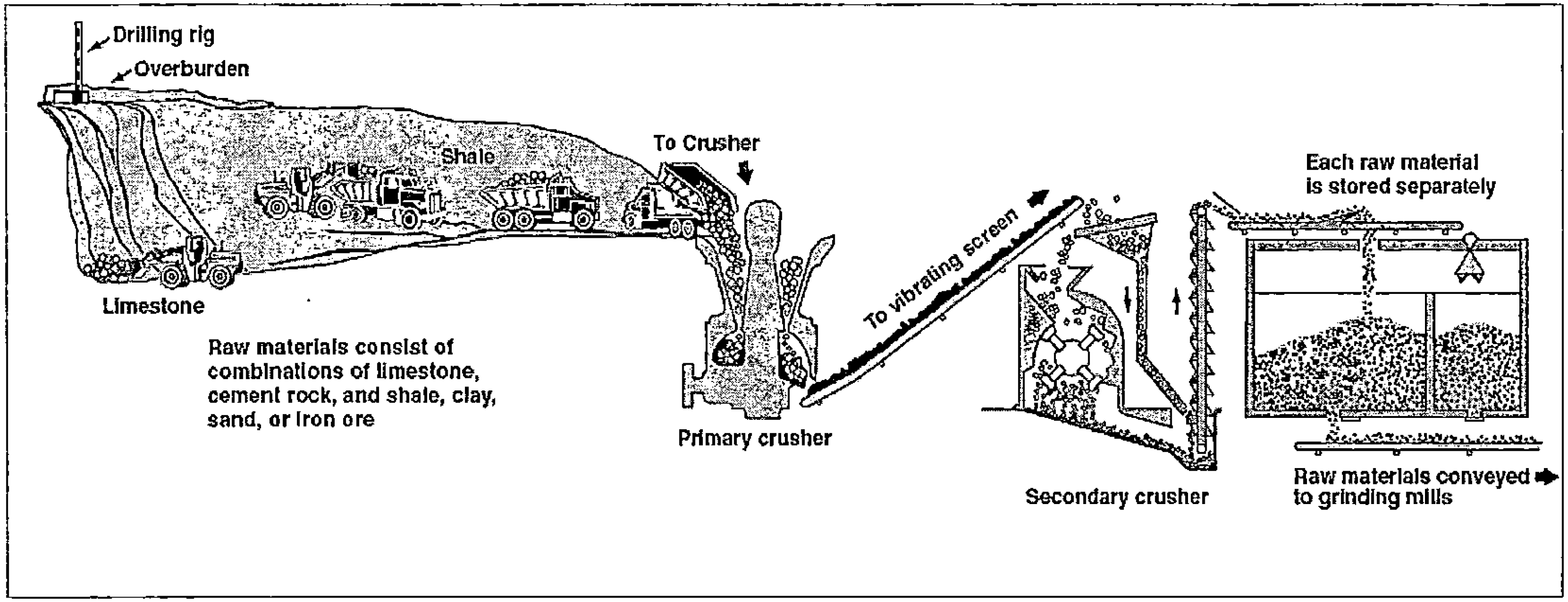

Figure 1. The Quarry and Crushing Operations of Portland Cement Manufacturing.

Kosmatka, Steven H.; Kerkhoff, Beatrix; Panarese, William C. *Design and Control of Concrete Mixtures*, 14th Editions. Portland Cement Association: USA, 2002; pp. 21-56.

The stacker/reclaim portion of the cement manufacturing process is where all the ingredients finally come together, forming the "raw meal" of cement production (*3*). Just as a baker mixes together flour, sugar, and eggs to form batter for a cake; "raw meal" represents the batter of the cement recipe. Raw meal is customarily a mixture of calcium carbonate-bearing material (generally limestone) and an argillaceous material (a co-mixture of silica and alumina sources) (*6*). A list of common raw meal sources is listed on the following page in table 1.

Table 1. Sources of Raw Materials Used in the Manufacturing of Portland Cement.

| Calcium carbonate | Iron | Silica | Alumina | Sulfate |
|---|---|---|---|---|
| Alkali waste | Blast-furnace flue dust | Calcium silicate | Aluminum-ore refuse* | Anhydrite |
| Aragonite* | Clay* | Cement rock | Bauxite | Calcium sulfate |
| Calcite* | Iron Ore* | Clay* | Cement rock | Gypsum* |
| Cement-kiln dust | Mill scale* | Fly ash | Clay* | |
| Cement rock | Ore washings | Fuller's earth | Sopper slag | |
| Chalk | Pyrite cinders | Limestone | Fly ash* | |
| Clay | Shale | Loess | Fuller's earth | |
| Fuller's earth | | Marl* | Granodiorite | |
| Limestone* | | Ore washings | Limestone | |
| Mable | | Quartzite | Loess | |
| Marl* | | Rice-hull ash | Ore washings | |
| Seashells | | Sand* | Shale* | |
| Shale* | | Sandstone | Staurolite | |
| Slag | | Shale* | Traprock | |
| | | Slag | | |

*Most common sources

In review, the beginning of the stacker/reclaim system begins where the crushing system ends--that is, with the stacking and storing of the appropriately sized materials. Quite simply, the system, as it suggests, has two major operations: 1) to store and stack, and 2) to retrieve or reclaim the precursor materials of cement (*15*). Despite the simplistic sounding nature of this portion of the cement process, there is more science to the system than it implies. In order to maintain quality product throughout the production line, the raw materials are stacked and reclaimed in such a manner as to provide a consistent flow that upholds the desired chemical characteristics of the product (*15*). This can be achieved through the shape of the storage pile, as well as, the pattern in which the materials are stacked and reclaimed (*14*). This portion of cement manufacturing is critical to the process because it is the first portion of the system to designate the qualities and quantities of the ingredients (the calcium carbonate-bearing and argillaceous materials) needed for the age-old cement formula (*15*).

The stacker/reclaim system can be an enclosed or open system, or even a combination of the two (*3*). Commonly, the system begins with reclaimed limestone, usually collected with a motorized "reclaimer" that is equipped with a belt conveyor (*15*). Depending on the streaming quality of the material, additional material sources (sand, clay, iron, etc.) are deposited onto the belt conveyor, as well, from designated hoppers to achieve the necessary chemistry of the desired product (*3*). The individual cement precursors have finally come together, and are now destined for the raw milling system of the production line where they will be further pulverized into raw meal (*3*).

The next step in the cement manufacturing process is the raw milling portion in which the reclaimed materials are subjected to a grinding system yielding uniform, homogenized raw meal (*15*). The raw meal is a powder material with particle size ranging from 45 to 70 microns (*15*). Raw milling can either be distinguished as a dry or wet process depending on whether water is added to the system resulting in a "slurry" raw meal (wet process) or left dry (*3*). In all other respects, the wet and dry processes are parallel. Illustrations of the wet and dry process can be seen in figure 2 on the following page.

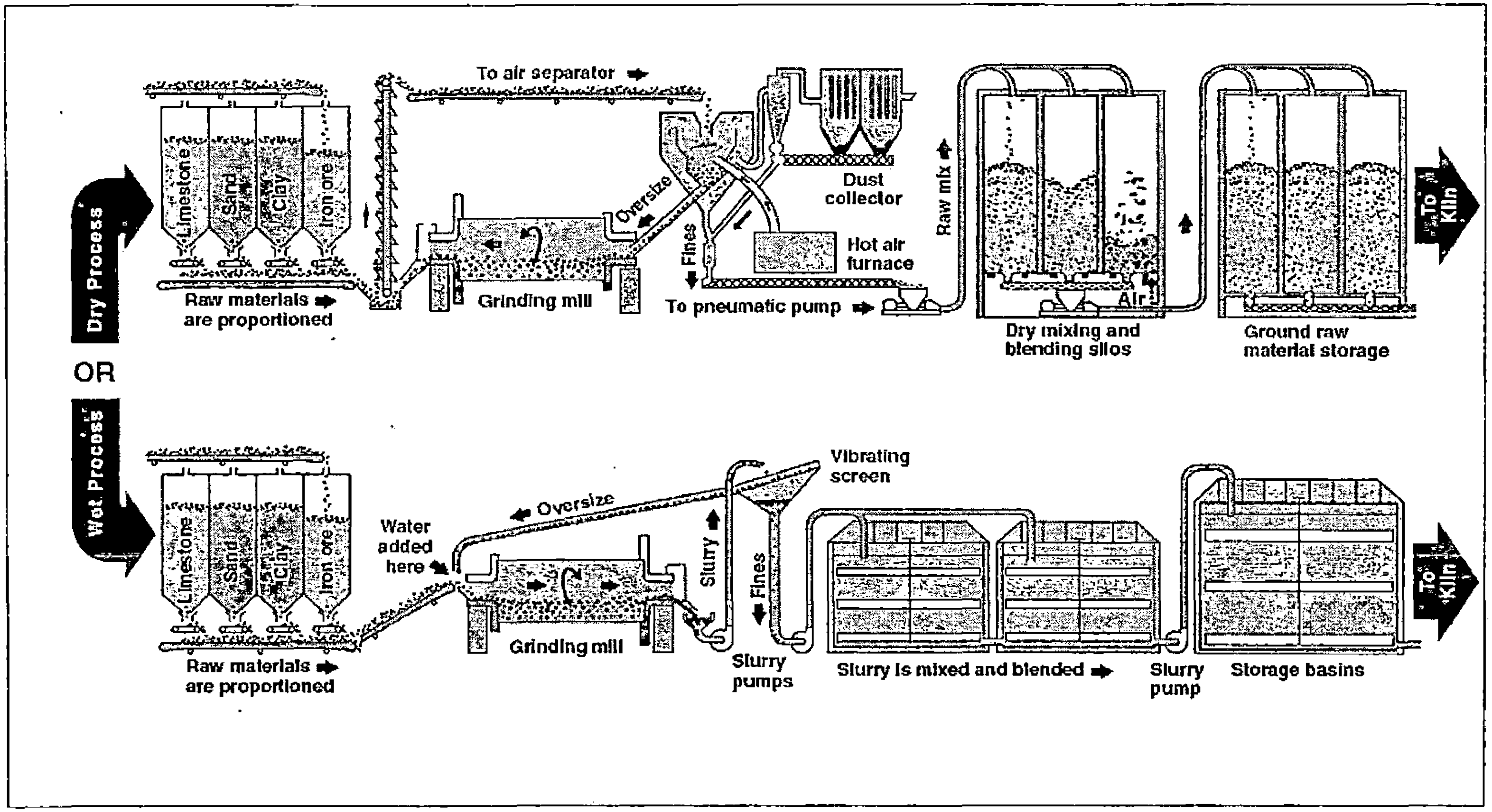

Figure 2. The "Dry Process" and "Wet Process" of Preparing the Raw Meal in Portland Cement Manufacturing.

Kosmatka, Steven H.; Kerkhoff, Beatrix; Panarese, William C. *Design and Control of Concrete Mixtures*, 14th Editions. Portland Cement Association: USA, 2002; pp. 21-56.

Traditionally, raw mill grinding has been achieved through the use of ball mills (*14*). A ball mill pulverizes material through the impact and attrition of grinding balls tumbling within a rotating cylinder, with the appropriately-sized raw meal collected via screens and separators (*15*). In contrast, more modern cement facilities employ roller mills in lieu of the classic ball mill, as they are far more efficient in terms of energy, maintenance, and production when compared to its historic counterpart (*14*). Roller mills consume less power, and crush raw materials with conical rollers that are hydraulically pressed onto a rotating grinding table, producing a steadily consistent flow of raw meal (*14*). The exiting pulverized raw meal is then sent to blending silos where it is further homogenized by means of mechanical, pneumatic fluidization, or gravity systems (*15*). The most common homogenizing techniques of blending systems are turbulence, in which the raw meal is tumbled by the injection of high volume air through the silo floor, or controlled flow, in which sequenced aeration causes layers of raw meal in the silo to descend at different rates (*14*). This final "mixing" period within the blending silos preps the raw meal "batter" for the kiln, and the intense heat that coaxes the chemical transformation of the raw material precursors into the molten material known as clinker, the main component of Portland cement (*15*).

Thus far in the cement manufacturing line the raw materials have been mined, selected, blended, ground, and homogenized into a fine, uniform raw meal. Now, the raw meal is destined to the exposure of enough heat to allow the clinkering reactions necessary to ultimately form cement (*16*). This portion of the manufacturing process is known as pyroprocessing, and involves preheating the raw meal, firing it with a rotary kiln to force the necessary chemical reactions, and cooling the clinker product so that it can be stored for the next stage of the cement process (*14*). The pyroprocessing stage is the heart of the cement manufacturing process. For this is the portion of the process in which successive combinations of endothermic and exothermic reactions occur, producing the calcium silicates that give cement its bonding strength (*16*). A detailed description of the specific chemistry associated with these reactions, and their corresponding contribution to greenhouse gas emissions, is in the next chapter of this paper.

There are many different pyroprocessing designs and enhancements, but in essence, the core process is the same. The raw meal is fed from the blending silos to a preheating system where it is warmed by the gases exiting the kiln portion (*14*). The preheating system may be as simple as metal chains hanging in the cold portion of the kiln that absorb the hot exhaust, and warm the raw meal as it flows over them, as in wet process kilns (*16,17*). In long dry kiln setups, the preheating section may also include metallic crosses and ceramic heat exchangers that split both the raw meal and the gas flow, resulting in significantly improved heat transfer and fuel efficiency (*16,17,18*). Another preheater design is that of the Traveling Grate Preheater Kiln. In this system, raw meal is heated as it travels through a preceding series of grates in which the hot exhaust gases penetrate upward through the grated screens (*19*). This system proves even more efficient in terms of heat recovery, and warms the raw meal to partial calcination status, that is, the desired chemical transformation to clinker (*19*). More commonly seen in cement manufacturing facilities, are Cyclone Preheater Kiln systems, in which cyclone separators promote heat exchange between the exhaust and raw meal by means of progressively hotter stages (*19,20*). Advancements in this particular design have optimized heat transfer, greatly improving fuel efficiency, and production rates (*14*). Production is increased as well as energy efficiency because some cyclone systems provide calcinating temperatures enabling clinker formation almost instantly as it enters the kiln (*4*).

Irrespective to which type of preheating and kiln system a particular cement manufacturing plant may employ, the result of the system is the same. Heat the raw meal enough and trigger the temperature dependent reactions necessary to form clinker (*3*). The kiln portion anteceding the preheating system ensures this process, which is to be expected, as it is nothing more than a rotating furnace (*20*). The kiln serves to propel the material as it is subjected to progressively hotter temperatures, striving for near perfect calcination rates (*20*). The portion of the kiln in which calcination is occurring, the hottest portion, is referred to as the "burning zone", and the clinker begins to cool immediately after passing through this section (*20*). The cooling of clinker occurs in two locations. The first, as mentioned above, occurs in the kiln as it exits the burning zone, and the second, more effective portion, occurs in designated clinker coolers (*16*). "The rate of cooling can be critical to the clinker quality and performance of cement" (*16*). The clinker exits the kiln at 1200°C and is cooled to less than 100°C by careful exchange of heat with ambient air to maintain clinker quality (*14*). The most preponderant type of clinker cooler is the Reciprocating Grate Cooler, consisting of a series of grate compartments exposed to individually controlled fans that are monitored to direct specific pressures and volumes of cooling air (*14*). Clinker cooler systems also serve to transport clinker from the kiln to the clinker storage (*16*). Figure 3 on the next page illustrates the complete pyroprocessing portion of the manufacturing process.

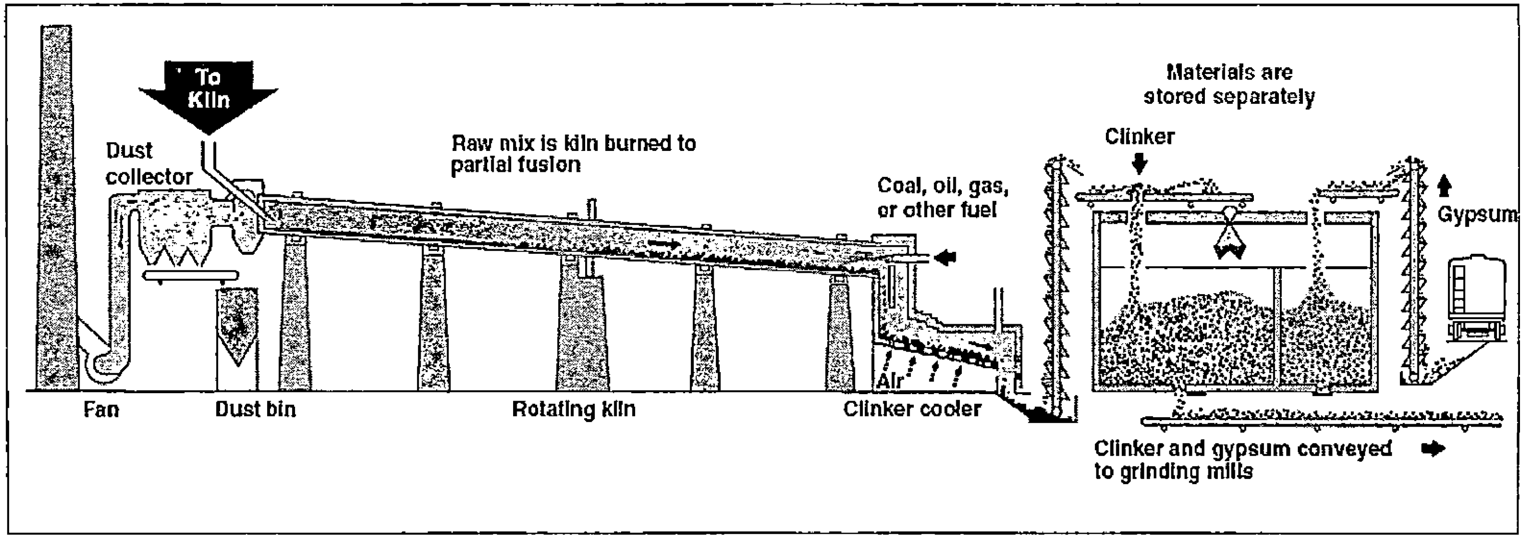

Figure 3. The Pyroprocessing System of Portland Cement Manufacturing.

Kosmatka, Steven H.; Kerkhoff, Beatrix; Panarese, William C. *Design and Control of Concrete Mixtures*, 14th Editions. Portland Cement Association: USA, 2002; pp. 21-56.

The final portion of pyroprocessing is clinker storage. Clinker is usually stored in designated silos according to its specific grade (16). At this point, there is one more round of grinding before the manufacturing process actually yields Portland cement. The concluding grinding operation is appropriately labeled "finish milling". The illustration on the following page, figure 4, describes the finish milling process in detail.

Finish Milling is the grinding together of clinker with 3-5% gypsum, and sometimes other additives, such as pozzolan, slag, and limestone, depending on the end use of the cement being produced (*14*). Similar to the other grinding/crushing systems in the cement manufacturing process, finish milling is achieved by ball or roller mill units, although ball mills are more abundant for finishing in cement operations (*21*). While ball mills consume more power than roller type mills, the design is more durable for grinding the coarse clinker than roller mills (*22*). The finish mill system must reduce the clinker, which is several centimeters in diameter, to a fine, gypsum-mixed powder with a maximum diameter of 100 micrometers (*21*).

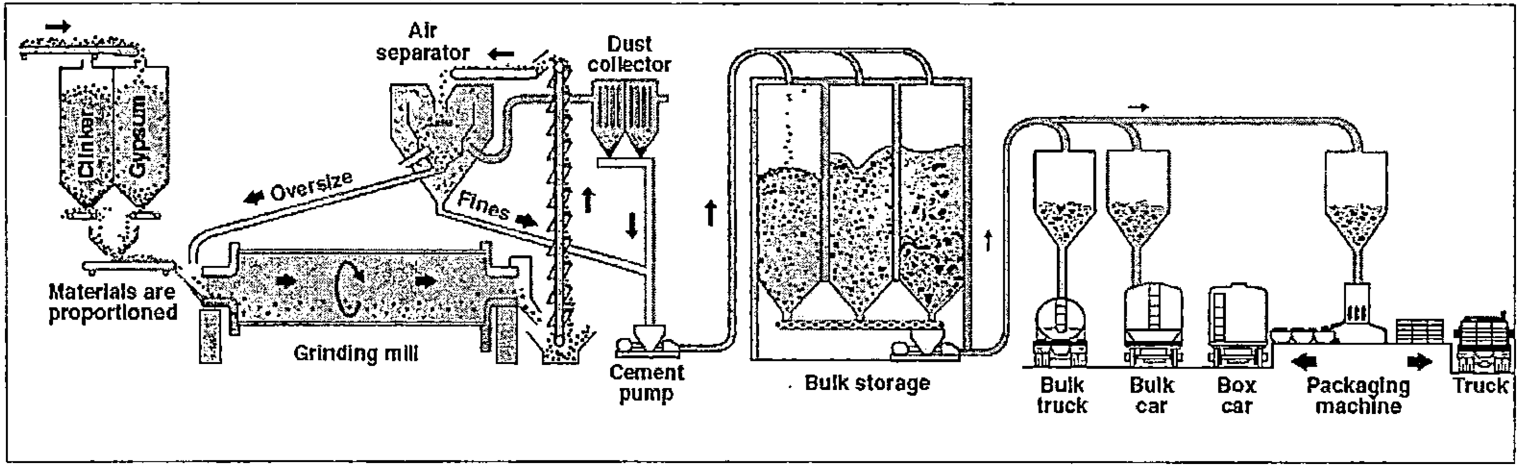

Figure 4. The Finish Milling Process of Portland Cement Manufacturing.

Kosmatka, Steven H.; Kerkhoff, Beatrix; Panarese, William C. *Design and Control of Concrete Mixtures*, 14th Editions. Portland Cement Association: USA, 2002; pp. 21-56.

The finish mill system is comprised of four basic components 1) feeders, 2) mill, 3) elevator, and 4) separator *(14)*. The feeders are modified belt conveyors that are calibrated to dump the appropriate amounts of clinker and gypsum into the grinding mill *(21)*. The mill, is the actual grinding unit of the system, most commonly a ball mill *(14)*. Ball mills typically consist of an inner cylindrical shell equipped with designated wear-resistant liners that provide increased lift and charge to the tumbling balls within *(22)*. Ball mills are able to pulverize the coarse clinker and gypsum material into a fine powder by passing the material through sequential compartments outfitted with successively smaller grinding balls and liner patterns *(22)*. Discharge material from the mill is then carried by the elevator portion of the system where the cementitious material is then screened by a separator, allowing the fine powder (the final cement product) to exit out to storage, while re-circulating any coarse material *(21)*.

The manufacturing line is now complete. The finished cement powder product is stored in silos where it is destined for bulk loading or to a packing house where it is bagged for shipment *(3)*. "Different types of Portland cement are manufactured to meet various normal physical and chemical requirements for specific purposes" (*3*). Portland cements are designed to meet the specifications of the American Society for Testing and Materials (ASTM) C150, *Standard Specification for Portland Cement*, which defines eight types using Roman numeral designations (*23,24*). Table 2 on the next page lists the eight types, the ASTM C150 specification, and their general applicable use. Specifications for the three types of air-entraining Portland cement types (IA, IIA, and IIIA) are similar to the composition in ASTM types I, II, and III except for the addition of an air-entraining material which is mixed with the clinker in the finish mills (*23,24*). This gives the Portland cement type an improved resistance to cold temperatures, where structures may be subjected to freezing and thawing sequences (*24,25*).

Table 2. American Society for Testing and Materials (ASTM) C150 Classifications of Portland Cement and their Applicable Use.

| Type | ASTM C150 | General Use |
|---|---|---|
| I | Normal | Suitable for all uses where the special properties of other types are not required. |
| IA | Normal, air-entraining | Same uses as Type I, where air-entrainment is desired. |
| II | Moderate sulfate resistance | Used where precaution against moderate sulfate attack is important such as structures exposed to soil or ground waters. |
| IIA | Moderate sulfate resistance, air-entraining | Same uses as Type II, where air-entrainment is desired. |
| III | High early strength | Used when forms need to be removed as soon as possible or when the structure must be put into service quickly. |
| IIIA | High early strength, air-entraining | Same uses as Type III, where air-entrainment is desired. |
| IV | Low heat of hydration | Used where the amount of heat generated from hydration must be minimized such as in massive concrete structures such as gravity dams. |
| V | High sulfate resistance | Used in concrete exposed to severe sulfate action, such as soils and ground waters with high sulfate content. |

What ever the project may be, Portland cement is most likely a component necessary for its completion. There are 39 cement companies in the United States alone, operating 118 cement plants in 38 states, with annual shipments estimated around 8.6 billion dollars (*18*). Like most building materials, the cement industry is closely tied to that of the construction industry. So long as there is a need to have skyscrapers and highways, so will there be a need for the age-old product of Portland cement.

## Portland Cement Chemistry

As discussed in the manufacturing chapter of this paper, Portland cement is essentially comprised of two constituents, clinker and gypsum. While the actual cement product is not formed until the induction of gypsum during the last stages of finish milling, almost the entire manufacturing process is delegated to producing clinker. For this reason, and to focus on the connection between Portland cement manufacturing and greenhouse gas emissions, the first subsection of this section will explore the clinkering chemistry in more detail. The second subsection focuses on the second major source of greenhouse gas emissions in Portland cement manufacturing, the combustion of fossil fuels.

### Clinkering Chemistry and Carbon Dioxide Production

To review, clinker is the nodular, molten product of igniting a mixture of primarily calcium carbonate ($CaCO_3$), typically limestone, aluminum silicates, such as clay, and small amounts of additives, such as iron, within the rotary kiln (*6*). "The raw material composition, mineralogical composition, and the time and temperature profile of the materials in the kiln determine the ultimate composition and mineralogy of the clinker, which in turn determines the performance of the cement produced" (*16*). Therefore it is pertinent that the appropriate balance of mineralogy and temperature are maintained in the kiln to ensure the proper chemical reactions needed to maintain quality product (*26*).

As discussed, there is an array of kiln designs operating in cement manufacturing facilities, but in essence, the same material transformation occurs in all of them (*16*). Free water immediately begins to evaporate from the raw meal as it enters the preheating portion of the kiln (*16*). Removal of absorbed water in clay materials as well as chemically bound water occurs between 100°C and 900°C, peaking as the raw meal enters the feed end of the kiln at around 500°C (*6*). Clays are composed of a host of different hydrated aluminosilicates which harbor varying ratios of silicon dioxide ($SiO_2$), also known as quartz or silica, and aluminum oxide ($Al_2O_3$) (*6*). The reaction below depicts the endothermic decomposition of a common clay, Kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$), as it is exposed to 500°C temperatures.

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O + {\sim}500^{\circ}C \rightarrow 2SiO_2 + Al_2O_3 + 2H_2O \qquad (1)$$

As the gravity fed raw meal continues to travel down the rotary kiln, increasing temperatures and mixing coax more chemical transformations (*20*).

Although not yet mentioned, magnesium carbonate ($MgCO_3$) is a common compound found in limestone deposits, yet it contributes nothing to the integrity of the final product (*4*). At about 400°C, the calcination of magnesium carbonate occurs, that is the decomposition of magnesium carbonate ($MgCO_3$), forming magnesium oxide ($MgO$) and liberating carbon dioxide ($CO_2$) as a gaseous by-product as seen in equation 2 below (*4*).

$$MgCO_3 + {\sim}400^{\circ}C \rightarrow MgO + CO_2(g) \qquad (2)$$

It is necessary to mention the calcination of magnesium carbonate to demonstrate the carbon dioxide ($CO_2$) liberation, as well as to point out the magnesium oxide ($MgO$) product, which may compete for the required clinkering reactions requiring free lime ($CaO$). As the above reaction shows, for about every 84 tons of $MgCO_3$ (MW = 84.31) consumed, about 44 tons of $CO_2$ (MW = 44.01) is generated.

Also known as calcium oxide, free lime (CaO), forms through the calcination of calcium carbonate ($CaCO_3$), the prime component of the limestone deposit (*4*).

$$CaCO_3 + \sim1000^\circ C \rightarrow CaO + CO_2(g) \qquad (3)$$

This reaction shows that it takes about 100 tons of $CaCO_3$ (MW = 100.09) to yield about 44 tons of $CO_2$ (MW = 44.01). In the calcination of calcium carbonate ($CaCO_3$) however, the dissociation occurs slowly at around 800°C, at an accelerated speed near 900°C, and rapidly at 1400°C (*6*). It is important to note that the chemical reactions within the kiln do not occur separately, but rather are co-dependent upon the completion of reactions occurring at different temperatures and areas of the kiln (*6*). For instance, at the beginning portions of the kiln, the decomposition of clays, iron ores, and limestone, frees up silica, alumina, ferric and calcium oxides ($SiO_2$, $Al_2O_3$, $Fe_2O_3$, and CaO respectively), which then react together in later portions of the kiln (*4*).

As the ratio of free lime, or calcium oxide (CaO), and that of the silica, alumina, and ferric oxides increases, an array of co-dependent reactions begin to occur (*4*). Below 800°C, free lime (CaO) and the oxides aluminum and iron begin to react, forming calcium aluminate and calcium ferrite ($CaO \cdot Al_2O_3 + CaO \cdot Fe_2O_3$), as seen in equation 4 below:

$$2CaO + Al_2O_3 + Fe_2O_3 + \sim 800^\circ C \rightarrow CaO \cdot Al_2O_3 + CaO \cdot Fe_2O_3 \quad (4)$$

Mono-calcium silicates ($CaO \cdot SiO_2$) began to form at around this temperature as well, but are readily converted to di-calcium silicates, or belite ($2CaO \cdot SiO_2$), almost completely by 1200°C (*6*). Belite is one of the four primary compounds in Portland cement, and is also referred to as "$C_2S$" (*25*). The formation of belite is seen in equation 5 below:

$$2SiO_2 + 3CaO + \text{heat } (900^\circ C \text{ to } 1200^\circ C) \rightarrow CaO \cdot SiO_2 + 2CaO \cdot SiO_2 \quad (5)$$

As the rotating mixture continues to warm as it travels through the kiln, aluminum and ferric oxides begin to react with the free lime (CaO) at accelerated rates, yielding tri-calcium aluminate and tetra-calcium aluminoferrite ($3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) between 1200-1300°C (*4*). Tri-calcium aluminate ($3CaO \cdot Al_2O_3$) and tetra-calcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) are two more of the four primary compounds of Portland cement and are commonly referred to as "$C_3A$" and "$C_4AF$", respectively (*25*).

Near 1300°C, the major phases present within the kiln are belite ($2CaO \cdot SiO_2$), free lime (CaO), and calcium aluminates and ferrites ($CaO \cdot Fe_2O_3$, $C_3A$, and $C_4AF$) (*6*). A summary of the reactions and temperatures occurring within the kiln can be seen in table 3 on the next page. Only a minor amount of liquid is formed at this stage, but contributes to the activation of reactions to follow (*6*).

Table 3. The Temperature and Corresponding Compound Formation within a Portland Cement Kiln.

| **Temperature (°C)** | **Compound Formation** | **Compound Name(s)** |
|---|---|---|
| Below 800 | $CaO.Al_2O_3$<br>$CaO.Fe_2O_3$ | Calcium aluminate<br>Calcium ferrite |
| 800-900 | $CaO.SiO_2$ | mono-calcium silicate |
| 900-950 | $5CaO.3Al_2O_3$ | penta-trialuminate |
| 950-1200 | $2CaO.SiO_2$ | di-calcium silicate, belite, $C_2S$ |
| 1200-1300 | $3CaO.Al_2O_3$ | tri-calcium aluminate, $C_3A$ |
|  | $4CaO.Al_2O_3.Fe_2O_3$ | tetra-calcium aluminoferrite, $C_4AF$ |
| 1260 | Liquid formation occurs | N/A |
| 1260-1450 | $3CaO.SiO_2$ | tri-calcium silicate, alite, $C_3S$ |

Tri-calcium silicates ($3CaO \cdot SiO_2$), the fourth primary compound of Portland cement, also known as $C_3S$, form slowly near 1300°C as seen in equation 6 below, but the presence of alumina and ferric oxides ($Al_2O_3$ and $Fe_2O_3$) greatly increases its production (*4*).

$$SiO_2 + CaO + CaO \cdot SiO_2 + 2CaO \cdot SiO_2 + >1300^{\circ}C \rightarrow 4CaO \cdot 3SiO_2 \quad (6)$$

The alumina and ferric oxides (primarily $C_3A$, and $C_4AF$), at this temperature have now converted to the liquid phase, and the only solids present are $C_3S$, $C_2S$, and small amounts of free lime (CaO) (*6*). The liquefied aluminates and ferrites ($C_3A$, and $C_4AF$) provide the reactive media necessary for the smaller belite crystals ($C_2S$) and free lime (CaO) to react and form the larger alite ($C_3S$) crystals more readily (*25*). As these crystals combine, the first notable nodules of clinker begin to form (*25*). Figure 5 is a phase diagram showing all the mineral phases involved in the clinker formation process as a function of temperature within the kiln.

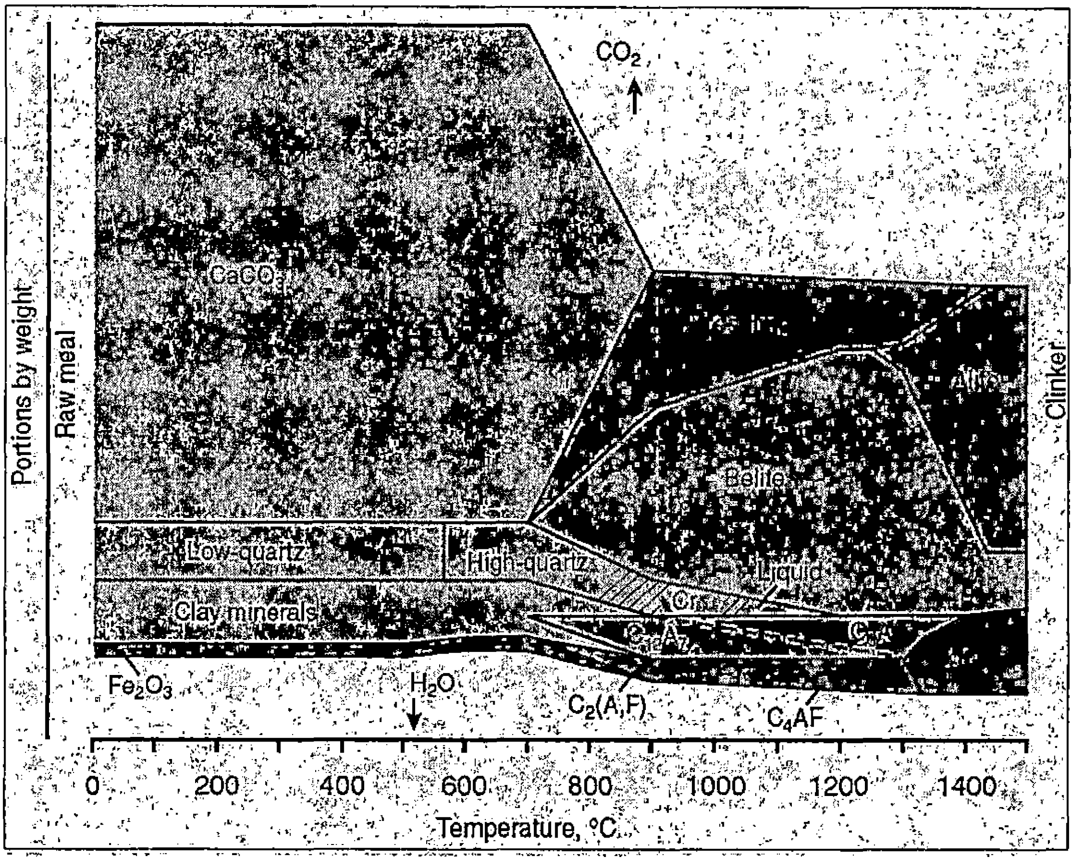

Figure 5. The Clinkering Reactions of Raw Meal as a Function of Temperature within a Portland Cement Kiln.

Kosmatka, Steven H.; Kerkhoff, Beatrix; Panarese, William C. *Design and Control of Concrete Mixtures*, 14th Editions. Portland Cement Association: USA, 2002; pp. 21-56.

As the clinkering nodules progress down the kiln, and temperatures cool to between 1300°C to 1250°C, the crystallization of the remaining liquid again produces tri-calcium aluminate and tetra-calcium aluminoferrite ($C_3A$ and $C_4AF$) compounds (*6*). The grayish-black pellets, about 20mm in diameter are carefully cooled as they exit the kiln and enter the cooling system (*15*). In summary, the four primary compounds of Portland cement are now evident within the clinker. "Alite constitutes 50% to 70% of the clinker, whereas belite accounts for only 15% to 30%. Aluminate compounds constitute about 5% to 10% of the clinker, and ferrite compounds 5% to 15%" (*4*).

Each of the four compounds has a unique contribution to the final product, as do the hydration reactions that occur when it is mixed with water to form concrete. Alite, $C_3S$, is the compound affecting the early strength of the cement, and is responsible for the initial set of the product (*3*). The tri-calcium aluminate, $C_3A$, also assists in early strength by liberating a great deal of heat during hydration, which provokes hardening (*3*). In contrast, belite, or $C_2S$, hydrates and hardens more slowly than the other compounds, contributing to increased strength with age (*25*). The last clinker compound, tetra-calcium aluminoferrite, $C_4AF$, does not contribute to the overall strength of the cement product, but it is the hydration of $C_4AF$ that offers cement its grayish hue. Gypsum, or calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), is added in the final cement product to react with the tri-calcium aluminate, $C_3A$, forming ettringite, or calcium tri-sulfoaluminate ($6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 2H_2O$), which controls the rate of hydration (*25*).

$$CaSO_4 \cdot 2H_2O + 3CaO \cdot Al_2O_3 \rightarrow 6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 2H_2O \qquad (7)$$

The rate of hydration is important to ensure that the product sets correctly without shrinkage or cracks that may lead to failure (*22*). This rate of hydration also allows masons to mold and shape the concrete before it sets (*22*).

## Fossil Fuel Combustion Chemistry and Carbon Dioxide Production

As seen in the description of the Portland chemistry, the clinkering reactions require extreme temperatures to proceed effectively. Not yet discussed, is how these intense temperatures, in some kiln systems topping out near 1900°C, are achieved. The answer is through the combustion of fossil fuels. While the raw meal is fed through the upper "feed end" of the kiln, fuel such as coal, coke, oil, natural gas, and other alternative fuels are forced into the lower end of the kiln (*20*). In the lower end of the kiln, gas, oil, or pulverized solid fuel is sent directly into the kiln through a "burner pipe" that upon ignition generates a fierce concentric flame (*14*). This is the hottest portion of the kiln, the burning zone, where raw meal reaches peak temperatures as it passes under the intense flame (*14*). The traditional fuels used to generate these hot kiln temperatures are natural gas, oil, and coal, however, the particular selection is highly dependent upon price and availability (*5*). Many cement manufacturing facilities today, are incorporating a variety of alternative fuels such as biosolids, woodchips, and tires as a means of competing with fuel cost, availability, and environmental consciousness (*5*). Table 4 on the following page lists some common kiln fuels consumed in cement manufacturing and their corresponding heat values.

Table 4. List of Common Fuels Used in Cement Manufacturing and Corresponding Heat Values.

| Fuel | Approximate Heat Value (Btu/lb) | Unit |
|---|---|---|
| Biosolids | 9500-10500 | Btu/lb |
| Carbon flyash | 900-1500 | Btu/lb |
| Coal tar sludge | 7000-10000 | Btu/lb |
| Coal* | 12000-14000 | Btu/lb |
| Hazardous Waste | 8000-13000 | Btu/lb |
| Meat & bone meal | 4000-8000 | Btu/lb |
| Municipal refuse | 4000-8000 | Btu/lb |
| Natural gas* | 1,029 | Btu/scf |
| Oils (including used) | 3.0-6.5 | MMBtu/barrel |
| Petroleum coke* | 12000-14000 | Btu/lb |
| Plastics | 10000-16000 | Btu/lb |
| Rice hulls | 6000-8000 | Btu/lb |
| Spent activated carbon | 10000-12000 | Btu/lb |
| Spent toner | 12000-15000 | Btu/lb |
| Spent water treatment resins | 6000-12000 | Btu/lb |
| Tires | 13000-15000 | Btu/lb |
| Wood products | 5000-8000 | Btu/lb |

*Traditional fuels

"The physical and chemical characteristics of fuels play a major role in the combustion process, in the clinker production process, and in the emission of atmospheric pollutants" (*5*). Kiln fuel relies on the chemical and thermal energy release of energy-rich bonds, such as carbon-carbon, hydrogen-hydrogen, or carbon-hydrogen (*20*). These essential bonds, consisting essentially of carbon, hydrogen, nitrogen, and sulfur vary from fuel to fuel, as does their specific heat, thermal conductivity, heating value, and flash point (*14*). While carbon and hydrogen provide the greatest energy contribution, nitrogen and sulfur yield significantly less energy, and all can form environmental contaminants (*5*). All kiln fuels consist of varying chains of impure hydrocarbons containing minimal amounts of sulfur and nitrogen (*27*). These hydrocarbons are great reducers, and when exposed to the right conditions, such as the ambient air (the oxidant) and an ignition source (activation energy) within the kiln, rapid, self-sustainable, exothermic chemical reactions occur, that of combustion (*4,27*). When hydrocarbons ($C_nH_{2n+2}$) are combusted, heat, water vapor ($H_2O$), and carbon dioxide ($CO_2$) are the primary products released (*28,29*). For example, the combustion of methane, a common component of natural gas, is shown in equation 8 below:

$$CH_4(S) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \text{heat} \qquad (8)$$

Because fossil fuels often contain trace amounts of nitrogen and sulfur impurities, corresponding oxides of nitrogen and sulfur ($NO_X$ and $SO_X$) are also emitted, which have implications affecting both clinker quality and the environment (*5,29*).

In addition to nitrogen containing fossil fuels, oxides of nitrogen ($NO_X$) form anytime a fuel is fired in the presence of atmospheric air, which contains approximately 79% of nitrogen naturally (*5*). The generation of oxides of nitrogen forming from atmospheric nitrogen ($N_2$) and oxygen ($O_2$) is called "thermal $NO_X$" (*5*).

$$N_2 + 3/2O_2 \rightarrow NO + NO_2 \qquad (9)$$

These thermal $NO_X$ species are dependent upon temperature, and are latent to combustion itself (*5,29*). Oxides of nitrogen ($NO_X$) formed from fuels containing chemically bound nitrogen impurities, are referred to as "fuel $NO_X$" (*5*). Fuel $NO_X$ formation is dependent upon the oxidation of nitrogen organic compounds present in the fuel, and can be summarized by the following reaction:

$$R_3\text{-}N + O_2 \rightarrow NO + NO_2 + CO_2 + H_2O \qquad (10)$$

While there are many intermediation reactions that can occur in fuel $NO_X$ formation, after nitrogen oxide is formed (NO), it is quickly oxidized into nitrogen dioxide ($NO_2$) at low temperatures, however all $NO_X$ is environmentally threatening (*5,28,29*). Nitrogen dioxide ($NO_2$) released from fuel combustion can react with water, forming two corrosive acids: nitrous acid ($HNO_2$) and nitric acid ($HNO_3$) (*5*). When this contact occurs via rainwater, highly concentrated nitrogen dioxide ($NO_2$) can cause acid rain, harming vegetation, animals, and infrastructure (*5*).

Perhaps even more environmentally menacing is the contribution of nitrogen oxides ($NO_X$) to photochemical smog. Photochemical smog is atmospheric pollution produced from sunlight, nitrogen oxides ($NO_X$), and volatile organic compounds (VOCs) reacting in the atmosphere (*30*). Figure 6 on the following page illustrates the key roles $NO_X$ plays in photochemical smog formation.

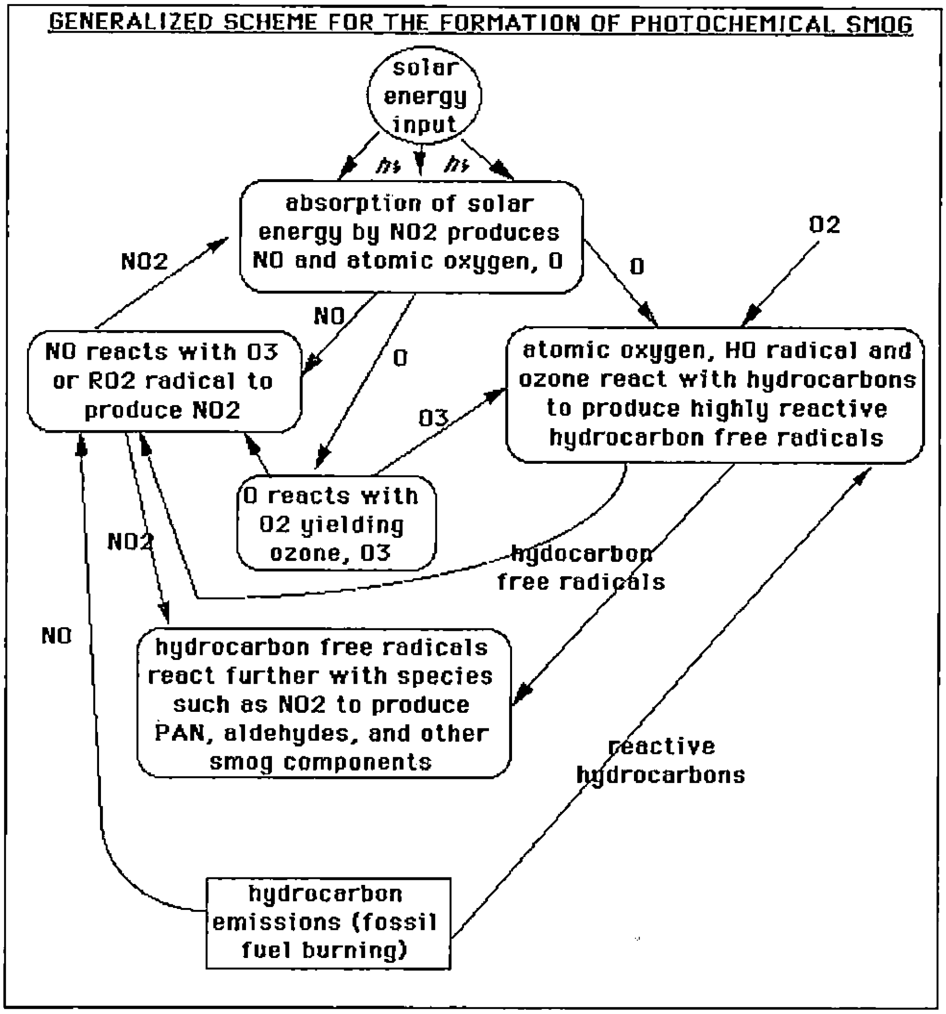

Figure 6. The Chemical Formation of Photochemical Smog.

Sillman, S. Troposheric Ozone and Photochemical Smog. *Environmental Geochemistry*. Elsevier: Amsterdam, 2005; pp. 407-431.

Nitrogen oxide (NO) and nitrogen dioxide ($NO_2$) can both be involved in various atmospheric reactions that yield smog directly, or its harmful precursors, such as atomic oxygen, ozone, and free radicals of hydroxyl and hydrocarbon compounds (*30*). Photochemical smog can be irritating to the eyes, skin, and lungs, especially to children and the elderly, and those with decreased immunity (*30*). Some of the stronger oxidants, such as ozone ($O_3$) can even damage lung tissue, plant cells, and materials such as rubber and paint (*30*).

Just as with the formation of nitrogen oxides ($NO_X$), kiln firing of sulfur containing hydrocarbons results in the generation of oxides of sulfur ($SO_X$)as shown in equation 11 below (*5*).

$$R_3\text{-}S + O_2 \rightarrow SO_2 + SO_3 + CO_2 + H_2O \tag{11}$$

In the presence of excess oxygen ($O_2$), sulfur dioxide ($SO_2$) can form at high temperatures, and sulfur trioxide ($SO_3$) at lower temperatures, which are precursors to sulfurous acid ($H_2SO_3$) and sulfuric acid ($H_2SO_4$), both environmentally relevant acids, that can contribute to acid rain (*5*).

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{12}$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulfur oxides ($SO_X$) emissions from cement kilns are relatively low, when compared to the other emissions generated, because a significant portion of the sulfur is incorporated into the clinker through reactions occurring between sulfur dioxide ($SO_2$) and alkalis found in the raw meal (*5,29*). Sulfur fuel impurities can therefore pose a threat to clinker quality if the $SO_x$ concentrations are too high.

In addition to environmental concerns stemming from the production of $NO_x$ and $SO_x$, the combustion of fossil fuels also yields precursors of dioxins and polycyclic aromatic hydrocarbons (PAHs) (*29*). Dioxins and PAHs are serious pollutants because they are carcinogenic, mutagenic and teratogenic (5). While PAHs are prone to heavier fuels, dioxins are common in fuels with chlorine components such as in wastes that may be used as an alternative fuel (5). Both are dangers in incomplete combustion and their concern in fuel use should be heavily surveyed (*5*). While it is important to keep in mind that just as cement cannot be made without raw meal, neither can it be made without fuel. Consequently, fuel choice should be a selection that balances technical, economical, and environmental concerns in order to ensure cost, quality, and environmental sustainablity.

## Global Warming and Greenhouse Gas Consciousness

On September 27, 2006, Governor Arnold Schwarzenegger signed the Global Warming Solution Act (AB 32) into effect, initiating California as a national and international leader in a commitment to reduce global warming emissions. Global warming emissions, or greenhouse gases, are chemical compounds found in the earth's atmosphere (*8*). When the sunlight reaches the earth's surface, some of it is absorbed and warms the surface while the rest is reflected back toward space as heat (*8*). Absorbed sunlight is shortwave energy, that of the visible and ultraviolet portion of the spectra, whereas the reflected light is longer-wave infrared energy or heat (*8*). Greenhouse gases absorb this longer-waved energy, impeding most of the heat from reentering space, thus trap it in the earth's lower atmosphere (*8*). This 'greenhouse' effect keeps the earth's temperature relatively constant, as the amount of energy sent from the sun equalizes with the amount of energy radiated back to space (8).

Many gases exhibit greenhouse properties. Some naturally occur in the atmosphere such as carbon dioxide ($CO_2$), methane ($CH_4$), water vapor ($H_2O$), and nitrous oxide

($N_2O$), while others are primarily man-made, like chloroflourocarbons (CFCs) or hydrochlorofluorocarbons (HCFCs) (*31,32*). $CO_2$, $CH_4$, $H_2O$, and $N_2$ are constantly cycled through the atmosphere by natural process involving respiration and decay of plants and animals (*31,32*). These natural processes, unaltered by human influence, generally do not affect the greenhouse gas concentrations that contribute to earth's natural greenhouse effect and normal temperature range (*31,32*). In contrast, man-made products containing halogen elements, do. CFCs and HCFCs are halocarbons that contain chlorine, and are used in air conditionings, fire extinguishers, and propellants (*30*). Halocarbons such as these containing chlorine, or others such as bromine-containing compounds, can undergo solar-radiation induced reactions contributing to the stratospheric depletion of ozone ($O_3$) (*30*). Ozone within the stratosphere helps to maintain earth's steady temperature, and depletion allows for potentially damaging ultraviolet light to reach its surface (*30*). Other halogenated substances, such as the fluorine-containing compounds of hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride ($SF_6$), do not deplete ozone within the stratosphere, but are potent greenhouse gases due to their powerful ability to absorb reflected infrared radiation (*30*).

Each of these greenhouse gases in the atmosphere, whether natural or anthropogenic, contributes to the greenhouse effect differently. Greenhouse gases can have a direct effect by absorbing solar radiation directly, or indirectly through radiative forcing transformations that prolong the lifetimes of other greenhouse gases, or produce other greenhouse gases all together (*31,32*). In order to quantify the capability of greenhouse gases, the Intergovernmental Panel on Climate Change (IPCC) developed the Global Warming Potential (GWP) concept. The GWP compares the ability of each greenhouse gas to trap solar radiation in the atmosphere relative to $CO_2$ (*33*). It is a ratio of the time-integrated radiative forcing from the instantaneous release of 1 kilogram of a trace substance relative to that of 1 kg of $CO_2$ (*33*). A list of common greenhouse gases and their corresponding GWP can be found in table 5 on the following page.

Table 5. The Global Warming Potential (GWP) of Common Greenhouse Gases and their Corresponding Tropospheric Concentrations.

| Greenhouse gas | Chemical Formula | Tropospheric Concentration (ppb) | GWP |
|---|---|---|---|
| Carbon dioxide | $CO_2$ | 368,400 | 1 |
| Methane | $CH_4$ | 1,745 | 21 |
| Nitrous oxide | $N_2O$ | 312 | 310 |
| Trichlorofluoromethane | CFC-11 | 0.262 | 1320 |
| Sulphur hexafluoride | $SF_6$ | 0.005 | 23,900 |

Carbon dioxide ($CO_2$) is chosen as the reference gas because it is the highest concentrated greenhouse gas in the atmosphere (*32,33*). It should be noted that while it is evident that concentration is a very important term to consider in understanding the effects of greenhouse gases, the GWP is an equally important counterpart (*32,33*). While a particular greenhouse gas concentration may be low, its GWP may be excessively high; therefore, it may generate as much of an environmental concern as a greenhouse gas with a high atmospheric concentration. Methane ($CH_4$), for instance, has a lower atmospheric concentration than $CO_2$, but it is 20 times more effective at trapping heat in the atmosphere (*32*). An important component to consider is the atmospheric lifetime of the greenhouse gas. Sulfur hexafluoride ($SF_6$), for example, can remain in the atmosphere for 3,200 years, while $CO_2$ can remain as little as 5 (*32*). In summary, the environmental impact of a greenhouse gas is dependent upon its concentration, GWP, and lifetime residence, and each must be equally weighed in evaluating its effects.

Despite the fact that direct greenhouse gases ($CO_2$, $CH_4$, $N_2O$, and $H_2O$) occur naturally, human activities have contributed to changed atmospheric concentrations (*30*). Concentrations of $CO_2$, $CH_4$, and $N_2O$ have increased globally by 36, 148, and 18 percent respectively, from the years following the industrial revolution, 1750 to 2005 (*32*). In the United States, alone, greenhouse gas emissions have increased by 14.7 percent between 1990 to 2006 (*8*). Many studies suggest that there is direct correlation to anthropogenic activities and increased greenhouse gas concentrations. In 2006, the largest source of $CO_2$, and of greenhouse gases overall, was the combustion of fossil fuels (*8*). Methane, $CH_4$, was primarily emitted from domestic livestock, landfills, and natural gas systems (*28*). Agricultural uses, such as fertilizers, and the combustion of fossil fuels within automobiles were the leading sources of $N_2O$ emissions (*28*). Ozone depleting substances were released in the development of substitute

HFCs, while electrical transmission and distribution systems account for the release of $SF_6$ (*28*). All of these greenhouse gas emissions are heavily connected to human activity.

Over the past century, the earth's temperature has increased by about 0.5 degrees Celsius, and many scientists believe this 'global warming' to be attributed to an increase in the atmospheric concentrations of greenhouse gases (*28,34*). Many environmental concerns have arisen concerning the effects of climate change; however, the debate is not without controversy. While many argue that an increase in global temperature is resulting in severe floods and droughts, rising sea levels, and irregular insect and animal behavioral patterns, others believe that it is just a natural process of our planet's cycle (*8*). For the time being, neither side is positively assured of its effects, but one thing is undeniable; greenhouse gas emissions are increasing and only recently has there been any attempt to reduce them.

### Assembly Bill 32: Global Warming Solutions Act

AB 32 is the first state-wide program within the United States to place caps on greenhouse gas emissions from major industries, and upholding penalties for noncompliance (*9*). California is the 12th largest source contributor of $CO_2$ in the world, the largest quantity greenhouse gas in the atmosphere (*9*). With the legislation of AB 32, California has taken responsibility to reduce its share of emissions, setting an example to lead the other states and countries in implementing policies and technologies that reduce potentially negative environmental effects. The Global Warming Solutions Act requires a three-step reduction in California's greenhouse gas emissions. It calls for an 11% decrease by reducing greenhouse gas emissions to 2000 levels by 2010, an estimated 25% decrease by reducing to 1990 levels by 2020, and an estimated 80% decrease to 1990 levels by 2050 (*8,34,35*).

To begin this colossal three step movement, the California Air Resources Board began with estimating the 1990 emissions, to serve as the baseline and target goal for 2050. The 1990 baseline was established using statewide and regional sources such as the California Energy Balance Report (CALEB), Energy Information Administration (EIA), California Energy Commission Quarterly Fuel and Energy Report, Petroleum Industry Information Reporting Act Data, and stakeholder input (*34*).

The final baseline was made public on January 1, 2008 and can be viewed in Appendix A. Concurrently, a mandatory reporting regulation was adopted into state law in December of 2007. The rule requires mandatory greenhouse gas emission reporting from the largest sources in California, approximately 800 separate industrial and commercial stationary sources which, combined, contribute 94 percent of statewide greenhouse gas stationary emissions (*8*). Typically these facilities emit more than 25,000 metric tons of $CO_2$ a year, and include electricity generating facilities, electricity retail providers, oil refineries, hydrogen plants, cement plants, and co-generation facilities (*8,9*). The first year is to be reported the beginning of 2009, consisting of 2008 greenhouse gas emissions data (*9*).

In October of 2008, the California Air Resources Board released the Proposed Scoping Plan to further implement AB 32. The Proposed Scoping Plan is an overall scope of specific actions California can take to reduce its greenhouse gas emissions (*8*). Some of these actions include expanding and strengthening energy efficiency programs, developing a cap-and-trade program, establishing individual targets for transportation-related greenhouse gas emissions, adopting and implementing measures pursuant to existing state laws and policies, and creating target fees (*8*). Implemented in conjunction, these actions will improve the environment, reduce dependence on oil, diversify energy sources, save energy, create new jobs, and promote pubic health (*8,9,35*). Policies, such as California's Global Warming Emission Standard for vehicles and renewable energy and efficiency requirements will move the state half-way toward its 2020 goal, showing the effectiveness of environmental policy (*8*). In the meantime, current progression of AB 32 implementation lies with mandatory reporting regulation. This regulation forces industries to establish greenhouse gas inventories, subsequently promoting a new beginning of emissions monitoring and greenhouse gas awareness. The cement industry, a top industrial contributor to greenhouse gas emissions, is no exception.

# CHAPTER TWO

# STATEMENT OF PROBLEM

## Introduction

In the United States alone, there are 39 companies operating 118 cement plants in 38 states (*18*). The $CO_2$ emitted from the cement production industry is the second largest industrial source of emissions in the United States (*36*). For this reason, cement plants are targeted as a major source in the California Code of Regulations to implement the Global Warming Solutions Act of 2006, AB 32, and to report and reduce their emission accordingly (*9*). In review, greenhouse gases, primarily $CO_2$, are emitted from the production of Portland cement through the chemical process itself, calcination, and energy consumption, the combustion of fossil fuels.

## Statement of Problem

This research focuses on projected greenhouse gas emissions of three Portland cement production facilities in southern California: CEMEX California Cement LLC (case study 1), Mitsubishi Cement Corporation (case study 2), and

TXI Riverside Cement Company (case study 3). For case studies 1 and 2, two greenhouse gas inventories were estimated. One represents a case in which the facility operates only on coal and 10% natural gas, and the other, represents the facility operating on alternative fuels in combination with coal, as specified by their permit to operate conditions listed in their corresponding Title V permits. In addition, two greenhouse gas inventories were generated for case study 3, one for the "old plant" in operation from the early 1950s to July of 2008, and the "new plant" in current operation as of July of 2008.

# CHAPTER THREE

# METHODS

## Introduction

The projected greenhouse gas emissions were calculated using the mandatory reporting requirements designated by AB 32 in section 95110 of the California Code of Regulations. This section is specific to cement manufacturing facilities, and focuses on the key greenhouse gas reporting requirements necessary for AB 32 compliance. According to the regulation, the required information includes reporting year emissions of process $CO_2$ emissions, stationary combustion emissions, fugitive emissions of coal storage, indirect energy usage, and efficiency metrics. Total emissions are to be reported in metric tons and include $CO_2$, $CH_4$, and $N_2O$ totals. A complete list of the data required for a typical cement manufacturing plant to report its greenhouse gas emissions to comply with this regulation can be seen in Appendix B. This research, however, is based on data obtained from public documents. Many assumptions were made throughout the emission calculations of these case studies because much of the required data is plant specific and confidential. The formulas represented, however, have not been altered from the reporting regulation methods, and represent valid totals using projected data. Because the two most contributing elements in Portland cement manufacturing are, in fact, calcination of clinker, and the combustion of fuels, these are the two areas of focus for the three case studies *(36,37)*. Fugitive emissions from coal storage and indirect energy (purchased electricity) have been omitted from the case studies. Efficiency metrics, however, were calculated for each case study comparison. The following subsections demonstrate the detailed methods on how the greenhouse gas emissions were generated for the case studies.

## Process Carbon Dioxide Emissions

Estimating process $CO_2$ emissions for cement manufacturing can be computed in two manners and conform with the mandatory reporting requirements. If the kiln is equipped with continuous emissions monitoring systems (CEMS) that directly monitors $CO_2$, then it is not necessary to compute and report process emissions because they are reported in unrelated, required kiln combustion reports.

However, if a $CO_2$ CEMS is not in use, then the process emissions are to be calculated using the Clinker-Based Methodology. All the process emissions estimated in this research were done so using the Clinker-Based Methodology. Because it is the calcination reactions of clinker formation that liberate $CO_2$, the clinker-based approach calculates $CO_2$ emissions based on the volume and composition of the clinker produced. The process-related emissions are derived from the annual clinker produced plus the amount of cement kiln dust not recycled to the kiln. The clinker-based $CO_2$ emissions were calculated for each of the case studies as follows, with two totals being calculated for case study 3, one for the "old plant" and one for the "new plant". There was no need to calculate two totals for each of the case studies 1 and 2 because fuel efficiency does not change the chemistry of the calcination reactions. The calculation is as follows:

$$\text{Clinker-based } CO_2 \text{ Emissions} = [(Cli)*(EF_{Cli})] + [(CKD)*(EF_{CKD})] + \text{TOC } CO_2 \text{ emissions}$$

Where:

Cli = Quantity of clinker produced (metric tons)

$EF_{Cli}$ = Clinker emission factor (metric tons $CO_2$/metric ton of clinker)

CKD = Quantity of Cement Kiln Dust discarded (metric tons)

$EF_{CKD}$ = CKD emission factor (metric tons $CO_2$/metric ton CKD)

TOC $CO_2$ emissions = Total organic carbon $CO_2$ emissions (metric tons of $CO_2$)

In order to compute the clinker-based $CO_2$ emission equation, the clinker and CKD emission factors must first be calculated. The clinker emission factor ($EFC_{li}$) is based on the quantity of clinker produced, the CaO and MgO content of the clinker produced, the quantity of non-carbonate sources used in the clinker produced, as well as the CaO and MgO content of those non-carbonate sources. The formula for calculating the clinker emission factor ($EF_{Cli}$) is listed below:

$$EF_{Cli} = [CaO\% - NC\ CaO\%) * (MR\ CO_2/CaO)] + [MgO\% - NC\ MgO\%) * (MR\ CO_2/MgO)]$$

Where:

$EF_{Cli}$ = Clinker emission factor (metric tons of $CO_2$/metric ton of clinker)

CaO% = CaO content (by weight) of clinker produced (%)

NC CaO% = Non-carbonate CaO content (by weight) fraction of clinker produced (%)

MR $CO_2$/CaO = Molar mass ratio = 0.785

MgO% = MgO content (by weight) of clinker produced (%)

NC MgO% = Non-carbonate MgO content (by weight) fraction of clinker produced (%)

MR $CO_2$/MgO = Molar mass ratio = 1.092

The CaO and MgO contents of the clinker produced are specific to the cement facility and are obtained from lab analysis for quality control (*9,37*). Different cement types have different ratios, for the case studies presented in this research, all process $CO_2$ emissions were assumed to be generated from the manufacturing of type II/V clinker, which is the most common type produced by each of the cement facilities in the case studies. The CaO and MgO content of type II/V clinker range between 55 to 65% for CaO, and 1 to 10% for MgO (*4*). For this research the mid values for each were used in the calculation (CaO = 60% and MgO = 5%).

Additionally, CaO and MgO contents of any non-carbonate source must be determined in order to calculate the clinker emission factor. Non-carbonate sources are any additive material used in the pyroprocessing section that do not contain carbonate ($CO_3^{2-}$). Examples of non-carbonate sources that may be used include fly ash, slag, calcium silicates, bauxite, etc. As illustrated in the clinker emission factor equation, these non-carbonate sources of CaO and MgO are subtracted from the corresponding contents of clinker. This is because any non-carbonate sources of CaO and MgO do not contain any carbonate that liberate $CO_2$ and therefore should not be counted toward the process $CO_2$ emissions generated. In fact, these sources of CaO and MgO are the products of calcining reactions that have occurred in the process that generated that particular material. Slag, for example is a metallic by-product material that is produced from smelting ore (*4*). During the smelting process, small amounts of $CO_2$ are liberated through the calcination of carbonate compounds. Because the calcination process occurs in the smelting plant where slag is produced, it does not need to be accounted for in the cement manufacturing process, otherwise it would be accounted for twice. For simplicity, it was assumed that there were no non-carbonate sources consumed in the cement process of the three case-studies. The CaO and MgO attributed to non-carbonate sources is fairly minimal, and generally contributes less than 1% of the total process $CO_2$ emissions generated (*37*).

Now that the clinker emission factor is computed, the CKD emission factor can also be tabulated. The CKD emission factor adjusts the process $CO_2$ emissions generated for the amount of uncalcinated $CaCO_3$ and $MgCO_3$ contained in CKD that is not recycled back into the system. CKD is dust generated by the rotary kiln during the pyroprocessing stage and contains uncalcined and partially calcined materials *(37)*. The CKD emission factor accounts for the amount of these uncalcined products, and is based on the clinker emission factor and the calcination rate, and is calculated as follows:

$EF_{CKD} = [(EF_{Cli}/(1 + EF_{Cli}))*d]/[1-(EF_{Cli}/(1+EF_{Cli})*d)]$

Where:

$EF_{CKD}$ = Cement kiln dust emission factor (metric tons of $CO_2$/metric ton of clinker)

$EF_{Cli}$ = Clinker emission factor (metric tons of $CO_2$/metric ton of clinker)

d = Calcination rate (%)

The calcination rate (d) is the amount of $CO_2$ associated with creating CKD and is based on loss-on-ignition data. According to the standard specifications of Portland cement, most cement types have a loss-on-ignition maximum value of 3% *(24)*. For the case studies presented in this research, a mid-value of 1.5% was used for the calcination rate. It was also assumed that there was no CKD produced that was not recycled back to the kiln for any of the three case study facilities. All three cement plants in this research do, in fact, recycle all CKD back into the system, with the exception of case study 3's "old plant" (38,39,40). The "old plant" research, however, is for comparison of technology advances, and the process $CO_2$ emissions are not expected to change, since the chemistry of cement remains unchanged. Because all CKD is recycled, no uncalcined product is lost, and therefore, the CKD emission factor for the three case studies is zero.

Once the clinker emission factor and the CKD emission factor have been determined the overall clinker-based $CO_2$ emission equation can be calculated. The final step in generating the overall process $CO_2$ emissions is to calculate the $CO_2$ emissions from organics in the raw meal. Some of the materials used to make the raw meal will contain trace amounts of organic material that can contribute to $CO_2$ emissions. To account for this release, an approximation is made assuming that 0.2% of the raw material is carbon by weight, according to the regulation's protocol (9). The emissions generated from organic carbon in the raw meal can be determined using this equation:

$\text{TOC } CO_2 \text{ emissions} = (TOC_{RM})*(RM)*(MR\ CO_2/C)$

Where:

$\text{TOC } CO_2$ emissions = Total organic carbon $CO_2$ emissions (metric tons of $CO_2$)

$TOC_{RM}$ = Total organic carbon content of raw meal (regulation protocol suggests using default of 0.2%)

RM = The amount of raw meal consumed (metric tons/year)

$MR\ CO_2/C$ = Molar mass ratio = 3.664

For the case studies in this research, the amount of raw meal consumed was determined by taking the annual clinker produced and multiplying it by 1.55, which is a default factor provided by the California Climate Action Registry's Cement Reporting Protocol for computing greenhouse gases (*37*). The annual clinker produced for each of the case studies was determined from plant specific public documents obtained from their local air district, Mojave Desert Air Quality Management District. The public documents used for obtaining any necessary plant specific data for this research were the Title V operating permits for each of the cement facilities. Title V operating permits are federally required under Title V of the federal Clean Air Act amendments passed in 1970, to help large facilities reduce air pollution (*41*). These permits are plant specific and describe explicit equipment and operations used at each facility and also describe the means by which air pollution is reduced. For this research, all the data needed was either obtained from these public Title V permits, or is a designated default as identified.

In summary, the total process $CO_2$ emissions were projected using the clinker-based methodology as seen in the first equation presented in this subsection. The clinker CaO and MgO contents were assumed as 60% and 5% respectively, and it was also assumed that there were no non-carbonate sources used in the raw meal. It was also assumed that all the CKD was recycled to the kiln, making the CKD emission factor equal to zero. Total organic carbon contributing to the process $CO_2$ emissions, assumes 0.2% of the raw material is organic carbon by weight. All formulas and calculations for these case studies were computed using Microsoft Excel spreadsheets. The spreadsheet used to calculate the process $CO_2$ emissions for the three case-studies in this research can be seen in Appendix C.

## Stationary Fuel Combustion Emissions

The mandatory greenhouse gas emission reporting requirements also requires the reporting of stationary fuel combustion emissions. In consonance with the regulation, it requires all cement plants to report emissions generated by all fuels consumed by stationary combustion sources at the facility (*35*). This includes kiln fuels as well as stationary compressors, generators, etc, and excludes all portable or mobile equipment (*9,35*). For the three case studies in this research, only the combustion emissions from kiln fuels were calculated. It was not possible to obtain all the individual information on the smaller stationary equipment in use at each of the facilities in order to account for them properly. These smaller compressor and emergency generator units most likely contribute a very small fraction of the overall combustion totals, and their omission should not affect the efficiency of the fuels. As specified in sections 95100(b) and (d) of the regulation, reporting stationary fuel combustion emissions begins with determining the types of fuels used at each facility. For this research, the kiln fuel types were determined from the corresponding Title V permits. Most all Portland cement plants use coal as the primary fuel source in manufacturing for its cost and heat content (*5*). Natural gas is the most common fuel used for kiln start-ups and shut-downs (*5*). Natural gas, on the other hand is quite expensive in comparison to coal, and is only used to heat the kiln to a hot enough temperature to allow the coal to combust on injection. For this reason, natural gas is only used for kiln start-ups and shut-downs, and only contributes between 5 and 15% of all kiln fuel consumption in most cement facilities (*2*). For this research, natural gas consumption is assumed at the mid-range value of 10% for total kiln usage.

For case studies 1 and 2, two stationary combustion emission totals were generated. One represents the cement facility running strictly on traditional fuel, coal, the major fuel source used in cement manufacturing facilities, and 10% natural gas for kiln start-ups and shut-downs. This total is referred to as "traditional fuels". The other stationary combustion emission total represents the cement facility running on coal and 10% natural gas, as well as permitted alternative fuels designated in the correlating permit, and is referred to as "alternative fuels". The permitted alternative fuels chosen for Case study 1 were tires and woodchips, and for case study 2, tires and biosolids. Despite the fact that the cement plants in this research may operate more than one kiln, only one kiln was chosen. Greenhouse gas emission totals are reported per ton of product and are not influenced by quantity irrespectively (the number of kilns generating product). For case study 3, two stationary combustion emission totals were also generated, but fuel types did not vary, the comparison here is between the "old plant" and "new plant". The "old plant" stationary combustion emission total was generated using coal, 10% natural gas, and tires, while the "new plant" total was generated using coal and 10% natural gas only.

After all of the fuel types have been identified, the next step in reporting stationary combustion emissions is to determine the annual totals of each of the fuels consumed. The regulation suggests obtaining this data from invoice purchasing data; however, this data was not available for this research. In order to estimate annual fuel consumption by type for each of the case studies, the amount of heat energy required to run the kiln was obtained from the Title V operating permits. This value is designated on the kiln operating permit within the Title V and is expressed in MMBtu per hour. The annual heat energy input for the kiln was then tabulated assuming the facility runs 24 hours a day, 365 days a year, with 90% uptime operation. Depending on the permit conditions of each fuel allowed to combust in the kiln, a percentage of total fuel for each of the fuels was documented. While there is no limit for the amount of coal that can be consumed by the kilns, there are designated limits for each of the alternative fuels: tires, woodchips, and biosolids. The maximum limit for each of the alternative fuels was assumed to be consumed in each of the case studies. The annual energy produced in MMBtus per year for each fuel were calculated by multiplying the energy input required for kiln operation and the alternative fuel limits allowed as a percent. The amount of coal used was determined by taking the energy input required for kiln operation and subtracting by the energy produced from the alternative fuels. This assumes that whatever energy input necessary that remains after the maximum permitted amount of alternative fuels have been used, is supplemented by coal. The spreadsheet used to generate the stationary combustion emission totals can be seen in Appendix D. For the "traditional fuels" stationary combustion emission totals, the alternative fuel limits were changed to zero, assuming that no alternative fuels are used to heat the kiln.

Once the annual fuel totals for each of the fuels consumed in the kiln were determined in MMBtus per year, $CO_2$, $N_2O$, and $CH_4$ combustion emissions were calculated per the regulation request using specific emission factors for each greenhouse gas. However, emissions of $CH_4$ and $N_2O$ were omitted for biomass fuels of woodchips and biosolids because these emissions are not likely significant due to the combustion conditions of the kiln (e.g. high temperatures and long residence times) *(33)*. The heat content of each of the permitted fuels for the particular kiln in question was then researched and documented. The amount of $CO_2$, $N_2O$, and $CH_4$ emitted from the annual amount of a specific fuel combusted is calculated by multiplying the annual fuel consumed (MMBtu/year) by the specific emission factor for that particular fuel (kg of gas/MMBtu). The heat contents of each of the fuels, as well as the emission factors for each fuel were either provided directly by the regulation or were obtained from other reliable greenhouse gas emission reporting sources such as the California Climate Action Registry or the World Business Council of Sustainable Development.

It should be noted, that according to the regulation, woodchips and biosolids are considered "biomass fuels" and although it is required to report the totals of biomass fuels consumed, they should not be included in the total for stationary combustion $CO_2$ emissions, for these fuels are considered "carbon-neutral" (*9,33*). For this research, the biomass fuel totals were deducted from the stationary combustion $CO_2$ total as specified in the regulation, but an additional total was also tabulated which included the biomass fuels, one for each case study, to determine the projected effects of woodchips and biosolids on $CO_2$ emissions. It is the focus of this research to project greenhouse gas emissions from the cement industry according to the specific mandatory reporting requirements of the regulation. These additional totals generated are an aside to the research, and shall be presented as such.

## Efficiency Metric

Pursuant to section 95110(e) of the regulation, cement plants are required to compute metrics that relate the plant's $CO_2$ emissions to a production variable (*9,10,37*). These metrics provide a comparison of emission rates relative to the facility's production. The regulation requires two metrics to be reported. The first is a clinker metric and is determined using the following equation:

$EM_{Cli}$ = Direct $CO_2$ produced / [(clinker consumed or added to stock) + (clinker sold)]

Where:

$EM_{Cli}$ = Efficiency metric of clinker ($CO_2$ metric tons/metric ton clinker)

Direct $CO_2$ produced = total $CO_2$ emissions from cement manufacturing ($CO_2$ metric tons)

Clinker consumed or added to stock = any clinker produced from the reporting facility that is consumed to make cement product or is stored for later use (metric tons)

Clinker sold = any clinker produced from the reporting facility that is sold (metric tons)

For this research, two clinker efficiency metrics were calculated for each of the three case studies. For case studies 1 and 2, a clinker efficiency metric was determined for the "traditional fuels" scenario, and one for the "alternative fuels" scenario. For case study 3, a clinker efficiency metric was calculated for both the "old plant" and the "new plant". In all the case studies, it was assumed that all the clinker produced was consumed to make cement product. For this research, "direct $CO_2$ produced" represents the total process $CO_2$ emissions calculated plus the total $CO_2$ emissions generated from stationary combustion of fuels. It should be noted that the "direct $CO_2$ produced" neglects to include $CH_4$ and $N_2O$ totals emitted from stationary combustion of fuels. It is currently not required by the regulation to include $CH_4$ and $N_2O$ in the efficiency metric calculations, so these metrics only reflect $CO_2$ emission rates.

The second efficiency metric required by the mandatory reporting regulation is for cementitious product. This efficiency metric is more inclusive than the clinker efficiency metric because it does not just include the clinker produced, but also any additional materials used by the cement facility such as cement substitutes and gypsum (*28*). This means that this efficiency can be adjusted in contrast to the clinker efficiency metric. The cementitious product efficiency metric is calculated as follows:

$EM_{CP}$ = Direct $CO_2$ produced / [(clinker consumed or added to stock) + (clinker sold) + (gypsum) + (cement substitutes)]

Where:

$EM_{CP}$ = Efficiency metric of cementitious product ($CO_2$ metric tons/metric ton clinker)

Direct $CO_2$ produced = total $CO_2$ emissions from cement manufacturing ($CO_2$ metric tons)

Clinker consumed or added to stock = any clinker produced from the reporting facility that is consumed to make cement product or is stored for later use (metric tons)

Clinker sold = any clinker produced from the reporting facility that is sold (metric tons)

Gypsum = the amount of gypsum blended with the clinker to make cementitious product (metric tons)

Cement substitutes = the amount of any cement substitutes such as limestone, CKD, or clinker

substitutes that are blended to make
cementitious product (metric tons)

As illustrated by the above formula, this efficiency metric demonstrates an approach where clinker, gypsum, and cement substitutes are a reduction strategy for $CO_2$ emissions. The spreadsheet used to calculate the efficiency metrics can be seen in Appendix E. In this research, two cementitious product efficiency metrics were tabulated for each of the case studies, in similar correlation to the clinker efficiency metrics. One each for the "traditional fuels" and "alternative fuels" scenarios, for case studies 1 and 2, and one for both "old plant" and "new plant", for case study 3. Again, it was assumed that all clinker produced was consumed. Gypsum was assumed to be 5% of the final cement product, as most II/V cement product is approximately 5% gypsum (*22*). According to the standard requirements of ASTM C 150 (Portland cement) the maximum limit of limestone sent to the finish mills is 5% of final product (*24*). For this research, a mid-value of 2.5% limestone of final product was used. It was also assumed that none of the case study facilities consumed any other cement substitute other than limestone. Since limestone is the most commonly consumed, all other substitutes must have limits less than 5% of final product to meet ASTM specifications, which is negligible to emission totals (*24*).

# CHAPTER FOUR

# RESULTS AND DISCUSSION

## Results

The results of the clinker-based approach to project the process $CO_2$ emissions of each of the three case studies can be seen in table 6.

Table 6. The Annual Clinker Produced for the Three Case Studies in Question and the Corresponding Carbon Dioxide Generated from the Clinker Forming Process Based Upon the Clinker-based Method.

| **Case Study** | **Annual Clinker produced (metric tons)** | **Process $CO_2$ Emissions (metric tons)** |
|---|---|---|
| 1 | 1,642,500 | 882,611 |
| 2 | 1,653,097 | 888,305 |
| 3 "old plant" | 197,100 | 105,913 |
| 3 "new plant" | 1,971,000 | 1,059,133 |

The annual clinker produced by the chosen kiln researched for each case study facility is presented along with the annual corresponding $CO_2$ emissions generated by that kiln. As seen in the table, there are two totals presented for case study 3, one for the "old plant" and another for the "new plant". This is because these process emission totals represent different facility operations, most notably, significantly different kilns.

Case study 2 was projected to produce the most clinker at 1,653,097 metric tons, and proportionately produce the greatest amount of process $CO_2$ emissions at 888,305 metric tons. The smallest producer of process $CO_2$ emissions projected was that of case study 3, the "old plant", coinciding with its annual mere 197,000 metric tons of clinker production for this small kiln capacity of just 25 metric tons per hour (*39*). Case study 3's "new plant", in contrast produces ten times as much clinker than its older relative, and exactly ten times as much process $CO_2$ emissions, as well. Case study 2 projected totals came in just below case study 3's "new plant" at 1,642,500 metric tons of annual clinker production, and 882,611 metric tons of $CO_2$ process emissions. The results suggest that there is definite correlation between annual clinker production and process $CO_2$ emissions generated, which is to be expected since it is the calcinating reactions of clinker that primarily contribute to $CO_2$ liberation (*7,31*).

The projected stationary combustion emission results are listed in tables 7 and 8.

Table 7. The Annual Energy Input Required by the Case Study Kiln in Question.

| Case Study | Required Energy Input of Kiln (MMBtu/year) |
|---|---|
| 1 "traditional fuels" | 4,927,500 |
| 1 "alternative fuels" | 4,927,500 |
| 2 "traditional fuels" | 5,920,884 |
| 2 "alternative fuels" | 5,920,884 |
| 3 "old plant" | 1,024,920 |
| 3 "new plant" | 5,676,480 |

Table 7 shows the required amount of energy needed for kiln operation, while table 8 displays the total $CO_2$, $CH_4$, and $N_2O$ annual emissions released in order to generate that amount of energy required. Case study 2 appears to require the greatest amount of energy input for kiln operation at 5,920,884 MMBtu per year, and consequently, produces the largest amount of $CO_2$ emissions when running on "traditional fuels" of coal and 10% natural gas. Remarkably, the stationary combustion emission total of 529,445 metric tons of $CO_2$ from "traditional fuel" usage dropped significantly to 352,258 metric tons of $CO_2$ with "alternative fuel" usage of tires and biosolids in this case study.

Table 8. Emissions Generated from Stationary Combustion of Kiln Fuels in Each of the Case Studies.

| Case Study | Stationary Combustion $CO_2$ Emissions (metric tons) | Stationary Combustion $CH_4$ Emissions (metric tons) | Stationary Combustion $N_2O$ Emissions (metric tons) |
|---|---|---|---|
| 1 "traditional fuels" | 440,617 | 52 | 7 |
| 1 "alternative fuels" | 346,360 | 69 | 9 |
| 2 "traditional fuels" | 529,445 | 63 | 9 |
| 2 "alternative fuels" | 352,258 | 35 | 5 |
| 3 "old plant" | 95,410 | 7 | 1 |
| 3 "new plant" | 519,057 | 62 | 9 |

Case study 1 reduced their projected stationary combustion $CO_2$ emissions by about 94,000 metric tons when "traditional fuels" were replaced with "alternative fuels" of tires and woodchips. Case study 3 illustrates a significant increase in required energy input with the "new plant" operation, and as expected, a correlating increase in stationary combustion emissions.

The table also shows that a very minimal amount of $CH_4$ and $N_2O$ are produced relative to $CO_2$. "Traditional fuel" usage contributes more $CH_4$ and $N_2O$ than "alternative fuel" use with the exception of case study 1 whose alternative fuels included tires and woodchips.

Table 9 illustrates the stationary combustion $CO_2$ emissions generated for case studies 1 and 2's "alternative fuel" projection, comparing the inclusion and exclusion of biomass fuels.

Table 9. The Effects of Biomass Fuels on Stationary Combustion Carbon Dioxide Emissions Generation.

| **Case Study** | **Stationary Combustion $CO_2$ Emissions (metric tons) Excluding Biomass Fuels*** | **Stationary Combustion $CO_2$ Emissions (metric tons) Including Biomass Fuels** |
|---|---|---|
| 1 "alternative fuels" | 346,360 | 438,869 |
| 2 "alternative fuels" | 352,258 | 572,723 |

* As required by AB 32 regulation.

The table suggests that excluding these carbon-neutral fuels significantly reduces the amount of $CO_2$ emissions of case study 1 were reduced by 92,509 metric tons with the exclusion of biomass fuels, and emissions generated from combustion. The projected $CO_2$ case study 2, by 220,465 metric tons.

Table 10 displays the results of the projected efficiency metric totals for each of the case studies.

Table 10. The Annual Projected Efficiency Metrics for Each of the Case Studies, Comparing Fuel Scenarios for Case Studies 1 and 3, and the Facility Modifications for Case Study 3.

| Case Study | Clinker Efficiency Metric (metric tons of $CO_2$/metric ton of clinker) | Cementitious Product Efficiency Metric (metric tons of $CO_2$/metric ton of clinker) |
|---|---|---|
| 1 "traditional fuels" | 0.8076 | 0.7513 |
| 1 "alternative fuels" | 0.8072 | 0.7509 |
| 2 "traditional fuels" | 0.8600 | 0.8000 |
| 2 "alternative fuels" | 0.7504 | 0.6981 |
| 3 "old plant" | 1.008 | 0.9381 |
| 3 "new plant" | 0.8027 | 0.7467 |

The middle column compares the clinker efficiency metric of the "traditional fuels" scenario compared with the "alternative fuels" scenario for case studies 1 and 2, and the "old plant" versus the "new plant" for case study 3. Similarly, the column on the right compares the cementitious product efficiency metrics of each of the case studies respectively. Both the clinker and cementitious product efficiency metric values seemed to have decreased with the projected "alternative fuels" scenario for both case studies 1 and 2, however, the metrics decreased more significantly in case study 2. This suggests an increased $CO_2$ efficiency when the facility runs on alternative fuels. For example, the clinker efficiency metric declined from 0.8600 metric tons of $CO_2$ per metric ton of clinker to 0.7504 in case study 2, and only 0.8076 to 0.8072 in case study 1. The cementitious product efficiency metric decreased by only 0.0004 metric tons of $CO_2$ per metric ton of cementitious product for case study 1, while case study 2 decreased by 0.1019.

Figures 7 and 8 on the next two pages show individual comparisons of the efficiency metrics for case studies 1 and 2. Figure 7 displays the decreased efficiency metric values for case study 1, and figure 8 shows the decreased metric values for case study 2. Both indicate a decreased value trend, indicating less $CO_2$ is produced per ton of clinker or cementitious product when the case study facility is fueled on alternative fuels.

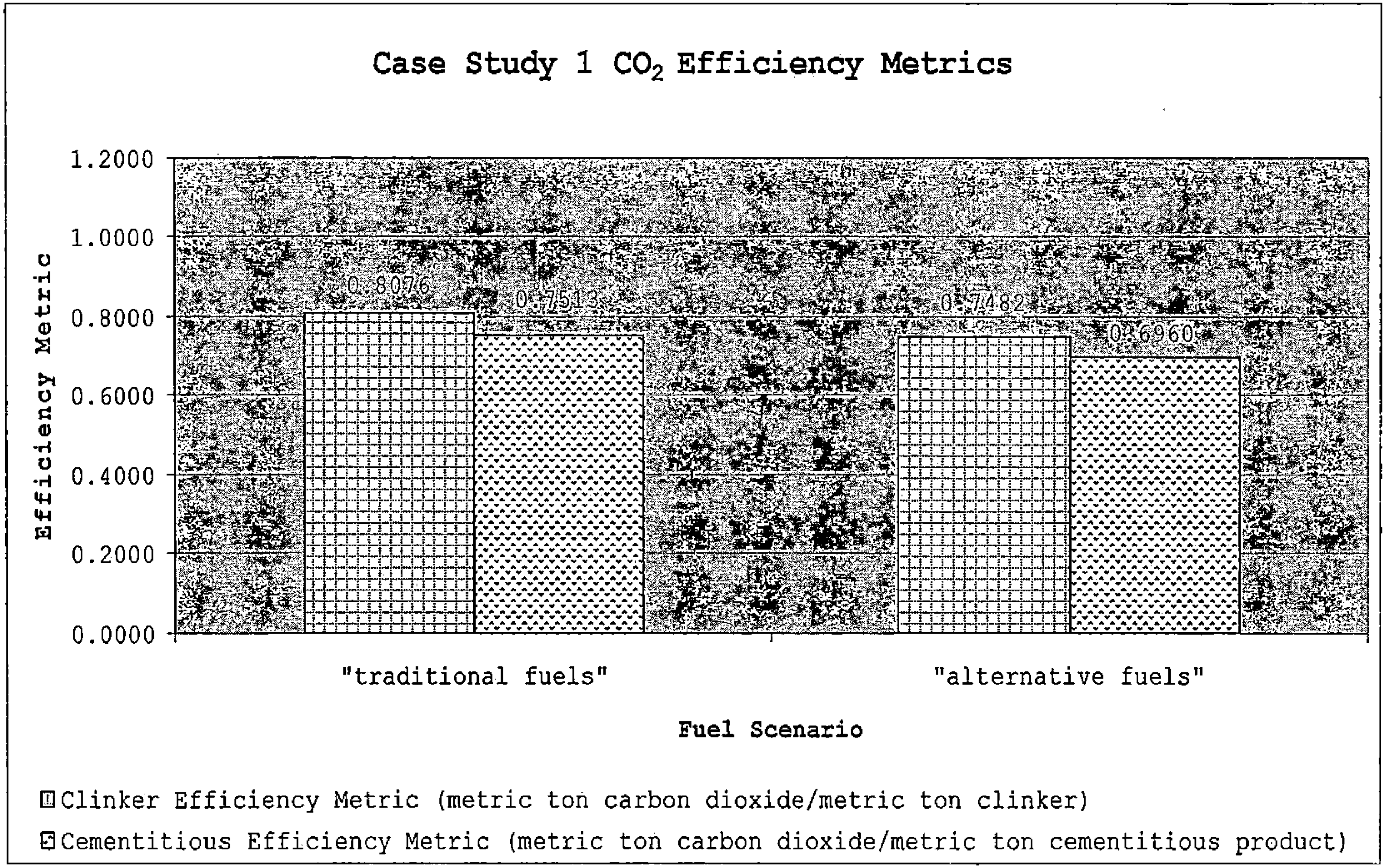

Figure 7. Comparison of Efficiency Metric and Cementitious Product Efficiency Metric for Case Study 1.

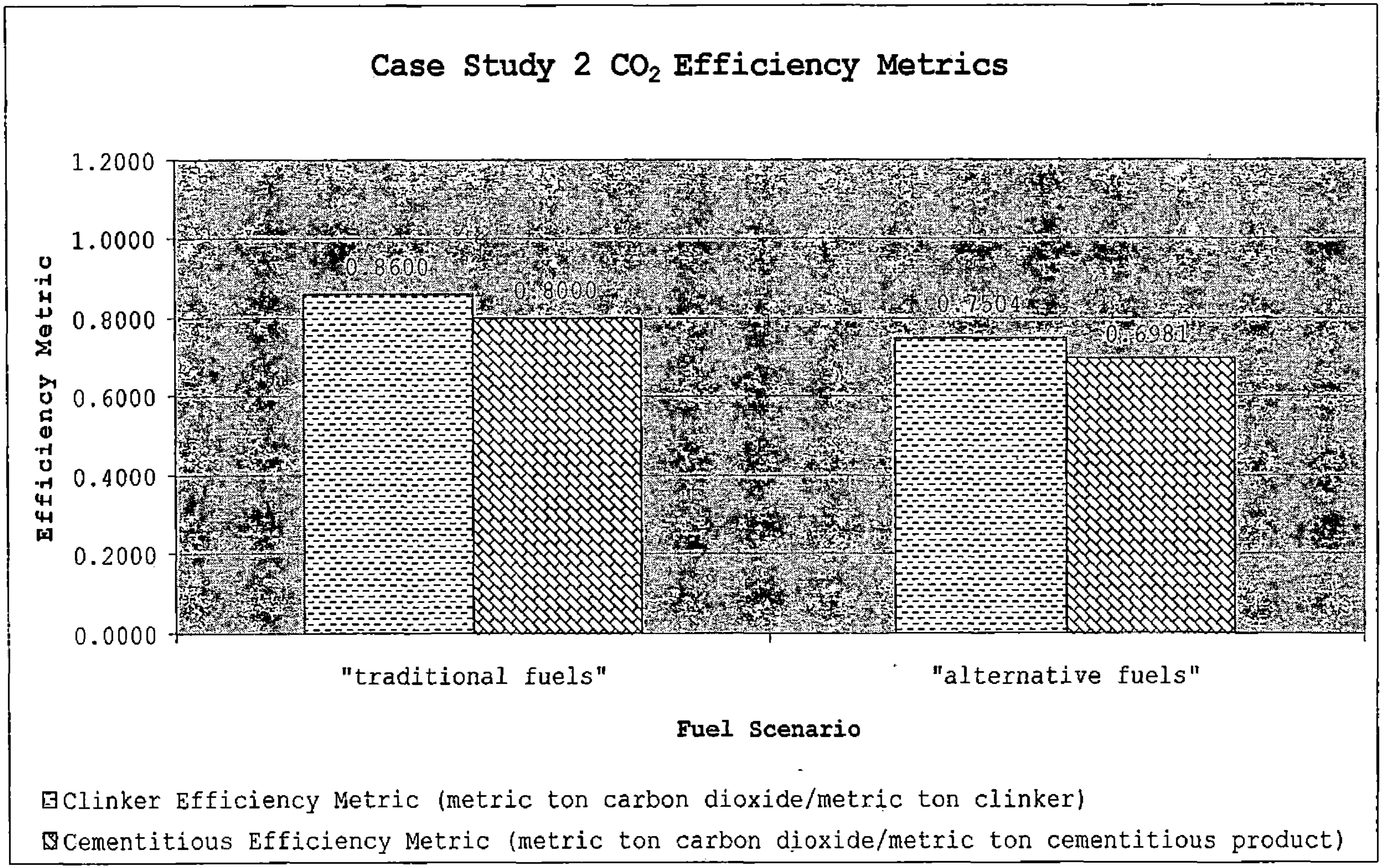

Figure 8. Comparison of Efficiency Metric and Cementitious Product Efficiency Metric for Case Study 2.

Both of the efficiency metrics appeared to have a decreased value in case study 3 as well. Case study 3's "old plant" resulted in a projected 1.008 metric tons of $CO_2$ per metric ton of clinker for the clinker efficiency metric, and 0.9381 metric tons of $CO_2$ per metric ton of cementitious product for the cementitious product efficiency metric. Both of these projected values significantly decreased with the "new plant" operations, with a clinker efficiency metric result of 0.8027 metric tons of $CO_2$ per metric ton of clinker, and a cementitious efficiency metric of 0.7467 metric tons of $CO_2$ per metric ton of cementitious product. Figure 9 on the next page illustrates the comparison of both efficiency metrics for both the "old plant" and "new plant" of case study 3. Again, the figure suggests a decreased efficiency metric value for both metrics, corresponding to an increased $CO_2$ efficiency for the "new plant" facility.

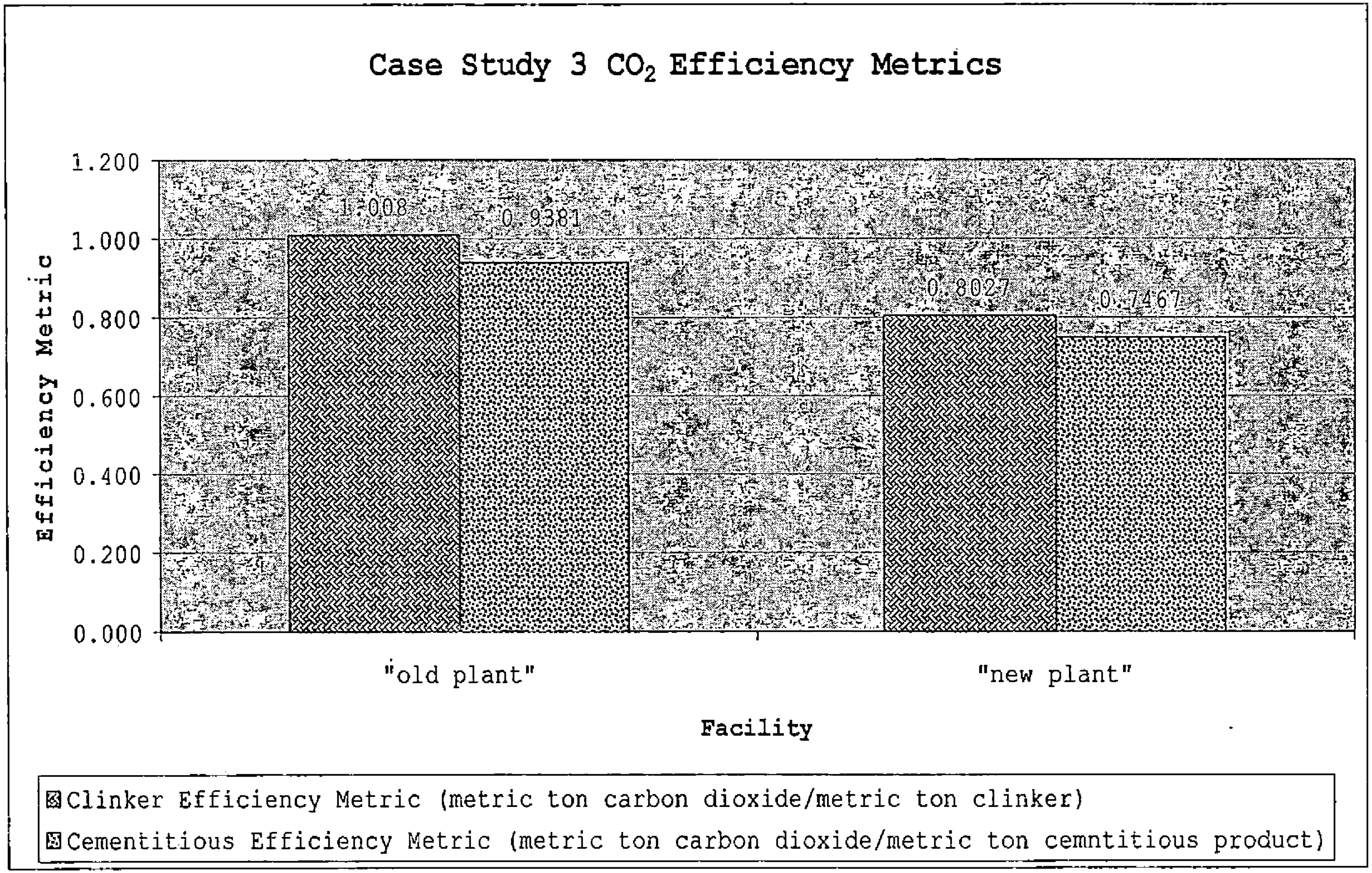

Figure 9. Comparison of Efficiency Metric and Cementitious Product Efficiency Metric for Case Study 3.

The last figure presented, figure 10 on the following page, displays the projected efficiency metrics for the alternative fuel scenarios of case studies 1 and 2. This chart illustrates both the clinker efficiency metric and the cementitious product efficiency metric for alternative fuel usage, including and excluding biomass fuels, which in this research are woodchips, in case study 1, and biosolids, in case study 2. Figure 10 suggests that the inclusion of these biomass fuels increases both the projected clinker and cementitious product efficiency metric values in each of the case studies. This correlates to more metric tons of $CO_2$ actually released per ton of clinker and cementitious product. For instance, case study 1's projected clinker efficiency metric value increased from 0.7482 metric tons of $CO_2$ to 0.8046 with the inclusion of these biomass fuels in the emissions reporting. A 7.5 % decrease in efficiency. All the metric values increased in both case studies 1 and 2, with case study 2 having a more significant projected increase, suggesting that the biomass fuel used in this case study (biosolids), emit more $CO_2$ than the biomass fuel consumed in case study 1 (woodchips). The cementitious product efficiency metric value rose 17.7% with the inclusion of biosolid emissions.

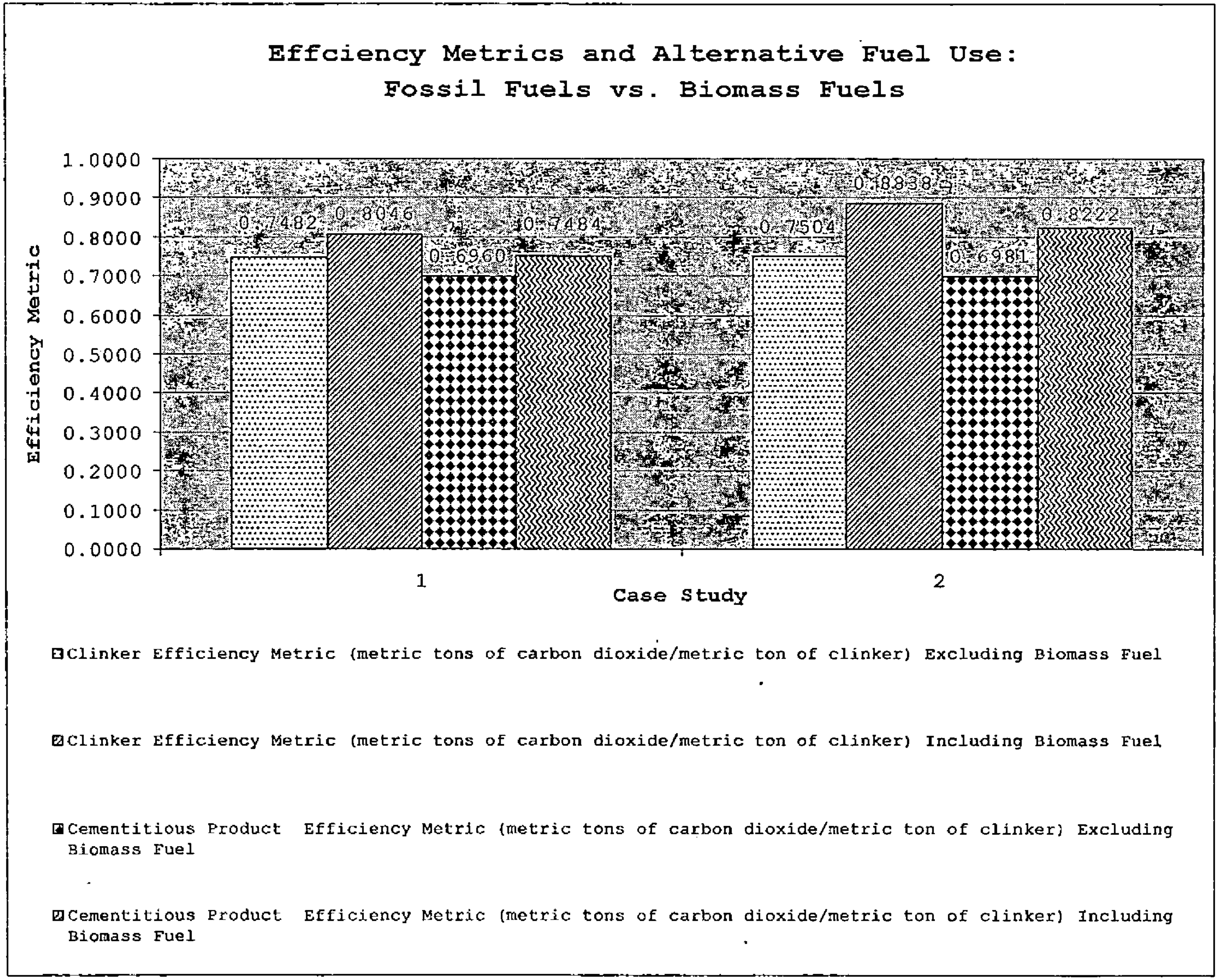

Figure 10. Comparison of the Effects of the Inclusion of Biomass Fuels on Emission Efficiency.

# Discussion

The findings in this research suggest that process $CO_2$ emissions increase as the production of clinker increases. This seems to correlate with previous studies, stating that it is the calcination of clinker that generates nearly 50% of all $CO_2$ emitted from cement production due to the $CO_2$ liberation of these clinker reactions(7). It is apparent from the projected results of this research that an increase in clinker production correlates to an increase in the required calcining reactions, which in turn, liberates an increased amount of $CO_2$ by-product. As indicated in the "Portland Cement Chemistry" chapter of this research, it is these calcining clinker reactions that are the heart of Portland cement clinker. Without the calcination reactions that free lime (CaO), the four trademark compounds of Portland clinker would not be able to form, for, as discussed previously, they are dependent upon the ratio of free lime and that of silica, alumina,, and ferric oxides (4). These findings lead to two conclusions: 1) process $CO_2$ emissions are, in fact, produced from the calcining reactions that form clinker, and 2), it is not likely that the chemistry of the process can be altered to reduce $CO_2$

emissions, and still produce the trademark clinker of Portland cement. Since Portland cement chemistry cannot be changed, some studies suggest the use of low-energy cements as an alternative. One study, discusses the alternative production of low energy belite cement. It is produced under reduced temperatures and lower lime saturation factors compared to traditional Portland cements, and therefore, produces much less $CO_2$ per ton of clinker(*42*). The reduced temperatures correspond to a decrease in fuel usage, and hence, a decrease in stationary combustion $CO_2$ emissions. The lower lime saturation factor also contributes to decreased fuel usage in that it requires less energy to calcine the raw materials (*42,43*). The lower lime saturation factor also showed a decline in $CO_2$ generated from calcination because there is less $CaCO_3$ in the raw feed in general, resulting in less $CO_2$ by-product formation (*5,42*). In summary, the study suggests that the energy required to produce low energy belite cement is 500-540 kJ/kg of clinker less than that required to produce Portland cement (*42*). The low energy cement also showed a longer hardening period, which after 90 days of curing, demonstrated an increased compressive strength in comparison to traditional Portland cement (*42,43*). "Such low energy cements may provide a cheap alternative to Portland cement with properties that are acceptable for many applications and the additional benefit of possible durability" (*42*).

Another study suggests an additional strategy in reducing process $CO_2$ emissions through the use of pozzolans. Pozzolans are reactive aluminosilicates that when added to the raw materials of Portland cement, serve as a secondary reactant with free lime (*1*). The pozzolanic reactions are rather slow, which is in fact the advantage of these pozzolan-mixed cements because while the formation of alite and belite occur fairly quickly, the slower pozzolanic reactions serve to use up any remaining free lime in the mix (*1*). By using up the remaining free lime, the efficiency of the cement manufacturing is increased since less lime will be required because less is wasted, and subsequently less calcining reactions will occur (*1*). A draw back to pozzolan use is that it requires elevated curing temperatures to insure good strength development (*43*). While the study did not elaborate on the extent of the required curing temperature, it seems that the elevated temperatures may partially negate the any $CO_2$ emissions saved from the manufacturing process to some extent.

It appears that although there may be alternatives to Portland cement that in turn reduce process $CO_2$ emissions, these alternatives are, in fact, alternatives, and do not yield traditional Portland cement, which is the most widely used concrete material in the world (*2*). Since Portland cement chemistry and its calcining reactions cannot be altered without altering its trademark clinker, it is logical that greenhouse gas reduction methods focus on that of fuel efficiency and technology.

The projected greenhouse gas emissions tabulated according to the mandatory reporting requirements of the regulation, indicated that the results of both case studies 1 and 2 showed a significant drop in stationary combustion $CO_2$ emissions when the facilities consumed alternative fuels (please see table 8). Case study 1 reduced their projected stationary combustion $CO_2$ emissions by 94,257 metric tons with the addition of tires and woodchips, and case study 2, reduced their projected stationary combustion $CO_2$ emissions by 177,187 metric tons with the addition of tires and biosolids. Correspondingly, both of the efficiency metrics for case studies 1 and 2 also declined, suggesting that less $CO_2$ per ton of clinker, or cementitious product, is generated. It should be noted that these projected totals reflect the requirements of the regulation, in which $CO_2$ emissions generated from biomass fuel combustion (woodchips and biosolids) are excluded from the totals because they are deemed carbon-neutral by the regulation.

An interesting aside to this research, suggests that when the $CO_2$ emissions generated from the combustion of biomass fuels are included, the total amount of projected stationary combustion $CO_2$ emissions actually increases (please see table 9). In this research, the projected use of tires, woodchips, and biosolids consumed as specified in permitted conditions listed in the corresponding Title V permits, assuming half the allowed limit, led to an increase in $CO_2$ emissions. The reasoning behind the exclusion of $CO_2$ emissions generated from biomass fuel, according to the World Business Council of Sustainable Development, is that the carbon in biomass fuels is of biogenic origin, meaning it was recently contained in living tissues, in contrast to carbon in fossil fuels which have been trapped for millennia in geologic formations (*9,33,44,45,46*). Because of their biogenic origin, biomass fuels are considered carbon-neutral since they do not disrupt the net zero carbon emission balance (*9,33,44,46*). That is, they offset the amount of carbon released with an equivalent amount sequestered due to their biogenic origin and relatively quick turnover (*9,33,44,46*). However, "if, at the national level, biomass harvests exceed growth and regeneration, the resultant depletion of biomass stocks results in a net emission" (*44*). For this reason, the regulation requires that all biomass fuels consumed are to be reported, although tabulated separately, and excluded from the stationary emission totals (*44,46*).

Returning to the original intention of this research, projecting the stationary combustion $CO_2$ emissions according to the specifications in the mandatory reporting requirements of the regulation, biomass fuels are, in fact excluded. Although the brief aside into their inclusion may not be easily ignored, studies suggest that the use of alternative fuels do offer some more promising benefits, both ecologically and economically speaking. First and foremost, alternative fuels consists of industrial, municipal, and hazardous wastes and mixtures thereof (*47*). These wastes are only applicable as a fuel sources if they have appropriate chemical energy content and do not ultimately affect the quality of the clinker (*48*). Just as fossil fuels such as coal, oil, and natural gas contain hydrocarbons, waste, or alternative, fuels must also contain viable amounts of combustible organic content (*47*). For example, waste tires are an excellent source of alternative fuel, for they have a higher fuel value, pound for pound, compared to coal (*49*). With hundreds of millions of used tires generated annually, that are otherwise disposed of in incinerators, recycling them into a kiln fuel can actually recover their energy (otherwise lost), and conserve fossil fuel resources (*49,50*). In specific regards to the cement industry, the United States Environmental Protection Agency states that tire-derived fuel contains 25% more energy than coal, and with every metric ton of tire-derived fuel consumed, the cement facility can replace 1.25 metric tons of coal (*48*).

In contrast, other waste fuels such as woodchips and biosolids have lower fuel values than traditional coal, however, these fuels are not without similar benefit. Burning wastes such as woodchips and biosolids, or any waste fuel, essentially lessens the environmental burden of waste disposal sites and specially designed incinerators (*51,52,53,54,55*). The cement kiln, as it turns out, is an optimal waste incinerator. Some of the most notable factors contributing to its success are the kiln's extremely high temperatures (sometimes reaching near

1400°C), kiln length, long time period the fuel/waste remains inside the kiln, and the alkaline environment within the kiln (*47,49,50,52*). Perhaps even more remarkable, unlike designated disposal incinerators, cement kilns do not generate any waste residue. "The process of fuel combustion in rotary cement furnaces is a non-waste process, as the ash created as a result of incineration is contained in the clinker produced" (*49*).

Some studies even suggest that the burning of alternative fuels in combination with the highly alkalinity of the kiln helps to reduce other pollutants such as $NO_x$, $SO_x$, and VOCs emitted from the manufacturing process (*52*). Even with waste fuels such as municipal solid waste or sewage sludge, in which heavy metals and salts are abundant, the extreme temperatures of the kiln incinerate the waste as fuel without emitting harmful levels of heavy metals, dioxins, or furans (*54*). Ultimately other studies indicate that cement production can be a feasible alternative for waste management (*48,49,51,52*). "Application of alternative fuels made from waste may allow one to reduce the amount of waste to be disposed of by up to 50%" (*49*).

Because waste fuels are waste products, they not only offer ecological benefits but also economical benefits. Alternative or waste fuels are significantly cheaper to acquire than traditional fossil fuels such as coal and oil, since they do not have to be mined or refined, costs are most often limited to transportation and equipment modifications (*53*). The average energy required to produce one metric ton of cement about 3.3 GJ which correlates to about 120 kg of coal (*47*). The use of alternative fuels can reduce the amount of coal consumed, and the environmental load associated with the transport of alternative fuels is still lower when compared to the transport of coal, even with the corresponding decrease associated with fossil fuel production and transport (*53*).

In summary, continued use of alternative fuels in the cement industry may prolong the economic and ecological benefits of their use by diverting waste from landfills and reducing the dependence upon fossil fuels. The incineration of waste in cement kilns has proven to be a safe method for disposal and is both economically abiding and profitable for the industry. From a greenhouse gas standpoint, currently the exemption of biomass fuels promotes their use as well, although their careful monitoring in the global carbon flux appears to be an important factor in their stability. Another interesting point, similar to that of the biomass fuel exemption, is that waste fuels are also often given a $CO_2$ emission factor of zero, despite their contribution to $CO_2$ emissions often exceeding that of coal, since the input of waste ultimately replaces an equivalent amount of fossil fuel-derived energy (*56*). For example, according to the California Climate Action Registry, the $CO_2$ emission factor of biosolids is 116 kg per million Btu whereas the $CO_2$ emission factor for coal is 93.46 kg per million Btu, indicating that more $CO_2$ is actually emitted with the use of an alternative fuel (*28*). The justification behind this exemption is that the waste, whose $CO_2$ would have otherwise been released into the atmosphere, is now being utilized for energy consumption (47,57,58). This exemption, like that of the biomass fuel exemption seems to provide another loop-hole that promotes alternative fuel use.

After examining the projected results of process and stationary $CO_2$ emissions and the emission mitigation options for each of these major emission sources of cement production, there is one more aspect of this research to discuss. Case study 3 compared the projected emissions of two scenarios: 1) the "old plant" consisting of predominantly 1950s cement manufacturing technology, and 2) the "new plant" representing state-of-the-art cement manufacturing technology in operation since July of 2008. The most valuable comparison in these two scenarios are the efficiency metrics, for they represent the efficiency of each of the facilities ton per ton and not by production totals. As seen in figure 9, both the clinker efficiency metric and the cementitious product efficiency metric projected values decreased significantly, suggesting that the "new plant" facility is more efficient in operation than the "old plant" facility. This suggests that the technology of the "new plant" is capable of reducing $CO_2$ when compared to the 1950s technology of its "old plant" precursor. According to the corresponding Title V permits, the "old plant" kiln used in this study is described as a "long dry kiln" with a capacity of 600 short tons of clinker per day. In contrast the "new plant" permits describe their kiln as a "5-stage preheater/precalciner dry kiln" with a capacity of 6,000 short tons of clinker per day. Already, the significance of the advancements in technology can be seen, for the "new plant" kiln produces ten times as much clinker as the "old plant" kiln, and yet the projected clinker efficiency metric value decreased from 1.008 metric tons of $CO_2$ per metric ton of clinker to 0.8027. Both kilns being "dry kilns" have a significant efficiency increase over "wet kilns" utilized in the wet process, for a tremendous amount of energy is saved due to the already dry materials utilized in the dry process (*53*). In fact, the conversion of primarily wet process facilities to dry process facilities between 1970 and 1997 lead to an average 4% decrease per year in overall energy consumption (*2*).

Even though both are "dry kilns", the "5-stage preheater/precalciner kiln" of the "new plant" demonstrates even more efficiency than the "old plant's" simple "long dry kiln". Preheater kilns greatly improve efficiency by warming the raw meal before it enters the kiln with hot kiln exit gases in a tower of heat exchange cyclones (*19*). The most common design is a parallel four stage preheater (see figure 11 on the following page), in which the top, #4, stage reaches temperatures of 340°C (*20*).

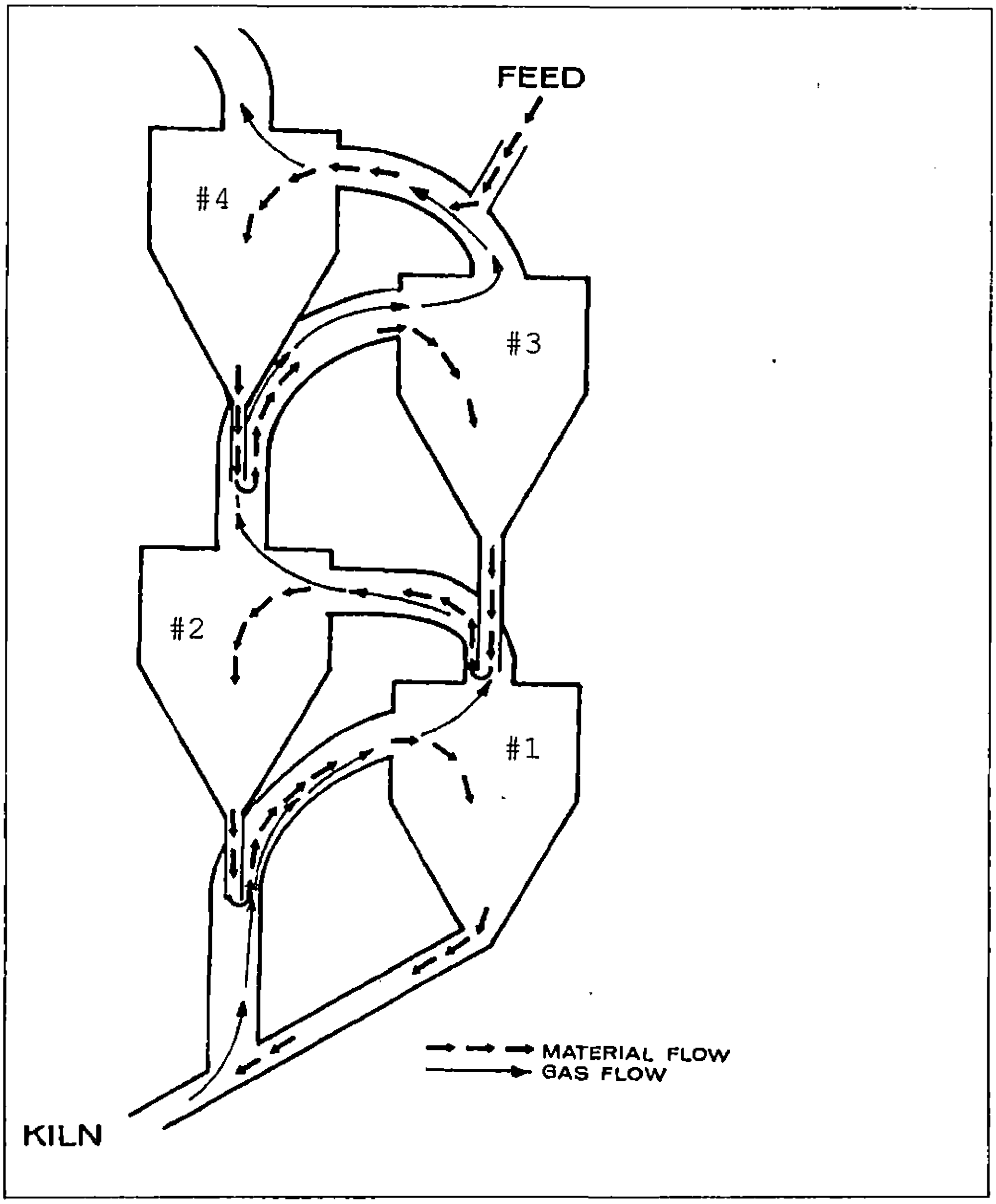

Figure 11. Illustrations of a Parallel Four-Stage Preheater Tower.

Alsop, Philip A. *The Cement Plant Operations Handbook*, $2^{nd}$ Edition. Tradeship Publications Ltd: Houston, 1998; pp. 3-73.

One drawback to this preheater design is that plug-ups can occur in the lower cyclone stage and kiln inlet due to high concentrations of volatile constituents such as alkalis, sulfur, and chlorides in the exhaust (*19*). Despite this hitch, suspension preheater kilns are the most energy-efficient types of kilns offered in the industry (*56*). Precalciners, are essentially preheaters with an additional secondary firing system, or furnace, at the lower stage of the tower at the feed end of the kiln (*20*). It is this secondary furnace that makes these types of kilns slightly less efficient than preheater kilns, however, the additional firing at the feed end of the kiln, reduces the amount of fire needed near the burning zone of the kiln, improving the overall refractory life (*19*). Another bonus is the precalcining furnace is also capable of consuming lower-grade cheaper fuels without altering the quality of the product (*20*). The intense, cheaply produced fire at the inlet of the kiln, begins to calcine the raw meal as it enters the kiln (*22*). Preheater and precalciner kilns are, therefore, much more efficient in terms of greenhouse gas emissions, primarily $CO_2$, because the warming of the raw meal prior to its entrance to the kiln decreases the amount of energy, and thus fuel, required in traditional dry kilns, since the waste heat provides optimal warming that promotes the necessary calcining reactions of clinker (*17*). The "old plant's" simple "long dry kiln" was not equipped with such preheaters/precalciners, and the "long" portion of the kiln name is most likely attributed to the characteristically long length of kilns from that time period. "Long dry kilns" were typically longer because they required the raw meal to remain in the furnace longer in order to achieve effective calcination (*22*). The only "preheating" of sorts that these older kilns did harbor was that of a conducting "hanging chain section" near the inlet, which also attributed to their increased length (*22*).

The kiln and pyroprocessing portion of the cement manufacturing process is not the only area in which efficiency may be gained. Chiefly, energy savings, which subsequently reduce greenhouse gases associated with fuel combustion, are another significant target. Raw material preparation and finish grinding, in particular, are two other areas where energy efficiency may be gained (*56*). Although the indirect generation of $CO_2$ emissions from electricity consumption was omitted from this research, this sector contributes heavily to anthropogenic emissions, and equipment modifications that consume less electricity are excellent ways to reduce $CO_2$ emissions (*28,59*). For instance, installing more efficient transport systems, and high-efficiency roller mills may significantly reduce energy costs and $CO_2$ generation (*56*). Raw material and finish grinding is the highest unit consumption of power in the cement manufacturing process, and the installation of roller type mills can decrease this consumption by nearly half (*14*). In addition, some designs of vertical-type roller mills combine raw material drying with grinding by recycling large quantities of waste heat from the kilns or clinker coolers (*56*). In regards to coolers, there are also more efficient clinker cooler designs such as rotary coolers, which do not require electric air fans to push air along, in contrast to the predominantly used grate cooler (*56*). In essence, energy conservation plans may include full scale equipment modifications such as these, as well as, measures as simple as changes in staff behavior and attitude that change a company's approach to energy efficiency and day-to-day practices (*56,59*). There seems to be no savings too big or too small to consider. A study of the Indian cement industry, investigating efficiency improvements, resulted in an improvement potential near 33%

when utilizing commercially available technology such as those described *(60)*. The study also generated an estimate of future technologies sequestering almost 48% of energy savings that would lead to $CO_2$ emission reductions of 27% *(60)*.

In addition to equipment modifications and energy conservation, modern cement facilities are also often equipped with emission control devices and technologies to further reduce the amount of pollutants entering the atmosphere. As discussed in the chemistry section of this research, there is an array of subsequent gaseous pollutants emitted from cement manufacturing, as well as a significant amount of particulate matter (PM). "The principal gaseous emissions from the pyroprocessing system in a typical descending order by volume are nitrogen, $CO_2$, water, oxygen, $NO_x$, $SO_2$, CO, and hydrocarbons *(29)*. The progressing environmental consciousness of today has lead to required monitoring enforced by governing air pollution control districts of pollutants, which exhibit greenhouse effects, as well as, other threatening environmental effects such as smog and acid rain *(30)*. As discussed previously, Continuous Emission Monitoring Systems (CEMS) can be used to monitor the individual concentration of each of these pollutants, to ensure that their emittance is below permitted limits. No two kilns operate exactly alike, and concurrently, there may be no apparent reason for the difference in behavior for identically appearing kiln systems operating at the same time, and therefore, no control measure is a perfect solution for all kiln systems (*61,62*). Table 11 on the following page lists the gaseous pollutant-control technologies that are currently available for cement kiln along with their synergetic and counteractive effects.

Table 11. Existing Control Technologies for Gaseous Pollutants Emitted from Portland Cement Manufacturing.

| Existing Control Technology | Targeted Pollutant | Synergistic Effects | Counteractive Effects |
|---|---|---|---|
| Inherent scrubbing | $SO_2$ | Process specific | Process specific |
| Oxygen increase | $SO_2$, CO | | $NO_x$, $CO_2$ |
| Oxygen decrease | $NO_x$ | $CO_2$ | $SO_2$, CO, product color and quality |
| Fuel substitution (lower sulfur) | $SO_2$ | Fuel specific | Fuel specific |
| Raw material substitution (containing lower sulfide) | $SO_2$ | Material specific | Material specific |
| Raw material substitution (containing lower organics) | CO | Material specific | Material specific |
| Raw material alkali/sulfur balance | $SO_2$ | Material specific | Material specific |
| In-line raw mill | $SO_2$ | AG*, $NH_3$*, D/F* detached plume | detached plume |
| Preheater upper stage hydrated lime injection | $SO_2$ | D/F* | PM* |
| Calcined feed recirculation | $SO_2$ | | $NO_x$, $CO_2$ |
| Cement kiln dust internal scrubber | $SO_2$ | AG*, D/F* | |
| Preheater upper stage trona injection | $SO_2$ | AG*, D/F* | CKD disposal |
| Calcium-based internal scrubber | $SO_2$ | D/F*, detached plume, waste disposal | |
| Pyroprocessing system design | $SO_2$ | process specific | process specific |
| Low- $NO_x$ burner | $NO_x$ | Burner/application specific | Burner/application specific |
| Process improvements | $NO_x$ | Project specific | Project specific |
| Low- $NO_x$ calciner | $NO_x$ | | CO |
| Staged combustion | $NO_x$ | | CO |
| Mixing air fan | $NO_x$, CO | $SO_2$ | |
| Cement kiln dust insufflation | $NO_x$ | | CO, $CO_2$, $SO_2$ |
| Biosolids injection | $NO_x$ | | CO, $NH_3$*, detached plume, metals |
| Regenerative thermal oxidizer | CO | Detached plume, D/F* | $NO_x$, $CO_2$, $SO_3$, AG*, waste disposal |

*AG = Acid Gases, $NH_3$ = Ammonia, D/F = Dioxins/Furans, HCl = Hydrogen chloride, PM = Particulate Matter

As illustrated, there is an extensive list of mechanical and chemical options for reducing pollutants; however, their applicability is heavily dependent upon equipment compatibility, typically limited to more modern facilities, or retrofits (*61,62,63*). It should also be noted that many of these emission controls have counteractive effects, often producing more harmful pollutants than are eliminated. This also contributes to the individuality of their use, as described, there is no suit-all solution since the behavior of any kiln operation is strictly unique (*20*).

In summary, there are multiple emission mitigation strategies that can reduce greenhouse gas emissions, predominantly $CO_2$, in cement manufacturing. While some are more easily incorporated than others, all avenues explored in this research seem to have one element in common: the ultimate goal of reducing $CO_2$ emissions. This correlation may beg the underlying question: Are there any alternative measures of controlling greenhouse gas emissions other than reduction? One pending research is challenging that very question. The Holcim Cement Plant in Jerez, Spain is breaking technology boundaries with their new approach on tackling $CO_2$ emissions that contribute to global warming by a "$CO_2$-recycling" method. The cement facility, in partnership with an Australian company, is testing the use of algae bioreactors that uptake $CO_2$ emissions from kiln flue gases ultimately resulting in high-value feeds, foods, and fuels (*64*). These GreenFuel bioreactors, as the company calls them, can be retrofitted to existing smokestacks, such as the Holcim kiln exhaust, or even coal-fired power-stations (*64*). Relatively feasible, these non-evasive bioreactors are 2 meters high and filled with green microalgae suspended in nutrient-rich water (*65*). "A stream of gas is drawn from the smokestack by a blower and passed through the bioreactor where the algae, bathed in sunlight, consume the $CO_2$ component for photosynthesis" (*65*). From here, the algae multiply, in which a portion is drawn off periodically into a dewatering station where the algae is concentrated into a thick, solid, algal cake from which biofuel can be extracted through transesterification, or other types of processing can yield food sources (*64*). Preliminary results indicate that the fast-growing algae not only consume 82% of waste $CO_2$ emissions on sunny days, but also 85% of $NO_x$ emissions (*65*). With 98% of the process water being returned to the bioreactors, the entire process is quite energy efficient (*65*). Waste heat is also captured and used to help dry the algal cakes before its conversion into biodiesel (*64*). Ethanol is another valued product from the algae, and has a key advantage over corn or soy beans production in that it requires significantly less space, in addition to the fact that it is recycling waste $CO_2$ (*66*). While these new-age innovative studies are still in progress, this approach in tackling $CO_2$ emissions is most certainly unparalleled by other reduction strategies, in that it "recycles" instead of "reduces" emissions associated with cement manufacturing. However, just as in the discussed process and fuel modifications; what ever the method, the underlying goal is in parallel: to reduce $CO_2$.

# CHAPTER FIVE

# CONCLUSION

## Conclusion

The projected results of this research indicate that the calcination of clinker and the combustion of fossil fuels are major contributors to greenhouse gas emissions, primarily $CO_2$, in the production of Portland cement. There are essentially three approaches to mitigating $CO_2$ emissions in the cement industry: 1) alterations in process, 2) alterations in fuel use, and 3) alterations in technology. Alterations in process seemed to be the most limited aspect in reducing $CO_2$ emissions, since it is not easy to alter the chemistry of Portland cement without altering the trademark clinker itself. Low energy cements, such as belite cement, are a feasible alternative that produce a durable product with decreased lime and fuel consumption. Blended cements, such as pozzolan-mixed cements, are another alternative to traditional Portland cements, since their process requires less lime, which corresponds to less $CO_2$ liberated by calcining reactions. While these alternatives do reduce the amount of $CO_2$ generated, the options do not yield traditional Portland cement. Portland cement is the most widely used element of concrete in the world, and conversion to alternative cements may be costly and slow (2).

Alterations in fuel use prove to be more promising in $CO_2$ reductions than process alternations. Alternative fuel use significantly reduces the amount of $CO_2$ generated from stationary combustion in cement facilities. Biomass fuels, typically derived from organic waste, are carbon-neutral and result in no net increase in the global carbon flux.. Biomass and other alternative fuels, specifically those derived from waste, provide both ecological and economical benefits. Cement kilns are excellent incinerators that can recover energy from waste that is otherwise sent to landfills while containing any ash residue within the clinker. Alternative fuels appear to be more cost-effective than traditional fuel use, as they do not require additional mining and refining fees. Burning alternative fuels, overall, seems to be a logical answer in reducing $CO_2$ emissions; however, their often propitious perception is not without caution. While the biomass fuel exemption and void emission factors of some of these alternative fuels provoke their consumption in many industries, there may be some skepticism to the stability of their source and emission immunity.

Alterations in technology also prove to be a viable solution in alleviating $CO_2$ emissions. Renovating older cement manufacturing with energy efficient modifications such as kiln upgrades, roller mills, rotary coolers, or even smaller staff-involvement plans, can equate to a staggering amount of emission savings. Emission monitoring systems such as CEMS allows companies to better control what they emit by allowing them to evaluate and install specific control measures for specific pollutants where needed. Continued research and technologies seem to yield even more emission mitigation opportunities that may begin to change mainstream approaches to greenhouse gas emissions, such as gas recycling.

Although these mitigation strategies do share a promise in reducing greenhouse gas emissions, primarily $CO_2$, it does not appear that their implementation in the cement industry will be that significant in obtaining the goals of AB 32 legislation. The cement industry is responsible for 5% of global anthropogenic greenhouse gas emissions, and even if mitigations strategies such as these allow for a 20% reduction within the industry, that is still only a 1%

decrease statewide (*1*). While every contribution shouldn't be taken lightly, AB 32 fails to set a reduction across all industries (35). So perhaps, it is left to the larger contributors, such as the power industry, to compensate for the hefty savings needed to reach the greenhouse gas emission target set by AB 32.

While these mitigation strategies in the cement industry may fall short in regards to AB 32, their implementation may yield a far greater impact on environmental reckoning as a whole. Whether it be through alterations in process, fuel use, or technology, these three approaches are linked by a common thread of emission consciousness. For there is an important balance that should be recognized between the cement industry and the environment; while cement has proven a necessity in industrial advancement for thousands of years, it has also proven that it is dependent upon the abundant elements and resources of our planet. Only though careful management and constant awareness of the environment will the cement industry persist in harmony.

# APPENDIX A

# CALIFORNIA STATE-WIDE 1990 GREENHOUSE GAS EMISSION BASELINE

## California Greenhouse Gas Inventory for 1990 (millions of tonnes of CO2 equivalent)

*(CO2 equivalence based upon IPCC Second Assessement Report's Global Warming Potentials)*

*Categories Included in the Inventory.*

| | |
|---|---|
| 1 - Energy | 386.41 |
| ***1A - Fuel Combustion Activities*** | ***381.16*** |
| **1A1 - Energy Industries** | **157.33** |
| 1A1a - Main Activity Electricity and Heat Production | 115.84 |
| 1A1ai - Electricity Generation | 90.502 |
| 1A1aii - Combined Heat and Power Generation (CHP) | 25.341 |
| 1A1b - Petroleum Refining | 27.63 |
| 1A1c - Manufacture of Solid Fuels and Other Energy Industries | 13.86 |
| 1A1cii - Other Energy Industries | 13.858 |
| **1A2 - Manufacturing Industries and Construction** | **24.24** |
| 1A2c - Chemicals | 0.96 |
| 1A2d - Pulp, Paper and Print | 1.91 |
| 1A2e - Food Processing, Beverages and Tobacco | 3.07 |
| 1A2f - Non-Metallic Minerals | 5.12 |
| 1A2g - Transport Equipment | 0.53 |
| 1A2h - Machinery | 1.33 |
| 1A2i - Mining (excluding fuels) and Quarrying | 0.03 |
| 1A2j - Wood and Wood Products | 0.24 |
| 1A2k - Construction | 0.67 |
| 1A2l - Textile and Leather | 0.38 |
| 1A2m - Non-specified Industry. | 9.04 |
| **1A3 - Transport** | **150.02** |
| 1A3a - Civil Aviation | 5.13 |
| 1A3aii - Domestic Aviation | 5.113 |
| 1A3b - Road Transportation | 137.99 |
| 1A3bi - Cars | 63.746 |
| 1A3bii - Light-duty Trucks | 44.754 |
| 1A3biii - Heavy-duty Trucks and Buses | 29.031 |
| 1A3biv - Motorcycles | 0.426 |
| 1A3c - Railways | 2.33 |
| 1A3d - Water-borne Navigation | 2.21 |
| 1A3di - International Water-borne Navigation (International Bunkers) | 0.548 |
| 1A3dii - Domestic Water-borne Navigation | 1.662 |
| **1A4 - Other Sectors** | **48.19** |
| 1A4a - Commercial/Institutional | 14.03 |
| 1A4b - Residential | 29.66 |
| 1A4c - Agriculture/Forestry/Fishing/Fish Farms | 4.50 |
| **1A5 - Non-Specified** | **1.38** |
| ***1B - Fugitive Emissions from Fuels*** | ***5.25*** |
| **1B2 - Oil and Natural Gas** | **2.94** |
| 1B2a - Oil | 0.14 |
| 1B2aiii - All Other | 0.139 |
| 1B2b - Natural Gas | 1.50 |
| **1B3 - Other Emissions from Energy Production** | **2.31** |

## California Greenhouse Gas Inventory for 1990 (millions of tonnes of CO2 equivalent)

*(CO2 equivalence based upon IPCC Second Assessment Report's Global Warming Potentials)*

| *Categories Included in the Inventory.* | |
|---|---|
| 2 - Industrial Processes and Product Use | 18.34 |
| *2A - Mineral Industry* | *4.85* |
| 2A1 - Cement Production | 4.62 |
| 2A2 - Lime Production | 0.23 |
| *2B - Chemical Industry* | *2.34* |
| 2B2 - Nitric Acid Production | 0.53 |
| *2D - Non-Energy Products from Fuels and Solvent Use* | *2.29* |
| 2D1 - Lubricant Use | 1.13 |
| 2D2 - Paraffin Wax Use | 0.00 |
| 2D4 - Other (please specify) | 1.16 |
| *2E - Electronics Industry* | *0.59* |
| *2F - Product Uses as Substitutes for Ozone Depleting Substances* | *0.04* |
| *2G - Other Product Manufacture and Use* | *3.18* |
| 2G1 - Electrical Equipment | 2.58 |
| 2G1b - Use of Electrical Equipment | 2.58 |
| 2G4 - Other (Please specify) | 0.61 |
| *2H - Other* | *5.05* |
| 2H3 - Other (please specify) | 5.05 |
| 3 - Agriculture, Forestry and Other Land Use | 19.11 |
| *3A - Livestock* | *11.67* |
| 3A1 - Enteric Fermentation | 6.67 |
| 3A1a - Cattle | 6.25 |
| 3A1ai - Dairy Cows | 3.632 |
| 3A1aii - Other Cattle | 2.618 |
| 3A1c - Sheep | 0.17 |
| 3A1d - Goats | 0.00 |
| 3A1f - Horses | 0.24 |
| 3A1h - Swine | 0.01 |
| 3A2 - Manure Management | 5.00 |
| 3A2a - Cattle | 4.68 |
| 3A2ai - Dairy Cows | 4.359 |
| 3A2aii - Other Cattle | 0.324 |
| 3A2c - Sheep | 0.02 |
| 3A2d - Goats | 0.00 |
| 3A2f - Horses | 0.03 |
| 3A2h - Swine | 0.07 |
| 3A2i - Poultry | 0.20 |
| *3B - Land* | *0.19* |
| 3B1 - Forest Land | 0.19 |

## California Greenhouse Gas Inventory for 1990 (millions of tonnes of CO2 equivalent)

*(CO2 equivalence based upon IPCC Second Assessment Report's Global Warming Potentials)*

| | |
|---|---|
| *Categories Included in the Inventory.* | |
| *3C - Aggregate Sources and Non-CO2 Emissions Sources on Land* | 7.26 |
| 3C1 - Emissions from Biomass Burning | 0.12 |
| 3C1b - Biomass Burning in Croplands | 0.12 |
| 3C2 - Liming | 0.07 |
| 3C4 - Direct N2O Emissions from Managed Soils | 5.20 |
| 3C5 - Indirect N2O Emissions from Managed Soils | 1.44 |
| 3C7 - Rice Cultivations | 0.41 |
| 4 - Waste | 9.42 |
| *4A - Solid Waste Disposal* | 6.26 |
| 4A1 - Managed Waste Disposal Sites | 6.26 |
| *4D - Wastewater Treatment and Discharge* | 3.17 |
| 4D1 - Domestic Wastewater Treatment and Discharge | 2.83 |
| 4D2 - Industrial Wastewater Treatment and Discharge | 0.34 |
| Summary of Categories Included in the Inventory. | |
| **Gross California Emissions** | **433.29** |
| **Sinks and Sequestrations from Rangelands and Forestry** | **-6.69** |
| **Net California Emissions** | **426.60** |
| *Categories Excluded from the Inventory.* | |
| 1 - Energy | 59.02 |
| *1A - Fuel Combustion Activities* | 59.02 |
| 1A3 - Transport | 59.02 |
| 1A3a - Civil Aviation | 33.95 |
| 1A3ai - International Aviation (International Bunkers) | 14.597 |
| 1A3aii - Domestic Aviation | 19.357 |
| 1A3d - Water-borne Navigation | 25.06 |
| 1A3di - International Water-borne Navigation (International Bunkers) | 25.062 |
| Summary of Categories Excluded from the Inventory. | |
| **Gross California Emissions** | **59.02** |
| **Net California Emissions** | **59.02** |

# APPENDIX B

# PLANT DATA REQUIRED FOR GREENHOUSE GAS EMISSION INVENTORY

## Plant Data Required

| | |
|---|---|
| **Process-related Emissions** | |
| Annual Clinker Produced* | short tons |
| Annual Average of CaO Content of Clinker | % |
| Annual Average of MgO Content of Clinker | % |
| Annual Kiln feed | short tons |
| Loss on Ignition | |
| * If more than one type of clinker is produced obtain additional set of data for each type produced. | |
| **Stationary Combustion Emissions** | |
| Annual Fuel to Kilns* | short tons |
| * If more than one type of kiln fuel is used, obtain annual totals for each fuel. | |
| **Electricity-Generated Emissions** | |
| Annual Electricity Consumed | kWh |
| Annual Electricity Produced | kWh |
| **Emission Totals** | |
| Annual Clinker Consumed in Finish Mills | short tons |
| Annual Gypsum Consumed in Finish Mills | short tons |
| Annual Limestone Consumed in Finish Mills | short tons |

# APPENDIX C

# SPREADSHEET FOR CALCULATING PROCESS-RELATED EMISSIONS

# Process-related Emissions

| | | |
|---|---|---|
| **Activity Data for Clinker-Based $CO_2$ Estimation Method using the California Climate Registry Protocol** | | |
| **II/V Clinker Production and Composition** | | |
| II/V Clinker Produced | | metric tons |
| CaO Content of II/V Clinker | 60.00 | % |
| MgO Content of II/V Clinker | 5.00 | % |
| Total Clinker Produced | | metric tons |
| | | |
| Total CaO Amount | | metric tons |
| Total MgO Amount | | metric tons |
| Total Clinker $CO_2$ Emissions | | metric tons |
| **Clinker Emissions Factor** | | **tons $CO_2$/metric ton clinker OR** |
| | | |
| **Cement Kiln Dust Sources** | | |
| CKD Not Recycled to Kiln | 0.00 | metric tons |
| **Cement Kiln Dust Emission Factor** | 0.000 | **tons $CO_2$/metric ton CKD** |
| | | |
| **Organic Carbon from Raw Material Sources** | | |
| II/V Kiln feed | | metric tons |
| **$CO_2$ emissions from total organic carbon in raw material** | | **metric tons $CO_2$** |
| | | |
| **Emission Factors for Process Emissions** | | |
| Total Organic Carbon Content of the Raw Materials | 0.20 | % |
| Calcination Rate | 1.00 | |
| | | |
| **Conversion Factors** | | |
| short ton-metric ton Conversion Factor | 1.10231 | |
| $CO_2$/CaO Stoichiometric Ratio | 0.785 | |
| $CO_2$/MgO Stoichiometric Ratio | 1.1 | |
| $CO_2$ to C Molar Mass Ratio | 3.664 | |
| **Total Process-related $CO_2$ Emissions** | | **metric tons $CO_2$** |

# APPENDIX D

# SPREADSHEET FOR CALCULATING STATIONARY COMBUSTION EMISSIONS

## Stationary Combustion $CO_2$ Emissions

| **Annual Fuel Totals** | |
|---|---|
| Annual Coal to Kilns | MMbtu |
| Annual Natural Gas to Kilns | MMbtu |
| Annual Alternative Fuel to Kilns* | MMbtu |

* List each additonal alternative fuel consumed in the kilns separately.

| **Calculations of Stationary Combustion Emissions** | Total $CO_2$ | Total $CH_4$ | Total $N_2O$ |
|---|---|---|---|
| Coal Emissions | metric tons | metric tons | metric tons |
| Woodchips Emissions | metric tons | metric tons | metric tons |
| Natural Gas Emissions | metric tons | metric tons | metric tons |
| Tires Emissions | metric tons | metric tons | metric tons |

| **Emission Factors for Stationary Combustion** | $CO_2$ | | $CH_4$ | | $N_2O$ | |
|---|---|---|---|---|---|---|
| Emission Factors for Industrial Coal | 93.46 | kg $CO_2$/ MMbtu | 0.0111 | kg $CH_4$/MMbtu | 0.0016 | kg $N_2O$/MMbtu |
| Emission Factors for Natural Gas | 53.06 | kg $CO_2$/ MMbtu | 0.0059 | kg $CH_4$/ MMbtu | 0.0001 | kg $N_2O$/ MMbtu |
| Emission Factors for Alternative Fuel* | 93.87 | kg $CO_2$/ MMbtu | 0.0351 | kg $CH_4$/ MMbtu | 0.0047 | kg $N_2O$/ MMbtu |

* List each additonal emission factor for each additional alternative fuel consumed in the kilns.

| **Conversion Factors** | |
|---|---|
| metric ton-million btu Conversion Factor for Coal | 24.790 |
| metric ton-million btu Conversion Factor for Coke | 30.232 |
| TCF-million btu Conversion Factor for Natural Gas | 1.03 |
| MCF-TCF Conversion Factor | 1 |
| $CH_4$-$CO_2$ Conversion Factor | 21 |
| $N_2O$-$CO_2$ Conversion Factor | 310 |

**Total Stationary Combustion $CO_2$ Emissions** metric tons $CO_2$

# APPENDIX E

## SPREADSHEET FOR CALCULATING EMISSION TOTALS AND EMISSION EFFICIENCY METRICS

## Emission Totals and Efficiency Metric

| **$CO_2$ Emission Totals** | |
|---|---|
| Total Process-related $CO_2$ Emissions | metric tons $CO_2$ |
| Total Stationary Combustion $CO_2$ Emissions | metric tons $CO_2$ |
| Combined Annual Total $CO_2$ Emissions | metric tons $CO_2$ |

| **Cement Content Totals** | |
|---|---|
| Annual Clinker Used | metric tons $CO_2$ |
| Annual Gypsum sent to Finish Mill | metric tons $CO_2$ |
| Annual Limestone sent to Finish Mill | metric tons $CO_2$ |

| **Conversion Factors** | |
|---|---|
| short ton-metric ton conversion factor | 1.10231 |

| **$CO_2$ Emissions per Ton of Clinker** | **Efficiency Metric** |
|---|---|
| | metric tons of $CO_2$/metric ton of cement |

| **$CO_2$ Emissions per Ton of Cementitous Product** | **Efficiency Metric** |
|---|---|
| | metric tons of $CO_2$/metric ton of cement |

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