Energy and Emission Reduction Opportunities for the Cement Industry

Prepared for:

Industrial Technologies Program
Energy and Emission Reduction Opportunities for the Cement Industry

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Cover: Rotary kilns represent the largest energy consumer and carbon dioxide emission source of the cement/concrete industry. The cover diagram shows a thermal image of an operating kiln. The high temperature of the kiln surface (300°F to 400°F) accounts for about a 5% energy efficiency loss. The diagram on the cover depicts a kiln that has lost insulating refractory material and shows hot spots and a hot ring that will require future repair.
Acknowledgments

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Executive Summary

Cement is a gray, finely ground combination of minerals which, when mixed with water, sand, gravel, and other materials forms concrete. Cement provides the chemical bonds that hold the other materials together to form a dense rocklike substance. Concrete is the world’s most commonly used construction material and second only to water as the most-consumed substance on Earth. Demand for cement is directly tied to the use of concrete in building construction and public works projects. It closely follows GDP growth in the United States and in developing countries. Nearly all cement is used to produce concrete. Cement manufacturing and concrete production are bound together in the Life Cycle Analysis of energy use and emissions of these industries.

The United States has 118 cement manufacturing facilities operating 192 kilns. These plants manufactured over 88,900,000 tonnes of cement in the year 2001. On average, they required 4,982,000 Btu to produce one metric ton (tonne) of cement, not including the energy required for quarrying raw materials. The production of concrete consumes nearly all manufactured cement. Ready Mixed Concrete is produced in more than 2,700 plants and accounts for over 75% of all concrete production. Over 390,646,000 cubic yards (687,000,000 tonnes) of ready mixed concrete were produced in 2002. Concrete blocks and precast products account for 13%, on-site concrete mixing accounts for 6%, and the remaining 6% of concrete production is used in well lining, mining operations, and other activities. Concrete accounts for about 20% of the energy and 12% of the CO₂ emissions associated with cement/concrete.

The cement/concrete industry operates at less than 40% thermal efficiency. This low efficiency suggests that there are significant opportunities to improve energy efficiency and reduce emissions. Diagram A shows the proportion of the more than 550 x 10¹² Btu (0.55 quad) that were consumed in 2000 for U.S. quarrying, cement manufacturing, and concrete production. Cement manufacturing requires very high temperatures, 2,700°F (1,500°C), to initiate the reactions and phase changes necessary to form the complex mineral compounds that give cement its unique properties. Pyroprocessing in large rotary kilns is the operational step that provides the energy and environmental conditions necessary for the reactions and phase changes. This operation dominates the energy consumption and environmental impacts associated with the manufacture of cement and use of concrete and accounts for 74.2% of the industries’ energy consumption. U.S. pyroprocessing systems, on average, operate at roughly 34% energy efficiency.
More than 104 x 10^6 tonnes of CO₂ emissions were associated with U.S. quarrying, cement manufacturing and concrete production. Diagram B shows the proportion by source of these emissions. The raw materials used in cement manufacturing undergo chemical reactions during pyroprocessing that result in the generation of carbon dioxide (CO₂). These chemical reactions produce 0.54 tonnes of CO₂ per tonne of cement, about 48 x 10^6 tonnes annually. Nearly 60% of the 68.9 x 10^6 tonnes of CO₂ produced annually in the United States from non-combustion industrial sources (chemical reactions) originate from cement manufacturing.1 Industrial non-combustion CO₂ sources account for approximately 1.2% of all U.S. CO₂ emissions. In addition, the fuels burned to supply the energy necessary for pyroprocessing produce roughly 0.43 tonnes of CO₂ per tonne of cement. In total, pyroprocessing generates nearly 0.97 tonnes of CO₂ for each tonne of cement produced (86 x 10^6 tonnes annually) and accounts for 81% of the CO₂ emissions associated with the use of cement/concrete. The CO₂ produced from the chemical reactions is not influenced by changes in technology, equipment, or pyroprocessing energy efficiency. A consequence of the large portion of CO₂ generated from chemical reactions is that a 25% reduction in pyroprocessing energy use results in only an 11% reduction of total CO₂ emissions.

The greatest gains in reducing energy consumption and lowering emissions in the cement/concrete industry will be obtained with improvements in pyroprocessing. Process improvement will come from better energy management, upgrading existing equipment, adopting new pyroprocessing technologies, and in the longer term, performing the research and development (R&D) necessary to develop new cement manufacturing processes. Pyroprocessing is ideally suited to utilizing biomass and other non-traditional alternative fuel sources. Its extremely high operating temperature and long residence time ensure complete combustion of these fuel sources. Biomass fuels are considered to provide energy with near net-zero carbon-based emissions. R&D directed at developing the systems necessary to prepare and feed biomass fuels into pyroprocessing equipment will dramatically lower carbon-based emissions. Many industrial, manufacturing and consumer wastes are suitable alternate fuels for pyroprocessing (e.g., used oils, solvents, tires, and other wastes). R&D directed at safely increasing the use of alternate fuels provides an indirect means of improving energy efficiency. Alternate fuels are frequently assumed to have no energy requirement for their manufacture and their feedstock energy (energy inherent to the material) is normally associated with the finished product not the used product. Hence, when alternate fuels that are typically disposed of in landfills are utilized as fuels they provide a source of “free” energy.

Energy efficiency improvements and emission reductions can also result from changes in
the Product Formulation of cement. Research has shown that modifications to the cement formula are possible without a loss in desired properties or performance. These modifications include the addition of cement-like (pozzolanic) materials (e.g., fly ash, furnace slag, or other materials) that do not require the large energy inputs associated with pyroprocessing. Changes to cement product formulations require significant time to be incorporated into ASTM standards and be accepted in the marketplace. Concrete producers specify cement based on ASTM standards in order to guarantee the performance characteristics of concrete. Changes to these formulations are perceived as “risky” because change represents a move away from standards that have a very long and well-documented performance history. There is a trend in public works projects of specifying newer “low-energy” product formulations.

This report describes the cement industry and its technology. It provides background information necessary to develop realistic work plans to reduce energy usage and to lower CO₂ emissions. This report finds that opportunities exist both in the near-term and in the long-term for reducing energy usage and lowering emissions. Immediate and near-term improvements can be achieved by implementing demand-side energy management measures to improve energy efficiency and reduce electricity and fuel use. These improvements can come from utilizing free and low-cost options that include: motor, compressed air and process heater optimization software tools; participating in local and regional energy management training, workshops, and seminars; and conducting university-based energy assessments. Other site-specific near-term energy and environmental improvements can be achieved with contracted formal energy audits. Changes in product formulation also offer significant near-term energy and environmental improvements. Longer-term improvements could come from advanced research and development programs. However the cement industry, like most of the commodity materials industries, does not have the resources or incentives to conduct advanced and significant R&D on their own. Successful research and development programs will require significant collaboration between industry, government, and academia.
Introduction

Cement is a gray, finely ground combination of minerals which, when mixed with water, sand, gravel, and other materials forms concrete. Cement provides the chemical bond that holds the other materials together. Concrete, when newly mixed, is plastic and malleable, which allows it to be cast into shapes to build homes, sidewalks, superhighways, dams, skyscrapers and many other objects. Concrete is inert, nontoxic, naturally waterproof, and fire resistant. It is the world’s most commonly used construction material.

The words cement and concrete in every day usage are frequently interchanged, even though cement is only one of the multiple materials used in the making of concrete (Is it a cement sidewalk or a concrete sidewalk?). Cement manufacturing and concrete production are bound together in any analysis of energy use and emissions.

The raw materials used to produce cement are primarily limestone, clay, shale, and silica sand (Appendix A Table A.3). These materials are quarried, crushed, and, for economy, are usually transported to a nearby cement plant. The cement plant proportions the raw materials to the correct chemical composition and grinds the material to a fine consistency. Small quantities of iron ore, alumina, and other minerals may be added to adjust the raw material mixture. The finely ground raw material, “raw meal,” is fed into large rotary kilns, cylindrical furnaces 10 to 25 feet in diameter and 200 to 1,000 feet in length. The rotary cement kiln is the world's largest moving manufacturing machine and one of the hottest. It is typically set on a slight incline and rotates from 1 to 4 revolutions per minute. A large kiln may “pyroprocess” more than 300 tonnes of raw meal an hour. The raw meal is heated in the kiln to extremely high temperatures, about 1,500°C (2,700°F). The high temperature pyroprocessing causes the raw meal to react and form complex mineral compounds. These compounds exit the kiln as a hard nodular material called “clinker.” Many newer cement plants use the hot exiting kiln gases to preheat the raw meal. Clinker is cooled and ground with approximately 5% gypsum (which controls concrete setting time) and other minor additives to produce cement.

Concrete is produced by blending cement with fine aggregate (sand), coarse aggregate (gravel or crushed stone), and frequently with small amounts of chemicals, called “admixtures.” Admixtures are used to accelerate or retard setting time, control early plasticity properties, increase strength, improve resistance to acid and sulfates, control shrinkage, and improve freeze/thaw cracking. When water is added to the concrete mix at the job site, it forms a slurry that coats the surfaces of the aggregate and fills the voids to form rock-solid concrete. The process of hardening or setting is the result of the water hydration chemical reaction of the cement. The properties of concrete are determined by the exact chemical composition of cement.
used, the additives, and the overall proportions of cement, aggregate, and water. Concrete contains about 12 weight percent cement. Because of the relatively small cement content, concrete is not energy intensive when compared to other construction materials.²

**ENERGY AND EMISSION METRICS**

Technologies, practices, and product use determine the energy consumption and environmental impact of a product. The energy values and emissions studied and presented in this report are based on a “value chain” analysis of the cement/concrete industry. Value chain analysis allows for the capture of the direct energy and feedstock inputs of each processing step (link) to build a cumulative value along the chain. A value chain analysis is an integral part of a Life Cycle Assessment (LCA) and provides valuable information and data values for organizations performing a complete LCA. LCAs are important to ensure that process improvements in one area are not merely shifting the energy and environmental burdens to another area. Numerous LCAs and energy inventories have examined the cement/concrete industry.³ These are valuable references.

On-site energy values are based on actual process measurements taken within a facility. These measurements are valuable because the on-site values are the benchmarks that industry uses to compare performance between processes, facilities, and companies. On-site measurements, however, do not account for the complete energy and environmental impact of manufacturing a product. A full accounting of the impact of manufacturing must include the energy used to produce the electricity, the fuels, and the raw materials used on-site. These “secondary” or “tacit” additions are very important from a regional, national, and global energy and environment perspective.

The “tacit energy” associated with the production and transportation of fossil fuels used for combustion adds roughly 3% to the energy values of the fuels. Tacit electrical energy and environmental impact measurements account for the fact that substantial electrical generation inefficiencies and transmission losses occur outside the cement manufacturing facility. It can take as much as three units of hydrocarbon or coal calorific energy to produce one unit of electric energy. Saving 1 kilowatt hour (kWh) of on-site electricity is equivalent to saving over 3 kWh of the energy contained in the petroleum or coal-based fuels used to generate electrical power. Typical U.S. grid electricity requires about 9,935 Btu of energy to deliver 1 kWh of on-site electricity (3,412 Btu) for use (Appendix A Table A.16). Industrial tacit energy values also account for feedstock energy. Feedstock energy is defined as the energy inherent in fuels that are used in the manufacturing as materials rather than fuels. The feedstock energy associated with cement and concrete production is near-zero. This report, for clarity, distinguishes between on-site energy values and tacit energy values with the use of a superscript *(Any value that is a tacit energy value is preceded by a superscript, e.g., X superscript 2)*.
value is denoted with the superscript “t,” e.g., 1.0 kWh).

OVERALL ENERGY USE AND EMISSIONS

The annual cement/concrete energy “value chain analysis” from quarrying raw material to the final placement of concrete is shown in Table 1. The United States produced approximately 89,000,000 tonnes of cement in 2002. In total, the cement/concrete industry consumed over 550 x 10^12 Btu (0.55 quad). Cement manufacturing is the most energy-intensive link, accounting for nearly 80%, 447 x 10^12 Btu (0.447 quad) of the on-site energy consumed in the cement/concrete energy value chain.

The amount of energy required to produce one tonne of cement averaged 4,982,000 Btu/tonne of cement for U.S. plants (not including the energy required for quarrying the raw materials).
The most energy efficient U.S. plant required 3,230,000 Btu/tonne of cement while the least efficient used 8,150,000 Btu/tonne of cement. One unit operation, pyroprocessing accounts for 74.2% of the total on-site energy, more than 410 x 10^{12} Btu (0.41 quad), requiring nearly 4,617,000 Btu per tonne of cement for pyroprocessing alone.

The CO₂ emissions associated with the cement/concrete value chain are also presented in Table 1. Kilns and ancillary equipment used for pyroprocessing produce 83.1% of the CO₂ emissions. These emissions are generated by two mechanisms:

- **Reaction-based CO₂ Generation** – the thermochemical decomposition reaction or calcining of limestone (CaCO₃ → CaO + CO₂) and other minor raw materials produce CO₂
- **Fuel-based CO₂ Generation** – the combustion of fuels, used to obtain the high temperature needed for the calcining reactions, produce CO₂.

The calcium carbonate calcining reaction (CaCO₃ → CaO + CO₂) produces 0.785 tonnes of CO₂ per tonne of CaO. There is no technological or physical way to reduce calcination reaction emissions. Many cements contain about 61% CaO. Hence, the calcining reaction produces roughly 0.48 tonnes of CO₂ for each tonne of cement manufactured. This report calculated reaction CO₂ emissions to be 0.544 tonnes of CO₂ per tonne of cement based on the raw materials used by the U.S. cement industry (Appendix A Table A.11 and A.3). This difference can be accounted for by recognizing that the MgCO₂ portion of the raw materials also contributes to CO₂ emissions. Industrial emissions of CO₂ that are not caused by the combustion of fossil fuels, **Reaction-based CO₂ Generation**, accounted for 1.2% (68,900,000 metric tons of CO₂ equivalent) of total U.S. CO₂ emissions in 2000. The cement industry contributed 61% of this non-fuel value.

The level of CO₂ emissions from fuels depends on the cement process and the fuels used. These emissions can be controlled to some degree by fuel selection, burner choice, burner controls, kiln operation, and heat recovery equipment. The fuel mix and operating systems that supplied the energy necessary to pyroprocess in U.S. cement kilns in 2001 produced roughly 0.433 tonnes of CO₂ per tonne of cement. In total, pyroprocessing generates nearly 0.977 tonnes of CO₂ for each tonne of cement produced (Appendix A Table A.11).

Cement manufacturing also generates other emissions of environmental concern. Particulates (dust) become airborne during the grinding, pyroprocessing, milling operations and with the conveying of raw materials and product within the cement plant. Large volumes of gases mixing with finely powdered material naturally result in airborne particulates. On-site airborne dust is captured and controlled through optimal design and application of electrostatic precipitators and bag-house filtration systems. These fine particulates can be difficult to capture and when they escape collection systems can spread over a large area.

Emissions of non-CO₂ gaseous pollutants are minimal because of the high temperatures and long residence times associated with kiln operations. Fuels and waste fuel materials are completely combusted and limestone in the raw meal acts as a natural "dry scrubber" that
captures many potential pollutants. Sulfur dioxide (SO$_2$) emissions from a cement manufacturing plant are dependent upon the sulfur content of the raw materials and fuels used. If a raw material or fuel with little or no sulfur content is used within a kiln, then there will be little or no SO$_2$ emissions. If there is a high sulfur content within the raw meal then the sulphide and organically combined sulphur will combust in the preheating stage, the majority of SO$_2$ formed is scrubbed out by the raw meal and only a small portion may be emitted to the atmosphere.$^7$

Other emissions from fuel combustion include nitrogen oxides (NO$_x$) and carbon monoxide (CO). NO$_x$ is produced during combustion due to the elevated temperatures in the kiln and to the presence of nitrogen in the air/fuel mixture. The temperatures at the firing end of the kiln approach 1,870°C (3,400°F). NO$_x$ is produced in this environment due to the reaction of nitrogen in air with excess oxygen. The amount of NO$_x$ produced is dependent upon the temperature and the amount of oxygen present. The higher the temperature or higher excess oxygen used in the kiln, the higher the resultant NO$_x$ emissions will be. CO can result from poor solid-fuel feed systems in which sub-stoichiometric combustion will produce CO.$^8$ However, the high temperature and long residence time associated with kiln operations provide little opportunity for CO emissions to occur.

The energy consumed for concrete production is associated mainly with three operations: quarrying fine and course aggregates; mixing and blending cement, aggregates, and admixtures; and transporting the concrete mix to the work site. The energy associated with concrete production is about 19.3% of the total energy associated with all quarrying, cement manufacturing, and concrete production.

CO$_2$ emissions associated with concrete production results from quarrying, blending, and transportation. Emissions from concrete account for 10.9% of the CO$_2$ emissions associated with both cement manufacturing and concrete production (Table 1). CO$_2$ emissions for concrete relative to energy input are smaller than for cement manufacturing, which produces CO$_2$ from both reaction chemistry and fuel use.
The U.S. Cement Industry

The U.S. Cement Industry produced 89,000,000 metric tons (tonnes) of building cement in 2002.9 The total value of cement plant sales was about $8.6 billion.2 U.S. cement industry plants directly employ about 16,400 workers. The United States ranks third in the world in overall cement output, behind China and India. Cement production worldwide is about 1,700,000,000 tonnes.10

Building cements accounts for about 95% of the cement sold in North America. This was used in the production of more than $40 billion of concrete in the United States in 2001.2 Masonry cement accounts for the remaining 5% of cement sales in the United States. Masonry cement is a combination of building cement and 30% to 50% limestone. It is used as mortar for blocks, bricks, stucco, and other building projects.

Cement manufacturing is a highly capital-intensive industry requiring large-scale equipment to be economically competitive. The capital investment per worker in the cement industry is among the highest in all industries. The high capital intensity limits the financial incentive to build new plants or update old plants. There are 118 cement facilities that operate 192 kilns in the United States (Diagram 1). Over 45% of U.S. kilns were built before 1980 and 5% of operating kilns were built prior to 1955.11 The U.S. cement industry currently operates at an average 80% kiln utilization rate.12

The industry is diverse, involving 39 companies with no single company controlling more than 13.1% of the market based on tonnes produced. The five largest companies control nearly 50% of the market. Roughly 80% of the cement production capacity in the United States has foreign ownership or affiliation. Based on plant capacity, the top six countries with U.S. plant ownership are France (14.5%), Mexico (14.4%), Switzerland (14.3%), Germany (13.8%), Italy (9.6%), and Japan (5.4%). These countries each have two corporations present in the United States, except for Switzerland, which has only one. The top six

**Table 2 - 2001 U.S. Cement Industry**

<table>
<thead>
<tr>
<th>Number of Companies</th>
<th>39</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Plants</td>
<td>118</td>
</tr>
<tr>
<td>Number of Kilns</td>
<td>192</td>
</tr>
<tr>
<td>Number of States with Plants</td>
<td>38</td>
</tr>
<tr>
<td>Largest Company Market Share (tonnes)</td>
<td>13.1%</td>
</tr>
</tbody>
</table>

companies in terms of U.S. capacity are Holcim, Ltd. (Switzerland - 13.1%), Lafarge Coppee (France - 12.7%), CEMEX S.A. de C.V. (Mexico - 12.2%), Heidelberger Zement AG (Germany - 8.25%), Ash Grove Cement Co. (United States - 6.5%), and Buzzi UNICEM SpA (Italy - 4.4%).

The cement industry has reduced the amount of energy needed in cement production by more than 33% since the early 1970s (Appendix A, Table A.9). Cement manufacturers achieved greater energy efficiency by closing small plants and modernizing others. Energy savings were primarily achieved by shifting from the energy-intensive wet manufacturing process to the dry manufacturing process. Wet processing plants use water in raw meal grinding operations. This water must be evaporated in the pyroprocessing area. In 1974, 234 cement kilns used the wet process, currently only 54 wet process cement kilns are in operation. Cement plants have also reduced energy consumption and costs by taking advantage of excess heat from pyroprocessing to preheat the raw meal before it enters the kiln.

Pyroprocessing energy costs are significant and cement manufacturers attempt to utilize the lowest-cost energy supplies to reach the high temperatures required. Many cement plants routinely burn a mix of fuels in order to minimize energy costs. They are able to switch among a variety of conventional fuels and alternate waste fuels.

Table 3 shows the significant shift in fuel sources over the past thirty years. Cement manufacturers have switched from natural gas and petroleum based fuels to coal and petroleum coke for pyroprocessing. This switch was initially a result of federal legislation in response to the “1973 Energy Crisis.” The Energy Supply and Environmental Coordination Act of 1974 (ESECA, Public Law 93-319) compelled “Major Fuel Burning Installations” to stop burning natural gas and petroleum and to burn coal. The Powerplant and Industrial Fuel Use Act of 1978 (Public Law 95-620) required Congressional approval and a waiver from the Department of Energy for the use of fuels other than coal in heating plants over 50 x 10^6 Btu/hr. In 1987, Public Law 100-42 amended the Powerplant and
Industrial Fuel Use Act to repeal prohibitions against the use of natural gas and petroleum. Fuel switching is costly in terms of capital costs and today’s lower cost/Btu of coal compared to petroleum or natural gas economically favor coal as the fuel of choice.

The switch from petroleum and natural gas results in an increase in CO₂ fuel emissions per Btu consumed. Coal produces about 1.8 times more CO₂ than natural gas and about 1.2 times more than residual oils on a Btu basis. Overall the industry has lowered their CO₂ emission by 15% between 1971 and 2000. This was accomplished with improvements in energy efficiency that produced a reduction in the Btu/tonne requirement for production of cement by over 33%. If year 2000 plants were operating on the 1971 fuel mix, emissions would have been lowered by 21% (Appendix A Table A.9).

Kilns are ideally suited to recycling alternate/wastes for recovering their energy value because of the intense heat of pyroprocessing. The cement industry has steadily increased its use of waste materials to fuel cement kilns, and currently relies on the combustion of waste materials for 8.2% of its energy needs. Cement plants can burn many household and industrial wastes, including waste solvents, scrap tires, used motor oils, surplus printing inks, dry-cleaning solvents, paint thinners, petroleum sludge, and agricultural wastes such as almond shells and rice hulls.

Nearly all cement is used to produce concrete. Ready Mixed Concrete, concrete mixed at local plants for delivery in the familiar trucks with revolving tanks, accounts for over 75% of all concrete production. Concrete masonry (e.g., 8 x 16 inch blocks) and precast concrete products account for 13%, contractor (on-site concrete mixing) accounts for 6%, and the remaining 6% of concrete production is used in well lining, mining operations, and other activities. The United States has about 2,700 ready mixed concrete companies that operate 5,000 to 6,000 plants and utilize 70,000 to 80,000 trucks for delivery. Ready mixed companies employ between 126,000 and 144,000 workers. They supplied more than 390,646,000 cubic yards of concrete in 2002, enough to build a road ten feet wide, four inches thick that encircles the globe 51 times.
Cement

Cement is the key ingredient in concrete products. Comprising roughly 12% of the average residential-grade ready mixed concrete, cement is the binding agent that holds sand and other aggregates together in a hard, rock-like mass. Building cement or portland cement accounts for about 95% of the cement produced in North America. Portland cement was patented in 1824 by Joseph Aspdin, an English stonemason, and named after a quarried stone it resembled from the Isle of Portland.

The properties of concrete depend on the quantities and qualities of its components. Because cement is the most active component of concrete and usually has the greatest unit cost, its selection and proper use are of paramount importance in obtaining the most economical balance of properties desired for any particular concrete mixture. Different types of portland cement are manufactured to meet different physical and chemical requirements for specific purposes, such as durability and high-early strength.

The American Society for Testing and Materials (ASTM) Specification C-150 provides for eight types of portland cement (Appendix B). ASTM standards serve as the basis for manufacturing, procurement, and regulatory activities. In 2001, more than 88% of the portland cement produced in the United States was ASTM Type I and II (or Type I/II); Type III accounted for about 3.5% and Type V accounted for 4.4% of cement production. Air-entraining cements Type IA, IIA, and IIIA are available but have little market share. Concrete producers prefer to use admixture for air-entraining during concrete production, where they can have better control in obtaining the desired air content.

The chemical composition of cement is what distinguishes one type from another. Portland cements are made up of clinker and gypsum (CaSO₄•2H₂O). The four main compounds in clinker are: tricalcium silicate (3CaO•SiO₂), dicalcium silicate (2CaO•SiO₂), tricalcium aluminate (3CaO•Al₂O₃), and tetracalcium aluminoferrite (4CaO•Al₂O₃•Fe₂O₃). The industry commonly uses an abbreviated notation differing from normal chemical formulae. These compounds are designated as C₃S, C₂S, C₃A, and C₄AF, where C stands for calcium oxide (CaO, lime), S for silica (SiO₂), A for alumina (Al₂O₃), and F for iron oxide (Fe₂O₃). The approximate composition of compounds in typical portland cement is listed in Table 4.

Table 4 - Final Composition of Typical Portland Cement

<table>
<thead>
<tr>
<th>Cement Compound</th>
<th>Weight Percentage</th>
<th>Chemical Formula</th>
<th>Abbreviated Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>50 %</td>
<td>Ca₃SiO₅ or 3CaO•SiO₂</td>
<td>C₃S</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>25 %</td>
<td>Ca₂SiO₄ or 2CaO•SiO₂</td>
<td>C₂S</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>10 %</td>
<td>Ca₃Al₂O₆ or 3CaO•Al₂O₃</td>
<td>C₃A</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>10 %</td>
<td>Ca₄Al₂Fe₂O₁₀ or 4CaO•Al₂O₃•Fe₂O₃</td>
<td>C₄AF</td>
</tr>
<tr>
<td>Gypsum</td>
<td>5 %</td>
<td>CaSO₄•2H₂O</td>
<td></td>
</tr>
</tbody>
</table>

-9-
The industry frequently reports the composition of cement as a percentage of the raw materials and not as a percentage of the final compounds formed. The composition of portland cement falls within the range of 60% to 67% lime (CaO), 19% to 25% silica (Si), 3% to 8% alumina (Al₂O₃), and 0.3% to 6% iron oxide together with 1% to 3% sulphur trioxide, derived mainly from the added gypsum, 0.5% to 5% magnesia, and 0.3% to 1.3% alkalis. Titanium oxide is usually present to the extent of 0.1% to 0.4%. Manganese oxide is usually present only in small amounts, except when blast-furnace slag is used as a raw material, then it may rise to 1%.

The proportions of components in the final composition results from obtaining a phase equilibrium of all components in the raw meal, ash from fuels, and from other additions. The final compounds reflect the effects of kiln temperatures, residence time, quenching, oxygen availability, and many other kiln conditions. The actual final components are complex chemical crystalline and amorphous structures. Diagram 2 is a phase diagram of the major raw meal pyroprocess products. About 20% to 30% of the raw materials become liquid at the highest temperatures in the kiln. Portland cement composition is noted in one small area. Complex reactions and phase changes occur at the surfaces of the solids and within the liquid. The behavior of each type of cement depends on the mixture of final components.
CEMENT MANUFACTURING PROCESS

Cement manufacturing requires exacting measurements and careful controls to produce a product that meets precise chemical and physical specifications. The first step in the cement manufacturing process is the quarrying of a combination of raw materials (Appendix A - Table A.3) that when sized, blended, and processed yield the exact chemical composition required. These raw materials then undergo a series of high temperature chemical reactions and physical changes after which they are ground into a very fine, carefully sized powder.

Quarrying

Generally, cement raw materials consisting of mainly limestone (71%) and combinations of cement rock (16%), shale, clay, sand, or iron ore are extracted from a quarry near the cement plant. Limestone and cement rock are the most common source of CaCO₃ for cement production, making up about 87% of the raw materials (Appendix A - Table A3). Typically, the limestone used in cement production contains 75% to 90% CaCO₃ with the remainder predominately MgCO₃ and minor impurities. Limestone is typically categorized as high-calcium (<5% MgCO₃), magnesium-limestone (5% to 20% MgCO₃), or dolomitic-limestone (>20% to <45.6% MgCO₃). Cement rock is impure limestone possessing the ideal balance of silica, alumina, and CaCO₃ for portland cement.

A typical limestone/cement rock quarrying process for producing crushed and broken stone includes:
- removal of the overburden (i.e., soil, clay, and loose rock overlaying the deposit)
- blasting of the limestone deposit
- loading and transporting the blasted limestone to the crushing plant
- Crushing to reduce stone to about 5 inches (125 mm) in primary crushers, then to roughly 3/8 inch to 3/4 inch (10 mm to 19 mm) in secondary crushers.

The total energy required to quarry and process limestone/cement rock is 29,932 Btu/tonne. The quarrying of the limestone/cement rock consumes approximately 88% of the total energy requirement and the crushing of the ore accounts for the remaining 12% of the energy requirement. Table 5 provides a detailed listing of the equipment used and the Btu per tonne consumed for each equipment operation. Appendix A Table A.5 lists quarrying fuels and consumption values. In the quarrying of the limestone/cement rock, diesel fuel is the main source of energy and provides about 80% of the quarrying operations energy. Diesel fuel is used to run the heavy machinery in the limestone quarry’s daily operation. Utilization of biodiesel provides an opportunity for quarrying operations to lower lifecycle emission profiles.
Primary crushing reduces quarried stone to about 5 inches. Primary crushed stone is fed into secondary crushers where it is broken down to a size (~0.375 to ~0.75 inch) suitable for feed to the fine grinding machines located at the cement manufacturing plant. Crushing consumes an estimated 2,927 Btu/tonne of limestone.

Limestone/cement rock account for 87% of the raw materials used to produce cement. The energy and emissions associated with quarrying of the remaining 13% of raw materials has been estimated using the limestone/cement rock data (Appendix A Table A.6).

The environmental issues related to quarrying are mostly local and are common to most surface mines. These issues include dust, increased sediment loads to local streams, noise, and ground vibrations from blasting.

**Raw Material Preparation**

When raw materials arrive at the cement plant, they are stored in dry sheds or silos. These materials are then carefully proportioned accounting for combustion fuel ash and other additives to create a cement with a specific chemical composition. Two different methods, dry-process and wet-process, are used to grind raw materials. In the dry-process, raw materials are proportioned, ground to a powder, blended together and fed to the kiln in a dry state. In the wet-process, a slurry is formed by adding water to the properly proportioned raw materials. The grinding and blending operations are then completed with the materials in slurry form. This significantly lowers dust levels but requires additional energy to later remove the water from the raw meal.

Limestone, ~0.375 inch to ~0.75 inch in size, is blended with other raw materials (Appendix A Table A.3) and fed into grinding mills where it is reduced in size until approximately 70% to 85% passes a 200-mesh screen (0.0027 inch, 0.069 mm screen opening). Raw meal grinding equipment

### Table 5 - Energy Consumption for Surface Limestone Quarrying

<table>
<thead>
<tr>
<th>On-site Operations</th>
<th>Btu/ Tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>QUARRYING</td>
<td></td>
</tr>
<tr>
<td>Percussion Drill</td>
<td>6,140</td>
</tr>
<tr>
<td>Hydraulic Shovel</td>
<td>5,670</td>
</tr>
<tr>
<td>Rear-Dump Truck</td>
<td>4,030</td>
</tr>
<tr>
<td>Bulldozer</td>
<td>3,420</td>
</tr>
<tr>
<td>Pick-Up Trucks</td>
<td>2,250</td>
</tr>
<tr>
<td>Water Tanker</td>
<td>1,170</td>
</tr>
<tr>
<td>Service Truck</td>
<td>1,120</td>
</tr>
<tr>
<td>Lighting Plant</td>
<td>66</td>
</tr>
<tr>
<td>Front-End Loader</td>
<td>187</td>
</tr>
<tr>
<td>Bulk Truck</td>
<td>147</td>
</tr>
<tr>
<td>Pumps</td>
<td>2,250</td>
</tr>
<tr>
<td>Grader</td>
<td>7</td>
</tr>
<tr>
<td><strong>subtotal</strong></td>
<td><strong>26,457</strong></td>
</tr>
<tr>
<td>CRUSHING</td>
<td></td>
</tr>
<tr>
<td>Conveyor</td>
<td>182</td>
</tr>
<tr>
<td>Screens</td>
<td>366</td>
</tr>
<tr>
<td>Primary Crushers</td>
<td>1,830</td>
</tr>
<tr>
<td>Secondary Crushers</td>
<td>1,097</td>
</tr>
<tr>
<td><strong>subtotal</strong></td>
<td><strong>3,475</strong></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>29,932</strong></td>
</tr>
</tbody>
</table>

raw meal grinding has a significant effect on pyroprocessing and clinker quality. The raw meal quality (fineness, the amount and nature of oversized particles), and flowability (kiln circulating and separation patterns, and conductive energy transfer) affect the final clinker quality.

Raw material grinding consumes about 2% of the on-site energy associated with cement manufacturing. Grinding and milling are electrically driven processes. In addition to the electricity consumed on-site, electric processes have large tacit energy requirements associated with the generation and transmission of electricity. Grinding raw materials for cement manufacturing consumes approximately 93,885 (273,235') Btu/tonne of cement (Appendix A Table A.11). Grinding energy is a function of numerous factors including how the material fractures (under slow pressure, under impact), compressive strength, coefficient of elasticity, hardness, starting and finish size, desired particle distribution, etc. The exact amount of work required for grinding is difficult to calculate. Grinding efficiency ranges from 6% to 25% based on the thermal measurements. Since grinding consumes electricity, a costly energy source, cement manufacturers work to improve grinding efficiency. On-site grinding efficiency improvements provide significant offsite energy savings related to electric generation and transmission losses.

Kiln Operations

Pyroprocessing in giant rotating furnaces or kilns represent the major technical process common to all cement plants. It is also the most technically complex and energy-intensive operation from quarrying to concrete placement. Rotary cement kilns are cylindrical, refractory-lined steel furnaces that range from 200 to more than 1,000 feet long and from 10 to over 25 feet in diameter. Cement kilns are the world’s largest piece of moving industrial process equipment - and one of the hottest.

Blended raw material is fed into the upper end of the tilted rotating kiln. As the kiln slowly rotates (1 to 4 revolutions per minute), the raw material tumbles through progressively hotter zones toward the flame at the lower end of the kiln. The mixture passes at a rate controlled by the diameter and rotational speed of the kiln. The flame is fueled by powdered coal, petroleum coke, natural gas, oil, recycled materials, or other fuels. A 1870°C (3400°F) flame heats the mixture to 1480°C (2700°F). The extreme heat triggers a series of chemical reactions. The raw materials break down (calcine), become partially molten, and fuse together into nodules called "clinker."
The raw meal undergoes complex chemical and physical changes as it tumbles, then flows, through the kiln. These chemical reactions and changes can be viewed as a sequence of thermal events, some of which may occur outside the kiln in a preheater and/or precalciner section. The following describes the sequence of chemical and physical changes:

- Evaporation of uncombined water from raw material preparation in the wet process as material temperature increases to 100°C (212°F).
- Dehydration: the evolution of bound water from the material as temperatures increase from 100°C to approximately 550°C (1,020°F) to form the unhydrated oxides of silicon, aluminum, and iron.
- Calcination of the calcium carbonate (CaCO₃) to calcium oxide (CaO) and magnesium carbonate (MgCO₃) to magnesium oxide (MgO) with the evolution of carbon dioxide (CO₂) between 900°C (1,650°F) and 980°C (1,800°F). The CO₂ gas fluidizes the raw materials, which changes raw material movement from tumbling to flowing.
- Reaction of CaO with silica to form dicalcium silicate.
- Reaction of CaO with the aluminum and iron-bearing constituents to form the liquid molten phase.
- Formation of the clinker nodules. Reactions bonding the calcium oxide and silica oxide to form dicalcium and tricalcium silicates, and small amounts of tricalcium aluminate and tetracalcium aluminoferrite. These compounds form the four principal components that determine the properties of the cement manufactured.
- Evaporation of volatile constituents (e.g., sodium, potassium, chlorides, and sulfates).
- Reaction of excess CaO with dicalcium silicate to form tricalcium silicate.
- Formation of clinker as material approaches the exit of the kiln at temperatures of approximately 1,500°C (2,700°F).

Clinker is discharged red-hot from the lower end of the kiln and transferred to various types of coolers to recover thermal energy and lower the clinker to handling temperatures. Clinker, when cooled, is typically gray, glass-hard, spherically shaped nodules that range from 0.3 to 5.0 centimeters (0.125 to 2.0 inches) in diameter.

Kilns are divided into two groups, dry-process (80.5% of U.S. capacity) and wet-process depending on how the raw materials were prepared. Wet-process kilns are fed raw material as a slurry with a moisture content of 30% to 40%. A wet-process kiln needs additional length to evaporate the water contained in the raw material feed. Nearly 33% additional kiln energy is consumed in evaporating the slurry water. Wet-process kilns tend to be older fully capitalized operations. The last wet-process kiln to be built in the United States was constructed in 1975.

Dry-process kilns are fed dry powder raw materials. Three major variations of dry-process kilns are in operation: no-preheater kiln, preheater kiln, and precalciner kiln. Dry-process kilns operate with high exiting gas temperatures. In most dry-process no-preheater
operations the kiln is equipped with metal chain sections at the
gas exit end. These chains hang from the refractories in the gas
path. The gases pass through the chains, which absorb heat
from the gas stream. As the kiln rotates, the chains intermix and
become covered by the feed raw materials at the bottom of the
kiln. The chains transfer their thermal energy by conduction to
the raw material entering the kiln.

Most dry process plants preheat the finely ground raw
material before it enters the kiln. The preheating takes place
typically in a tall tower consisting of multistage countercurrent-
flow cyclones, Diagram 6. These towers can be over 450 feet
tall. Multiple solid/gas cyclone heat exchangers swirl the raw
materials with the hot exit gases from the kiln and heat them
quickly and efficiently. Some preheater towers include a special
preheater section which contains a fuel combustion chamber.
These sections provide some of the precalciner energy and are
referred to as precalciner.

Today, the most common type of cement kiln
(accounting for 80% of capacity in the United States) is a dry-process kiln, in which the raw
meal is processed dry. Many older kilns (20%) still in operation use the wet-process. Table 6
provides an inventory of U.S. cement kilns. Each kiln, wet-process and the three versions of dry-
process, operate with a different energy efficiency. The theoretical energy requirement for
pyroprocessing (i.e., the minimum energy required to remove hydrated water, calcine, and raise
the temperature to obtain the phases necessary for cement clinker) is about 1,710,000 Btu/tonne
of clinker. The thermal efficiencies for various kiln processes are also shown in Table 6. On
average, pyroprocessing operations run at about 34% thermal efficiency. This leaves ample
opportunities to improve thermal performance. The last chapter of this report, Opportunities for
Improving Energy Efficiency and Reducing CO₂ Emissions, and in particular Table 9, examines
the thermal balance of the kiln and kiln losses and suggests where efficiency improvement could
have a major impact.
Table 6 - Approximate Energy Consumption in U.S. Kilns by Number and Process

<table>
<thead>
<tr>
<th>Kiln Type</th>
<th>U.S. Kilns¹</th>
<th>Percent of Kilns</th>
<th>2000 Clinker Production, tonnes</th>
<th>Percent of U.S. Capacity</th>
<th>Million Btu per tonne ³</th>
<th>Percent Thermal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total U.S. Kilns</td>
<td>192</td>
<td>100%</td>
<td>71,860,000²</td>
<td>100%</td>
<td>4.98</td>
<td>34%</td>
</tr>
<tr>
<td>Wet Process Kiln Plants</td>
<td>54</td>
<td>28.4%</td>
<td>14,030,000²</td>
<td>19.5%</td>
<td>6.25</td>
<td>27%</td>
</tr>
<tr>
<td>Dry Process Kiln Plants</td>
<td>136</td>
<td>71.6%</td>
<td>57,830,000²</td>
<td>80.5%</td>
<td>4.67</td>
<td>37%</td>
</tr>
<tr>
<td>No Preheater or Precalceriner</td>
<td>59</td>
<td>31.1%</td>
<td>12,950,000²</td>
<td>18.0%</td>
<td>5.64</td>
<td>30%</td>
</tr>
<tr>
<td>Preheater (only)</td>
<td>35</td>
<td>18.4%</td>
<td>13,830,000²</td>
<td>19.2%</td>
<td>4.58</td>
<td>37%</td>
</tr>
<tr>
<td>Precaliner</td>
<td>42</td>
<td>22.1%</td>
<td>31,050,000²</td>
<td>43.2%</td>
<td>4.31</td>
<td>40%</td>
</tr>
<tr>
<td>Preheater/Precalceriner</td>
<td>77</td>
<td>40.5%</td>
<td>44,880,000³</td>
<td>62.4%</td>
<td>4.39</td>
<td>39%</td>
</tr>
</tbody>
</table>

1 - Kiln process types were provided by the Portland Cement Association. Two kilns were not classified and are not listed as wet or dry process kilns. These data represent approximately 92% of U.S. clinker production and about 93% of U.S. kilns (Appendix A Table A.1).
4 - Includes plants that are preheater only, precalciner only and combinations

Clinker Cooling

Red-hot clinker tumbles from the kiln onto a grate and is cooled by recirculating air. The hot air recovered from this cooling process is recycled back to the kiln or preheater system to recover its thermal energy. After energy is recovered from the process gases, the gases are routed to pollution control devices. Electrostatic precipitators or fabric filters remove particulate matter (dust) from the gases before they are discharged to the atmosphere. Particulate removal efficiencies of 99.7% are common throughout the industry.

Cement Milling

Cooled clinker is combined with approximately 3% to 6% gypsum and ground/milled into an extremely fine gray powder. This fine gray powder is cement. Gypsum is used to control the setting time of concrete.

Finish milling usually uses tube or ball mill equipment. Clinker is milled so finely
that nearly all of it passes through a 200 mesh (0.0027 inch, 0.069 mm) screen that will hold water. The final powder has a surface area of 3,000 to 5,000 cm²/g and about 85% to 95% of the powder will pass through a 325-mesh screen (0.0017 inch, 0.043 mm). The fineness of the cement is an important property and affects the rate of hydration. The finer the milled cement, the more surface area is available for hydration. The greater area for hydration causes greater early strength and more rapid generation of heat. Cements are classified by their fineness with Type III containing a more finely milled cement than Type I cement.

Clinker milling uses the same general type of equipment as raw meal grinding. However, the final product is much finer and requires almost three times the energy 270,610 (778,043) Btu/tonne of cement as raw meal grinding requires (Appendix A Table A.11). Clinker milling is not energy efficient and typical cement milling systems can consume nearly twenty times their theoretical energy requirement. After milling, portland cement is ready to be bagged or shipped in bulk by truck or rail to concrete producers.

Storage and Dispatch

Cement is stored at the cement manufacturing facility or a cement terminal until it is shipped to a customer. Storage of bulk cement is in watertight bins or silos. About 40% of manufactured cement is shipped by rail and barge to directly to terminals. Direct customer shipments are predominately made by truck. All transportation vehicles should be equipped with watertight, properly sealed compartments. Cement is very moisture-sensitive and must be stored in a dry environment. When kept dry it will retain its quality indefinitely. If stored in contact with damp air or moisture, cement will set more slowly and have lower concrete strength than dry cement. Cement stored for long periods of time should undergo standardized tests for strength and loss on ignition before use.
Concrete

Concrete is produced by mixing cement with fine aggregate (sand), coarse aggregate (gravel or crushed stone), and water. Small amounts of chemicals, called admixtures, are frequently added to the concrete mix to control setting time and plasticity. A properly designed concrete mixture will possess the desired workability for the fresh concrete and the required durability and strength for the hardened concrete. Typically, a concrete mix is by volume about 10% to 15% cement, 60% to 75% aggregates and 15% to 20% water. Entrained air bubbles in many concrete mixtures may also take up another 5% to 8% of the volume. Table 7 shows a typical weight percent mix. The character of concrete is determined by the quality of the cement and the mix ratios. Higher-quality concrete is produced by lowering the water-cement ratio as much as possible without sacrificing the workability of fresh concrete.

When water is added to the concrete mix, it combines with the cement to form a slurry or gel that coats the surfaces of the aggregate and fills the voids of the concrete mix. The water and cement compounds undergo hydration reactions that slowly form the complex hydrated microstructure that sets the concrete and makes it solid. These reactions continue after the concrete is set and are not complete for months (and even years) after placement. The microstructure of the cement hydrates determine the mechanical behavior and durability of the concrete.

The strength developed in concrete depends on its composition and the fineness to which the cement is ground. Cements high in C$_3$S (3CaO•SiO$_2$), especially those that are finely ground, will hydrate more rapidly and lead to higher early strength. However, rapid hydration can lead to a lower final strength. C$_2$S is mainly responsible for the strength developed in the first week of hardening. Cements high in C$_5$S (2CaO•SiO$_2$) will hydrate much more slowly, leading to a denser structure with higher long-term strength. The alumina and iron compounds in cement make little contribution to final strength.

Concrete can deteriorate from attack by some natural or artificial chemicals. The alumina compound C$_3$A (3CaO•Al$_2$O$_3$) is the most vulnerable to chemical attack in damp soils containing sulphate salts or in seawater, while the iron compound C$_4$AF (4CaO•Al$_2$O$_3$•Fe$_2$O$_3$) and the two calcium silicates (C$_3$S and C$_2$S) are more resistant.

Cement liberates heat when it hydrates. Consequently, concrete placed in large masses, as in dams, can cause the temperature inside the mass to rise as much as 72°F (40°C) above the outside temperature. Subsequent thermal stresses when cooling cause cracking in the concrete.
structure. The highest heat of hydration is shown by C₃A, followed in descending order by C₃S, C₄AF, and C₂S.

Ready mixed concrete consisting of cement, aggregates, water, and admixtures mixed at local plants for delivery to a work site by truck accounts for over 75% of all concrete production. Concrete masonry (e.g., 8 x 16 inch blocks) and other precast concrete products (e.g., pipes) account for 13%, contractor (on-site concrete mixing) accounts for 6%, and the remaining 6% of concrete production is used in well lining, mining operations, and other activities.

Ready mixed facilities store, convey, measure, and discharge cement, aggregates and admixtures into trucks for transport to a job site. These facilities typically receive raw materials by rail, truck, or barge. Cement is transferred and stored in elevated dry-storage silos. Sand and coarse aggregate are stored and transferred to elevated bins as needed. The raw materials are typically fed by gravity into weigh hoppers, where they are proportioned in the exact amounts specified for the concrete mix. Approximately 75% of ready mixed concrete is “transit mixed.” Transit mix trucks are loaded with sand, aggregate, cement, and water by gravity from weigh hoppers. The materials are mixed and blended in a rotating truck mounted drum while being transported to a work site. About 25% of the ready mixed concrete is blended at the ready mixed facility. The premixed and blended concrete is placed in open bed dump or agitator trucks for transport to a work site. Dry batching, with concrete mixed and hauled to the construction site dry is uncommon.

The water, sand, and gravel or crushed stone used in ready mixed concrete production are abundant and usually sourced as close to the ready mixed plant as possible. The distance and quality of the sources have an impact on transportation energy use (costs), water use for washing, and dust generation. The energy consumed for ready mixed concrete production are associated mostly with three operations (Appendix A Table A.13):

- Quarrying (fine and course aggregates) 160,700 Btu/tonne cement
- Mixing and blending (cement, aggregates and admixtures) 353,700 Btu/tonne cement
- Transporting the concrete mix to the work site 697,300 Btu/tonne cement

Ready mixed concrete production from U.S. manufactured cement is estimated to have consumed about 117.7 x 10¹² Btu in 2001, approximately 1,211,700 Btu/tonne of cement (Appendix A Table A.13).

Concrete block, pipe and other precast products follow the same production steps (quarrying and blending) as ready mixed concrete, but are cast at a manufacturing site and then transported to the work site. Hence, the total energy requirement for precast product is similar to ready mixed. The difference between the two products is location of where the concrete sets. Likewise contractor, well-lining concrete operations, and mining concrete all transport quarried aggregates and then blend on the work site. These operations result in overall energy use and emissions similar to ready mixed concrete. For simplicity, this report uses the ready mixed energy use and emissions data to calculate values for all industrial concrete products. Hence, in
total, the quarrying, mixing, and transportation operations account for 2.6% (14.3 x 10^{12} \text{ Btu/yr}), 5.7% (31.4 x 10^{12} \text{ Btu/yr}), and 11.2% (62.0 x 10^{12} \text{ Btu/yr}), respectively, of the on-site energy use for all cement and concrete (Appendix A Table A.10).

CO_2 emissions associated with concrete production can be calculated based on the fuels used. The three major concrete operations, quarrying, blending, and transportation, account for 1.2%, 5.4%, and 4.3% respectively, a total of 10.9% of the CO_2 emissions associated with both cement manufacturing and concrete production (Appendix A Table A.10). CO_2 emissions for concrete relative to energy usage are smaller than for cement manufacturing, which produces CO_2 from both reaction chemistry and fuel use.
Opportunities for Improving Energy Efficiency and Reducing CO₂ Emissions

Many opportunities exist for improving energy efficiency and reducing CO₂ emissions in the cement/concrete industry. These opportunities come from both changes in the manufacturing and production processes and from changes in the chemical formulation of cement. Process changes range from energy management improvements to investments in equipment upgrades or new technologies. Formulation changes have been demonstrated to save energy and reduce emissions but their widespread adoption is slowed by the burdens of developing new industrial standards.

The largest opportunities for improving energy efficiency and reducing CO₂ emissions related to energy inputs in the cement/concrete industry are mostly related to cement manufacturing. Table 8 lists the annual energy use and emissions associated with cement/concrete industry. Pyroprocessing accounts for 74% of the cement/concrete industries’ energy consumption (93% of cement’s manufacturing energy requirement) and operates at roughly 34% thermal efficiency. This low thermal efficiency provides many opportunities to improve performance. If it were possible to operate at the theoretical minimum energy requirements to produce clinker, nearly 400 x 10¹² Btu per year (0.4 quad) in energy savings could be obtained. Realistic and cost-effective energy savings are smaller, but achievable.

Grinding and milling account for 5.8% (12.3%) of cement/concrete energy consumption. These operations consume electricity and have energy efficiency ranging from 6% to 25%. They offer a large opportunity for energy reduction considering that each kWh saved on-site saves nearly 3 kWh of tacit energy at the electric generation site.

The potential opportunities for improving energy efficiency and lower emissions in quarrying and concrete production are smaller in terms of Btu and CO₂ emissions than in cement manufacturing. Quarrying and

| Table 8 - Annual Energy Use and CO₂ Emissions Associated with Cement and Concrete Production |
|-----------------------------------------------|-----------------------------------------------|
| On-site Energy | CO₂ Emissions |
| 10⁹ Btu | % | 10⁶ tonne | % |
| RAW MATERIALS: QUARRYING and CRUSHING | |
| Cement Materials | 3,817 | 0.7% | 0.36 | 0.3% |
| Concrete Materials | 14,287 | 2.6% | 1.28 | 1.2% |
| CEMENT MANUFACTURING | |
| Raw Grinding | 8,346 | 1.5% | 1.50 | 1.4% |
| Kiln: fuels | 410,464 | 74.0% | 38.47 | 36.8% |
| reactions | | 48.35 | 46.3% |
| Finish Milling | 24,057 | 4.3% | 4.32 | 4.1% |
| CONCRETE PRODUCTION | |
| Blending, Mixing | 31,444 | 5.7% | 5.65 | 5.4% |
| Transportation | 61,933 | 11.2% | 4.53 | 4.3% |
| TOTAL | 554,409 | 100% | 104.50 | 100% |

See: Appendix A Table A.10
transportation related to concrete production consume significant quantities of diesel fuel, approximately $74 \times 10^{12}$ Btu/year (550 x 10^6 gallons). Replacement of diesel fuel with biodiesel offers an opportunity to effectively lower lifecycle emission profiles. Biodiesel is a renewable energy fuel source, typically containing the mono alkyl esters of long-chain fatty acids derived from vegetable oils (commonly soybean oil) or animal fats. It can be blended at any level with petroleum diesel to create a biodiesel blend and can be used in compression-ignition (diesel) engines with little or no modifications. It has lower emissions compared to petroleum diesel, is less toxic than table salt, and bio-degrades as rapidly as sugar. Total U.S. production of biodiesel was 25.4 x 10^6 gallons in 2001. Total U.S. production represent only 4.6% of the diesel fuel requirement of the cement/concrete industry. Hence biodiesel availability will limit the opportunity to substitute for petroleum based diesel fuel.

Normally, energy efficiency improvements proportionally reduce the emissions of CO$_2$ generated from fossil fuel combustion and electricity generation. However, reducing cement manufacturing CO$_2$ emissions by a percentage proportional to energy efficiency improvements is not possible. More than half of the CO$_2$ emissions associated with cement/concrete are a result of the chemical reactions necessary for converting raw materials and not a result of the energy required to produce these reactions. If a near-zero CO$_2$ emitting fuel (e.g., nuclear, biomass) were utilized for all pyroprocessing energy needs, then CO$_2$ emissions could be reduced by 54%, from approximately 104 x 10^6 tonnes/yr to 48 x 10^6 tonnes/yr. It is also possible to reduce reaction CO$_2$ emissions by changing the product formulation with the substitution of raw materials, which provide cement-like properties.

The opportunities for reducing energy usage and lowering environmental impact are described in the Pyroprocessing and Product Formulations sections below. Briefly, these improvements will come from:

- Managing energy more efficiently
  - performing energy assessment/audits, utilizing energy management training, and implementations programs
- Upgrading existing equipment
  - shifting to more energy-efficient processes (e.g. from wet to dry process, from dry process to preheater)
  - installing improved heat recovery systems from clinker coolers
  - installing new design high-efficiency crushing, grinding, and milling equipment
- Adopting new pyroprocessing technologies
- Performing the R&D necessary to develop new cement manufacturing processes
- Utilizing biomass fuels
- Utilizing waste fuels
- Replacing high-carbon fuels by low-carbon fuels (e.g. shifting from coal to natural gas) *(This lowers CO$_2$ emissions, however at current fuel prices it increases operating costs.)*
• Changing cement product formulations, applying a lower clinker to final cement mixture ratio (i.e., increasing the ratio of cement additives that do not require pyroprocessing)
• Utilizing alternative cements (mineral polymers)
• Sequestering CO₂ from the gas streams

Cement manufacturing is a highly capital intensive and competitive industry. This fact combined with the long economic life of existing facilities will constrain the rate of upgrading exiting technology or adopting new technology. The near-term energy and emission-reduction opportunities will mainly come from better energy management practices, changes to “greener” fuels, and, to a smaller degree, changes in product formulation.
PYROPROCESSING OPPORTUNITIES

The greatest opportunities in reducing energy consumption and lowering emissions associated with cement/concrete will be obtained with improvements in cement pyroprocessing. On average, pyroprocessing systems in the United States operate at about 34% thermal efficiency. This low efficiency implies that there are potentially significant process and system improvements to improve energy and environmental performance. These process improvements will come from better energy management, upgrading existing equipment (e.g., replacing wet kilns, upgrading to preheater and precalciners), adopting new pyroprocessing technologies (e.g., fluidized bed systems) and, in the longer term, performing the R&D necessary to develop completely new concepts for the cement manufacturing processes.

The typical energy balances for the major pyroprocessing systems are shown in Table 9. These balances show where energy losses occur (areas where no useful work is accomplished). Any area, other than the theoretical requirement, that is losing energy represents an

<table>
<thead>
<tr>
<th>Table 9 - Thermal Energy Balances to Produce Clinker in Process Kilns</th>
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<tr>
<td>Energy Use Area</td>
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<td></td>
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<tr>
<td>Theoretical Requirement</td>
</tr>
<tr>
<td>Exit Gas Losses</td>
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<tr>
<td>Evaporation of Moisture</td>
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<tr>
<td>Dust in Exit Gas</td>
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<tr>
<td>Clinker Discharge</td>
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<tr>
<td>Clinker Stack</td>
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<tr>
<td>Kiln Shell</td>
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<tr>
<td>Calcination of Waste Dust</td>
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<tr>
<td>Unaccounted Losses</td>
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<tr>
<td>TOTAL</td>
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opportunity for improving energy efficiency and lowering fuel-based emissions. The large energy efficiency difference between cement processes, from 5,536,000 Btu/tonne of clinker for wet process to 3,424,000 Btu/tonne of clinker for dry process with preheater, shows the significant gains that can be made by upgrading to the more efficient process. The individual energy use areas (e.g., clinker discharge, kiln shell, etc) in Table 9 show the area and the magnitude of the opportunities available from managing energy losses by improving specific
equipment or practices.

**Pyroprocessing Energy Audits**

Energy audits, including kiln system performance testing and calculation of mass and heat balances, are the most comprehensive approaches to improving an existing system's energy efficiency. These audits can identify specific opportunities for improving energy efficiency and lowering CO₂ emissions. A cement manufacturing energy audit should at a minimum address the energy use areas identified in Table 9 and recommend potential actions. Typically the following actions will improve energy efficiency.

- Lower kiln exit gas losses
  - install devices to provide better conductive heat transfer from the gases to the materials (e.g., kiln chains)
  - operate at optimal oxygen levels (control combustion air input)
  - optimize burner flame shape and temperature
  - improve or add additional preheater capacity

- Lower moisture absorption opportunities for raw meal and fuels (avoiding the need to evaporate adsorbed water)

- Lower dust in exhaust gases by minimizing gas turbulence (dust carries energy away from the kiln where it is captured in dust collectors. The dust is recycled into the raw meal and fed into the kiln where it is reheated.)

- Lower clinker discharge temperature (retaining more heat within the pyroprocessing system)

- Lower clinker cooler stack temperature
  - recycle excess cooler air
  - reclaim cooler air by using it for drying raw materials and fuels or preheating fuels or air

- Lower kiln radiation losses by using the correct mix and more energy efficient refractories to control kiln temperature zones

- Lower cold air leakage
  - close unnecessary openings
  - provide more energy efficient seals
  - operate with as high a primary air temperature as possible

- Optimize kiln operations to avoid upsets

**Upgrading Existing Technology** – The addition of preheater sections, precalcination sections, or
more efficient clinker coolers would allow less efficient operations to maximize heat recovery. The impact of upgrading can be seen by comparing the processes shown in Table 6. If all U.S. plants upgraded pyroprocessing to the technology of the best U.S. plant (a dry process, preheater with precalciner system), the industry would lower its energy consumption by approximately 30% to approximately 3,230,000 Btu/tonne of cement and lower CO₂ emissions by 13% to 75.3 x 10⁶ tonnes/year.

**Adopting New Technology** – Large pilot-scale fluidized-bed kilns (200 tonnes/day) have been developed (1996) and have demonstrated significant energy savings. It is estimated that a full-scale fluidized-bed (3,000 tonnes/day) system will consume about 2,800,000 Btu/tonne of clinker – as efficient as the most advanced U.S. kiln utilizing a preheater and precalciner and 37% more efficient than the average U.S. plant. Fluidized-bed systems are estimated to have capital costs equivalent to 88% of the capital costs of a modern cement facility and operating costs equivalent to 75% of a modern cement facility’s operating costs. They have smaller footprints and their superior combustion characteristics of fluidized beds enable the use of lower-grade, lower cost coal.

Fluidized-bed systems do not provide “Shutdown Economics.” That is, their operating and capital costs are not less than the operating costs of older, fully capitalized kiln-based plants. This slows their adoption by the industry, since they are likely to be considered only for future capacity expansion. The U.S. cement industry currently operates at an average 80% kiln utilization rate. Another barrier to adoption is the natural reluctance to invest in the large capital expenditures associated with new plant construction. The risks associated with building a new technology commercial-scale plant, based on the successful demonstration of a one-tenth scale facility, are considered high.

**Cogeneration** – Large industrial thermal energy demand offers opportunities for cogeneration of electricity and/or steam production, particularly if the cogeneration system is part of the initial plant design. Cogeneration has demonstrated that it can significantly improve the overall energy efficiency of some manufacturing operations. Five cement manufacturing plants cogenerate electricity on-site. Currently, about 38% of U.S. cement capacity does not take advantage of preheater and/or precalciner systems. These plants typically have large heat losses (waste heat streams). Utilization of waste heat in preheater heat exchange systems is usually more energy efficient than the cogeneration of electricity with its inherently low conversion efficiency of thermal to electrical energy (typically about 9,935 Btu are required to produce 1 kWh (3,412 Btu)). Cogeneration of steam at a cement plant is possible, but typically cement plants require little steam and are located in isolated areas where markets for excess steam generation are not available.

**Biomass Fuels** – Trees, plants, and crops (biomass) incorporate (sequester) CO₂ as carbon compounds as they grow. On a life-cycle basis, where the life-cycle includes both the growth phase and the use phase (combustion), there is a near net-zero emission of CO₂ associated with the use of biomass fuels (Net life-cycle emissions are not zero, because energy is used to gather, increase density, reduce moisture, deliver, and store biomass fuels). Therefore the use of biomass
fuels for pyroprocessing can provide energy with low-net CO\textsubscript{2} emissions.

Cement pyroprocessing is suited to utilizing biomass as an ancillary fuel. Careful system design is required to account for biomass combustion characteristics (moisture load, flowability, burn temperature,...) and byproducts (ash composition). Biomass fuels do not improve energy efficiency per se, however they do replace conventional fuels and lower life-cycle CO\textsubscript{2} emissions. Burning biomass fuels can offer other indirect benefits:

- U.S. dependence on imported fuels is reduced,
- crops grown exclusively for energy production can provide economic opportunity for underutilized agricultural lands,
- energy crops require fewer herbicides and pesticides compared to row crops, and
- chemical runoff into surface water and groundwater is reduced.

An additional benefit of burning biomass over fossil fuels is the reduction of sulfur dioxide (SO\textsubscript{2}) emissions. Most forms of biomass contain small amounts of sulfur; therefore, biomass being burned emits little sulfur dioxide (SO\textsubscript{2}). For example, using biomass for 5% of a coal-fired heat input would reduce SO\textsubscript{2} emissions by approximately 5%. This benefit may not be fully realized in cement kiln operations. Limestone in the cement kiln’s raw meal acts as a natural SO\textsubscript{2} scrubber resulting in low SO\textsubscript{2} emissions. Hence biomass fuels will not significantly change the SO\textsubscript{2} emissions associated with cement kiln operations.

\textit{Alternate/Waste Fuels} – Utilization of alternate/waste fuels does not directly improve the energy efficiency or lower the CO\textsubscript{2} emissions of cement manufacturing. However, it does reduce the use of conventional fuels, lowers U.S. dependence on imported fuels, and reduces waste material sent to landfills. Depending on the alternate/waste fuel used it can be argued that there are real indirect energy savings and emission reductions. Placing a quantitative value on these indirect energy savings and emission reductions however is problematic.

Cement pyroprocessing is currently used for and highly suited to the disposal of alternate or waste fuels, such as used solvents, oils, tires, carpets, and other hazardous wastes (see fuel mix, Table 3). In the case of many hazardous wastes, cement pyroprocessing is more advantageous than commercial incinerators. Time, temperature, and turbulence are the three most important factors to ensure the destruction of organic and/or hazardous organic wastes. Cement pyroprocessing systems have a high degree of mixing, have long gas residence times, and burn hotter (30% higher than the temperatures in a commercial hazardous waste incinerator) than a typical thermal waste treatment facility. Cement kilns are very large and have a high heat capacity. Temperatures cannot change quickly due to process "upsets," ensuring that waste destruction is complete. Limestone also acts as a natural "dry scrubber" inside the kiln to capture chlorine and sulfur compounds, as well as some metals. Organic materials are completely combusted. Cement kilns easily achieve a Destruction and Removal Efficiency of at least 99.99 percent, as required by U.S. Environmental Protection Agency regulations for most organic wastes. However, care must be taken for high volatile elements (i.e., mercury, thallium, etc.).
Kilns operate with a temperature profile along their length that controls the sequence of kiln reactions and phase changes. Waste materials combust and burn at different temperatures under different conditions. Solid waste fuels need to be introduced into the kiln in such a manner as to not significantly change the temperature profile and chemical reactions. It is sometimes necessary to add solid waste through a hatch or valve structure in the kiln shell. This is technically challenging and creates an additional source of thermal and emission losses.

Receiving and handling of alternate or waste fuels can raise technical, liability, and political concerns. Cement manufacturing companies do not desire to be labeled as handlers of hazardous wastes and surrounding communities have valid concerns about hazardous waste transport and final emissions. These concerns can be difficult to address and in some cases are perceived as a financial liability to the cement manufacturer.

**GRINDING AND MILLING OPPORTUNITIES**

Grinding and milling operations are notoriously energy inefficient. Typical systems routinely run at 6% to 25% on-site energy efficiency.\(^1\) Although these systems do not account for a large portion of the on-site energy consumption profile of a cement plant, they do offer significant opportunities for energy improvement. Raw material grinding and finish mill systems should be evaluated for both efficiency of energy usage and cement quality. Modern finish mill systems may comprise several units of process equipment – high-pressure, twin-roll presses, tube mills, ball mills, and conventional or high-efficiency separators. Air flow, and material and heat balances should be measured and evaluated. Optimization of these systems may include:

- Adjustment of ball charges
- Studies of circulating loads
- Analyses of Tromp curves
- Modifying particle size distribution
- Controlling gypsum dehydration
PRODUCT FORMULATION CHANGES TO IMPROVE ENERGY EFFICIENCY

Energy efficiency improvements and emission reductions can also result from changes in the Product Formulation of cement. Research has shown that energy-saving modifications are possible without a loss in concrete performance. These modifications include the addition of limestone and other cement-like materials (e.g., fly ash, furnace slag, or other pozzolanic materials) that do not require the large energy inputs and emissions associated with pyroprocessing.

Changes to cement product formulations require significant time to be incorporated into ASTM standards and be accepted in the marketplace. An ASTM committee (C01.10) is considering a proposal to allow 5% limestone in portland cement. This formulation is supported with over thirty years of research and 20 years of field experience that confirms that this formulation change meets all chemical and physical property requirements. Current European (EN197) and Canadian (CSA A5) specifications allow this formulation. This change in product formulation results in roughly a 5% decrease in energy use and a 2.6% reduction in CO₂ emissions. Concrete producers specify cement based on ASTM standards in order to guarantee the performance characteristics of concrete. Changes to these formulations are perceived as “risky” because change represents a move away from standards that have a long and well-documented performance history.

Pozzolan

Materials that can be added to cement to extend its volume without a significant loss of properties are known as “pozzolans.” They are named after the ash deposits adjacent to the Pozzol volcano that the Romans used as cement. The Pantheon in Rome is a testament to the high strength and durability of pozzolan cement. Its hemispherical dome, 141 feet (43 meters) in diameter, is made completely from pozzollan cement and does not contain any reinforcing bars. It has been in use since 135 A.D. (for comparison the U.S. Capital dome is 96 feet in diameter)

The addition of pozzolan to cement will modify its characteristics. Depending on the type of pozzolan chosen, the density and compressive strength of the formed concrete may be increased and porosity reduced. Pozzolanic materials can combine with uncarbonated lime (calcium hydroxide) to form stable compounds, thus reducing the risk of early leaching or frost damage and increasing the potential durability of the mortar.

Pozzolan materials, in general, do not require pyroprocessing and, hence, can save very significant quantities of energy and lower emissions when supplementing regular cement. Concrete research is now calling for increased usage and high-volume usage of pozzolans, especially fly ash. Some have suggested that all concrete should contain fly ash. The economic and environmental advantages of adding pozzolan would seem to indicate that their regular and high-volume use will become standard practice in the concrete industry. The U.S. Environmental Protection Agency requires fly ash content in concrete to be used in buildings that receive
Coal-fired power fly ash is sometimes used as a source of silica in cement manufacturing, but more commonly is used in concrete production as a substitute for a portion of the cement. This is beneficial in two ways: it reduces solid waste and overall energy use since it does not require pyroprocessing. Fly ash can readily be substituted for 15% to 35% of the cement in concrete mixes and in some applications fly ash content can be up to 70%. These addition change the performance characteristic of the concrete. Of the 68 million short tons of coal fly ash produced in 2001, 12.4 million short tons were used in cement and concrete products\textsuperscript{28}. Fly ash can contain elements (e.g., carbon), compounds (e.g., ammonia) and other constituents that are detrimental to concrete performance.

Fly ash and slags react with any free lime left after the hydration to form calcium silicate hydrate, which is similar to the tricalcium and dicalcium silicates formed in cement curing. This process increases strength, improves sulfate resistance, decreases permeability, reduces the water ratio required, and improves the pumpability and workability of the concrete. Western coal-fired power plants produce better fly ash for concrete than eastern plants, because of lower sulfur and lower carbon content in the ash. Fly ash from incinerators cannot be used. Portland cement with fly ash added is sometimes identified with the letter P after the type number (e.g., Type IP).

Other industrial waste products, including blast furnace slag, cinders, silica fume and steel mill scale are sometimes substituted for some of the aggregate in concrete mix. Recycled concrete can be crushed into aggregate and reused in the concrete mix. However, the irregular and higher surface area of crushed concrete aggregate is more costly than sand or crushed stone because it takes more cement slurry to coat the surface.
Endnotes:


   This CD contains 31 reports with a focus on concrete. Cement is a key component in a LCA and data are presented in many of these reports.


12. *U.S. Cement Industry Factsheet*, Table 14


19. *Energy and Environmental Profile of the U.S. Mining Industry*, page 9-8


22. *Chemical Engineering Handbook*, page 8-8


