



# **Background Facts and Issues Concerning Cement and Cement Data**

By Hendrik G. van Oss

Open-File Report 2005-1152

**U.S. Department of the Interior**

**U.S. Geological Survey**

## **U.S. Department of the Interior**

Gale A. Norton, Secretary

## **U.S. Geological Survey**

P. Patrick Leahy, Acting Director

For product and ordering information:

World Wide Web: <http://www.usgs.gov/pubprod>

Telephone: 1-888-ASK-USGS

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:

World Wide Web: <http://www.usgs.gov>

Telephone: 1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted material contained within this report.

## Preface

This report is divided into two main parts. Part 1 first serves as a general overview or primer on hydraulic (chiefly portland) cement and, to some degree, concrete. Part 2 describes the monthly and annual U.S. Geological Survey (USGS) cement industry canvasses in general terms of their coverage and some of the issues regarding the collection and interpretation of the data therein. The report provides background detail that has not been possible to include in the USGS annual and monthly reports on cement. These periodic publications, however, should be referred to for detailed current data on U.S. production and sales of cement. It is anticipated that the contents of this report may be updated and/or supplemented from time to time.

Because some readers will choose to access only specific sections of this report, the individual sections have been written on a more stand-alone basis than might have been otherwise. A variety of technical terms related to cement (in this report and elsewhere) have definitions that may differ from the same terms as used in other fields. Most terms in this report have been defined at first usage in the text, but a brief glossary of technical terms has been provided to limit sectional repetition of definitions. A short table of units of measure has also been included.

The table of contents contains links to the appropriate section headings. It can be accessed either by scrolling to the beginning or by using the bookmarks tab, which is to the left of the document. The glossary can be accessed at any time by using the bookmarks tab. When toggling between the glossary or table of contents and your location in the primer, use the back arrow provided with the Adobe Reader rather than the back arrow provided with the browser. The Adobe navigation arrows are found at the window bottom to the right of the current page number. A right-click in the document with the mouse can also be used to access the forward or back navigation options.

## Units of measurement

For the most part, this report makes use of metric units despite the fact that the U.S. cement (and concrete) industry, at the time of writing, continues to use nonmetric units for commerce and a mix of units for internal accounting. Nonmetric units are also commonly encountered in the literature on cement. Conversion of units is provided below for the convenience of the reader. It is important to note that some of the conversion factors are given here to more significant figures than can generally be justified in reporting cement data.

The cement industry tends not to distinguish between units of weight and mass but almost invariably conducts its business in the sense of weight. Thus the metric ton, a unit of mass, is treated as if it were a unit of weight; strictly, the conversions to weight are applicable only at mean sea level.

Barrel (bbl) as a unit of cement weight (not volume) is no longer used by the cement industry but is frequently encountered in the historical literature. Its weight conversion has varied over the years by type of cement, reporting source, and by reporting region. For original (not re-converted) U.S. data reported by the U.S. Government, equivalences are as follows:

<b>Cement Type</b>	<b>Years</b>	<b>Weight (lbs) of 1 barrel</b>
Portland cement:	through 1919	380
	1920 onwards	376
Natural cement:	through 1920	300 (imposed*)
	1921 onwards	276
Pozzolanic and slag cements:	through 1915	380
	1916-1920	300
	1921 onwards	376
Masonry cement:	through 1960	376
	1961 onwards	280
Generic cement data:	All years	376

\*USGS-imposed (in original reports) conversion so as to standardize industry-submitted data that ranged from 265 to 300 pounds per barrel

Thus the general conversions:

- 1 metric ton = 5.80163 bbl (of 380 lbs);
- 5.86335 bbl (of 376 lbs);
- 7.87365 bbl (of 280 lbs).

1 bag (in USA) of portland cement = 94 lbs (this could change if the industry switches to kilogram-denominated bags).

1 bag (in USA) of masonry cement = 70 lbs (this could change if the industry switches to kilogram-denominated bags).

## Units of measurement and their equivalents

<b>Units of Weight and Mass</b>		
1 metric ton	1,000 kilograms	1.10231 short tons
1 short ton	2,000 pounds avoirdupois (lbs)	0.907185 metric tons
1 kilogram	2.20462 lbs	
<b>Units of Length</b>		
1 meter	3.28084 feet	39.3701 inches
<b>Units of Volume</b>		
1 cubic meter	1,000 liters	1.3079 cubic yards
1 cubic meter	264.172 U.S. gallons	35.3147 cubic feet
1 barrel (volume) of fuel	42 U.S. gallons	158.9878 liters
<p><i>Note:</i> When initially reported in metric tons, the conversion of fuels to volume units (e.g., to use volume-related heat or energy equivalences) varies by type of fuel. For petroleum-based liquid fuels, a rough (first approximation) equivalence is: 1 metric ton of liquid fuel = 7 barrels (range is about 6-9 barrels).</p>		
<b>Units of Energy</b>		
1 kilowatt hour (electricity)	3,412.14 British thermal units (Btu)	3.6000 megajoules (MJ)
1 British thermal unit (Btu)	1.055056 kilojoules (kJ)	
1 million Btu (Mbtu)	1.055056 gigajoules (GJ)	
<b>Temperature</b>		
°F	$32 + 9/5$ °C	
°C	$5/9$ (°F – 32)	
<b>Prefixes</b>		
kilo (k)	$= 10^3$	
mega (M)	$= 10^6$	
giga (G)	$= 10^9$	
tera (T)	$= 10^{12}$	
peta (P)	$= 10^{15}$	
exa (E)	$= 10^{18}$	

## Contents

Preface .....	iii
Units of measurement.....	iv
Part 1: Overview of Hydraulic Cements.....	1
Introduction .....	1
Brief history of hydraulic cement .....	1
Ancient use of cements.....	2
Post-Roman use of cements.....	2
The first portland cement.....	3
Early use of portland cement in the United States .....	5
Growth of the market for portland cement.....	5
Types of hydraulic cement.....	7
Hydraulic lime.....	7
Natural cements.....	7
Portland cement.....	8
Portland-limestone cements.....	10
Blended cements .....	10
Pozzolan-lime cements .....	11
Masonry cements .....	11
Aluminous cements .....	12
Mechanisms of cementation, and the chemistry and mineralogy of portland cement.....	12
Mechanisms of cementation .....	12
Carbonation.....	12
Hydration .....	13
Chemical composition of portland cement and clinker .....	13
Mineralogy of portland cement and its clinker .....	14
Hydration of portland cement.....	17
Clinker manufacturing process .....	20
Raw materials for clinker.....	21
Pyroprocessing.....	22
Kiln technology .....	22
Pyroprocessing functions of kiln lines .....	23
Process chemistry .....	25
Calcination zone reactions.....	25
Sintering zone reactions.....	26
Manufacture of finished cement from clinker .....	28
Energy requirements for clinker and cement manufacture .....	29
Environmental issues of cement manufacture.....	32
Mining of raw materials.....	32
Manufacture of clinker and finished cement .....	32
Particulate emissions.....	33
Gaseous emissions .....	33
Nitrogen oxides .....	33
Sulfur Oxides.....	35

Carbon dioxide.....	35
Environmental benefits of cement manufacture.....	40
References Cited in Part 1 .....	42
Glossary of terms.....	45
Links to other sources of information on cement and concrete.....	57
Part 2: Issues related to cement industry canvasses and data interpretation .....	58
Protection of proprietary data .....	58
Types of cement canvasses .....	59
Reporting units and accuracy .....	59
Monthly canvass and data.....	62
Sales destination data .....	62
Cement origins data.....	62
Breakout of blended cement .....	63
Clinker production.....	63
Treatment of trade data collected by the D16 canvass.....	63
Issues concerning the D16 monthly canvass .....	64
Timeliness.....	64
Completeness .....	64
Accuracy .....	64
Miscellaneous reporting problems with the D16 form.....	65
Revisions to monthly data .....	66
Annual canvass and data.....	66
Page 1 information.....	67
Page 2 information.....	67
Page 3 information.....	67
Page 4 information.....	72
Issues concerning the D15 annual canvass .....	72
Timeliness.....	72
Completeness issues.....	73
Accuracy issues.....	73
Sales and production tonnage issues.....	73
Other data related to sales tonnages.....	74

## Figures

Figure 1. World production of hydraulic cement, by region. ....	6
Figure 2. U.S. production and consumption of portland cement. ....	7
Figure 3. Simplified flow sheet of cement manufacture.....	20
Figure 4. Diagram of functional zones for different kiln technologies .....	25
Figure 5. Time-temperature profile for material in a preheater-equipped dry kiln. (After Glasser, 2004).....	31

## Tables

Table 1. Typical chemical composition of clinker and portland cement.....	14
Table 2. Typical mineralogical composition of modern portland cement.....	15
Table 3. Typical range in mineral proportions in modern portland cements.....	15
Table 4. Evolution of typical average mineral ratios in modern portland cements.....	16
Table 5. Nonfuel raw materials for clinker and portland cement manufacture in the United States.....	22
Table 6. Sequential functional zones in a wet kiln tube.....	24
Table 7. Summary of fuel and electricity consumption by the U.S. cement industry in 2000.....	29

# Part 1: Overview of Hydraulic Cements

## Introduction

Hydraulic cements are the binding agents in concretes and most mortars and are thus common and critically important construction materials. The term *hydraulic* refers to a cement's ability to set and harden under, or with excess, water through the hydration of the cement's constituent chemical compounds or minerals. Hydraulic cements are of two broad types: those that are inherently hydraulic (i.e., require only the addition of water to activate), and those that are pozzolanic. Loosely defined, the term *pozzolan* (or pozzolanic) refers to any siliceous material that develops hydraulic cementitious properties when interacted with hydrated lime [ $\text{Ca}(\text{OH})_2$ ], and in this overview includes true pozzolans and *latent cements*. The difference between true pozzolans and latent cements is subtle: true pozzolans have no cementitious properties in the absence of lime, whereas latent cements already have some cementitious properties but these are enhanced in the presence of lime. Pozzolanic additives or extenders may be collectively termed *supplementary cementitious materials* (SCM).

*Concrete* is an artificial rock-like material (in effect, an artificial conglomerate) made from a proportioned mix of hydraulic cement, water, fine and coarse aggregates, air, and sometimes additives. The cement itself can either be a pure hydraulic cement or a mix of hydraulic cement and SCM. Concrete mix recipes vary, but most have compositions (in volumetric terms) in the range of about: 7%–15% cement powder, 15%–20% water, 0.5%–8% air, 25%–30% fine aggregates (e.g., sand), and 30%–50% coarse aggregates (e.g., gravel or crushed stone) (Kosmatka and others, 2002). The cement powder and water together form *cement paste*. The aim in a good concrete mix is to have a completely unsorted (by size) mix of the aggregate particles, all bound together with just enough cement paste to completely coat all of the aggregate grain surfaces and fill all unintentional voids. For a typical concrete mix, 1 metric ton (t) of cement (powder) will yield about 3.4–3.8 cubic meters ( $\text{m}^3$ ) of concrete weighing about 7–9 t (that is, the density is typically in the range of about 2.2–2.4  $\text{t}/\text{m}^3$ ). Although aggregates make up the bulk of the mix, it is the hardened cement paste that binds the aggregates together and contributes virtually all of the strength of the concrete, with the aggregates serving largely as low cost fillers. Hydraulic *mortars* are similar to concrete, except that only fine aggregates are incorporated and the cement used is formulated so as to be somewhat more plastic in character. A few mortars use nonhydraulic binders such as lime. Mortars are used to bind together bricks, blocks, or stones in *masonry* construction. In the older literature, “mortar” can sometimes also be a casual term for cement itself.

Current (2004) world total annual production of hydraulic cement is about 2 billion t (Gt), and production is spread very unevenly among more than 150 countries. This quantity of cement is sufficient for about 14–18 Gt/yr of concrete (including mortars), and makes concrete the most abundant of all manufactured solid materials. The current yearly output of hydraulic cement is sufficient to make about 2.5 metric tons per year (t/yr) of concrete for every person on the planet.

## Brief history of hydraulic cement

The use of various cements in construction is a very ancient practice but some of the details as to who first made, or used, what form of cement are still uncertain. Nevertheless, a general sequence of developments can be described; much of the following synopsis is derived from Lea (1970, ch. 2), Bogue (1955, ch.1), Klemm (2004), Lesley (1924, ch. 1-2), and Wilcox (1995).

## Ancient use of cements

The earliest binder used in masonry construction was plain mud (with or without straw) and mud binders are still used, mainly for adobe construction, in many parts of the world today. Bitumen (natural asphalt) was used as a binder in some parts of ancient Mesopotamia. Some of the earliest use of true mortars was in ancient Egypt, Greece, and Crete. In Greece and Crete, lime mortars were made, as today, from the burning of limestone. In contrast, the Egyptians mainly used crude gypsum (plaster) mortars, although they had access to abundant limestone and did make some lime mortars. The Egyptian practice of using gypsum (a much rarer material than limestone) appears primarily to have been because of a shortage of fuels; the conversion of limestone to lime requires significantly higher temperatures (hence more fuel) than that of gypsum to plaster. Some foundations for ancient Egyptian buildings even made use of gypsum concrete (Kemp, 1994), in which limestone quarry and/or construction debris comprised the coarse aggregates. Some of the Greek mortars used hydraulic lime made from impure limestones, and still other hydraulic mortars were made by mixing lime with certain volcanic ashes, most notably that from the island of Thíra (or Thera; now called Santorin or Santorini).

The ancient Romans learned about various types of mortars from the Greeks, but because the Romans improved the quality and methods of application of hydraulic mortars and made far more extensive use of them, it is the Romans who are commonly given the lion's share of the credit for the development of hydraulic cement. Most significant was the Roman use of pozzolan-lime cements incorporating volcanic ash. A volcanic ash particularly favored by the Romans for this purpose was that quarried in large quantities from the distal slopes of Mt. Vesuvius near the village of Pozzuoli. This material became known as *pozzolana* (also spelled puzzolana, pouzzolana, pozzuolana) based on this village's name; likewise, the more general terms pozzolan and pozzolanic. Pozzolana has come to be applied to all volcanic ashes (such as santorin earth and trass) having pozzolanic character. Where pozzolana was unavailable, the Romans made use of crushed tiles or potshards as an artificial pozzolan; the Greeks may have earlier made similar use of crushed ceramics.

The Roman pozzolan-lime cements were so strong that, in practice, the proportion of aggregates in the mortars could be significantly increased over that used in unmodified lime mortars. Even coarse aggregates (commonly demolition debris) could be incorporated to form a bulk building material in its own right, i.e., concrete. Roman engineers used pozzolan-lime mortars and concrete throughout the Roman Empire, not only in a multitude of buildings (perhaps the best known surviving example of which is the Pantheon in Rome), but also in applications such as the waterproof lining of aqueducts and the construction of sea walls for artificial harbors.

## Post-Roman use of cements

Hydraulic mortars and concretes made in the first few centuries following the fall of the Roman Empire were of lower quality, owing either to poor understanding of the techniques of cement and lime manufacture or a lack of pozzolans in some places, or both. Regular lime mortars appear to have fared better, however. Sporadic interest remained in reproducing the quality of the old Roman cements, and in the 18th century active research into improving the quality of cements was becoming fairly widespread in Western Europe.

A major breakthrough in the understanding of hydraulic cement resulted from the research of John Smeaton following his being awarded, in 1756, the contract to build a replacement lighthouse on the Eddystone Rocks, offshore from Plymouth, England. For this project, Smeaton conducted experiments to make a mortar that could withstand especially severe marine conditions. Smeaton discovered that strong

hydraulic lime mortar could be made from calcining limestones that contained appreciable amounts of clay—his key insight being the link between the clay component and the development of hydraulic character. He found that an even better mortar could be made by combining this hydraulic lime with pozzolans, and it was a hydraulic lime-pozzolan mortar (specifically, hydraulic lime made from Aberthaw, Wales limestone and Italian pozzolana) that he used to build the new Eddystone lighthouse, which then stood for 126 years before needing replacement. Smeaton published the results of his research on hydraulic limes in 1791.

In 1796, a patent was granted to James Parker (Joseph Parker in some writeups) in England for hydraulic cement made from argillaceous limestone nodules (septaria). Within a few years, cements derived from a variety of argillaceous limestones were being marketed under the misleading but persistent term Roman cement. The name was based on the claim that the cement was as good as, and of similar reddish color to, the ancient Roman product, but was despite the fact that the new material contained no pozzolana and was compositionally quite unlike its namesake. Because the new cement (better termed *natural cement*) possessed good strength and hydraulic properties and set and hardened fairly quickly, its popularity grew rapidly, and natural cement remained the dominant cement type produced in England and most of the rest of Europe until the mid-19th century.

Production of cement of any type came later in the United States than in Europe, with the initial impetus being a need for waterproof mortars for the lining and lockworks for the Erie Canal, New York. Construction of the canal began in 1817 and, in the following year, deposits of argillaceous limestone suitable for the manufacture of natural cement were discovered near the canal. Manufacture of natural cement began shortly thereafter. The argillaceous limestone was locally called *cement rock*. The natural cement industry in the United States grew steadily as cement rock deposits were subsequently discovered in eastern Pennsylvania and elsewhere. Until the early 1870's, the only cements made in the United States were natural cements and slag-lime cements (chiefly based on quenched iron furnace slag).

Natural cements in the United States and in Europe exhibited significant regional variations in quality, owing to differences in processing methods and in the composition of the cement rock raw material. Smeaton's discovery of the importance of clay to the development of hydraulic character in lime mortars inspired research into ways to improve the quality, and/or reduce the variability, of natural cements. An ultimately more important avenue of research was that into the making of so-called artificial cement. Probably the most influential researcher in this area of investigation was the French engineer Louis J. Vicat. His research was first published in 1818 and showed how, in the absence of argillaceous limestones or cement rock, high quality hydraulic limes could be made with ordinary limestone, provided that controlled amounts of clay or shale were added. A more comprehensive review was published in 1828, and was translated into English in 1837 (Vicat, 1837).

## The first portland cement

The findings of Smeaton, Vicat, and other researchers appear to have been fairly well disseminated, and a number of patents were issued in England and France for various types of hydraulic limes and cements. In 1810, Edgar Dobbs received a patent in England for a cement that utilized clay, road dust (from limestone) and lime. The Dobbs patent expired in 1824, and this may have inspired Joseph Aspdin, a brick mason and experimenter from Leeds, England, to file later that year a patent for what superficially appears to be a similar product. Aspdin's December 15, 1824 patent "An improvement in the modes of producing an artificial stone" (British patent 5022) was for a product that he called *Portland Cement*. This name alluded to Portland stone, a well-regarded, very tough, dimension stone

quarried on the Isle of Portland along the South Dorset coast. The Portland stone comparison also had been used, much earlier, by Smeaton in extolling the qualities of his own cement. Aspdin's patent is interesting by modern standards in that it reveals remarkably little specific information about the product or its manufacture; indeed it would seem to be a rather tenuous foundation for a future major industry! Omitting the introductory remarks and salutations, the patent's technical description reads:

“My method of making a cement or artificial stone for stuccoing buildings, waterworks, cisterns, or any other purpose to which it may be applicable (and which I call Portland Cement) is as follows: I take a specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle, or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labor or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan until the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it to the consistency of mortar, and this applied to the purposes wanted.”

The first portland cement (the name, commonly, is no longer capitalized) plant was set up at Wakefield, England by Aspdin shortly after receiving his patent. His son, William Aspdin, later set up plants on the Thames and at Gateshead-on-Tyne. In the early years of the British portland cement industry the expensive new cement found difficulty in capturing market share from the well-regarded natural cements. Marketing of portland cement received a major boost in 1838 when it was chosen for the prestigious project to construct the Thames River tunnel.

Early efforts by others to duplicate the quality of Aspdin's portland cement were largely unsuccessful and led to speculation that Aspdin's patent lacked (perhaps deliberately) critical details regarding the cement's manufacture. The duplication efforts, however, yielded by the mid-1840s important ideas as to what those missing details were, most notably the need to heat the raw materials in the kiln to much higher temperatures than that merely needed to calcine the limestone. Empirical evidence for this was the discovery that over-burned, partially vitrified, material (hitherto discarded) from the kilns yielded better quality cement; a rival cement maker, Isaac C. Johnson, is generally credited with making public this need for high-temperature burning. It was eventually determined that the improvement in cement quality was because of the presence of hydraulic dicalcium silicate in the vitrified material (clinker) and, even more important, the presence of tricalcium silicate (discussed in more detail later). There remains debate as to whether Aspdin's original portland cement contained either of these minerals or whether it was merely a well made hydraulic lime, relying on heat-activated clay pozzolans. It is now known that both dicalcium silicate and (minor) tricalcium silicate were present in at least some of the later portland cements made by Joseph Aspdin (Stanley, 1999; Campbell, 1999, p. 1-3), and were certainly present in cements made by his son. Through trial and error, numerous improvements to the manufacturing process and mineralogic composition of portland cement were made in England and elsewhere over the course of the following decades. Improvements still continue and there remains only superficial similarity between modern portland cements and those manufactured in the mid- to late-19th century. The portland cement name has been retained by the industry largely because the modern material

is still an artificial cement made from limestone and argillaceous raw materials and because the name has an unrivaled cachet.

## Early use of portland cement in the United States

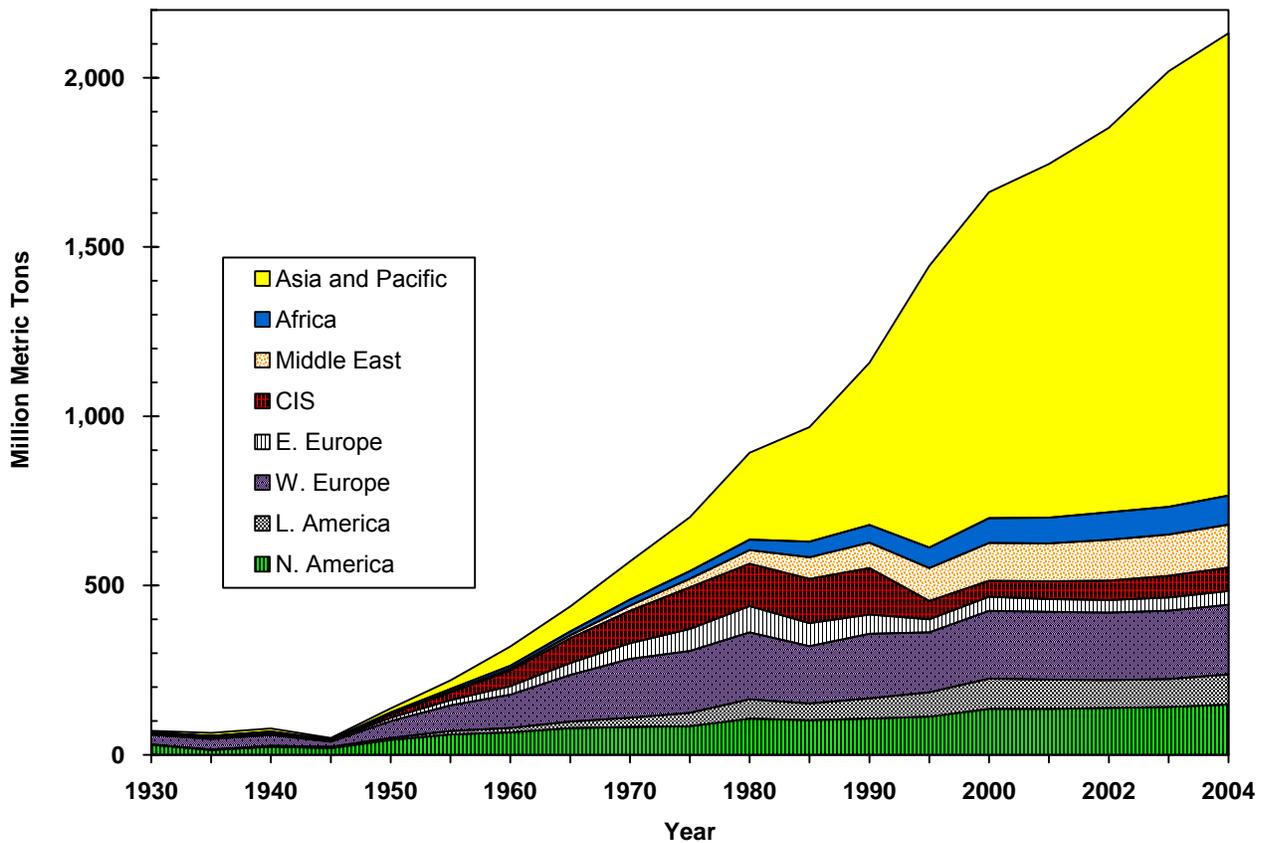
The first portland cement plants outside of England were constructed in Belgium and Germany around 1855. Portland cement imports into the United States began in the late 1860s and reached a peak level of about 0.5 million metric tons (Mt) in 1895 before declining owing to increased local production. The first portland cement plant in the United States was established in 1871 by David Saylor at Coplay, Pennsylvania; natural cement had been made there since 1850. The initial portland cement made at Coplay was not very satisfactory. However, by 1875, Saylor had more or less overcome problems of low kilning temperatures and inadequate mixing of raw materials and was making a high-quality product. The superiority of portland cement led to a proliferation of portland cement plants elsewhere in the United States; a detailed review of the history of the early (through about 1920) portland cement industry in the United States is provided by Lesley (1924). Output of portland cement in the United States grew rapidly from about 1890 onwards. By 1900, U.S. production had reached 1.46 Mt, exceeding for the first time the combined U.S. output (1.22 Mt) of natural and slag-lime cements.

## Growth of the market for portland cement

Overall growth in demand for concrete was given a great boost by the invention of reinforced concrete in the late 1860s. Because concrete is strong in compression but relatively weak in tension, this innovation of incorporating reinforcing steel bar to provide tensile strength opened up a number of new uses for the concrete, such as for high-rise buildings and suspended slab structures (such as bridge decks).

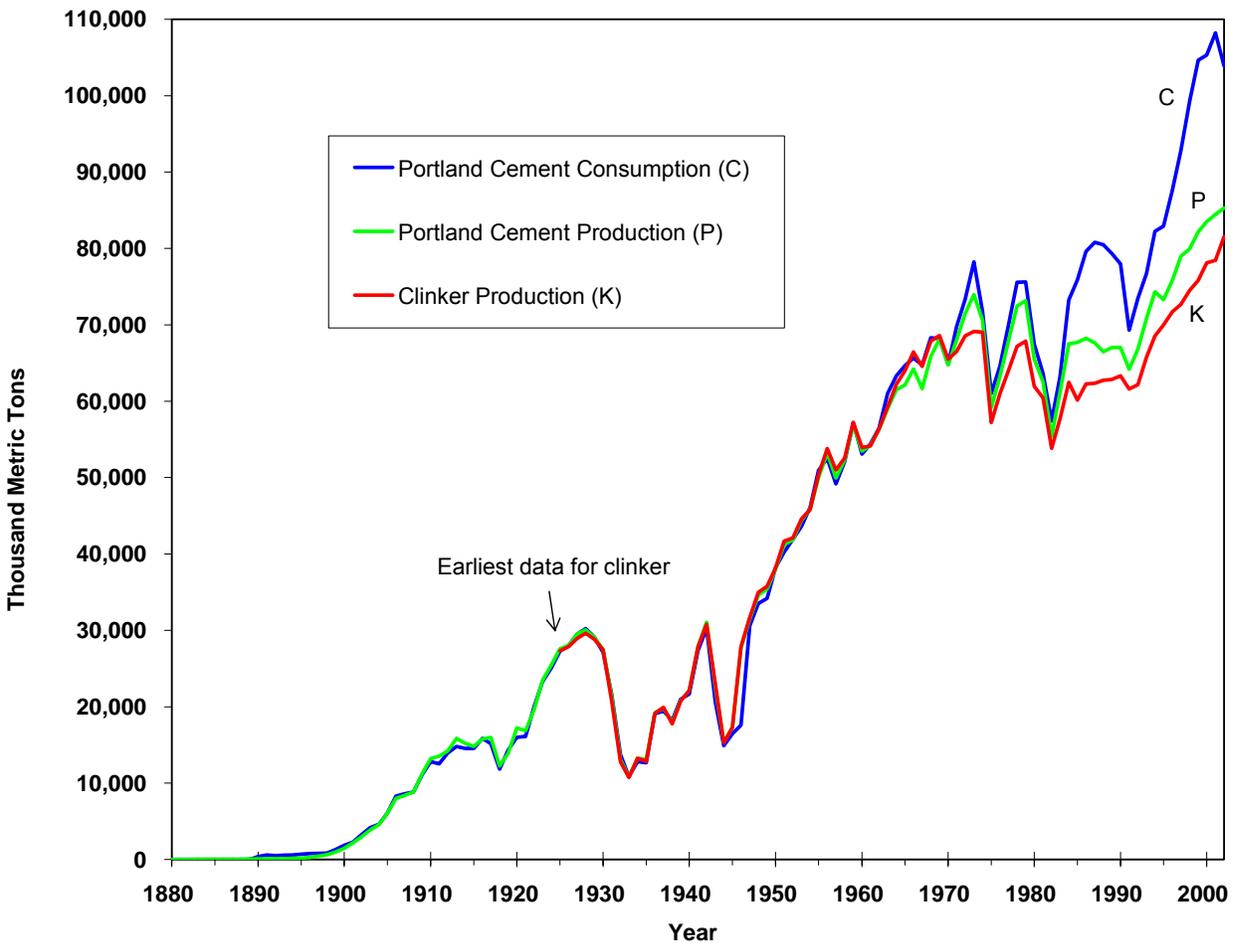
All of the early portland and natural cements were made on a batch basis in vertical shaft or chimney-type kilns. A major advance in output capacity and in thoroughness of mixing and heating of the raw materials came with the invention in 1873 of the rotary kiln. The English engineer F. Ransome patented an improved version of the rotary kiln in 1885 that allowed continuous throughput of materials. Thomas Edison developed the first high capacity rotary kilns in 1902; Edison's kilns were about 46 meters (m) long, as opposed to just 18–24 m for the rotary kilns up to that time.

In the first half of the 20th century, world use of concrete, and hence production of cement, grew erratically, experiencing major ebbs during the two World Wars and the Great Depression. World hydraulic cement production does not appear to have reached 100 Mt/yr until 1948 (see figure 1). However, since World War II, cement production has experienced steady, strong growth, with output in 2004 at about 2 Gt, as noted earlier. Today, there are very few countries that do not have at least one cement plant. As can be seen in figure 1, the greatest growth in cement output since 1950 (and especially since 1980) has been in Asia, which currently accounts for more than half of total world production. Much of Asia's overall growth has been by China. In 1950, China produced only about 2 Mt of cement, whereas output in 2004 was about 950 Mt. Currently, the top five world producers are, in descending order, China, India, the United States, Japan, and the Republic of Korea. The vast majority of cement produced in the world today is portland cement or closely related cements having portland cement as a base.



**Figure 1.** World production of hydraulic cement, by region.

Because of its important use in construction, cement production and consumption trends in developed countries tend to mirror those for the general economy. The historical graph for the United States (see figure 2) is illustrative; most of the major national economic perturbations, such as the World Wars, Great Depression, and the energy crises, can be seen as short-term disruptions to a generally increasing demand for cement. The general increase is largely owing to the combination of a shift in construction preferences to concrete and the rapidly rising population. The very rapid growth beginning in the early 1950s is due to the commencement of construction of the interstate highway network. Until 1970, U.S. production and consumption of portland cement and production of clinker were in balance. Since that time, however, U.S. production of clinker has fallen behind production of portland cement, and cement output has fallen greatly behind consumption. The production shortfalls have been met by imports of clinker and cement. Details of U.S. cement production, consumption, and trade can be found in the USGS Minerals Yearbooks and monthly Mineral Industry Surveys.



**Figure 2.** U.S. production and consumption of portland cement.

## Types of hydraulic cement

As partly enumerated in the historical review above, there are a number of different types of hydraulic cement, most of which are still in at least occasional use today. The main ones are:

### Hydraulic lime

This lime contains certain variable amounts of hydraulic silicates (mostly as calcined clay pozzolans but some varieties could contain small amounts of dicalcium silicate) as well as free lime, and is made from calcination of clay-rich limestones. Hydraulic lime was the active ingredient in natural cements. Today, hydraulic lime is used in some specialized mortars, but is not widely produced.

### Natural cements

Commonly and misleadingly called Roman cement in some older U.S. and English literature, natural cements are made from argillaceous limestone or cement rock or intimately interbedded limestone and clay or shale, with few, if any, additional raw materials. Some natural cements were made at relatively low temperatures, and the cementing properties were substantially due to the formation of clay

pozzolans. Better quality natural cements were made at much higher temperatures, and some may thereby have included hydraulic dicalcium silicate. Because significant blending of raw materials is not done, the quality of natural cements is dependent (assuming similar manufacturing parameters) on the composition of the local cement rock and so can vary regionally. Although of great historical importance, natural cements were generally found to be inferior to portland cement, and most natural cement plants worldwide eventually switched to the production of portland cement.

## Portland cement

Portland cement is an artificial cement in that its manufacture involves the mixing of raw materials (details on its manufacture and mineralogy are given in a later section), which allows for a uniform composition of the raw material feed to the kiln and which, in turn, allows for uniform properties of the finished cement, regardless of where it was made. The blending of raw materials and the fact that portland cements are made at higher temperatures are key difference between portland and natural cements. Today, straight (i.e., fitting within the specifications of ASTM C-150—see below) portland cement is defined as a finely interground mixture of portland cement clinker (an intermediate product in cement manufacture described in more detail later) and a small quantity (typically 3%–7% by weight) of calcium sulfate, usually in the form of gypsum. The ASTM C-150 standard for portland cement was revised recently to allow the incorporation of up to 5% of ground limestone as a filler.

By modifying the raw material mix and, to some degree, the temperature of manufacture, slight compositional variations in the clinker can be achieved to produce portland cements with slightly different properties. During the 20th century, the mineralogical ratios and particle size distribution in portland cement have been changed to favor faster and greater development of strength; this has been achieved principally by increasing the proportion of tricalcium silicate relative to dicalcium silicate, and grinding the clinker more finely.

Similar varieties of portland cement are made in many parts of the world, but go by different names. In the United States, the different varieties of straight portland cement are denoted per the American Society for Testing and Materials (ASTM) standard C-150, as:

*Type I:* general use portland cement. In some countries, this type is known as *ordinary* portland cement.

*Type II:* general use portland cement exhibiting moderate sulfate resistance and moderate heat of hydration.

*Type III:* high early strength portland cement.

*Type IV:* portland cement having a low heat of hydration.

*Type V:* portland cement having high sulfate resistance.

For Types I, II, and III, the addition of the suffix A (e.g., Type IA) indicates the inclusion of an *air-entraining* agent. Air entraining agents impart myriad tiny bubbles to the concrete containing the hydrated cement, which can offer certain advantages to the concrete, especially improved resistance to freeze-thaw cracking. In practice, many companies market hybrid portland cements; Type I/II is a common hybrid and meets the specifications of both Types I and II. Another common hybrid is Type

II/V. Because the uses and mineralogic composition (see table 3 below) of modern Type I and II portland cements are so similar, many statistical compilations (including those of the USGS) do not distinguish between them.

Portland cements are usually gray, but a more expensive *white* portland cement (generally within the Type I or II designations) can be obtained by burning only raw materials of very low contents of iron and transition elements. Both gray and white portland cement can be the basis of colored portland cements through the incorporation of pigments.

Notwithstanding the ASTM C-150 specifications, it is important to note the common industry practice, and that of the USGS, to include within the portland cement designation a number of other cements not within ASTM C-150 that are composed largely of portland cement and which are used for similar applications (e.g., concrete). These include blended cement (see below), block cement, expansive cement, oil well cement, regulated fast setting cement, and waterproof cement. However, plastic cements and portland-lime cements are not part of the portland cement umbrella, being instead grouped by the USGS and by most cement companies within the *masonry cement* designation (see below). In Europe and some other regions, the term portland cement, used loosely, may also include cement more properly termed *portland-limestone* cement (see below); this cement is not currently in use in the United States.

Some statistical compendia, including USGS Minerals Yearbook chapters and pre-1998 monthly Mineral Industry Surveys reports, also include *blended* cement (see below) within the portland cement designation. Blended cements have the same uses as Types I, II, IV, and V portlands, but generally not instead of Type III portland. Some jurisdictions allow certain (usually Type I) portland cements to contain small amounts (1%–3%) of inert and/or cementitious extenders while retaining the portland cement name. A relatively common example of this is where (unground) granulated blast furnace slag has been added in the finish mill to act as a clinker-grinding aid in the production of Type I cement. In this instance, the slag is converted (through grinding) into an SCM component to the finished portland cement. Because the use of SCM is increasing, interest is growing in having the cement requirements in construction project specifications change from a compositional basis (e.g., based on ASTM C-150) to a performance basis. The current performance-basis standard is ASTM C-1157, which identifies the following basic performance types of cement (essentially irrespective of composition) for concrete and similar applications:

*Type GU*: general use cement (performance equivalent to Type I in ASTM C-150)

*Type HE*: high early strength cement (performance equivalent to Type III)

*Type MS*: a cement providing moderate sulfate resistance (i.e., equivalent to Type II)

*Type HS*: a cement providing high sulfate resistance (i.e., equivalent to Type V)

*Type MH*: a cement providing moderate heat of hydration (i.e., equivalent to Type II)

*Type LH*: a cement providing low heat of hydration (i.e., equivalent to Type IV)

Any of the ASTM C-1157 cements can be further specified as requiring *Option R*, which indicates a requirement that the cement exhibit low reactivity with alkali-reactive concretes. This is to avoid alkali-silica or alkali-aggregate reactions between the cement paste and the aggregates in the concrete.

For low heat of hydration applications, Type IV cement has now been virtually entirely replaced with blended cements (generally incorporating fly ash) meeting the requirements of ASTM C-1157 Type LH.

## Portland-limestone cements

These are cements wherein relatively large amounts (6% to 35%) of ground limestone have been added as a filler to a portland cement base. Although not in use, as yet, in the United States, portland-limestone cements are reported to be in common use in Europe for certain relatively low strength general construction applications (Moir, 2003).

## Blended cements

Blended cements (called *composite* cements in some countries) are intimate mixes of a portland cement base (generally Type I) with one or more SCM extenders. The SCM commonly makes up about 5%–30% by weight of the total blend (but can be higher). In many statistical compendia (including some by the USGS), blended cements are included within the term portland cement; however, beginning with the January 1998 edition, the USGS monthly Mineral Industry Surveys on cement list blended cements as a separate category.

In blended cements, the SCM (or pozzolans) are activated by the high pH resulting from the lime released during the hydration of portland cement (see chemistry of hydration discussion below). The most commonly used SCM are pozzolana, certain types of fly ash (from coal-fired powerplants), ground granulated blast furnace slag (GGBFS—now increasingly being referred to as *slag cement*), burned clays, silica fume, and cement kiln dust (CKD). In general, incorporation of SCM with portland cement improves the resistance of concrete to chemical attack, reduces the concrete's porosity, reduces the heat of hydration of the cement (not always an advantage), may improve the flowability of concrete, and produces a concrete having about the same long-term strength as straight portland cement-based concretes. However, SCM generally reduce the early strength of the concrete, which may be detrimental to certain applications.

Blended cement, strictly, refers to a finished blended cement product made at a cement plant or its terminals, but essentially the same material can be made by doing the blending within a concrete mix. Indeed, most of the SCM consumption by U.S. concrete producers is material purchased directly for blending into the concrete mix; concrete producers buy relatively little finished blended cement. Increasingly, cement and concrete companies would prefer the flexibility of offering their products on a performance basis rather than on a recipe (specific type of portland cement) basis. Performance specifications for cements are covered under ASTM Standard C-1157-02 as noted above. A recent detailed review of blended cements is provided by Schmidt and others (2004).

The designations for blended cements vary worldwide, but those currently in use in the United States meet one or the other of the ASTM Standards C595 and C-1157. The definitions of blended cements given in ASTM Standard C-595 are summarized below.

*Portland blast furnace slag cement* (denoted IS [pronounced “one-S”]) contains 25%–70% GGBFS. Type IS cements are for general purpose uses, and can be designated for special properties: Type IS(MS) has moderate sulfate resistance; Type IS(A) is air-entrained; and Type IS(MH) has moderate heat of hydration.

*Portland-pozzolan cement* contains a base of portland and/or IS cement and 15%–40% pozzolans. The pozzolan type is not specified. There are two main types of portland-pozzolan cement: Types IP (“one-P”) and P.

Type IP cements are for general use; and Types IP(MS), IP(A), and IP(MH) share the same modifiers as the IS cements above.

Type P cements are for general uses not requiring high early strength. Again, there are the same P(MS), P(A), and P(MH) varieties, as well as Type P(LH); the LH designates low heat of hydration.

*Pozzolan-modified portland cement*: Designated I(PM); the base is portland and/or Type IS cement, with a pozzolan addition of less than 15%. Type I(PM) is for general use; and Types I(PM)(MS); I(PM)(A); and I(PM)(MH) share the same modifiers as the IS cements above.

*Slag-modified portland cement*: Designated I(SM), these cements contain less than 25% GGBFS. Type I(SM) is for general use; and Types I(SM)(MS), I(SM)(A), and I(SM)(MH) share the same modifiers as the IS cements above.

*Slag cement*: Under C-595, slag cement is designated Type S, defined as having a GGBFS content of 70% or more. The slag can be blended with portland cement to make concrete or with lime for mortars; the latter combination would make the final cement a pozzolan-lime cement. Type S(A) is air-entrained.

It is important to note that true Type S cements are no longer commonly made in the United States. Instead, the name *slag cement* (but with no abbreviation) is now increasingly given to the unblended 100% GGBFS product; this use of the term has led to some confusion because the material is not used directly (i.e., on its own) as a cement. The GGBFS is sold as an SCM either to cement companies to make blended or masonry cements, or to concrete manufacturers as a partial substitute for portland cement in the concrete mix (in effect making a IS or I(SM) blended cement paste as the binder).

## Pozzolan-lime cements

These include the original Roman cements (c.f., the natural cements above) and are an artificial mix of one or more pozzolans with lime (whether or not hydraulic). Little, if any, of this material is currently manufactured in the United States (but slag-lime cements were once popular) and these cements are now relatively uncommon elsewhere as well.

## Masonry cements

These are hydraulic cements based on portland cement to which other materials have been added primarily to impart plasticity. The most common additives are ground limestone (unburned) and/or lime, but others, including pozzolans, can be used. In a true masonry cement, the typical mix will incorporate about 50%–67% portland cement (or its clinker plus gypsum equivalent) and the remainder will be the additives. Masonry cements are used to make hydraulic mortars for binding blocks together, and controlling their spacing, in masonry-type construction.

In addition to true masonry cements, USGS and many other statistical compendiums include within this category two other cements of similar application. These are *plastic cements*, which are portland cements to which only small amounts (generally <12%) of plasticizers have been added, and

*portland-lime* cement. Portland-lime cements can be, and commonly are, made at the construction site by combining purchased portland (generally Type I) cement with hydrated lime.

## Aluminous cements

Also known as *calcium-aluminate* cement, high-aluminous cement or, for some versions, *ciment fondu*, aluminous cements are made from a mix of limestone and bauxite as the main raw materials. Aluminous cements are used for refractory applications (such as for cementing furnace bricks) and in certain rapid-hardening concrete applications. These cements are much more expensive than portland cements and are made in relatively tiny quantities by just a few companies worldwide. Currently, there is only one production facility in the United States. Data on production and sales of aluminous cement are almost always proprietary and hence unavailable.

## Mechanisms of cementation, and the chemistry and mineralogy of portland cement

As noted earlier, portland cement and some other cements based on it are overwhelmingly the dominant hydraulic cements produced today. The chemistry and mineralogy of portland cement can and will be described simply and qualitatively in the following overview. It should be stressed, however, that the simple descriptions and explanations provided below are mere representations of more complex reactions into which research is still ongoing. The same comment applies to the mechanisms of binding or cementation.

### Mechanisms of cementation

A number of binding mechanisms can occur in a mix of a cementing agent and aggregate particles. Qualitatively, one can envision the ultimate strength of the cemented material being due primarily to any or a combination of the mechanical strength of the hardened cement paste itself, the degree to which the hardened paste physically interlocks with the aggregate particles or chemically binds or otherwise reacts with the particles, the mechanical strength of the aggregate particles themselves, and the degree to which the aggregate particles and paste have been properly mixed.

Geologically speaking, a binding agent may be thought of as a material that has cooled from a melt, settled from suspension, precipitated from aqueous solution, or is a preexisting material that has undergone a change (perhaps through diagenesis) in morphology, mineralogy, or chemical composition. It is this last aspect that is of chief importance in artificial cements, and the changes of interest are *carbonation* and *hydration*. Hydraulic cements rely on hydration as their cementing mechanism.

### Carbonation

Ordinary (nonhydraulic) lime mortars harden through carbonation (rarely, but incorrectly, called carbonisation) of free lime. Lime (CaO) is formed by heating a source of calcium carbonate (CaCO<sub>3</sub>) such as calcite (the main mineral in limestone) to high temperatures (for practical purposes, about 950°C or more). The resulting *calcination* reaction to drive off carbon dioxide (CO<sub>2</sub>) is simple: CaCO<sub>3</sub> + heat → CaO + CO<sub>2</sub>↑. The carbonation reaction for lime is simply the slow reversal of this reaction by the lime's gradual absorption of atmospheric carbon dioxide. In lime mortars, the actual lime species present is hydrated or slaked lime (or *portlandite*) and is formed simply by the hydration reaction CaO + H<sub>2</sub>O → Ca(OH)<sub>2</sub>. The carbonation reaction for hydrated lime is: Ca(OH)<sub>2</sub> + CO<sub>2</sub> → CaCO<sub>3</sub> + H<sub>2</sub>O. The ultimate strength of the lime mortar will depend on the completeness of the carbonation; the

hydrated lime particles develop a shell of  $\text{CaCO}_3$  which, to one degree or another, slows  $\text{CO}_2$  diffusion to the residual lime particle cores and thus slows further carbonation. But when the carbonation process is complete (months to decades or more), lime mortars can be quite strong.

It is important to note that binders that rely on carbonation to harden and gain strength are not hydraulic cements. Ordinary lime, therefore, is not a hydraulic cement, but hydraulic lime is, although it may also develop some strength through carbonation.

## Hydration

A simple example of cementation by hydration is that of gypsum or plaster mortars. The common mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), when heated to about  $150^\circ\text{C}$ , partially dehydrates to the hemihydrate phase ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ), called *plaster of Paris* or simply plaster. If either gypsum or hemihydrate is heated to about  $190^\circ\text{--}200^\circ\text{C}$ , all the structural water is lost and “soluble” *anhydrite* ( $\text{CaSO}_4$ ) is formed. In the presence of water, soluble anhydrite fairly readily rehydrates to hemihydrate. Hemihydrate very quickly rehydrates to gypsum. However, if anhydrite is formed at temperatures above about  $200^\circ\text{C}$ , its ability to rehydrate slowly diminishes and, at about  $600^\circ\text{C}$ , is lost entirely. The rehydration of hemihydrate to gypsum is the binding reaction in plaster mortars. In addition, it is the defining reaction in the manufacture of gypsum wallboard.

Most hydraulic cements rely on far more complex hydration reactions to set and develop strength than those of plaster. The hydration reactions of portland and related cements will be discussed below, following an introduction to the chemistry and mineralogy of portland cement.

## Chemical composition of portland cement and clinker

Modern straight portland cement is a very finely ground mix of portland cement clinker and a small amount (typically 3%–7%) of gypsum and/or anhydrite. The chemical composition and mineralogy of the portland cement itself can be described fairly simply, but first the shorthand notation used in cement chemistry needs to be introduced, as it simplifies the presentation of hydration and other reactions and is commonly encountered in the cement literature.

Cement chemistry is generally denoted in simple stoichiometric shorthand terms for at least the major constituent oxides. This notation can be initially confusing to readers familiar only with standard forms of chemical notation (geologists, however, use an almost identical shorthand for AFM diagrams and similar compositional representations.) Consider, for example, a non-cement example such as the familiar feldspar mineral *anorthite*. The formula for anorthite is generally shown in the geological literature using standard chemical notation:  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . This can be recast in terms of oxide groupings:  $(\text{CaO})(\text{Al}_2\text{O}_3)(\text{SiO}_2)_2$  for mass balance computational purposes, or in such a way as to show structural or crystal chemistry relationships. Cement shorthand merely abbreviates the oxides; in this shorthand, anorthite’s formula becomes  $\text{CAS}_2$ .

The shorthand notation for the major oxides in the cement literature is given in table 1 below, which also shows the chemical composition of a typical modern portland cement and its clinker. For clinker, the oxide compositions would generally not vary from the rough averages shown in Table 1 by more than 2%–4% absolute (i.e., relative to 100% total oxides). Likewise, the oxide composition of portland cement would vary slightly depending on its actual gypsum fraction (5% is shown but the range

is generally 3%–7%), or if anhydrite substitutes for any of the gypsum, or if any other additives are present.

**Table 1.** Typical chemical composition of clinker and portland cement

Oxide Formula	Shorthand notation	Percentage by mass in clinker <sup>1</sup>	Percentage by mass in cement <sup>1,2</sup>
CaO	C	65	63.4
SiO <sub>2</sub>	S	22	20.9
Al <sub>2</sub> O <sub>3</sub>	A	6	5.7
Fe <sub>2</sub> O <sub>3</sub>	F	3	2.9
MgO	M	2	1.9
K <sub>2</sub> O + Na <sub>2</sub> O	K + N	0.6	0.6
Other (incl. SO <sub>3</sub> <sup>-</sup> )	...(… S)	1.4	3.6
H <sub>2</sub> O	H	"nil"	1
	Total:	100	100

<sup>1</sup>Values shown are representative to only 2 significant figures.

<sup>2</sup>Based on clinker shown plus 5% addition of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

Because the shorthand just conveys the oxide chemistry, a given shorthand formula will apply to all minerals or compounds having the same formula. Accordingly, many cement chemists confine the use of shorthand notation to the common or major cement minerals or chemical phases, and may use conventional chemical notation for less common cement minerals or compounds or for others (such as the mineral anorthite) not generally associated with cement. So a mix of notations may be encountered in a single equation. Cement shorthand is particularly convenient for denoting stoichiometric balances.

## Mineralogy of portland cement and its clinker

The major oxides in clinker are combined essentially into just four cement or clinker minerals, denoted in shorthand: C<sub>3</sub>S; C<sub>2</sub>S; C<sub>3</sub>A; and C<sub>4</sub>AF. It is important to note that these mineral formulas are not completely fixed; they are more or less averages and ignore the fact that, in real clinker, the minerals are commonly somewhat impure. For example, C<sub>4</sub>AF is actually the mean value of a solid solution with end members C<sub>6</sub>A<sub>2</sub>F and C<sub>6</sub>AF<sub>2</sub>. The ratios among these four minerals (and gypsum) in typical modern portland cements, and major functions of the minerals, are shown in table 2.

**Table 2.** Typical mineralogical composition of modern portland cement

Chemical formula	Oxide formula	Shorthand notation	Description	Typical percentage	Mineral function (see notes)
$\text{Ca}_3\text{SiO}_5$	$(\text{CaO})_3\text{SiO}_2$	$\text{C}_3\text{S}$	Tricalcium silicate ('alite')	50-70	(1)
$\text{Ca}_2\text{SiO}_4$	$(\text{CaO})_2\text{SiO}_2$	$\text{C}_2\text{S}$	Dicalcium silicate ('belite')	10-30	(2)
$\text{Ca}_3\text{Al}_2\text{O}_6$	$(\text{CaO})_3\text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$	Tricalcium aluminate	3-13	(3)
$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	$(\text{CaO})_4\text{Al}_2\text{O}_3\text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$	Tetracalcium aluminoferrite	5-15	(4)
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$(\text{CaO})(\text{SO}_3)(\text{H}_2\text{O})_2$	$\text{C}\bar{\text{S}}\text{H}_2$	Calcium sulfate dihydrate (gypsum)	3-7	(5)

(1) Hydrates quickly and imparts early strength and set.

(2) Hydrates slowly and imparts long-term strength.

(3) Hydrates almost instantaneously and very exothermically. Contributes to early strength and set.

(4) Hydrates quickly. Acts as a flux in clinker manufacture. Imparts gray color.

(5) Intergrinds with clinker to make portland cement. Can substitute anhydrite ( $\text{C}\bar{\text{S}}$ ). Controls early set.

Although not shown in table 2, the typical "free" or uncombined lime ( $\text{C}\bar{\text{S}}$ ) in portland cement or clinker is generally within the range of 0.2%–2.0% (a very low value is sought). As noted in the table 2 footnotes, the minerals in clinker have different functions relating either to the manufacturing process or the final properties of the cement. Thus, for example, the primary function of the "ferrite" mineral ( $\text{C}_4\text{AF}$ ) is to lower the temperature required in the kiln to form, in particular, the  $\text{C}_3\text{S}$  mineral, rather than impart some desired property to the cement. In contrast, the proportion of  $\text{C}_3\text{S}$  determines the degree of early strength development of the cement. Accordingly, it is no surprise that the mineralogical ratios differ for the different functional types (I-V) of portland cement defined earlier. Table 3 shows typical (not extreme) mineralogical ranges among these cement types.

**Table 3.** Typical range in mineral proportions in modern portland cements

ASTM C-150 Cement Type	Clinker Mineral (%)*				Properties of cement
	$\text{C}_3\text{S}$	$\text{C}_2\text{S}$	$\text{C}_3\text{A}$	$\text{C}_4\text{AF}$	
I	50-65	10-30	6-14	7-10	General purpose
II	45-65	7-30	2-8	10-12	Moderate heat of hydration, moderate sulfate resistance
III	55-65	5-25	5-12	5-12	High early strength**
IV	35-45	28-35	3-4	11-18	Low heat of hydration
V	40-65	15-30	1-5	10-17	High sulfate resistance

\*Range of minerals is empirical and approximate rather than definitional

\*\*High early strength is typically achieved by finer grinding of Type I cement.

During the 20th century the mineral ratios in portland cements have been changed in response, mainly, to a growing demand for faster development of strength and greater strength overall. The principal change has been a gradual increase in the ratio of  $C_3S$  to  $C_2S$ . Typical  $C_3S$  to  $C_2S$  ratios in the first quarter of the 20th century were more like the reverse of that shown in table 2, and the ratios have continued to evolve in recent years. Table 4 shows the evolution of (empirical) average mineralogical ratios between those made in the 1960-80s (approximately), and those made more recently, as reported by the PCA.

**Table 4.** Evolution of typical average mineral ratios in modern portland cements

ASTM C-150 Cement Type	Clinker Average Mineral Ratios (%) and Period Ranges <sup>1,2</sup>							
	$C_3S$		$C_2S$		$C_3A$		$C_4AF$	
	Older	Newer	Older	Newer	Older	Newer	Older	Newer
I	55	54	19	18	10	10	7	8
II	51	55	24	19	6	6	11	11
III	56	55	19	17	10	9	7	8
IV <sup>3</sup>	28	42	49	32	4	4	12	15
V	38	54	43	22	4	4	9	13
White <sup>4</sup>	33	63	46	18	14	10	2	1

<sup>1</sup>Except where indicated as white, data are for gray portland cement. Data are empirical averages and do not sum horizontally to 100%.

<sup>2</sup>“Older” is the period of about 1960-80s; data are from Kosmatka and Panarese (1994); “Newer” refers to about 1990 onwards; data are from Kosmatka and others (2002).

<sup>3</sup>Essentially no Type IV is currently made; it has been replaced by IP cement incorporating fly ash.

<sup>4</sup>All forms of white portland cement (i.e., Types I-V).

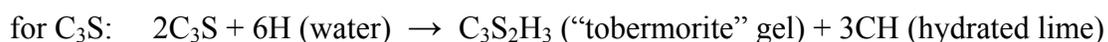
Although very small changes over time in the averages shown in table 4 (e.g.,  $C_3S$  in Types I and III) are probably of no statistical significance for these empirical data, some shifts are noteworthy. The average  $C_3S$  content of Type IV (rarely made today) and Type V portland cement has been increased significantly, and  $C_2S$  decreased; in the case of Type V possibly reflecting the need for faster hydrating sulfate resistant concrete in areas of rapid population growth in the American Southwest (e.g., Arizona, southern California, Nevada). For some portland cement types, not only has the average  $C_3S$  content increased (table 4), but the upper end of its proportionality range (table 3) has increased (to about 65%, from about 55% in older Type I cements and from about 50% for Type II). At the upper end of the range, Types I and II cements now can have  $C_3S$  contents that used to be more typical of Type III cements, and reflect the fact that many modern Type III cements are merely more finely ground versions of Type I cement. The overall iron content (reflected by  $C_4AF$ ) has increased modestly, possibly reflecting an increased need for its fluxing role (to increase formation of  $C_3S$ ) in clinker manufacture, as will be discussed in the process mineralogy section below.

The largest compositional shift is seen for white portland cements, for which the  $C_3S$  contents have been more or less doubled, at the expense of the  $C_2S$  contents. As will be discussed later, this has interesting process chemistry implications. White cements continue to have extremely low  $C_4AF$  contents to avoid the coloring effects of iron.

## Hydration of portland cement

Portland cement hydration reactions are complex and not completely understood. Part of the problem is that hydration (hydrated mineral) shells form around the cement mineral particles. The shells shield the remaining cores from easy observation, slow the hydration of the as-yet-unreacted or partly-reacted cores, and affect the actual hydration reaction stoichiometries. Nonetheless, it is possible to note a few general “net” equations that are representative of the larger family of reactions that are likely taking place. Much of the following discussion is based on the summary article by Young (1985).

The important strength-developing hydration reactions are those of  $C_3S$  and  $C_2S$ . Typical hydration reactions (in shorthand notation—see table 1) would be:



The formula shown for *tobermorite* is only approximate, and some texts denote it as  $C_3S_2H_4$ , in which case both hydration equations above would need an additional water (H) to start with. Actually, instead of just tobermorite, a whole family of similar *calcium silicate hydrates* (C-S-H) may be formed, and C-S-H is the preferred general term for these compounds. It is the C-S-H colloid or gel that is the actual binder in hydrated portland cement. The ultimate strength of the hardened cement paste will depend not only on the original total content of  $C_2S$  and  $C_3S$  but also on the completeness of their hydration.

Although the net hydration reactions for both  $C_3S$  and  $C_2S$  are similar, the reaction for  $C_3S$  is relatively fast, and C-S-H from it is responsible for virtually all of the early (e.g., within 3 days of curing) strength development of the cement. Typically, about 60% (by mass) of the  $C_3S$  has hydrated to C-S-H within the first 5 days of curing and about 70% has hydrated within about 10 days. Because of the formation of protective hydration shells, the remaining unreacted  $C_3S$  particle cores hydrate much more slowly, reaching about 75% hydration after 20 days of curing, about 80% hydration after 28 days (a standard measurement interval), and 85% after 60 days. Beyond 60 days, the rate of  $C_3S$  hydration slows dramatically and the incremental hydration and strength contribution is of little practical importance.

In contrast, the hydration of  $C_2S$  is relatively slow, with only about 20% hydration after 5 days of curing, about 30% after 10 days, 35% after 20 days, about 40% after 28 days, and only about 55% at 60 days. Its rate of hydration slows further after 60 days. Accordingly, the C-S-H derived from the hydration of  $C_2S$ , while making little contribution to the early strength of the concrete, contributes a significant proportion of the strength gain after the first week or so of curing.

The presence of large amounts of  $C_3S$  can be considered a defining characteristic of modern portland cement. In contrast, the very earliest portland cements probably contained little, if any,  $C_3S$ , and those of the latter half of the 19th century probably no more than about 15%–20%  $C_3S$ .

The 19th century portland cements instead relied primarily on the hydration of  $C_2S$ . It is unclear if the original (1824) portland cement even contained much  $C_2S$ ; the patent description describes only a calcination process. If the patent was indeed a full description of the original process, then the resulting hydraulic species would have been primarily clay pozzolans (as with hydraulic limes and natural cements)

although, as described in the process chemistry discussion below,  $C_2S$  formation could have been possible given the poor temperature control characteristic of the lime kilns of the day.

As shown above, the  $C_3S$  and  $C_2S$  hydration reactions release free lime. Based on the typical clinker mineral proportions and their hydration reactions, it can be shown that the net free lime release during clinker hydration, overall, is roughly 25%–33% of the original CaO content of the clinker. Free lime in hardened concrete is not particularly desirable because it increases the chemical reactivity of the surface (including along cracks) and can leach out in an unsightly fashion. On the other hand, by maintaining a high pH in the aqueous phase, free lime can help protect steel reinforcing bars (rebar) in the concrete from corrosion should water and oxygen reach the rebar via cracks. The lime is also available to react with any pozzolans that may have been added to the cement or concrete mix.

Alkalis, particularly sodium ( $Na_2O$ , or N in shorthand), can combine with C-S-H to form complex hydrates (e.g., C-S-N-H) that are unstable and prone to swelling compared with regular C-S-H. Alkalis can also react with forms (amorphous, opaline, or very fine grained crystalline) of silica in some aggregates used in concrete, forming highly hygroscopic alkali-silicate hydrates (e.g., N-S-H), and generally weakening the bond between the aggregates and the cement paste and forming higher-volume phases. These and similar reactions, collectively called *alkali-silicate reactions* (ASR) or *alkali-aggregate reactions*, can cause cracking of hardened concrete. The cracks not only weaken the concrete but render its interior susceptible to additional alkali or other chemical attack, and to freeze-thaw damage in cold weather regions. Approaches to controlling ASR reactions include selecting portland cements having lower alkali contents (e.g., ASTM C-150 provides for a low-alkali cement designation if the cement has a total alkali content [defined as  $Na_2O + 0.658 K_2O$ ] content of 0.60% or less), testing of aggregates for reactivity, and the incorporation of pozzolans into the cement paste. Pozzolans contain active silica which “sacrificially” combines with the alkalis in the paste (thus leaving less alkalis available to react with the aggregates), and significantly reduce the hardened concrete’s porosity. A review of ASR is provided by Leming (1996).

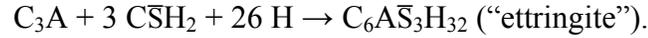
The other two clinker minerals,  $C_3A$  and  $C_4AF$ , have complex hydration reaction paths that are similar to each other, but those of  $C_3A$  are more important because they are much more rapid and exothermic. Having  $C_3A$  in the cement primarily enhances initial set and speeds, via release of heat, the hydration of  $C_3S$  (the presence of  $C_3A$  also has benefits to the cement manufacturing process because it speeds the overall formation of the clinker). In the absence of significant sulfate,  $C_3A$  very rapidly—almost instantaneously—forms  $C_3A$ -hydrates, many of which are unstable and may subsequently convert to other forms. One of the many possible sequential hydration reactions is:



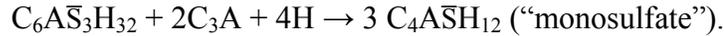
A minor, but lime-consuming, reaction is:



The hydration of  $C_3A$  in the absence of sulfate can be so rapid as to cause the undesirable condition known as *flash set*. This is controlled through the addition of sulfate, usually as gypsum and/or anhydrite. Plaster is only rarely used because it hydrates so quickly back to gypsum that its use is rather counterproductive. The use of plaster also increases initial water consumption. A typical hydration reaction of  $C_3A$  in the presence of rate-controlling sulfate (here shown as gypsum) would be:



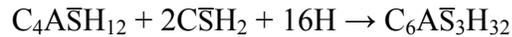
Flash set is controlled because ettringite forms a shell around the  $C_3A$  particles, which slows water diffusion to, and hence the hydration of, the residual  $C_3A$  cores. Ettringite is stable only in the presence of excess sulfate. If this condition is not met (i.e. not enough gypsum present, or in the evolving conditions at the ettringite-residual  $C_3A$  core interface), then ettringite reacts with  $C_3A$  to form a monosulfate phase:



Alternatively,  $C_3A$  hydration under low sulfate conditions can be expressed by:

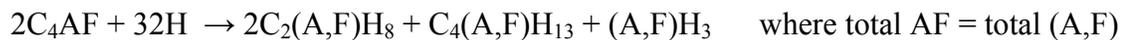


An important property of the monosulfate phase is that, in the presence of sulfate ions, it can re-form ettringite, such as by the reaction:

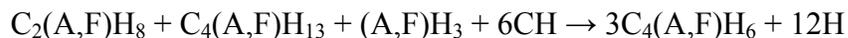


Ettringite has a molar volume of about 735 cubic centimeters ( $cm^3$ ) per mole and monosulfate about 313  $cm^3$  per mole (Bentz 1997). Because of this volume difference, re-formation of ettringite from monosulfate can cause expansion of the concrete. This is not much of an issue while the cement paste has yet to harden, but if ettringite re-forms in hardened concrete, the result can be cracking or spalling of the concrete. This process is known as *sulfate attack* and is prevalent in regions (commonly desert areas) having sulfate-rich groundwater, or it can occur if too much gypsum is present in the cement. Thus the proportion of gypsum in the cement is important. Where sulfate attack from groundwater is likely, concretes are better made using a sulfate resistant portland cement, such as Type II, or better yet, Type V; both have low concentrations of  $C_3A$  (table 3). A Type IV cement would also show resistance to sulfate attack, but would be less desirable for most applications because its relatively low  $C_3S$  content would cause it to develop strength relatively slowly. Alternatively, sulfate resistance is improved by using a blended cement, as addition of pozzolans lowers the overall  $C_3A$  content of the cement paste and reduces the porosity (hence sulfate entry potential) of the concrete.

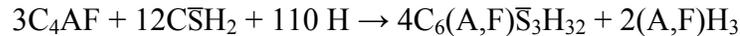
The ferrite mineral  $C_4AF$  does not play a critical role in cement hydration. The chief value of ferrite is in its effects on kiln reactions to form  $C_3S$  (see process mineralogy discussion below). The hydration of  $C_4AF$  is broadly similar to that of  $C_3A$ , although the reactions tend to be slower and much less exothermic. The reaction stoichiometries will vary given the fact that, as noted earlier,  $C_4AF$  is merely a mean composition for the ferrite solid solution having end members  $C_6A_2F$  and  $C_6AF_2$ . In the absence of sulfate, the F partially substitutes for some of the A (partial substitution denoted as A,F) in the analogous  $C_3A$  hydration products, as shown in the reaction:



In the presence of hydrated lime (from  $C_3S$  and  $C_2S$  hydration), however, the formation of  $(A,F)H_3$  is suppressed and a stable AF-hexahydrate ( $C_4(A,F)H_6$ ) is formed that is analogous to  $C_3AH_6$ , with a possible net reaction being:



Even more so than with  $C_3A$  hydration, the hydration of  $C_4AF$  is slowed in the presence of sulfate by the formation of an ettringite-like phase, with a possible reaction being:

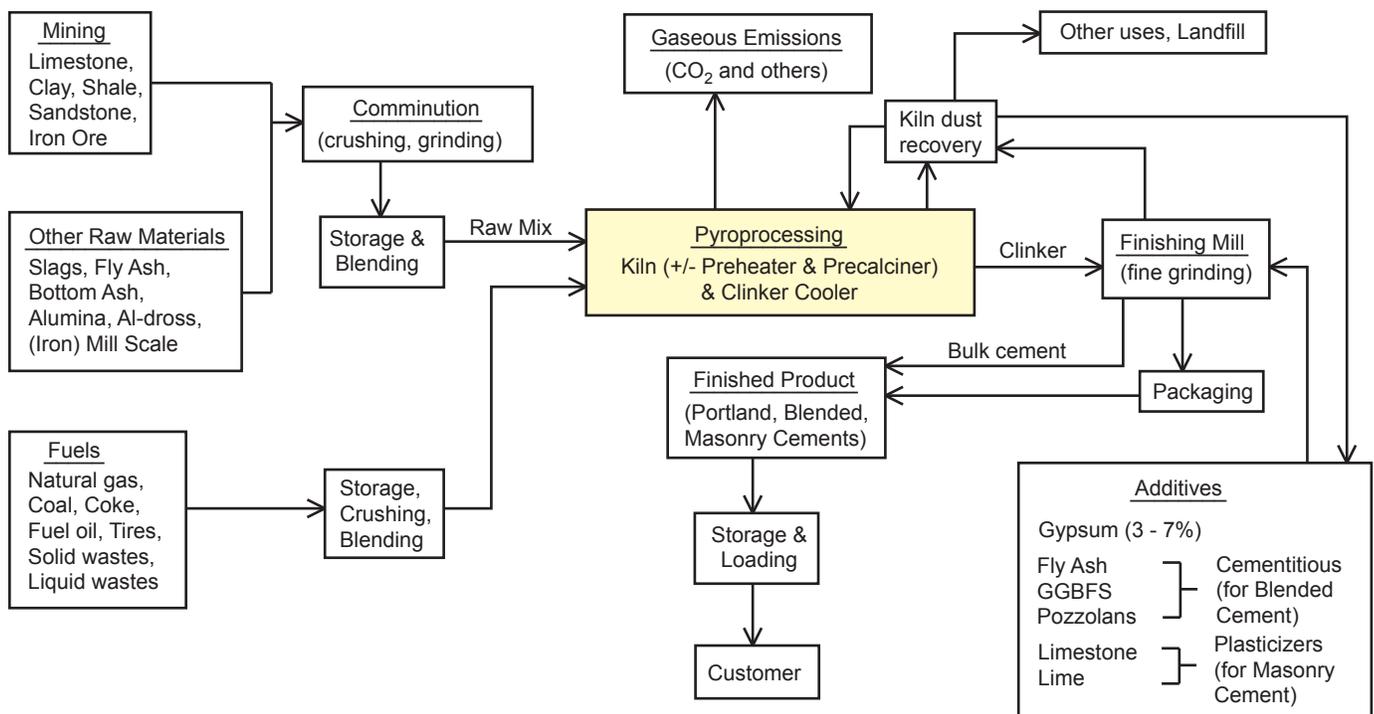


And, analogous to  $C_3A$ , if the sulfate concentration is insufficient, the “AF” ettringite becomes unstable and forms an “AF” monosulfate phase:



## Clinker manufacturing process

Portland cement manufacture involves two main steps: manufacture of clinker followed by fine grinding of the clinker with gypsum and sometimes other materials like pozzolans to make the finished cement product. Integrated plants perform both steps, whereas *grinding plants* make cement by grinding clinker that was made elsewhere. Clinker manufacture itself involves two main steps. First, appropriate raw materials must be quarried, crushed, and then proportioned and blended into a kiln feed called the raw mix or raw meal. Second, the raw mix must be converted into the clinker minerals. This is a thermochemical conversion and because it involves direct flame interaction, the overall procedure is referred to as pyroprocessing. Figure 3 is a generalized flow sheet of cement manufacture.



**Figure 3.** Simplified flow sheet of cement manufacture.

## Raw materials for clinker

The nonfuel raw materials for cement must yield the oxides required for clinker in the approximate proportions noted in table 1. Individual raw materials generally provide more than one oxide. Primary raw materials are those that are always used in relatively large quantities by a specific plant. To correct for minor deficiencies in one or more oxides in the primary raw materials, accessory or “sweetener” materials, generally of high purity, may be added. Certain oxides can also be partly supplied by the fuels; for example, the ash in coal supplies a portion of the silica requirements for clinker, and the steel belts in waste tires (a supplementary fuel) supply iron oxide. When a plant evaluates its raw materials, consideration is given not only to each material’s potential contribution of major oxides (CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>), but also to the content, if any, of undesirable trace elements (e.g., excess MgO, alkalis, toxic species). Consideration also is given to the ease of prepping the material (usually ease of crushing), and the material’s “burnability,” that is, the heat energy required to break down the material to activate or make accessible its component oxides.

The major oxide requirement for clinker is CaO (table 1) and large amounts of “accessible” CaO-bearing material are thus required for clinker manufacture. In practical terms this means limestone or similar material (e.g., marble). However, because of the need for other oxides, a high purity (>95% CaCO<sub>3</sub>) limestone is not required, although it is usable. Basically, a cement plant will first analyze its limestone, and then, to the degree that the limestone lacks the other requisite oxides, they will be added from other sources. Argillaceous limestones that supply a more or less complete oxide package are sometimes called *cement rock*; such material is not particularly common but was the key raw material and location determinant for natural cement plants (most of which eventually converted to portland cement production). Preparation of the raw mix for the kiln is a process of constant adjustment based on the frequent chemical testing of the raw materials, the raw mix itself, and the clinker. Generally, most, but not all, of the raw materials are mined adjacent to or within a few miles of the cement plant; the low unit value of most of the raw materials means that few can support the cost of long-distance transport to the plant. Long distance sourcing of major raw materials (i.e., limestone) is generally only economical if waterborne transport of the materials is available.

The USGS Minerals Yearbook chapters on cement show current consumption of raw materials split out by major oxide contribution and (in recent editions) whether the material is used to make clinker or is added to the clinker in the finish (grinding) mill to make finished cement. Table 5 shows an average annual consumption of raw materials for recent years by the U.S. cement industry and also shows some of the variety of materials that can be used. Some accessory raw materials (not necessarily split out in table 5) are waste products of other industries. Examples of these are spent potliners and catalysts from aluminum smelters, lime kiln dust and sludges, mill scale from steel mills, and a variety of ashes and slags from power plants and smelters.

Individual plants will have similar oxide ratios among materials, but may differ significantly in the specific raw materials consumed. Typically, about 1.7 t of nonfuel raw materials (about 1.5 t of which will be limestone or similar calcareous rocks) are required to make 1 t of clinker (table 5). The main reasons for this large ratio are the substantial mass loss (of CO<sub>2</sub>) from the calcination of limestone (see environmental discussion below), and the generation of large amounts of cement kiln dust (CKD), which, although captured, is not necessarily returned to the kiln as part of the feed stream.

**Table 5.** Nonfuel raw materials for clinker and portland cement manufacture in the United States (average for 1995-2000)

(Million metric tons per year)

Major oxide	Materials	Amount
CaO	Limestone, cement rock, marl, marble, CKD, other:	111.0
SiO <sub>2</sub>	Sand, sandstone, ferrous slags, fly ash, other ash:	6.0
Al <sub>2</sub> O <sub>3</sub>	Clay, shale, bauxite, other:	9.1
Fe <sub>2</sub> O <sub>3</sub>	Iron ore, millscale, other:	1.4
Other:	Gypsum, anhydrite, other:	4.5
Total raw materials:		132.0
Raw material content of imported clinker <sup>1</sup> :		6.1
Total equivalent raw materials:		138.1
Clinker production:		75.0
Total raw materials per ton of clinker <sup>2</sup> :		1.7
Cement production <sup>3</sup> :		84.4
Total raw materials per ton of cement:		1.6

<sup>1</sup>Calculated as tons of clinker x 1.7.<sup>2</sup>Excludes gypsum and anhydrite.<sup>3</sup>Includes cement made from imported clinker.

## Pyroprocessing

The heart of the cement manufacturing process is the kiln line, where raw materials undergo pyroprocessing to make clinker (figure 3). Almost all of the raw materials and most of the total energy consumed in cement manufacture are consumed during pyroprocessing.

In the following discussions, the technology of the kiln or pyroprocessing line and the process chemistry of clinker manufacture will be briefly described.

## Kiln technology

Early natural and portland cements were made in small vertical chimney-type kilns operating on a batch-process basis. These were slow, labor-intensive, and fuel inefficient, and the quality of the cement was difficult to control. As demand for cement grew, both in terms of quantity and quality, efforts were made to improve the manufacturing technology. The invention of the rotary kiln (1873), its improvement (1885), and significant enlargement (1902) allowed for superior mixing of raw materials, better control of temperature and other processing conditions, and continuous throughput of materials. Further design refinements to rotary kiln lines have been made throughout the 20th century. In most countries today, rotary kilns account for virtually all of the cement made (100% of U.S. production). The most significant exception is China, where a majority of production is still from small vertical shaft kilns (VSK), although the VSK fraction is declining rapidly; Lan (1998) provides a brief review of Chinese VSK technology.

Although VSK are improvements over the old, chimney-type kilns in that some VSK allow for continuous processing, they are considered to be less energy efficient than the rotary kilns, and VSK clinker (and hence cement) is generally considered to be of lower quality. Still, well-operated VSK technology can be appropriate to supply very small (village-scale) markets. The broad thermochemical functions of VSK do not differ significantly from rotary kilns, and the remaining discussion pertaining to rotary kilns will also apply broadly to VSK.

Rotary kilns consist of enormous, gently inclined and slowly rotating steel tubes lined with refractory brick, and are said to be the largest pieces of moving manufacturing equipment in existence. In all rotary kilns, the finely ground raw mix is fed into the upper, “cool” end of the kiln and is gradually heated and transformed into semifused clinker nodules as the material progresses down the kiln. In its simplest form, heating is from a white-hot jet of flame projecting up-kiln from a burner tube at the lower end. The clinker emerges from the lower, discharge end, and falls into a clinker cooler, where the clinker temperature is reduced to a safe handling level (about 100°C) for grinding into cement.

The oldest and largest (dimension) kilns in operation today use *wet* technology; these kilns typically range from about 120–185 m in length (a few are much longer) and about 4.5–7.0 m in internal diameter. Wet kilns derive their name from the fact that they are fed their raw materials in an aqueous slurry; such slurries were an early but effective solution to the problem of achieving a thorough mix of the crushed raw materials. *Dry* (technology) kilns take a dry powder feed and are of three main types. In order of increasing technological advancement, the main dry kiln line types are *long dry* kilns, *preheater* dry kilns, and *preheater-precalciner* dry kilns. Dimensionally, long dry kilns are about 90–120 m or more in length; preheater dry kilns can be the same length but most are somewhat shorter; and preheater-precalciner kilns—the most modern technology—are typically 45–75 m long. Dry kilns typically have internal diameters in the range of 3.5–4.5 m. The main reason for dry kilns having shorter tubes than wet kilns is that dry kiln tubes perform fewer thermochemical functions, as discussed below. Among kilns of the same technology, specific tube length and diameter may reflect throughput capacity (bigger tubes having larger capacity), and whether (any) preheaters and/or precalciners were installed as retrofit upgrades (original kiln tube length being retained or mostly so) or as an integral part of an entirely new kiln line (generally using a short, but large diameter tube). Although the largest (output) capacity kilns today are preheater-precalciner kilns, kiln size and technology, themselves, are not good guides to output capacity.

It must be emphasized that the overall pyroprocessing or thermochemical functions casually ascribed to the kiln generally refer to those of the complete kiln *line*, which consists of the kiln tube itself plus any preheaters and precalciners ahead of the kiln tube, plus the clinker cooler at the discharge end of the kiln tube. All kiln *lines* perform identical pyroprocessing functions, but those performed in the kiln *tube* itself depend on the type of kiln technology.

## Pyroprocessing functions of kiln lines

Wet kiln tubes perform the full range of functions of a kiln line, and the basic clinker manufacturing process is most easily described using a wet kiln example. The four major clinker line functions are: drying, preheating, calcining, and sintering (a.k.a. burning or clinkering). Each of these functions is performed sequentially in specific and progressively hotter parts of the wet kiln, described here as *functional zones* (note, the boundaries of adjacent functional zones overlap to some degree) and the temperature ranges shown are for the main functions of the zone (table 6).

**Table 6.** Sequential functional zones in a wet kiln tube

(Listed in order from upper end to lower end of the kiln)

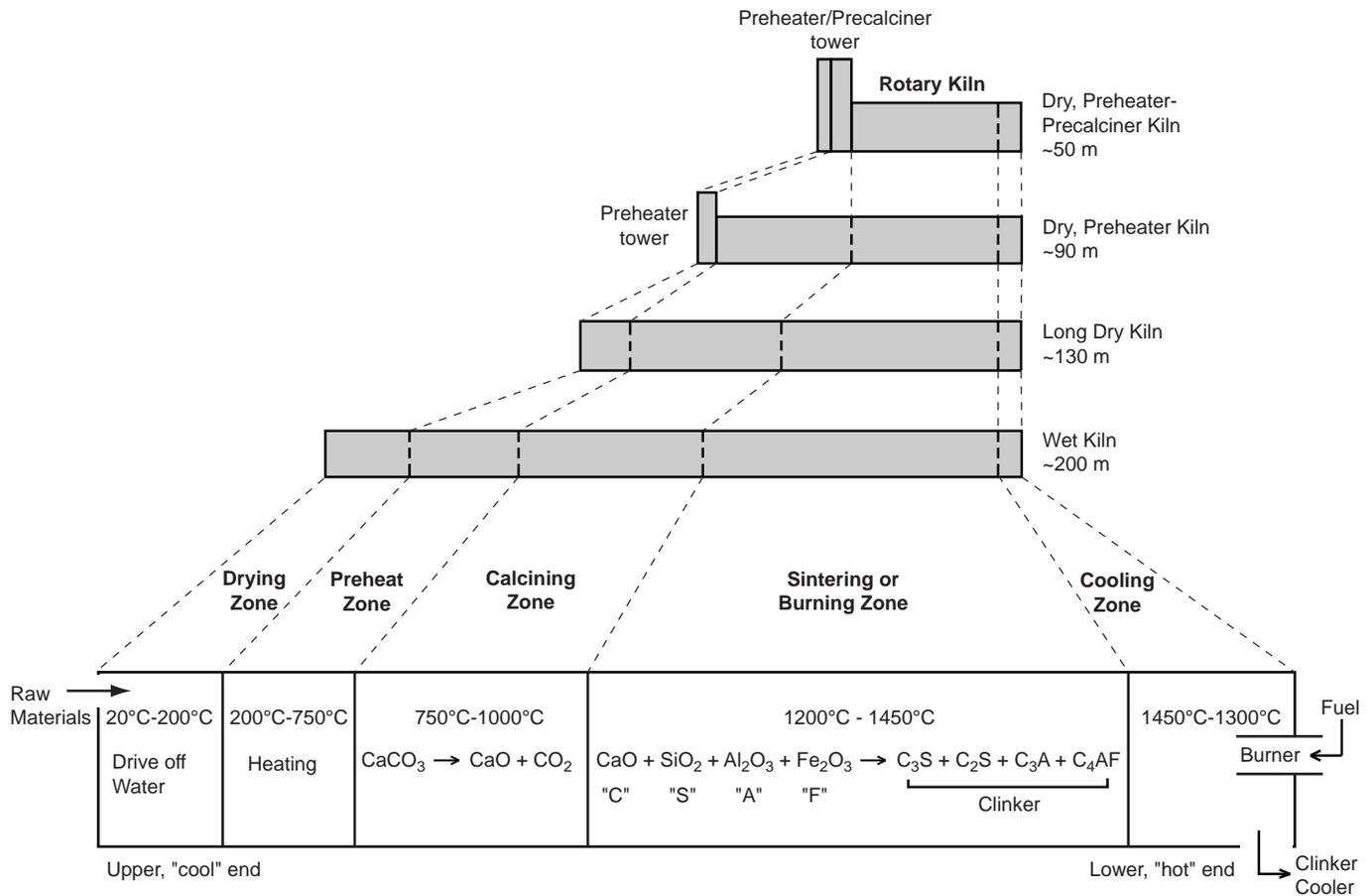
Functional zone	Approximate range of temperature (°C)	Activity
Drying <sup>1</sup> :	<100 – 200	Drive off water (wet slurry becomes dry powder).
Preheating <sup>2</sup> :	200 – 550	Drive off structurally-bound water (from clays etc.)
Calcination <sup>3</sup> :	750 – 1000	Drive off carbon dioxide from carbonate minerals.
Sintering <sup>4</sup> :	1200 – 1450	Form clinker minerals; form clinker nodules.
Cooling <sup>5</sup> :	<1450 – 1300	Cool slightly (no longer in path of flame).

<sup>1</sup>This function is essentially obviated in dry kiln lines.<sup>2</sup>This function is mostly performed by a separate preheater in a preheater dry kiln line.<sup>3</sup>This function is mostly performed in a separate precalciner in a preheater-precalciner dry line.<sup>4</sup>Also known as "burning" or "clinkering".<sup>5</sup>This cooling happens before the clinker enters the clinker cooler apparatus.

Again, the boundaries of the functional zones are approximate and do not involve complete cutoffs of activity. The drying and preheating zones together occupy roughly the upper one-third of the wet kiln tube, the calcination zone roughly the middle third, and the sintering zone most of the remainder. In the sintering zone, there is not only the thermochemical formation of the individual clinker minerals but also of a liquid phase (i.e., there is partial melting) such that the minerals form an intimate physical mix within semifused nodules or pellets of clinker about 1–10 centimeters in diameter. After their formation, the clinker nodules move into the kiln's short cooling zone—a slightly cooler region beneath the burner tube. When the now slightly cooled clinker reaches the discharge end of the kiln, it drops out of the kiln tube into the clinker cooler apparatus, where the real cooling occurs and the clinker temperature is reduced to about 100°C. The heat from the clinker is recaptured by recycling the hot air from the clinker cooler to the kiln line to be used as combustion air.

The technological progression over the years from wet kilns to preheater-precalciner dry kilns has been accompanied by a successive shortening of the kiln tubes. In succession, the wet kiln's drying zone is obviated in the long dry kiln; the long dry kiln's preheating zone is replaced by a tower-mounted cyclone preheater apparatus in a preheater kiln; and, finally, most of the calcination function is transferred to a (pre)calciner apparatus attached to the preheater in a preheater-precalciner kiln line. Thus, in a modern preheater-precalciner kiln line, the kiln tube itself basically only performs the sintering function, and can be as little as one quarter the length of a wet kiln tube of similar output capacity.

Residence time for material in kilns ranges from about 2 hours or more in wet kilns to as little as 20 minutes in preheater-precalciner kilns. The residence time in a preheater-precalciner tower itself is only about 20 to 90 seconds. Used alone, preheaters can be heated with hot kiln exhaust gases, but precalciners require their own, separate heating source, and commonly are designed to burn about 60% of the total kiln line fuel supply. Hot air from the clinker cooler apparatus is used as combustion air in the kiln to save energy. Additional details on the form, function and operation of rotary kilns can be found in Alsop and others (2005) and, in more detail, Duda (1985) and Bhatta and others (2004).



**Figure 4.** Diagram of functional zones for different kiln technologies

## Process chemistry

Although all of functions of a kiln line (table 6) involve a great deal of heat energy, the thermochemical reactions most important to the formation of clinker occur in the calcination and sintering zones. As noted above, there is no sharp transition between these or the other functional zones in the kiln; the terminology refers to the critical reactions occurring dominantly in the particular zone.

### Calcination zone reactions

The main oxide in clinker and portland cement is CaO (table 1), and a source of CaO is sought that is abundant, inexpensive, and easily processed to make this oxide available for clinker mineral formation. Limestone and similar rocks are the main raw material sources of CaO (table 5); cement plants are almost invariably located within a few miles of their limestone quarries. The main CaO-bearing mineral in limestone and related rocks is calcite ( $\text{CaCO}_3$ ), and calcination simply strips the carbon dioxide from this mineral (or any other carbonate minerals present):  $\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2 \uparrow$

If a dolomite [ $\text{Ca}, \text{Mg}(\text{CO}_3)_2$ ] or magnesite ( $\text{MgCO}_3$ ) phase is present, calcination via an almost identical equation will yield an MgO component in addition to CaO. This calcination will require somewhat lower temperatures than for calcite, but because the MgO component of cement is kept very small (table 1), the actual calcination temperature for the raw mix overall is not significantly affected. As will be discussed later, the calcination release of carbon dioxide is of great environmental concern.

Within much of the calcination zone temperature range, clay minerals in the raw mix break down into their component oxides or other reactive phases, and other silicate minerals in the mix begin to break down also. There is initial formation of  $C_2S$  by the net reaction  $2C + S \rightarrow C_2S$ . This process continues into the sintering zone.

### Sintering zone reactions

A distinction can be made between reactions that straddle the calcination-sintering zone transition (about  $900^\circ\text{C}$  to about  $1200^\circ\text{C}$  or so), and true sintering (or clinkering) reactions occurring mostly above about  $1300^\circ\text{C}$ . The transitional or lower temperature reactions are mainly of two types: a continuation of reactions that began in the calcination zone that involve the thermal decomposition of noncarbonate (mainly silicate) raw materials into their component oxides or other reactive phases, and those that form some of the lower temperature clinker minerals or their immediate precursors from those oxides or phases. The true sintering reactions are mainly those that require high temperatures and which center on the formation of  $C_3S$ . For the purpose of the following discussion, the “sintering” reactions will be restricted to those that combine (even at lower temperatures) component oxides into the clinker minerals. These reactions are many and complex, but in terms of an overall oxide balance, the approximate net reaction to form clinker (mineralogical ratios comparable to those in table 3) would be:



All of the classic books on cement chemistry have chapters that discuss in detail the sintering reactions in the kiln; the following brief discussion is based on Bogue (1955), Welch (1964), Lea (1970), Taylor (1997), and, especially, the summary by Roy (1985). These references may be consulted for the relevant phase diagrams. It is important to note that the discussions in the chemistry books, as well as that here, tend to focus on pure chemical or mineral phases. In reality, the raw mix and clinker mineral compositions usually contain modest amounts of impurities, and these can affect reaction paths, rates, and temperatures.

Most of the mineral-forming reactions that occur below about  $1200\text{--}1300^\circ\text{C}$  are in the solid state and tend to be slow and relatively confined to individual raw material particles or to the contacts between adjacent particles. However, in the higher temperature range of the sintering zone there is significant formation of liquid (i.e. partial melting), and this allows oxide combination, and hence clinker mineral formation, to occur much more rapidly and completely. The rate of reaction is important because the clinker raw mix is continuously progressing through the kiln and the residence time in the highest-temperature zone is limited.

Which clinker minerals form, and at what temperatures, depend on the oxides present in the raw mix. The formation and stability of the four clinker minerals ( $C_3S$ ,  $C_2S$ ,  $C_3A$ , and  $C_4AF$ ) can be described within the confines of a 4-component (quaternary) system covering the four major component oxides (C, S, A, F). However, it is best to first consider simpler phase systems and then build to the quaternary system, with the goal of understanding how large quantities of  $C_3S$  (the dominant mineral in portland cement) can be formed economically—that is, as quickly, and at as low a temperature, as possible.

For a simple binary mix of  $\text{CaO}$  and  $\text{SiO}_2$  (i.e., a C-S system), most or all of the available silica will have been taken up from solid state reactions into  $C_2S$  (assuming sufficient  $\text{CaO}$ ) by the time the temperature reaches  $1200^\circ\text{C}$ . Initial formation of  $C_2S$  begins around  $700^\circ\text{C}$ , but most forms in the range of  $1100\text{--}1200^\circ\text{C}$ . Solid-state binary system formation of the critical  $C_3S$  mineral (by the exothermic

reaction  $C_2S + C \rightarrow C_3S$ ) starts in the range of 1250–1400°C. However, the reaction is extremely slow at these temperatures and remains so even at 1500°C. Rapid formation of  $C_3S$  in the C-S binary system does not occur until a melt forms, and this does not happen below about 2050°C, which is well above the practical material temperatures achievable in a kiln. Fortunately for the portland cement industry, the presence of other oxides ( $Al_2O_3$ ,  $Fe_2O_3$ ) dramatically lowers the temperature range at which a melt forms.

For example, in the C-A-S ternary system (important because it accommodates about 90% of the clinker composition),  $C_3A$  is a critical phase that lowers the temperature needed to form a melt. This mineral and its aluminates precursors begin to form by solid state reactions at calcination zone temperatures. The three clinker minerals  $C_3S$ ,  $C_2S$ , and  $C_3A$  are in stable coexistence with a melt phase at a temperature as low as 1455°C, although there will not be much melt, or much  $C_3S$ , at this temperature. Further, 1455°C is still a difficult material temperature to sustain or significantly exceed in a rotary kiln. Thus, as a practical matter, the amount of  $C_3S$  that can be made in a C-A-S ternary component system is limited unless higher temperatures can be achieved or fluxes are used.

The occurrence of  $Fe_2O_3$  in clinker raw materials brings the reactions into the C-S-A-F quaternary system, which is highly advantageous to practical clinker production. The key ferrite ( $C_3AF$ ) phase, which begins to form by solid state reactions at temperatures of about 800°C, acts as a flux to lower the temperature of melt formation. Within the C-A-F ternary subset of the C-S-A-F quaternary system,  $C_4AF$  coexists with  $C_3A$  plus liquid at the relatively modest temperature range of 1310–1389°C. Likewise, the minerals  $C_3S$ ,  $C_2S$ , and  $C_3A$  are in equilibrium with a liquid phase at 1400°C, compared with 1455°C in the pure C-A-S ternary system. In the full C-S-A-F quaternary system, the four minerals  $C_3S$ - $C_2S$ - $C_3A$ - $C_4AF$  plus liquid coexist at even lower temperatures. Although the temperature reduction is not all that large with just a few percent  $Fe_2O_3$  in the system, at about 10%  $Fe_2O_3$  the temperature drops significantly. The quaternary eutectic for  $C_3S$ - $C_2S$ - $C_3A$ - $C_4AF$  plus liquid is 1338°C, with a modest upwards range of equilibrium point temperatures because of the fact that somewhat different clinker mineral stoichiometries may be present (c.f., the “pure” mineral formulae shown). In any case, the equilibrium temperatures for these four minerals and melt are now in a range readily attainable and sustainable in a kiln, but at the lowest end of this melt temperature range not much liquid is present and so formation of the critical  $C_3S$  mineral is still not very rapid. The rate of  $C_3S$  formation, and hence the amount of  $C_3S$  that will form within a given residence time in the sintering zone of the kiln, increases as the proportion of liquid is increased. For an “average” clinker C-S-A-F composition such as that in table 1, the amount of liquid at about 1340°C is about 20%, and it reaches about 30% (a satisfactory melt component for adequate rate of  $C_3S$  formation) at temperatures of 1400–1450°C. Consequently, 1400–1450°C is the approximate targeted maximum temperature range for the sintering zone in the kiln.

In actual clinker manufacture, other compounds that can act as a flux may be present in the raw mix. Among these, MgO and alkalis are the most likely to be naturally present in the raw materials, and fluorine is sometimes added in the form of fluorspar ( $CaF_2$ ). However, the amount of these materials must be kept low to avoid certain subsequent problems with the operation of the kiln and/or the quality of the finished cement.

Interestingly, in the manufacture of white portland cement, the iron content must be kept very low to avoid iron’s coloring effect, and so there forms no (or insufficient)  $C_4AF$  to act as flux. In effect, the conditions in a white cement kiln, in the absence of other fluxes, are essentially confined to the C-A-S ternary system. Formation of large percentages of  $C_3S$  in line with modern requirements for white cement (table 4) is difficult, and requires that the kilns be operated very hot (sintering temperatures of approximately 1500°C) and the residence times in the sintering zone be extended.

Cooling of clinker in the clinker cooler not only allows for safe subsequent handling, but also stops further changes of the clinker mineral phases and assemblages. The cooling of white clinker must be especially rapid (essentially via water quenching) to minimize any reversion of  $C_3S$  to  $C_2S$  and to prevent the oxidation of any (slight) iron present to ferric ( $Fe^{+3}$ ) valence (ferric iron imparts more color than does ferrous iron).

## Manufacture of finished cement from clinker

After clinker has been cooled to about  $100^\circ C$ , it is ready to be ground into finished cement in a grinding mill, more commonly referred to as a *finish mill*. At most integrated cement plants, the output or grinding capacity of the finish mill will be at least as large as the sum of the clinker capacity plus the additives to be interground in the finished product. That is, an integrated plant with a clinker capacity of 1 Mt/yr would be expected to have a grinding capacity of at least 1.05 Mt/yr if the usual product is a straight portland cement having a fairly typical 5% gypsum content, but the mill capacity could be significantly higher if the product line involves a lot of ground additives (i.e. to make blended and/or masonry cements). Likewise, finish mill capacity will be higher if the plant was designed to routinely grind supplementary clinker from an outside source. In a few cases, plants report seemingly excess grinding capacities, but include mills that are, in fact, being used to grind granulated blast furnace slag destined to be sold directly to concrete companies as a cement extender (SCM). A few plants have large excess clinker production capacities; these plants routinely transfer out or sell their surplus clinker. A few independent grinding facilities (*grinding plants*) rely on outside sources for all of their clinker.

Generally, separate grinding and/or blending finish mill lines will be maintained at a plant for each of its major product classes (finished portland cements, blended cements, masonry cements, ground slag). In the United States, about 95% of the masonry cement is made directly from a clinker + gypsum + additives feed, with the remainder being made from a (finished) portland cement + additives feed. Additives that commonly require grinding at the mill include gypsum, limestone, granulated blast furnace slag, and natural pozzolans. Additives that generally do not require significant grinding include fly ash, GGBFS, and silica fume, but the finish mill does provide intimate mixing of these with the portland cement base.

Portland and related cements are ground to an extreme fineness (much finer than cosmetic talcum powder). Cement particles average about 10 micrometers in diameter and approximately 85%–95% of cement particles are smaller than 45 micrometers in diameter. This fine particle size helps insure rapid and uniform hydration of the cement and enhances the ease with which it can be mixed into the concrete batch. The fineness of cement is determined using tests that measure the total surface area of a given unit mass of cement powder. Fineness of cement is usually expressed relative to the *Blaine* air-permeability test (ASTM C-204), either in units of  $m^2/kg$  or  $cm^2/g$  (the latter being more common), but sometimes denoted simply as Blaine, where the reader is expected to know the units based on the number itself. Thus, for example, one might see the fineness of a particular cement casually expressed as either 400 Blaine or 4,000 Blaine; these represent, and would be more rigorously expressed, as  $400 m^2/kg$  (Blaine) or  $4,000 cm^2/g$  (Blaine), respectively. Typically, portland cement in the United States is ground to 3,700–4,000  $cm^2/g$  (Blaine), except that Type III (high early strength) cements are ground much finer (about 5,500  $cm^2/g$ ) to speed the hydration of  $C_3S$ . As shown in Kosmatka and others (2002, p. 42), white cement is also typically ground very fine (typically about 4,900  $cm^2/g$  (Blaine), but some specifications are ground much finer still). In “older” white cements having low  $C_3S$  contents (table 4), this fine grinding helped increase the speed of hydration of the cement, allowing it to meet Type I performances. Modern formulations of white cement have very high  $C_3S$  contents and the fine grinding is done mainly to

improve the whiteness and brightness of the product. Along with the high heat requirements for white clinker formation, this fine grinding increases the overall energy requirements and hence manufacturing cost of white cement and makes it necessary to sell this product at significantly higher prices (roughly double) than those for gray portland cements of similar structural performance.

### Energy requirements for clinker and cement manufacture

Given the huge size of cement kilns, it takes a great deal of fuel (heat energy) to generate and sustain the very high temperatures inside them needed to make clinker and, in the case of wet kilns, to evaporate the water from the raw feed slurry. Likewise, it takes a lot of electricity to crush and grind the raw materials into kiln feed and the clinker into finished cement, as well as to operate the kiln line.

Data on the type and quantity of fuels and electricity consumed by the U.S. cement industry are collected and published annually (Minerals Yearbook) by the USGS. The data are grouped separately by plants operating wet kilns, dry kilns, and those operating both technologies. Data on the heat content of the fuels consumed are also collected by the USGS but have not been routinely published. A summary of recent data for the U.S. industry overall is given in table 7 below, and a compilation for the period 1950-2000 can be found in van Oss and Padovani (2002).

**Table 7.** Summary of fuel and electricity consumption by the U.S. cement industry in 2000 1/ 2/

Fuel	Quantity	Unit	Fraction of contributed	
			Heat	Total Energy
Coal	10.1	3/	67%	60%
Coke, petcoke	1.8	3/	14%	13%
Natural gas	338.3	4/	3%	3%
Fuel oils	123.7	5/	1%	1%
Used tires	0.4	3/	3%	3%
Solid wastes	1.0	3/	6%	5%
Liquid wastes	929.1	5/	6%	5%
Electricity	12.6	6/	nil	10%
<u>Average unit consumption of energy 2/:</u>				
Electricity	143.9 kilowatt hours per metric ton of cement.			
Heat	4.7 million Btu (7/) per metric ton of clinker.			
Total energy 8/	4.9 million Btu per metric ton cement.			

1/ Source of data: USGS annual survey of U.S. plants.

2/ Fuel and energy consumed reflect the U.S. mix of wet and dry kilns; values likely would differ in countries operating a different mix of technologies.

3/ Million metric tons.

4/ Million cubic meters.

5/ Million liters.

6/ Billion kilowatt-hours.

7/ British thermal units; 1 million Btu = 1.055056 gigajoules.

8/ Includes electricity.

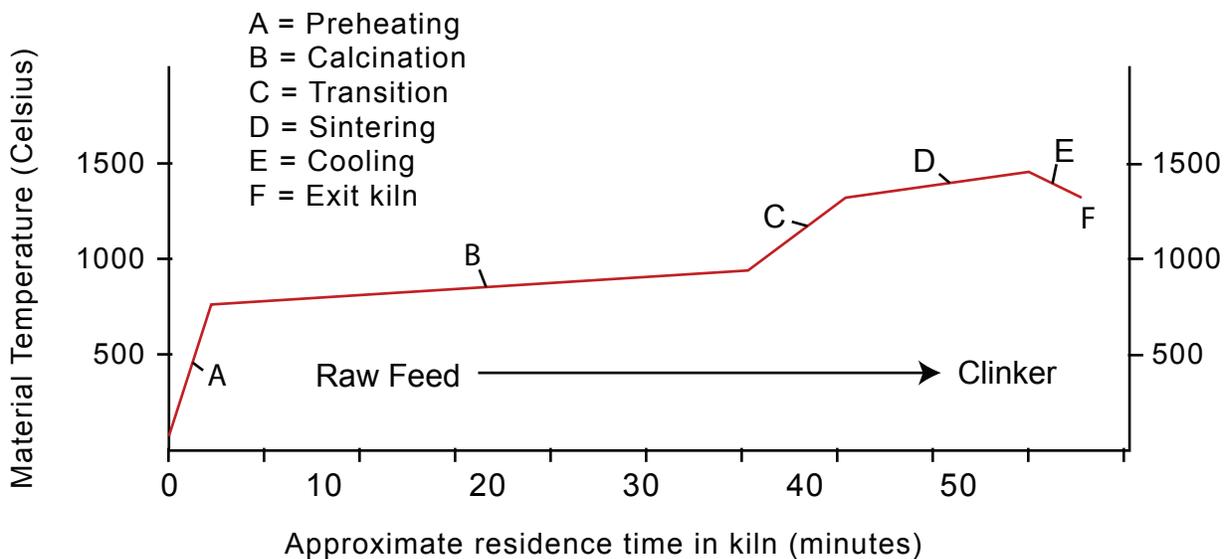
As can be seen from table 7, coal (currently all bituminous) is overwhelmingly the dominant fuel used by the U.S. cement industry; all but a tiny handful of U.S. cement plants burn coal as their primary heat source. However, many U.S. plants routinely burn more than one fuel. For example, when firing up a cold kiln, natural gas or fuel oil is commonly used for the slow, warm-up phase necessary to prevent thermal overstressing of the kiln's refractory brick lining. Once the kiln is sufficiently hot, it will be switched over to coal and/or coke (generally petroleum coke) for production operations. Most U.S. plants are technically capable of burning a variety of fuels, even if they do not routinely do so. Depending on the kiln technology, which may need to be modified, various materials can be burned as alternative or supplementary fuels. An impressive variety of solid and liquid waste materials, including many types of hazardous wastes, can be burned in clinker kilns as supplements or partial replacements to the regular fossil fuels. Some alternative materials used as fuels contribute high unit energy contents (e.g., petroleum coke and used tires), while others are less valued in this respect but are still utilized because the plant is paid to take them. Where waste fuels are incorporated, their contribution to the total heat in the kiln will generally be no more than about 10%–30%. Examples of solid wastes include whole or shredded tires, shredded paper and pulp, spent catalysts, sawdust, scrap wood, rubber residues, shredded packing containers, bone meal, scrap fabrics, dried sewage sludges, oil-contaminated soils, and scrap plastics. Examples of liquid waste fuels include a wide range of spent lubricants and solvents, substandard petroleum refinery products, tars, paints and inks, and miscellaneous chemicals, slurries, and sludges.

Although not shown on table 7, both heat and electricity consumption vary significantly with kiln technology and, for a given technology, tend to be higher for plants operating multiple kilns than for plants with a single kiln of the same overall capacity. Wet kilns consume more fuel on a unit basis than do dry kilns because of the need to evaporate the water in the slurry feed and the much larger size of the wet kilns. In 2000, wet kiln plants in the United States averaged 5.7 million Btu (Mbtu) per ton clinker (fuels only), whereas dry kiln plants averaged 4.4 MBtu/t clinker (USGS data). Data from the Portland Cement Association (PCA) 2000 energy survey of its members (a large subset of the entire U.S. industry) are comparable: 5.8 Mbtu/t clinker for wet plants and 4.2 MBtu/t clinker for dry plants. The PCA's slightly lower values may reflect the exclusion of the white cement plants, which are exceptionally energy-intensive. On a unit clinker basis, fuel consumption tends to be lower in larger capacity kilns and, in the case of dry kilns, decreases with the incorporation of preheaters and precalciners. The PCA 2000 energy survey data illustrate these trends (all data per ton clinker): wet kilns <0.5 Mt/yr capacity (6.2 MBtu); wet kilns  $\geq 0.5$  Mt/yr (5.6 MBtu); dry kilns <0.5 Mt/yr (4.9 MBtu); dry kilns  $\geq 0.5$  Mt/yr (4.1 MBtu); long dry kilns (5.1 MBtu); dry preheater kilns (4.1 MBtu); dry preheater-precalciner kilns (3.8 MBtu). Both the USGS and PCA heat data are based on reported or assigned standard values for the high or gross heat contents of fuels and, for the gaseous and liquid fuels in particular, these will be higher than values for the same fuels reported on a low or net heat basis (as is done in most other countries).

Despite the very much higher temperature requirements for sintering than for calcination, as noted in the kiln functional zone and process chemistry discussions earlier, the actual heat energy input requirements are the opposite. The major heat requirements are for the drying, preheating and calcination functions, not for sintering. For a dry technology kiln line, of the total theoretical heat inputs to make clinker (i.e., based on reaction thermodynamics, thus ignoring heat losses through the kiln shell and the drying requirements of a wet kiln's feed), about 40% is taken up in the preheating, about 48% in the calcination reaction, and about 12% additional heat is required in the transitional reactions leading to the earliest sintering reactions. The main sintering reaction to make alite ( $C_2S + C \rightarrow C_3S$ ) is exothermic; the sintering process actually yields a net return of heat energy equivalent to almost 9% of the total heat inputs. Thus the total theoretical heat requirements to make clinker are only about 92% of the requirements to preheat and calcine the raw materials. These heat relationships are reflected in the

material temperature vs. residence time profiles for a kiln. Figure 5 illustrates this for a typical preheater-equipped dry kiln; very little temperature gain is seen while calcination is ongoing because this reaction is absorbing so much heat energy. For a kiln equipped with a calciner, the ‘B’ part of the curve (calcination) would be much shorter, as about 80% of the calcination function would overlap the profile of part ‘A’ (preheating).

In reality, the true heat requirements to make clinker are much higher than the theoretical requirements because of various inefficiencies (totaling about 50%)—mostly heat losses through the kiln shell and, for wet kilns, the enormous heat requirements to evaporate slurry water. On the other hand, most plants will be designed to recover as much heat as possible from the exit gases. For example, hot air from the clinker cooler will be used as combustion air in the kiln. The heat saved by reuse of hot gases can be equivalent to about 50% of the total theoretical heat requirements to make clinker.



**Figure 5.** Time-temperature profile for material in a preheater-equipped dry kiln. (After Glasser, 2004)

Surprisingly, the energy (unit fuel or heat) savings noted above for dry kilns is commonly not seen in the plants’ electricity consumption, although logic would dictate that a short (hence lighter) dry kiln tube would take less electricity to rotate than a long wet tube. Likewise, there is no inherent reason why the comminution circuits at dry plants should be more efficient than those at wet plants, save that the dry plant category has the majority of the more modern grinding facilities. But for the U.S. industry in 2000, USGS data indicate that wet kiln plants averaged 131 kWh/t cement and dry kilns 148 kWh/t. These values have declined only very slowly and slightly over the years. Comparable data for 2000 from the PCA are 135 kWh/t for wet kilns and 146 kWh/t for dry. The main reason for dry kilns having overall higher unit electrical consumption is that the various fans and blowers associated with preheaters and precalciners are electricity-intensive. However, when examined by type of dry kiln technology, the PCA survey data do not fully support this generalization. For example, long dry kilns averaged about 153 kWh/t cement; preheater kilns about 150 kWh/t cement; and preheater-precalciner kilns about 141 kWh/t

cement. Thus, it is evident that other factors are also important determinants of electricity consumption, most probably economies of scale, age of the facility or its upgrade(s), the grinding technology installed, and the type of kiln dust recovery system used. Also, USGS plant survey data (not shown here) reveal that plants that operate multiple kilns (of any technology) have higher unit electricity consumption overall than do plants having similar technology and overall capacity but which have just one kiln. Dedicated clinker-grinding plants typically have electricity consumption rates of 70–80 kWh/t cement. This is about 10%–15% higher than would be expected for a finish mill of similar capacity at an integrated cement plant, and reflects the fact that a grinding plant is a stand-alone facility.

## **Environmental issues of cement manufacture**

Cement manufacturing, as noted earlier, involves two major types of activity: 1) obtaining and preparing raw materials (and fuels), and 2) manufacturing clinker and finished cement. Some of the environmental issues related to these activities will be briefly covered here; the major issue of CO<sub>2</sub> emissions will be covered in some detail. Although the U.S. cement industry is subject to a variety of environmental regulations (most not specific to the industry), it is beyond the scope of this review to describe the regulations and regulatory issues.

### **Mining of raw materials**

The environmental aspects of mining of cement raw materials generally do not attract widespread public attention; certainly not by comparison to the attention accorded to the mining of, for example, metals and coal. The environmental issues for cement raw materials tend to be quite local and are similar to those for aggregates; a review of the latter is provided by Langer (1999). Most raw materials for cement are from surface quarries. A few plants mine underground in cases where, because of stratigraphy, terrain, land acquisition or mine permitting problems, or a need to protect the viewscape, there is a lack of surface reserves. Cement plants generally will not be constructed unless adjacent raw material reserves are sufficient for at least 50 years of operations. Over this time span, the plants' limestone quarries can become quite large even though their operational rate will only be on the order of a few thousand tons per day. As with aggregates, the low unit value of limestone and other raw materials precludes high stripping ratios, and thus overburden quantities will be minimal. Likewise, long-distance (more than a few miles) transportation of the major raw materials is generally precluded. Cement raw materials typically are geochemically benign, so issues such as acid mine drainage tend not to apply. Overall, issues with mining of cement raw materials mostly relate to noise, vibrations and dust from blasting (usually not done daily) and haulage equipment (mostly short-haul transport), as well as aesthetic concerns. Environmental factors related to the procurement of fuels (coal mining, etc...) for cement manufacture are generally not an issue for the cement industry itself. A significant exception is where a cement plant burns waste fuels, which need to be gathered, transported to a location for blending, and then delivered to the cement plant. Especially in cases where hazardous wastes are being used, various aspects of waste fuel handling will likely require environmental permitting.

### **Manufacture of clinker and finished cement**

The major environmental issues associated with the cement manufacture are, in fact, associated with the manufacture of clinker rather than with the subsequent intergrinding of clinker and various additives to make cement itself. With clinker manufacture, the environmental issues concern particulate and gaseous emissions from the burning of large quantities of fuels and raw materials—chiefly limestone.

## Particulate emissions

All cement plants generate a great deal of fine dust from the kiln line; these dusts will be collectively labeled *cement kiln dust* (CKD). The material in CKD varies among plants and even over time from a single kiln line, but includes particulates representing the raw mix at various stages of burning, particles of clinker, and even particles eroded from the refractory brick and/or monolithic linings of the kiln tube and associated apparatus. In the early days of the portland cement industry, and perhaps still the case at obsolete plants in countries substantially lacking air pollution regulations, CKD was vented to the atmosphere and the resulting dust clouds were no doubt viewed unfavorably by the local communities. Today, however, at all plants in the United States, and at all modern plants worldwide, CKD venting to the atmosphere has been reduced to minute quantities generally invisible to the naked eye. This is because the plants are now equipped with dust scrubbers, either in the form of electrostatic precipitators or filtration baghouses, or both. At many plants, the captured CKD is fed back into the kiln (“recycled”). Likewise, at many kiln lines, CKD-laden exhaust is directly rerouted to the kiln for recycling.

Except to monitor stack emissions (residual venting), CKD generation by cement plants is not routinely measured; indeed, this would be difficult to do for CKD exhaust directly rerouted to the kiln. Consequently, there are only limited data on total CKD generation by cement plants. Some of the available data merely refer to the material captured by the scrubbers. Informal conversations with plant personnel at U.S. plants suggest that typical CKD generation is equivalent to about 15%–20% of the weight of the clinker produced (or about 12–15 Mt/yr at current U.S. clinker output levels).

Apart from environmental concerns, cement plants prefer to recycle (to the kiln) as much CKD as possible, sometimes including material from old CKD piles, because the accumulated CKD represents material that has a substantial value in that its precursors had to be mined, crushed, and burned, and so should not be wasted. However, certain contaminants such as alkalis and some heavy metals tend to concentrate in the CKD, and recycling of CKD to the kiln can thus only be done to the extent that the clinker quality is not compromised. This is a particular issue where local aggregates (for concrete) are susceptible to alkali-silica reactions with the cement. Where not recycled to the kiln, CKD can sometimes be used as a soil conditioner (liming agent), or as a somewhat cementitious material for roadfill, and occasionally as a filler or cementitious extender for finished cement. Where no uses can be found, however, CKD must be landfilled—an increasingly undesirable and costly option. Informal data suggest that about 60%–70% of generated CKD at U.S. plants is currently being recycled to the kilns (7–8 Mt/yr, but only a fraction of this is recorded in the CaO-contributing raw materials in table 4), less than 10% is being used for other purposes, and the remainder is being landfilled..

## Gaseous emissions

The principal gaseous emissions from cement plants are nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>), and CO<sub>2</sub>. The cement industry is considered to be a significant overall, and large point source of NO<sub>x</sub>, a modest source of SO<sub>x</sub>, and a very large point and collective source of CO<sub>2</sub>. Nevertheless, for all three, the cement industry’s collective emissions are dwarfed by those of thermal powerplants, and by those of motor vehicles for NO<sub>x</sub> and CO<sub>2</sub>.

### Nitrogen oxides

The high-temperature combustion of large quantities of fuels, as in cement kilns, can be expected to release NO<sub>x</sub> in significant amounts, with the nitrogen being derived mostly from the atmosphere and

the fuels, but also to a limited degree from the nonfuel raw materials. The formation of NO<sub>x</sub> in rotary kilns is complex and not fully understood; useful reviews of the subject are given by Haspel (2002), Smart and others (1998) and Young and von Seebach (1998). As noted in these reviews, NO<sub>x</sub> emissions are dominantly NO (90% or more of the total), with lesser NO<sub>2</sub>, and four principal categories or formation mechanisms of NO<sub>x</sub> are typically identified, namely “thermal” NO<sub>x</sub>, “fuel” NO<sub>x</sub>, “feed” NO<sub>x</sub>, and “prompt” NO<sub>x</sub>.

Thermal NO<sub>x</sub>, the dominant type (typically >70% of total), is that formed by direct oxidation of atmospheric nitrogen and forms chiefly by two reactions, both of which are dependent on the dissociation of atmospheric O<sub>2</sub> and N<sub>2</sub>:



Thermal NO<sub>x</sub> begins to form at temperatures above 1200–1500°C, which is well below the burner flame temperature in cement kilns. The formation of thermal NO<sub>x</sub> increases rapidly with even small increases in temperature when temperatures are in the range of 1370–1870°C, the higher end of which approximates the gas temperatures in the sintering zone of the kiln. Thus, even small shifts in oxygen content of combustion gas in the kiln’s sintering zone can have a pronounced influence on the amount of thermal NO<sub>x</sub> formed.

Fuel NO<sub>x</sub> refers to NO<sub>x</sub> formed by the combustion of nitrogen-containing compounds in the fuel. Most fuels (the major exception being natural gas) contain nitrogen in some amount. The oxidation of nitrogen in fuels occurs throughout the entire temperature range of combustion in the kiln line. Based on its nitrogen content, coal has the highest potential to generate fuel NO<sub>x</sub> and natural gas the least (nil). However, total NO<sub>x</sub> emissions from kilns burning coal are much lower than from gas-fired kilns, which illustrates the overwhelming importance of thermal NO<sub>x</sub> in total emissions (natural gas flame temperatures are higher than coal flame temperatures). On the other hand, NO<sub>x</sub> emissions from calciners are predominantly fuel NO<sub>x</sub>, as the calciner temperatures can be kept low relative to the sintering zone of the kiln. The formation paths for fuel NO<sub>x</sub> are very complex, as they are an interplay of oxidizing and reducing reactions (by intermediate nitrogen compounds such as HCN and NH<sub>2</sub><sup>·</sup> radicals), and thus vary both with the overall temperature, the amount of oxygen available, and the position (within the flame) of the reaction.

Feed NO<sub>x</sub> is from the oxidation of nitrogen compounds in the clinker raw materials, and tends to form at relatively low heating temperatures (330–800°C), especially where the rate of heating is slow. Thus feed NO<sub>x</sub> contributions tend to be greater in wet and long dry kilns than in preheater and precalciner kilns.

Prompt NO<sub>x</sub> refers to the NO formed in fuel-rich (reducing) flames that is in excess of what would be expected to form by thermal NO<sub>x</sub> reactions. Prompt NO<sub>x</sub> appears to be formed by the reaction of CH<sub>2</sub><sup>·2</sup> and other fuel-derived radicals with atmospheric nitrogen to form cyanide radicals (CN<sup>·</sup>) and nitrogen radicals (N<sup>x·</sup>); the cyanide and nitrogen radicals subsequently oxidize to NO. Prompt NO<sub>x</sub> is a relatively minor contributor to the total NO<sub>x</sub> emissions of the kiln line.

As shown by Young and von Seebach (1998), total NO<sub>x</sub> emissions at cement plants are highly variable over short and long time intervals (minutes to days), and frequent sampling over long periods is required to provide useful data sets for statistical analysis. The majority of emissions (computed as NO<sub>2</sub> and expressed as daily averages) in the long dry kiln example these authors studied in detail were within a

range of 0.15%–0.45% of the weight of the clinker produced. Because of the lower fuel requirements and shorter residence times, a preheater-precalciner kiln would be expected to have lower (perhaps by 30%–40%) average overall NO<sub>x</sub> emissions than a long dry kiln. Johnson (1999) noted EPA 30-day average emissions target guidelines (with NO<sub>x</sub>-control technology installed) for wet kilns of 0.3% (of the weight of the clinker) for wet kilns, 0.26% for long dry kilns, 0.19% for preheater kilns, and 0.14% for preheater-precalciner kilns.

Approaches to reducing NO<sub>x</sub> emissions include most general technology upgrades that will reduce fuel consumption or residence times in kiln lines, recycling of CKD, low NO<sub>x</sub> burners (Johnson, 1999), staged combustion (especially to reduce thermal NO<sub>x</sub> in precalciners, and via mid-kiln injection of some of the fuel), reduction of excess air, injection of urea or ammonia into the precalciner to reduce oxidizing conditions, switching among major fuels, burning of waste materials (especially whole tires) to create reducing conditions, and, for precalciner kilns, to lower the kiln flame temperatures through water injection (Haspel, 2002). This last would seem to be counterintuitive, but it takes advantage of the fact that, of all the heat energy required to produce clinker, much is consumed in calcination. The subsequent heat requirement to achieve sintering temperatures (about 1450°C) is less than one might expect because some of the sintering reactions (especially that forming C<sub>3</sub>S from C<sub>2</sub>S and lime) are exothermic. Thus, if most of the calcination is achieved in a precalciner, the actual kiln's flame temperatures can be reduced somewhat from what would be needed in a kiln lacking a precalciner. All emissions reduction strategies benefit from improvements in process controls.

### Sulfur oxides

Sulfur from sulfide minerals (mainly pyrite) and from kerogens in both the raw materials (minor) and the fuels yields sulfur oxide (SO<sub>x</sub>) emissions, almost all of which will be SO<sub>2</sub>. Sulfur in fuel oxidizes in the sintering zone of the kiln and in any precalciner apparatus. In contrast, the sulfur in raw materials mostly oxidizes in the preheater apparatus or preheating zone of the kiln. As noted by Schwab and others (1999), much of the SO<sub>x</sub> evolved in the preheater combines with alkalis to make stable alkali sulfates (e.g., Na<sub>2</sub>SO<sub>4</sub>), some of which winds up as a buildup or coating in the cooler sections of the kiln line, and some of which becomes resident in the clinker. Scrubbing of SO<sub>x</sub> by reaction with lime or limestone feed materials (making anhydrite) also occurs during preheating, but the anhydrite is less stable and tends to decompose and rerelease the sulfur (as SO<sub>x</sub>) as the feed enters the (much hotter) precalciner or calcination zone in the kiln. This SO<sub>x</sub> is carried with the system air back into the preheating zone and tends to overwhelm the alkali scrubbing capacity of the feed, thus there remains a net evolution of SO<sub>x</sub> in the exhaust gases. Typical concentrations of SO<sub>x</sub> in exhaust gases are about 100–200 parts per million, but are highly variable depending on the sulfur content of the fuels and feed materials. Where SO<sub>x</sub> emissions are in excess of regulatory limits, or where they appear frequently as visible detached plumes, there is pressure on cement companies to install SO<sub>x</sub> scrubbers. Such scrubbers are readily available, and make use of limestone or lime to form synthetic gypsum.

### Carbon dioxide

By far the major environmental issue of concern today related to clinker manufacture is that of carbon dioxide (CO<sub>2</sub>) emissions. Interest in calculating CO<sub>2</sub> emissions stems from the global warming debate and the role therein of anthropogenic greenhouse gases. Although the emissions by powerplants that burn fossil fuels and the exhaust from motor vehicles are by far the largest source of anthropogenic CO<sub>2</sub>, the cement industry is more or less tied with the iron and steel industry as the largest “industrial” (other than powerplants) emitter of the gas. Overall, the U.S. cement industry emits about 1.4% of total U.S. anthropogenic CO<sub>2</sub> emissions (U.S. Environmental Protection Agency, 2002); in many countries

worldwide, the contribution is relatively higher—probably closer to 5%—because of a lower “intensity” of thermal power generation (relative to the overall economy) and less use of motor vehicles.

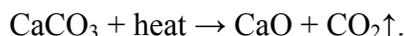
The emission of CO<sub>2</sub> from clinker manufacture stems from both the calcination of carbonate minerals in the raw feed, and the combustion of fuels. However, many statistical compilations detailing CO<sub>2</sub> emissions by the cement industry and other industrial sources (e.g., U.S. Environmental Protection Agency, 2002) do not directly link the combustion emissions to the specific industries; instead, combustion emissions are only shown as lumped within an all-sources national fuel total. Thus, the industry-specific emissions data may be very incomplete.

Calculation of CO<sub>2</sub> is more properly done on the basis of clinker production data than on data for cement output. This is because a link to cement production assumes that the clinker content of the cement is precisely known. However, with many country-level cement production data, no information is available as to the type(s) of cement produced. As noted earlier, blended cements and masonry cements both contain large fractions of material other than clinker. Two approaches are reasonable using clinker production data as the basis for the CO<sub>2</sub> calculation. For plants calculating their own emissions, it is feasible to calculate CO<sub>2</sub> based on the precise chemical compositions and quantities of the raw materials and fuels consumed. Detailed data like these, however, are generally lacking for the purposes of compiling national or regional emissions totals. For regional totals, the practical approach is to start with clinker production data and work backwards to calculate the CO<sub>2</sub>. This approach works well for calcination CO<sub>2</sub>, but is more equivocal for fuel combustion emissions.

### *Carbon dioxide from calcination*

For CO<sub>2</sub> generated through calcination, the easiest calculation approach is that advocated in the “good practices” methodology detailed by the Intergovernmental Panel on Climate Change (IPCC) (2000). The IPCC method yields an estimate of emissions good to no better than 5% but generally within 10% based on certain compositional assumptions and typical errors found within reported production and compositional data.

As noted earlier, the calcination reaction for calcium carbonate is:



The basic assumption in the IPCC method is that all of the CaO and CO<sub>2</sub> are derived from CaCO<sub>3</sub>, but the method advises compensating for cases where it is known that a significant amount of CaO is being contributed from non-carbonate sources, such as ferrous slags. It does not matter if all of the CaCO<sub>3</sub> is within limestone. Given the range of CaO values in typical clinkers (60%–67%), the clustering of most values in the range of 64%–66%, and imprecisions in the compositional control in manufacture and chemical analysis of clinker, a default composition of 65% CaO (e.g. per table 1) for clinker is a satisfactory assumption in the absence of more specific data.

In the calcination equation given above, the CaO fraction is 56.03% of the original weight of the CaCO<sub>3</sub>, and the CO<sub>2</sub> fraction is 43.97%. Accordingly, the amount (X) of CaCO<sub>3</sub> required to yield 1 t clinker containing 0.65 t CaO (i.e. 65%) would be:

$$X = 0.65 \text{ t} / 0.5603 = 1.1601 \text{ t (unrounded).}$$

This weight of  $\text{CaCO}_3$  yields  $\text{CO}_2$  in the amount of:

$$1.1601 \text{ t} \times 0.4397 = 0.5101 \text{ t (unrounded); } = 0.51 \text{ t (rounded).}$$

This amount (0.51 t  $\text{CO}_2$  per ton of clinker) is the IPCC default emissions factor for calcination  $\text{CO}_2$  and, again, assumes that 100% of the  $\text{CaO}$  is from  $\text{CaCO}_3$ . For comparison, 1 t of clinker of 60%  $\text{CaO}$  content would back-calculate to 0.47 t (rounded) of  $\text{CO}_2$ , and a 67%  $\text{CaO}$  clinker would calculate to 0.53 t of  $\text{CO}_2$ .

The IPCC method (2000, but currently is being updated) offers little guidance for cases where carbonates other than  $\text{CaCO}_3$  are present in clinker feeds, but this turns out to be a relatively insignificant problem. Examples of such carbonates would include dolomite  $\text{CaMg}(\text{CO}_3)_2$ , magnesite ( $\text{MgCO}_3$ ), siderite ( $\text{FeCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ), and various solid solutions among these. The effects of these carbonates on  $\text{CO}_2$  emissions can be easily calculated by the same procedure as for  $\text{CaCO}_3$  above.

For example,  $\text{MgO}$  is commonly present in small amounts in clinker raw materials—it is present in many limestone feeds where it typically forms a minor dolomitic phase, even though pure dolomite would not commonly be used as a kiln feed, and magnesite even less so. And  $\text{MgO}$  is also common in many non-carbonate clinker feeds, such as the silicate minerals in shales and slags. If the assumption is made, however unrealistic, that 100% of the  $\text{MgO}$  comes from a carbonate phase, then it can be shown that, for a clinker of 65%  $\text{CaO}$ , the default calcination  $\text{CO}_2$  emissions factor would become, in unrounded terms:

$$[0.5101 + M(0.011)] \text{ t } \text{CO}_2 \text{ per ton clinker}$$

where the 0.5101 is the emissions factor (see above) for a pure  $\text{CaCO}_3$  system, and  $M$  is the percentage of  $\text{MgO}$  in the clinker. This modest  $M(0.011)$  component would be a maximum  $\text{MgO}$  contribution to  $\text{CO}_2$ . For the small amount of  $\text{MgO}$  in clinker (e.g., 2% in table 1; the amount in portland cement is limited to a maximum of 6%, per ASTM standard C-150, and few U.S. portland cements would approach this limit), it may be argued that the  $\text{Mg}$ -carbonate contribution to calcination is small enough to be ignored because it would be subsumed within the 5%–10% overall error range of the IPCC methodology. The effect of iron carbonates is smaller still: for a clinker of 65%  $\text{CaO}$ , the combined emissions factor, if iron is assumed to be 100% from carbonate (very unlikely), becomes just:

$$[0.5101 + F(0.0055)] \text{ t } \text{CO}_2 \text{ per ton clinker (unrounded terms)}$$

where  $F$  is the percentage  $\text{Fe}_2\text{O}_3$  in the clinker. Thus, for the modest amount of iron in clinker (e.g., 3%  $\text{Fe}_2\text{O}_3$  in table 1), an iron-carbonate contribution to  $\text{CO}_2$  will be trivial. Accordingly, for regional clinker data, it is reasonable to look just at  $\text{CaCO}_3$  and to ignore the effects of the other carbonates. For plant-level reporting, sufficient compositional data may be available to warrant including the other carbonates, if present.

A remaining issue in the calculation of calcination  $\text{CO}_2$  emissions is the component represented by “lost” CKD. This component is very difficult to quantify. As noted earlier, total generation of CKD is large at all cement plants. In most countries today, and at all modern plants, essentially all of the CKD that is generated is either directly rerouted to the kiln’s raw material feed stream or is captured by electrostatic precipitators or filtration baghouses. Captured CKD can be recycled to the kiln (the preferred use for it), used for other purposes, or landfilled. The  $\text{CO}_2$  emissions associated with the CKD rerouted or recycled to the kiln becomes part of the clinker emissions calculation. All the other CKD, however, is

“lost” to the CO<sub>2</sub> calculation because the dust is not part of the clinker production tonnage. How much CO<sub>2</sub> this lost CKD represents depends upon the weight of the lost CKD, the degree to which the CKD represents an original carbonate (i.e., CO<sub>2</sub>-bearing) feed, and the degree to which this carbonate material was calcined. Data on all these factors are generally poor or lacking, but within very broad constraints, the IPCC recommended a “best practice” default addition of 2% to the calcination CO<sub>2</sub> calculated for the clinker itself for plants or regions where it is believed that significant amounts of CKD are not being recycled to the kilns.

### *Carbon dioxide from fuel combustion*

Few data exist on the CO<sub>2</sub> emissions from fuel combustion by the cement industry because most major compendia (e.g., EPA, IPCC) choose the expedient of combining emissions from fuel combustion from all sectors of the economy rather than attempt to show (or survey) each of the myriad emissions sources (fuel consumers) separately. Nevertheless, the contribution from fuel combustion is required to have a reasonably complete picture of CO<sub>2</sub> emissions by the cement industry. It is generally assumed that carbon monoxide released by cement plants (a relatively small amount because of the high combustion efficiencies of cement kilns) is ultimately oxidized to CO<sub>2</sub>.

It is more difficult, and much less precise, to calculate CO<sub>2</sub> emissions from the combustion of fuels than emissions from calcination because of uncertainties in the reported quantities and identification of fuels (particularly differentiating among the many types of waste fuels), and the different reported (or assigned) heat “contents” (the heat energy released from burning) of the fuels. Data on the heat contents are required because they are integral components of published fuel carbon factors. Instead of tables showing how much carbon (from which CO<sub>2</sub> is readily calculated) is in a ton of a given fuel, carbon factor data instead are presented in terms like “million tons of carbon equivalent per quadrillion Btu” for the fuel in question. Thus, the energy content of the fuel is needed to isolate the carbon content. Where heat contents must be assigned in the absence of (correctly) reported data, a complication is faced in that published standard heat contents commonly show significant ranges for individual fuels. Few published data exist for the heat or carbon contents of waste fuels; further, waste fuels commonly are consumed in diluted or impure forms. Finally, because the reporting units commonly are in terms with large exponents (e.g., quadrillion Btu and petajoules, both of which involve 10<sup>15</sup>) and are rounded, these carbon-isolation calculations are very prone to propagation of rounding errors. Overall, calculated combustion emissions, whether presented rounded or not, should be viewed as being good to within a range of 5%–10% at best, and probably a 15%–20% error range would be safer.

With the foregoing in mind, the 2000 fuel data in table 6 yield U.S. average unit emissions of about 0.43 t CO<sub>2</sub>/t clinker (van Oss and Padovani, 2003). Although earlier years’ fuel consumption data are not shown here, annual average unit emissions calculated for them show a gradual decline over the years from about 0.63 t CO<sub>2</sub>/t clinker in 1950. The decline reflects an increased reliance on dry kiln technology and parallels a decline in unit energy consumption. The U.S. industry in 2000 had about 76% of its clinker output from dry plants (not all of which operated modern, preheater-precalciner technology, however), with the remainder from wet plants. Countries with a high proportion of modern (i.e., dry) cement plants likely have unit emissions somewhat lower than the U.S. average.

### *Overall carbon dioxide emissions*

Calcination emissions (about 0.51 t per ton of clinker—more or less worldwide), and combustion emissions (current U.S. level about 0.43 t per ton of clinker) noted above, sum to a total of about 0.94 t CO<sub>2</sub>/t clinker. Given the likely imprecision of the combustion emissions calculation, and changes with

time in fuel use, the combined calcination and combustion emissions is better rounded to about 0.9 or even 1 t CO<sub>2</sub>/ t clinker. This is a good average for first order emissions estimates for most countries or regions.

Not included in this average is an estimate of the CO<sub>2</sub> released in generating the electricity purchased by the cement plant. Its exclusion is the norm, and is reasonable because the outside electricity would customarily be assigned to electric utilities in national emissions inventories. The amount of electricity CO<sub>2</sub> would depend on the fuels used to generate the electricity and would vary nationally and regionally. But, overall, for the U.S. cement industry and electrical grid, the purchased electricity consumption of integrated cement plants would equate to an additional 7%–8% of current total (calcination plus combustion) emissions. In contrast, electricity cogeneration at cement plants (currently, very rare in the U.S. industry) utilizes waste heat from the kiln line and should not directly add to the CO<sub>2</sub> output.

Instead of relating CO<sub>2</sub> emissions to clinker, some studies casually quote a 1:1 mass ratio for CO<sub>2</sub> and (portland) cement; the rationale given for the cement linkage is that cement production data are more readily available than clinker data for most regions. Given that a straight (clinker + gypsum) portland cement will have a clinker ratio or clinker factor of about 93%–97% (95% being a useful average for estimation purposes), this generalization is reasonable for cases where the cement production data actually refer to straight portland cement. Unfortunately, this is not a safe assumption for USGS and most other country-level tabulations of cement production data. These data sets normally are for total hydraulic cement, which, although likely dominated by portland cement, may include for some countries significant quantities of blended cements, portland-limestone cements, and masonry cements, and perhaps even misassigned cementitious admixtures (SCM or pozzolans) as yet uncombined within finished cement. Blended and masonry cements have lower (commonly much lower) clinker factors than straight portland cements, and the admixtures (other than CKD) have zero clinker factors. For masonry cements that incorporate lime as the main additive, there is a separate CO<sub>2</sub> legacy related to lime manufacture (generally done at a different facility), but it will be somewhat lower for lime than for the equivalent weight of clinker because of the lower temperatures (and hence fuel consumption) to achieve calcination for lime (as a product) than that to achieve clinker formation. For countries believed to have significant output of these other cements, an overall clinker ratio of 75%–85% may be a better approximation; the IPCC “good practices” suggestion is to use a 75% ratio for these countries.

### *Strategies to reduce carbon dioxide emissions*

There are four main strategies to reduce CO<sub>2</sub> emissions by the cement industry. The first is to switch to lower carbon fuels, such as from coal to natural gas. Many plants are equipped to switch among fuels, but a fuel switch is not always desirable. One issue is that a switch could lead to fuel cost/availability problems. This is a particular problem with switching to natural gas—a low carbon fuel. More importantly, a fuel switch can adversely affect the performance of the kiln because fuels vary in heat contents and in the heat-transfer and shape characteristics of the flames they generate. A fuel switch may counter efforts to reduce NO<sub>x</sub>; as noted earlier; natural gas, because it burns with a hotter flame, generates more thermal NO<sub>x</sub> than relatively high-nitrogen content coal. An alternative fuel switching strategy is to burn a measure of waste fuels, as these may have lower carbon contents, or the plant might receive some form of carbon “credit” for them because of the reduced consumption of standard fuels.

The second major strategy is to upgrade the kiln line to be more fuel-efficient. There are many options for this, such as by the installation of more efficient burners and improved process control systems, and innumerable minor “tweakings” that cumulatively make the plant more efficient. But for major fuel reductions, a plant generally needs to go through a major upgrade, such as converting from wet

(or older dry) kiln technology to modern preheater-precalciner systems. Major technological conversions are expensive (tens of millions of dollars or more) and may thus not be economical for an old plant lacking long-term (say, 50-years) reserves of raw materials, or that is located in a small market. Fuel-reduction strategies essentially target combustion  $\text{CO}_2$ .

The third reduction strategy is to target calcination  $\text{CO}_2$  emissions by using raw materials that will contribute part of the  $\text{CaO}$  needed to make clinker from a source other than  $\text{CaCO}_3$ . Many plants already get minor amounts of  $\text{CaO}$  from various silicate minerals in the feed, but this type of contribution can be increased by incorporating feeds such as slags and fly ash or bottom ash. The key consideration in such a  $\text{CaO}$ -source substitution is to make sure the alternative source does not require significantly more heat (and hence fuel) to process. A highly promising  $\text{CaO}$  source has proven to be steel slag. This material had been tried at various time in the past and, although chemically suitable, had been viewed unfavorably because it was difficult (hence costly) to grind. A key discovery regarding steel slag was made by the cement company Texas Industries, Inc. as a result of a program to find a more beneficial use (than as coarse aggregate) for slag produced by an adjacent electric arc furnace steel plant owned by a subsidiary company. The discovery, patented under the name CemStar, was that the slag did not require fine crushing or grinding. With just coarse crushing (to about 2–2.5 cm diameter), the material proved to be easily incorporated by a cement kiln. The slag's mineralogy already contained  $\text{C}_2\text{S}$  and/or compounds (including iron) that made  $\text{C}_2\text{S}$  at low temperatures, and because the slag melted easily (just 1260–1300°C), it provided a relatively low-temperature melt environment for the  $\text{C}_2\text{S}$  to combine exothermically with lime (from calcination) to rapidly form the critical  $\text{C}_3\text{S}$  clinker mineral. Using CemStar, additional clinker is produced in roughly a 1:1 ratio to the slag added, the unit fuel consumption is reduced, as are the unit calcination  $\text{CO}_2$  emissions. Typical slag additions with CemStar are as a 3%–10% substitution for limestone (or, more properly, a kiln's throughput capacity can be increased by these percentages by using CemStar). A review of the process is provided by Perkins (2000).

The fourth strategy to reduce  $\text{CO}_2$  emissions is to reduce the clinker content of finished cement through the use of SCM additives (i.e. make more blended cements) or admixtures; on a societal level, this strategy would also mean encouraging concrete companies to increasingly use SCM as a partial substitute for portland cement. At both levels, increased SCM use can only proceed to the degree that construction codes allow it. A similar substitution is that of ground limestone or similar “inert” material to finished straight portland cement, in an amount of 1%–5%. This limestone substitution is common in Europe and, at the low range shown has been proposed and accepted by ASTM as a modification of the standard for portland cement (ASTM C-150); higher substitution levels are common in Europe. In all cases with substitution, the emphasis is not on reducing absolute clinker production but the clinker fraction of finished cement. This allows increased production of finished cement without adding a commensurate amount of clinker production capacity.

## **Environmental benefits of cement manufacture**

In the increasingly popular industrial ecology paradigm, it is desirable to have industries and industrial processes that are interconnected and interdependent, particularly in the context of having no, or greatly reduced, net wastes by the entire multi-industry complex. In other words, it is desirable to have industries that consume other industries' waste products (the CemStar process, mentioned earlier, is a good example of this). Given that cement and concrete are produced and consumed in huge quantities worldwide, the manufacture of cement to meet this demand insures that enormous quantities of raw materials and fuels will also be required. The manufacture of cement (actually clinker) has virtue in its inefficiencies of high requisite temperatures and long residence times for clinker formation. These allow

for the complete destruction or conversion into clinker and/or heat of virtually anything that enters the kiln, including a wide variety and large quantities of waste fuels and other waste materials, some of them classified as hazardous. This use of wastes saves on standard fossil fuels and more costly disposal or storage strategies for the wastes. It is in this production of a valuable product from the destruction of other industries' wastes that the cement industry is seen as an ideal driver in existing and future industrial ecosystems (van Oss and Padovani, 2003; Vigon, 2002).

## References Cited in Part 1

- Alsop, P.A., Chen, H., Chin-Fatt, A.L., Jackura, A.J., McCabe, M.I., and Tseng, H.H., 2005, The cement plant operations handbook, 4th ed.: International Cement Review, Tradeship Publications Ltd. UK, 257 p.
- Bentz, D.P., 1997, Three-dimensional computer simulation of portland cement hydration and microstructure development: *J. American Ceramics Society*, v. 80, No. 1, p. 3-21.
- Bhatty, J.I., Miller, F.M., and Kosmatka, S.H., (eds), 2004, Innovations in portland cement manufacturing: Skokie, IL, Portland Cement Association, 1367 p.
- Bogue, R.H., 1955, The chemistry of portland cement, 2nd. ed., New York, Reinhold Publishing Corp., 793 p.
- Campbell, D.H., 1999, Microscopical examination and interpretation of portland cement clinker, 2nd ed.: Skokie, IL, Portland Cement Association, 202 p.
- Duda, W.H., 1985, Cement-data-book, 3rd ed.: Weisbaden, Bauverlag GmbH, vol. 1., 636 p.
- Glasser, F.P., 2004, Advances in cement clinkering: in Bhatty, J.I., Miller, F.M., and Kosmatka, S.H., (eds), 2004, Innovations in portland cement manufacturing: Skokie, IL, Portland Cement Association, p. 331-368.
- Haspel, David, 2002, Lowering NOx for less: *International Cement Review*, January, p. 63-66.
- Intergovernmental Panel on Climate Change, 2000, Good practice guidance and uncertainty management in greenhouse gas inventories: Intergovernmental Panel on Climate Change, p. 3.1-3.18.
- Johnson, S.A., 1999, Low NOx burners-what are the options?: *World Cement*, vol. 30, no. 10, p. 82-86.
- Kemp, B.J., 1994, Concrete Bover three thousand years in the making: *International Cement Review*, February, p. 52-53.
- Klemm, W.A., 2004, Cement manufacturing—A historical perspective: in Bhatty, J.I., Miller, F.M., and Kosmatka, S.H., (eds), 2004, Innovations in portland cement manufacturing: Skokie, IL, Portland Cement Association, p. 1- 35.
- Kosmatka, S.H., and Panarese, W.C., 1988, Design and control of concrete mixtures: 13th ed., Skokie, IL, Portland Cement Association, 205 p.
- Kosmatka, S.H., Kerkoff, B., and Panarese, W.C., 2002, Design and control of concrete mixtures: 14th ed., Skokie, IL, Portland Cement Association, 358 p.
- Lan, Wang, 1998, Advances in Chinese VSK technology: *World Cement*, vol. 29, no.12, p. 44-48.

- Langer, W.H., 1999, Environmental impacts of mining natural aggregates: Proc. 35th Forum on the Geology of Industrial Minerals—The Intermountain West Forum, Utah Geol. Survey Misc. Pub. 01-2; p. 127-137.
- Lea, F.M., 1970, The chemistry of cement and concrete: 3rd ed., New York, Chemical Publishing Co., 727 p.
- Leming, M.L., 1996, Alkali-silica reactivity mechanisms and management: Mining Engineering, v. 48, no. 12, p. 61-64.
- Lesley, R.W., 1924, History of the portland cement industry in the United States: Chicago, International Trade Press, Inc., 330 p.
- Moir, G. K., 2003, Gaining acceptance: International Cement Review, March, p. 67-70.
- Perkins, David, 2000, Increased production and lower emissions: World Cement, vol. 31, no. 12, p. 57-59.
- Portland Cement Association, 2000, U.S. and Canadian labor-energy input survey: Skokie, IL, Portland Cement Assoc., 48 p.
- Roy, D.M., 1985, Portland cement—Constitution and processing, Part II—Cement constitution and kiln reactions: in Roy, D.M., ed., Instructional modules in cement science: J. Materials Education, p. 73-92.
- Schmidt, M., Middendorf, B., Vellmer, C., and Geisenhansluekke, C., 2004, Blended cements, in Bhatti, J.I., Miller, F.M., and Kosmatka, S.H., (eds), 2004, Innovations in portland cement manufacturing: Skokie, IL, Portland Cement Association, p. 1107- 1148.
- Schwab, J., Wilber, K., and Riley, J., 1999, And SO<sub>2</sub> can you: International Cement Review, January, p. 54-55.
- Smart, J.P., Mullinger, P.J., and Jenkins, B.G., 1998, Combustion, heat transfer and NO<sub>x</sub>: World Cement, vol. 29, no. 12, p. 14-25.
- Smeaton, J., 1791, A narrative of the building and a description of the construction of the Eddystone lighthouse with stone: London, H. Hughes. 198 p.
- Stanley, C., 1999, Where it all began: World Cement, v. 30, no. 12, p. 20-24.
- Taylor, H.F.W., 1997, Cement chemistry: 2nd ed., London, Thomas Telford, 459 p.
- U.S. Environmental Protection Agency, 2002, Inventory of U.S. greenhouse gas emissions and sinks, 1990-2000: U.S. Environmental Protection Agency, p. ES-3 and 3.2-3.7.
- van Oss, H.G., and Padovani, A.C., 2002, Cement and the environment; Part I—Chemistry and technology: J. of Industrial Ecology, vol. 6, no. 1, p. 89-105.

- van Oss, H.G., and Padovani, A.C., 2003, Cement and the environment; Part II—Environmental challenges and opportunities: *J. of Industrial Ecology*, vol. 7, no. 1, p. 93-126.
- Vicat, L.J., 1837, *A practical and scientific treatise on calcareous mortars and cements, artificial and natural*: trans. J.T. Smith. London. John Weale. 302 p.
- Vigon, Bruce, 2002, *Industrial ecology in the cement industry*: World Business Council for Sustainable Development, Substudy 9: *Toward a sustainable cement industry*; Battelle, 103 p.
- Welch, J.H., 1964, Phase equilibria and high-temperature chemistry in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and related systems: in Taylor, H.F.W., ed., *The chemistry of cements*, London, Academic Press, v. 1, p. 49-88.
- Wilcox, Simon, 1995, From the mists of time...: *International Cement Review*, July, p. 73-75.
- Young, J.F., 1985, Hydration of portland cement: in Roy, D.M., ed., *Instructional modules in cement science*: *J. Materials Education*, p. 5-21.
- Young, G.L., and von Seebach, Michael, 1998, NO<sub>x</sub> variability and control from portland cement kilns: *Proc. 34th International Cement Seminar*, Salt Lake City, UT, p. 13-44.

## Glossary of terms

Brief definitions are provided below of technical terms and abbreviations found in this report as well as some other terms found in the external literature on cement and concrete. For many of the terms, fuller definitions or additional information can be found in the text of the report. Words in italics are defined elsewhere in the glossary.

<b>A</b>	1) Cement chemistry shorthand for alumina ( $\text{Al}_2\text{O}_3$ ). 2) As a capitalized suffix (e.g., Type IA portland cement) it denotes the addition to the cement of an <i>air-entraining</i> agent.
<b>AAR</b>	Alkali-aggregate reactivity. Adverse reactions within concrete between certain aggregates and the alkali hydroxides in cement. The most common type of AAR is alkali silica reactivity ( <i>ASR</i> ).
<b>Accelerator</b>	An agent (admixture) added to concrete to speed <i>setting</i> and hardening, and/or to speed <i>hydration</i> , and/or to speed strength development; c.f. <i>retarder</i> .
<b>Additive</b>	Material intermixed with hydraulic cement to form a different finished cement product.
<b>Admixture</b>	Ingredient (other than cement, water, and aggregates) added to a concrete mix.
<b>Aggregates</b>	Particulate materials such as sand, gravel, crushed stone, and crushed <i>slag</i> , used in construction.
<b>Air-entraining agent</b>	Chemical agent added to cement or concrete that causes the formation of tiny bubbles in the resulting concrete.
<b>Alite</b>	A cement mineral, generally equated to $\text{C}_3\text{S}$ but usually somewhat impure.
<b>Alumina</b>	Aluminum oxide ( $\text{Al}_2\text{O}_3$ ; or A in cement chemistry shorthand). 1) As a solid material, its major use is in the production of aluminum metal, but it also has refractory and chemical applications (including as a secondary raw material or <i>sweetener</i> in clinker manufacture). 2) term pertaining to the aluminum oxide content of a material.
<b>Aluminate</b>	a) Casual term for the cement mineral $\text{C}_3\text{A}$ ; b) referring to $\text{C}_3\text{A}$ or similar phases containing aluminum oxide in cement chemical reactions.
<b>Aluminous cement</b>	Hydraulic cement based on clinker made from a mix of <i>limestone</i> and <i>bauxite</i> . Used for certain high temperature and rapid-setting applications.
<b>Anhydrite</b>	Anhydrous calcium sulfate ( $\text{CaSO}_4$ or, in cement chemistry shorthand, $\text{CS}$ ). A mineral sometimes interground with portland cement clinker to control setting times in portland cement; in this role it partially substitutes for <i>gypsum</i> .
<b>Aragonite</b>	A mineral composed of calcium carbonate ( $\text{CaCO}_3$ ).
<b>ASR</b>	Alkali-silica reactions or reactivity. Undesirable reactions in concrete between disordered silica in some aggregates and alkali hydroxides in the cement.

<b>ASTM</b>	American Society for Testing and Materials; organization has now been renamed ASTM International. Sets standards for testing and performance of construction and other materials.
<b>AASHTO</b>	American Association of State Highway Transportation Officials. An alternative to ASTM for setting of standards; however, many cement- related AASHTO standards are similar or even identical to those of ASTM.
<b>Bauxite</b>	An earthy material consisting of a mix of iron and aluminum oxides, hydroxides and silicates. It is processed into <i>alumina</i> for subsequent reduction to aluminum metal and for various chemical and refractory applications. Bauxite can be a supplementary raw material for portland cement clinker production, and is a major raw material for <i>aluminous cement</i> production.
<b>Belite</b>	A cement or clinker mineral, generally equated to $C_2S$ but usually somewhat impure.
<b>Blended cement</b>	A hydraulic cement made of a mixture of portland cement (or clinker plus gypsum) plus <i>pozzolans</i> or other <i>SCM</i> .
<b>Blending plant</b>	An independent (of a <i>portland</i> cement company) facility that purchases cement and then blends it with other materials to make a different type of cement, typically blended cements (by addition of <i>SCM</i> ), <i>colored</i> cements (by addition of pigment) or <i>masonry</i> cements (by addition of crushed limestone or other materials). Blending plants are considered to be <i>final customers</i> .
<b>Burning</b>	An imprecise term referring variously to a) the combustion of fuels in the cement plant; b) the extreme heating and <i>thermochemical</i> decomposition of raw materials into their component oxides; c) the hottest part (zone) of the kiln where the actual clinker minerals are formed; a.k.a. <i>sintering</i> or <i>clinkering</i> .
<b>Burnability</b>	An informal term, generally encountered in the context of choosing raw materials for clinker manufacture, pertaining to the relative amount of heat energy required to break down the specific raw material into its component oxides. High burnability, then, refers to a material that breaks down easily, requiring relatively little heat input.
<b>C</b>	1) Cement chemistry shorthand for calcium oxide (CaO); 2) conventional chemical notation for carbon.
<b>C<sub>2</sub>S</b>	Cement chemistry shorthand for calcium disilicate, one of the four principal minerals in portland cement clinker. Sometimes referred to as <i>belite</i> .
<b>C<sub>3</sub>S</b>	Cement chemistry shorthand for calcium trisilicate, the dominant of the four principal minerals in modern portland cement clinker. Sometimes referred to as <i>alite</i> .
<b>C<sub>3</sub>A</b>	Cement chemistry shorthand for tricalcium aluminate, one of the four principal minerals in portland cement clinker. Commonly referred to as <i>aluminate</i> (as in aluminate content or phase).

<b>C<sub>4</sub>AF</b>	Cement chemistry shorthand for tetracalcium aluminoferrite, one of the four principal minerals in portland cement clinker. Strictly, C <sub>4</sub> AF is the mean compositional value of a solid solution between C <sub>6</sub> A <sub>2</sub> F and C <sub>6</sub> AF <sub>2</sub> . Commonly referred to as <i>ferrite</i> (as in ferrite content or phase).
<b>C-S-H</b>	Cement chemistry shorthand for calcium silicate hydrate. A colloidal gel made up of a family of related calcium silicate hydrates (e.g., C <sub>3</sub> S <sub>2</sub> H <sub>3</sub> ; C <sub>3</sub> S <sub>2</sub> H <sub>4</sub> ) formed, chiefly, from the hydration of the cement minerals C <sub>3</sub> S and C <sub>2</sub> S. In the older literature, the simplest of the C-S-H formulations is sometimes called <i>tobermorite</i> . C-S-H is the dominant contributor of strength to concrete.
<b>Calcination</b>	1) The heat-induced removal, or loss, of chemically-bound volatiles, usually other than water. 2) In cement and lime manufacture, it involves the thermal decomposition of calcite and other carbonate minerals to a metallic oxide (mainly CaO) plus carbon dioxide.
<b>Calciner</b>	See <i>precalciner</i> .
<b>Calcite</b>	A mineral composed of calcium carbonate (CaCO <sub>3</sub> ); the dominant mineral in limestone and hence the most common single mineral raw material for portland cement manufacture.
<b>Carbonate</b>	1) Refers to a mineral containing the carbonate radical CO <sub>3</sub> <sup>-2</sup> ; 2) the act of <i>carbonation</i> .
<b>Carbonation</b>	The re-formation of carbonate minerals through the absorption of carbon dioxide by metallic oxides (e.g., carbonation of <i>lime</i> yields <i>calcite</i> ).
<b>Cement</b>	1) A binding agent. In construction, this agent is a powder to which water is added and which develops binding properties either through hydration of the component minerals in the cement ( <i>hydraulic</i> cement) or through <i>carbonation</i> (e.g., <i>lime</i> mortars). 2) informal term for <i>cement paste</i> .
<b>Cement chemistry shorthand</b>	The use of single letters to denote the most common oxides in cement chemistry; e.g., C for CaO. See <i>individual letters</i> .
<b>Cement paste</b>	A mix of hydraulic cement plus sufficient water to insure full hydration of the cement minerals. Cement paste contributes virtually all of the strength to concrete and mortars.
<b>Cement rock</b>	1) An impure limestone containing a complete set of oxides, and in the correct proportions, to make clinker or cement with little or no addition of other raw materials; 2) less commonly, a term used in a quarry to distinguish the limestone that is mined for cement manufacture from other rock that is unsuitable for cement; 3) less commonly, a term denoting the major limestone feed to the kiln as opposed to other limestone used less frequently (perhaps as a <i>sweetener</i> ).

<b>C.i.f.</b>	Cost, insurance, and freight. A common value indicator and is inclusive of the base cost (see <i>customs value</i> ; <i>f.o.b.</i> ) of a shipment, plus insurance and freight to an agree-upon destination (typically a port or land terminal). It does not include costs of unloading the material and other port or terminal fees, or any import duties or tariffs. For U.S. trade data, the c.i.f. valuation is generally based on the location (port) of official entry into the country.
<b>Ciment fondu</b>	A type of <i>aluminous cement</i> .
<b>CKD</b>	Cement kiln dust; casually refers to all dust generated in the <i>kiln</i> or <i>pyroprocessing line</i> .
<b>Clinker</b>	An intermediate product of hydraulic cement manufacture. Clinker is produced in a kiln and consists semifused nodules that contain a controlled and intimate mix of clinker (or cement) <i>minerals</i> . <i>Portland cement</i> clinker consists, chiefly, of the four minerals $C_3S$ , $C_2S$ , $C_3A$ , and $C_4AF$ . Clinker is finely ground to make finished cement; in the case of portland cement, the clinker is interground with a small amount of <i>gypsum</i> and/or <i>anhydrite</i> .
<b>Clinkering</b>	The <i>thermochemical</i> formation of the actual clinker minerals, especially to those reactions occurring above about 1300°C; also the zone in the kiln where this occurs. A.k.a. <i>sintering</i> or <i>burning</i> .
<b>Clinker ton</b>	A unit of measure used at some plants to directly relate clinker production to the potential output of portland cement: 1 clinker ton of clinker is sufficient to make 1 ton of portland cement. The actual weight or mass of a clinker ton, therefore, is dependent on the particular plant's recipe for portland cement; that is, its ratio of clinker to other ingredients in the cement.
<b>Colored cement</b>	A cement to which pigments have been added. Excludes <i>white</i> cement (although white and colored cements have a common tariff code); see also <i>gray cement</i> .
<b>Comminution</b>	Reduction of particle size by crushing and/or grinding.
<b>Composite cement</b>	<i>Blended cement</i> .
<b>Concrete</b>	A proportioned mix of <i>hydraulic</i> cement, water, fine and coarse <i>aggregates</i> , and sometimes additives, that hardens to a tough, rocklike material used for construction.
<b>Curing</b>	The process of maintaining the moisture content of concrete to allow full hydration of the component hydraulic cement minerals and hence the development of full strength.
<b>Customs value</b>	In trade data, it is the base value or price of the merchandise being imported and generally equates to the <i>f.o.b.</i> value. It excludes onward shipping and insurance costs (see <i>c.i.f.</i> ), ship unloading and other destination terminal costs, and import duties and tariffs.

<b>Dead burned</b>	Refers to a material, generally a metallic oxide, that has been heated to a point where it is no longer chemically reactive (relative to its lower temperature reactivity). For example, dead burned magnesia or <i>periclase</i> ( <i>M</i> in cement chemistry shorthand) no longer readily <i>carbonates to magnesite</i> , whereas reactive magnesia readily does so.
<b>Dehydration</b>	Removal or loss of chemically or structurally bound water; c.f. <i>drying</i> .
<b>Dolomite</b>	A mineral composed of calcium magnesium carbonate $\text{CaMg}(\text{CO}_3)_2$ . Also a sedimentary rock composed primarily of this mineral.
<b>Drying</b>	Removal of water other than that which is chemically and structurally bound; c.f. <i>dehydration</i> .
<b>Dry kiln (plant)</b>	Refers to a kiln for which the raw materials are crushed, ground, proportioned, and fed into the kiln line in a dry state; c.f. <i>wet kiln</i> .
<b>Ettringite</b>	A mineral (formula $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$ in cement chemistry shorthand) formed by the hydration of the cement mineral $\text{C}_3\text{A}$ in the presence of excess sulfate.
<b>Extender</b>	As in ‘cement <i>extender</i> ,’ term used in some countries to denote cementitious <i>admixtures</i> or <i>SCM</i> .
<b>F</b>	1) Cement chemistry shorthand for ferric oxide ( $\text{Fe}_2\text{O}_3$ ); 2) conventional chemical notation for the element fluorine.
<b>F.a.s</b>	Free alongside ship. The base value or price of merchandise delivered to an agreed-upon port or terminal of debarkation (e.g., export) and placed alongside the ship (or train). It excludes the cost of loading the ship and all other onward costs (see <i>customs value, c.i.f.</i> ).
<b>Ferrite</b>	Casual term for the cement mineral $\text{C}_4\text{AF}$ . The formula represents the mean value of a solid solution with end members $\text{C}_6\text{A}_2\text{F}$ and $\text{C}_6\text{AF}_2$ .
<b>Final customer</b>	A term of convenience used in the cement industry to denote a purchaser of cement other than a rival cement company or a sister plant or terminal owned by the selling company. As a practical reporting matter, most final customers are concrete companies, construction contractors, or building material suppliers, and are not individual citizens or companies owning the location where the concrete or mortar was actually put into place. <i>Blending plants</i> independent of the originating or rival cement companies are included as final customers. In the case of <i>swaps</i> , the final customer is that which paid the originating company for the cement.
<b>Finished cement</b>	A cement ready for sale, i.e., which needs no further processing. The product(s) of a cement plant’s <i>finish mill</i> .
<b>Finish mill</b>	The section of a cement plant where <i>clinker</i> and other ingredients are finely ground and combined into <i>finished cement</i> .

<b>Flux</b>	1) A material that reduces the temperature and/or energy input requirements of a chemical reaction or physical change (such as melting). 2) In <i>clinker</i> manufacture, a material that lowers the temperature and energy requirements of the clinker-forming (especially the <i>sintering</i> ) reactions by promotion of the development of a liquid phase. Casually synonymous with <i>mineralizer</i> .
<b>Fly ash</b>	Fine grained glassy <i>silicate</i> particles released through the burning of coal in power plants and recovered by scrubbers. Some varieties of fly ash are useful as <i>pozzolans</i> or <i>SCM</i> and others can be used as raw material for clinker manufacture and as fine-grained construction <i>aggregates</i> .
<b>F.o.b.</b>	Free on board. The base value of merchandise at an agreed-upon location from which the material will be sent to the customer, or at which the customer will pick up the merchandise. It includes the cost of loading the onward carrier (truck or train or ship). It is thus comparable to the <i>f.a.s.</i> price plus loading costs.
<b>GGBFS</b>	Ground granulated blast furnace slag. A form of blast furnace <i>slag</i> produced by quenching molten slag in a water stream to form sand-sized grains of glass. When finely ground, this material is a <i>latent cement</i> , although it is generally included as a <i>pozzolan</i> or <i>SCM</i> . Increasingly, GGBFS is being sold under the imprecise term <i>slag cement</i> . See also <i>pelletized slag</i> .
<b>GHG</b>	Greenhouse gas(es). A gas (e.g., carbon dioxide) that causes retention of heat in the atmosphere; usually cited in the context of the global warming debate.
<b>Granulated slag</b>	A form of blast furnace <i>slag</i> that quenched through a water stream so as to form sand-sized grains of silicate glass. When very finely ground ( <i>GGBFS</i> ), this material is an <i>SCM</i> . Can also be used as a <i>grinding aid</i> in the <i>finish mill</i> .
<b>Gray cement</b>	Cement other than <i>white</i> or <i>colored</i> varieties. Generally synonymous with gray <i>portland</i> cement, but would include other, similar use cements (e.g., <i>blended cements</i> ). It may or may not include gray <i>masonry</i> cement.
<b>Grinding aid</b>	A material added in the <i>finish mill</i> to aid in the grinding of clinker into <i>finished cement</i> .
<b>Grinding circuit</b>	The parts of a cement plant where grinding of raw materials is done ( <i>raw mill</i> ) or where clinker is ground into finished cement ( <i>finish mill</i> ).
<b>Grinding plant</b>	A stand-alone cement manufacturing facility that grinds clinker that was made at another (usually foreign) location; c.f. <i>integrated plant</i> .
<b>Gypsum</b>	Calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or in shorthand $\text{C}\bar{\text{S}}\text{H}_2$ ); it is a mineral component of portland cement and its function is to control setting time.
<b>H</b>	1) Water ( $\text{H}_2\text{O}$ ) in cement chemistry shorthand notation; 2) hydrogen in conventional chemical notation.
<b>Hydration</b>	Chemical combination of water with another compound. Hydration of cement minerals (to form new minerals called <i>hydrates</i> ) is the key reaction in the hardening and development of strength in concrete. 2) absorption of structural water into a crystal lattice.
<b>Hydrate(d)</b>	Refers to a mineral or compound formed from another mineral or compound

that has undergone hydration, e.g., *CSH*; *hydrated lime*.

<b>Hydrated lime</b>	The compound $\text{Ca}(\text{OH})_2$ ; also called slaked lime. In solid form, sometimes called <i>portlandite</i> .
<b>Hydraulic (cement)</b>	Refers to a cement's ability to set and harden under, or with excess, water through the hydration of the cement's constituent chemical compounds or minerals.
<b>Integrated plant</b>	An informal term used to describe a cement plant that produces both clinker and finished cement; c.f. <i>grinding plant</i> .
<b>K</b>	1) Cement chemistry shorthand for potassium oxide $\text{K}_2\text{O}$ . 2) Potassium in conventional chemical notation
<b>Kiln</b>	The heating apparatus in a cement plant in which <i>clinker</i> is manufactured. Unless otherwise specified, may be assumed to refer to a <i>rotary kiln</i> .
<b>Kiln line</b>	A.k.a. <i>pyroprocessing line</i> . The part of the cement plant that manufactures clinker; comprises the kiln itself plus any preheaters and precalciners, plus the clinker cooler apparatus.
<b>Latent cement</b>	An infrequently encountered term referring to material having some cementitious character but whose hydraulic cementitious properties are significantly enhanced when interacted with free hydrated lime. The term is most commonly associated with <i>GGBFS</i> .
<b>Lime</b>	A general term for: 1) the compound $\text{CaO}$ (denoted C in cement chemistry shorthand), also called quicklime; 2) the hydrated compound $\text{Ca}(\text{OH})_2$ (denoted CH in shorthand) that is more properly termed <i>hydrated lime</i> or slaked lime. Solid hydrated lime is sometimes called <i>portlandite</i> . 3) the foregoing plus high magnesian or dolomitic forms, e.g., $\text{CaO}\cdot\text{MgO}$ or $(\text{Ca},\text{Mg})(\text{OH})_2$ ; 4) <i>hydraulic lime</i> , which contains hydraulic silicates.
<b>Limestone</b>	1) A sedimentary rock composed primarily of calcium carbonate (generally as the mineral <i>calcite</i> ). Limestone is generally the main raw material for cement manufacture. 2) locally, any rock (e.g., limestone, cement rock, marble) composed primarily of calcium carbonate and used by the plant as its primary raw material in cement manufacture.
<b>M</b>	Cement chemistry shorthand for magnesia $\text{MgO}$ .
<b>Masonry</b>	1) Refers to construction using natural or manufactured blocks (e.g, bricks, dimension stone, cinderblock), either shaped or unshaped; 2) see <i>masonry cement</i> .
<b>Masonry cement</b>	A general term for cements used as the binder in mortars. Commonly consists of a mix of portland cement plus plasticizing agents such as lime or ground limestone. Loosely, the term includes true masonry cements, portland-lime cements, plastic cements, and cements for <i>stucco</i> .
<b>Magnesite</b>	A mineral composed of magnesium carbonate $\text{MgCO}_3$ .

<b>Mill net value</b>	The total or unit value of cement (or clinker) sold to <i>final customers f.o.b.</i> the plant, regardless of whether the cement was, in fact, sold from an associated terminal. It thus excludes all shipping costs from the plant to the terminal. It includes any packaging charges, but excludes any discounts. For sales from an independent or stand-alone terminal (usually an import terminal) reporting separately from the plant, the comparable valuation is the <i>terminal net</i> value.
<b>Mineral</b>	1) In geology, a naturally occurring inorganic material (or synthetic version thereof) having a defined chemistry and crystal lattice and which has defined physical and chemical properties. 2) In the literature on cement, <i>mineral</i> has its geologic meaning but also refers to various synthetic solid phases in clinker or cement that may or may not occur in nature.
<b>Mineralizer</b>	Casually synonymous with <i>flux</i> , but more properly refers to an addition to the <i>raw mix</i> that both promotes the development of a liquid phase and promotes the formation of specific <i>clinker minerals</i> , especially <i>alite</i> .
<b>Monosulfate</b>	Informal term for a certain compounds that form during the hydration of the cement mineral $C_3A$ when sulfate is not present in excess. The presence of monosulfate makes the concrete susceptible to later <i>sulfate attack</i> .
<b>Mortar</b>	1) The binder in masonry construction. Generally a proportioned mix of masonry (or similar) cement, water, and fine aggregates. 2) In the oldest historical literature, sometimes used synonymously with <i>cement</i> .
<b>N</b>	1) Sodium oxide ( $Na_2O$ ) in cement chemistry shorthand; 2) Nitrogen in conventional chemical notation.
<b>Ordinary</b>	As in <i>ordinary portland cement (OPC)</i> : a designation used in some countries for <i>straight</i> portland cement for general purpose use; OPC is generally comparable to an ASTM C-150 Type I portland cement.
<b>PCA</b>	Portland Cement Association. The principal U.S. private organization representing the cement industry.
<b>Pelletized slag</b>	Blast furnace slag cooled by quenching with water to generate copious steam and hence a vesicular texture in the slag; a form of expanded slag. Most commonly used for lightweight aggregate, it can also be used as an <i>SCM</i> if very finely ground.
<b>Periclase</b>	A mineral composed of magnesia $MgO$ .
<b>Plaster</b>	1) Short term for <i>plaster of Paris</i> , which is ground calcium sulfate hemihydrate $CaSO_4 \cdot \frac{1}{2}H_2O$ and which hydrates to <i>gypsum</i> . 2) A plastic material used to coat and/or decorate walls and similar surfaces (see <i>stucco</i> ).

<b>Portland cement</b>	The most common hydraulic cement. A proportioned and finely interground mixture of portland cement <i>clinker</i> and a small amount of calcium sulfate (generally as <i>gypsum</i> ). In practice, minor amounts of other additives may also be incorporated. Strictly, the term in the United States is limited to the Types I through V varieties (and their air-entrained variants) as defined in ASTM C-150; these types are also collectively called <i>straight</i> portland cement. Apart from the straight varieties, “portland cement” when used loosely (a common industry practice) can also include a number of similar hydraulic cements, including <i>blended</i> cements, that are based on portland cement clinker plus gypsum.
<b>Portlandite</b>	A mineral composed of hydrated lime $\text{Ca}(\text{OH})_2$ (denoted CH in shorthand).
<b>Pozzolan(ic)</b>	1) A natural or synthetic <i>silicate</i> material that develops <i>hydraulic</i> cementitious properties when interacted with hydrated lime. Pozzolans and similar materials are commonly lumped under the term <i>SCM</i> . 2) used loosely, the term is synonymous with <i>SCM</i> .
<b>Pozzolana</b>	A pozzolanic volcanic ash or tuff.
<b>Precalciner</b>	A kiln line apparatus, usually combined with a <i>preheater</i> , in which partial to almost complete calcination of carbonate minerals is achieved ahead of the kiln itself, and which makes use of a separate heat source. A precalciner reduces fuel consumption in the kiln, and allows the kiln to be shorter, as the kiln no longer has to perform the full calcination function.
<b>Preheater</b>	An apparatus used to heat the <i>raw mix</i> before it reaches the dry kiln itself. In modern dry kilns, the preheater is commonly combined with a <i>precalciner</i> . Preheaters make use of hot exit gases from the kiln as their heat source.
<b>Premix</b>	A bagged product containing proportioned dry ingredients for concrete (i.e., sand, gravel, and cement powder); the customer adds the required amount of water (for cement hydration) at the jobsite.
<b>Pyroprocessing</b>	Chemical transformation using intense heat from a flame. In cement, it refers to the manufacture of clinker, which is achieved in a kiln utilizing the flame from an internal burner tube. The pyroprocessing circuit or line is also called the <i>kiln line</i> of a cement plant.
<b>Quartz</b>	A common mineral having the formula $\text{SiO}_2$ . A major source of additional silica in clinker manufacture.
<b>Quicklime</b>	The compound $\text{CaO}$ ; see <i>lime</i> .
<b>Raw mill</b>	The part of the cement plant in which the raw materials are crushed, ground, and proportioned to form the feed for the kiln.
<b>Raw mix/ meal/feed</b>	The crushed, ground, proportioned, and thoroughly mixed raw material-feed to the <i>kiln line</i> .

<b>Ready-mix(ed)</b>	Also spelled as one word ( <i>readymix</i> ). Common type of <i>concrete</i> in which all the ingredients, including water, are preproportioned at the concrete plant and placed into the rotatable drum of a mixing truck. The concrete is then thoroughly mixed via drum rotation while the truck is in transit from the concrete plant to the jobsite. Data on ready-mixed concrete generally include similar concrete made at semimobile batch plants positioned near the jobsite. Batch plants are used where the jobsite is too far from the main concrete plant to allow convenient delivery of ready-mixed concrete by truck.
<b>Retarder</b>	An agent ( <i>admixture</i> ) added to a concrete mix to delay <i>setting</i> and hardening; c.f. <i>accelerator</i> .
<b>Rotary kiln</b>	A kiln consisting of a gently inclined, rotating steel tube lined with refractory brick. The kiln is fed with raw materials at its upper end and heated by flame from, mainly, the lower end, which is also the exit end for the product (clinker); c.f., <i>vertical shaft kiln</i> .
<b>S</b>	1) Cement chemistry shorthand for <i>silica</i> ( $\text{SiO}_2$ ); 2) conventional chemical notation for sulfur.
<b>S</b>	Cement chemistry shorthand for the sulfite (sulfur trioxide) radical ( $\text{SO}_3^-$ ).
<b>SCM</b>	Supplementary cementitious material(s). Materials that can be incorporated within blended cements or in concrete mixes as partial substitutes for portland cement. Common examples are <i>GGBFS</i> , <i>fly ash</i> , <i>silica fume</i> , and <i>pozzolana</i> . Casually synonymous with <i>pozzolan</i> .
<b>Semidry kiln (plant)</b>	A plant in which an initially wet (slurry) raw material feed is dried before pyroprocessing in a dry kiln line.
<b>Set or setting</b>	Hydration-induced stiffening of cement paste or concrete. Initial set is the loss of fluidity and plasticity of the material; final set is the development of a certain degree of hardness. Concrete is difficult to work once setting has commenced.
<b>Silica</b>	1) Silicon dioxide, $\text{SiO}_2$ ; denoted S in cement chemistry shorthand. 2) pertaining to the silicon dioxide content of a material.
<b>Silica fume</b>	Ultrafine particles of disordered <i>silica</i> formed as a byproduct of the manufacture of silicon metal, silicon carbide, and silicon alloys (e.g., ferrosilicon). It is used as a <i>pozzolan</i> or <i>SCM</i> .
<b>Silicate</b>	Refers to minerals or compounds whose formulae include silica as a component oxide.
<b>Sintering</b>	In clinker manufacture, refers to the process of, or the <i>thermochemical</i> reactions, forming the actual clinker minerals, especially those reactions occurring above about $1300^\circ\text{C}$ . The sintering zone of a kiln is that part of the kiln where the sintering reactions occur; it is the highest temperature zone of the kiln. A.k.a. <i>clinkering</i> or <i>burning</i> .
<b>Slag</b>	A silicate melt produced during metal smelting and which essentially is the

residuum of the fluxing agents used and the impurities from the metal ores and fuels or reductants. The term also applies to the silicate material after it has cooled to a solid. In the general context of cement and concrete, *slag* (unmodified) refers to iron or steel (furnace) slag. More specifically, as a cementitious component of finished cement or concrete admixture, *slag* refers to the *granulated* variety used either unground as a grinding aid in the finish mill or ground (*GGBFS*) as an *SCM*. As a raw material for clinker manufacture, *slag* generally refers to steel furnace slag. As an aggregate in concrete, *slag* generally refers to air-cooled blast furnace slag.

<b>Slag cement</b>	1) Properly, an ASTM C-595 <i>blended</i> cement (Type S), defined as having $\geq 70\%$ <i>GGBFS</i> ; 2) Increasingly on the U.S. market, the term <i>slag cement</i> is used for a 100% <i>GGBFS</i> product that is sold as an <i>SCM</i> .
<b>Slaked lime</b>	1) <i>Hydrated lime</i> ; see also <i>lime</i> . Also refers to a liquid solution containing hydrated lime.
<b>Slurry</b>	1) A suspension of insoluble particles in a liquid (generally water) which overall still flows like a liquid; 2) denoting the raw material feed to a wet kiln.
<b>Straight</b>	Refers to portland cement defined in the strict sense (i.e., straight portland cements are those within ASTM standard C-150), as opposed to the general grouping “portland cement” which may also include a variety of other, similar, cements that are based on portland cement clinker.
<b>Stucco</b>	A mix of portland cement (or sometimes lime), plasticizers, fine aggregates, and water that will adhere to a steep surface and retain imposed surface impressions and textures, and which is used for coating walls and other surfaces. Also called portland cement <i>plaster</i> .
<b>Sulfate attack</b>	Deleterious expansion of concrete caused by reaction of certain hydrated <i>monosulfate</i> phases in the cement with sulfate-bearing groundwater or soils. The reaction re-forms <i>ettringite</i> (a higher-volume phase).
<b>Sweetener</b>	An informal term used for a clinker raw material, generally of high purity, that is added to the <i>raw mix</i> to rectify a small deficiency in one or more oxides. For example, silica sand is a common sweetener to boost silica.
<b>Terminal net value</b>	The total or unit value of cement or clinker sold to <i>final customers</i> at a terminal, including any packaging costs and charges for loading the onward conveyance vehicle (typically a train or truck), but excluding onward delivery charges and customer discounts. For import terminals, the terminal net would be comparable to the <i>c.i.f.</i> value, plus all terminal charges and markups. Terminal net is analogous to <i>mill net</i> for a plant.
<b>Thermochemical</b>	Refers to chemical reactions induced by high heat (as in the making of clinker in a kiln).
<b>Tobermorite</b>	A somewhat discredited name for the gel phase resulting from the hydration of the cement minerals $C_3S$ and $C_2S$ . The formula of tobermorite, in shorthand,

is  $C_3S_2H_3$  (sometimes denoted  $C_3S_2H_4$ ). Because  $C_3S$  and  $C_2S$  actually hydrate to form a whole family of compounds of related formulation, the more general name ‘calcium silicate hydrate’ or *C-S-H* is preferred to tobermorite.

- Transfer-in** In USGS cement reporting, the receipt by cement plant X, or its terminals, of material from sister (same company) cement plant Y or its terminals. The term includes cement from Y that was directly delivered to a final customer of X, where X was paid by the customer for the cement. See also *transfer-out*.
- Transfer-out** In USGS cement reporting, a shipment of material from cement plant X or its associated terminal(s) to sister (same company) cement plant Y, Y’s terminals, or Y’s final customers (where the customer pays Y). The transfer-out transfers “ownership” of the cement from X to Y. A shipment from a cement plant to its own terminal is not a transfer-out, nor is any shipment to rival (different company) cement companies. See also *transfer-in*.
- Vertical shaft kiln** A vertical, cylindrical or chimney-type kiln, heated from the bottom, which is fed either with a batch or continuous charge consisting of an intimate mix of fuel and raw materials. Generally considered obsolete for cement manufacture.
- VSK** *Vertical shaft kiln.*
- Wet kiln (plant)** Refers to a kiln that takes its crushed and ground raw material feed as a wet (aqueous) slurry; compare with *dry kiln*.
- White cement** A cement made from white *clinker*, and is based upon raw materials having very low contents of iron (oxides) or other transition elements to avoid the coloring effects of these elements. Unless otherwise specified (e.g., white *masonry* cement), white cement generally is confined to white *portland* cement. White cement is used to make white *concrete* and *mortar*, and serves as a base for *colored* cements, and is generally much more expensive than equivalent-performance *gray* cement varieties.

## Links to other sources of information on cement and concrete

American Society of Civil Engineers (ASCE): <http://www.asce.org>

ASCE National Concrete Canoe Competition: <http://www.asce.org/inside/nccc2006>

American Coal Ash Association: <http://www.aaa-usa.org>

American Concrete Institute: <http://www.aci-int.org>

ASTM International: <http://www.astm.org>

AASHTO: <http://www.transportation.org>

Cement Kiln Recycling Coalition: <http://www.ckrc.org>

European Cement Association (Cembureau): <http://www.cembureau.be>

The Fly Ash Resource Center: <http://www.rmajko.com/flyash.html>

National Institute of Standards and Technology (NIST): <http://www.nist.gov>

NIST (Virtual Concrete): <http://ciks.cbt.nist.gov/vcctl>

National Ready Mixed Concrete Association: <http://www.nrmca.org>

National Slag Association: <http://www.nationalslagassoc.org>

Portland Cement Association: <http://www.cement.org>

Silica Fume Association: <http://www.silicafume.org>

Slag Cement Association: <http://www.slagcement.org>

U.S. Environmental Protection Agency (EPA): <http://www.epa.gov>

EPA: Coal Combustion Products Partnership:

<http://www.epa.gov/epaoswer/osw/consERVE/c2p2/>

U.S. Geological Survey (Home page): <http://www.usgs.gov>

U.S. Geological Survey (Minerals information): <http://minerals.usgs.gov/minerals>

World Business Council for Sustainable Development —Cement: <http://www.wbcscement.org>

## Part 2: Issues related to cement industry canvasses and data interpretation

The U.S. Government has been collecting data on the domestic cement industry for more than a century, mostly through canvasses sent directly to the producers. Annual production and sales data extend back to 1879, and some decadal summations go back to the middle of the century. Monthly sales data have been collected since about the mid-1960s. Collection and reporting of cement data was conducted by the USGS through the 1923 data year, by the U.S. Bureau of Mines (USBM) for the data years 1924-94 (and most of 1995 for monthly data), and again by the USGS for the data years 1995 onwards (monthly data were 1996 onwards). However, for simplicity, reference hereafter to USGS canvasses and publications on cement will include those by the now-closed USBM. Annual data compilations and commentaries have been published as chapters on cement in the USGS Minerals Yearbooks, whereas the monthly data have been published as individual Mineral Industry Surveys reports. In recent years, hard copy distribution of cement reports has been supplemented by electronic dissemination of reports, most recently via the Internet.

The purpose of Part 2 is to better familiarize readers with the USGS periodic canvasses of the U.S. industry, and to discuss some of the issues associated with the physical collection of the data, their completeness and accuracy, and their interpretation. The discussion will make better sense if the reader has at hand a copy of a monthly MIS and an annual report, both of which are available on the Web at URL: <http://minerals.usgs.gov/minerals>. Although we believe that the U.S. cement industry data published by the USGS are the best, most complete, and sometimes the only data available, the data are not perfect. It is hoped that the following discussion will clarify the limitations of the cement data beyond what is possible with footnotes to the actual data tables or with explanations in the periodic reports' texts. Further, although there will be no mention of specific companies, plants, or personnel (except on a fictitious example basis), it is hoped that the discussion will help respondents to the USGS cement industry canvasses complete their data reporting.

The canvasses sent out by the USGS to the cement industry are filled out on a voluntary basis and the high response rate over the years is quite remarkable given the highly proprietary nature of the information requested. It also is a testament to the usefulness of the data to the industry. The USGS reports are neutral sources of consumption and production data that support the accurate evaluation of cement market conditions by interested parties in the cement and concrete industries, academe, and Government agencies.

### Protection of proprietary data

Data received through the USGS canvasses are checked for accuracy and are aggregated into non-proprietary tabulations of State or district totals for public dissemination. Protection of proprietary data is done primarily through two tests. The first is the Rule of Three (ROT) test, wherein unless a specified region has three or more companies active (not just plants), the regional total must be withheld (symbolized in tables as W/) or combined with other regions until enough companies are present. Where ROT is not an issue, the data are then examined relative to the Dominant Company (DC) test. The DC test is failed if any one company in a region accounts for 75% or more of the activity, or any two combined account for 90% or more of the activity. A DC test failure requires that the regional total be withheld or combined. Exceptions to the ROT and DC rules are where the USGS has written permission from all of

the critical companies in the region to publish the regional total. Thus, for example, in a region having just two producing companies (fails the ROT test), both companies would need to provide written permission to print the regional total. The USGS questionnaires include a question asking (Yes or No) whether the data in the form may be revealed in a nonproprietary way. With rare exception, this question is either left unanswered or is answered 'NO.' If left blank, a 'NO' answer is assumed.

## **Types of cement canvasses**

Currently, the USGS sends out two types of cement surveys. The first is the D16 form, which is a monthly canvass of, primarily, sales of cement to final customers. Some D16 forms are filled out on a specific plant (including its distribution terminals) or independent terminal basis, and others are filled out on a consolidated basis where a single form covers the activities of more than one plant or terminal. Currently, approximately 100 forms are sent out monthly, and the response rate is generally 100%, if not always on a timely basis. This survey misses a few, mostly small, importers that have yet to agree to take part in the survey. The second canvass (D15) is the annual questionnaire, which covers a range of activities of plants or terminals, and is sent to individual plants or independent (mostly import) terminals. Currently, approximately 140 annual forms are sent out, and although the response rate is generally high, the timeliness of the responses is a common problem.

Because both the monthly and annual canvasses are official Government forms, substantive changes to the forms themselves are made only with concurrence of the U.S. Office of Management and Budget, and generally only after negotiation with the industry as to the need for the changes. However, minor changes, such as in rewording of instructions for better clarity, may be made at the discretion of the USGS. Substantive changes have been fairly infrequent.

## **Reporting units and accuracy**

Currently, all of the USGS cement data are collected in nonmetric units, as these are believed to be more familiar to the majority of U.S. cement industry personnel (hence fewer reporting errors), and because they remain the units of domestic cement commerce. More than 80% of the U.S. cement industry is now foreign-owned and is becoming increasingly consolidated and dependent on centralized metric unit bookkeeping. Thus, the industry and the PCA may eventually prefer the USGS to switch to metric unit canvasses, and may even start selling cement in metric units. The USGS cement data have been published in metric units for several years and the ASTM standards to which the industry adheres are in metric units.

In recognition of inherent inaccuracies in determining the weight of shipments and production for most mineral commodities, the USGS rounds most commodity data to 3 significant digits. Given a perfectly accurate original datum having more than 3 significant digits, rounding to 3 significant digits maintains the integrity of the original number to within 0.5%. For most commodity measurements, 3 significant digit reporting will in fact provide more precision than is warranted by the accuracy of the original data. Nevertheless, the U.S. cement industry likes to track cement sales on the basis of individual tons, and has indicated a strong preference that the USGS not round its published cement data except where required for brevity (e.g., tables showing units in thousands). Despite the industry's tracking their activities on the basis of individual tons, it is not uncommon for the USGS to receive revisions to data, some quite large. While it is the current policy of the USGS to accommodate the cement industry's preference for unrounded data, the USGS believes that the unrounded cement data are not accurate to more than 3 significant figures. Exceptions to reporting unrounded data are where estimates have been incorporated; unless qualified by a footnote, such estimated data will have been rounded to no more than 3 significant digits.



D16

UNITED STATES  
DEPARTMENT OF THE INTERIOR  
U.S. GEOLOGICAL SURVEY  
986 NATIONAL CENTER  
RESTON, VIRGINIA 20192

INDIVIDUAL COMPANY  
DATA - PROPRIETARY

Unless authorization is granted in the section above the signature, the data furnished in this report will be treated in confidence by the Department of the Interior, except that they may be disclosed to Federal defense agencies, or to the Congress upon official request for appropriate purposes. Unless objection is made in writing to the USGS, the information furnished in this report may be disclosed to the respondent's State Geological Survey (or similar State Agency) if the State has appropriate safeguards to prevent disclosing company proprietary data.

PORTLAND, BLENDED, AND MASONRY CEMENT

(Please correct if name or address has changed.)

FACSIMILE NUMBER  
1-800-543-0661

Public reporting burden for this voluntary collection of information is estimated to average 30 MINUTES per response. A Federal agency may not conduct, sponsor, or require a person to respond to a collection of information unless it displays a valid OMB control number. Comments regarding this collection of information should be directed to: U.S. Geological Survey, Statistics and Information Systems Section, 988 National Center, Reston, VA 20192. **Please do not mail survey forms to this address.**

Collection of nonfuel minerals information is authorized by Public Law 96-479 and the Defense Production Act. This information is used to support executive policy decisions pertaining to emergency preparedness, national defense, and analyses for minerals legislation and industrial trends. The USGS relies on your voluntary and timely response to assure that its information is complete and accurate. Please complete and return the form in the enclosed envelope or fax to the above toll-free number **BY THE 10TH OF THE MONTH** following the report month. Use zero (0) when appropriate. Do not report decimals or fractions. Additional forms are available upon request.

You may report on an individual plant basis or on a consolidated basis. For each month, complete Question A and all of page 2.

If you have any questions concerning completion of this form, please contact the Mineral Commodities Data Unit, U.S. Geological Survey, 985 National Center, Reston, VA 20192, Telephone (703) 648-7960.

Name and title of person to be contacted regarding this report			Tel. area code	No.	Ext.
Address	No.	Street	City	State	ZIP Code

**A. This report is (check one) (a)  Plant report (b)  Consolidated report**

If you checked (a): Is the plant covered in this report the one appearing in the address imprint?  Yes  No

If you checked (b): Number of plants covered \_\_\_\_\_

**COMPLETE ONLY ON THE JANUARY REPORT OR IF A CHANGE OCCURS IN PLANT STATUS OR COVERAGE.**

1. If you checked A (a), give

Name of plant \_\_\_\_\_  
Location of plant State \_\_\_\_\_ County \_\_\_\_\_ Nearest city \_\_\_\_\_

2. If you checked A (b), complete the following item for each plant covered by the consolidated report. If necessary, continue on a supplemental sheet.

- \* Name of plant \_\_\_\_\_  
Location of plant State \_\_\_\_\_ County \_\_\_\_\_ Nearest city \_\_\_\_\_
- \* Name of plant \_\_\_\_\_  
Location of plant State \_\_\_\_\_ County \_\_\_\_\_ Nearest city \_\_\_\_\_
- \* Name of plant \_\_\_\_\_  
Location of plant State \_\_\_\_\_ County \_\_\_\_\_ Nearest city \_\_\_\_\_
- \* Name of plant \_\_\_\_\_  
Location of plant State \_\_\_\_\_ County \_\_\_\_\_ Nearest city \_\_\_\_\_

3. Status of the reporting establishment(s)

Operated as a subsidiary  Yes  No

If yes, give name and address of controlling company \_\_\_\_\_



]

## Monthly canvass and data

The D16 monthly canvass collects data on the disposition of cement sales and the production of clinker. The data gathered via this canvass, together with trade data from the U.S. Census Bureau, are published in the monthly Mineral Industry Surveys (MIS) for cement. The D16 form is a 2-page document, the first page of which, however, has only the address and identification codes for the company or facility in question, and solicits news of changes as to which facilities are being covered by the form.

## Sales destination data

Page 2 of the D16 canvass is divided into 3 sections. The first section tracks the cement sales tonnages to final customers by the State of *destination* (location of the customer). The sales are broken out into three cement types: portland cement, blended cement, and masonry cement, and include sales of imported cement and cement made domestically from imported clinker. A few States are subdivided (north vs. south or east vs. west), and two metropolitan areas (Chicago and New York) are broken out, reflecting sufficient market activity to warrant the additional detail. The State sales data are considered to represent the consumption of cement in that State. These data are published in the monthly MIS publications for cement as the tables 2 and 3 series; and (summed for the year) as tables 9 and 10 in the annual reports. In these tables, data for all States are revealed separately. Because a great deal of cement is transported across State lines, and in highly variable quantities, the State destination or consumption totals are generally not subject to proprietary protections.

The destination data are primarily used by analysts interested in regional and temporal comparisons of consumption levels, and by cement and concrete companies seeking to determine their individual market shares in a given State. Although not a problem with market share analyses, general State-level consumption analyses are complicated by the fact that the term *final customer* is taken to mean a concrete company or similar customer (e.g., a building contractor), and, the destination State could simply be that of the customer's headquarters or an address printed on the order invoice instead of the actual concrete plant or cement storage facility owned by the customer. Importantly, the final customer is not the person whose concrete driveway is being redone. A sale to a ready mixed concrete company in eastern Pennsylvania could easily involve delivery of cement to a concrete batch plant along a highway in New Jersey, or the delivery may have been to a concrete plant in Eastern Pennsylvania, but the concrete was then transferred by truck to a jobsite in western New Jersey. Thus, the State destinations data, although defined as the State consumption levels, may actually include some ultimate consumption in adjacent States.

## Cement origins data

The second data section of the D16 form breaks out the total sales of each type of cement to final customers in terms of the State(s) and/or countries of origin. Origin is defined as the location where the finished cement was manufactured (ground from clinker). These data are a proxy for monthly production by State, but do not truly equate to this because the cement sales can include material from stockpiles. Because of the link to actual production sites, the cement origins data are subject to ROT and DC proprietary protections, and many States thus require grouping into districts for the totals to be shown. A number of States are not listed at all because they lack cement plants. Origins data are published in the table 1 series in the monthly reports, but appear in the annual report (table 9) only as overall sums showing total domestic vs. foreign origins. Origins data (as a proxy for production) are mainly used to look at

production capacity utilization levels in given regions, by comparing the data with grinding capacity data for individual plants published by the PCA. For example, high capacity utilization rates in a given area combined with even higher consumption levels suggest opportunities for a company to add to its existing production or cement distribution (terminals) capacity in a given area.

A significant problem has come to light in recent years with the data on cement origins. As the industry has consolidated, and as cement sales have been by means of an increasingly complex network of plants and terminals (perhaps involving intra- and intercompany transfers), cement companies are finding it increasingly difficult to identify where the cement that they sold in a given month was ground. Instead, the origins being reported increasingly just represent the point of last possession by the company; such data are of little use in the analysis of production capacity utilization.

## **Breakout of blended cement**

Prior to January 1998, the D16 canvass collected data on the disposition (destinations and origins) only of portland and masonry cement, and blended cement data were included with portland cement. Following discussions with the industry, the D16 form and the resulting published tabulations were altered, starting with the January 1998 report, to show blended cements separately from portland cement. The blended cement category (published as table 2b) was created to better track what was perceived to be a rapidly growing market for this material. However, the origins data for blended cement continue to be published as totals combined with portland cement (table 1a). This is because the origins are supposed to refer to the plant location where the cement (i.e., the clinker) was ground and not, as is the case for some blended cement, the location of a terminal where the blending (SCM addition) took place.

Table 3 in the monthly report shows combined portland and blended cement consumption for the given month over a 5-year interval; the combination of the two cement types reflects the fact that they both feed essentially the same concrete markets. In any multiyear comparison of consumption levels (monthly table 2 series) for “portland” cement, it is important to compare pre-1998 portland cement with 1998 and later data for portland cement plus blended cement.

## **Clinker production**

The third section of the D16 canvass also was added in January 1998 at the request of the industry, and captures State-level production of clinker during the month. This addition followed a negotiated decision to define cement origin as being the location where the clinker was ground into finished cement, not where the clinker was manufactured. Clinker production data are subject to ROT and DC proprietary protection. The data are published in the table 4 series of the monthly MIS publication, and the State groupings are usually the same as for the cement origin data.

## **Treatment of trade data collected by the D16 canvass**

Although the D16 form captures the sales and country origins of imported cement, these import data are kept completely proprietary, except that they are summed for the entire industry to a single line total (as “foreign” origin) in the monthly MIS table 1 series. The D16 canvass includes many multiplant/terminal consolidated forms, so much of the country-specific import data recorded therein cannot be linked to a specific cement plant or terminal. And the canvass does not ask for the name of the port handling the imports. Instead, the USGS publishes nonproprietary import data collected by U.S. Customs and made available by the U.S. Census Bureau. These data (monthly MIS tables 5-7), however, do not show who the importers were, or where the cement was consumed. There is thus a complete break

between the published trade data (which show import tonnages by country of origin and Customs District of entry) and the State-level consumption data collected through the D16 canvass.

## Issues concerning the D16 monthly canvass

The major issues or problems concerning the monthly surveys concern timeliness, completeness, and accuracy. There is an inherent assumption to the survey—one based on general industry and PCA agreement—that companies will report completely and accurately; they will not knowingly misreport their data (to attempt to influence the market or confound their competitors).

### Timeliness

Currently, although the USGS is getting a 100% response rate, or very close to it, on the monthly canvass, many responses are slow to arrive. In accordance with an informed agreement between the PCA and the USGS, companies are requested to return their D16 forms (by mail, fax, or Email) so that they will arrive at the USGS within 10 days following the end of the data month in question. But, in fact, many of the responses arrive later than this—sometimes more than 30 days later—and sometimes reminder notices to the nonrespondents must be sent by the USGS. With this response pattern and the time requirements for data entry, computer processing, and data checking, the USGS is currently able to meet its guidelines to 1) electronically disseminate the preliminary monthly tables within 45 days after the end of the data month, and 2) to issue the full report electronically within 60 days. To meet the day 45 preliminary data target release date, all major company data must be in hand by day 43; data still missing from small companies may be obtainable at the last minute during the data checking on day 44 and incorporated. It is important to note that, in fact, the USGS time requirements to process and release the monthly data are only about 5 working days; thus, if the industry met its day 10 day reporting target, the USGS could advance its monthly data releases by as much as 30 working days.

### Completeness

The current response rate is essentially 100% of the facilities or companies canvassed. However, the D16 canvass currently misses some of the independent importers of cement. Most of these importers are directly tied to specific concrete companies that are using the material to supply their own cement requirements (rather than selling cement into the open market). These concrete companies already know their own markets, so have little incentive to contribute to the USGS voluntary canvass. Most of the missing import volumes are relatively small, but can still be important in the local market because they represent material not being purchased from domestic producers.

### Accuracy

The cement industry tries very hard to supply accurate monthly (and annual) data, both by agreement with the PCA and the USGS, and because their own market analysts are major users of the USGS reports. The main accuracy issue has long been the elimination of double-counting of cement sales. As noted earlier, respondents are only supposed to report, in terms of destinations, the cement sales to *final customers*, not transfers-out of cement to sister cement plants and/or terminals nor sales of cement to rival cement companies. Thus, if cement company A were to report sales to cement company B as if to a final customer, then this cement would be double counted when company B properly reported the sale of the same cement to a true final customer. This mischaracterization of the buyer is fairly common and can lead to large errors if not caught and corrected. For example, in a recent year, a correction for double

counting among three companies led to a downward revision of that year's cement consumption in Florida of approximately 500,000 tons.

Situations particularly prone to double counting are those where a cement company arranges for a rival cement company to supply cement to one of the first company's final customers. Such an arrangement could stem from unforeseen production shortfalls at the first cement company, the customer's requirement for a cement type only made by the rival cement company, or a location of the customer much closer to the rival cement company. And the arrangement could be bidirectional (i.e., a swap). The problem is to determine which cement company should report the sale to the USGS. The answer basically is that the reporting to the USGS should be by the cement company that receives payment from the final customer.

Consider an example involving a swap arrangement between "Peach" Cement Co. in Georgia and "Orange" Cement Co. in Florida. For geographical convenience, Peach arranges for Orange to supply 10,000 t of portland cement to a Peach customer in Florida. The Peach customer pays Peach for the cement and so Peach should report (to the USGS) a sale of 10,000 t of portland cement into Florida. In turn, Peach agrees to supply 12,000 tons to an Orange customer in Georgia. The Orange customer pays Orange for the cement received from Peach, so Orange should report a sale of 12,000 tons into Georgia. These reporting "vectors" are regardless of the fact that neither cement company ever had possession of the cement sold into the other's State. And the reporting vectors are unaffected by whether or not the sales arrangement between Peach and Orange involved an exchange of money between the two cement companies or whether it was based simply on supplying comparable tonnages or values of cement to each other's customers.

## Miscellaneous reporting problems with the D16 form

a) *Identification of cement type:* Another type of reporting error on the D16 canvass is where a company may report sales of certain types of cement in the wrong cement category. Examples of these errors include inclusion of plastic cements with portland cement (the correct assignment would be with masonry cement), and putting masonry cements into the blended cement category or vice versa. These errors, particularly where consistently made, are difficult to detect. Also difficult to detect is where a company may omit its sales of white or colored cements—these are supposed to be included with the reporting of gray cement.

b) *Assignment to State:* A very common error (both by cement company respondents and the USGS in data entry) is where cement sales are attributed the wrong State; the tonnage is usually misreported in the State immediately above or below the correct State on the form. Where the tonnage involved is large, or the mislocation obvious (such as a southern California plant reporting sales into Maine), the error is quickly spotted on the computer printouts and corrected. But it is easy to miss location errors where the shipments are small and typically erratic. The company may actually sell the occasional truckload of cement into a very distant State, but the inclusion or lack thereof in a given month's canvass could instead be an error. Similarly, a sudden large increase in sales into a certain State could be an error or could represent a short-term, but large, sales contract.

c) *Assignment to State subdivision:* In some USGS published cement tables, four States (CA, NY, PA, and TX) are subdivided (eastern-western or northern-southern) and two metropolitan areas are split out (metropolitan Chicago from IL, and metropolitan New York from NY). Cement shipments are

sometimes reported into the wrong State division and this error, unless breaking a pattern, can be very difficult to identify. Accordingly, consumption levels of State subsets must be viewed as being potentially less accurate than that for the total State. For the divided States, and for the Chicago and New York metropolitan areas, the USGS publishes a list of the counties included in, or defining the critical boundaries between, the State subsets (see table 2 in the annual report).

d) *Clinker production*: With clinker production, the most common reporting error stems from the fact that clinker production is generally not routinely weighed. Instead, the amount is calculated by the plant based on the amounts and ratios of raw materials consumed by the kiln. Plants will periodically conduct audits of the calculation, where clinker production for a time will actually be weighed and/or the actual weight of clinker in a storage facility of known volume or capacity will be determined. Such audits commonly reveal a need to revise the monthly data. This revision may be apportioned over several months or the entire tonnage correction accumulated over several months between audits may be credited to the current or next month's production figure. The latter adjustment gives unwarranted spikes in the data.

Another clinker issue is that of reporting units (clinker tons instead of short tons); this will be discussed under the annual canvass section below.

## Revisions to monthly data

Companies are encouraged to promptly submit revisions to data should they or the USGS discover errors in past reporting. Revisions are accepted back to January of the preceding year, but no farther. The USGS may choose to ignore very small revisions. It is evident that some companies are not submitting revisions for many of their "small" (single tons to a few hundreds of tons) monthly errors, except where such are part of a long string of errors (wherein, the tons in question have cumulatively become "large"). In the monthly MIS tables, revised data will be indicated a footnote next to the new number (e.g., 20,232 <sup>1</sup>) or sometimes alongside column or row headers. The revision indicator footnote will appear only in the publication issue that first shows the revised number; subsequent issues of the report will not indicate the presence of a revision. It is important in the analysis of time-series data to always work backwards in time so as to catch any revisions to data.

The monthly Census Bureau trade data sometimes contain errors; these will be discussed under the annual form section below.

## Annual canvass and data

The D15 annual canvass and the data derived from it differ from the monthly (D16) canvass in some important aspects. Unlike the monthly canvass, all of the annual canvass responses represent individual plants (or plant complexes, including their distribution terminals) or independent terminals; that is, there is very little consolidated reporting. Except for the facility location itself, no regional information is gathered; that is, data are not collected on the destination of sales. The annual canvasses focus on the characterization of the total cement tonnages sold, the fuels and raw materials consumed by the plants, and the performances and capacities of individual kilns. The D15 canvass consists of a 4-page questionnaire plus a sheet of detailed instructions.

## Page 1 information

The first page of the D15 questionnaire has a preprinted name and address for the specific plant, plus identification codes, but asks that the respondent supply the county and nearest city information. A few, but important, summary questions follow that ask for the production of clinker, clinker purchases, the beginning and yearend clinker stockpiles, and the total plant grinding capacity. In Section 4, a mass balance is set out for portland cement (loosely defined and including blended cement) activity in terms of beginning stockpiles, inflows, outflows, and ending stockpiles. The inflows are split among cement production, transfers-in, purchases from other domestic cement companies, and imports. The outflows consist of shipments to final domestic customers, transfers-out, sales to other cement companies, exports, cement transferred to production of masonry cement, and cement consumed by the plant for miscellaneous purposes.

Subtraction of the outflows from the inflows yields an entry for yearend final stockpiles, or a combination of an inventory adjustment and the actual stockpiles.

## Page 2 information

The second page is all based on the tonnage reported on page 1 (section 4 line 240) for the total sales of portland cement to final domestic customers, and is divided into sections 5 through 7. Section 5 asks for the sales to be broken out by tonnage in terms of the types of cement involved. Currently, 15 varieties of portland cement are identified, including Types I-V portland cement and 5 general types of blended cements. Gray portland sales are reported in a separate column from those of white portland cement. *Mill net values* are requested on the total sales of gray portland cement and the total sales of white portland cement. The mill net values are the ex-factory or f.o.b. factory values, inclusive of any bagging charges, but exclusive of any onward transportation costs (to customer or terminal) and discounts. The value may be reported as total dollars or as average dollars per ton—the former is preferred. If the reporting facility is an independent terminal, then the value sought is a *terminal net value*, which is the c.i.f. cost of the cement, plus all terminal unloading and storage charges, any bagging charges or other value added, and the normal terminal markup. Onward shipping costs and discounts are excluded.

Section 6 on page 2 asks for the total sales to final customers to be apportioned among about 15 types of final customers (e.g., ready mixed concrete producers, brick and block manufacturers, road pavers, etc...). Section 7 asks for the total sales to be apportioned among various methods of transportation (rail, truck, boat or barge) to final customers and/or terminals, subdivided between bulk shipments and bag shipments.

## Page 3 information

Page 3 also has three sections (8-10). Section 8 is a mass balance among the inflows, outflows, and stockpiles for masonry cement (including portland-lime and plastic cements), much like the balance for portland cement in section 4 on page 1. Section 9 requests information on the quantities and total heat contents of the individual fuels burned by the kiln line, and electricity consumed by the entire plant. Section 10 asks for information on the performance and technological specifications of the plant's kiln lines.



**DO NOT INCLUDE MASONRY, PORTLAND LIME, AND PLASTIC CEMENT IN SECTIONS 5-7**

**5. Domestic shipments, by type, of finished portland and blended cement. (in short tons)**

*Mill or terminal net value equals the value of shipments to domestic customers, f.o.b. this reporting facility (i.e., the actual value of shipments less all discounts, allowances, freight charges to customers, and freight charges from domestic producing facilities to distribution facilities.)*

Portland and Blended Cement Types (include air-entrained versions) (1)	Code	Gray		White	
		Quantity (2)	Mill Net Value (3)	Quantity (4)	Mill Net Value (5)
Types I, II, general use and moderate heat.....	310				
Type III, high-early-strength.....	320				
Type IV, low-heat.....	330				
Type V, high-sulfate-resistance.....	340				
Block.....	345				
Oil-well (API Spec. 10).....	350				
Portland-natural pozzolan blended.....	360				
Portland-blast furnace slag blended.....	361				
Portland-fly ash blended.....	362				
Portland-silica fume blended.....	363				
Other blended portland (exclude PC Lime).....	365				
Expansive (ASTM C845).....	370				
Regulated fast setting.....	375				
Waterproof.....	380				
Other (please specify).....					
<b>TOTAL (equals CODE 240, SECTION 4).....</b>	<b>399</b>		\$		\$

**6. Domestic shipments of finished portland and blended cement by customer type. (in short tons)**

Type of customer or user (1)	Code	Quantity (2)
Ready-mixed concrete.....	870	
Building material dealers.....	810	
Concrete product manufacturers (please specify below): .....	820	
Brick/Block.....	821	
Precast/Prestress.....	822	
Pipe.....	823	
Other concrete products.....	824	
Contractors (please specify below): .....	830	
Airport.....	831	
Road paving.....	832	
Soil cement.....	833	
Other.....	834	
Federal, State, and local government agencies.....	840	
Oil well drilling.....	850	
Mining (other than oil).....	860	
Waste stabilization.....	880	
Other (please specify).....		
<b>TOTAL (equals CODE 240, SECTION 4).....</b>	<b>899</b>	

**7. Shipments of finished portland and blended cement to final domestic customer by mode of transportation. (in short tons)**

*Total shipments in SECTION B, CODE 649 should equal CODE 240, SECTION 4.*

Mode of transportation (includes pick-up by customer)	Code	A. Shipments to terminal as first destination		B. Shipments to final customer (COLUMNS 3-6 should equal LINE 240, SECTION 4)			
		Plant to terminal		Plant to final customer		Terminal to final customer	
		Bulk (1)	Bag or package (2)	Bulk (3)	Bag or package (4)	Bulk (5)	Bag or package (6)
Rail.....	610						
Truck.....	620						
Barge or Ship.....	630						
Other (please specify).....							
	649						

**PREPARED MASONRY, PORTLAND LIME, AND PLASTIC CEMENT**

*Report the quantity of prepared masonry, portland lime and/or plastic cement actually produced, received, and shipped. Mill or terminal net value equals the value of shipments to domestic customers, f.o.b. this reporting facility (i.e., the actual value of shipments less all discounts, allowances, freight charges to customers, and freight charges from domestic producing facilities to distribution facilities.)*

**8. Production, receipts, shipments, and stocks of prepared masonry, portland lime, and/or plastic cement. (in short tons)**

(400) Specify in percent, the quantity produced as: Gray \_\_\_\_\_% White \_\_\_\_\_% Colored \_\_\_\_\_%

Item (1) <i>(Include all terminals controlled by reporting facility)</i>	Code	Quantity (2)	Mill Net Value (3)
Stocks at beginning of year <i>(include stocks at distribution terminals)</i> .....	410		
Produced at this plant: From clinker.....	421		
From portland and blended cement.....	422		
<b>PLUS</b>			
Transfers-in <i>(domestic plant-to-plant within company)</i> .....	430		
Purchases from other domestic producers.....	431		
Imports from outside the United States and Puerto Rico.....	432		
<b>TOTAL (CODES 410 through 432)</b> .....	439		
<b>LESS</b>			
Shipments to final domestic customer <i>(from plant and/or from distribution terminal)</i> .....	440		\$
Invoiced shipments to other domestic cement producers and/or cement suppliers.....	441		
Transfers-out <i>(domestic plant-to-plant within company)</i> .....	442		
Exports out of the United States and Puerto Rico.....	443		
Consumption at facility.....	444		
<b>TOTAL (CODES 440 through 444)</b> .....	449		
Inventory adjustments (+/-).....	450		
End of year inventory <b>(CODE 439 - 449 +/- 450)</b> .....	460		

**PRODUCTION FACILITY INFORMATION**

**9. Fuel and energy used at this plant for all operations during the year. (exclude fuels used at distribution facilities)**

Item (1)	Code	Unit of measure (2)	Quantity (3)	Million BTU's (4)	Fuel used for:			
					Kiln	Power plant	Dryer	Other
Natural gas.....	901	Thousand cubic feet (MCF)			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Fuel oil.....	902	Thousand gallons			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Coal								
Bituminous.....	903	Thousand short tons			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Anthracite.....	904	Thousand short tons			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Coke <i>(from coal)</i> ...	905	Thousand short tons			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Petroleum coke.....	906	Thousand short tons			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Waste fuel:					Specify type of waste fuel:			
Tires.....	921	Thousand short tons						
Other solid.....	922	Thousand short tons						
Liquid.....	923	Thousand gallons						
Electric energy								
Generated.....	916	Thousand kilowatt hours						
Purchased.....	917	Thousand kilowatt hours						

**10. Kiln data for the report year.**

*Please list each kiln separately. Exclude data for idle kilns that cannot be restarted in less than six months.*

Code	Number of days NOT in production			Total length of each kiln (feet) (4)	Internal diameter of lined kiln (feet)		Maximum output for each kiln per 24 hour day (short tons) (7)	Pollution control equipment (number)		Pre-heater (10)	Pre-calciner (11)	Type of process	
	Total (COL. 2 + 3) (1)	Routine maintenance downtime ONLY (2)	Other days NOT in production (3)		Upper end (5)	Lower end (6)		Glass bag house (8)	Electrostatic precipitator (9)			Wet (12)	Dry (13)
701										<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
702										<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
703										<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
704										<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
705										<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

**11. RAW MATERIALS CONSUMED IN THE PRODUCTION OF CLINKER AND FINISHED PORTLAND AND MASONRY CEMENT.**

Report quantity of each material consumed during the year at this facility. Check whether the material was mined (M) or purchased (P) by you. The materials (quantities) consumed in the production of finished cement exclude those consumed for the production of clinker. Report quantities in short tons, if possible; otherwise please specify the units used.

Raw material (1)	Code	QUANTITY TO MAKE		Raw material (1)	Code	QUANTITY TO MAKE	
		M	P			Clinker (1)	Finished cement (2)
<b>Clinker (purchased):</b>				<b>Siliceous and pozzolanic:</b>			
Imported (foreign)...	533			Sandstone.....	521		
Domestic.....	534			Silica, other sand..	522		
<b>Calcareous:</b>				Quartzite.....	523		
Cement rock.....	501			Calcium silicates...	524		
Limestone.....	502			Pumice, tuff.....	516		
Marl.....	503			Pozzolana.....	563		
Oyster, seashells...	504			Other rock pozzolans.....	577		
Chalk.....	505			Other igneous rocks.....	571		
Marble.....	506			Rice husk ash.....	583		
Aragonite.....	507			Silica fume.....	584		
Coral.....	508			Other micro-crystalline silica..	592		
Cement kiln dust...	561			Granulated blast furnace slag.....	586		
Lime.....	593			Other blast furnace slag.....	587		
Other (specify)				Steel furnace slag.....	589		
<b>Aluminous:</b>				Other slag (specify)	591		
Shale and schist...	511			Fly ash.....	536		
Clay (all kinds).....	512			Other ash (specify)	598		
Staurolite.....	513			Other pozzolans and cementitious additives (specify)	520		
Bauxite.....	514			Other:			
Aluminum dross...	515			Gypsum.....	538		
Alumina.....	518			Anhydrite.....	539		
Other (specify)				Fluorspar.....			
<b>Ferrous:</b>				Other (specify)	540		
Iron ore (all types)..	528						
Pyrite cinder.....	529						
Mill scale.....	530						
Other (specify)							

**12. List any noteworthy changes in quarry or mill equipment made at this plant during the year**

**13. List any expansions/modernizations to plant/quarry during reporting year**

Name of person to be contacted regarding this report			Tel. area code	No.	Ext.
Address	No.	Street	City	State	ZIP Code

May tabulations be published which could indirectly reveal the data reported above?

Value data  (1) Yes  (2) No Other (including quantity) data  (1) Yes  (2) No

Signature	Title	Date
-----------	-------	------

## Page 4 information

Section 11 is mainly a list of nonfuel raw materials, grouped by major oxide contribution, wherein the plant's actual consumption (in tons) of each is split between materials burned in the kiln to make clinker and those introduced afterwards to the finish mill to make finished cement. Consumption of outside clinker, split between domestic and foreign manufacture, is also requested.

Data from the D15 annual questionnaire are collated and published by State or district for most items, as national totals for some others (e.g., raw materials consumption, types of portland cement sold), and split between wet and dry technology plants for still others (fuels and electricity consumption). The State-level presentations are subject to ROT and DC proprietary data protection and, thus, many of the State totals require the aggregation of individual data within districts. The data are published in the USGS annual MIS report for cement. This report becomes the cement chapter in the Minerals Yearbook (MYB). These reports also contain U.S. annual trade data supplied by the U.S. Census Bureau, presented in somewhat more detail than in the monthly MIS. The annual report, as with the monthly reports, is available electronically at: <http://minerals.usgs.gov/minerals>.

## Issues concerning the D15 annual canvass

As with the monthly survey, the annual canvass is subject to timeliness, accuracy, and completeness issues.

### Timeliness

The D15 canvass is mailed out by the USGS in early January following the data year in question, with a requested return due date of March 1. Typically, only 10%–20% of the forms have been returned to the USGS by the requested return date, perhaps 50% are in by the end of April, and about 80% by the end of May. Companies that have not responded by the end of March receive reminder telephone calls from the USGS. Generally, the remaining forms come in June and July, with the last few coming in either August or not at all.

The timeliness problem of the annual canvass reflects the fact that the industry relies less on the annual report than on the monthly reports. In the case of the monthly surveys, both the respondents and users of the data typically are the marketing divisions of the plants or companies and the data are used in monthly economic analyses critical to the business of the company. In contrast, the annual reports are seen as historical documents. Although useful to a company seeking long-term trend data for the purpose of evaluating plans to build new or added capacity or doing other long-term analyses, the corporate need for the annual data appears to be less pressing than for the monthly data.

Another factor in the lateness of annual responses is that cement sales activities and data are increasingly being centralized within companies, which means that the actual production site personnel are commonly unfamiliar with data pertaining to cement sales. That is, the plant's job is mostly just to make cement and ship it to a terminal or make it available for pickup at the plant. Accounting now tends to be done at central or regional sales offices. Thus, plant personnel may find it difficult to fill out sections 4–8 of the D15 canvass, as these sections pertain to sales, and may thus postpone filling out the form. Apart from causing general delays to the publication of the annual report, late responses make more difficult the resolution of any errors found on individual forms. A particularly frustrating problem is where

respondents have relied heavily on the previous year's form for guidance in filling out the current form; this leads to errors being perpetuated.

Where, after perhaps repeated telephone requests, data still have not been reported to the USGS, estimates for the missing data will be made, using monthly data and previous years' annual reporting for guidance. The estimated data, while generally a small fraction of national totals, can be significant for specific regions of the country.

## Completeness issues

The D15 annual form is sent to all of the currently operational integrated production facilities in the United States and Puerto Rico, and as many grinding plants and independent distribution and import facilities of which the USGS is aware and which agree to participate in the survey. Currently, several independent import terminals are not part of the survey.

For the facilities canvassed, response rates have generally been high (covering commonly 90% or more of the facilities and the total U.S. tonnages). The missing import terminals are a small part of the overall tonnage nationally, but can be important locally.

Even for forms returned to the USGS, it is common for certain questions to have been skipped by the respondents. Where the missing data cannot be obtained by follow up inquiry, they are estimated.

## Accuracy issues

Discussion of accuracy will be grouped by topic.

### Sales and production tonnage issues

In a typical year, U.S. total cement sales to final customers reported monthly (and summed for the year in tables 9 and 10 in the annual report) may significantly exceed the shipments to final domestic customers plus exports reported on the annual forms. The difference has been as high as 7 million metric tons (Mt) in some recent years (i.e., about 6%–8% of sales). To locate and reduce the discrepancies, all annual forms are now compared with the monthly data and an attempt is made to resolve at least the large discrepancies (say, more than 1% of a plant's total sales). A common source of discrepancies is when a plant's annual form fails to include associated or other terminals that were included on its monthly forms. In such a case, a possible solution is for the company to submit a separate annual form for the missing terminal(s). Another common problem is when a plant's shipments are allocated improperly among sales to final customers, sales to other cement companies, and transfers-out to sister cement plants. The third most common problem is where, contrary to instructions, masonry cement is included in the portland and blended cement data. A careful comparison of annual to monthly sales data has succeeded in reducing the sales tonnage discrepancy significantly; it was just 4 Mt or about 3.8% of total sales for portland cement in 2000, less than 0.2 Mt in 2001 and 2002, about 1.7 Mt in 2003, and less than 0.1 Mt in 2004. However, as a matter of practicality, it is generally not possible for a given plant to resolve most differences in portland cement sales of about 20,000 t or less for the year. This approximate threshold is typically less than about 3% of the given plant's total sales. In most cases, the sales discrepancies have been found to be the result of errors in the annual form.

In contrast, clinker production data—the other data directly comparable between the monthly and annual forms—tend to show only small (< 1%) discrepancies or none at all. The errors in the clinker data have generally been with the monthly reports, and then only with a few months' entries. The errors stem from the fact that plants do not routinely weigh their clinker output; instead they calculate it based on raw materials consumed and then do periodic audits to check their calculations. The USGS is not always informed of the revisions resulting from the audits. Another problem, of unknown extent but which was revealed by one plant's recent survey, was that of reporting clinker in "clinker tons" rather than short tons. A "clinker ton" is a unit of convenience for a cement plant and is defined as that weight of clinker that will yield 1 short ton of portland cement. The weight of a clinker ton varies plant-to-plant; in this particular instance, the clinker ton was 1,915 lbs.

Although monthly origins of sales data are proxies for actual cement production, they are, in fact, rather poor checks against annual production data. This is because the origins data can include stockpiled material and may erroneously reflect a location of last possession instead of production. Also, as with clinker, plants do not routinely weigh their cement output. Cement sales, in contrast, are weighed very precisely.

Another data check done with the annual forms is to see if the clinker production (adjusted for clinker purchases, transfers-in, changes to stockpiles, and for consumption of pozzolans and gypsum) is sufficient to make the finished cement quantities reported.

The reported grinding (or cement) capacity is checked to see if it is adequate for the cement production shown. A problem sometimes encountered is where the grinding capacity appears to be too small. In some cases, this is because it has been misreported (perhaps does not account for a mill upgrade). In some other cases, the low number represents the correct capacity to grind clinker, rather than the capacity needed to grind clinker plus the additives to make the finished cement.

Regionalized production and related data for portland and masonry cement are given in tables 3 and 4, respectively, of the annual report. For portland cement, the reported grinding capacity also is shown, as is a capacity utilization percentage (production/capacity). The capacity utilization data shown in table 3 of the annual report are entirely based on portland plus blended cement output and are thus conservative (ideally, utilization would be compared to the production of total hydraulic cement).

Some regions show an apparently abnormal (usually low) cement or clinker capacity utilization percentage. In most cases, this is an artifact of the USGS policy of including all capacity that was in operation during the year, regardless of for how long. Thus, a new plant that came on-stream late in the year, or an old plant that was closed early in the year, will have its full capacity included in the regional total, but will have little offsetting actual cement or clinker production for the year.

## Other data related to sales tonnages

### *Types of cement sold*

Where major differences in total sales to final customers have been resolved, company annual data as to the types of portland cement sold are generally quite accurate in terms of tonnages, except that they may indicate an erroneous type of blended cement (e.g., fly ash blended cements reported as natural pozzolan blended cements), and sometimes are inconsistent as to how hybrid portland cements are

reported (e.g. will a Type II/V hybrid be registered on the entry line for (combined) Types I,II or for Type V?).

### *Mill net values of sales*

A far more common problem is where the mill net value of the total portland cement sold has been omitted or is in error. Most omitted values can be obtained through follow-up inquiries, but some cannot, either because the company finds value data to be too sensitive to release or where the canvass form is not returned. For the remaining missing data (typically 10%–15% of the total forms), estimates are made using values from plants that did provide data and which are in the same market area. For plants reporting values in the form of an average value per ton, a total value (rounded) is calculated by the USGS. The mill net values reported on some canvass forms appear to be too low, and likely reflect the omission of bagging and pallet charges (bagged cement is invariably more expensive per ton than bulk cement). Occasionally, a very low unit value will prove to reflect the erroneous reporting of a production cost (this, normally, would be less than the sales price).

In the annual report, separate tabulations (tables 12–14 in reports through 2003, and 11–13 for 2004) show regionally reported mill net values for portland cement (gray and white combined) and masonry cement. Gray cement sales dominate the total value for portland cement, but the unit value of white cement is much higher. For the national average values, a separate tabulation provides the split out unit value averages for gray portland cement, white portland cement, total portland cement, masonry cement, and total cement. The white cement average shown is likely somewhat too high because it includes both primary sales and resales (with markups).

Although the regional average value data are generally presented in the annual report unrounded, the annual report cautions readers that the data contain estimated components and should not be taken too literally; regional or temporal value differences of less than \$0.50– \$1.00/t are probably not significant.

### *Sales by customer type*

Portland and blended cement sales are broken out by the major construction activities of the customer (customer type) rather than the actual uses of the cement sold; the former classification is believed to be easier for cement companies to track.

Although a noticeable improvement has been seen in recent years, a number of facilities still fail to provide customer-type breakouts of sales. In some cases, the respondents claim not to track this information at all; this is rather surprising for a company overall but may be reasonable for production personnel isolated at the plants themselves. The USGS encourages respondents that lack adequate data to put in their best estimates of the customer types; it is virtually certain that company-provided estimates are preferable to the USGS estimates that would have to be made otherwise. Estimates by the USGS and, it appears, some by the companies, favor the major customer-type categories over the minor ones. Another difficulty is that a company may categorize its customers in ways that do not match the breakouts on the USGS form. In addition, some of the D15 breakout categories are overlapping. A perennial example of this overlap is characterizing cement sales to ready-mixed concrete producers (the largest category) that are also engaged in road-paving (one of the subcategories of “contractors”). Also, the general categories “Concrete products” and “contractors” each include a subcategory called “other” that is intended to capture miscellaneous customers, but instead is used by a few respondents as a catch-all to register undifferentiated sales within the more general category.

### *Sales by mode of transportation*

The final section of the D16 form related to portland cement sales is fairly complicated but seeks to apportion shipments to final customers by method of transportation (rail, truck, boat), form of sale (bulk vs. bag or packages) and location of transfer to the customer (plant vs. terminal). The section asks for the quantity in tons of cement destined for final customers that were transferred during the year from the plant to terminals. This transfer does not require that the cement be fully sold during the year (i.e., some can remain in stockpiles at yearend). Transfers from plant to terminal exclude imported cement, but sales to customers from the terminals include imported material. Thus, there can be a fundamental disconnect in tonnage between domestic loading of terminals and total sales from terminals.

Another problem with this section that has surfaced recently is confusion regarding the split between “bulk” and “container” shipments. The form’s instructions explain that jumbo bags (aka. “supersacs”) are to be registered as “containers” despite their common use for bulk shipments to terminals unequipped for true bulk cement handling. But the term “container” also is an example of how word meanings can change over time. Through about 1970, cement shipment data were still being reported in barrels (1 barrel = 376 lbs), even though no cement had actually been shipped in a barrel in the United States for many decades. Instead, cement was increasingly being shipped in bulk form or, for the non-bulk deliveries, in various (usually 94-lb) bags, sacks, or packages. For brevity, the word “container” was adopted to describe all these non-bulk shipments, and proved satisfactory for many years. However, “container” now is sometimes confused with the large rectangular wood or steel-sided general cargo containers carried on the decks of general freighters, by “ro-ro” ships, and as full loads for tractor trailers and individual railcars. Little, if any, cement gets sold or carried in these rigid containers. So, rather than erroneously register non-bulk sales as (rigid) container sales, some annual respondents have instead erroneously included their bag or package shipments in the “bulk” category. It is unknown how long this error has been occurring, but it has led to a wording change from “container” to “bag or package” on the D15 form.

### *Regional presentation of data*

Cement and clinker production data in the annual report are presented as regional tabulations showing the locations of manufacture. However, with the exceptions of tables 9 (and 10 in reports prior to 2004), it is important to note that the annual reports’ State and district breakouts of cement sales represent the location of the reporting facility, not the location of consumption. For example, data shown for “...cement shipped by producers...” in eastern Pennsylvania represent the sales tonnages reported by the producers located in eastern Pennsylvania, including their sales into adjoining States, but the data exclude sales into eastern Pennsylvania from producers outside eastern Pennsylvania. The true consumption of cement in eastern Pennsylvania (and the other States, shown individually) is given in table 9. Individual State production in tons shown in table 9 will not match those in the other tables. The totals for the United States overall, however, should match among all tables, but commonly do not because of reporting errors already noted. A problem with the regional representation of sales occurs if a plant erroneously reports all of its cement shipments as sales to final customers. Some of this material could have been transferred out to sister cement plants in other States.

### *Fuel and electricity data*

Data on fuels burned by the cement industry are of increasing interest for environmental studies, chiefly those regarding CO<sub>2</sub> emissions. In the D15 canvass, plant-level fuel consumption is broken out by fuel type, both in terms of the quantity of fuel and the heat energy realized for each. The fuel types

specified are coal (bituminous vs. anthracite), metallurgical coke, petroleum coke, natural gas, fuel oil, and three types of waste fuels: tires, "other solid wastes," and liquid wastes.

A number of problems have been encountered with the reporting of fuel data. The most common is with the reporting units. The D15 form currently specifies nonmetric units of "thousand short tons" for the solid fuels, "thousand cubic feet (MCF)" for natural gas, and "thousand gallons" for the liquid fuels. If other units are, in fact, used, the respondent is asked to specify them precisely. The problem is that respondents commonly report fuel data in full rather than thousand-units. This becomes obvious for solid fuels: no single plant burns 67,525 thousand short tons of coal; the entry should have been 67.525 (or 68) thousand tons. The same error is far less obvious, however, for the liquid and gaseous fuels, as they may be burned in relatively small amounts to warm up a cold kiln or in large quantities as a major fuel or co-fuel during regular kiln operations. Natural gas is especially difficult to pin down, as plants track this fuel from the gas company invoices, and these are generally denoted in MCF (thousand cubic feet), which many respondents misinterpret to mean "million cubic feet." The gas may even be reported as some very large number (actual cubic feet) annotated "MCF" or worse, "MMCF". Since the addition by the USGS of the "MCF" qualifier to the units specification on the form, it is believed that the incidence of errors has decreased significantly.

A check on the fuel units is possible when the company also provides, as requested, the heat (in million Btu, high or gross heat value basis) realized for each fuel. Where Btu data are provided, a Btu/ton fuel ratio can be calculated and compared with standard gross heat values to check for order of magnitude errors in the fuel reporting units. Unfortunately, heat data are commonly omitted or are sometimes reported in amounts that make no sense regardless of the fuel reporting unit. Where omitted, standard heat values can be applied to see if the overall plant's heat consumption appears reasonable, but this is a crude check at best. It is increasingly common for plants to report heat energy on a low or net heat basis instead of the high or gross heat basis requested. A few plants erroneously apportion heat values among the fuels based on the total unit heat consumption per ton of clinker and the mass ratios among the fuels. Because the quality of the heat data provided are so poor, the USGS has not routinely published heat data. However, corrections to the Btu data are being increasingly sought and the quality of the collected data is improving.

Another problem is that the fuel splitout on the D15 form is not very comprehensive. No space is offered for gasoline, for example, although it is known that some plants' consumption (generally very small) is included, for lack of a better place, with fuel oil. And "fuel oil" does not distinguish between distillate fuel oils (like diesel) and residual fuel oils; their heat values are somewhat different. Likewise, no provision is made for liquid petroleum gas. For many years, the D15 form did not distinguish between metallurgical coke (i.e., devolatilized coal) and the completely unrelated petroleum coke (petcoke). Petcoke is by far the more common fuel but is sometimes erroneously put on the metallurgical coke line. Finally, only rarely do respondents identify the waste fuels burned (other than as tires vs. other solid wastes vs. liquid wastes); it is difficult to evaluate or assign Btu values for unidentified waste fuels, or for that matter, liquid wastes identified merely as mix of "spent oils, solvents, alcohols, inks, lubricants, etc..."

Electricity data are commonly reported in total kilowatt-hours instead of the "thousand kilowatt-hours" requested; this error is easily spotted and corrected. Occasionally, a plant will record purchased electricity as having been cogenerated. These errors usually are spotted. For many years, electricity consumption was reported on a per-ton portland cement basis instead of, more properly, on a total cement basis. Although U.S. masonry cement output is equivalent to only about 5% of the portland cement

production, most is made directly from clinker rather than from portland cement, and so imposes a significant electricity burden within the grinding mill.

### *Raw materials data*

Instead of just requesting the total tonnages of various raw materials consumed, the D15 form now asks that the respondent indicate whether the particular raw material was used to make clinker or was added in the finish mill to make finished cement. This cement vs. clinker distinction caused some confusion when it was introduced for the 1998 canvass, but the industry appears now to have become accustomed to the split. A few materials are, perhaps by habit, still reported in the wrong usage columns, but most of these errors are easily spotted. A few materials are habitually underreported. For example, the CKD space is generally left blank, despite the fact that, at many plants, CKD is returned to the kiln. The problem is that this flow is not routinely measured, and the plant thus has very incomplete or no data on it. Material reported as limestone one year might become marble the next year, or cement rock. The data for gypsum will include natural gypsum and may include synthetic gypsum (a product of flue gas desulfurization at thermal power plants) or the synthetic gypsum may be put in the space for “Other” raw materials (but usually identified) or, unfortunately, it may be put in the space for anhydrite.

The raw materials data are published in table 6 of the annual report. A grand total tonnage is shown at the bottom of the table but it is misleading because, until recently, it included the actual tons of imported (foreign) clinker consumed. Although imported clinker can be viewed as a raw material (because the cement produced from it is counted as U.S. production), it is better if the imported clinker is first converted to an approximate weight of raw materials used to make that clinker. This conversion commenced with the 2002 report.

### *Kiln data*

Data are collected separately for each “operational” kiln at a plant. Operational kilns are those that had clinker production during the year as well as some idle kilns. An idle kiln is deemed operational if it can be restarted, with all operating permits in hand, within a period of 6 months or less; very few U.S. cement plants report idle kilns at present. The data collected for each kiln include its length and internal diameter, its daily (24-hour) clinker output capacity, its technology (wet, dry, dry with preheater, dry with preheater-precalciner, and type of dust control system), and the number and characterization of downtime days.

The characterization of downtime is between that for routine maintenance (previously called “scheduled” downtime) and all other downtime combined. The key datum here is the days for routine maintenance (M); this is used in conjunction with the reported daily capacity (C) to calculate an apparent annual capacity (AC) by the formula:

$$AC \text{ (tons/year)} = (365 - M) \text{ days/year} \times C \text{ (tons/day)}$$

The “working year” component (365 - M) becomes (366 - M) for leap years.

A serious problem derives from how “routine” or “scheduled” maintenance is defined at individual plants, USGS instructions notwithstanding. It is supposed to cover all the planned outages for routine maintenance, including and generally concurrent with the annual or semiannual task of rebricking the kiln,

and it is the amount of time that this work is expected or planned to take. Any extensions to this expected work period (delay in arrival of parts, condition of equipment worse than expected, etc.), all breakdowns, all shutdowns for poor market conditions, shutdowns for major upgrades (in excess of routine maintenance done at the same time) are to be entered as “other” downtime. Most kilns need 10–30 days annually for routine maintenance, taken in one or two scheduled kiln outages. However, some plants do not schedule a set period for routine maintenance; they wait for the first problem requiring a shutdown to occur, and then do the routine work as well as the needed repair and “plan” on taking as much time as it takes. Some plants include all of the time for upgrades, arguing that this work was certainly planned and scheduled. For these plants, excessively long routine maintenance periods are shown, and this leads to a calculated apparent annual capacity that is too small, and an annual capacity utilization (clinker production/AC) that is too high; not uncommonly > 100%.

The daily capacities reported for the kilns are supposed to represent a realistic maximum 24-hour sustained output, which may well exceed the conservative ratings provided by the kiln manufacturers. Daily capacities should change (year-to-year) if the equipment has been upgraded, a bottleneck has been removed, or the raw mix changed in some way so that the throughput increases. A potential problem of unknown magnitude is when plants report daily clinker capacities in “clinker tons” rather than short tons. As noted earlier, a clinker ton is a measure of convenience and represents the amount of clinker in 1 short ton of portland cement.

Regionalized kiln performance and clinker production data are published as (currently) table 5 in the annual report. A frequent question is why the published regional daily capacities and average routine maintenance downtimes do not yield the regional annual capacities shown, using the footnoted formula for apparent annual capacity. The answer is that the regional daily and apparent annual capacities are the sums of the actual (not average) individual daily and annual capacities, respectively, for each kiln, whereas the average downtime figure is an average of all the kilns.

### *Trade data*

Trade data, other than single-line totals for cement imports and exports, are not collected on the annual canvass. Instead, as with the monthly reports, nonproprietary U.S. Census Bureau data are utilized for the annual report. Currently, seven trade tables (17–22 through the 2003 report; 16–21 for 2004) are published, all showing quantities (tons) and values. Table 17 lists U.S. exports of hydraulic cement and clinker (combined), by country of destination, and is the only export table in the report. Table 18 shows a summary of combined hydraulic cement and clinker imports, by country of origin. Table 19 breaks out the table 18 data by country of origin and the customs district (“port”) of entry into the United States (including San Juan, Puerto Rico). Table 20 is a subset of table 18 showing just the imports of gray portland cement, by country of origin. Table 21 does the same thing for white portland cement, and table 22 shows the subset for imports of clinker.

Values shown on the trade tables are “free alongside ship” (f.a.s.) for exports, and both “customs” and “cost, insurance, freight” (c.i.f.) values for imports.

Removing the portland cement imports (tables 20-21) and clinker imports (table 22) from table 18 leaves a small residuum of imports representing other forms of hydraulic cement. Some of these imports calculate to very high unit values and likely represent either aluminous cement or some highly specialized material.

As earlier noted, both the monthly and annual canvasses miss the activities of a few, mostly small, importers, but the activities of these importers are included in the trade tables. Except for antidumping tariffs still imposed on imports from Mexico and Japan, cement imports into the United States are not subject to import tariffs so there is no incentive to smuggle the material or misreport its tariff code to U.S. Customs. Nevertheless, apparent errors in the monthly or annual trade tables are occasionally discovered by, or brought to the attention of, the USGS. Some of the data on white cement imports calculate to unit values (\$/t) that are unrealistically low for white cement. In at least some of these cases, the USGS has determined that the low unit values actually represent gray portland cement (or even gray clinker) imports that the importer had mistakenly invoiced under the white cement tariff code. This mistake is understandable if one considers the abbreviated explanatory wordings offered in some older code tabulations. For example, under the Harmonized Tariff Schedule of the United States (HTS), item HTS code 2523.21.000 is commonly described just as “portland cement” and the next code 2523.29.00 is described as “portland cement, other than white and colored.” It is only by reading the second code that one realizes that the first code is actually for white (and/or colored) cement; more recent tabulations now have code 2523.21.00 reading “Portland cement, white or colored.” The second code is the correct one for gray portland cement.

Another issue with official trade data is that they do not include relatively low-valued (<\$2,000 customs valuation on the shipment) entries for commodities lacking import tariffs or are otherwise deemed innocuous. This omission has been noticeable for clinker imports from Canada that come in by truck into the Seattle, WA (and possibly the Detroit, MI, and Milwaukee, WI) Customs Districts. At least some finished cement entering by truck from Canada appears also to be missing from the official data, but the magnitude of such has been hard to determine, as the tonnages are likely small compared with large waterborne or train-conveyed bulk cement imports from that country.

Where trade data errors appear to be significant, the USGS informs the Census Bureau of the problem, but does not unilaterally issue corrections.