

Cement Manufacture and the Environment

Part II: Environmental Challenges and Opportunities

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Keywords

alternative fuels
carbon dioxide
clinker
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Summary

Construction materials account for a significant proportion of nonfuel materials flows throughout the industrialized world. Hydraulic (chiefly portland) cement, the binding agent in concrete and most mortars, is an important construction material. Portland cement is made primarily from finely ground clinker, a manufactured intermediate product that is composed predominantly of hydraulically active calcium silicate minerals formed through high-temperature burning of limestone and other materials in a kiln. This process typically requires approximately 3 to 6 million Btu (3.2 to 6.3 GJ) of energy and 1.7 tons of raw materials (chiefly limestone) per ton (t) of clinker produced and is accompanied by significant emissions of, in particular, carbon dioxide (CO₂), but also nitrogen oxides, sulfur oxides, and particulates. The overall level of CO₂ output, about 1 ton/ton clinker, is almost equally contributed by the calcination of limestone and the combustion of fuels and makes the cement industry one of the top two manufacturing industry sources of this greenhouse gas. The enormous demand for cement and the large energy and raw material requirements of its manufacture allow the cement industry to consume a wide variety of waste raw materials and fuels and provide the industry with significant opportunities to symbiotically utilize large quantities of by-products of other industries.

This article, the second in a two-part series, summarizes some of the environmental challenges and opportunities facing the cement manufacturing industry. In the companion article, the chemistry, technology, raw materials, and energy requirements of cement manufacture were summarized. Because of the size and scope of the U.S. cement industry, the article relies primarily on data and practices from the United States.

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Introduction

Construction materials constitute some 70% of the nonfuel materials flows in the United States (Wernick et al. 1997). Concrete and mortars are critically important construction materials; concrete is used as a bulk building material in its own right, and mortars are used to bind together bricks, stone, or other blocks in masonry-type construction. Concretes and most mortars rely on hydraulic cement binders for their strength and durability, but despite this, the dry cement component in these materials is rather small (e.g., about 10% to 12% by volume of the concrete mix). Most of the concrete, which is essentially an artificial conglomerate, is a mix of sand and gravel or other fine and coarse aggregates (65% to 80%), water (about 14% to 21%), and air (0.5% to 8%). The combination of cement and water in the concrete mix is called cement paste. Compositionally, mortars differ from concrete chiefly in the fact that they contain only fine aggregates and the hydraulic cement contains plasticizing agents. Typically, 1 ton (t)¹ of cement suffices for about 3 to 4 cubic meters (m³) of concrete, weighing about 7 to 9 t. Current world output of hydraulic cement exceeds 1.6 gigatons (Gt).

This article is the second of a pair. As noted in part I (van Oss and Padovani 2002), hydraulic cements are those that can set and harden underwater through the hydration of the component cement minerals. By far the most common hydraulic cements in use today are either portland cements or similar-use cements (called “blended” or “composite” cements) that are made of a portland cement base plus cementitious or pozzolanic additives; blended cements are commonly included within the portland cement designation in the economic research and technical literature. A pozzolan is a siliceous material that develops hydraulic cementitious properties when interacted with free lime (CaO) and water.

Straight portland cement is made by grinding together portland cement clinker (the intermediate product of cement manufacture) with a small amount, typically 5% by weight, of calcium sulfate, usually in the form of the mineral gypsum. Summarizing from part I, the chemical

composition of a typical portland cement clinker is almost entirely just four oxides: calcium oxide or lime (CaO), about 65%; silica (SiO₂), about 22%; alumina (Al₂O₃), about 6%; and iron oxide (Fe₂O₃), about 3%. In cement industry shorthand, these four oxides are written as C, S, A, and F, respectively, and most clinkers do not show deviations in these oxide proportions of more than 2 to 4 percentage points. The remaining 4% or so of the clinker composition is divided among oxides of magnesium, potassium, sodium, sulfur, and others. Clinker is primarily made up of four clinker minerals, denoted in shorthand as C₃S, C₂S, C₃A, and C₄AF. The C₃S and C₂S are the main contributors to the performance of portland cement and together make up about 70% to 80% of the weight of the clinker. During their hydration, C₃S and C₂S combine with water by similar reaction paths to form calcium silicate hydrate (its variable composition is denoted “C-S-H”) plus lime; the C-S-H is a colloidal gel that is the actual binding agent in the concrete. The bulk of the C₃S hydrates rapidly (hours to days) and provides most of the early strength of the concrete, whereas the C₂S hydrates slowly (days to weeks) and is responsible for most of the concrete’s long-term strength. The lime by-product of hydration activates any pozzolans that may be present in the concrete mix.

As was reviewed in part I, the manufacture of clinker involves the thermochemical processing of large quantities of limestone and other raw materials, typically about 1.7 t/t clinker, and requires enormous kilns and related equipment, sustained very high kiln temperatures (the materials reach temperatures of about 1450°C in order to form the key C₃S mineral), and the consumption of large amounts of energy (fuels and electricity); total energy consumption is about 3 to 6 million British thermal units (Btu)/t clinker (1 million Btu = 1.055 GJ). Clinker manufacture results in significant emissions, particularly of carbon dioxide (CO₂). Apart from the technological aspects of cement manufacture, part I discussed the main environmental considerations of the mining of cement raw materials. The remaining environmental challenges and opportunities relating to clinker and cement manufacture are the subject of this article.

Environmental Considerations

Where the public is aware of the cement industry at all, it is usually in an environmentally negative context (i.e., pollution); less well known are the environmentally beneficial aspects of the industry. The main environmental issues associated with cement manufacture are discussed, first in terms of those that are problems² and second in terms of those that are benefits.

Cement manufacture involves both mining and manufacturing steps. Although covered in part I, a few summary remarks concerning the mining of nonfuel raw materials are warranted here. About 1.7 t of nonfuel raw materials are consumed to make 1 t of cement; the bulk (about 85%) of the raw materials is limestone or similar rocks, to which is added clay or shale and other materials to achieve the correct chemical proportions. These are, for the most part, geochemically benign materials, and their mining generally does not lead to significant problems of acidic or otherwise chemically contaminated drainage. Although individual quarries and mining rates for cement raw materials are not particularly large relative to mines for many other minerals, the existence of thousands of cement plants worldwide ensures that their quarries' cumulative yearly output of cement raw materials is huge. Current world cement output requires almost 3 Gt/yr of nonfuel raw materials; associated fuel consumption is roughly 200 million tons (Mt) per year in straight mass terms (i.e., not on a common fuel basis), or about 0.15 to 0.2 t fuel/t clinker. The concrete and mortars (about 13 to 14 Gt/yr) incorporating this cement require a total of about 15 Gt/yr of raw materials, mostly aggregates. Reserves of cement (and concrete) nonfuel raw materials are geologically abundant, although they may be quite limited for individual plants for a variety of reasons.

Although not discussed in part I, and generally not stressed in discussions of raw materials for concrete and mortars, the current annual worldwide consumption of raw materials for these includes about 1 Gt water/yr for cement hydration. Water is also required in some cement plants, especially to form the raw materials slurry feed for wet-process kilns (this water is not

needed with dry-kiln technology). Slurry water amounts to about 30% to 35% of the weight of the slurry, or roughly 0.8 t water/t (wet process) clinker, and is ultimately evaporated (and thus lost) in the kiln line. Lacking comprehensive international data distinguishing wet- from dry-process clinker production, the total amount of water consumed worldwide for wet-process slurry is not known, but would amount to about 16 Mt for the United States in 2000 (table 5 in part I; table 7 in van Oss 2002). The main issue concerning water for cement or concrete is not pollution of it by the cement or concrete industries, but its adequate supply and quality (the broader issue of sediment loading or other contamination of water bodies as a result of general construction industry activity is neglected here). For various reasons, water for concrete manufacture should be of essentially potable quality (Kosmatka and Panarese 1988).

As was argued in part I, and notwithstanding the significant tonnages involved, the effects of mining of cement raw materials are considered to be local in impact, at least compared to some other mining sectors. Far more important are the environmental issues relating to cement manufacturing itself, specifically the manufacture of the clinker intermediate product, and the remainder of the article focuses on these issues. Clinker manufacture has significant emissions of particulates and gases, of which one in particular (CO₂) has garnered international attention and is routinely singled out in national and international emissions data compendia. Although quantitatively small relative to CO₂, emissions by individual plants of the other substances can be of considerable local concern, especially for older plants in countries (or in past times) where strong emissions regulations are/were lacking. And even in modern, state-of-the-art facilities, so-called minor emissions can be of public concern where the emitted substance has gained notoriety from instances, perhaps elsewhere, of major releases or poor handling, where the substance is classified as toxic, or where it has an alarming appearance (e.g., visible nonsteam emissions plumes). Further, emissions levels that are "minor" on an individual plant basis can reach substantial cumulative totals when summed for the world. Except for CO₂, emissions

(in the sense of escaping the plant) can be controlled or reduced in modern cement plants, although not all modern plants are necessarily equipped to control all emissions.

Particulate Emissions from the Manufacturing Process

Particulate emissions, including dust, of various types derive intermittently and diffusely from quarrying activities and more or less continuously on a point-source basis from the comminution circuits (i.e., crushing and grinding of raw materials and clinker), from the pyroprocessing or kiln line, and from landfilled cement kiln dust (see below). In general, fugitive emissions of coarse particulates (particularly of particle diameters $> 10 \mu\text{m}$), if not controlled, are considered to be more of a local nuisance than a health hazard. Fine particulates (those $< 10 \mu\text{m}$ and especially $< 2.5 \mu\text{m}$ diameter known in U.S. regulatory parlance as "PM₁₀" and "PM_{2.5}," respectively), in contrast, are of greater concern, because of their respirable nature and because, both for cement raw materials and manufactured products, they may contain potentially harmful concentrations of toxic metals and compounds. Even where emissions of fine particulates by cement plants do not exceed statutory limits, they can augment already high ambient particulate levels (from other sources) in the air. The U.S. Environmental Protection Agency (U.S. EPA) provides extensive summary tabulations, most related to plant process and control technologies, of emissions of particulates, both in terms of total mass and chemistry. Most of the data in the tabulations are rated by the U.S. EPA as having been measured by techniques of low reliability, and the agency cautions, therefore, that the data are order-of-magnitude indicators only (U.S. EPA 1994, 1995).

The amount of dust from comminution is highly variable from plant to plant and is dependent on the type and character (e.g., hard, soft, wet, dry) of the materials involved and on the design, condition, and operational practices of equipment at individual plants. With even rudimentary dust-control procedures, generally such dust, especially the PM₁₀ fraction, is not considered a problem, or its effects do not extend

beyond or much beyond (a few hundred meters) the confines of the plant property. Where captured, much of the comminution dust is suitable for incorporation into the raw material feed (raw mix) for the kiln.

Dust from the pyroprocessing line is loosely called "cement kiln dust" (CKD) and includes fine particles of unburned and partially burned raw materials, clinker, and material eroded from the refractory brick lining of the kilns. As used in this article, CKD includes both the main stack particulate emissions and emissions from the alkali bypass system (see below), as well as emissions from the clinker cooler.

Very few public data are available on national, or even plant-specific, total generation of CKD. This is basically because there has been little economic or regulatory incentive to collect such data in the past and, in any case, CKD generation is not easily measured. At many plants, as much CKD as possible is directly routed back with return air to the kiln (effectively joining the raw mix stream), and the dust content of this return flux would be very difficult to determine. In modern plants and most plants in countries having particulate emissions restrictions, plants route exhaust through electrostatic precipitators (ESPs) and/or fabric filtration baghouses to remove CKD. The amount recovered this way is readily measurable, although where done, tends to be on an episodic basis (e.g., when the filtration bags are purged or cleaned). Recovery by ESP and/or baghouses is generally quite efficient (commonly 99% or better with modern equipment, based on measured emissions) (Duda 1985). Modern scrubber systems are capable of meeting current U.S. particulate emission standards for kilns of 0.15 kg/t (or 0.015%) of dry raw kiln feed (U.S. EPA 1999a), which is roughly equivalent to 0.009% on a clinker weight basis; emissions from clinker coolers are limited to 0.05 kg/t clinker. Return of CKD to the kiln, either via direct rerouting or after capture by ESPs or baghouses, makes sense chemically and economically because the CKD typically has a major oxide composition very close to that of the raw mix feed or the clinker, and such a return of CKD thus saves on raw materials and energy.

Because of the difficulty of completely measuring the material, the relatively few data on

CKD output or production commonly are limited to (1) that material first captured by the ESP and/or baghouse, (2) perhaps only that fraction of captured CKD that is returned to the kiln, or (3) perhaps just that portion sent to landfills. In other words, most CKD production data should at least be suspected of underrepresenting the true total or gross CKD generation. Despite the scarcity of data, it is generally agreed that the amount of CKD generation is highly variable among plants and over time at individual plants. Based on limited, informal data and conversations with various U.S. plant personnel, an estimate of CKD generation as about 15% to 20% (by weight) of the clinker output is useful as a first approximation, which has implications for rigorous calculations of CO₂ emissions as discussed below and in Appendix A.

A 15% to 20% CKD to clinker ratio implies a significant disposal problem, if only in terms of quantity, for plants that do not recycle the CKD to the kiln or that cannot find outside customers for it, given the fact that most plant clinker capacities fall in the range of 0.2 to 2.0 Mt/yr. The informal data from, and conversations with, producers noted above revealed that in the United States, typically about two-thirds of the generated CKD is returned to the kiln, leaving one-third for landfill disposal (the majority) or sale. Landfill disposal is becoming increasingly unsatisfactory for environmental and cost reasons (i.e., landfill space is increasingly at a premium and is unsightly; some countries now require that new CKD pits be lined to prevent escape of leachate). Landfill disposal also represents a loss of potential revenue from material that not only has been mined and at least partially processed, but is close to the finished saleable product (i.e., cement) in composition. In this respect, CKD waste differs from wastes of some other industries where the wastes are dissimilar to the saleable product.

Some contaminants (trace elements or compounds) from the raw materials and fuels tend to concentrate in the CKD, and these contaminants may constrain the degree to which a cement plant can recycle the dust to the kiln if the clinker quality thus becomes compromised. This is a particular problem with alkalis (e.g., sodium and potassium), which can cause adverse effects (volume expansion and bond-weakening alkali-

silica reactions) between the cement paste and certain amorphous silica-rich rock types used as aggregates for concrete in some areas (Kosmatka and Panarese 1988; Lea 1970). Preheater and preheater-precalciner dry plants having raw materials with high alkali contents commonly incorporate an alkali bypass system ahead of the kiln or precalciner to reduce condensation of alkalis (coatings) in the kiln line and the alkali content of the clinker and/or CKD.

The presence of contaminants other than alkalis may limit the ability of CKD to be used for other purposes, notably the traditional use as a liming agent for soils (Palmer 1999), although they would be less likely to affect the suitability of CKD for other common uses, such as the stabilization of sludges, wastes, and soils; as road fill; or as a cementitious additive in blended and masonry cements (as yet a minor use). Further information on alternative uses of CKD can be obtained from Bhatta (1995).

Health concerns regarding CKD relate to its dispersal through the air (dust from the kiln line, material disturbed during transportation, or wind action on existing CKD piles) and to leachate from CKD piles and generally have to do with the concentrations of heavy metals in the CKD itself or in leachate from CKD piles. As noted earlier, the U.S. EPA (1994, 1995) summarized a number of studies into the mass and chemistry of particulate, particularly airborne, emissions. In cement plants lacking dust controls, particle size analysis of emissions of particulates from wet-process kiln lines showed that 24% of the particulates were of diameters of less than 10 μm and 7% were smaller than 2.5 μm ; dry-process lines showed 42% of emissions having particle diameters of less than 10 μm and 18% less than 2.5 μm (U.S. EPA 1994, table 11.6-5). For plants having dust-control technology, very little coarse dust was escaping; both wet and dry lines showed that about 85% of the remaining escaping particles were of diameters of less than 10 μm . Wet-process plants using ESP scrubbers showed an average of 64% of the particles at less than 2.5 μm diameter, and dry plants equipped with baghouses showed 45% of escaping particles in the less than 2.5 μm size fraction.

A summary of U.S. EPA studies into health and related environmental issues concerning

CKD (particularly that in landfills), as well as proposed CKD landfill disposal and management practices, is found in U.S. EPA's proposed standards for CKD (U.S. EPA 1999b). The U.S. EPA report noted that, whereas most metal concentrations in CKD were at safe levels for use of CKD as a soil liming agent, this was equivocal for cadmium (Cd), lead (Pb), and thallium (Tl). Accordingly, maximum concentrations were set for CKD for soil liming use at 22 ppm for Cd, 1,500 ppm for Pb, and 15 ppm for Tl. Limits were also placed on the concentration of dioxins and furans (see below). Although no limits were proposed for hexavalent chromium in the U.S. EPA report, general concerns about Cr⁺⁶ toxicity and the fact that it can be a component of CKD have contributed to a decline in the use of "chrome" (magnesia chromite) refractory bricks in the kiln lines (Nievoll 1997). An overview of the chemistry and utilization of CKD was given by McCaffrey (1994). Apart from the studies cited by the U.S. EPA in various reports (U.S. EPA 1994, 1995, 1999b), compendia of heavy metal and other trace elements and compounds in CKD can be found in publications of Haynes and Kramer (1982), Delles and colleagues (1992), and PCA (1992). Gossman (1993) provides data on certain toxic elements from particulate emissions for about 30 U.S. cement plants, all of which burned hazardous waste fuels.

Gaseous Emissions from the Clinker Manufacturing Process

Gaseous emissions from cement plants include large quantities of CO₂ (a major focus of this article), smaller amounts of carbon monoxide (which is considered to ultimately oxidize to CO₂ and is discussed along with CO₂), sulfur and nitrogen oxides, and trace amounts of dioxins and furans. These are discussed below. In addition, cement plants can emit variable, but generally much smaller, quantities of a variety of other pollutants (e.g., volatile organic compounds other than dioxins and furans), but it is beyond the scope of this review to cover these relatively minor emissions; publications by the U.S. EPA (1994, 1995) provide some emissions data on these compounds. All the pollutants mentioned are all at least potentially subject to

emissions regulations and, increasingly, plants are being designed or retrofitted with various monitoring devices for these compounds. Likewise, the operational practices of some plants are being modified to reduce some of these emissions. Emissions standards and testing procedures vary among countries; however, it is beyond the scope of this review to provide a comparison of these different standards and procedures.

Sulfur Oxide Emissions from Clinker Manufacturing

Anthropogenic sulfur oxides (SO_x) emissions are of general interest primarily for their role in the generation of acid rain, and the bulk of these emissions are generally attributed to fossil-fuel-fired power plants and base-metals smelters. Locally (particularly in humid areas), major point sources of SO_x can generate acidic mists that can engender potential health concerns.

In cement manufacturing, SO_x emissions mainly derive from the combustion of sulfur-bearing compounds in the fuels (e.g., from pyrite [FeS₂] in coal and various sulfur compounds in oil and petroleum coke) but can, to a lesser extent, also come from pyrite, sulfate minerals, and kerogens in the nonfuel raw materials. Fuel-derived SO_x forms in the main burning zone of the kiln tube (figure 4 in part I) and in the independently heated precalciner apparatus (if so equipped), whereas raw-material-derived SO_x forms in the preheating apparatus or section of the kiln line. Given the large quantities of coal and other sulfur-bearing fuels consumed in cement manufacture (table 1), the cement industry would be considered a fairly large SO_x source were it not for the significant self-scrubbing nature of the clinker manufacturing process; indeed, the ability to handle high-sulfur fuels is considered to be an asset of the industry. The amount and location of SO_x formation and emissions in clinker kiln lines can vary with the kiln-line technology (e.g., wet versus dry lines). A brief summary is provided below, but a more detailed review of these variables, and of SO_x abatement strategies, was given by BCA (1997) and by Terry (2000).

Although the proportions are quite variable from plant to plant, many of the SO_x and

Table 1 Fuel consumption and carbon dioxide emissions for the U.S. cement industry

Fuel consumption	Year												
	1950	1955	1960	1965	1970	1975	1980	1985	1990	1995	1998	1999	2000
Coal (kMt)	7,206	7,918	7,591	8,288	7,227	6,509	10,601	10,087	9,098	8,241	9,066	9,206	10,095
Coke (from coal) ¹ (kMt)	nd	nd	nd	nd	nd	nd	nd	nd	nd	455	432	343	442
Petroleum coke ¹ (kMt)	nd	nd	nd	nd	nd	357	488	442	379	1,475	1,197	1,622	1,351
Fuel oil (ML)	836	1,352	641	710	1,594	1,166	653	120	299	42	73	134	124
Natural gas (Mm ³)	2,751	3,721	4,859	5,621	5,998	4,518	1,718	301	294	1,069	720	653	338
Tires (kMt)	nd	nd	nd	nd	nd	nd	nd	nd ²	nd ²	158	269	685	374
Other solid waste (kMt)	nd	nd	nd	nd	nd	nd	nd	nd ²	nd ²	68	74	816	1,016
Liquid waste (ML)	nd	nd	nd	nd	nd	nd	nd	nd ²	nd ²	885	1,268	905	929
Carbon dioxide emissions (t/t clinker)													
Case A: fuel only ³	0.69	0.63	0.56	0.54	0.53	0.52	0.55	0.47 ⁴	0.41 ⁴	0.46	0.46	0.49	0.48
Case A: total ^{3,5}	1.20	1.14	1.07	1.05	1.04	1.03	1.06	0.98 ⁴	0.92 ⁴	0.97	0.97	1.00	0.99
Case B: fuel only ⁶	0.63	0.57	0.52	0.50	0.48	0.48	0.49	0.43 ⁴	0.37 ⁴	0.41	0.41	0.44	0.43
Case B: total ^{3,6}	1.14	1.08	1.03	1.01	0.99	0.99	1.00	0.94 ⁴	0.88 ⁴	0.92	0.92	0.95	0.94
Clinker output (kMt)	38,679	51,093	55,349	63,991	67,123	58,549	63,341	60,941	64,356	71,257	75,842	77,337	79,656

Source: Table 4 of van Oss and Padovani (2002).

Note: nd. = no data; likely small or nil except for 1990.

¹ For years labeled "nd," consumption, if any, may be included in data for coal.

² Waste fuel data were not collected until 1993, but the fuels were being consumed beginning in the mid-1908s.

³ Calculated based on standard gross (high) heat values for fuels. Values exceed those calculated using net (low) heat values by about 0.02 unit (1950–1975), 0.00 to 0.01 unit (1980–1990), and 0.01 unit (1995–2000).

⁴ Data are undervalued because of the lack of waste fuel data for 1985 and 1990; see footnote 2.

⁵ Includes calcination emissions of 0.51 t/t clinker.

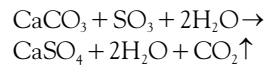
⁶ Calculated based on actual heat values (gross heat basis) for fuels reported by plants to the USGS in 2000.

volatile alkalis derived from the raw materials combine within the preheating zone or apparatus in the kiln line to form stable alkali sulfates (e.g., Na_2SO_4) or calcium-alkali sulfates [e.g., $\text{K}_2\text{SO}_4(\text{CaSO}_4)_2$], some of which wind up as buildups or coatings in the cooler parts of the kiln line and some of which become incorporated within the clinker and/or the CKD. The kiln-line coatings help to protect the refractory brick linings from damage but, if allowed to build up excessively, can clog or otherwise impede the movement of material through the kiln.

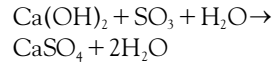
Some of the SOx formed during preheating is scrubbed by limestone or lime in the raw material feed and forms anhydrite (CaSO_4), but, although much of it can become part of the clinker, at least part of the anhydrite tends to decompose and rerelease SOx as the feed enters the (much hotter) calcination zone or apparatus in the kiln line. Anhydrite surviving in the clinker (provided that the amount is neither too variable nor too high) is generally viewed favorably, as its presence can reduce the need for gypsum addition later in the finish mill. Overall, typically more than 70% of the original SOx winds up incorporated in one compound or another in the coatings, the clinker, and the CKD. The SOx from anhydrite decomposition in the calcination zone, and that derived from fuels in the sintering zone of the kiln, is carried back with the system air into the preheating zone and can overwhelm the lime and alkali scrubbing capacity of the raw material feed. Thus, there can be a net evolution of SOx in the exhaust gas in concentrations commonly of 100 to 200 ppm, but they are variable. Very approximately, 100 ppm SOx in the exhaust corresponds to an emissions rate of about 0.5 kg SOx/ton clinker. The U.S. EPA noted typical SOx emissions for wet and long dry kilns of 4.1 to 4.9 kg/t clinker, whereas preheater and preheater-precalciner kiln lines had much lower emissions of about 0.27 to 0.54 kg/t (table 11.6-7 of U.S. EPA 1994). U.S. statutory emissions limits are typically around 2.75 kg SOx/t clinker (Schwab et al. 1999). Where SOx emissions routinely exceed local regulatory limits, or where they frequently appear as visible detached plumes, cement plants can install scrubbers on the exhaust gases (Olsen et al. 1998). Similar, but of smaller scale, to those for thermal power

plants, these scrubbers react the SOx with limestone or lime to make gypsum, such as by the net reactions (shown for SO_3):

limestone scrubber:



lime scrubber:

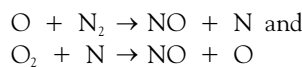


Likewise, this type of SOx scrubbing can occur if hot exhaust gases are used as a heat source for drying the (calcareous) raw materials in the raw milling circuit. A cement plant can further reduce SOx emissions by selecting low-sulfur raw materials and fuels, but these may be of limited availability or high cost.

Nitrogen Oxide Emissions from Clinker Manufacturing

High-temperature combustion of fuels in the kiln line releases nitrogen oxides (NOx), with the nitrogen being mainly derived from the atmosphere but also to some degree from the fuels themselves; a minor contribution also comes from some types of raw materials. The formation of NOx in cement kilns is complex and as yet incompletely understood; useful reviews of the subject are found in publications by Haspel (2002), Lanier and Hanson (2000), Smart and colleagues (1998), Terry (2000), and Young and von Seebach (1998). As noted in these studies, 90% or more of NOx emissions are NO, with the rest NO_2 ; the cement industry generates almost no nitrous oxide (N_2O), a powerful greenhouse gas (GHG) (U.S. EPA 2002). Four mechanisms of NOx formation are recognized: thermal, fuel, feed, and prompt.

Thermal NOx makes up about 70% or more of total NOx from clinker kilns and is formed by direct oxidation of atmospheric nitrogen through the dissociation of O_2 and N_2 :



Thermal NOx begins to form at temperatures as low as 1200°C, but rapid formation requires about 1600°C, which is well below the burner-flame (not material) temperatures in clinker kilns. Thermal NOx formation increases rapidly

with even small temperature increases when within the range of 1370° to 1870°C; the high-end temperature approximates that of the gas temperatures in the kiln's sintering zone. Given the high kiln temperatures, even small shifts in the amount of combustion oxygen can have a pronounced effect on the amount of thermal NO_x formed.

Fuel NO_x is formed from the burning of nitrogen compounds in the fuels; most fuels contain at least some nitrogen. Of the major fuels, coal, the most common fuel, contains the most nitrogen and natural gas the least (essentially nil). Fuel NO_x forms throughout the entire range of combustion temperatures, but mainly when in excess of 800°C, and the mechanisms of formation are complex. In the fuel-rich (reducing) zone of kiln flames, fuel NO_x is reduced to N₂, which remains stable, typically, until the temperature reaches about 1600°C, when it reoxidizes to NO_x. Based on the higher nitrogen content in the fuel, one would expect coal-fired kilns to have higher total NO_x emissions than natural gas-fired kilns, but the opposite is true because of the dominance of thermal NO_x formation in the sintering zone and the fact that natural gas generally generates higher flame temperatures than coal. As noted in part I, precalciners have their own burners and operate at lower temperatures than those in the sintering zone of the kilns themselves; accordingly, NO_x formation in precalciners (alone) is dominated by fuel NO_x.

Feed NO_x is derived from nitrogen compounds in the raw mix or feed to the kiln and is formed slowly during the preheating (350° to 750°C) phase of pyroprocessing. Feed NO_x production tends to be greater in wet and long dry kilns because of the relatively slow rates of preheating with these older technologies.

Prompt NO_x refers to NO formed in the reducing (i.e., fuel-rich) flame in excess of that which would be expected from thermal NO_x-forming reactions. Prompt NO_x appears to be formed by the reaction of CH₂ and similar fuel-derived radicals with atmospheric nitrogen to form cyanide (CN) radicals and N, both of which subsequently oxidize to NO.

As noted by Young and von Seebach (1998), overall output rates of NO_x from individual plants are highly variable even over short to medium periods (minutes to days); their study de-

tailed the example of one long dry kiln that had absolute NO_x output rates varying between about 1 and 6.5 kg NO_x/t clinker (converted from reported English units), or about 0.1% to 0.7% of the weight of the clinker, with most values in the range of 0.15% to 0.45% and what looks like a 1 standard deviation range encompassing NO_x emissions of about 0.2% to 0.4% of the weight of the clinker. These values illustrate the typical variability of NO_x measurements to be expected for kilns, but absolute NO_x emissions would likely show a somewhat larger range for a large population of plants or kiln technologies. The lower end of the range noted would be fairly typical of precalciner-equipped kilns because of the reduced amount of very high temperature fuel combustion in the kiln compared with that burned at lower temperatures in the precalciner; likewise the more modern kilns have shorter material residence times (and hence lower unit emissions). An alternative general metric is that kilns produce about 0.5 to 2 kg NO_x per million Btu (or per gigajoule [GJ]).

A 0.2% to 0.4% (of the weight of the clinker) NO_x emissions range would imply NO_x emissions by the U.S. cement industry within the range of 0.16 to 0.32 Mt in 2000, based on a clinker output of about 79.66 Mt in that year (table 1). This may be compared with total non-agricultural U.S. NO_x emissions of about 22 Mt/yr, of which about 19% are so-called industrial and commercial sources (U.S. EPA 1997, 1998). Although an output of about 1% of total U.S. nonagricultural NO_x emissions is modest compared to that of motor vehicles and electrical utilities, cement plants are nonetheless significant point-source NO_x contributors and are increasingly being required to install NO_x-monitoring equipment and reduce emissions. This is particularly true in regions that suffer from high levels of ambient ozone, the most widespread urban air pollutant in the United States, which is largely a secondary air pollutant resulting from the precursors NO_x and hydrocarbons.

Approaches to reducing NO_x emissions include technological upgrades to reduce fuel consumption and material residence times in the kilns, installation of low NO_x burners, recycling of CKD, adoption of staged combustion to reduce thermal NO_x in precalciners, midkiln firing

of fuels, reduction of excess air (oxygen), switching among major fuels (i.e., burning more coal), burning of waste fuels to induce reducing conditions, and, for precalciner kilns, introduction of water injection to reduce flame temperatures in the sintering zone (Haspel 2002). All reduction strategies benefit from improved kiln process controls (Lanier and Hanson 2000).

Dioxin Emissions from Clinker Manufacturing

Cement manufacturing releases small but variable amounts of a variety of volatile organic compounds; the U.S. EPA (1995) listed some of these and showed a general emission of these compounds, in total, in the range of only 0.014 to 0.090 kg/t clinker. At their low individual emissions levels, most of these compounds do not raise health concerns. One class of these compounds, dioxins and furans, has attracted significant scrutiny, however.

Dioxins and furans are general names applied to a large, complex group of polychlorinated organic compounds, many of which are highly toxic even in trace amounts. For simplicity, the quantity and toxicity of individual dioxins and furans, as well as those of the similar polychlorinated biphenyls (PCBs), are commonly expressed relative to that of the compound 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (TCDD), the most toxic and well-studied member of the group (U.S. EPA 2000). The toxic equivalency factor (TEF) of TCDD is assigned a value of 1.0, and most of the other compounds have TEFs of no more than 0.1; many are 2 to 4 orders of magnitude lower.

Trace amounts of dioxins and similar compounds (hereafter collectively labeled "dioxins") can be formed from the combustion of organic compounds in fuels and raw materials in cement manufacture, especially as a result of the combustion of certain waste fuels. The potential to increase emissions of dioxins may inhibit a plant's use of the offending fuel where emissions cannot be controlled by varying the combustion conditions in the kiln, where this control precludes efficient kiln operations, or where obtaining permits to burn the fuel would be too time consuming or costly. Dioxin emissions likely

would not be the sole criterion in a plant's decision or ability to burn waste fuels, however.

Dioxin emissions by cement plants are in trace amounts only, but there is not an abundance of plant-specific data available on the actual outputs. Emissions for a limited number (about 30) of U.S. kilns were measured in 1995 by the U.S. EPA (2000); about half of the facilities burned a portion of hazardous waste fuels. Based on TEFs developed by the World Health Organization in 1998, the U.S. EPA found that kilns that did not burn hazardous wastes had dioxin emissions, in toxicity mass equivalents (TEQ) relative to TCDD, averaging 0.29 ng TEQ/kg clinker (1 ng/kg = 0.001 ppb). Kilns burning hazardous wastes (types unspecified) emitted an average of 22.48 ng TEQ/kg clinker (with a range of 1.11 to 30.70 ng TEQ/kg clinker); that is, emissions from kilns burning hazardous waste were about 100 times higher than those from kilns burning regular fuels (coal).

The U.S. EPA also found that for kilns burning hazardous wastes, emissions differed significantly between kilns having "hot" exhaust gases (as measured at the CKD scrubber) > 450°F (232°C) and those having "cool" exhausts < 450°F. The hot exhaust emissions averaged 30.69 ng TEQ/kg clinker, whereas the cool emissions were just 1.11 ng TEQ/kg clinker. Further, post-1995 measurements by the U.S. EPA showed that for hot exhaust systems, scrubber outlet emissions of dioxins could be significantly higher than those at the scrubber inlet. Evidently, dioxins were being formed within the hot scrubber, and this discovery has led, since 1995, to a number of plants installing water spray cooling to the exhaust gases ahead of the scrubbers to reduce scrubber emissions.

Overall, for 1995 the U.S. EPA (2000) projected total national emissions from U.S. kilns burning hazardous wastes of 156.1 g TEQ (of which 154.7 g TEQ was from hot exhaust kilns) and just 17.8 g TEQ from kilns not burning hazardous wastes, for a grand total of 173.9 g TEQ. By comparison, total U.S. airborne dioxin emissions in 1995 from all anthropogenic sources were estimated at 3,125 g TEQ. Importantly, the U.S. EPA noted that because of the installation of exhaust cooling, noted above, the total U.S.

cement industry emissions are now (post-1995) much lower, closer to about 14 g TEQ annually. Although considered representative and adequate for first-order approximations, the absolute levels of these dioxin emission levels by cement plants must be considered to be of low statistical confidence (U.S. EPA 2002). Apart from cooling the exhaust gases to prevent formation in the scrubbers, overall dioxin generation from combustion is kept very low if fuel materials in the kiln are kept in excess of 1200°C for several seconds or more, limits that are in line with normal kiln operating conditions (Krogbeumker 1994). Dioxin limits in recovered CKD that is intended to be sold as a soil liming agent in the United States have been set by the U.S. EPA at 40 ng TEQ/kg clinker (reported as 0.04 ppb TEQ; U.S. EPA 1999b).

Carbon Dioxide Emissions from Clinker Manufacturing

In recent years, there has been increased international concern about the long-term effects of anthropogenic emissions of GHGs on global climate. The most important of these gases is carbon dioxide (CO₂), not because it has the highest unit heat retention of the GHGs but because the quantity of emissions is so large that its effects overall are dominant. For the United States, the U.S. EPA currently produces annual U.S. inventories of emissions data for GHGs other than water vapor. In terms of warming potential, CO₂ accounted for about 83.5% of the total U.S. GHG emissions in 2000 (U.S. EPA 2002). Unlike the cement industry's emissions of SO_x and NO_x (considered to be relatively modest), the emissions of CO₂ by the cement industry are enormous and have led to the industry being one of a very few singled out in the calculation of international GHG emissions levels. Prominent in this attention to the cement industry is the Intergovernmental Panel on Climate Change (IPCC), which has the responsibility of helping to promulgate the Kyoto Protocol and to derive methodologies for establishing national GHG emissions inventories (see below).

Industrial emission of CO₂ arises universally from the burning of fossil fuels, but it is relatively uncommon from other industrial pathways. Both

the IPCC and the U.S. EPA segregate emissions resulting from fuel combustion (dominated by those of power plants and motor vehicles) from other pathway sources. The logic behind this combustion segregation is that, on a national basis, it is easier to determine the total quantity of fuels burned (based on apparent consumption calculated from national data on fuel production, stockpile, sales, and trade) than to survey the myriad individual consumers of fuels. This combustion segregation does not clearly demonstrate the full CO₂ impact of the cement industry, however, nor that of the two other industrial sources (the iron/steel and lime industries) identified as having major noncombustion CO₂ emissions.

As shown in figure 1, combustion of fuels accounted for about 97% of total U.S. anthropogenic CO₂ emissions (about 5.8 Gt) in 2000, and almost two-thirds of the total combustion emissions were from power plants and motor vehicles. All of the remaining individual combustion sources were small by comparison, but of these sources, the iron/steel and cement industries were the largest.

Overall, the U.S. cement industry accounted for only 0.6% of the country's total CO₂ emissions from combustion, or 1.3% of total emissions from all sources. The cement contribution would be 3.4% of total emissions from all sources excluding motor vehicles and power plants. Because most countries do not have as proportionally large a thermal power generation infrastructure as the United States or a comparable intensity of motor vehicle use, the relative cement contribution to total CO₂ emissions is lower in the United States than in many other countries having substantial cement industries. A number of studies (e.g., Hendriks and colleagues 1998; Worrell and colleagues 2001) have suggested that, worldwide, the cement industry contributes about 5% of total anthropogenic CO₂ emissions; an estimate of 2.4% was given by Marland and colleagues (1989), but this does not account for the combustion emissions by the industry and so would need to be approximately doubled for the full emissions picture.

Given the magnitude of the cement industry's CO₂ output, considerable interest has been expressed in quantifying these emissions. The IPCC (1996, 2000) developed a detailed meth-

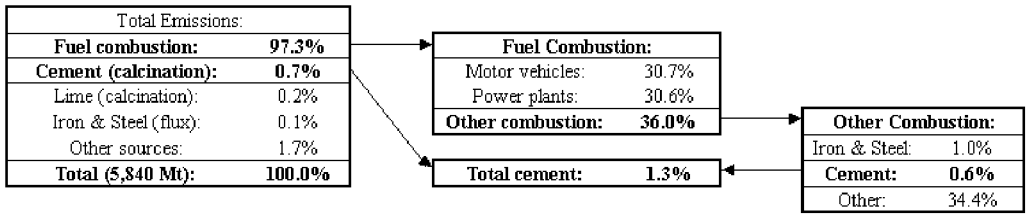
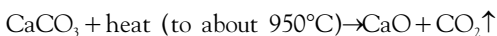


Figure 1 The contribution of the cement industry to total U.S. anthropogenic CO₂ emissions in 2000. The cement industry is a large source of CO₂, but its total contribution is only a small fraction of that from the combustion of fuels by power plants and motor vehicles. For countries having economies that are less power plant and motor vehicle intensive, the proportion of total emissions from the cement industry is generally higher. *Source:* Based on data from U.S. EPA (2002).

odology to estimate (to within 5% to 10%) the calcination CO₂ emissions from cement manufacture in individual countries. The IPCC method is based on national statistics (but applicable also to data for individual plants) on clinker production rather than cement itself. A problem with a clinker approach is that clinker production data are currently lacking or not readily available for most countries, although the data probably could be easily collected in the future by national statistical agencies. National hydraulic cement production data are far more available but commonly are rounded (see, e.g., table 23 of van Oss 2002). Also, as is discussed below, the accuracy of the calculation using cement is highly dependent on the clinker fraction of the cement, which can be quite variable. One could also estimate emissions derived from the cement industries' combustion of fuels, provided that data exist for the types and quantities of fuels consumed. Lacking such data for most countries, one can still make crude approximations for them based upon existing combustion emissions data for the U.S. industry, owing to similar cement plant technologies in use worldwide; this approach is less valid for China because of its preponderance of vertical shaft kiln (VSK) plants.

CO₂ Emissions from Calcination

As noted in part I, the calcination of calcium carbonate (from limestone, the major raw material in cement) releases CO₂ by the simple reaction



In theory, the amount of calcination CO₂ released could be calculated from the component formula weight ratios for this equation based on the amount of limestone and similar rocks burned in the kiln (table 3 of part I). For this, one needs data on both the tonnage and composition of the raw materials, and these data are generally lacking on a national basis. The only practical, general, country-level approach is to work backward from clinker production, from which may be derived a calcination emissions factor of 0.51 t CO₂/t clinker, assuming a 65% CaO content of the clinker. Appendix A provides a detailed discussion of this calculation.

The 0.51 t CO₂/t clinker emissions factor for calcination, which has been adopted as a default by the IPCC (2000), is very similar to those used in some other studies (e.g., U.S. EPA 2002; Vanderborgh and Brodmann 2001; Worrel et al. 2001); some of the differences disappear with rounding (component data quality does not warrant precision to more than two decimal places, and most final results should be rounded further). The methodologies in some of these other studies (e.g., Vanderborgh and Brodmann 2001), however, work forward from the raw materials—the procedures are proposed for individual plant reporting—but the equations are the same and thus subject to essentially the same error ranges. As noted by the IPCC (2000) and discussed further below, unless one knows the net clinker fraction (about 95% for a straight portland cement; typically 55% to 80% for blended or composite cements and 45% to 60% for masonry cements) of a country's specific cement output mix, there

is no CO₂ emissions factor for cement production that can be used without the potential for significant error (up to about 35%).

An assumption apparently common to all clinker-based methodologies for calculating CO₂ emissions is that one is dealing with portland cement clinker or something very similar to it. This assumption, which basically refers to the amount and source of CaO in the clinker, would not hold very well for clinker for aluminous cement (made by burning a mix of bauxite and limestone). Aluminous cement, however, is manufactured in tiny (<1%) quantities, and in just a few countries, relative to portland and related cements. Production data on aluminous cement are almost invariably proprietary and hence unavailable. Within any realistic assessment of the accuracy of current international data on clinker and cement compositions and production levels, satisfactory first-order national or regional estimates of calcination CO₂ emissions for the cement industry can be made using the assumption of a 65% CaO content in clinker and a calcination emissions factor of 0.51 t CO₂/t clinker.

CO₂ Emissions from Combustion

The determination of CO₂ emissions from fuel combustion is complex and imprecise compared to that from calcination because the combustion emissions are dependent on the types and quantities of the actual fuels burned, together with their interrelated carbon and heat factors (contents). Specific data for all of these for the cement industry are generally lacking, especially on a country basis. Further, the calculation of CO₂ from combustion invariably makes the assumption that all of the carbon monoxide (CO) generated through combustion ultimately is converted to CO₂ and may thus be treated as CO₂ for GHG calculation purposes. The generation of CO and the methodology used in this article to calculate combustion CO₂ are discussed in Appendix B. Unlike the case with calcination emissions, the net combustion CO₂ factors derived from data for one country's cement industry may be only approximately applicable to other countries because the quantity (and to some degree the type and composition) of fuels burned

depends significantly on the kiln technologies in use, fuel availability, and to a lesser degree on the nonfuel raw materials consumed.

Table 1 shows the basic fuel consumption breakdown for the U.S. cement industry for 1950 through 2000, as well as the derived unit emissions of CO₂. Two sets of CO₂ emissions data are shown; both utilize the gross or high heat contents (values) of the fuels to calculate the fuels' carbon contents. Gross heat is the basis of fuel energy reporting by the U.S. cement industry, whereas net or low heat values are used almost everywhere else. Gross heats are preferred for CO₂ calculations, as they are more complete. Fortunately, there is very little difference between gross and net heats for coal, coke, and most other solid fuels, and as these are the dominant fuels for the cement industry, the CO₂ emissions series in table 1 would not change significantly if it were recalculated using net heats.

As seen in table 1, combustion emissions in 2000 for the U.S. industry were 0.43 t CO₂/t clinker according to actual heat data supplied by the plants, or 0.48 t CO₂/t clinker using standard gross heat assignments for each fuel; the equivalent output using standard net heats is 0.47 t CO₂/t clinker. All of the CO₂ data series show a general decline since 1950, although the data for 1985 and 1990 are slightly and significantly too low, respectively, because they do not include waste fuels. Burning of significant amounts of waste fuels in U.S. cement kilns began around the mid-1980s, but data on this activity were not collected before 1993.

As noted in part I, and as with unit energy requirements, the general decline in unit CO₂ emissions from 1950 to 2000 reflects the modernization of the U.S. industry over this period, specifically the increasing use of dry (vs. wet) process technology in clinker manufacture, as well as technological upgrades at many existing dry-process kilns. Data for the earlier years in table 1 could be viewed as comparable to values that would be expected in countries presently running mostly old kilns. Countries having all very modern dry preheater-precalciner kilns, however, could be expected to have somewhat lower combustion emissions than the lowest values shown in table 1.

Summarizing CO₂ Emissions from Calcination and Combustion

Table 1 also shows total emissions of CO₂, which are simply the combustion emissions plus the calcination emissions of 0.51 t CO₂/t clinker noted above. Total unit emissions by U.S. cement plants amounted to about 0.94 t CO₂/t clinker in 2000. Total emissions for the majority of countries would likely be within the range of 0.9 to 1.2 t CO₂/t clinker, perhaps slightly higher for countries such as China and India that operate a large number of VSKs. As noted earlier, the IPCC (2000) calculation methodology used for calculating CO₂ is good to within 5% to 10% for individual country calculations, and this or greater uncertainty would apply to most competing methodologies. Given likely uncertainties in international clinker production and other data and in the CO₂ calculation methodologies, a simple ratio of 1 t CO₂/t clinker production is a reasonable first-order approximation by which to compare total emissions among countries.

For a straight portland cement (typically 95% clinker), the corresponding total emissions would be about 0.95 t CO₂/t cement and, indeed, the casual literature commonly quotes “cement” emissions of 1 t CO₂/t cement. A 1:1 ratio for cement, however, will not accurately allocate national CO₂, except for countries that produce only straight portland cement, because of the variable clinker fraction that can be accommodated within the term “hydraulic cement.” Even where data are available for a country’s production mix of straight and blended cements, the actual clinker fractions of the blended cements is often unknown or available only as estimated averages or as a range of compositions. For example, the recipe for one of the common blended cements in the United States (type IS, general-use portland blast-furnace slag cement) allows for a ground granulated blast-furnace slag (GGBFS) content of 25% to 70%. Assuming a 5% gypsum content in the portland cement fraction, a type IS cement could thus have a clinker factor of 28.5% to 71.3%.

Where clinker fraction data are lacking, the IPCC (2000) recommends using a default clinker fraction of 75%. Humphreys and Mahasenan (2002) gave world regional clinker factors esti-

mated for the mid-1990s by the International Energy Agency ranging from 81% (western Europe average) to 89% (Africa and the Middle East), but there likely is variation within the regions as well. These authors estimated total world output of CO₂ from the cement industry output for 2000 at 1.4 Gt. Worrell and colleagues (2001) used average clinker factors of 84% for industrialized countries and 87% for the rest of the world and showed a breakout for 1994 of about 30 countries that revealed clinker fractions of 74% to 99% and a world average of 85%. A regional tabulation of approximate CO₂ emissions potentials based on data for clinker capacities is given in table 2. CO₂ emissions³ for the world’s cement industry are on the order of 1.7 Gt; about one-half of this potential resides in plants in Asia. Figure 2 is a map showing country-level CO₂ emissions potentials.

CO₂ Emissions from Electricity Use

Table 1 does not include the CO₂ derived from the generation of electricity because it is likely that, in the analysis of national GHG emissions, such emissions would be allocated to the commercial power plants in the case of cement manufacturers purchasing all or most of their electricity (e.g., the U.S. industry). Electrical generation by a cement plant itself generally would make use of waste heat from the kiln and not involve further fuel consumption. If data are available on electricity purchases, approximate overall electricity CO₂ can be calculated by assuming that the cement industry accesses an “average” national power grid and so has indirect CO₂ emissions from electricity proportional to cement’s share of a country’s total power generation and derived emissions. By this means, unit electrical consumption by the U.S. cement industry (see discussion and table 5 in part I) of 151 kWh/t portland cement (144 kWh/t total cement)⁴ in 2000 would correspond to about 0.07 to 0.08 t CO₂/t cement; that is, total CO₂ emissions including purchased electricity are about 7% to 8% more than the unit CO₂ emissions levels shown in table 1 totaled just for calcination and combustion.

Table 3 is a summary of emissions and other data for cement manufacture.

Table 2 Regional tabulation of hydraulic cement production and carbon dioxide emissions potential

Region	Cement production (Mt)*	Percent of world production	Emissions potential (Mt CO ₂ /yr) [†]
United States	89.5	5.5	80.2
Canada	12.6	0.8	14.4
Mexico	31.7	1.9	43.3
Central America and Caribbean	12.8	0.8	13.0
South America	75.3	4.6	91.5
Western Europe	189.9	11.6	191.0
Eastern Europe	42.1	2.6	56.7
Former Soviet Union	46.9	2.9	105.3
Middle East	103.6	6.3	125.7
Africa	71.8	4.4	78.7
Asia and Pacific	963.6	58.8	940.5
Total world	1,639.8	100.0	1,740.3

Source: USBM (U.S. Bureau of Mines) and USGS minerals yearbooks (cement); Cembureau (1996) and other sources (clinker capacities).

* Data are for 2000.

† Data are based on clinker capacities variously for the years 1996–2000.



Figure 2 World distribution of annual cement industry CO₂ emissions potential based on country clinker capacities in the mid-1990s. By far, the greatest emissions potential is in Asia. Source: Based on data in Cembureau (1996).

Environmental Benefits and the Industrial Ecology of Cement Manufacture

Although generally not widely discussed, there are environmental benefits to cement manufacturing and the use of cement or concrete. One of the general benefits claimed by the cement and concrete industries is that concrete is “better” than competing construction materi-

als. In terms of overall construction tonnage equivalence, it is difficult to quantitatively compare emissions levels (or other environmental effects) of cement with those of its potential substitutes, and most of these materials do not substitute for cement or concrete on a 1:1 mass basis; defining the appropriate basis of comparison (i.e., the functional unit) is a challenge fa-

Table 3 Salient data for cement and clinker manufacture

Item	Approximate quantity per metric ton		
	Clinker	Cement ¹	Units
Raw materials			
Nonfuel ²	1.7 ³	1.8 ⁴	Tons
Fuel	0.2	NA	Ton
Energy emissions	4.7 ⁵	4.9 ⁶	Million British thermal units ⁷
Cement kiln dust	0.2 ⁸	NA	Ton
SOx	0.5–1	NA	Kilograms
NOx	1–4	NA	Kilograms
Carbon dioxide			
From calcination	0.51 ⁹	0.49	Ton
From combustion	0.43 ¹⁰	0.41	Ton
Dioxins ¹¹	300–3,000	NA	Nanograms TEQ ¹²

Note: NA = not applicable.

¹ Portland cement.

² Excluding water (used for wet kiln slurry).

³ About 1.5 t of this is limestone or equivalent.

⁴ Assumes 5% gypsum.

⁵ Gross heat basis, average for U.S. industry in 2000. Excludes electricity. Most plants are in the range of 3 to 6 million Btu/ton clinker.

⁶ Includes electricity.

⁷ 1 million Btu = 1.055 GJ.

⁸ Total generation, not fugitive emissions.

⁹ Assumes CaO in clinker of 65% and 100% derivation from carbonate.

¹⁰ Gross heat basis; U.S. average in 2000. Most plants are in the range of 0.4 to 0.6 ton/ton clinker.

¹¹ Dioxins, furans, and similar chemicals.

¹² Nanograms toxic mass equivalents relative to the dioxin TCDD.

miliar to life-cycle assessment (LCA) practitioners. A few points in this regard relative to steel and wood are made here.

Structural steel is a common competitor with concrete for projects such as office buildings and bridges. In terms of a comparison of GHG emissions, Price and colleagues (1999) cited CO₂ emissions for a few countries' steel industries in the range of 1.2 to 3.6 t CO₂/t steel overall, but their data include steel derived from both ores and scrap, making comparisons complicated.⁵ Here it is not important to provide exact CO₂ emissions or emissions range for iron or steel but to note that steel derived from iron ores via a blast furnace has unit CO₂ emissions that are higher than those for cement.

Another environmental comparison is the respective energy requirements of manufacture. Freuhan and colleagues (2000) provided a num-

ber of theoretical energy requirements for iron- and steelmaking for several selected conditions and compared them to actual energy requirements (which are higher). Using hot metal (crude iron) from a blast furnace, primary steel made in a basic oxygen steel furnace has actual energy requirements of about 24 to 26 GJ/t steel, of which 13 to 14 GJ/t is the energy required to produce the hot metal charge (i.e., the blast-furnace component). Steel from an electric arc furnace (EAF) requires 2.1 to 2.4 GJ/t. Price and colleagues (1999) provided an energy comparison between cement and steel manufacture for a number of countries. They showed energy requirements for primary steel (made from iron produced in a blast furnace) of about 23 to 41 GJ/t steel, whereas steel from scrap feed (EAF) only requires about 5.5 GJ/t; the latter is comparable to the energy requirements to make ce-

ment (see part I). Their energy requirements (4.0 to 5.8 GJ/t) for cement are comparable to the range we showed for the U.S. industry in part I.

Glover and colleagues (2002) compared the embodied energy in concrete, steel, and wood used in house construction and showed that the highest embodied energy is for steel and the lowest is for wood; their study also showed the great sensitivity of the results to the many variables in the analysis. Their energy values for the cement in concrete are at the high end of the range that we showed in part I.

In addition to embodied energy, an environmental comparison of cement (concrete) and wood (mainly for houses) is of interest, even in just qualitative generalizations, because the cement industry is actively trying to capture market share in housing construction (walls and roofing, not just the almost ubiquitous concrete foundations). Concrete buildings are more durable than wooden structures in terms of fire resistance and the strength needed for multifloor construction (but concrete's advantages in terms of the seismic resistance of houses and similarly sized structures are less clear and depend on many construction variables). Concrete is "abundant" (13 to 15 Gt/yr worldwide manufacture or consumption), as are its component mineral resources (but they are nonrenewable). Wood, particularly softwood, is a renewable resource, but its availability is constrained by severe deforestation and/or slow growth rates in some parts of the world and it is naturally scarce in other areas. Wood is considered to be more or less CO₂ neutral because its atmospherically derived carbon is modern (relative to fossil fuels) and, if burned to completion, returns all the carbon to the atmosphere (as CO₂). Börjesson and Gustavsson (2000) presented a GHG comparison of a wood- versus concrete-framed house in a materials and energy flow study, which additionally well illustrates the potential complexity of a quantitative comparison of dissimilar construction materials.⁶

Alternative Fuels for Cement Manufacture

Apart from possible advantages in using cement (concrete) instead of competing construction materials, cement manufacture itself has

environmental benefits. Although the practice varies among individual plants, cement manufacture can consume significant quantities of industrial by-products as fuel (table 1) and nonfuel raw materials (table 3 in part I). This consumption reflects the combination of long residence times and high temperatures in clinker kilns that ensures the complete breakdown of the raw materials into their component oxides and the recombination of the oxides into the clinker minerals. The ability to consume large quantities of waste products is what makes cement manufacture attractive from an industrial ecology viewpoint.

Cement kilns, after appropriate modifications, are particularly adept at burning alternative or waste fuels, which can be almost anything, solid or fluid, that can combust,⁷ including used motor vehicle tires, municipal biowastes, and hazardous (but not radioactive) wastes; Degré (1998) and Jenkins and Mather (1997) provide lengthy lists of these materials.⁸ Waste fuel burning in a cement kiln has several advantages for the cement plant and for the environment and society in general. Consumption of waste fuels reduces a plant's consumption of conventional fossil fuels. In reality, because of impurities in waste fuels, the very large dimensions of kilns, a choice of introduction points for the waste fuels (main burner, midkiln, upper end), and certain technical complications that waste fuels may impose on kiln operations, exact heat equivalence in fuel replacement may not always be possible. Nonetheless, the use of waste fuels in cement kilns allows the displaced fossil fuels to be utilized by other industries that lack fuel flexibility. Waste fuels cost less than conventional fuels on a heat equivalence basis (Boarder 1997; Gilling 1999) and generally are used for the sake of economy; in some countries, especially the United States, the cement plants are in fact paid to take the wastes. According to plant personnel, in some cases, such revenues can completely offset the remaining conventional fuel costs (i.e., zero net fuel costs) or even exceed them and thus function as a source of net income for the plant. Lower fuel costs from waste fuels are of especial benefit to wet and long dry process plants, as both are older technologies having relatively high unit energy requirements (see part I). The

large dimensions of these older technology kilns, and long material residence times associated with them, contribute to their ability to efficiently burn waste materials.

A clinker kiln converts a worthless waste material, or one that could otherwise incur substantial disposal or storage costs (especially for hazardous wastes), through its use as a fuel into a product typically worth \$50 to \$100 or more per ton as finished cement; by comparison, a commercial waste incinerator burns fossil fuels to dispose of the wastes and may produce a modest amount of electricity. Because the waste fuel (heat) component of total fuels is generally limited to 30% or less (some plants are permitted to burn a higher component even where they do not actually do so), cement kilns can make use of fuels with lower unit heat values than could be tolerated by most other industrial furnaces.

Burning waste fuels can convey additional advantages in terms of reduced emissions (Mishulovich 2003). For example, some hydrocarbon-containing waste fuels have a higher hydrogen to carbon ratio than conventional fuels and thus yield less CO₂ when burned. Incorporating fuels that induce reducing conditions can reduce NO_x emissions from kilns, as noted earlier. At least one plant in the United States burns a proportion of semidry municipal sewage ("biosolids") solely for NO_x control; the material is energy neutral (Mayfield and Biggs 1997; Kahn 1998). Some forms of biomass fuel such as sawdust may generate CO₂ that might be subtractable from "regular" process CO₂ for a plant's environmental accounting purposes where biomass is considered to be CO₂ neutral.

In terms of community relations, burning of waste fuels, assuming that it is fully permitted, saves the community alternative disposal or storage costs, and the cement plant could be considered a safer destination for the wastes than certain disposal alternatives. A community might only see this as an advantage if the waste fuels are generated locally, however. In cases where kilns have been adapted to take whole (as opposed to shredded) tires, the plant may allow the general public to individually deliver their worn-out tires directly to the facility, a practice that may be more convenient and cheaper for the public than disposal at the local landfill and, for

the landfill operator, reduces the size, and hence fire risk, of large tire accumulations.

For a cement company, a decision to burn waste fuels involves many factors. A potentially lengthy and expensive environmental permitting process may be required, which may involve public input. The economic analysis of the decision considers the suitability of the existing kiln technology at the plant or which could be installed (e.g., modification to an existing kiln or construction of a new kiln), the straight cost savings or other benefits, and the cost of complying with environmental restrictions (if any) on the fuel (such as storage and handling costs, emissions monitoring costs, penalties for emissions violations, and whether burning of waste fuels would force emissions monitoring and limits for plants hitherto exempt from such requirements).

Fuel-handling considerations include physically moving the material about, any costs to prepare the fuels (crushing, screening, blending, quality control, etc.), safety issues (flammability, toxicity), and possibly aesthetic (odor) considerations. A key consideration, given the fact that the plant would prefer a consistent waste fuel mix, is whether there is a sufficient and reliable supply of the waste(s) available within a reasonable transportation (cost) distance. Thus, for many wastes (especially tires), a plant needs to be fairly close to a large metropolitan area, and for most nonhazardous wastes, the appropriate source industry or other accumulation site should be reasonably close to the cement plant. Hazardous wastes generally involve high handling, storage, and transportation costs; these costs can be relatively insensitive to distance.

A related consideration is the cost and logistics of collecting the waste fuels even from a convenient distance. Commonly, either the producers deliver to the cement plants, or private contractors are engaged for this purpose. Especially with liquid and liquid hazardous wastes, there may exist (or the cement company may help form) a company specifically charged with collecting the materials, blending them to an acceptable degree of consistent quality, storing the individual materials and blended fuel mix, and delivering it to the cement plant as required. Such fuel companies offer operational advantages to the cement plant, are a practical way for

the cement plant to tap into an otherwise inconvenient diversity of fuel sources, and may reduce the regulatory burdens of using the fuels on the cement company itself. Likewise, such a fuel company might provide an entire diverse industrial complex with a convenient means of disposing of part or all of its wastes (Vigon 2002).

A disadvantage to certain waste fuels is their potential to induce or increase kiln emissions (Gossman 1993). Certain hazardous wastes, for example, may increase the chances of a plant emitting higher amounts of dioxins and furans (U.S. EPA 2000), as noted earlier. Highly heterogeneous fuels may require extensive preparation prior to burning to screen out or sufficiently dilute components such as toxic metals (e.g., nickel, chromium) and to blend to ensure consistent heat contents and ease of burning.

Local or national building codes and project specifications commonly cite cement types or performance specifications that indirectly may not allow for burning waste fuels, or may limit the type(s) burned, because of the potential for changing the trace-element composition of the cement (or concrete) and, potentially, its performance. For example, a project to build a concrete-lined municipal water reservoir could indirectly discourage the use of waste fuels in cement manufacture (for this project) that would increase the cement's content of potentially leachable heavy metals (see the particulates discussion above). Wastes that might increase a cement's alkali content could preclude that cement's use for projects in areas where alkali-silica reactions might become a problem.

Transportation, storage and handling, and burning of, in particular, hazardous wastes may prove uneconomical or bothersome for the cement plant and could invite lawsuits and generally deteriorating public relations (it is unlikely that a cement company can count on the automatic public approval of proposed waste fuel burning). Regarding the latter, companies seeking to avoid public opposition to proposed waste fuel burning often provide local communities with factual data relating to the project and solicit public commentary well in advance of the proposed startup date and, commonly, in advance of the official permitting process.

Alternative Raw Materials

Clinker manufacture can make use of a wide variety of raw materials, most of which are selected on a supplementary basis to make up for chemical deficiencies of the primary limestone feed. As noted in part I, these supplementary materials may, for example, supply nearly all of the alumina or silica, or they may be added as "sweeteners" to boost one oxide or another. Examples of sweeteners include high-purity limestone, or calcite itself, to boost the lime content; silica sand, silica fume, or diatomite to boost silica; alumina or aluminum dross to supply alumina; or millscale for iron. Apart from the oxide content of a proposed alternative material, plant operators consider the material's thermochemical accessibility (Mishulovich 2003). For example, silica sand is a commonly used supplementary silica source, yet it is hard to grind (thus increasing electricity consumption) and the component quartz (SiO_2) requires high temperatures and a long exposure in the kiln to activate the silica. If available, a more easily grindable and/or more reactive silica source might be preferable; examples include diatomite, ferrous slag, or a material containing amorphous silica, such as fly ash.

Although many of the supplementary materials are mined products, any number of other materials, including wastes, are potentially suitable, especially if they are of low cost. Some materials contribute both oxides and energy, for example, deinking sludge from recycling and shredder fines from paper plants. Some of these materials offer process advantages; for example, certain aluminum smelter by-products (pot liners, catalysts) not only contribute alumina, but also sufficient fluorine or calcium fluoride to act as a flux (Mishulovich 2003). Fly ash and bottom ash from coal-fired power plants, as well as ferrous slags, are consumed in large quantities (see below and table 3 in part I) as supplementary silica, alumina, and lime sources for clinker. Noncarbonate lime sources are of particular interest in an environmental context because they reduce the calcination CO_2 component of the process; this is discussed in more detail later. The criteria for selecting waste materials for the kiln include appropriate chemistry (composition and

reactivity), resulting cement quality, material availability, material costs (base, transportation, storage, handling, and preparation), regulatory compliance and general environmental impacts (similar to those for waste fuels, as discussed above), and public and government acceptance.

As discussed in part I, pozzolans and similar cementitious extender materials may be added to produce blended cements and masonry cements. Waste products used as extenders include some types of fly ash, GGBFS, burned rice husk ash, CKD, burned clays (“metakaolin”), and silica fume. In regions or countries where cement specifications or building codes allow the practice (without renaming the product), extenders may be incorporated as a minor bulking agent for portland cements; a common example is the incorporation of 1% to 3% GGBFS introduced (in unground form) in the finish mill as a grinding aid.

Cementitious extenders allow the production of a finished cement with lower clinker content and hence proportionally lower unit equivalent energy and raw materials inputs and emissions outputs. Although blended cements can have lower early strength development, their final strength (measured at 28 days) is generally comparable to straight portland cements. Blended cements generally exhibit a reduced heat of hydration, which is usually, but not always, an advantage. Other advantages to using extenders include improved flowability of concrete during placement and the fact that the hardened concrete generally has lower porosity, reduced lime reactivity (the pozzolans consume the lime released through cement hydration), and increased resistance to other forms of chemical attack, notably by sulfate-rich groundwater. A large literature on cement extenders exists, for example the collected papers in Frohnsdorff (1986) and Malhotra (1989); Detwiler (1996) provided a short overview.

Cementitious extenders are generally added on about a 1:1 clinker (or portland cement) substitution basis. These materials may or may not reduce the cost of making the finished cement, depending mainly on the procurement cost of the extender and whether and to what extent the material needs to be ground. Granulated blast-furnace slag, for example, may be added in

ground form (GGBFS) to cement or concrete or in unground form (as a grinding aid) in the finish mill. Because it is less hydraulically reactive, GGBFS needs to be ground considerably finer than portland cement to make a satisfactory cement extender. Thus, if a plant decided to grind a substantial quantity of slag, it likely would incur higher unit grinding costs and electricity consumption, and the mill apparatus assigned to the slag would have a lower output capacity than if it had been kept on clinker-grinding duty. Some cement plants operating large grinding facilities for GGBFS produce a surplus and sell much or all of this material directly to the concrete industry. Fly ash generally does not require grinding, and silica fume particles are already very much finer than cement.

Industrial Symbiosis Involving Cement

In an industrial ecology context, cement plants are of interest not only where they simply consume waste materials of other industries, but even more so to the degree that a cement plant may be directly tied to a plant of a different industry or vice versa (Nemerow 1995). Cement plant materials acquisition interactions can take several forms. The cement plant could simply consume wastes of other plants (as discussed above), with every possibility of changing waste suppliers or types as conditions warrant. A variation on this theme is where a parent company seeks to link subsidiary cement plants with subsidiary plants manufacturing other products.

Of greater industrial ecology interest is where a cement plant is constructed to take advantage of the availability of wastes or by-products; the location might be entirely or partially governed by the waste source, depending on what the waste contributes and the economics of its transportation. An existing or proposed cement plant might be modified to take advantage of waste availability. Similarly, a waste-generating industrial facility could be sited to take advantage of proximity to a cement plant, or a factory might alter the composition or physical form of its waste stream to make it attractive for use in cement manufacture. Both the industrial plant and the cement plant might enter into partnership to form a waste-handling company. More than one

facility can be involved in these relationships, and some might be nonindustrial operations (a farm, for example). In any industrial relationship, sound economic reasons may dictate subsequent switches to other raw materials and sources; cement plants are remarkably flexible in what they can consume and would be well poised to take advantage of new industries in the market area or to survive the cutoff or shortages of materials being used.

A comprehensive review of the industrial ecology of cement was given by Vigon (2002), but a few examples here would suffice to illustrate some of the linkages that make cement an interesting industry from an industrial ecology standpoint. A well-known case is that of Texas Industries, which operates a cement plant in Texas adjacent to the EAF steel plant of a subsidiary company. The EAF steel slag had for some time been marketed as a road aggregate selling for a few dollars per t, a typical price for such material. The company's research into alternative uses resulted in the patenting of the CemStar process, which introduces steel slag into the cement kiln raw mix as a source of CaO and SiO₂. Use of steel slag was well known in the cement industry but traditionally not favored because of the difficulty in crushing it. The key discovery behind CemStar was that the material did not, in fact, need to be crushed to finer than about 5 cm diameter to melt easily in the kiln. Once introduced, steel slag acts as a flux (indeed, it is exothermic) and provides the important clinker mineral C₂S. Its use as a substitute for some of the limestone feed yields clinker in about a 1:1 tonnage ratio to the slag input, increases the throughput of an existing kiln by several percent, and has the added benefit of supplying some or all of the Fe₂O₃ needed to form the C₄AF clinker mineral. Steel slag thus reduces the amounts of limestone and fuel required to produce clinker and allows for reduced emissions of both CO₂ and NO_x (Perkins 2000; Forward and Mangan 1999).

One of the most popular cementitious extenders is GGBFS. This material differs from ordinary (air-cooled) blast-furnace slag in that the granulated slag has been cooled by quenching through a water stream. This quenching forms sand-sized particles of glass. Unground, granu-

lated blast-furnace slag finds a modest market among cement producers as a grinding aid in cement manufacture. Finely ground into GGBFS, it is used to make blended cements or is sold to concrete manufacturers as a partial portland cement substitute. In the United States, only about 0.3 Mt/yr of granulated slag is consumed by the cement industry itself, and of this, about two-thirds is as a grinding aid and the rest (as GGBFS) within blended cement (van Oss 2002). But a substantially larger market for GGBFS exists within the concrete industry. Although published data for the United States are incomplete, the size of this growing market would probably be at least 3 Mt/yr overall, based on the 2.3 Mt reported GGBFS sales in 2001 (Prusinski 2002) for member companies of the newly formed Slag Cement Association, capacities of granulated slag-grinding plants, and U.S. Geological Survey (USGS) data on the production and imports of slag. The number of operating blast furnaces in the United States is in major decline, however, and most of them just produce air-cooled slag for aggregate; accordingly, U.S. production of granulated slag is currently inadequate to meet demand. Some of the excess demand has been met by imports of unground material, which is then ground at U.S. facilities. To boost U.S. production of GGBFS, some cement companies have found it worthwhile to enter into arrangements with steel companies wherein granulation cooling is installed at the blast furnaces and the cement companies construct the requisite grinding plants; two such granulators were installed in 2001 (Holcim 2002; Cement Americas 2001). In this way, the previous air-cooled slag by-product, worth a few dollars per t as an aggregate, is converted to a GGBFS co-product, worth about \$30 to \$40 per t when sold directly, or is incorporated within a blended cement selling for substantially more. This cooling conversion is not inexpensive; the granulation equipment costs several million dollars and a grinding plant about \$40 million or more.

Coal-fired electric power utilities have long supplied fly ash and bottom ash to the cement industry for use as a raw feed and fly ash to both the cement industry and, especially, concrete industry for use as a pozzolan. Power plants are under pressure to reduce NO_x emissions, and one

way to do this is to lower combustion temperatures (which reduces thermal NO_x). A disadvantage of this reduction is that it often results in a less complete combustion of fuels, which causes an increase in the carbon content of the fly ash waste product. This additional carbon makes the fly ash unsuitable for direct pozzolan use in blended cement and many concrete applications. To remedy this problem, the fly ash can be washed, but it adds to the cost of the ash. Carbon in fly ash or other ashes is not a problem, however, when the ash is used as a raw material for cement kilns.

Another ash that has potential use as raw feed for cement kilns is that from municipal waste incinerators. The pioneering application of this material has been in Japan. The concern in using this secondary waste is that it can contain high and variable levels of toxic metals (Suto and Kaneko 2000).

Another linkage between electrical utilities and cement plants is that the SO_x-scrubbing apparatus of the power plant commonly uses limestone or lime as a reagent. As noted in the SO_x discussion, synthetic gypsum is thereby formed in the scrubber (SO_x scrubbers at cement plants can also make this mineral). This synthetic gypsum, if sufficiently clean, has market applications including substitution for natural gypsum in cement manufacture. Although consumption data are incomplete for synthetic gypsum (it is commonly reported in with natural gypsum on USGS annual cement plant surveys), in 2000 at least 5% of the gypsum consumed by the U.S. cement industry was obtained from SO_x scrubbers.

One of the better examples of a cement plant being constructed to take advantage of an existing by-product is that of the Cajati (formerly the Jacupiranga) mine in Brazil. The mine exploits an apatite [Ca₅(PO₄)₃F]-bearing carbonatite (an igneous carbonate complex) to supply phosphate for an adjacent fertilizer plant. The mine's processing plant has a waste stream of carbonatite rock, composed of calcite and dolomite. Owing to the low grade of the phosphate reserves, a cement plant was constructed near the mine in the early 1970s to use the calcite wastes and so provide an additional revenue stream to the mine complex; the cement plant is now owned by another company. Because portland cement manufacture cannot tolerate much MgO in the raw

materials (part I), to date both mining and ore processing have had to keep the calcite adequately segregated from the dolomite, which contains significant MgO (Alves 2002). Efforts are underway, however, to utilize some of the dolomitic material as a cement feed by segregating low MgO dolomitic material (blendable into the raw feed in low proportions) from that of higher MgO content. Cajati thus also illustrates a situation whereby a waste-generating entity can modify its operating procedures to favor the waste consumer. The Cajati cement plant is also being converted over to the partial burning of waste fuels (Vigon 2002).

The Geopolitics and Mitigation of Emissions from Cement Manufacture

As noted earlier, emissions from cement manufacture are relatively small compared with other industrial or economic sectors, with the significant exceptions of CKD (the effects of which are local) and CO₂. But even for CO₂, emissions from cement manufacture are small compared with those from the combustion of fuels by power plants and motor vehicles. Thus, it is fair to question why there is concern about CO₂ emissions from cement manufacture and why much of that concern is expressed by the cement industry itself. Part of the concern stems simply from the fact that the issue of global warming has been widely publicized, as has the role of CO₂ therein. In addition, the overwhelmingly dominant CO₂ emissions from combustion have been segregated by many major reporting agencies, especially the IPCC, from so-called industrial emissions. Under this segregation, cement manufacture stands out for scrutiny as one of the two largest industrial emitters of CO₂. The cement industry fears that it may be negatively impacted by CO₂ reduction policies resulting from the Kyoto Protocol or other emissions-reducing treaties in the future. Here the worry is that efforts to force reductions by the sectors emitting considerably larger quantities of CO₂ may impact the cement industry disproportionately to its more modest role (about 5% of total anthropogenic emissions).

One of the reduction strategies particularly feared by the cement industry is the imposition of a large carbon tax on fossil fuels throughout

the economy. Depending on the size and stipulations of the tax, a significant increase in production costs for clinker could be incurred. Some of the proposals are on the order of \$50/t carbon or a proportionate sum expressed per t of fuel (Humphreys and Mahasenan 2002; Nisbet 1996). Such a high tax on fuels would increase fossil fuel costs to a cement plant by approximately 100% or typically about \$12/t clinker. Although data on production costs are notoriously scarce, unreliable, and often proprietary, costs in the United States appear to be in the range of \$27/t to \$44/t (cement), and for some modern plants in developing countries, as low as \$15/t. Whatever the case, a \$12/t production cost increase would be crippling for most plants because only rarely can large production cost increases be passed along to the customers given the highly competitive nature of the cement market in many countries or regions. Within individual U.S. market regions, for example, proprietary USGS data show that it is uncommon to find cement prices among producers varying by more than \$1/t to \$2/t. Some carbon tax proposals, however, apply only for emissions levels above a certain amount, and still others allow for emissions trading (Hoening and Schneider 2002).

Depending on the actual carbon tax, it is likely that some of the older, least-efficient plants would become uneconomic and would be closed, whereas for other plants the tax would certainly be an added inducement (beyond those of the normal market) to seek opportunities to reduce fuel consumption levels or costs, such as by switching partially to waste fuels. Not all CO₂ reduction strategies by governments would necessarily involve carbon taxes: Tax rebates and reductions, for example, could be offered to companies to reduce emissions.

Because only a few countries would initially be bound to the Kyoto Protocol, cement producers in countries not so bound would be less likely to incur added production costs related to emissions reductions, and so, if they are exporters, they would be at a competitive advantage to producers in signatory (developed) countries that import significant quantities of cement. The U.S. cement market currently has an import dependence of more than 20% (van Oss 2002) and absorbs approximately 25% of the total world cement trade; the domestic cement industry would

be vulnerable to international production cost differentials resulting from the unequal application of emissions reduction strategies, especially carbon taxes.

In the case of unequal application of large, Kyoto Protocol–related, carbon taxes, Nisbet (1996) concluded that the effects on the U.S. cement industry would be severe; competition from cheap imports would likely force the closure, at a minimum, of smaller, less fuel-efficient cement plants (especially wet-process plants). Further, the resulting production shortfalls might even encourage the establishment of large export-oriented plants in nearby, nonsignatory countries. Nisbet's study, however, did not consider the mitigative effects of protective tariffs that might be imposed on imports that are not carbon taxed, nor the fact that transportation costs might shield some otherwise vulnerable producers from import competition. This latter protection, however, might not be as widespread as supposed, because cement can, in fact, be economically transported over long distances by train and barge, and large tonnages (of both domestic and imported cement) are so moved in the United States (van Oss 2002).

In the face of import (or general) competition, cement companies can, to protect their market share, instigate business strategies such as vertical integration, the purchase of control of import terminals, and growth through the purchase of other cement companies, particularly those overseas. Although the potential replacement of older technology production capacity in the United States by newer, more cost-efficient, capacity elsewhere might be viewed as beneficial from a global standpoint, it would only be so if the replacement plants had lower net emissions; a mere transfer of emissions sources from one location to another would not directly benefit the global climate.

Emissions Reduction Strategies

Many cement companies are trying to reduce fuel consumption and associated CO₂ emissions for purely economic reasons, but some of the actions are also seen as an essential business strategy for the future. Notable in this regard and in terms of a shift in corporate philosophy is the recently released report *Toward a Sustainable Cement Industry* (Battelle 2002) and a set of asso-

ciated substudies (e.g., Vigon 2002), sponsored by ten of the world's largest cement companies. These studies have identified many issues facing the cement industry and have suggested ways in which the industry can improve its specific performances (operational practices, emissions, profitability), operate using concepts from industrial ecology, and, through these improvements, receive more widespread and favorable public exposure. The study also encourages governments to help their country's cement industries employ strategies based on the principles of industrial ecology.

A number of emission reduction strategies are available to the cement industry. Given its chemistry, the calcination of limestone emits CO_2 , but the partial substitution of other CaO sources reduces the quantities of limestone needed. Alternative CaO sources are being sought, the key requirement being that they not demand even more energy for CaO access than is needed for the calcination of limestone. One promising material, discussed above, is steel slag (CemStar), which not only provides CaO without calcination but also plays a fluxing role (i.e., reduces the energy and hence fuel requirements for the sintering reaction in clinker manufacture). A number of fluxes are available, such as fluorspar (Lea 1970), but these may have more limited application.

Similar to fluxes would be materials that, even if they do not change the temperature requirements of clinker formation, are more thermodynamically accessible, that is, they require less residence time in the kiln. An example of this would be the substitution of reactive slag for silica sand (Mishulovich 2003). A decrease in residence time allows for a higher kiln throughput capacity for the same fuel burned and thus lowers the unit heat consumption and associated combustion CO_2 and NO_x . Energy savings can also be achieved through choosing materials that require less preparation (such as crushing) prior to burning.

Reduction of CO_2 can also be accomplished by upgrading plants to more efficient technologies and by switching to lower-carbon-content fuels. Many technological changes also reduce emissions of other pollutants. Regarding technological changes, strategies can include the

physical conversion of wet kilns to dry technology; the upgrade of dry kilns and precalciner systems to more efficient versions; the replacement of wet kilns and VSKs with entirely new, modern, preheater-precalciner dry kilns; the optimization of kiln burner designs; the upgrade of clinker coolers; and the installation of computerized control technology (expert systems). Good reviews of these options include those published by Hendriks and colleagues (1998) and especially by Martin and colleagues (1999). These upgrades generally reduce unit energy consumption levels, as discussed in part I. It should be noted, however, that many of these options are very expensive, commonly costing well in excess of \$10 million, and might not be economically feasible for some small, older plants or plants lacking sufficient limestone reserves (approximately 50 years' worth). The limestone reserve picture is important, because the projects are generally seen as having very long payback periods and price increases for cement cannot always easily be passed on to customers. Switching to lower carbon fuels, such as from coal to natural gas, is technically feasible at many plants, but it can involve problems of fuel cost and availability, may increase thermal NO_x output, and may require technical alterations to the kiln line.

Another CO_2 reduction strategy would be to allow the use (in some applications) of lower-quality portland or similar cements. One of the ways to do this is by reducing the clinkering temperature, either directly or effectively by increasing material throughput speed. This would affect the process chemistry, resulting in less C_3S and more C_2S in the clinker and thus resulting in reduced early strength. This could result in a cement that is satisfactory for some applications where early strength is not essential. Another, but indirect, strategy, and one that is in use in Europe, would be to grind the cement less finely, thereby reducing the unit electricity consumption. A less finely ground cement would be less reactive (lower overall surface area) and would thus tend to develop strength more slowly than a more finely ground cement. Yet another strategy is using a bulked-out cement, such as portland-limestone cement, as discussed below.

In the long run, there is a limit to how much CO_2 can be reduced through technical or oper-

ational improvements at the plant. As noted by Ruth and colleagues (2000), the unit energy savings through efficiency improvements, although significant (about 10%), is much smaller than those achievable by incorporation of by-product extenders—especially those not requiring additional heat inputs to manufacture—in the finished cement (15% to 30% or more).

Extenders can be cementitious (i.e., blended cements as discussed earlier) or inert or relatively so. The most common relatively inert extender is ground limestone. This can be added in small proportions (about 3% or so) without significantly altering the properties of the portland cement; this is as yet not allowed in the United States. Ground limestone can also be added in larger proportions (6% to 35%) to make portland-limestone cement; this has captured significant market share in some countries in Europe and elsewhere (Moir 2003).

Extenders reduce the clinker component of the cement and allow a plant to increase production capacity without the expense of actually upgrading or adding new equipment. Blended cements are in common use in many parts of the world, but, as noted in many studies, there is much remaining growth potential worldwide, notably in the United States and China (e.g., Detwiler 1996; Soule et al. 2002). The usual substitution ratio is 1:1, that is, the extender displaces an equal weight of portland cement. A few extenders (such as silica fume) may displace more than their weight of portland cement. Blended cements are rarely sold with more than about 30% extenders, although concrete manufacturers may themselves mix in up to 50% or more (some projects up to 75% to 80%) as a partial substitute for portland cement. Extenders may or may not be locally available or abundant. Of the common extenders, fly ash is available in many countries and could be utilized more, but such use, as noted earlier, could be constrained if NO_x restrictions on power plants become widespread, resulting in a high-carbon product. The use of GGBFS is subject to fairly severe availability constraints, as discussed earlier. A potential growth area in extenders is the use of CKD; such a use would allow the cement plant the added benefit of being the source of the extender. The use of ground limestone extenders to make portland-lime cements

has a large potential for growth, but they generally exhibit lower long-term strength than straight portland cements or blended cements (Moir 2003).

Currently, the United States is the world's third largest cement market; about 1% of cement sales are of blended cements, and, on average, extenders make up at least 10% of the "cement" in U.S. concrete (van Oss 2002). A 10% extender substitution in concrete means, for the United States, a current pozzolan consumption on the order of 11 to 15 Mt, based on an annual plus blended portland cement consumption of about 111 Mt. The true cement consumption in the country, therefore, is about 10% higher than USGS reported sales data suggest. The volume of pozzolons consumed also implies that if the economics of cement and concrete shifted to favor the concrete companies purchasing blended cements for 100% of their extender needs, then the cement companies could significantly increase their effective cement capacities by providing these cements. If building codes were altered to allow the use of more blended cements or, similarly, the official cement specifications were changed from the current composition basis (e.g., type V portland cement) to a performance basis (e.g., sulfate-resisting cement), then the market for blended cements or equivalent concretes in the United States could increase dramatically, with a proportional decrease in average clinker factors and unit emissions of finished cements. In a growing cement market, a shift to blended cements would allow growth without increased clinker output, assuming that the extra demand would not be met simply through imports.

Beyond the estimated 10% reduction in CO₂ emissions possible by technical upgrades at plants, the 10% to 15% from noncarbonate CaO substitution in raw materials, and the 30% achievable through blending (not all of these savings would be additive), further reduction of CO₂ emissions from cement manufacturing would require more extreme developments in technology; the widespread adoption of radically different, more efficient, technology; the introduction of CO₂ sequestration technologies (as yet, the economics of this do not appear attractive [Hendriks et al. 1998]); or a shift to different,

non-clinker-based, cements. Martin and colleagues (1999) discussed some of the possible new production technologies. It should be noted that given the huge capital investments resident in individual cement plants (kiln lines themselves typically cost \$50 million or more) and the long-lived nature of the equipment, near-term widespread shifts away from rotary kilns are unlikely.

In the long term, significant reductions in emissions may also require the development of entirely new cements for general construction purposes. Both Martin and colleagues (1999) and Uchikawa (2000) discussed several new cements, and there are a number of others, some of which allow blending. An interesting new concept is that of cements based on activated magnesia (MgO) derived from calcination of magnesite (MgCO₃) or dolomite [CaMg(CO₃)₂]. Magnesite calcination occurs at a substantially lower temperature than does that of calcite, which saves energy. No clinker is made, but the magnesia is blended with a small amount of portland cement (for additional strength) and pozzolan (to tie up the lime from portland cement hydration), and the magnesia develops strength, ultimately, through the carbonation of the material (or, rather, its hydroxide) back to magnesite (TecEco 2002). Carbonation of activated magnesia is faster and more pervasive than is the case for lime, but remains a diffusive process, and the reaction rate thus slows with time. Thus, the favored uses of an activated magnesia cement would be in high-surface-area applications, such as building blocks. The relatively high rate of carbonation of magnesia could allow for the reabsorption of a significant proportion of the calcination CO₂ evolved in the cement's manufacture.

A final approach to reducing the overall environmental impacts of cement manufacture is to develop stronger cements and more durable concretes, either of which, if not overly expensive, would allow for less material use for the same application. One approach to increased concrete durability is through the introduction into the concrete mix of so-called engineered cementitious composites (ECCs), such as fibers that impart much of the tensile strength currently contributed by steel reinforcing bars (Li 2002). Among other attributes of ECC concretes, the

elimination of rebar in concrete could dramatically reduce concrete failure owing to rebar corrosion, a very common problem with bridges and similar structures exposed to deicing salts.

Overall and per capita, annual cement and concrete production and consumption are likely to increase steadily; for the world overall per capita production of concrete (and mortars) already exceeds 2 t per year. As indicated in part I (figures 1 and 2) and in figure 2 and table 2 of this current article, the developing world has the bulk of current cement output and capacity and will likely experience the greatest growth in both. Asia currently has more than 50% of world production; China itself has approximately one-third of the total world cement output (van Oss 2002) and capacity, spread among several thousand cement plants.

The size and growth of the industry makes the reduction of its environmental impacts very important. The cement industry is presently highly consolidated worldwide; estimates vary, but approximately 40% of world production and capacity is controlled by just a dozen international companies. As noted above, ten of these companies have joined forces in investigating industrial ecology strategies and have committed to their implementation. Other companies are likely to follow suit. Industrial symbiosis or industrial ecosystems tend to be thought of in somewhat geographically restrictive terms of industrial complexes, sometimes having a few outlier facilities (Vigon 2002); however, the cement industry, on the corporate level, can expand the concept to a global scale. A single large multinational cement company operates dozens of plants worldwide. Each of these plants is or can be tied into a central information exchange and marketing and credit network. Each plant (and the corporate headquarters) is thus able to draw on the expertise resident in the other plants' personnel and to evaluate numerous technologies, operational practices, and raw materials performances at different plants and scales. This, in effect, is a linkage of at least the informational aspects of multiple local industrial ecosystems, with potential linkages with respect to the movement of some materials. Ultimately, given appropriate international agreements, this globalization may allow for a worldwide system of

environmental charges and credits in the cement industry so that emissions of a less well-performing individual plant might be charged against emissions credits of a lower emissions facility.

In that cement manufacture is a highly materials- and energy-intensive process and has significant associated emissions, the industry can be thought of as highly inefficient. But these very inefficiencies, coupled with the ability to utilize a wide variety and large quantities of waste raw materials and fuels, can be thought of as virtues—a veritable silk purse out of a sow's ear—in that they provide the opportunity and incentive for the cement industry to engage in industrial ecology practices. Indeed, the cement industry may be a better driver of such practices than any other manufacturing industry.

Acknowledgments

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Notes

1. Unless otherwise noted, “ton” refers to metric ton (1 metric ton = 1 Mg [SI] and is about 1.1 short tons).
2. This article does not examine environmental impacts of cement during the use or end-of-life phases of the cement product (i.e., concrete) life cycle.
3. These emissions are described as potential emissions because they are based on clinker capacities rather than actual production.
4. Electrical consumption for 2000 was assigned entirely to portland cement to be consistent with the reporting practice for the 1950–1995 data in table 5 of part I. Electricity consumption is better

expressed in terms of total (including masonry) cement and for this could be further broken out as 131 kWh/t for wet plants and 148 kWh/t for dry plants (table 2 of van Oss 2002).

5. Steel is basically an alloy of iron and a small amount (rarely more than 1% and commonly much less) of carbon and other elements. The iron in steel can be derived from iron ores, scrap (i.e., remelted) steel, or a combination of the two. Blast furnaces in one form or another account for the vast majority (93% in 2000) of world iron production from ores (Fenton 2002); the U.S. fraction in 2000 was 97%. Very simply, a blast furnace strips the oxygen from iron oxide ore (or its sinter) by reducing it at high temperatures with carbon (generally from coke) to form carbon monoxide (CO), which ultimately is oxidized to CO₂ and removes silica and other impurities from the ore by reacting it with a limestone and/or dolomite [(Ca,Mg)CO₃] flux to produce blast furnace slag and CO₂ (from flux calcination). Thus, both ore reduction and slag formation ultimately produce CO₂ in large quantities (see below).

The iron ore, flux, and coke charges or burden to a blast furnace will vary somewhat, depending principally on the chemical composition of the iron ore and whether any ferrous scrap is being added (Bray 1942; USS 1964). Very approximately, for a furnace burden that does not include ferrous scrap, the production of 1 t of crude iron will involve the consumption of 0.5 to 1.0 t of coke as fuel and reductant and 0.2 to 0.5 t of carbonate flux. Except for about 4% carbon remaining in the crude iron, all of the carbon in coke will ultimately become CO₂; for the coke proportion noted above and typical carbon contents therein, the emissions yield would be about 1.6 to 3.2 t CO₂/t crude iron. The IPCC cites default emissions for coke of 3.1 t CO₂/t iron (IPCC 2000). For the carbonate flux, the tonnage range shown would yield calcination emissions (see methodology in Appendix A) of about 0.1 to 0.2 t CO₂/t crude iron (at this level of rounding, limestone and dolomite yield the same emissions levels). Thus, at a minimum, the total unit CO₂ emissions would be about 1.7 t CO₂/t crude iron (again, provided that ferrous scrap was not involved), which is almost double that for clinker or cement as shown earlier. Fruehan and colleagues (2000) listed somewhat lower emissions of 1.45 to 1.56 t CO₂/t crude iron, but their calculations assumed a remaining carbon in the crude iron of 5%.

In the conversion of crude iron to steel, the carbon content will be reduced by oxidation (to CO₂) from about 4% to about 1% or less as noted above, which will yield further emissions of 0.036 t CO₂/t steel for every 1% (absolute) carbon reduction. Steel made from remelted scrap has considerably lower associated emissions.

6. Part of the Börjesson and Gustavsson (2000) study appears flawed by their estimates of the amount of CO₂ capture by the "carbonisation" (carbonation) of hardened concrete. The carbonation reaction is $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ and is a surficial process that very and increasingly slowly diffuses inward and along crack surfaces in the concrete. The authors appear to assume that all of the calcination CO₂ released from the manufacture of cement would be reabsorbed through carbonation, whereas, in fact, the process principally affects free lime released through the hydration of clinker minerals; significant carbonation of the silicate minerals is extremely slow (centuries). It can be shown that the net free lime from clinker hydration is only about one-third of the total CaO contained in the original clinker minerals (having the mineralogical ratio shown in table 2). Accordingly, only about one-third of the calcination CO₂ could be reabsorbed through carbonation if the process went to completion, but this is unlikely on a scale of decades and assumes that none of the free lime has been chemically bound by pozzolans. In a reconnaissance study, Gaijda (2001) provided data that show that, for a 50 year (1950–2000) mass of concrete emplaced in the United States, 50 years' worth of carbonation accounts for (very approximately) only about 2% of the total calcination CO₂ released in the manufacture of the cement in the concrete; as a result of some ambiguous wording, the study appears to claim this amount as being annual absorption, but this would be an incorrect interpretation of the data presented.
7. Most recently it has been proposed that cement kilns burn bonemeal from the carcasses of cows suspected of carrying so-called mad cow disease; (uncontaminated) bonemeal has already been used as fuel for cement kilns in several European countries for some time (ICR 2001).
8. Although a huge variety of waste materials can be burned, a given plant will generally use only a few materials, or a preblended mix of materials (especially common with liquid wastes), to keep the kiln burning conditions optimized and as uniform as possible and so as not to compromise

clinker quality. In this respect, the kiln may be less flexible than municipal incinerators.

9. Vanderborgh and Brodmann (2001) may have been misled by the fact that the IPCC report (IPCC 2000, 3.11, footnote 1) misstated the total output of CKD (itself) as 1.5% to 2.0% of the weight of the clinker; this typographical error was not present in the original draft of the document. The CO₂ contribution from the CKD, however, remains correct in the footnote.
10. USGS "energy" data for cement have been cited in certain reports (e.g., Martin et al. 1999) but in fact were independent energy conversions of the actual USGS data on the types and quantities of fuels, and electricity, consumed.

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Appendix A. Methodology for Calculating CO₂ Emissions from the Calcination Reaction in Clinker Manufacture

Given the large amounts of CO₂ evolved during cement manufacture and the desire to establish national GHG inventories, there has been considerable interest in precisely calculating CO₂ emissions by the cement industry. Essentially all emissions of CO₂ during cement manufacturing are from the manufacture of the clinker intermediate product and is from two pathways: the calcination of calcium carbonate and the combustion of fuels. The methodology to calculate the emissions from calcination is presented here; that for fuel combustion is discussed in Appendix B. Rival methodologies to calculate calcination emissions make use of identical equations (both are based on the basic calcination reaction, $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2\uparrow$) but differ in their approach (back-calculation from clinker or forward calculation from raw materials) and to a slight degree in the emissions factors utilized. For a country-level emissions calculation, the approach taken in this article, data availability favors the back-calculation from clinker approach, although much of the discussion is applicable to a raw materials approach as well. The methodology described here is based on that adopted by the IPCC (1997, 2000).

As discussed in part I (see table 1 of part I, van Oss and Padovani 2002), a typical portland cement clinker has a CaO content of about 65% (the range is 60% to 67%, with most clinkers in the range of 63% to 66%, skewed toward the upper end.) For the calcination CO₂ calculation, the important assumption is made that all of the CaO comes from CaCO₃, regardless of whether the CaCO₃ comes from limestone (the main raw material) or another type of rock. The CaCO₃ source assumption generally introduces only a small (1% to 3%) error on a country scale. On an individual plant basis, however, if it is known that a given plant burns a large quantity of raw materials containing noncarbonate CaO (such as Ca silicates in igneous rocks or in slags and ashes), then an adjustment for this source should be made in the CO₂ calculation. Another assumption is that all of the CO₂ comes from

CaCO_3 and not from other carbonates, such as those of magnesium (see below), iron, or manganese; the error in this assumption is small unless one knows that these other carbonates are present in the raw materials in significant quantities.

In the calcination equation given above, the CaO fraction is 56.03% of the original weight of the CaCO_3 and the CO_2 fraction is 43.97%. Accordingly, the weight (X) of CaCO_3 required to yield 0.65 ton CaO in 1 ton of clinker (i.e., 65% CaO) would be $X = 0.65 \text{ ton} / (0.5603) = 1.1601$ tons (unrounded). This weight of CaCO_3 yields CO_2 in the amount of $1.1601 \text{ ton CaCO}_3 (0.4397) = 0.5101$ ton CO_2 (unrounded) or 0.51 ton CO_2 (rounded).

By comparison, 1 ton of a 60% CaO clinker would back-calculate to 0.47 ton (rounded) of calcination CO_2 , and for a 67% CaO clinker, the CO_2 release would be 0.53 ton. The ratio 0.51 ton CO_2 /ton clinker (of 65% CaO) was adopted as the default calcination emissions factor by the IPCC (2000). Given imprecisions in the reported weights and chemical specifications of clinker produced, in the assumptions regarding the derivation of oxides as noted above, and in the inclusion of a CKD "correction" factor (see below), the use of the 0.51 ton calcination CO_2 /ton clinker emissions factor yields a calcination CO_2 emissions estimate expected to be accurate to within 5% to 10% of actual emissions (IPCC 2000).

Forward calculation from raw materials may be preferable for individual cement plants calculating their own emissions, as the plants have detailed data on their raw materials. These plant-specific raw materials data (both tonnage and chemical composition), however, are essentially unavailable on a country basis. As correctly noted in an article by Vanderborgh and Brodmann (2001) describing the main rival methodology, the IPCC (2000) method presented above does not consider the MgO content of clinker. Vanderborgh and Brodmann prefer a slightly higher, MgO modified, calcination emissions default factor of 0.525 ton CO_2 (total)/ton clinker, based on the assumption that the MgO is from an MgCO_3 (magnesite) phase in the limestone. The average MgO content they used for clinker was 1.4% (versus the 1% shown in table

1 of part I). Although it is more likely that MgO would be present as a dolomite [$\text{CaMg}(\text{CO}_3)_2$] phase rather than as magnesite (the latter being a comparatively rare mineral), the stoichiometric effect on CO_2 is the same for both minerals if one also corrects for the CaO contribution by the dolomite. Using a comparable arithmetic approach as for the pure CaCO_3 example above, it can be shown that for an MgO bearing clinker of 65% CaO, the default emissions factor would be (per ton of clinker) $[0.5101 + M(0.011)]$ ton CO_2 (result to be rounded to two decimal places), where M is the percent MgO in the clinker. This would be a *maximum* contribution and would need to be reduced proportionally for any MgO from noncarbonate sources (highly likely). Because the small MgO contribution to CO_2 would be subsumed in the overall 5% to 10% error range of the general calculation, it may be argued that the additional CO_2 from consideration of MgO is insignificant, at least for country-level calculations, and for this reason MgO has been ignored in this article.

Another criticism of the IPCC (2000) methodology made by Vanderborgh and Brodmann (2001) was that the methodology may inadequately correct for the contribution to CO_2 emissions by the generation of any CKD not subsequently recycled to the kiln.⁹ A high (but variable) proportion of CKD represents material incorporating calcined calcium carbonate. Where CKD is returned to the kiln, it becomes part of the clinker, and the CO_2 emissions associated with this CKD are subsumed within those calculated for the clinker. But the emissions calculated for the clinker would not include those from "lost" CKD, which is CKD not returned to the kiln because it was either landfilled or used for other purposes; a correction for this lost material is desirable in a rigorous calculation. Although Vanderborgh and Brodmann (2001) provided a complex formula for plant-level calculations of lost CO_2 from CKD, the calculation is impractical for country-level determinations. In the absence of better CKD data, the IPCC method provides for a default emissions addition for lost CKD of 2% of the amount of CO_2 calculated for the clinker itself. In fact, this 2% default addition is not unreasonable assuming a total generation of CKD equivalent to 15% to 20%

of the weight of the clinker produced, a calcination factor of the CKD of 33%, and a 33% nonrecycling (to the kiln) ratio. Such ratios would be applicable to modern, rotary kiln lines but could significantly understate the lost CKD CO₂ from VSKs or older rotary kilns lacking efficient CKD recovery systems. Given the 5% to 10% error of the IPCC method (this error range would also be applicable to the rival methodologies), a 2% CKD correction can be safely omitted for first-order estimations of country-level emissions of calcination CO₂.

Appendix B. Methodology for Calculating CO₂ Emissions from the Combustion of Fuels in Clinker Manufacture

Emissions of CO₂ from cement manufacturing are both from calcination of limestone and from fuel combustion. Although calcination emissions can be calculated fairly precisely (Appendix A), the calculation of CO₂ from fuel combustion is significantly more difficult and less precise; the methodology is described here.

Combustion (oxidation) efficiencies are commonly (if casually) expressed as being 100% in cement kilns, based on the high combustion temperatures and long residence times. But, unlike clinker raw materials, the residence times for the fuels and combustion gases are actually not all that long (typically seconds to minutes), and not all parts of the kiln are at the high temperatures of the sintering zone (part I). Further, kerogen or other organic matter in the clinker raw materials (as opposed to the fuels) commonly burns in the preheating and or precalcining sections of the kiln line, where temperatures are more modest and combustion may therefore be incomplete. Incomplete combustion can lead to the formation of CO rather than CO₂. The amount of CO released is quite variable, but it is extremely small by comparison with CO₂. According to the U.S. EPA (1995), cement kilns typically emit CO in the range of about 0.06 to 1.8 kg/ton clinker. As with other studies of combustion contributions to GHGs (e.g., IPCC 2000), it is assumed in this article that any CO released by cement kiln lines ultimately is converted to CO₂ and may thus be ignored as a distinct species (i.e., should be calculated as if it were CO₂).

Theoretical energy (and hence fuel) requirements to make clinker from a proportioned mix of pure oxides or from a theoretical mix of raw materials are invariably much less than the actual fuel requirements for the kiln. The reasons for this difference stem from variations in plant design and operating parameters, heat losses, highly variable energy requirements to break down different raw materials and recombine them into the clinker minerals, and variations in the chemical composition and energy yield of fuels. Given adequate data, a rigorous approach to combustion CO₂ based on actual fuel consumption is practical on a plant-specific basis, but these data are generally lacking on a country basis. For the very few countries for which annual fuel consumption data (by type) are available for the cement industry, there are generally no specific compositional data associated with the fuels. One could, however, apply standard carbon contents data for each fuel to derive approximate combustion CO₂ emissions, with the significant caveat that data on waste fuels (such as type, tons, dilution factors, energy yields, and carbon contents) are almost invariably poor or lacking entirely.

Given type and tonnage data for fuels, the CO₂ calculation based on standard carbon contents of fuels is complicated by the fact that most published conversion factors ("carbon factors") are not reported in terms of tons of carbon per ton of fuel, but are instead expressed as tons of carbon per unit energy yield of the fuel (e.g., coal at 25.75 Mt carbon-equivalent per 10¹⁵ Btu). The carbon factors thus require fuel-specific energy yield data in order to isolate the carbon, which may then be converted to CO₂ (tons carbon × 3.6642 = tons CO₂). Both the carbon factor and energy data have significant potential for rounding errors in actual use. Further, for some fuels, a range of standard energy values may be provided, and the carbon and energy data commonly are based on laboratory testing conditions rather than on actual industrial combustion experience (which usually realizes lower heat yields). For liquid and gaseous fuels in particular, the standard energy yield data vary significantly depending on whether the data are for net (or low) heat contents values or gross (high) heat contents, yet this distinction is rarely made

in the literature. Net heats are more realistic for computing process-available energy yields of fuels (they account for typical impurities and heat losses from evaporation of residual moisture) and appear to be the basis of energy reporting, where available, for the cement industries of most countries other than the United States. Gross heat values, however, which are used by the U.S. cement industry, are probably better than net values for computing the true total energy requirements to make clinker (table 4 in part I) and, especially, the CO₂ yields of fuels, as the energy values are more complete. Gross heat values would yield higher CO₂ emissions per ton of liquid or gaseous fuel, but where solid fuels are dominant (most U.S. plants), the overall increase in combustion CO₂ over that for net heats is only 0.01 to 0.02 ton CO₂/ton clinker.

Because the U.S. cement industry continues to utilize a variety of rotary kiln technologies and has plants varying widely in age that burn a broad variety of fuels, the range of energy consumption (table 4 in part I) and combustion CO₂ emissions (table 1), per ton of product, may be taken as broadly comparable to the range for rotary plants outside the United States. Two sets of combustion emissions data for the U.S. industry are shown in table 1. Data for the first set are based on the carbon factor data published by the U.S. EPA (2001), standard heat content data published by the U.S. National Energy Information Center (U.S. NEIC 1977) and Degré (1998) (for waste fuels); data for the second set are based on plant-specific gross heat data reported to the USGS in 2000. Estimates for heat yield and carbon content were made for undifferentiated waste fuels not listed in these sources. Data on the type and quantity of fuels consumed were those collected by the USGS as part of its annual cement industry surveys. The quality of these data is considered to be good, except possibly for natural gas and for waste fuels in the early years of their use (mid-1980s through 1992). Natural gas data for individual plants are subject to order-of-magnitude reporting errors that can be diffi-

cult to identify because the fuel can be used both for warming up the kiln and for full kiln operation. Data on consumption of waste fuels was not collected prior to 1993, despite their use actually having begun in the mid-1980s or possibly even earlier at a few plants. Further, the waste fuel data, other than tires, are collected only in terms of broad categories (e.g., other solid wastes, liquid wastes) that do not adequately distinguish among the wide variety of waste fuels (hence carbon and heat contents) burned.

Data from the USGS surveys on the energy yields of fuels consumed by the cement industry have not been routinely published.¹⁰ Annual energy consumption data for the U.S. and Canadian cement industries are, however, available for recent decades from the Portland Cement Association (e.g., PCA 2002), but the data only cover its member companies' plants and share some of the same data collection and reporting problems as the USGS surveys. The average energy consumption values for both U.S. data sets are similar; the USGS values are about 5% higher (see part I).

Although it is evident from table 1 that different combustion CO₂ emissions values can be derived for the same fuel consumption data, the differences among the values for any one year amount to only 8% to 12% for combustion CO₂ and only 5% to 6% for total (combustion plus calcination) CO₂. Given uncertainties in the base fuel quantities, the time series analysis of the data in table 1 (and probably comparable data, where available, for other countries) should be considered accurate to within about 5% at best; that is, year-to-year variations of less than 5% may not be real.

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