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Industrially interesting approaches to "low-CO_2" cements☆

Ellis Gartner*

Lafarge Laboratoire Central de Recherche, 95 Rue du Montmurier, St. Quentin Fallavier 38291, France

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Abstract

This article discusses the practicality of replacing portland cements with alternative hydraulic cements that could result in lower total CO_2 emissions per unit volume of concrete of equivalent performance. Currently, the cement industry is responding rapidly to the perceived societal need for reduced CO_2 emissions by increasing the production of blended portland cements using supplementary cementitious materials that are principally derived from industrial by-products, such as blast-furnace slags and coal combustion fly ashes. However, the supplies of such by-products of suitable quality are limited. An alternative solution is to use natural pozzolans, although they must still be activated either by portland cement or lime or by alkali silicates or hydroxides, the production of all of which still involves significant CO_2 emissions. Moreover, concretes based on activated pozzolans often require curing at elevated temperatures, which significantly limits their field of application.

The most promising alternative cementing systems for general concrete applications at ambient temperatures currently appear to be those based at least in part on calcium sulfates, the availability of which is increasing due to the widespread implementation of sulfur dioxide emission controls. These include calcium sulfoaluminate–belite–ferrite cements of the type developed in China under the generic name "Third Cement Series" (TCS) and other similar systems that make good use of the potential synergies among calcium sulfate, calcium silicate and calcium aluminate hydrates. However, a great deal more research is required to solve significant unresolved processing and reactivity questions and to establish the durability of concretes made from such cements. If we are to use these potentially more CO_2-efficient technologies on a large enough scale to have a significant global impact, we will also have to develop the performance data needed to justify changes to construction codes and standards.

Keywords: Cement; Energy; Carbon dioxide; Environment; Sustainable development

1. Introduction

The portland cement manufacturing industry is under close scrutiny these days because of the large volumes of CO_2 emitted in the manufacture of portland cement clinker. Some estimates put the cement industry total as high as 5% of total global anthropogenic CO_2 emissions [1]. However, CO_2 emissions are only a minor part of the larger issue of the role of the construction industry in the sustainable development of our civilisation. According to the World Business Council on Sustainable Development, the three "pillars" of sustainable development are economic growth, ecological balance and social progress, and one cannot have any one without the others. Thus, in looking for ways to reduce the global CO_2 emissions related to cement manufacture, we must consider not only the cement manufacturing process but also where and how the raw materials resources will be found, where and how the product will be used and with what overall impact on the global community. There can be no doubt that the portland cement industry takes the issue of sustainable development very seriously. This is typified by the stance of the world's largest cement manufacturer, Lafarge, which has recently published a corporate report on economic, societal and environmental performance [2] and made a public commitment to reduce its total global CO_2 emissions by 15%, and its mean specific CO_2 emissions per ton of cement by 20%, over the period 1990–2010.

Concrete, based mainly on portland cement, is the most widely used material on Earth. Current estimates of world cement manufacture are of the order of 1.7×10^9 t/year, enough to produce well over 6 km^3 of concrete per year or

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* Tel.: +33-474821890; fax: +33-474828011.

E-mail address: ellis.gartner@lafarge.com (E. Gartner).

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at least 1 m^3 per person. For the production of each cubic meter of concrete, average CO_2 emissions are about 0.2 t, which amounts to about 0.08 t CO_2 per ton of concrete. While these figures sound high, they are actually quite low compared with many other construction materials. For example, the specific CO_2 emissions for steel production usually exceed 1 t per ton of steel, the exact value depending on the technology used [3]. However, it is difficult to compare steel and concrete directly on either a weight or a volume basis, because they are used in different types of application. A true comparison of the CO_2 efficiency of construction requires the comparison of equivalent structures made from alternative sets of materials, and such detailed comparisons are not generally available. Moreover, a more fundamental analysis of the CO_2 efficiency of a structure also involves an estimate of the lifetime of the structure and the CO_2 emissions associated with its use and maintenance. (For example, a well-insulated concrete building should require much less energy for heating or air conditioning during its useful life than a poorly insulated wooden structure.) We are clearly not yet in a position to give reliable detailed comparisons of this kind in most cases.

Given that there is no practical alternative to concrete for many modern constriction projects, we have an interest in ensuring that the overall CO_2 emissions associated with concrete construction be minimised to the greatest extent economically feasible. Of course, not all of the cement used to make concrete is pure portland cement; in fact, much of it already contains secondary cementitious materials and fillers. This makes our challenge all the greater. Is it possible to go beyond the current approach of the cement industry, that of maximising the use of industrial by-products such as blast-furnace slag and fly ash as supplementary cementitious materials, to an approach based on alternative cementitious systems that are inherently less CO_2 intensive? This article attempts to answer this fundamental question.

2. A historical perspective

It should be remembered that a similar pressure for change arose in the mid-1970s, when the OPEC oil embargo forced the cement industry to reduce its dependence on oil and, more generally, improve its overall energy efficiency. That crisis gave rise to a period of intense R&D activity, much of it process oriented, which led to the rapid refinement and commercialisation of what are still the current "best" portland cement manufacturing technologies [i.e., high-capacity multistage preheater/precalciner kilns coupled with vertical raw mills (to recover waste heat for drying the raw feed), high-efficiency closed-circuit finish mills and improved clinker coolers]. There was also a rapid change away from oil and toward coals, cokes and a wide variety of waste fuels as the primary combustible in the kiln [4]. The shock provided by the OPEC oil embargo provided the short-term economic incentive necessary to force the industry to adopt new process technologies; these new technologies turned out to have long-term benefits for the overall efficiency of the industry, reducing the average specific kiln fuel energy requirement for clinker manufacture (in North America) by about 40% during the two decades starting in 1973, as estimated below.

2.1. CO_2 emissions vs. energy consumption

The comparison of the current situation with the 1970 oil shock is important, because most anthropogenic CO_2 emissions result directly from the combustion of fossil fuels to produce usable forms of energy. Thus, almost any approach to decreasing fossil fuel consumption should have a similarly beneficial effect in reducing CO_2 emissions per unit of product. Clearly, a modern cement plant produces much less CO_2 per ton of product than an average plant predating 1974, and the strong incentive to minimise the relatively high fraction of cement manufacturing costs associated with energy has in most cases also served to minimise average specific CO_2 emissions. We are therefore starting from a fairly high level of energy efficiency for the best available portland cement manufacturing technology, and it seems very unlikely that new manufacturing process research can offer very significant further improvements. Nevertheless, many cement plants around the world still operate at well below the levels of efficiency of the best available technology, which still leaves considerable room for improvement provided that the capital is available for investment.

It is not easy to find completely comparable sets of data for the global energy consumption or CO_2 emissions associated with cement manufacturing, partly because each country has its own reporting system and partly because the methods of calculation vary slightly from one source document to another. Thus, this article does not attempt to provide a thorough statistical analysis of all of the factors involved. However, information on the energy efficiency of the U.S. cement industry in 1973 is contained in Ref. [4], and many useful data on the energy efficiency of the global cement industry two decades later are contained in Refs. [1,3]. Data in Ref. [4] show that average kiln fuel energy consumption in the United States was about 7 GJ/t in 1973 (relative to clinker), whereas current best available technology allows clinker to be manufactured with as little as 3 GJ/t under ideal conditions. According to Ref. [3], the actual energy efficiency of U.S. plants in the mid-1990s was still about 25% above the "best practice" benchmark (i.e., about 4 GJ/t). Similar figures can be deduced from the data in Ref. [1], which show a total primary energy consumption of 5.4 GJ/t of cement in North America in 1994, from which we must deduct the primary energy equivalent of the electric power consumption in cement manufacturing. The average electricity consumption in cement manufacturing is given as 0.38 GJ/t in direct electrical energy (106 kW h/t), which is equivalent to about 1.2 GJ/t in primary energy if we assume a typical figure of about 33% for the energy efficiency of electricity production from fossil fuels. This suggests that North American kiln fuel consumption in 1994 averaged about 4.2 GJ/t. These comparisons also highlight the fact that the CO_2 emissions associated with electric power generation are by no means negligible in regard to cement manufacturing; in fact, they account for about 0.08 t CO_2 per ton of cement manufactured [3] on average, given that most electricity production in North America is based on fossil fuels. Grinding of raw materials and clinker accounts for well over half of the total electrical energy consumption [4], and it is important, in this context, to note that alternative cements that require extremely fine grinding of hard materials, such as belite or blast-furnace slag, can often lose in grinding energy a good fraction of whatever they may save in clinkering energy.

Detailed estimates of the total CO_2 emissions associated with cement manufacture in 1994 show that, for the then global world cement production of 1.381 Gt, total CO_2 emissions were 1.126 Gt [1]. Of this, 0.587 Gt originated from the raw materials and 0.539 Gt from the combustion of fossil fuels, including the fuels required to generate the electricity for plant operation. In specific terms, these 1994 world averages amounted to 0.815 t CO_2/t cement, of which 0.425 came from the raw materials and 0.390 from fuels. These figures take into account the fact that the cements produced in 1994 were not all pure portland cements; many were blended cements containing supplementary cementitious materials. The proportion of blended cement production varied widely from country to country, and this partially accounts for the wide variations in energy and CO_2 efficiency observed.

It has been suggested that portland cements could be produced with lower associated CO_2 emissions by processes that do not directly make use of fossil fuels (e.g., electric furnaces) or even solar- or nuclear-powered furnaces. Many such ideas were seriously investigated in the 1970s, but with little practical success. Electric furnaces are rarely the most energy-efficient approach for the bulk thermal processing of materials because most electricity is itself made from fossil fuels at an energy efficiency of generally well below 40%. Nuclear reactors are clearly not a solution that would please most environmentalists and can be discounted for the same reasons that nuclear electric power generation, despite its negligible CO_2 emissions, is no longer being considered as a serious option by most developed societies. Finally, although it should be possible, theoretically, to make portland cement clinker in a specially designed solar furnace, the practical difficulties would be enormous. A huge solar collection and focussing device would be required to run a typical cement plant, and it could only operate in strong direct sunlight, so it would lose all of the advantages of continuous operation. Intermittent operation clearly leads to severe energy and operational inefficiencies.

2.2. The importance of raw materials selection

In addition to the relatively straightforward issue of energy efficiency, we are also faced with the problem of raw materials and the “potential CO_2” contained within them. Portland cements are very rich in calcium. The principal concentrated source of calcium in the Earth’s crust is limestone, which is essentially calcium carbonate ($CaCO_3$). To make portland cement clinker, in which the principal active component is alite (impure Ca_3SiO_5), limestone is heated with a source of silica in a kiln at temperatures of well over 1350 °C. The simplest form of the basic reaction is shown in Eq. (1); the mass proportions are given in italics:

$$\begin{array}{lcccccc} 3CaCO_3 & + & SiO_2 & \Rightarrow & Ca_3SiO_5 & + & 3CO_2 \\ 300 & & 60 & \Rightarrow & 228 & & 132 \\ \text{calcium carbonate} & + & \text{silica} & \Rightarrow & C_3S\text{(or alite)} & + & \text{carbon dioxide gas} \end{array} \tag{1}$$

Two important facts are to be observed here. Firstly, for every ton of C_3S produced from $CaCO_3$ in this way, 579 kg CO_2 gas are liberated as a chemical by-product, irrespective of the process used and its fuel efficiency. Secondly, the enthalpy change, ΔH, of this reaction is about +416 kJ/mol at 20 °C, which means that the theoretical minimum amount of thermal energy required to produce 1 t C_3S from limestone and quartz is 1.83 GJ. (In practice, one cannot hope to come very close to this minimum, as explained later.) In addition, the reaction will not proceed at all at temperatures lower than about 1250 °C (even with a catalyst), and it is usually necessary to heat the materials to more than 1400 °C to get the reaction to go at a rate high enough to be commercially useful.

Calcium sources other than limestone can, in theory, be used as raw materials, but it turns out that there are not really any other sufficiently widespread and sufficiently concentrated sources of calcium available. Calcium sulfates (gypsum and anhydrite) are abundant in some locations and have historically been used to make portland cement clinkers, but the major complication is that the principal by-product in this case is not CO_2 but instead sulfuric acid, as shown by the following (intentionally simplified) reaction equation:

$$\begin{array}{lcccccccc} 3CaSO_4 & + & SiO_2 & + & 3H_2O & \Rightarrow & Ca_3SiO_5 & + & 3H_2SO_4 \\ 408 & & 60 & & 54 & \Rightarrow & 228 & & 294 \\ \text{anhydrite} & + & \text{silica} & + & \text{water} & \Rightarrow & C_3S\text{ (or alite)} & + & \text{sulfuric acid} \end{array} \tag{2}$$

This process was, in fact, practiced industrially primarily as a means of producing sulfuric acid, with the by-product being portland cement clinker, but it fell out of favour relative to other less complicated and less expensive methods of sulfuric acid manufacture. As with all processes that attempt to obtain two useful products at the same time, relative economic fluctuations in the raw materials supply and in the market for both products made it difficult to operate profitably for long periods of time. In addition, the overall thermal efficiency and environmental impact of the cement–sulfuric acid process was considerably worse than that of the normal cement manufacturing process. The total global demand for portland cement is roughly an order of magnitude greater than that for sulfuric acid, meaning that it would never be practical to produce more than a small percentage of cement in this way. Moreover, good deposits of calcium sulfate are less abundant than good deposits of limestone, making this an important issue in locating a factory. Nevertheless, the process could be looked at again for suitable locations, if the market conditions were also right.

It therefore appears almost impossible to make the majority of portland cements from sources other than limestone; limestone-based cement manufacture inherently gives rise to very high CO_2 emissions even if the minimum theoretical energy consumption can be obtained. Therefore, it is worth looking at alternative cementing systems to see whether any of them might in the future be capable of offering many of the advantages of portland cement but with significantly lower inherent CO_2 emissions. It should be added that the principal economic advantage of portland cement is its low delivered cost in most important locations due principally to the ready availability of the necessary raw materials. One can make cements with better performance for specialised applications, but none of them can currently be produced at a competitive price for ordinary construction applications.

3. Raw materials CO_2 vs. fuel-derived CO_2

It is clear from the previous discussion that we have to separate the CO_2 emissions from any manufacturing process into two categories: those simply derived from carbon compounds in the raw materials that are converted to CO_2 during the manufacturing process, which we refer to as "raw materials" CO_2 ($RMCO_2$), and those produced by the combustion of fossil fuel necessary to drive the manufacturing process, which we refer to as "fuel-derived" CO_2 ($FDCO_2$). The former is much easier to predict than the latter, because one usually knows very precisely the composition of the raw materials and the products. Thus, in the previous example, manufacture of 1 g C_3S from limestone and silica produces 0.58 g $RMCO_2$, whereas manufacture of the identical product from anhydrite and silica produces essentially no $RMCO_2$. On the other hand, calculation of the $FDCO_2$ emissions per unit of product requires a detailed knowledge of the processing equipment to be used and the way it is operated. It also depends on the specific fuel chosen. Thus, it is hard to obtain reliable data on $FDCO_2$ emissions except for industrial processes that are already operating and for which good statistical data can be obtained. As a result, this article does not attempt to estimate $FDCO_2$ emissions for most of the alternative cementing systems discussed.

To explain why it is so difficult to calculate the likely $FDCO_2$ emissions of a manufacturing process from fundamental physicochemical data, it is sufficient to use portland cement manufacture, which we understand very well, as an example. In practice, the thermal energy requirements for clinkering vary widely from plant to plant depending on the type of kiln system used. The most efficient modern coal-fired preheater (dry process) plants use as little as 3.06 GJ fuel energy per ton of clinker (GJ/t), whereas some older wet process plants can consume more than twice that amount. The wet process uses a lot of heat to evaporate water, but there are better alternatives even when the raw materials are naturally wet. The main justification for continued use of wet kilns is simply the high replacement cost.

Table 1 shows a calculation of the theoretical thermal energy requirement for the manufacture of portland cement clinker in the absence of heat losses. The total heat requirement is 1.76 kJ/g (or GJ/t), if we start with all raw materials at 20 °C, ending up with all products at 20 °C and there are no heat losses to the surroundings. However, this is impossible in industrial reality. Not only is there the problem of insulation of the kiln shell (it is not possible to make or use a perfectly insulated kiln because suitable materials do not exist), but there is also the problem of combustion thermal efficiency. Fuel is burned in air to produce a certain volume of hot combustion gases (ideally consisting only of N_2, CO_2 and H_2O). These hot gases then transfer some of their heat to the kiln charge by radiation and convection but, clearly, this transfer can only occur when there is a significant difference in temperature between the two. As can be seen readily from Table 1, about 2.2 GJ/t heat are needed at temperatures above about 900 °C for calcination and clinker

Table 1
Simplified ideal heat balance for the manufacture of portland cement clinker [5]

Position in kiln system	Temperature range (°C)	Process	Heat required (GJ/t) clinker
Preheater	20–900	Heating raw feed to 900 °C	+ 1.53[a]
	~ 450	Dehydration of clays	+ 0.17
	20–900	Cooling CO_2 and H_2O	– 0.59[b]
Calciner	~ 900	Dissociation of calcite	+ 1.99
	~ 900	Reactions of dehydrated clays	– 0.04
Rotary kiln	900–1400	Heating feed from 900 to 1400 °C	+ 0.52
	900–1400	Formation of clinker phases	– 0.31
Clinker cooler	20–1400	Cooling of clinker to 20 °C	– 1.51
		Net heat required:	+ 1.76

[a] Assumes dry limestone and clay as kiln feed.

[b] Industrially, it is not generally considered practical to recover heat from kiln exit gases below about 120 °C due to the problems engendered by condensation of water.

formation, whereas only about 1.1 GJ/t is needed below 900 °C for preheating dry raw materials. It turns out that the calcination temperature acts a kind of "thermal bottleneck" in the process, because no matter how much heat we have available below that temperature, it cannot be used to drive either the calcination or the clinkering reactions.

Ideally, therefore, we need a fuel that burns to give gases that are very much hotter than 900 °C, so that a significant proportion of the heat can be used for clinkering and calcining. One ton of good quality bituminous coal has a gross heating value of 32.6 GJ and produces 2.94 t CO_2 when burned stoichiometrically in air. In addition, the combustion gases include 8.26 t N_2 from the combustion air and 0.50 t water vapour from hydrogen in the coal. If the coal and air are initially at ambient temperatures (about 20 °C), 19.5 GJ/t fuel of this heat are available above 900 °C (i.e., about 60% of the gross heating value). However, this percentage is further degraded by the fact that typically about 10% excess air is used to assure complete combustion and by the fact that rapid heat transfer from the gases to the solids requires a significant temperature difference. Thus, to provide 2.2 GJ/t clinker above 900 °C, we would need to burn coal of gross heating value equal to at least 3.7 GJ. This situation is made even worse by any other heat losses (e.g., kiln shell losses) above 900 °C, but we also have one additional source of heat that makes a very useful contribution, which is the clinker itself. By cooling the hot clinker with the incoming combustion air in the clinker cooler, we can also recover a very significant amount of heat that can be used above 900 °C. The combination of all of these factors leads to the estimation that the practical thermal efficiency limit for a perfectly tuned coal-fired kiln using reasonably dry raw materials is about 3 GJ/t (which gives about 0.28 t per ton of coal-derived CO_2) relative to the theoretical 1.76 GJ/t (about 0.16 t per ton of coal-derived CO_2). If more energy-rich and carbon-poor fuels, such as methane, could be used, then that would help a little. In theory, the energy consumption and thus $FDCO_2$ emissions could also be further reduced by:

(a) Improving kiln shell insulation. However, this would be limited to saving at most about 0.3 GJ/t even if perfect insulating materials could be developed for this application (and this is not a practical proposition for many reasons).
(b) Reducing clinkering times and temperatures (e.g., by catalysts). This would indirectly help to reduce kiln shell losses above 900 °C, but in practice, the energy savings will be only a small fraction of the maximum possible savings (0.3 GJ/t) estimated for eliminating completely those kiln shell losses. Thus, they are likely to be insignificant.
(c) Reducing the volume of exhaust gases. Typically, the kiln exhaust gases are well over 60% nitrogen, and this carries a lot of heat away with it into the atmosphere, especially because it is not industrially practical to cool these gases to below about 120 °C to avoid condensation of liquid water in the gas ducts or on the raw feed. If the fuel could be burned in pure oxygen, a much higher percentage of its heat would be available over the bottleneck temperature of 900 °C and much lower total volumes of exhaust gases would be created. Thus, overall thermal efficiency could, in theory, be greatly improved. However, the practical difficulties are enormous; the materials required for the kiln burner and clinker cooler would have to be capable of resisting the extremely high temperatures developed and the risk of fire in metallic components (because most metals burn fairly readily in pure oxygen). In addition, air fractionation also consumes significant amounts of electrical energy, which would counterbalance some of the energy savings in the kiln system. Nevertheless, partial oxygen enrichment of the combustion air has been and may still be considered as one possible approach to further decreasing cement kiln fuel requirements and thus help further reduce the $FDCO_2$ emissions.
(d) Reducing the lime saturation factor of the kiln feed. This essentially means making clinkers with lower alite and higher belite contents. Clearly, the higher the belite content, the less limestone will be required. However, on going from a typical modern OPC with about 65% alite to a belite-rich OPC with little or no alite, the overall reduction in limestone consumption is no more than 8% of the total. Even allowing for the ensuing reductions in burning temperature, the likely maximum total CO_2 emissions savings are only of the order of 10%, and this must be balanced against the fact that high-belite OPC clinkers are very hard to grind (require more grinding energy) and also usually give very low rates of strength development that are considered unsatisfactory by most customers.

It is worth adding at this point that the phenomenon of "clinkering" is very important with respect to kiln efficiency. The raw feed can be dried efficiently as a fine powder in the raw mill (through which the kiln exit gases usually pass) and then preheated efficiently in the suspension preheater. However, if it did not self-nodulise into clinker balls of a reasonable diameter in the rotary kiln, the efficient operation of the kiln and clinker cooler would be endangered, with a very significant impact on overall energy requirements. Alternative kiln and clinker cooler designs can be envisaged for fine powders, but it is difficult to obtain the long residence times required for the slow reactions involved (principally, formation of C_3S). As a corollary, cement-making processes that require complete melting of the raw feed (such as the manufacture of certain calcium aluminate cements and of glass cements) face the problem of heat recovery from the melt. Currently, no reliable technology exists that will allow rapid but thermally efficient quenching of such melts, using only the incoming combustion air, at the enormous flow rates necessary for a full-scale cement plant. This is why quenched melts (e.g., blast-furnace slags) cannot be made efficiently as primary products.

From the above discussion, it is clearly impractical to make major gains in the fuel efficiency of the cement manufacturing process without changing the clinker chemistry radically to one that is much less limestone intensive. Essentially, this is because both the $RMCO_2$ and the $FDCO_2$ are roughly proportional to the $CaCO_3$ content of the kiln feed. This realisation leads us to look more closely into the question of raw materials.

4. Natural resources suitable for making hydraulic cements

Given the large volumes of portland cement required worldwide and its very low unit cost, any alternative would also have to be made from raw materials that are extremely abundant and widespread because transportation costs would otherwise dominate. If one looks at the relative abundance of minerals on the surface of the Earth, one finds that limestone is one of the most abundant and widely distributed. It is also a relatively pure and concentrated source of calcium, which itself is one of the most abundant metals in the Earth's crust. But what other minerals might conceivably be available in many locations and in such large quantities? A study made using public U.S. Geological Survey data suggests that, on this basis, only the following materials are reasonable alternative candidate raw materials for hydraulic cements:

- Clays: a source of Al and Si
- Calcium sulfates (gypsum or anhydrite): a source of S and Ca
- Iron oxides (iron ores): a source of Fe
- Silica (quartz, chert, etc.): a source of Si
- Coal ash (including desulfurisation products): a source of Si, Al and S.
- Sodium carbonate or sodium chloride: (a source of Na for alkali-activated cements)

In reality, other sources of the same elements may be available, but any particular source may be much less widespread. For example, bauxite is readily available in some locations but not very widespread, so we did not include it here. The same is true for magnesite and for phosphate ores. Thus, alternative cements that are very rich in Al, Mg or P seem less likely to be viable on a global basis, although they might be useful for local or specialised applications.

Based on the elements and minerals discussed above, we have calculated the $RMCO_2$ values for the known cementing phases that might be produced. These data are given in Table 2. $RMCO_2$ values are listed in two different units; the first, more commonly used form is on a mass basis (i.e., the mass of $RMCO_2$ liberated per unit mass of the resultant cementing phase). The second unit is relative to the unit volume of the cementing phase (i.e., in g CO_2/ml (kg/l or t/m^3) of the pure, anhydrous cementing phase). The interest of this second unit is that it may relate better to the rheology of the resulting fresh concrete because increased paste volume is generally associated with a more fluid concrete.

Table 2
$RMCO_2$ emitted in the manufacture of "pure" cement compounds

Cement compound	Raw materials used	$RMCO_2$ (g/g)	$RMCO_2$ (g/ml)
M (magnesia, periclase)	Magnesite	1.092	3.91
C (calcia, quicklime)	Limestone	0.785	2.63
C_3S (alite)	Limestone + silica	0.578	1.80
β-C_2S (belite)	Limestone + silica	0.511	1.70
C_3A (tricalcium aluminate)	Limestone + alumina	0.489	1.50
C_4AF (calcium aluminoferrite)	As above + iron oxide	0.362	1.29
NS (sodium metasilicate)	Soda + silica	0.361	–
CA (monocalcium aluminate)	Limestone + alumina	0.279	0.83
$C_4A_3\bar{S}$ (calcium sulfoaluminate)	As above + anhydrite	0.216	0.56

Note that some useful cementing phases (e.g., plaster, most pozzolans, and certain calcium phosphates) have essentially zero $RMCO_2$ values and are thus not included in this table.

It is interesting to note the widespread $RMCO_2$ values between these different compounds. In particular, there is a factor of about 2.7 (on a mass basis) between alite and calcium sulfoaluminate (3.2 on a volume basis). However, the difference between alite and belite is only a factor of 1.13 on a mass basis and even less (1.06) by volume. This is another reason why the idea of making belite-rich portland cements seems to be of rather limited interest, although belite-rich calcium sulfoaluminate cements may well be industrially interesting.

However, simplistic comparisons such as this can only get us so far, because it is unrealistic to imagine making pure cementing phases and it is also unreasonable to ignore the benefits that accrue from certain favourable combinations. A good example is that of pozzolans. Because the CO_2 emissions associated with the mining of natural pozzolans are very small, the interest in using activated pozzolan-based systems is clear. Similarly, because natural calcium sulfates also have negligible associated CO_2 emissions, cementing systems that make use of significant proportions of calcium sulfate appear very interesting.

Based on the above list of cement phases and potentially viable raw materials, it may be concluded that the most promising low-CO_2 alternatives to portland cement are probably to be chosen from the following major known classes of cementing system:

(A) Pozzolan-based cements.
(B) Calcium (sulfo)aluminate-based cements (made from low-grade alumina sources).
(C) Calcium sulfate-based cements.

These three classes are analysed in more detail below. Note that we have deliberately omitted blast-furnace slags from this list mainly because their production is slowly declining. Most good sources of such slags are already either being used or are earmarked for use in the manufacture of blended cements, and the technology for this is already very well established. In addition, much research is currently being done on the use of other metallurgical slags (principally, steel slags) in cement production, but this is a separate and complex subject, which is very much tied to the economics of the metallurgical industries.

5. Pozzolan-based cements

We define ''pozzolans'' as reactive aluminosilicates (A_xS_y), which can be either glassy (such as natural volcanic glasses or man-made glasses such as fly ash or silica fume) or semicrystalline (such as metakaolin). The best known and best-understood class of pozzolan-based cements is that based on lime activation, which includes activation by portland cement. This is based on the following generalised reaction:

$$A_xS_y + mCH + nH \Rightarrow C-S-H + C-A-H$$

$$\text{pozzolan} + \text{lime} + \text{water} \Rightarrow \text{calcium silicate hydrates} + \text{calcium aluminate hydrates} \qquad (3)$$

The precise composition of the C-S-H and C-A-H formed varies greatly with the reaction conditions and the presence of other components (e.g., sulfates, which preferentially enter the C-A-H phases). Mixed C-A-S-H phases can also form, especially in the absence of sulfates.

Eq. (3) is classically called the ''pozzolanic reaction,'' and it consumes lime, pozzolans and water to make new hydrated phases that occupy more volume that the original solid phases. The lime itself can also be obtained from an indirect source, which is usually the hydration of the alite (and to a lesser extent, the belite) in portland cement:

$$C_3S\ (C_2S) + 5.3\ (4.3)\ H \Rightarrow C_{1.7}SH_4 + 1.3\ (0.3)\ CH \qquad (4)$$

Traditional pozzolanic cements, as developed by the Romans, used lime as the activator, but this reaction is too slow at room temperature to be of use for most modern concrete applications. The advantage of using alite as the activator is that its hydration is sufficiently rapid to give reasonable early concrete strengths, while the slower pozzolanic reaction can then be used to ''mop up'' the free lime produced. It should be noted that the high C/S C-S-H formula used in Eq. (4) is (approximately) valid only when excess lime is present. In many pozzolanic cements, the ultimate C-S-H may have a lower C/S ratio, which allows for even more C-S-H to form (i.e., the high C/S C-S-H can contribute some of its own lime to a further pozzolanic reaction).

Considering these reactions in conjunction with the $RMCO_2$ values in Table 2 and making the most conservative assumption that the C-S-H has the same high C/S ratio, it can be seen that the overall CO_2 efficiency of portland cements is greatly improved by using pozzolans. For example, the hydration of alite plus silica fume should give the following stoichiometry:

$$C_3S + 0.76\ S + 7.04\ H \Rightarrow 1.76\ C_{1.7}SH_4 \qquad (5)$$

In this case, we produce 1.76 times as much C-S-H per unit of alite reacted. Because we assume silica fume to have zero $RMCO_2$, the effective $RMCO_2$ for C-S-H production from this pozzolanic cement is therefore reduced by 43% relative to the value for pure alite. Essentially, this argument depends on the fact that most people accept C-S-H to be the major binding phase in conventional concrete and that CH (portlandite) is a less effective and less desirable hydrate. Thus, every mole of CH persisting in concrete can be considered to represent 1 mol CO_2 emitted unnecessarily, and it should ideally be replaced by either C-S-H or C-A-H. This argument has its limitations, however, because some excess CH can be useful in certain cases (e.g., to ensure that the pH remains high enough to avoid steel corrosion in reinforced concrete). Free CH in hydrated OPC also makes a useful contribution in terms of volume filling and the resultant compressive strength, but C-S-H is preferable in terms of durability because it has a much lower solubility.

In addition to lime activation, certain pozzolans can also be activated by reaction with other bases. A particularly interesting case is the reaction between alumina-rich pozzolans (such as metakaolin) and alkali silicate solutions [RS_z (aq.)], where the alkali metal is usually sodium:

$$AS_y + RS_z\ (aq.) + nH = RAS_{(y+z)}H_n \qquad (6)$$

This reaction has been referred to by some as ''geopolymerization,'' but the term has no special scientific significance. A careful scientific study has clearly shown the alkali silicate/metakaolin reaction to be a kind of condensation reaction in which the dissolved alkali silicate cross-links with the reactive aluminosilicate to form a kind of ''low-temperature alkali aluminosilicate glass'' with chemistry close to that of a zeolite (in which each aluminum cation is in a tetrahedral environment surrounded by four shared oxide ions and requires an alkali cation to balance its net negative charge) but with an amorphous structure [6]. The products of this reaction are apparently very microporous but have a rather low chemically bound water content, so it is not really appropriate to refer to it as a hydration reaction. The reaction does have some cementing value, because the alkali silicate is initially present as a solute; thus, the overall solid volume increases significantly during the reaction. However, the kinetics is very different to those typical of cement hydration. Elevated curing temperatures are usually required for good strength development, especially with glassy aluminosilicates such as fly ashes and many natural pozzolans, and this limits applications. If very reactive (and also rather expensive) man-made pozzolans, such as metakaolin, are used, it is also difficult to obtain long working times. These constraints make it seem unlikely that such cementing systems will replace portland cement except perhaps in precast applications.

Under the assumed name of "geopolymers," several potential applications of alkali-activated pozzolan technology are currently under investigation worldwide, some making use of fly ash as the main raw material, but few good large-scale applications have yet been found and much further research needs to be done to understand these systems to the level where they can be considered truly predictable and reliable. Regarding overall CO_2 efficiency, the activator itself has significant $RMCO_2$ (see typical value in Table 1) and $FDCO_2$ values. Alkali silicates are usually made from alkali carbonates plus silica in furnaces similar to those used to make ordinary "bottle" glass, and the $FDCO_2$ should therefore be similar to that of ordinary glass. (In some cases, the activator can simply be an alkali hydroxide solution, but we assume that this also will have an equivalent $FDCO_2$ value.) The pozzolan may have very low associated CO_2 emissions if it is a natural pozzolan or a by-product, like fly ash, but metakaolin and related products are artificially heat-treated clays and thus have nonnegligible $FDCO_2$ values. Total CO_2 emissions reductions will, in many cases, depend primarily on the activator content, which can be as low as 10% by mass in some cases, leading to systems that could, in theory, be as much as 10 times lower (in terms of CO_2 emissions per unit volume of hardened concrete) than pure portland cement concretes.

A third reported possibility for the activation of pozzolans is by reaction with magnesium oxide or hydroxide following the same type of chemistry as given in Eq. (3) but substituting Mg for Ca. It has been claimed recently that such chemistry is feasible for the manufacture of concrete products [7]. However, it seems unlikely to be of widespread value as a low-CO_2 cementing system due to (a) the very low solubility of magnesium hydroxide, which will render its reaction with pozzolans very slow; (b) the very high $RMCO_2$ and $FDCO_2$ values associated with the manufacture of MgO from magnesite and (c) the relative global scarcity of good magnesite deposits. Claims that MgO-based cements carbonate more rapidly than portland cements have yet to be verified publicly, but both lime-based and magnesia-based hydrates will fully carbonate in air [equivalent to reversing Eq. (1)] if exposed for a long enough time, giving calcium or magnesium carbonate plus silica and alumina gels and absorbing all of the $RMCO_2$ emitted during their manufacture. The main limitation of this reaction is that it is diffusion controlled, so that, in large concrete pours, it may take many thousands or even millions of years. It is already well known that small- to medium-sized portland cement-based concrete products can be hardened by accelerated carbonation under factory conditions, but this is not a practical approach for concrete use on most construction sites, and such carbonated concretes also do not protect steel reinforcement from corrosion.

6. Calcium (sulfo)aluminate-based cements

As shown in Table 1, calcium sulfoaluminate ($C_4A_3\bar{S}$, sometimes called "Klein's compound") has a very low $RMCO_2$ relative to most other calcium-based cementing phases apart from the closely related phase monocalcium aluminate. $C_4A_3\bar{S}$ hydrates readily to give a combination of C-A-$\bar{S}$-H, C-A-H and AH phases depending on the availability of sulfate and lime. In terms of hydrate volume creation per unit of "clinker," its reaction with excess portlandite and gypsum to give ettringite is one of the most effective hydration reactions:

$$\begin{array}{ccccccccc} C_4A_3\bar{S} & + & 6CH & + & 8C\bar{S}H_2 & + & 74H & \Rightarrow & 3C_6A\bar{S}_3H_{32} \\ 610.3 & + & 444.6 & + & 1377.5 & + & 1333.2 & \Rightarrow & 3765.9\ (\mathrm{g}) \\ 234.1 & + & 198.3 & + & 596.3 & + & 1333.2 & \Rightarrow & 2121.6\ (\mathrm{ml}) \end{array}$$

$$\text{Solid volume ratio (hydrates/dry powder)} = \mathbf{2.06} \tag{7}$$

$$\text{Volume of hydrates per mass of initial dry powder} = \mathbf{0.87\ ml/g}$$

$$\text{Volume of hydrates per mass of } (C_4A_3\bar{S} + CH) = \mathbf{2.01\ ml/g}$$

$$\text{Volume of hydrates per mass of } C_4A_3\bar{S} = \mathbf{3.48\ ml/g}$$

Compare this to the complete hydration of a mixture of alite and reactive silica:

$$\begin{array}{ccccccc} C_3S & + & 0.76\ S & + & 7.04\ H & \Rightarrow & 1.76\ C_{1.7}SH_4 \\ 228.3 & + & 46.0 & + & 127.2 & \Rightarrow & 401.5\ (\mathrm{g}) \\ 73.1 & + & 20.9 & + & 127.2 & \Rightarrow & 200.8\ (\mathrm{ml}) \end{array}$$

$$\text{Solid volume ratio (hydrates/dry powder)} = \mathbf{2.14} \tag{8}$$

$$\text{Volume of hydrates per mass of initial dry powder} = \mathbf{0.73\ ml/g}$$

$$\text{Volume of hydrates per mass of } C_3S = \mathbf{0.88\ ml/g}$$

Both of the above equations are similarly effective in the creation of hydrate volume from total solid reactants, but Eq. (7) is much more efficient in terms of its use of "clinker" phases because it also combines a lot of gypsum that does not have to be heat treated in a kiln. This makes it potentially a much more efficient cementing system in terms of total CO_2 emissions. Similar conclusions apply to the hydration of monocalcium aluminate (CA) in suitable combinations with lime and calcium sulfates to give ettringite.

Eq. (7) is not the most typical embodiment of calcium sulfoaluminate cement technology, as there are many practical problems with such ettringitic cementing systems, especially the problem of controlling the expansion associated with the reaction. If one wishes to make use of ettringite as a major cementing phase, there is an older technology that still has great interest: that of "supersulfated" slag cements. Such cements, based on ground granulated blast-furnace slag (GGBFS) with fairly large amounts (10–20%) of gypsum or anhydrite, plus a very small amount of lime or portland cement as a catalyst, can give volume-stable concretes in which ettringite and C-S-H are the main hydrate phases. However, their strength development is slow compared with that of portland cements, and the concretes are more easily carbonated, sometimes leading to strength loss and corrosion of reinforcing steel. As a result, they have fallen out of favour with concrete users and most of the available GGBFS is instead currently used in blends with portland cement. Nevertheless, given that GGBFS is an industrial by-product and can thus be considered to have zero associated CO_2 emissions, supersulfated cements still appear to be a promising area for additional research.

Although calcium sulfoaluminate-based cements are increasingly being used in specialised applications where high early strengths and self-stressing or shrinkage compensation are required, their more general application to concrete is limited to China, where a wide range of $C_4A_3\bar{S}$-based cements have been developed and normalised under the name of the "Third Cement Series" (TCS) [8]. In the Chinese literature, it is stated that these cements, which are based on clinkers containing $C_4A_3\bar{S}$, belite and ferrite in various proportions as their major phases, can be used in a wide variety of applications depending on their different phase compositions and on the amount of gypsum or anhydrite interground to make the final cement. However, as far as we are aware, the TCS technology currently practiced in China is based mainly on clinkers with fairly high $C_4A_3\bar{S}$ contents (60–70%), aimed at the prestressed concrete sector in which the rapid strength development at moderate curing temperatures, plus self-stressing, are economic advantages. Such cements must usually be manufactured using bauxite as a principal raw material, and this makes them relatively expensive compared with portland cements. It should be noted that the same comment applies to the more traditional calcium aluminate cements, such as the classic "Fondu" cement, which is rich in monocalcium aluminate and thus has a fairly low $RMCO_2$. However, in addition to its higher raw materials cost, Fondu clinker is made by a melt process, which is not very energy efficient compared with the Chinese TCS approach (which makes use of conventional rotary kilns).

The TCS approach has also been reexamined recently in some eastern European countries [9], with the objective of making energy-efficient sulfoaluminate-belite cements with lower $C_4A_3\bar{S}$ contents and higher belite contents than those produced in China. However, published results are disappointing apparently due to the same problem of low belite reactivity that affects belite-rich portland cements, so it is not yet clear whether TCS cements are really capable of offering very significant global CO_2 savings.

7. Calcium sulfate-based cements

The hydration of calcium sulfate hemihydrate ("plaster") to give gypsum is probably the best known and most ancient cementing reaction and has the advantage of very rapid but controllable setting and hardening rates, good global raw materials availability and very low process energy requirements, although it creates less hydrate volume than Eqs. (7) or (8):

$$\begin{array}{lllll} C\bar{S}H_{0.5} & + & 1.5H & \Rightarrow & C\bar{S}H_2 \\ 145.2 & + & 27.0 & \Rightarrow & 172.2\ (g) \\ 53.1 & + & 27.0 & \Rightarrow & 74.5\ (ml); \end{array} \qquad (9)$$

$$\text{Solid volume ratio (hydrates/dry powder)} = \mathbf{1.40}$$

$$\text{Volume of hydrates per mass of initial dry powder} = \mathbf{0.51\ ml/g}$$

The $RMCO_2$ is zero and the $FDCO_2$ is very low even compared with calcium (sulfo)aluminate cements. The main disadvantage is the softness and high solubility of gypsum, which results in the low durability of gypsum-based mortars in outdoor exposure. Nevertheless, very dense (low-porosity) gypsum (alabaster) can be fairly durable and really quite strong. Thus, there may well be some circumstances in which gypsum-based cementing systems could be of interest for replacing portland cements, especially when the gypsum produced by hydration of plaster or anhydrite can be combined with moderate amounts of relatively inexpensive additives, such as calcium aluminates or silicates, to help further stabilise it toward softening by water. It has also been shown that addition of 25% of a suitable portland–pozzolan cement to gypsum plasters can strengthen and stabilise the material under completely wet conditions [10].

Of course, gypsum-rich cements are not well suited to use with ordinary steel reinforcement because they offer little corrosion protection. However, they are more compatible with glass fibre reinforcement, which could allow for the production of low-cost, low-energy gypsum-based composites. Thus, such systems appear to be another promising research avenue in the long-term quest to reduce the global CO_2 emissions associated with construction.

It is apparent that natural calcium sulfate sources contain no CO_2 and require very little processing energy for their activation, but they are also far less abundant and widespread than limestones. However, large volumes of by-product calcium sulfates are now being produced worldwide by gas desulfurisation processes, most frequently associated with coal- and oil-fired electric power plants; the abundance of such sources is likely to increase rapidly as more and more societies increase their demand for electricity and also adopt stringent sulfur dioxide emission controls. It is interesting to note that most SO_2 control technologies are actually net CO_2 emitters because they make either direct or indirect use of limestone as the neutraliser, the principal reaction being the formation of calcium sulfite hemihydrate:

$$2SO_2 + 2CaCO_3 + H_2O \Rightarrow 2CaSO_3 \cdot H_2O + 2CO_2 \qquad (10)$$

Thus, for each molecule of SO_2 captured, one molecule of CO_2 is emitted. Nevertheless, the environmental benefits of this process would be very evident to anyone living near the plant in question, because SO_2 is a toxic gas that causes severe respiratory problems at quite low concentrations, where as CO_2 is essentially nontoxic and is essential for all life on earth.

Calcium sulfite hemihydrate is a by-product that is hard to dewater and has few direct uses, so it is often oxidised to gypsum (by a catalytic process), giving the overall equation:

$$2SO_2 + 2CaCO_3 + 4H_2O + O_2 \Rightarrow 2CaSO_4 \cdot 2H_2O + 2CO_2 \qquad (11)$$

The resulting gypsum, known as flue gas desulfurisation (FGD) gypsum, is now widely used as an alternative to natural gypsum for the manufacture of gypsum products and could also be used to provide calcium sulfate for low-CO_2 cements.

8. Concluding remarks

Based on the present analysis, the most promising low-CO_2 alternative cementing systems appear to be those that make use of large amounts of either natural or artificial pozzolans or those that effectively stabilise hydrated calcium sulfates (e.g., as ettringite). There are several alternative cementing systems that could result in overall reductions in CO_2 emissions per unit volume of concrete relative to pure portland cements and even, to some extent, relative to portland cements that have been fully reacted with pozzolanic materials to convert all free lime into calcium silicate and aluminate hydrates. However, this article has not attempted to make any practical performance comparisons of such alternative cementing systems, mainly because very few published performance data exist for the systems that appear to be of most interest for CO_2 emissions reduction per unit volume of concrete.

Clearly, if any alternative cementing system is ultimately to have a real impact on global CO_2 emissions related to the construction industry, it will have to have performance and durability characteristics at least as good as the current generation of portland-based cements, and probably even better, because it is likely to be, at least initially, more expensive to the consumer. The establishment of the performance and durability of alternative cements and concretes to the level required for the introduction of the appropriate new standards and construction codes is likely to be a very expensive undertaking because a large number of tests (and committee meetings) will be required. It will evidently require the full participation and cooperation of industry, government, the scientific community and members of the general public. It is only by such a concerted effort that our society can hope to bring about the long-term changes necessary to make our built environment truly sustainable.

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