

# The Production of Low Energy Cements

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## 8.1 INTRODUCTION

Rising levels of ‘greenhouse’ gases in the atmosphere, and the associated increase in temperature of the environment, are potentially able to alter the ability of the planet to support present life forms.<sup>1</sup> These greenhouse gases are characterised by showing radiation absorption bands in the infrared region of the spectrum; examples are carbon dioxide, methane, ozone, NO<sub>x</sub> and chlorofluorocarbons.<sup>2</sup> The most important greenhouse gas is carbon dioxide due to the volume produced. While there are still some who question the validity of the accepted mechanism of global warming,<sup>3–6</sup> most of the scientific community find that greenhouse gases result in an increased temperature for the Earth’s troposphere. Action is being proposed on a worldwide scale to limit the use of fossil fuels which release CO<sub>2</sub> on combustion.<sup>7</sup> The Intergovernmental Panel on Climate Change<sup>7</sup> (IPCC) estimates that the average rise in temperature of the environment should reach between 1.9°C and 5.3°C in the next 100 years. In the European Union 2030 framework for climate and energy policies, they propose to reduce the EU domestic greenhouse gas emissions by 40% below the 1990 levels as part of the target of cutting greenhouse gas emissions by at least 80% by 2050.<sup>8</sup>

In addition to their contribution to global warming, fossil fuels are a relatively scarce resource with residual lives in the 100s of years and a view is slowly developing that they are too valuable to burn as fuels. As a consequence, the cement industry is now widely adopting the use of secondary fuels. These fuels range from crumbed tyres through waste organic solvents to domestic waste. As domestic waste often contains a significant proportion of plastics, the chloride content of the resulting cement increases and this is undesirable from a concrete producer’s viewpoint, see [Section 8.3](#). Nevertheless in 2006, 90% of the total energy used in cement production still came from conventional fuels, mainly coal.<sup>9</sup>

On a more philosophical level, should the focus not be on low energy but on carbon dioxide released into the atmosphere adding to global warming and on ensuring that our natural resources are available to future generations? Some means of producing energy do not add significantly to global warming. Hydro-electricity and tidal power do not add to global warming if the convention of not including the infrastructure is followed. All fossil fuels have a relatively short life when one takes into account the length of time we hope humanity will survive, and it can be argued that they are too valuable to be used as fuel. By focusing on any single aspect of sustainability, there can be unintended consequences. A large increase in the percentage of fuel from biofuels will lead to reductions in natural habitat, indigenous people losing access to land they have used for centuries, less land for agriculture and rising food prices and social consequences. Issues have to be assessed in the round and all aspects of sustainability taken into account.

The term ‘low energy’ is used in several ways. In its purest form it means ‘low energy’ in absolute terms. For example, a grinding aid is intended to reduce the energy needed to grind the clinker and this will have an absolute impact on energy use, provided the grinding aid does not use more energy to manufacture and transport than that saved during the manufacture of the clinker. ‘Low energy’ is also used when meaning low primary energy, which is energy from primary fuels such as coal and oil. The opposite of ‘primary fuels’ is ‘secondary fuels’ and this includes energy giving wastes, for example domestic waste, tyres, wood wastes and organic solvents, and byproducts such as petcoke. Petroleum coke (often abbreviated ‘pet coke’ or ‘petcoke’) is a carbonaceous solid delivered from oil refinery coker units or other cracking processes. Coking processes that can be employed for making petcoke include contact coking, fluid coking, flexi coking and delayed coking. Crops grown specifically for biofuels are classed as primary fuels and this has led to another understanding of ‘low energy’; meaning low energy in terms of non-renewable energy. In this case, biofuels would not be included in the calculation of ‘low energy’. In this chapter the term ‘low energy’ is taken as low energy in absolute terms, but accepted rules for allocation are taken into account.

The cement production industry has been identified as one of the most important users of carbon-based fuels as a source of heat energy and also as an industry in which the technology exists for large savings in this respect.<sup>10</sup>

Cement production is much higher in the developing world, in China and India for example, than in the Western countries, see [Table 8.1](#) and any attempt to limit CO<sub>2</sub> emissions (and Portland cement production) to below the 1990 levels (as proposed in Europe) will be unacceptable to the developing world. [Table 8.1](#) shows that even if the EU achieve its target for CO<sub>2</sub> reductions in Europe, it will have a relatively small impact on the total emissions from the cement industry.

**TABLE 8.1** Cement Production in 2013 (CEMBUREAU Data<sup>11</sup>)

World Cement Production in 2013 Was Around 4 Billion Tonnes	
Region	Total Production (%)
China	58.6
Asia excluding China, India and Japan	12.3
India	7.0
CEMBUREAU <sup>a</sup>	5.8
America excluding USA	4.9
Africa	4.8
Commonwealth of Independent States	2.6
USA	1.9
Japan	1.5
Oceania	0.3
Europe excluding CEMBUREAU <sup>a</sup>	0.2

<sup>a</sup>CEMBUREAU is the European Cement Association based in Brussels. Currently, its full members are the national cement industry associations and cement companies of the European Union (with the exception of Cyprus, Malta and Slovakia) plus Norway, Switzerland and Turkey. Croatia and Serbia are Associate Members of CEMBUREAU.

There are several approaches to producing low energy cements and these are introduced in [Section 8.2](#) and described in more detail in the subsequent sections.

In reality it is concrete, not cement that has to provide the structural strength and durability of the concrete infrastructure and buildings, and consequently any consideration of the global warming potential of cement is secondary to the consideration of the global warming potential of comparable functional elements. While the cement type is an important factor in the global warming potential of a concrete functional element, it is also affected by the size of the element, the w/c (water:cement) ratio and the cement content and these are considerations that are outside the present scope of this book.

## 8.2 APPROACHES TO PRODUCING LOW ENERGY CEMENTS

The main approaches to producing low energy cements may be grouped into:

- use of waste-derived materials to replace fossil fuels, see [Section 8.3](#);
- lowering the energy required in the production of Portland cement clinkers, see [Section 8.3](#);
- highly reactive Portland cement clinkers so that less is needed to achieve the same concrete strength, see [Section 8.4](#);
- belite cements, see [Section 8.5](#);
- blended cements by diluting Portland cement clinker with other constituents, see [Section 8.6](#);
- use of lower energy non-Portland cements, see [Section 8.7](#).

These approaches are often combined to produce cements that use less energy in their production. Low energy in terms of what is released during cement hydration, that is low heat and very low heat cements, is not within the scope of this chapter, but such cements are often also cements that use less energy in their production.

## 8.3 LOWERING THE ENERGY REQUIRED IN THE PRODUCTION OF PORTLAND CEMENT CLINKER

Over the past decade, there has been concerted effort to reduce the energy derived from fossil fuels to manufacture Portland cement. In the United Kingdom, waste-derived fuels are rigidly specified and sourced from among: used tyres (whole or chipped), secondary liquid fuels (recycled inks, solvents, thinners, oils and residues), wood, packaging wastes (non-recyclable paper, cardboard and plastics), sewage sludge (pellets), residual household waste, commercial and industrial waste and meat and bone meal (MBM). There can be significant regulation of these materials but generally environmental impact assessments have shown these materials to be acceptable to environmental regulators.

Both waste-derived fuels (called alternative fuels) and biomass are used as substitutes for fossil fuels. Waste-derived fuels, like fossil fuels, are predominantly hydrocarbons which, when burnt during cement manufacture, are almost entirely decomposed to carbon dioxide and water with insignificant amounts of more complex carbon-based compounds. A small residue of ash is formed from liquid fuels, larger quantities are formed from solid fuels but these are bound into the cement clinker.

As an example, tyres burn to give a residue that is mainly iron, thus reducing the need for additional iron ore to be added as a raw material component.

The use of waste-derived fuels and replacement raw materials in cement manufacture is a well-established practice in the United States and Europe and, most importantly, there have been no reported issues or adverse impact on concrete performance related to their use. Domestic waste in North America and Europe contains a significant proportion of plastics, and these increase the chloride level of the cement, but cement specifications put a limit on the chloride content of cements.<sup>12</sup>

At the global level cement manufacture used 7% alternative fuels and 3% biomass,<sup>9</sup> but there are significant variations. In some European countries the average substitution rate for the industrial sector reaches 50% and in individual plants reaches 80% as a yearly average.<sup>9</sup>

As well as the direct impact of using waste fuels for cement production, diverting these materials from landfill has an additional benefit as 60% of landfill gas is methane,<sup>9</sup> which is a gas that has a global warming potential in the range 28–36 times that of carbon dioxide over 100 years.<sup>9(a)</sup>

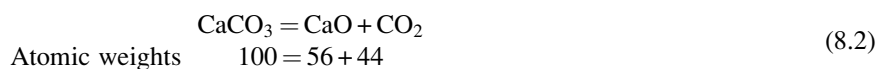
Although energy use in the cement manufacturing industry usually, but not always, results in the release of CO<sub>2</sub>, it is the release of CO<sub>2</sub> to the atmosphere and the use of relatively scarce fossil fuels that are chief concerns with respect to a sustainable future.

In June 2008, the International Energy Agency published a report<sup>10</sup> setting out road maps for 70 industries to achieve long-term carbon dioxide savings. This report includes the cement production industry as it is one of the most important users of carbon-based fuels as a source of heat energy and also as an industry in which the technology exists for large savings in this respect. In addition, calcination of limestone constituents, which is an initial step in traditional cement production, release additional CO<sub>2</sub> to the atmosphere. Portland cement production involves the sintering of raw feed (composed of limestone and clay) at about 1450°C and then grinding the cooled clinker with 5% gypsum rock and 5% of a minor additional constituent, usually limestone. The average energy to produce clinker is 3690 MJ/t with the 10% best plants achieving  $\leq 3100$  MJ/t and the worse 10% of plants being  $\geq 4400$  MJ/t.<sup>9</sup> The theoretical heat energy requirement to form Portland cement clinker is calculated to depend on the percentage of limestone employed, or the lime saturation factor (LSF),

$$\text{Lime saturation factor} = \frac{100\% \text{CaO} + 75\% \text{MgO}}{2.8\% \text{SiO}_2 + 1.18\% \text{Al}_2\text{O}_3 + 0.65\% \text{Fe}_2\text{O}_3} \quad (8.1)$$

rising from about 1570 to 1800 kJ/kg as the LSF is increased from 80% to 100%.<sup>11</sup> Depending upon the moisture content of the raw materials a further 200–1000 MJ/t corresponding to moisture contents of 3%–15% is needed to dry the materials.<sup>9</sup> This gives theoretical minimum energy demands of 1850–2800 MJ/t clinker for chemical and mineralogical reactions and drying. The ‘waste heat’ (kiln exhaust gas, bypass gas and/or cooler exhaust gas) is often used to dry the raw materials or generate electricity.<sup>9</sup> The energy efficiency of cement kilns is very high compared to many other industrial processes.<sup>9</sup>

Calcination of limestone (CaCO<sub>3</sub>) results in the release of CO<sub>2</sub> and, since natural limestone and chalk are the only large-scale sources of calcium available to the cement industry, this aspect of CO<sub>2</sub> release is only reducible by changing the chemical composition of the cement, see Chapter 4: *The Constitution and Specification of Portland Cements*. Accepting that the thermal energy requirement for very efficient Portland cement production may be 2930 kJ/kg, and that 1 kg of Portland cement requires the decomposition of 1.209 kg of CaCO<sub>3</sub>, then the production of 1 kg Portland cement clinker, or the decomposition of 1.209 kg of CaCO<sub>3</sub>, releases  $44/100 \times 1.209 = 0.5320$  kg CO<sub>2</sub> into the atmosphere since:



If carbon is the fuel used in firing the kiln:



releasing 94,052 cal/mol; or 7837.7 cal/g, equivalent to 32,792 J/g. To burn 1 kg of Portland cement clinker requires 2930/32,792 = 0.08935 kg of carbon to be burnt, thus releasing  $44/12 \times 0.08935 = 0.3276$  kg of CO<sub>2</sub> to the atmosphere.

Although energy use and release of CO<sub>2</sub> are closely related in the usual cement manufacturing industry, it is the release of CO<sub>2</sub> to the atmosphere rather than the consumption of energy which is of chief concern. The electrical energy required is additional to the above calculations. The average global energy consumption for cement manufacturing was 111 kWh/t with the best 10% being  $\leq 89$  kWh/t and the worse 10% being  $\geq 130$  kWh/t.<sup>9</sup> For the dry process this energy is split as 5% for raw material extraction and blending, 24% for raw material grinding, 6% for raw material homogenisation, 22% clinker production including solid fuel grinding, 38% cement grinding and 5% for conveying, packing and loading.<sup>9</sup> Assuming a 40% efficiency in the generation of electricity, this amounts to 1080 kJ heat energy/kg clinker. If carbon is again burnt then

$1080/32792.8 = 0.03293$  kg is required, or the release of a further 0.1208 kg CO<sub>2</sub> takes place. If fuel oil or natural gas is substituted for carbon in the burning of the clinker or the generation of electrical power, the quantity of CO<sub>2</sub> released is reduced. The generation of electricity by solar, hydro, tidal or nuclear sources will also reduce the CO<sub>2</sub> release of cement.

Traditional Portland cement clinker formation is being made more efficient and the energy requirements in the different steps reduced. The life of a cement plant is typically 30–50 years, but cement plants are subject to continual modernisation. While changes to the preheater cyclones, clinker cooler and separators are relatively easy to install changing to, for example, more efficient grinding is a major refit. The trends in cement production are clear, large capacity plants with the dry process, multiple cyclones, precalciner, clinker cooling, vertical roller mills or high pressure grinding rolls, high efficiency separators and sophisticated automatic control all giving improvements in the plant efficiency and represent best available technology (BAT). The various papers<sup>9,13–15</sup> describe the efficiency savings these different processes can achieve and these are summarised in [Table 8.2](#), see also Chapter 2: *Manufacture of Portland Cement*.

A completely new type of kiln design is under development, which uses fluidized bed technology. In this system finely ground raw meal is pneumatically conveyed to the fluidized bed along with fuel and preheated air from the bottom while fine recycled clinker particles are fed in at a higher level. The clinker grows on these recycled particles forming a clinker that is much finer than normal. Energy savings come from the efficient use of waste heat. This technology has only been used so far in small demonstration plants and it has shown a thermal energy saving of 300 MJ/t clinker but an increase in electrical energy of 9 kWh/t clinker and a potential net saving of about 20 kg CO<sub>2</sub>/t clinker.<sup>9</sup> The energy savings in full sized production units still has to be established.

Switching from coal to heavy oil or natural gas will reduce the carbon dioxide emissions (lignite coal 98 kg CO<sub>2</sub>/GJ, hard coal 95 kg CO<sub>2</sub>/GJ, heavy oil 78 kg CO<sub>2</sub>/GJ and natural gas 56 kg CO<sub>2</sub>/GJ)<sup>9</sup> but these fuels are also relatively scarce fossil fuels and such a change is only economic in oil and gas producing countries.

The cement industry already uses a wide range of alternative fuels, [Table 8.3](#). Biomass may be a waste from other processes but it may also be grown for the sole purpose of producing biofuels. The use of such fuels does not contribute directly to low energy cements, but they do reduce the use of primary fuels and waste. The high burning temperature within a cement kiln is also a very effective way of completely destroying organic compounds such as dioxins. Many of these wastes will also reduce the quantity of primary materials needed as their ashes form part of the cement. Plastic wastes tend to increase the chloride content of the cement and this is undesirable from a concrete producer's viewpoint. The trend to use larger quantities of alternative fuels and biomass will continue. While biofuels may appear to be the way forward, there might be serious social and economic impacts on local populations by following this route, for example, land not available for food production; crops being used for fuel and not food, rising food prices.

There is some scope, albeit limited to a few locations where suitable materials are available, to use raw materials that are already calcined. Examples of such materials are blastfurnace slag, lignite ash, coal ash, crushed concrete fines, some fractions of demolition wastes and the lime residues from the sugar industry. CO<sub>2</sub> savings come from not having to calcine these materials and possible reductions in fuel consumption. While fuel consumption may reduce, this might be due to the carbon in the fly ashes and when burnt, this will also produce CO<sub>2</sub>.

It seems that usually more than half the CO<sub>2</sub> released in the process of Portland cement production arises from the calcination of the raw feed, with a smaller fraction resulting from the burning of fuel. The release of this carbon dioxide to the atmosphere can be reduced by carbon capture and storage systems but this will result in an increase in the use of energy.<sup>9</sup> At present no cement plant is fitted with this technology and from an economic viewpoint, it is uneconomic involving very high capital costs and an increase in the use of electrical energy; however, achieving the European Union's target of an 80% reduction in CO<sub>2</sub> from 1990 levels by 2050<sup>8</sup> does not appear to be feasible without adopting this technology and this will require political action to ensure that such plants are not commercially disadvantaged.

**TABLE 8.2** Heat Consumption of Different Kiln Technologies<sup>13</sup>

Process	Heat Consumption (GJ/t)	Efficiency (%)
Vertical shaft kilns	Approximately 5.0	35
Wet process	5.9–6.7	26–30
Dry process		
Long dry process	4.6	38
One stage cyclone preheater	4.2	42
Two stage cyclone preheater	3.8	46
Four stage cyclone preheater	3.3	53
Four stage preheater + precalciner	3.1	56
Five stage preheater + precalciner (best available technology)	3.0–3.1	58

**TABLE 8.3** Calorific Values of Alternative Fuels<sup>16</sup>

Fuel Type	Net Calorific Value (MJ/kg)
Polyethylene	46
Light fuel oil/diesel (for comparison)	42
Heavy fuel oil (for comparison)	40
Tar	38
Animal fat	37
Rubber	36
Waste oils, refinery wastes	30–40
Petcoke (for comparison)	33
Waste tyres	28–32
Low ash bituminous coal (for comparison)	27
Combustible de substitution liquid (CSL, Seneffe) <sup>a</sup>	20–30
Plastic fluff	18–22
Landfill gas	16–20/Nm <sup>3</sup>
Animal meal	18
Dry wood, rice husks (10% water)	16
Impregnated saw dust (25% water, CSS, Seneffe) <sup>a</sup>	10–13
Dried sewage sludge (10% water)	10
Unsorted domestic refuse (30% water)	8.5

<sup>a</sup>Value specific to the product produced in Seneffe.

Carbon emissions are usually expressed as CO<sub>2</sub> e. This carbon dioxide equivalent is a unit of measurement of the release of all the gases that potentially impact global warming. It takes into account the relative impact of each gas on global warming. For example, methane has a global warming potential between 21 and 25,<sup>16(a)</sup> it means that 1 kg of methane has the same impact on climate change as 21–25 kg of carbon dioxide and thus 1 kg of methane would count as 21–25 kg of CO<sub>2</sub> e (for calculations the average value of 23 kg of CO<sub>2</sub> e is often used). Other publications, e.g. EPA<sup>9(a)</sup>, give higher values of global warming potential as the value depends upon the period being considered.

Embodied carbon is the CO<sub>2</sub> e emissions associated with energy consumption (embodied energy) and chemical processes during the extraction, manufacture, transportation, assembly, replacement and deconstruction of construction materials or products. Embodied carbon can be measured from cradle-to-gate, cradle-to-site, cradle-to-end of construction, cradle-to-grave, or even cradle-to-cradle. The typical embodied carbon datasets are cradle-to-gate. Embodied carbon is usually expressed in kilograms of CO<sub>2</sub> e per kg of product or material.

In the United Kingdom, indicative carbon dioxide equivalent (CO<sub>2</sub> e) for the main cementitious constituents of concrete have been published by the Mineral Products Association<sup>17</sup> (see Tables 8.4 and 8.5) and have been derived from calendar

**TABLE 8.4** CO<sub>2</sub> e of UK Portland Cement (CEM 1), Additions and Cementitious Material

Cement, Additions and Cementitious Material	CO <sub>2</sub> e (kg/t)
Portland cement CEM I: cradle to factory gate	913
Ground granulated blastfurnace slag (ggbs)	67
Fly ash (from coal burning power generation)	4
Limestone fines	75

**TABLE 8.5** CO<sub>2</sub> e of UK Factory Made Cements

Cement	Secondary Main Constituent (%)	CO <sub>2</sub> e (kg/t)
CEM II/A-LL or L Portland limestone cement	6–20	859–745
CEM II/A-V Portland fly ash cement	6–20	859–746
CEM II/B-V Portland fly ash cement	21–35	728–615
CEM II/B-S Portland slag cement	21–35	743–639
CEM III/A Blastfurnace cement	36–65	622–398
CEM III/B Blastfurnace cement	66–80	381–277
CEM IV/B-V pozzolanic (siliceous fly ash) cement	36–55	598–441



2010 data. Data are 'cradle to factory gate', so transport from the place of manufacture of the cementitious material to the concrete plant is not included.

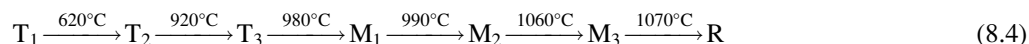
## 8.4 HIGHLY REACTIVE PORTLAND CEMENT CLINKERS

More efficient use of the Portland cement produced can be achieved by increasing its hydraulic activity, and thus encouraging the use of leaner concrete mixes or a higher proportion of a second main constituent. A modification of the raw feed in Portland cement clinker production, to include minor percentages (0.25%) of fluoride (F), for example, can lead to increased reactivity,<sup>18</sup> as can increasing the speed of cooling of the clinker. The reduced clinkering temperature possible by the use of mineralisers may bring about savings in energy, however the energy savings to be made by bringing the firing temperature down from 1450°C to 1350°C in industrial practice amount to only 5%.<sup>19,20</sup> Reduced firing temperature should allow low grade fuels to be utilised and will also reduce the emission of the greenhouse gas NO<sub>x</sub>.

If chloride is added, a salt melt forms and a modification to the clinker minerals is introduced, to give alinite in which oxygen ions are partially substituted by chlorine and silica by alumina, and it can be represented by the general formula: Ca<sub>10</sub>Mg<sub>1-x/2</sub>V<sub>x/2</sub>[(SiO<sub>4</sub>)<sub>3+x</sub>(AlO<sub>4</sub>)<sub>1-x</sub>]O<sub>2</sub>Cl (V: a lattice vacancy, 0.35 < x < 0.45).<sup>21</sup> The burning temperature of the clinker is stated to be reduced to between 1000°C and 1100°C, and an overall saving in heat plus electrical energy of up to 30% has been claimed.<sup>19</sup> The raw mix contains between 6% and 25% CaCl<sub>2</sub> with the remaining composition similar to that of Portland cement raw feed.<sup>22</sup> The presence of chloride in the clinker raises doubts concerning the suitability of this cement for use in steel-reinforced concrete. Substitution of CaF<sub>2</sub> for the chloride removes this problem and has been shown to lead to satisfactory clinkers at 1150°C.<sup>23</sup>

Subsequent dilution of these highly reactive Portland cements with low-energy waste material or ground limestone can be made without a reduction in performance from accepted levels for the blend (see Section 8.6).

Pure C<sub>3</sub>S exhibits seven distinct polymorphic forms, depending on the formation temperature and pressure. Although all forms of alite are metastable at temperatures below about 1252°C<sup>24</sup> and slowly transform to C<sub>2</sub>S plus CaO, transition temperatures for rapid transformations between the polymorphic forms have been established. The slow decomposition of C<sub>3</sub>S to C<sub>2</sub>S and CaO normally occurs at temperatures below about 1250°C:



where T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub> are the three triclinic polymorphs, M<sub>1</sub>, M<sub>2</sub> and M<sub>3</sub> are the three monoclinic polymorphs and R is a rhombohedral high temperature polymorph.<sup>25</sup>

The pure compound when cooled to room temperature is the T<sub>1</sub> polymorph of C<sub>3</sub>S. In production clinkers, due to the incorporation of foreign ions, the form present at room temperature is normally the M<sub>1</sub> or M<sub>3</sub> forms of C<sub>3</sub>S. The introduction of minor amounts of other components into the crystal composition enables the retention of higher temperature forms at lower temperatures.

The quantities of foreign ions that can be inserted into the crystal structure are limited. In general, greater quantities of foreign ions can be inserted at higher temperatures than at lower temperatures, so that the rhombohedral form is expected to be able to accommodate more foreign ions than the triclinic or monoclinic forms. Boikova<sup>26</sup> reported the stabilisation of the different forms of C<sub>3</sub>S with ZnO (T<sub>1</sub> up to 1%, T<sub>2</sub> and T<sub>3</sub> from 1% to 2%, M<sub>1</sub> from 2% to 2.5%, M<sub>2</sub> from 2.5% to 4%, and R from 4% to 5%). The greatest hydration activity was at 4% ZnO where the crystal structural arrangement was changing to the rhombohedral form.

Between 3% and 4% of the composition of Portland cement clinker can be designated as composed of minor components. The minor components P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, K<sub>2</sub>O and SO<sub>3</sub> primarily enter into solid solution with belite and the rate of combination of CaO to form alite is slowed down. The role of CaF<sub>2</sub> in the formation of cement clinker from phosphatic limestone has been examined in detail: the tolerance for phosphate is substantially greater in the presence of fluoride.<sup>27</sup> The effects of some additives (fluorspar, anhydrite, sodium and potassium sulfate) on the rate of the reaction C + C<sub>2</sub>S = C<sub>3</sub>S have been studied under isothermal conditions between 1350°C and 1500°C.<sup>28</sup> Fluorspar acts as an accelerator while the others retard the formation of alite. A compound (C<sub>3</sub>S)<sub>3</sub>CaF<sub>2</sub> is formed at ~1100°C.<sup>29</sup> A raw feed was given various additions of MgO, SO<sub>3</sub> and ZnO, and the specimens were burned at 1500°C.<sup>30</sup> Additions of SO<sub>3</sub> made sintering more difficult due to the increased viscosity of the liquid melt, and the alite crystals became larger. Addition of MgO reduced the viscosity of the melt, and the alite crystals became smaller; at least 1.5% MgO can be absorbed by the clinker minerals. ZnO was easily absorbed by the silicate minerals and the alite became more stable.

The use of combined fluoride and sulfate mineraliser has been explored.<sup>31–34</sup> The compound fluorellestadite (3C<sub>2</sub>S:3CaSO<sub>4</sub>:CaF<sub>2</sub>) appears as an intermediate phase and results in a decrease in the maximum clinkering temperature to 1175°C. Clinkers with high alite content can be obtained at 1300°C and a melt is formed at 1180°C. For a synthetic alite

raw feed,<sup>35</sup> it was established that the most effective sintering aids were ZnO, CaF<sub>2</sub> and MnF<sub>2</sub>, allowing burning to be completed at ~1100°C. Low-temperature alite cements have been prepared using 2% additions of ZnO or CaF<sub>2</sub> as fluxing agent,<sup>35</sup> firing at 1150°C and 1250°C, respectively. The reactivity of alites produced at lower temperatures is enhanced and the microstructures of the clinker allows easier grinding.

Production trials with Aether cement,<sup>36</sup> which is a cement made from limestone, clay, iron oxide and bauxite, confirmed a firing temperature in the range 1225°C–1300°C giving a 25%–30% reduction in CO<sub>2</sub> during the production process<sup>36</sup>; however, it was noted that the control of temperature is critical.

The effects of fluxes and mineralisers upon phase equilibria in the system CaO–Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> have been investigated.<sup>28,37</sup> In the presence of CaF<sub>2</sub>, the temperature for first liquid formation is reduced and in the phase diagram, the primary phase of C<sub>12</sub>A<sub>7</sub> is expanded, while the phase area for C<sub>3</sub>A is greatly decreased.<sup>38</sup> The effects upon phase relations and related kinetic phenomena appear to be favourable to cement clinker manufacture, resulting in greater kiln efficiency.

The amount of clinker melt has an effect on the rate of formation of alite,<sup>39</sup> and the beneficial effects of fluoride arises partly as a result of the increased quantity of melt. A linear relationship has been found between the amount of melt liquid and the rate of formation of alite. Segregation of the melt into two liquid phases, which may have very different viscosities and surface tensions, may complicate the above relationship. For clinker melts containing 1%–5% fluoride, chloride or sulfate, the tendency to form two liquid phases increases in the following order:



Sulfated melts separate only in the presence of alkali metal ions. The addition of MgO or Mn<sub>2</sub>O<sub>3</sub> to the liquid phase changes its properties and, when the amount of Mg<sup>2+</sup> is large, separation into two liquid phases is suppressed. For melts containing chloride or fluoride, separation into two melts takes place more readily than with sulfate additions.

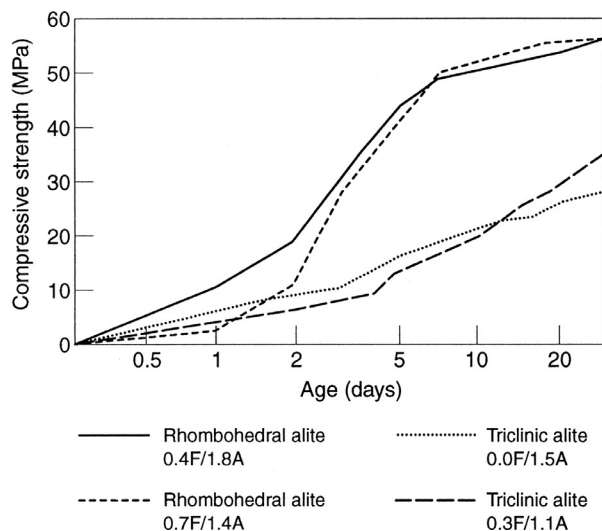
These salt melts have viscosities which may be half those of the usual oxide melts found in Portland cement clinker, and may have surface tensions one-quarter the value of the normal melt.

Fluorine-containing additives have a major influence on the composition of the liquid phase, and accelerate silicate mineral formation between 1200°C and 1300°C, permitting the formation of C<sub>3</sub>S below the usual stability range. MgO and K<sub>2</sub>SO<sub>4</sub> influence the partitioning of fluoride between silicate and interstitial phases, and have a further fluxing effect; the presence of MgO favours the partitioning of fluoride into the silicate phase while K<sub>2</sub>SO<sub>4</sub> increases volatilisation. The crystallisation of C<sub>3</sub>S results in the removal of fluoride from the interstitial phases, and causes a compositional shift from C<sub>11</sub>A<sub>7</sub> CaF<sub>2</sub> to C<sub>3</sub>A in the interstitial phase as the temperature is increased from 1100°C to 1300°C.

The effect of MgO content on unsoundness has been studied in relation to the speed of cooling and the C<sub>3</sub>A content.<sup>40</sup> Rapidly cooled clinker forms smaller alite and belite crystals, exhibits faster strength growth during hydration, and is able to accommodate the hydration of periclase (MgO). Slowly cooled clinkers containing 3% MgO are sound when containing 7% C<sub>3</sub>A but are unsound when C<sub>3</sub>A contents rise to 15%. The addition of 25% of a second main constituent (fly ash) effectively stabilises high MgO (10%) Portland cement clinker. In practice the requirement for a cement to be sound is specified by a performance test and not by compositional limits. For example EN 197-1<sup>12</sup> sets a limit of ≤10 mm when tested in accordance with EN 196-3.<sup>41</sup>

The strength performance of about 50 commercial cements has been analysed in terms of the types of alite and belite present.<sup>42</sup> High temperature forms (alite with high birefringence, and α-belite with a pale coloration) prove to be more hydraulically active and result in higher strengths. It is suggested that extended retention of the clinker at high temperatures, followed by quenching, allows crystal growth to occur and so restrains the crystal transformations and exsolution of impurities from the alite and belite crystals. Exsolution, which is a process by which a solid solution phase unmixes into two separate phases in the solid state, of dissolved Fe<sub>2</sub>O<sub>3</sub> results in the formation of orange-coloured particles of iron oxide within the belite crystals. The possibility of preparing cements with enhanced reactivity has been confirmed by the discovery of the exceptional properties for rhombohedral alite, the polymorph stable at the highest temperatures.<sup>43,44</sup> Surprisingly, the content of minor components in the high-temperature metastable transform (M<sub>3</sub>) is claimed to be less than in the low-temperature metastable transform (M<sub>1</sub>). The high-temperature metastable transform, with smaller amounts of minor and trace components, had a higher hydration reactivity and also a higher birefringence.<sup>45</sup>

Strength tests on mortar cubes have been reported for both pure and mineralised systems.<sup>46</sup> In all cases, mixes containing 0.5% fluoride (F) were substantially weaker than the corresponding mixes without fluoride, and this effect seemed unrelated to the polymorphic form produced. In contrast, the inclusion of fluoride plus Al<sub>2</sub>O<sub>3</sub> in the crystal lattice improved the stability range for the rhombohedral form of alite, and allowed its retention in quenched material.<sup>43</sup> Micro-concrete cube strength tests showed rates of strength growth up to twice that shown by the low-temperature (triclinic) form of alite (Fig. 8.1). The presence of fluoride causes a loss in hydraulic activity, but this can be restored by adding SO<sub>3</sub>.<sup>32,47</sup> The use of combinations of SO<sub>3</sub> and fluoride additions has been proposed<sup>31</sup> to allow the production of highly reactive Portland cements having increased alite content, with alite in the more reactive rhombohedral form (see Table 8.6).



**FIG. 8.1** Compressive strength of alites. (Source: Ono Y, Soda Y. *Effect of crystallographic properties of alite and belite on the strength of cement*. In: The cement association of Japan, 19th general meeting, Tokyo; 1965, Chapter 15. p. 78–82.)

**TABLE 8.6** Influence of Clinker Fluorine Content on Cement Quality<sup>31</sup>

Factor	1	2	3	4	5	6	7
K <sub>2</sub> O (%)	1.0	1.2	1.4	1.5	1.4	1.2	1.5
SO (%)	2.9	3.4	3.3	3.6	3.2	2.8	3.9
F <sub>2</sub> (%)	0.06	0.10	0.14	0.22	0.39	0.80	1.7
Free lime (%)	3.3	2.0	1.7	1.7	1.6	1.5	1.1
Standard consistence (%)	25.3	31.0	29.0	29.5	27.5	27.5	29.5
Initial set (min)	90	140	155	170	240	210	540
Final set (min)	110	175	205	220	310	260	660
<b>Concrete compressive strength (MPa)</b>							
8h	6.7	5.4	3.7	4.6	1.7	1.8	
16h	17.7	20.8	19.7	22.2	15.6	14.5	1.6
24h	22.9	30.0	29.3	33.2	26.6	19.4	11.6
3 days	33.9	41.9	43.2	46.5	47.5	44.6	38.6
7 days	42.3	48.2	50.2	52.0	55.3	57.1	46.8
28 days	51.9	54.0	56.2	60.7	65.9	66.4	56.0

The effects of fluoride-containing mineralisers and fluxes on the burnability of a series of synthetic raw mixes, ranging from the quaternary system CaO–Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> to more complex mixtures and industrial mixes, were determined.<sup>38</sup>

Factors that influence hydration and strength development (up to 28 days) have also been examined,<sup>38</sup> in most cases a significant increase in strength was obtained where mineralisers (CaF<sub>2</sub>, 0.5% F<sup>–</sup>) were present (Table 8.7), but a clinker containing a high alumina content ‘C’ showed reduced strength development at 1 and 28 days in the presence of CaF<sub>2</sub>.

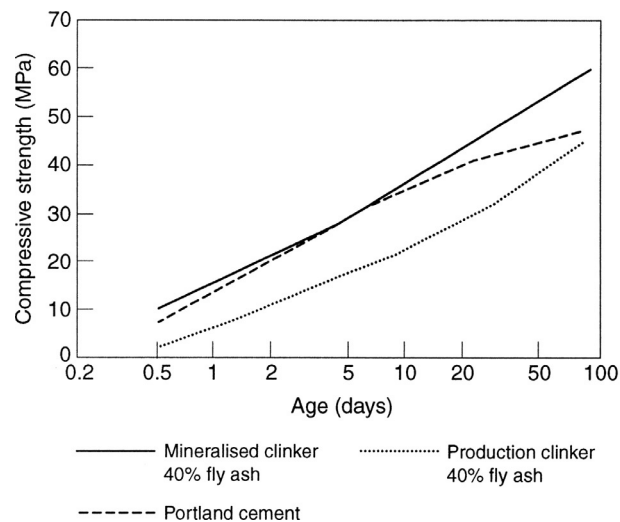
The action of different mineralisers has been investigated.<sup>23</sup> The use of mineralisers can be expected to reduce the burning temperature by over 100°C and give an energy saving of 2%–3%. A reduction in the sintering temperature by 200°C and in the calcining temperature by 50°C would be expected to give an energy saving of about 6%.<sup>23</sup> The performance of low-energy cements formed by mineralisation with CaF<sub>2</sub> and gypsum in sulfate solutions and sea water was reported to be satisfactory<sup>48</sup> and to be better than ordinary Portland cement (CEM 1). The mineralised clinker did not require the addition of gypsum to control the set since sufficient calcium langbeinite (K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) was present in the high-SO<sub>3</sub> clinker (2.6% SO<sub>3</sub> and 0.27% F<sup>–</sup>). It was concluded that only a limited saving of energy can be accomplished by the use of mineralisers and fluxes.<sup>20</sup> In one commercial production, the kiln temperature was reduced by 100°C and the fuel requirement by 3%. However, much larger savings were realised from the much longer life of the kiln linings and the 50% reductions in NO<sub>x</sub> emissions brought about by the reduced firing temperature. The mineralised cement was found to exhibit slightly reduced early strength, due to the



**TABLE 8.7** Compressive Strengths of Mortar Cubes Made From Synthetic Clinkers<sup>38</sup>

Cement Compositions (5% Gypsum) <sup>a</sup>	Compressive Strength (MPa)		
	1 Day	7 Days	28 Days
A + MgO + SO <sub>3</sub>	6.2	23.1	31.6
A + MgO + SO <sub>3</sub> + CaF <sub>2</sub>	10.1	29.2	34.8
B + MgO + SO <sub>3</sub>	7.3	22.6	33.6
B + MgO + SO <sub>3</sub> + CaF <sub>2</sub>	9.1	26.7	38.4
C + MgO + SO <sub>3</sub>	5.6	28.1	38.3
C + MgO + SO <sub>3</sub> + CaF <sub>2</sub>	1.2	20.8	32.5
Raw mix I + H <sub>2</sub> SiF <sub>6</sub> (0.3% F <sup>-</sup> )	10.8	31.1	35.6
Raw mix II + H <sub>2</sub> SiF <sub>6</sub> (0.6% F <sup>-</sup> )	6.3	28.1	33.6

<sup>a</sup>Synthetic clinkers, 1% additions of MgO, SO<sub>3</sub> as K<sub>2</sub>SO<sub>4</sub>, 0.5% F<sup>-</sup> burnt for 30 min at 1450°C.



**FIG. 8.2** Comparison of blended cement concrete strengths for mineralised and normal Portland cement clinker. (Source: Moir GK, Glasser FP. *Mineralisers, modifiers and activators in the clinkering process*. In: Proceedings of the ninth international congress on the chemistry of cement, New Delhi; 1992, vol. 1, p. 125–52.)

reduced lime saturation factor; however, the 28 day strength was increased as a result of the increased activity of the additional belite forms formed.<sup>19</sup>

The use of Portland cement clinkers which have enhanced activity due to the use of mineralisers allows the performance of blended cements to exceed those of pure Portland cement (CEM 1) (Fig. 8.2).<sup>49</sup> It has been shown that mineralised Portland cement clinker can be blended with limestone filler to give a cement with an exceptionally high early strength.<sup>18</sup>

The European Standard, EN 197-1,<sup>12</sup> for common cement types allows up to 5% addition of a minor additional constituent (MAC) to all of the cements covered by this standard.<sup>12</sup> EN 197-1 specifies the range of proportions of Portland cement clinker in each cement type<sup>12</sup> and for example, this is 95%–100% in CEM 1 (calcium sulfate and additives are not included in the composition calculations). While EN 197-1 permits a wide range of materials to be used for the MAC, in practice limestone is usually used as this material is available on site. A significant acceleration in setting and a reduction in bleeding have been found to occur where limestone is used for this 5% MAC, but the most important result of the adoption of the use of 5% MAC has allowed highly active Portland cement clinkers to be more coarsely ground. This reduces the rate of hydration and strength development at early ages but without increasing bleeding and segregation of mixes. The introduction of 5% MAC enables overall cement fineness to be maintained and 28 day strengths to be controlled over a range of levels, as required.

## 8.5 BELITE CEMENTS ( $C_2S$ CEMENTS)

Further reductions in  $CO_2$  emissions must involve a reduction in CaO content of the final cement, resulting in belite ( $2CaO \cdot SiO_2$ ) based cement rather than the present alite ( $3CaO \cdot SiO_2$ ) based cement. The substitution of a high-lime by a low-lime cement should lead to both energy saving and a reduction in  $CO_2$  emissions.<sup>20,50</sup> The belite formed normally has a low hydraulic reactivity with water and improvements are required if cement properties are to be maintained at present Portland cement levels. In order to increase the activity of the belite formed, it is frequently proposed that fast cooling should be adopted. This procedure leads to increased heat losses in the processing coolers, so the overall saving in fuel is questionable; however,  $CO_2$  emissions will be reduced in line with the reduction in lime standard, that is by about 25%.<sup>20</sup>

Work on the subject of belite cements can be split into three groups<sup>51</sup>:

1. hydraulic activity of the  $C_2S$  phase;
2. hydraulic activity of belite-rich cements without additional cementitious components;
3. hydraulic activity of belite-rich cements with additional components such as  $C_4A_3\bar{S}$ .

In group 3, low-energy production of a rapid-hardening, belite-rich cement is possible as a result of the sulfoaluminate content, even where the belite is in the usual P form having a low hydraulic reactivity.

The chemical composition of the blended raw feed and the final clinker may be represented using a number of component ratios in order to aid in the selection and control of manufacture. The lime saturation factor or lime standard is the most important of these ratios. It expresses the maximum amount of lime that can be combined with the various oxides present, based on the chemical formulae for the cement minerals being formed ( $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ ) and on the high-temperature phase diagram. A number of definitions of lime saturation factor are used in the literature,<sup>52</sup> for example, see Eq. (8.1).

One approach to a reduction in energy consumption and to a reduction in the release of  $CO_2$  in the production of cements is to reduce the lime saturation factor of the raw feed.<sup>53</sup> A reduction in lime saturation factor leads automatically to an increasing belite content and a decreasing alite content.<sup>51</sup> With lime saturation factor of 75%, a virtually alite-free clinker is obtained and  $C_{12}A_7$  is formed instead of  $C_3A$ .

A reduction in lime saturation factor from 100 to 75 results in a 12% reduction in theoretical heat requirement; however, a reduction of only 6% in  $CO_2$  emission occurs (Figs 8.3 and 8.4). This result appears to arise because of the reduced heat evolution during crystallisation of silicate minerals if they consist of belite rather than alite.

A predominantly belite cement has a theoretical heat of formation  $\sim 150$  kJ/kg less than a conventional alite cement.<sup>51</sup> In forming these cements, raw materials of lower lime content can be exploited. The reduction in  $CaCO_3$  content of the raw feed reduces the energy demand (by about 10% for a lime saturation factor of 80%–85%) and allows a satisfactory clinker to be formed at lower temperatures (lower by  $150^\circ C$ ) (Fig. 8.5).<sup>53</sup> Laboratory investigations have been carried out on cement raw feed based on natural marls, by heating 11 mm pressed cylinders up to clinkering temperature at  $50^\circ C/min$ , holding them at that temperature for 20 min, and then cooling at  $800^\circ C/min$ . Fig. 8.5 shows the reduction in firing temperature which is possible by reducing the lime saturation factor; however, clinkers with lime saturation factor  $III > 80\%$  still need to be fired at temperatures  $> 1250^\circ C$ .

A reduced lime saturation factor results in easier grinding. The compressive strength development for mortars made from laboratory cements of different lime saturation factor is shown in Fig. 8.6 fired at different temperatures according to Fig. 8.5.<sup>53</sup> The strength development for cements with lime saturation factors of 84% and above is adequate, even in the

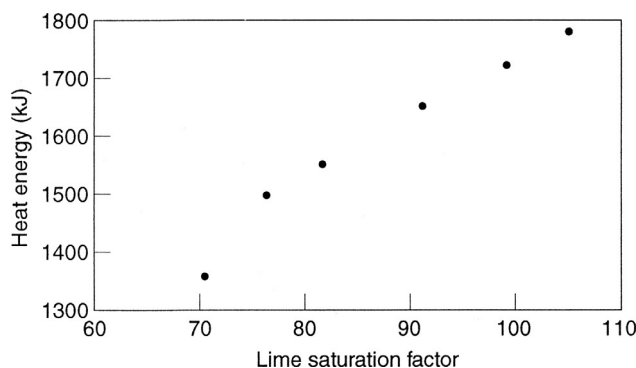
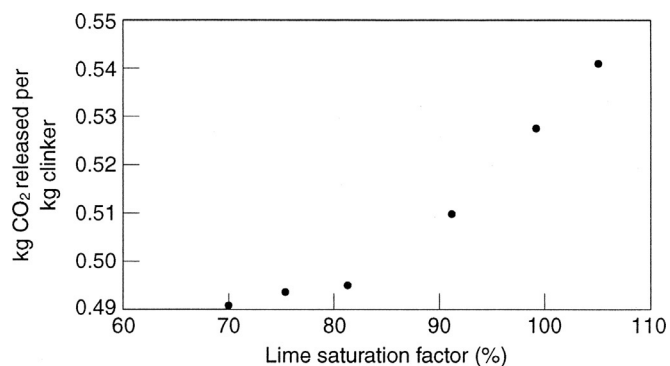
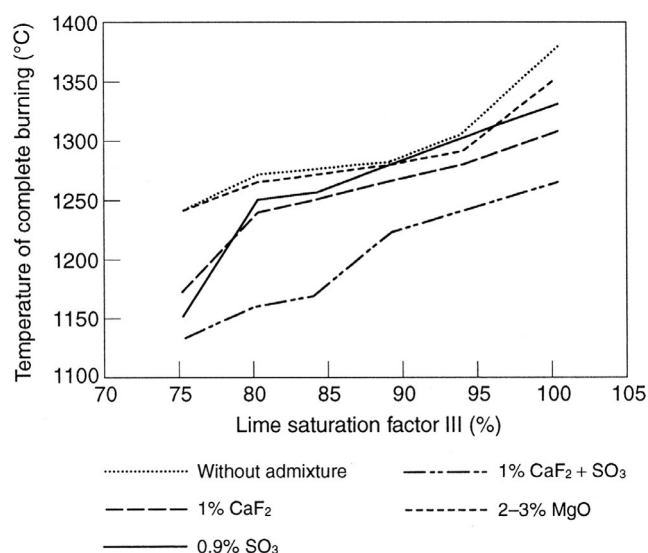


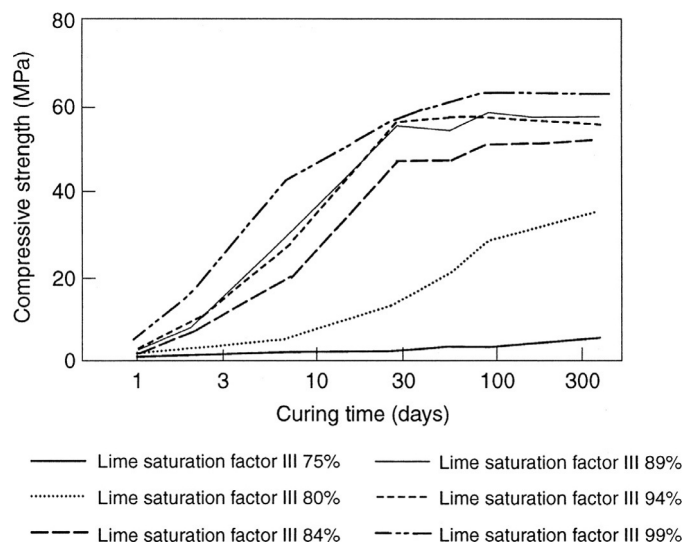
FIG. 8.3 Effect of lime saturation factor on heat energy required. (Source: Gygi H. *Thermodynamics of the cement kiln*. In: Proceedings of the third international symposium on the chemistry of cement, London; 1952. p. 750–79.)



**FIG. 8.4** Effect of lime saturation factor on the CO<sub>2</sub> released during clinker production. (Source: Gygi H. *Thermodynamics of the cement kiln*. In: Proceedings of the third international symposium on the chemistry of cement, London; 1952. p. 750–79.)



**FIG. 8.5** Burning temperature for complete combination (<2% free lime) versus lime saturation factor of cement raw feed based on natural marls. (Source: Ludwig U, Pohlmann R. *Investigation on the production of low lime Portland cements*. In: Proceedings of the eighth international congress on the chemistry of cement, Rio de Janeiro; 1986, Sub Theme 1.3, vol. II. p. 363–71.)



**FIG. 8.6** Effect of lime saturation factor on compressive strength. (Source: Ludwig U, Pohlmann R. *Investigation on the production of low lime Portland cements*. In: Proceedings of the eighth international congress on the chemistry of cement, Rio de Janeiro; 1986, Sub Theme 1.3, vol. II. p. 363–71.)

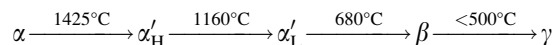
early period of hydration. The marked drop in reactivity for the cement with a lime saturation factor of 80% cannot be compensated by increased cement grinding or increased sulfate level. It is argued that a certain minimum percentage of alite is required in the cement ( $\sim 15\%$ ) for the cement to perform in a near normal manner<sup>20</sup>; this alite content may be derived either from the low-energy clinker or from normal Portland cement clinker blended with the low-energy clinker. The most effective cement feed for forming cement clinker at  $1250^\circ\text{C}$  is one containing  $\text{CaF}_2 + \text{SO}_3$  as a flux, but the use of this mineraliser does not result in cements showing adequate strength when the lime saturation factor is below about 90%. The rheological properties of belite cement pastes have been examined.<sup>54</sup>

### 8.5.1 Active Belite Cements

In order to produce Portland cements with adequate strength at lime saturation factors below about 85%, a belite which has improved reactivity is required. Several possible approaches to the improvement in reactivity of  $\text{C}_2\text{S}$  have been suggested<sup>53</sup>:

- rapid quenching of the clinker, in order to stabilise a high-temperature polymorph;
- the introduction of impurity ions during formation at high temperature (alkalis, sulfate, etc.) into the crystal structure, again to stabilise a high-temperature polymorph;
- the addition of normal Portland cement clinker to the  $\text{C}_2\text{S}$  clinker in order to accelerate the rate of hydration.<sup>20,53</sup>

Pure  $\text{C}_2\text{S}$  exhibits five polymorphic forms, depending on temperature and pressure during formation<sup>55</sup> all are metastable except the  $\gamma$  form.



In Portland cement the equilibrium temperature between  $\alpha$  and  $\alpha'_\text{H}$  is  $1280^\circ\text{C}$  and the conversion reaches a maximum rate at  $1100^\circ\text{C}$ . With decreasing cooling rate, the  $\alpha'_\text{H}$  phase tends to dominate, and finally the belite is composed entirely of this form, which transforms into  $\beta\text{-C}_2\text{S}$  after passing through the  $\alpha'_\text{L}$  form.<sup>56</sup>

The  $\beta$  form exists in Portland cement and is slowly reactive with water to form cementitious hydrates. The  $\alpha$  and  $\alpha'$  forms are also hydraulic. The speed of hydration of  $\beta\text{-C}_2\text{S}$  can be increased by imparting a stressed condition through thermal shock, or through the formation of small crystallites using gel techniques or spray drying in the preparation of the raw feed, followed by firing at temperatures in the range  $750^\circ\text{C}$ – $940^\circ\text{C}$ . For cement raw feed with lime saturation factor II of 80%–90%, and different alkali contents, quenching yields  $\alpha$ -belite at high alkali content (1.49% equivalent  $\text{Na}_2\text{O}$ ) at the fastest cooling rate, while at lower alkali contents a new polymorph  $\beta$  is identified, having increased hydraulic properties.<sup>57</sup>

The most important aim for the development of active belite cement is to reduce the energy consumption for cement manufacture. In addition, the maximum burning temperature may be reduced, leading incidentally to reduced  $\text{NO}_x$  formation. The production of active belite cement allows the use of lower grade limestone, the belite formed being activated either by thermal or by chemical means. Typically, the lime saturation factor lies in the range 75%–85%: thermal activation is achieved by quenching in the temperature range  $1300^\circ\text{C}$ – $900^\circ\text{C}$ , with a cooling rate of at least  $800^\circ\text{C}/\text{min}$ . This quenching procedure results in stabilisation of  $\alpha'$ -belite by the incorporation of alkalis or other foreign ions in amounts up to 5%. The deliberate addition of alkali sulfates fails to stabilise the  $\alpha'$ -belite modification and only quenching is able to achieve a high-strength belite. Pilot plant investigations yield cements with strengths between 16 and 22 MPa after 3 days and 50–60 MPa after 28 days. Production of an active belite cement with lime saturation factor between 80% and 82% allows a reduction in energy consumption of 10%–14%, and a decrease in burning temperature of  $100^\circ\text{C}$ . Both  $\beta$ - and  $\alpha'$ -belites have also been stabilised by  $\text{P}_2\text{O}_5$ ;  $\alpha'$  form was found to hydrate faster than the  $\beta$  form.<sup>58</sup>

Belite is a major phase in active belite cements and is chiefly present in the  $\alpha$  and  $\alpha'$  modifications, stabilised either by rapid cooling in the temperature range  $1300^\circ\text{C}$ – $900^\circ\text{C}$ ,<sup>21</sup> or by the use of higher alkali levels.<sup>59</sup> It has been suggested that the hydraulic activity of  $\beta\text{-C}_2\text{S}$  is related to the calculated strength of the  $\text{Ca-O}$  ionic bond.<sup>60</sup> A study of the relationship between crystal structure and hydraulic activity, including synthetic  $\beta\text{-C}_2\text{S}$  and samples separated from Portland cement, indicates that the electric field strength at the site of the  $\text{Ca}^{2+}$  ions in the crystal lattice determines the hydraulic activity.<sup>61</sup> The ease of early hydration increases for samples of pure  $\text{C}_2\text{S}$  that have been quenched in carbon tetrachloride ( $\text{CCl}_4$ ). Hydration rates of impure belite extracted from Portland cement are lower than those for pure  $\text{C}_2\text{S}$  quenched in  $\text{CCl}_4$ .

The work of Ono<sup>62</sup> shows that rapid cooling may result in 40% of the belite remaining in the  $\alpha$  modification sandwiched between fine lamellae of disordered  $\beta\text{-C}_2\text{S}$ ; exsolution of impurities fails to occur on cooling. The overall result from these studies led to the suggestion that among belites there is no hydraulic activity sequence of general validity (e.g.  $\alpha > \alpha' > \beta > \gamma$ ), and that the measured strength generation depends on the actual experimental conditions (burning temperature, cooling rate, foreign oxide content, etc.). In principle, it is claimed that both hydraulically highly active and nearly inactive forms may be possible for all belite modifications.<sup>57</sup>

Experiments have been conducted, using industrial limestone and clay, on kiln feeds designed to lime saturation factors between 70% and 101%. A range of firing temperatures from 1150°C to 1450°C, and a range of clinker cooling rates between 20°C and 3000°C/min, in the temperature interval 1350°C–700°C, were applied. An increase in strength is achieved for the lower range of lime saturation factors by increasing the cooling rate of the fired clinker (Fig. 8.7).<sup>51</sup> Strength is increased at both 3 and 28 days. Comprehensive investigations of the conditions necessary for the production of active belite have indicated that the rate of cooling of the clinker plays the important role where the lime saturation factor is below about 90%, especially as far as the 28 day strengths are concerned.<sup>51,59</sup> The increase in strength between quenched and slowly cooled clinker with a lime saturation factor of 80%, was 5 MPa after 3 days and 40 MPa after 28 days. In agreement with this result, rapid cooling of low-lime clinkers improved hydraulic activity<sup>63</sup> but had no influence on the activity of high-lime clinkers.<sup>51</sup> A lime saturation factor of 80%–82% allowed a reduction in energy of production of at least 10%–14%, and a reduction in temperature of clinkering of >100°C. The rate of cooling of the clinker in the temperature range 1300°C–900°C, in which belite is the main mineral, is the most important factor affecting the development of strength.<sup>64,65</sup> A cooling rate of 1000°C/min was achieved in a pilot plant and resulted in high early strengths of 16–22 MPa at 3 days and 50–60 MPa at 28 days. This high cooling rate was achieved by crushing the hot clinker. An addition of anhydrite rather than gypsum was made in order to control the setting.

An active belite cement has been produced in sufficient quantities to enable a concrete road to be constructed (in 1984). The concrete was tested for durability performance after 4 years<sup>66</sup> and found to have similar degrees of carbonation and freeze–thaw resistance to a concrete using Portland cement. The compressive strengths after 4 years were virtually identical, but somewhat smaller for the belite cement after 3 days (16.7 and 22.4 MPa) and after 28 days (45.9 and 53.0 MPa). The cement<sup>67</sup> exhibited a lime saturation factor (I) between 80.5 and 81.7. Its silica ratio lay between 2.7 and 2.9 and its alumina ratio lay between 2.3 and 2.6. Its mineralogical composition was alite: 27%–29%,  $\alpha'$ -C<sub>2</sub>S: 21%–30%,  $\beta$ -C<sub>2</sub>S: 14%–30%, C<sub>3</sub>A: 6%–7% and ferrite was 16%–18%. The theoretical heat required to form the cement was 1630–1680 kJ/kg of clinker. Rapid cooling was achieved in an air-fluidised trough, giving rates of temperature change of 1100°C/min, in a rotary cooler, or by hot comminution in an impact mill attached to the rotary kiln. Highest strengths were achieved using the air-fluidised bed cooler (28 day strengths varied between 43 and 59 MPa depending on the cooling rate).

The freeze–thaw resistance of cement paste and mortar specimens has been measured for cements formed from clinkers with lime saturation factors between 69% and 97%. The clinkers were burnt at temperatures between 1380°C and 1430°C.<sup>67</sup> The phase composition had C<sub>2</sub>S contents of 25%–71% and alite contents of 0%–43%. It was found that the strength retained after freeze–thaw cycles was higher for the high-belite cement than for Portland cements. It was proposed that the weak link in the microstructure was provided by the Ca(OH)<sub>2</sub> crystals and, as belite cements produce less Ca(OH)<sub>2</sub> on hydration, they are consequently better able to resist freeze–thaw damage. This view is based on the fact that reduced temperatures increase the solubility of Ca(OH)<sub>2</sub> and thus cause an increase in the porosity of the microstructure at the surface of the portlandite crystals during freeze–thaw cycling.

In another investigation, the normal processes of cement technology were adopted, except that the clinkering temperature was reduced by 100°C to 1365°C.<sup>68</sup> The influence of lime saturation factor and quenching rate were investigated: for a lime saturation factor of between 70% and 101%, cooling rate affects the hydration rate up to a lime saturation factor of 90%; beyond this, the cooling rate does not affect strength. Strengths after 3 and 28 days of approximately 15 and 60 MPa, respectively, were achieved.

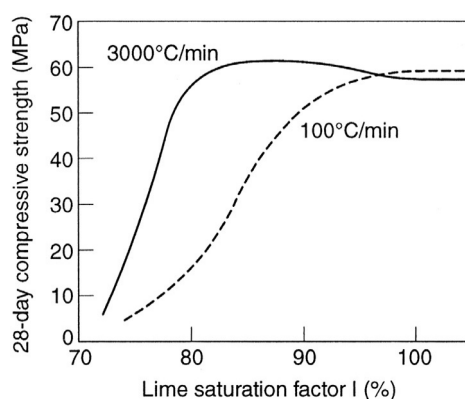


FIG. 8.7 Effect of the quenching rate of clinkers of different lime saturation factors on their strength generation capacity. (Source: Stark J, Müller A, Schrader R, Rümpler K. Existence conditions of hydraulically active belite cement. *Zement-Kalk-Gips*, 1981; 34: 476–81.)



The role of alkali in the stabilisation of  $\beta$ -C<sub>2</sub>S has been reviewed.<sup>49</sup> The influence of alkali on the stabilisation of high-temperature forms of dicalcium silicate, and the increased hydraulic activity of the dicalcium silicate phase has been studied.<sup>69,70</sup> K<sub>2</sub>O is found to be incorporated into the C<sub>2</sub>S phase and results in the stabilisation of the  $\alpha$  form. It is stated that the  $\alpha'_L$  form can be stabilised by the inclusion of barium, magnesium, manganese and boron oxides, or by inclusion of CaHPO<sub>4</sub>. Rapid cooling of the clinker assists in the stabilisation of this hydraulically active phase. The highest 7 day strengths are recorded for high-alkali samples, and generally water or air quenching improves the strength levels, the improvements being greatest for the highest alkali levels.

Alkali oxide in C<sub>2</sub>S-rich clinkers (particularly Na<sub>2</sub>O) induces an increase in the compressive strength for the corresponding cements, and modest strength enhancement is attained by high cooling rates for the low-lime clinkers at all alkali levels (Table 8.8). In general, active belite cements have lower early and higher late strengths compared to alite-rich Portland cement.

Active belite cements, stabilised with chromium oxide as a component in the raw feed, have also been examined.<sup>71</sup> Low- to medium-purity limestones are employed to produce clinkers in the laboratory, firing the mixes at 1350°C, 1400°C and 1450°C. The cements (with 4%–5% Cr<sub>2</sub>O<sub>3</sub> giving the highest strengths at 1 day and 28 days) were observed to be sound; the  $\beta$ -C<sub>2</sub>S does not convert to the  $\gamma$  modification. The lime saturation factor was maintained between 95% and 100%, the silica ratio between 1.7 and 1.8, and the alumina ratio between 1.2 and 1.3. An active belite can be produced from barium-contaminated waste.<sup>72</sup> Raw feed with lime saturation factors of 70%, 85% and 90% are blended with 1% barium waste. After firing at 1350°C or 1450°C, compressive strengths are determined up to 28 days. The strengths of the clinker containing barium are somewhat higher for the mix with a lime saturation factor of 70%. A reduction in heat consumption during manufacture is observed.

**TABLE 8.8** Effect of Alkali Content and Cooling Regime of Low-Lime Clinkers<sup>a</sup> on the Strength of the Corresponding Cements<sup>71</sup>

Alkali Oxide (%)				Compressive Strength (MPa)			
K <sub>2</sub> O	Na <sub>2</sub> O	Equivalent Na <sub>2</sub> O	Cooling Mode <sup>b</sup>	2 Days	7 Days	28 Days	90 Days
0.23	0.04	0.193	a	5	6	32	42
0.25	0.04	0.192	b	4	7	31	40
0.28	0.04	0.206	c	4	7	29	41
0.57	0.04	0.226	a	5	10	51	56
0.54	0.04	0.419	b	3	10	43	50
0.50	0.04	0.399	c	4	9	30	46
1.01	0.04	0.373	a	3	11	47	50
1.01	0.04	0.712	b	4	12	42	44
1.02	0.04	0.712	c	5	12	38	45
1.46	0.04	1.001	a	6	17	53	56
1.42	0.04	0.974	b	4	17	42	48
1.46	0.04	1.000	c	5	16	39	46
0.23	0.63	0.781	a	6	14	60	59
0.22	0.65	0.794	b	5	14	47	55
0.24	0.65	0.808	c	5	9	31	47
0.25	1.08	1.245	a	5	17	59	59
0.24	1.11	1.268	b	5	15	48	58
0.26	1.10	1.271	c	4	9	38	55
0.25	1.65	1.815	a	6	22	64	64
0.25	1.63	1.795	b	6	17	45	47
0.24	1.61	1.768	c	5	9	33	45
0.26	0.15	0.321	a	5	11	50	57
0.27	0.18	0.358	b	6	11	50	48
0.27	0.17	0.348	c	5	8	30	41
0.53	0.49	0.839	a	5	11	54	60
0.54	0.47	0.825	b	6	11	47	58
0.48	0.49	0.806	c	5	10	39	54
0.76	0.80	1.300	a	7	15	60	62
0.75	0.77	1.264	b	6	13	48	56
0.77	0.81	1.317	c	5	11	32	46

<sup>a</sup>Lime saturation factor II = 80%, silica ratio = 2.4, alumina ratio = 2.0.

<sup>b</sup>a, cooling in water; b, cooling in air; c, cooling in furnace.

In some investigations, the presence of pozzolanas, and to a lesser extent blastfurnace slag, has been found to accelerate the hydration of  $\beta$ -C<sub>2</sub>S.<sup>73</sup> In contrast, other investigations find the presence of blastfurnace slag reduces the rate of hydration of belite.<sup>74</sup> The  $\gamma$ -C<sub>2</sub>S is normally regarded as non-hydraulic,<sup>21</sup> although a slow hydration has been reported<sup>75</sup>; in the presence of silica fume, no hydration of  $\gamma$ -C<sub>2</sub>S took place. Synthetic belite and alite (as well as 70:30 and 30:70 mixtures) were hydrated with 2% SO<sub>3</sub> added as pastes at a water/cement ratio of 0.4, after casting as 10 × 10 × 60 mm prisms.<sup>74</sup> The influence of replacing these synthetic cements with commercial blastfurnace slag was explored by measuring compressive strength development and heat of hydration after curing for periods up to 365 days under water at 20°C. The hydration of belite was significantly retarded by the presence of blastfurnace slag. The presence of alite, or normal Portland cement clinker,<sup>21</sup> greatly accelerated the hydration of the belite and it was suggested that the presence of Ca(OH)<sub>2</sub> is required to ensure a full hydration rate for both blastfurnace slag and belite.

Further developments to yield greater savings can be made in theory by limiting the lime content of the clinker, and several encouraging lines of research have been explored and presented in the literature. Cements based on belite are attractive as a way of reducing the temperature of formation and consumption of calcium carbonate (emission of CO<sub>2</sub>) as the present production plant can be adapted. Many of the restraints currently placed on the use of low-grade fuels and alternative source materials, especially lime because of a lack of purity, would disappear. The major difficulty is the low hydraulic reactivity of belite compared to alite. A number of methods of increasing the reactivity of belites have been examined. The most interesting way round this difficulty seems to lie in rapid quenching of the clinker. Perhaps a saving of 10%–20% in energy and CO<sub>2</sub> emission may be expected.

Cements prepared at reduced temperatures may have other benefits, apart from the reduction in energy input. The ferrite phase becomes more hydraulic when prepared at low temperature, and cements can be formed to give reactive systems containing combinations of CA and  $\beta$ -C<sub>2</sub>S, which have good long-term performance. The abandonment of sintering in favour of solid–solid interaction in the production of cements seems to deserve further attention.

## 8.6 BLENDED CEMENTS MADE BY DILUTING CLINKER WITH OTHER CONSTITUENTS

The main approach to producing low energy cements is to dilute the Portland cement clinker with selected inorganic materials. The European standard for common cements, EN 197-1<sup>12</sup> permits the following as other main constituents of Portland cements:

- granulated blastfurnace slag;
- natural pozzolanas;
- natural calcined pozzolanas;
- fly ashes from furnaces fired with pulverised coal and sub-divided into siliceous fly ashes and calcareous fly ashes;
- burnt shale;
- limestone;
- silica fume.

Cement standards from other parts of the world have similar lists. As an alternative to using pre-blended cements, a number of these materials have their own product standards, for example fly ash,<sup>76</sup> ground granulated blastfurnace slag<sup>77</sup> and silica fume.<sup>78</sup> In this case these materials are called additions (Europe) or supplementary cementitious materials (North America) and they are added directly by the concrete producer into the concrete mixer. All these constituents of cement are considered to be traditional and well tried.<sup>12</sup> The use of these materials either in cement or directly in the concrete enhances some properties of concrete and have a negative effect on other properties; however, the durability provisions in most national standards permit a range of cement types all with the same maximum w/c ratio.<sup>79</sup>

The energy savings in cement depend upon the classification of these materials and the applicable co-allocation rules.<sup>80</sup> In Europe, the materials would be classified as primary, co-products and wastes. Natural pozzolans, natural calcined pozzolanas and limestone are primary materials but in some cases the limestone may be a waste from, for example, crushed rock aggregate production. With primary materials all the energy needed to produce and transport them to the cement works needs to be taken into account in the energy calculation.<sup>80</sup> According to EN 15804,<sup>80</sup> there is no allocation of energy to wastes until the end of waste stage is reached and therefore fly ashes and burnt shale contribute no energy other than that needed to transport to the cement works and the energy in processing. Granulated blastfurnace slag is made by quenching molten slag and so this material never enters a waste stream and therefore it should be classified as a co-product. The demand and price paid for silica fume is such that this material will also never enter a waste stream and so it should also be classified as a co-product.

The general principle of co-allocation is that it has to respect the main purpose of the process,<sup>81</sup> which in the case of blastfurnace slag is iron production and in the case of silica fume it is the production of pure silicon or ferrosilicon. The differences in revenue between iron and blastfurnace slag and pure silicon and silica fume are large and therefore the recommended way to allocate impacts is on economic value.<sup>80</sup> If the difference in economic value is high (one co-product is  $\leq 1\%$  of the economic value of the other co-product), it is usual to make no allocation to the co-product with the low economic value with respect to the material itself. This is the norm with fly ash, but both GGBS and silica fume have some allocation. FprCEN TR 16970<sup>81</sup> states:

*EN 15804:2012 + A1:2013, 6.4.3.2 states: 'Processes generating a very low contribution to the overall revenue may be neglected.' This cut off rule for neglecting allocation is intended to allow manufacturers to put all emissions onto the main product where it considers allocation too much effort for minor co-products. However, if a low value co-product is being used as an input into a production process, allocation rules are used to understand the impact connected to that product.*

*The term 'revenue' in EN 15804:2012 + A1:2013, 6.4.3.2 means the revenue coming from the co-product after co-product as it leaves the joint co-production process. The revenue is the price multiplied by the output. For both price and output, representative values should be identified (e.g. annual averages). Prices alone are not considered to be the appropriate basis for the decision.*

In all cases the impacts of processing the material and transport are fully allocated to the co-product and in the case of ground granulated blastfurnace slag (GGBS), the impacts of grinding are allocated fully to the GGBS.

The impacts of using such materials is significant and summarised in Table 8.9.

Cements are often classified by the proportion of the second (or more) main constituent, e.g. as in EN 197-1<sup>12</sup> and the trend is to provide cements with combinations of these materials and ever increasing proportions. For example, it is proposed that EN 197-1<sup>82</sup> is revised to include new CEM II/C with 36%–50% of slag–limestone, natural pozzolana–limestone or siliceous fly ash–limestone and a new group of cements CEM VI with 51%–65% slag–limestone.

The adoption of cements with non-traditional components is often a slow process. Non-traditional materials include fly ashes from sources other than power generation and slags other than the slag from iron production. There are many aspects to consider<sup>83</sup> including stability of the hydrates over time, durability, potential release of dangerous substances and uniformity of performance. Guidance on getting a new cement standardised is available,<sup>83</sup> but sometimes a first stage is achieving a technical approval at a national or regional level.

## 8.7 LOW ENERGY NON-PORTLAND CEMENTS

### 8.7.1 Calcium Sulfoaluminate Cements

Although most countries base their concrete construction on Portland cements,<sup>79,84</sup> there are alternatives perhaps most notably calcium sulfoaluminate cement (CSA), which is widely used in China. Historically, this is due to the availability of source rock material i.e. bauxite, rather than any technical necessity. Source rock remains a key issue for the manufacture of non-Portland cements to be commercially viable. Although bauxite is an abundant rock type in the Earth's crust, it tends to occur in limited geographies e.g. China, particularly when compared to the widespread availability of limestone. Thus the energy associated with transport can easily be greater than savings in lower clinkering temperatures.

**TABLE 8.9** Potential Impacts of Using Other Main Constituents<sup>9</sup>

Constituent	Worldwide Production in Million Tonne/Year	Typical % <sup>a,b</sup>	Thermal Energy Decrease, MJ/t Cement	Electrical Energy Decrease, kWh/t Cement	Total CO <sub>2</sub> Reduction, kg CO <sub>2</sub> /t Cement
GGBS	200	30–70	420–1880	None	100–430
Fly ash	500 <sup>c</sup>	25–35	220–600	15–27	58–159
Natural pozzolana	30 <sup>d</sup>	15–35	0 <sup>e</sup> –600	0–25	0–158
Limestone	Sufficient	25–35	220–600	12–23	56–156

<sup>a</sup>By mass of main and minor constituents if cement, or as the percentage of the mass of cement plus addition if added at the concrete mixer.

<sup>b</sup>The potential impacts are based on these percentages.

<sup>c</sup>About 25% of this fly ash is used in the cement and concrete industries.

<sup>d</sup>About 50% of these natural pozzolana are used in the cement and concrete industries.

<sup>e</sup>The zero values in this row relate to natural calcined pozzolana.

Widely used in China for over 35 years, (calcium sulfoaluminate) CSA-belite cements are made by heating/sintering industrial wastes such as coal fly ash, gypsum and limestone at 1200°C–1250°C in rotary kilns. In comparison with Portland cement, this can result in energy savings of around 25%, which combined with the low carbonate content gives a reduction in embodied CO<sub>2</sub> of around 20%.

CSA-belite (C<sub>2</sub>S i.e. dicalcium silicate) cements are made in a range of compositions but the structural grades made in China comprise a predominant phase of CSA of 35%–70%, a belite content below 30% and a ‘ferrite’ (calcium ferroaluminate) phase of 10%–30%.

Rapid early strength development can be problematic with these cements and careful selection of constituents is required, particularly the gypsum content. Although extensively used in China issues such as the effect on rheology, *E*-value, creep strain and durability are less well understood and, indeed may not be the same due to the various CSA chemistries. Some of these properties have been explored in laboratory work by the UK Building Research Establishment.<sup>85</sup>

### 8.7.2 Alkali Activated Cementitious Materials (AACM)

Alkali-activated cements gain their strength, and other properties, via chemical reaction between a source of alkali (soluble base activator) and aluminosilicate-rich materials. The alkali used as the activator tends to be an alkali silicate solution such as sodium silicate (water glass) but can also be sodium hydroxide solution, or a combination of the two, or other source of alkali (such as lime). The aluminosilicate-containing material—the pozzolana/latent hydraulic binder component of the cement—can be coal fly ash, municipal solid waste incinerator ash (MSWIA), metakaolin, blastfurnace slag, some steel slags or other slags, or other alumina-rich materials. Use of sodium silicate gives a low temperature sodium aluminosilicate glass, chemically similar to naturally occurring zeolites (a special class of hydrated aluminosilicates). Geopolymeric cements are particular examples of ‘alkali-activated pozzolanic cements’ or ‘alkali-activated latent hydraulic cements’. See Chapter 16: *Geopolymers and Other Alkali-Activated Materials*, for more information about geopolymers and alkali-activated cementitious materials.

All alkali-activated cements tend to have lower embodied energy/carbon footprints than Portland cements (up to 80%–90% less, but this is pozzolana dependent). Historically, short, erratic setting times restricted the use of these cements, although predictable performance in the fresh wet state is now claimed. Manufacture on a commercial basis is underway in Australia, United States and possibly, China and precast/prefabricated concrete products based on these cements are apparently available.

AACMs do not generally fit into the standard framework for traditional concretes and common cements covered by EN 197-1,<sup>12</sup> EN 206,<sup>86</sup> BS 8500-1<sup>87</sup> and BS 8500-2.<sup>88</sup> While many of the tests and considerations relevant to traditional concretes and common cements may broadly be applied to AACMs, some of the details do not and this may impede the use of AACMs when the existing standards are specified for a project. In the United Kingdom, a Publicly Available Specification PAS 8820<sup>89</sup> has been published that defines the specification for the use of alkali-activated cementitious materials in concrete. This aims to pave the way for these materials to be accepted and used in construction. It should be noted that this PAS does not deal with the long-term properties such as creep or drying shrinkage, or some aspects of concrete durability, and where such properties are important, further testing would be required, until sufficient field performance data and experience is built up.

The scope of PAS 8820<sup>89</sup> defines an AACM (including the activator) as a cement that may contain Portland cement <5% mass of ‘binder solids’ (defined as all solids and dissolved solids) and subsidiary constituents <25% of the mass of the cementitious material.

The alkali activator as ‘source of one or more elements in the alkali metals group (i.e. Group 1 of the Periodic table but with the exception of radioactive francium), and/or magnesium, and/or calcium, which when incorporated in aqueous or solid form, induces a reaction, setting and hardening of an AACM’. Examples of activator components are sodium silicate, potassium silicate, sodium hydroxide, potassium hydroxide, sodium carbonate, and sodium sulfate. It should be noted that activator doses in excess of that necessary to achieve the desired mechanical performance can result in efflorescence. There is limited data reporting on the risk of alkali–silica reaction of aggregates but aggregates with high reactivity or extreme reactivity should not be used with AACMs.

### 8.7.3 Magnesium Oxide-Based Cements

Magnesium oxide-based cements (MgO) are based on two chemical/mineralogical forms (and manufacturing processes) that is magnesium carbonate and magnesium silicates. Magnesium oxide cements hydrate to form magnesium hydroxide (brucite)

and/or magnesium silicate hydrates (depending on the cement formulation). In addition, brucite can carbonate producing a range of magnesium carbonates, which also have cementitious properties. See Chapter 13: *Special Cements*, for more information.

Magnesium oxide is produced by heating magnesium carbonate at atmospheric pressure, preferably as the mineral magnesite, to its dissociation temperature of about 800°C–1000°C. This does result in CO<sub>2</sub>, which their promoters claim will be re-carbonated rapidly from the atmosphere, making them carbon neutral. However, there is not sufficient evidence as yet to fully substantiate this claim.

As a result the alternative form of MgO manufacture using silicate rather than carbonate raw materials has been developed. Both the raw materials and manufacturing process are novel in that magnesium silicates are first carbonated under elevated temperature (170°C) and high pressure to produce magnesium carbonate. This is then heated at 700°C under atmospheric pressure to its dissociation temperature to produce reactive magnesium oxide; part of this is (re-) carbonated to produce hydrated magnesium carbonates [i.e. 4MgCO<sub>3</sub>·Mg(OH)<sub>2</sub>·4H<sub>2</sub>O] that are blended with reactive magnesium oxide to produce the final cement. There are several advantages to this chemistry as the raw material is not based on a carbonate and any CO<sub>2</sub> produced is incorporated into the cement and not released to the atmosphere. Indeed, the cement is promoted as being carbon negative. As yet the cement has not reached a commercial scale but work continues to refine the process.

It should be noted that the likely commercial viability of any of these cement is dependent on locally available mineral source and although magnesium silicate minerals for example, pyroxenes, olivine/forsterite, serpentine and talc are abundant in the Earth's crust, quarrying commercial quantities is not available in all countries.

#### 8.7.4 Municipal Solid Waste Incinerator Ash Cements

Municipal solid waste incinerator ash (MSWIA) can be used as a raw material for an alkali-activated pozzolanic/geopolymeric cement. The problem with this material is that it can contain high concentrations of chlorides as well as small amounts of toxic substances such as dioxins and heavy metals.

To overcome this problem in Japan, MSWIA has been used as a raw material for Portland cement manufacture during which the high temperatures will decompose any dioxins. Volatile heavy metals, such as lead, zinc, copper and cadmium vaporise during clinkering in the form of chloride salts and are trapped in the cement kiln dust (CKD), where they can be extracted by post-production processes and reused. One problem with this process is that MSWIA is often an irregular supply making it difficult to set up commercial contracts.

### 8.8 SUMMARY POINTS

It seems likely that Portland cements will remain the dominant binder types taken on an international basis. Portland cement production will continue to be the dominant cement type, albeit most commonly blended with fly ash, GGBS or limestone (although there is some uncertainty with regard to the future availability for the former two materials). The industry will continue to make further inroads into the use of non-fossil, alternative fuels and, in the longer term, carbon capture and sequestration may be economically viable. In the United Kingdom, alternative waste derived fuels account for around 40% of the fuel used to manufacture Portland cement and the industry is aiming to increase this to around 60% by 2050 and to reduce greenhouse gases by 81%.<sup>90</sup>

Lower energy non-Portland cements will have a role to play but probably for niche applications.

What will be important is for robust greenhouse gas emission data to be agreed for all cement materials. Figures for Portland cement, fly ash, GGBS etc. have been published but this is not the case for novel cements. Furthermore, it is important for designers and specifiers to note that it is the amount of embodied CO<sub>2</sub> in a particular concrete mix that matters rather than the cement itself.

### REFERENCES

1. Goreau TJ. Balancing atmospheric carbon dioxide. *Ambio* 1990;**19**(5):230–6.
2. Hilbertz WH. Solar-generated construction material from sea water to mitigate global warming. *Build Res Inf* 1991;**19**:242–55.
3. Barrett J. The roles of carbon dioxide and water vapour in warming and cooling the Earth's troposphere. *Spectrochim Acta* 1995;**51A**:415–7.
4. Houghton J. Comment on 'the roles of carbon dioxide and water vapour in warming and cooling the Earth's troposphere' by J. Barrett. *Spectrochim Acta* 1995;**51A**:1391–2.
5. Slime KP. Comment on 'The roles of carbondioxide and water vapour in warming and cooling the Earth's troposphere' by J. Barrett. *Spectrochim Acta* 1995;**51A**:1393–4.



6. Barrett J. Reply to comment on 'the roles of carbondioxide and water vapour in warming and cooling the Earth's troposphere' by J. Barrett. *Spectrochim Acta* 1995;**51A**:1395.
7. Houghton JT, Callander BA, Varney SK. *Climate change 1992: the supplementary report to IPCC scientific assessment*. London: Cambridge University Press; 1992.
8. European Union. 2030 climate & energy framework. Available on the web: [https://ec.europa.eu/clima/policies/strategies/2030\\_en](https://ec.europa.eu/clima/policies/strategies/2030_en), [accessed May 2018].
9. CSI. *Development of state of the art techniques in cement manufacturing: trying to look ahead*. CSI/ERCA—technology papers; Jun. 2009; (a) Environmental Protection Agency (USA). Understanding global warming potentials. <https://www.epa.gov/ghgemissions/understanding-global-warming-potentials>.
10. International Energy Agency. Energy technology Perspectives; 2008. Available for downloading from <http://www.iea.org/publications/freepublications/publication/energy-technology-perspectives-2008-.html>.
11. CEMBUREAU. Activity report; 2014. Available for free downloading from the CEMBUREAU web site <http://www.cembureau.eu/>.
12. EN 197-1. Cement—part 1: composition, specifications and conformity criteria for common cements.
13. Barcelo L, Kline J, Walenta G, Gartner E. Cement and carbon emissions. *Mater Struct* 2014;**47**:1055–65.
14. Madlool NA, Saidur R, Rahim NA, Kamalisarvestani M. An overview of energy savings measures for cement industries. *Renew Sustain Energy Rev* 2013;**19**:18–29.
15. Benhelal E, Zahedi G, Shamsaei E, Bahadori A. Review of global strategies and potentials to curb CO<sub>2</sub> emissions in cement industry. *J Cleaner Prod* 2013;**51**:142–61.
16. HOLCIM. Application of pre- and co-processing in cement production: Module 4, [www.coprocem.com/trainingkit/documents/module4/Presentation\\_4\\_Coprocessing\\_v31.pdf](http://www.coprocem.com/trainingkit/documents/module4/Presentation_4_Coprocessing_v31.pdf), [accessed May 2018]; (a) Greenhouse Gas Protocol. Global warming potentials. <http://www.ghgprotocol.org/files/ghgp/tools/Global-Warming-Potential-Values.pdf>, 2013.
17. Mineral Products Association. Embodied CO<sub>2</sub>e in UK cements, additions and cementitious materials, Fact Sheet 18.
18. Borgholm HE. *What is mineralised cement?* FL Smidth & Company, Highlights; Mar. 1996. p. 15–7.
19. Locher FW. Low energy clinker. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Principal paper: Sub theme 1.3, vol. I. p. 57–67.
20. Sahu S. Developments in low energy clinkers. *Ceramics—Silikáty* 1994;**38**:191–200.
21. Wu K, Shi H, De Schutter G, Guo X, Ye G. Preparation of alinite cement from municipal solid waste incineration fly ash. *Cem Concr Compos* 2012;**34**:322–7.
22. Motzet H, Neubauer J, Pöllmann H. Alinite-cement made from waste incineration residues—from basic research to application. In: *Proceedings of the 16th international conference on cement microscopy*, Richmond; 1994. p. 210–29.
23. Ludwig U, Urbonas L. Synthesis and reactivity of fluoralinites and fluoralinite cement. *Zement-Kalk-Gips* 1993;**46**:568–72.
24. Stracelsky J, Hanic F, Kapralik I, Kupcik F. The effect of pressure and temperature on phase stability of tricalcium silicate. *Silikáty* 1983;**27**:299–309.
25. Courtial M, de Noirfontaine M-N, Dunstetter F, Gasecki G, Signes-Frehel M. Polymorphism of tricalcium silicate in Portland cement: A fast visual identification of structure and superstructure. <https://hal.archives-ouvertes.fr/hal-00278373/document>, [accessed May 2018].
26. Boikova AI. Chemical composition of raw materials as the main factor responsible for the composition, structure and properties of clinker phases. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Sub-Theme 1.2, vol. I. p. 19–33.
27. Gutt W. Manufacture of Portland cement from phosphatic raw materials. In: *Proceedings of the fifth international symposium on the chemistry of cement*, Tokyo; 1968, vol. I. p. 93–105.
28. Christensen NH, Johansen V. Mineralizers and fluxes in the clinkering process. II. Kinetic effects on alite formation. In: *Proceedings of the seventh international congress on the chemistry of cement*, Paris; 1980, Communication Theme I, II: 1–1.
29. Gutt W, Osborne GJ. The system CaO–2CaOSiO<sub>2</sub>–CaF<sub>2</sub>. *Trans Brit Ceram Soc* 1970;**69**:125–9.
30. Tsuboi T, Ito T, Hokinoue Y, Matsuzaki Y. The effects of MgO, SO<sub>3</sub> and ZnO on the sintering of Portland cement clinker. *Zement-Kalk-Gips* 1972;**9**:426–31.
31. Moir GK. Improvements in the early strength properties of Portland cement. *Philos Trans Roy Soc Lond A* 1983;**310**:127–38.
32. Ikeda K. Cement along the join C<sub>4</sub>A<sub>3</sub>S–C<sub>2</sub>S. In: *Proceedings of the seventh international congress on the chemistry of cement*, Paris; 1980, vol. II. p. HI-31–6.
33. Blanco MT, García S, Giménez S, Palomo A, Puertas F, Vazquez T. The behaviour of a low energy cement and two blended cements in Na<sub>2</sub>SO<sub>4</sub> and sea water media. In: *Proceedings of the ninth international congress on the chemistry of cement*, New Delhi; 1992, vol. V. p. 329–34.
34. Giménez-Molina S, Blanco-Varela MT. Solid state phases relationship in the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–CaF<sub>2</sub>–CaSO<sub>4</sub> system. *Cem Concr Res* 1995;**25**:870–82.
35. Bürger D, Ludwig U. Synthesis of calcium silicates at low temperatures and influences on their reactivity. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Sub Theme 1.3, vol. II. p. 372–8.
36. Lafarge, Aether cements. [www.aether-cements.eu/results.html](http://www.aether-cements.eu/results.html), [accessed May 2018].
37. Sarkar AK, Roy DM, Smart RM. Mineralizers and fluxes in the clinkering process. I. Phase equilibria in the CaO–Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system with calcium fluosilicate. In: *Proceedings of the seventh international congress on the chemistry of cement*, Paris; 1980, Communication: Theme I, vol. II. p. 1-195–200.
38. Klemm WA, Jawed I. Mineralizers and fluxes in the clinkering process. III. Burnability of synthetic and industrial raw mixes. In: *Proceedings of the seventh international congress on the chemistry of cement*, Paris; 1980, Communication: Theme I, vol. II. p. 1-150–5.
39. Méric JP. Low energy clinker formation. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Principal paper: Sub Theme 1.3, vol. I. p. 51–6.
40. Narang KC, Ghosh SP, Sharma KM. Microstructural characteristics of sound and unsound clinkers with varying MgO content. In: *Proceedings of the third international conference on cement microscopy*, Houston, Mar. 1981. p. 140–53.

41. EN 196-3. Methods of testing cement—part 3: determination of setting times and soundness.
42. Ono Y, Soda Y. Effect of crystallographic properties of alite and belite on the strength of cement. In: *The cement association of Japan, 19th general meeting*, Tokyo; 1965, Chapter 15. p. 78–82.
43. Aldous RTH. The hydraulic behaviour of rhombohedral alite. *Cem Concr Res* 1983;13:89–96.
44. Glasser FP. The chemical environment in cements, and its modification by blending agents. In: *Beijing international symposium on cement and concrete* (Abstracts); 1985. p. 9.
45. Uchikawa H, Hanehara S, Shirasaka T. Relationship between zonal structure in alite, lamellar texture in belite and their production process, composition and crystal structure. In: *Proceedings of the ninth international congress on the chemistry of cement*, New Delhi; 1992, vol. II. p. 3–9.
46. Nurse RW, Midgley HG, Gutt W, Fletcher K. Effect of polymorphism of tricalcium silicate on its reactivity. In: *Symposium on structure of Portland cement pastes and concrete*, Highway Research Board Special Report 90; 1966. p. 258–62.
47. Kelham S. Active Portland cement clinker. Part 1: background, production and properties. In: *Institute of concrete technology, 23rd annual convention*; 10–12 Apr. 1995.
48. Giménez S, García S, Blanco MT, Palomo A. The behaviour of a low energy cement in  $\text{Na}_2\text{SO}_4$  and sea water media. *Cem Concr Res* 1992;22:793–803.
49. Moir GK, Glasser FP. Mineralisers, modifiers and activators in the clinkering process. In: *Proceedings of the ninth international congress on the chemistry of cement*, New Delhi; 1992, vol. I. p. 125–52.
50. Mehta PK. Investigations on energy-saving cements. *World Cem Technol* May 1980;166–77.
51. Stark J, Müller A, Schrader R, Rümpler K. Existence conditions of hydraulically active belite cement. *Zement-Kalk-Gips* 1981;34:476–81.
52. Spohn E, Woermann E, Knöfel D. A refinement of the lime standard formula. In: *Proceedings of the fifth international symposium on the chemistry of cement*, Tokyo; 1968, vol. I. p. 172–9.
53. Ludwig U, Pohlmann R. Investigation on the production of low lime Portland cements. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Sub Theme 1.3, vol. II. p. 363–71.
54. Grzeszczyk S. Rheological properties of belite cement pastes. *Adv Cem Res* 1994;6:155–9.
55. Hanic F, Kamarád J, Stracelský J, Kaprálik J. The p-T diagram of  $\text{Ca}_2\text{SiO}_4$ . *Brit Ceram Soc Trans J* 1987;86:194–8.
56. Maki I. Processing conditions of Portland cement clinker as viewed from the fine textures of the constituent minerals. *Cem Technol (Am Ceram Soc)* 1994;3–17.
57. von Lampe F, Seydel R. On a new form of  $\beta$ -belite. *Cem Concr Res* 1989;19:509–18.
58. Matkovic B, Young JF. Dicalcium silicates doped with phosphate. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Sub Theme 1.2, vol. II. p. 276–81.
59. Stark J, Müller A. International development trends in low-energy cements. *Zement-Kalk-Gips* 1988;41:162–4.
60. Xiuji F, Xinmin M, Congxi T. Study on the structure and characteristic of dicalcium silicate with quantum chemistry calculations. *Cem Concr Res* 1994;24:1311–6.
61. Tsurumi T, Hirano Y, Kato H, Kamiya T, Daimon M. Crystal structure and hydration of belite. *Cem Technol (Am Ceram Soc)* 1994;19–25.
62. Ono Y. Microscopical estimation of burning condition and quality of clinker. In: *Proceedings of the eighth international congress on the chemistry of cement*, Paris; 1980, vol. II. p. 1–206–11.
63. Müller A, Stark J, Rümpler K. Present position in developing an active belite cement. *Zement-Kalk-Gips* 1985;6:303–4.
64. Mielke I, Müller A, Stark J. Active belite cement. In: *Proceedings of the 9th international congress on the chemistry of cement*, New Delhi; 1992, vol. II. p. 399–405.
65. Stark J, Müller A, Seydel R, Jost K. Conditions of the existence of hydraulically active belite cement. In: *Proceedings of the eighth international congress on the chemistry of cement*, Rio de Janeiro; 1986, Sub Theme 1.3, vol. II. p. 306–9.
66. Müller A, Fuhr C, Knöfel D. Frost resistance of cement mortars with different lime contents. *Cem Concr Res* 1995;25:809–18.
67. Müller A, Stark J. Durability of concrete made with active belite cement. *Zement-Kalk-Gips* 1990;3:160–2.
68. Ghosh SN, Mathure VK, Chopra SK. Low temperature OPC-type cement containing superhydraulic  $\text{C}_2\text{S}$  phase. *Cem Concr Res* 1984;14:437–8.
69. Gutt W, Osborne GJ. The effect of potassium on the hydraulicity of dicalcium silicate. *Cem Technol* 1970;1:1–5.
70. Subba Rao VV, Narang KC. Potentials for making active belite cements with chromium oxide as modifier. *Zement-Kalk-Gips* 1987;40:434–7.
71. Gies A, Knöfel D. Influence of alkalis on the composition of belite-rich cement clinkers and the technological properties of the resulting cements. *Cem Concr Res* 1986;16:411–22.
72. Rajczyk K, Nocuń-Wczelik W. Studies of belite cement from barium containing by-products. In: *Proceedings of the ninth international congress on the chemistry of cement*, New Delhi; 1992, vol. II. p. 250–4.
73. Sharara AM, El-Didamony H, Ebied E, El-Aleem A. Hydration characteristics of  $\beta$ - $\text{C}_2\text{S}$  in the presence of some pozzolanic materials. *Cem Concr Res* 1994;24:966–74.
74. Yoshida K, Igarashi H, Ohsaki M. Heats of hydration and strength development of alite-belite-blastfurnace slag composite. *Cem Technol (Am Ceram Soc)* 1994;35–42.
75. Sun G, Young JF, Matkovic B, Paljevic M, Mikoc M. Long-term hydration of  $\text{CaSiO}_4$  with combined addition of silica fume, calcium sulfoaluminate and gypsum. *Adv Cem Res* 1994;6:161–4.105.
76. EN 450-1:2012. Fly ash for concrete—part 1: definition, specifications and conformity criteria.
77. EN 15167-1. Ground granulated blastfurnace slag for use in concrete, mortar and grout—part 1: definitions, specifications and conformity criteria.
78. EN 13263-1. Silica fume for concrete—part 1: definitions, requirements and conformity criteria.
79. CEN TR 15868. Survey of national requirements used in conjunction with EN 206-1:2000; 2009.

80. EN15804. Sustainability of construction works. Environmental product declarations. Core rules for the product category of construction products.
81. CEN Technical report 16970. Sustainability of construction works—Guidance for the implementation of EN 15804. Draft for voting dated 14 Dec. 2015.
82. prEN 197-1. Cement—part 1: composition, specifications and conformity criteria for common cements. Draft of EN 197-1 for public comment; Jun. 2014.
83. CEN Technical Report 16912. Guidelines for a procedure to support the European standardization of cements.
84. Taylor MG. *Novel cements: low energy, low carbon cements*. Mineral Products Association Cement Fact Sheet 12; 2013.
85. Quillin K. Calcium sulfoaluminate cements: CO<sub>2</sub> reduction, concrete properties and applications (BR 496); 2007.
86. EN 206. Concrete—specification, performance, production and conformity.
87. BS 8500-1. Concrete—complementary British Standard to BS EN 206-1—part 1: method of specifying and guidance for the specifier.
88. BS 8500-1. Concrete—complementary British Standard to BS EN 206-1—part 2: specification for constituent materials and concrete.
89. PAS 8820. Construction materials—alkali-activated cementitious material—specification. British Standard Institution; 2016.
90. Mineral Products Association (MPA). MPA cement GHG reduction strategy: roadmap to 2050; 2013.

## FURTHER READING

91. Gygi H. Thermodynamics of the cement kiln. In: *Proceedings of the third international symposium on the chemistry of cement*, London; 1952. p. 750–79.