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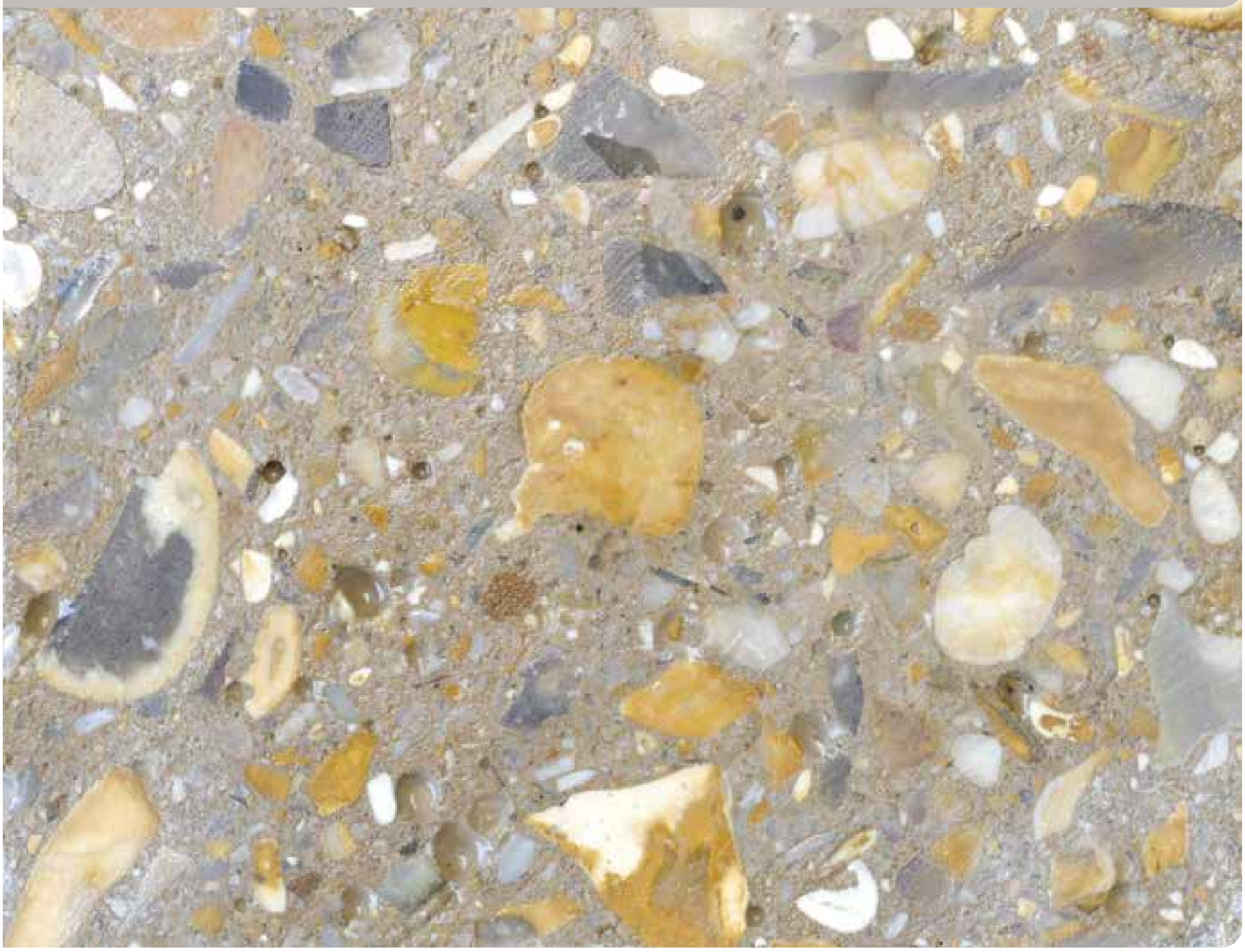

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Contents

Chemical formulae used in this guide

Al_2O_3	alumina
$C_2(A,F)$	ferrite phase (specific form found in Aether)*
C_2S	dicalcium silicate (belite)*
C_3A	tricalcium aluminate*
C_3S	tricalcium silicate (alite)*
$C_4A_3\$$	ye'elimite (calcium sulfoaluminate)*
C_4AF	calcium aluminoferrite (ferrite)*
$CaCO_3$	calcium carbonate (limestone comprises mainly calcium carbonate)
CaO	calcium oxide (lime)
CH	calcium hydroxide (portlandite)*
CO_2	carbon dioxide
Fe_2O_3	iron(III) oxide
K_2SO_4	potassium sulfate
Na_2O_{eq}	total alkalis Na_2O + K_2O (expressed as sodium oxide equivalent)
Na_2SO_4	sodium sulfate
NaOH	sodium hydroxide
SiO_2	silica
SO_3	sulfate

* Cement chemist's nomenclature has also been used as follows:

A	Al_2O_3	alumina
C	CaO	calcium oxide
F	Fe_2O_3	iron(III) oxide
S	SiO_2	silica
$	SO_3	sulfate

Executive summary

Concrete is likely to continue to be the primary volume construction material for most structural applications and its use is likely to grow in the future. Portland cement (PC) and blended PCs are currently the only economic binders for concrete that can match the performance and durability requirements under the wide range of conditions to which concrete is exposed.

Cement manufacture produces large amounts of CO_2 due to energy use and the calcination of $CaCO_3$. Cement manufacture consequently accounts for about 5% of total global anthropogenic CO_2 emissions.

The pressure to reduce energy consumption and CO_2 emissions during cement manufacture has led the industry to increase the extent to which Portland cement clinker is substituted in conventional cements by other ingredients that are currently approved for standard production, such as ground granulated blastfurnace slag (ggbs), pulverised-fuel ash (pfa or fly ash), natural pozzolans and limestone. However, there have until recently been few serious attempts to develop novel cements based on alternative clinkers with intrinsically lower energy requirements and CO_2 emissions on manufacture than conventional Portland cement clinkers.

This report summarises work on cements based not on C_3S (the major phase in PC) but instead on C_2S as the major phase, with $C_4A_3\$$ (calcium sulfoaluminate or ye'elimite) and C_4AF (ferrite) as the other two principal phases. It specifically focuses on the LafargeHolcim-patented Aether† cements as an example of this type of cement. These cements can be made from conventional raw materials, in existing industrial installations and offer similar performances to CEM I (ordinary) PC, but with 25–30% lower CO_2 emissions.

The work summarised in this report was funded under the EU LIFE+ and SILC programmes to assess the performance and durability of Aether concrete. It has shown that good-quality concretes can be made using a range of different batches of Aether cement. Specimens have been prepared to allow testing to continue over a number of years. To date, durability data for up to two years have been recorded. Results have shown the following:

- Good-quality concretes can be prepared using Aether cement. The compressive strength of Aether concretes at lower water:cement (w/c) ratios at least matches that of otherwise equivalent PC concretes at test ages of up to two years.
- The dimensional stability of Aether concretes stored in water at 5°C and 20°C is comparable to that of otherwise equivalent PC concretes at test ages of up to two years.
- Aether concretes stored in air at 20°C show less drying shrinkage than equivalent PC concretes.
- Aether concretes have not shown signs of deterioration on exposure to sulfate solutions over two years of exposure. Otherwise equivalent PC concretes show significant deterioration on exposure to sulfate solutions.
- Aether concretes deteriorate on exposure to citric acid solution. However, the rate of deterioration to these extremely aggressive conditions is comparable to that of otherwise equivalent PC concretes. In both Aether and PC concretes, acid resistance increases with concrete quality and curing.
- Whilst the carbonation front in Aether concretes is less well defined than in PC concretes, the rate of carbonation of Aether concretes appears to be higher than that of otherwise equivalent PC concretes stored in similar conditions. Further tests will be required to assess if there is any impact on the corrosion of embedded reinforcement.
- The gas permeability and chloride diffusion coefficient of Aether concretes are lower than those of otherwise equivalent PC concretes. These results are consistent with Aether concretes being durable, although other factors (such as exposure environment and mix design) need to be taken into account.
- A number of large reinforced concrete elements have been produced using Aether concretes. The elements were of good quality and will be stored on the BRE exposure site at an inland location in southern England to allow ongoing monitoring of performance.
- Specimens have been prepared to assess the susceptibility of Aether concretes to deterioration as a result of alkali–silica reaction (ASR) or delayed ettringite formation (DEF). Data available to date have not indicated a susceptibility to these processes, although the tests need to be continued over a longer period before conclusions regarding durability can be made.

† Aether is a registered trademark.

1 Introduction

1.1 Background

Concrete is likely to continue to be the primary volume construction material for most structural applications and its use is likely to grow in future. Portland cement and blended PCs are currently the only economic binders for concrete that can match the performance and durability requirements under the wide range of conditions to which concrete is exposed.

Global cement manufacture (including both ‘pure’ and ‘blended’ PCs) has risen from 594 million tonnes per annum in 1970 to 2.3 billion tonnes per annum in 2005 and to about 3.8 billion tonnes in 2012, with virtually all of this growth occurring in developing countries. The UK produced approximately 8 million tonnes of PC in 2012 (total sales were about 10.5 million tonnes if imports and other cementitious materials such as fly ash (also known as ‘pulverised-fuel ash’ or ‘pfa’) and ggbs are included)[1]. Global production is likely to increase significantly over the coming decades as the global population increases. Recent forecasts have indicated that global cement production could reach 5 billion tonnes per annum by 2030.

Cement manufacture is energy intensive. The raw materials must be finely ground and homogenised, and then heated to about 1450°C to form Portland cement clinker. Upon cooling, the hard nodules of clinker must be finely ground with small amounts of other ingredients such as gypsum to make the finished cement. Cement manufacture also produces large amounts of CO_2 due to energy use and the calcination of $CaCO_3$ – about 1.2 tonnes of $CaCO_3$ are required to produce 1 tonne of a typical modern Portland cement clinker. The amount of CO_2 produced per tonne of Portland cement clinker manufactured depends on a number of factors such as clinker, fuel and raw materials compositions and the energy efficiency of the specific kiln system. The amount of CO_2 produced per tonne of finished cement varies depending on factors such as cement composition (eg content of gypsum and other non-clinker ingredients) and manufacturing efficiency, and is therefore difficult to quantify. However, recent data on global CO_2 emissions from cement manufacture give an overall average of 0.88 tonnes per tonne of cement produced (the same data indicate a value for Europe of about 0.63 tonnes/tonne). British Cement Association data for the UK indicate that 0.82 tonnes of CO_2 are produced per tonne of CEM I cement. These and other industry data imply that about 1.5–2 billion tonnes of CO_2 per annum are produced from cement manufacture globally. Cement manufacture accounts for about 5.3% of total global anthropogenic CO_2 emissions[2], and about 1.4% of anthropogenic emissions in the UK*. It is reported to be the third-highest readily identifiable source of anthropogenic CO_2 emissions after fossil fuel combustion (eg for electricity and transportation) and deforestation[3].

The pressure to reduce energy consumption and CO_2 emissions during cement manufacture has led the industry to increase the extent to which Portland cement clinker is substituted in conventional cements by other ingredients that are currently approved in the existing norms, such as ggbs, pfa, natural pozzolans and limestone†. However, there have until recently been few serious attempts to develop novel cements based on alternative clinkers with intrinsically lower energy requirements and CO_2 emissions on manufacture than conventional Portland cement clinkers. Possible alternative cements have been reviewed elsewhere[4, 5, 6, 7].

1.2 Portland cement manufacture

Portland cement clinker is manufactured by heating an intimate mixture of limestone and clay, generally in a rotary kiln. Minor proportions of constituents such as iron ore, bauxite or sand may be required to achieve the correct overall composition. The raw meal, paste or slurry is finely divided, intimately mixed and therefore homogeneous. The clinker is then blended with additives to produce a cement. The process is summarised in Figure 1.

The main component of PC is C_3S (alite), although about 20% C_2S (belite) is typically present. The formation of a large percentage of C_3S requires that the raw feed be heated to a temperature of about 1450°C. Belite is typically formed at around 1200°C. It can exist in a number of polymorphs, although it is the β-form that is normally present in Portland cement clinker. Alite reacts more rapidly with water than β-C_2S. Under conditions typical of PC use, about 30% of the available β-C_2S and 70% of the available C_3S hydrate within 28 days. The hydration products are similar, although less CH is formed on hydrating C_2S, which correlates with the lower amount of $CaCO_3$ required for its manufacture.

Standard enthalpies of reaction can be used to calculate the theoretical enthalpies required to manufacture C_3S and C_2S from $CaCO_3$ and SiO_2. These are 1848 kJ/kg and 1337 kJ/kg respectively, although the actual values for manufacturing particular cements will depend on the starting materials used and the target compositions.

1.3 Cement composition

Cement clinker is blended with other materials such as calcium sulfate, limestone, ggbs and pfa to form a cement. BS EN 197-1:2011[9] summarises 27 products in the family of common cements (subdivided into five main types). Some of these products are included in Table 1 and show a wide range of compositions (although some of these products will be suitable for use only in limited, specific applications). Portland cement contains at least 95% clinker, with the remaining 5% made up of minor additional components. The final cement comprises the main clinker and minor additional constituents plus the necessary calcium sulfate and any additives (see BS EN 197-1, Section 5). However, as shown in Table 1, the clinker content in cements conforming to BS EN 197-1 can be as low as 5% and, assuming that CO_2 emissions associated with constituents other than clinker can be ignored, the CO_2 associated with 1 tonne of cement can vary considerably.

* Assuming total UK emissions of 490 million tonnes per annum.

† Limestones are sedimentary rocks comprising mainly calcium carbonate ($CaCO_3$).