EDUCATIONAL GUIDE TO
CEMENTITIOUS MATERIALS
# Cementitious Materials

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Cementitious Materials

Introduction

Cement is the adhesive or glue, which when set binds particles of fine aggregate together to produce mortar. When mixed with water the cement forms a paste, which is called the fine matrix. (When coarse aggregate is used as in concrete production the matrix is described as the fine and the coarse matrix). Cements are hydraulic materials, this means that they depend upon a reaction with water rather than air for strength development. When water is added to cement a chemical reaction called hydration commences immediately and continues while water is still present.

Lime mortars are believed to have been developed in ancient Egypt. These generally harden and gain strength by the evaporation of the water and the absorption of carbon dioxide from the atmosphere. This results in the gradual conversion of the lime into calcium carbonate.

It was the patenting of Portland cement by Joseph Aspin in 1824 that started the large-scale production of cements. There are a number of different types of cements, which may be used to produce mortar.

Portland cement

Manufacture

Portland cement is made from limestone or chalk and shale or clay (i.e. calcium carbonate and siliceous material). There are two main methods of cement manufacture, the wet process and the more modern dry process.

In the wet process, soft raw materials are reduced to a water suspended slurry in washmills, hard oversized material being separated by screens and ground in a tube mill. The slurry has a creamy consistency and a water content of approximately 40%. The slurry is pumped to storage tanks, which are continuously agitated to prevent the solid particles from settling out. Because the raw materials can contain varying amounts of calcium and silica, it may be necessary to blend different slurries in order to obtain the desired chemical composition before feeding into the kiln.

In the dry process, the materials are crushed and fed through a tube mill, which reduces them to a fine meal. The meal is then stored in a silo from where it is transported to the kiln pre-heater. The material then cascades downwards while warm exhaust gas from the kiln passes through it.

The raw materials are fed through the kiln, which can be up to 250m long, and 6m in diameter, the length of the kiln depending on which process is used. In the kiln-firing zone, the material reaches a temperature of 1400°C before leaving the kiln in the form of clinker.
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The clinker is rapidly cooled and stored until required for milling, when it is fed into tube mills where about 3-5% gypsum is added to control the setting of the finished product and the materials are ground to the required fineness. Increasingly, other additives which impart water-reducing properties to the cement and aid grinding are incorporated during the grinding stage. The cement is then fed to storage silos until required for delivery or diverted to a bagging plant.

Properties

The proportions of the raw materials and the manufacturing process can be varied to produce different cements with a range of properties.

Portland cement contains four main compounds these are:

- **Tricalcium silicate** (C₃S) - this reacts rapidly with water producing relatively large amounts of heat to form calcium silicate hydrate. It has a high strength and is the main contributor to the early strength of cement hydrate. The cement chemist's shorthand notation for this compound is C₃S.

- **Dicalcium silicate** (C₂S) - this reacts slowly with water to form the same product as C₃S. Because of the slow reaction, the heat evolved is dissipated before significant temperature rises occur. It increasingly contributes to strength at later ages.

- **Tricalcium Aluminate** (C₃A) - this compound reacts very rapidly with water, evolving a relatively large amount of heat and with a very rapid set. This reaction is retarded by the addition of gypsum during the grinding stage.

- **Tetracalcium aluminoferrite** (C₄AF) - this compound reacts rapidly with water but does not produce much heat or strength. C₄AF must be absent in white cement because of its pronounced colour.

The symbols C₃S, C₂S, C₃A and C₄AF are all cement chemist's shorthand notation.

**Minor compounds** - A number of minor compounds are present in cement, including free lime, alkalies and magnesia.

**Fineness** - since reaction with water is a surface one, increasing the fineness, which increases the surface area, speeds up the reaction.

British/European standards

The European Standard BS EN 197-1 which is entitled "Cement - Part 1 Composition, specification and conformity criteria for common cements" was published in 2000 and replaced a number of former British Standards which were withdrawn on 1st April 2002.

The Standards withdrawn in April 2002 were:

- BS 12 :1996 Specification for Portland cement
- BS 4246: 1996 Specification for high slag blastfurnace cement
- BS 6588: 1996 Specification for Portland pulverised fuel ash cement
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BS 7583 : 1996 Specification for Portland limestone cement
BS 146 (Specification for blastfurnace slag cements outside the scope of BS EN 197-1) and BS 6610 (Pozzolanic pulverised fuel ash cement) will continue to co-exist with modified requirements. For the foreseeable future BS 4027 (Specification for sulfate-resisting Portland cement) will continue in an unmodified form.

A European standard for Masonry cement BS EN 413 is nearing publication, when this is published BS 5224 will be withdrawn.

Nomenclature for cements

Cements are described in a format which indicates the cement type, main constituents, strength class and rate of early strength development.

a) BS EN 197-1 categorises cements into five types based on their composition, these are:

CEM I Portland cement; comprising Portland cement and up to 5% of minor additional constituents Note 1.

CEM II Portland composite cement; comprising Portland cement and up to 35% of certain other single constituents (the exception being Portland composite cement). Note 2

CEM III Blastfurnace cement; comprising Portland cement and higher proportions of blastfurnace slag than in a CEM II cement.

CEM IV Pozzolanic cement; comprising Portland cement and higher proportions of pozzolana than in a CEM II cement.

CEM V Composite cement; comprising Portland cement and combinations of blastfurnace slag and pozzolana or fly ash.

Notes 1 Minor additional constituents are inorganic materials, (limestone, fly ash or ground granulated blastfurnace slag), which because of their particle size can improve the physical properties of the cement, e.g. workability or water retention.

2 Portland composite cement may incorporate a mixture of up to 35% of any of the materials listed as secondary main constituents (See c).

b) All the cement types apart from CEM I have a designatory letter immediately after the Roman numeral indicating the cement type, this indicates the range of PC clinker proportions. Regrettably, for each of the cement types the same designatory letter indicates a different PC clinker range, this is a little confusing.

i) The cements described as CEM II which is a cement with a single secondary major constituent (the exception being Portland composite cement) have a designatory letter immediately after the CEM notation to indicate the level of Portland cement contained within the cement:
Cementitious Materials

A = high level (PC clinker content 80-94%) - CEM II/A  
B = medium level (PC clinker content 65-79%) - CEM II/B

ii) A similar system operates for CEM III cements which are cements containing a higher level of blastfurnace slag than permitted in a cement of type CEM II.

A = PC clinker content 35-64% - CEM III/A  
B = PC clinker content 20-34% - CEM III/B  
C = PC clinker content 5-19% - CEM III/C

iii) CEM IV cements contain a higher level of pozzolanic material than permitted in a cement of type CEM II, a designatory letter is used to indicate the PC content:

A = PC clinker content 65-89% - CEM IV/A  
B = PC clinker content 45-64% - CEM IV/B

iv) CEM V cements are composite cements but contain a higher level of the secondary constituent than CEM II cements (it is also permitted to have more than one major secondary constituent). The range of Portland cement clinker content is also indicated by the use of a designatory letter:

A = 40-64% PC clinker content - CEM V/A  
B = 20-39% PC clinker content - CEM V/B

c) CEM II cements also have an additional designatory letter after the letter indicating the Portland cement clinker level which indicates the second main constituent present in the cement. The letters are as follows:

S = blastfurnace slag  
P = natural pozzolana  
V = siliceous fly ash (e.g. pfa)  
T = burnt shale  
M = a composite cement  
D = silica fume  
Q = natural calcined pozzolana  
W = calcareous pfa (e.g. high lime pfa)  
L = limestone

d) For example a cement with the description BS EN 197- CEM II/ B-V 42.5 N indicates a Portland fly ash cement with a Portland cement clinker content in the range 65-79%, a pulverized fly ash content in the range 21-35%, a standard strength class of 42.5 and a normal rate of strength development as shown in Figure 1.
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BS EN 197 – CEM II/B-V 42.5 N

Figure I: BS EN 197-1 – description for a Portland fly ash cement

e) The standard strength class is the strength that will be achieved at twenty eight days by a prism of cement, sand and water of a fixed composition tested in a prescribed manner. There are three strength classes 32.5, 42.5 and 52.5. The appropriate standard lists the exact requirements for determining the class and the permitted range of strengths within each class. Not all cements are available in each class. The strength class is expressed in MPa (Mega Pascals), these units are numerically equivalent to N/mm².

f) Masonry cement has a different form of nomenclature. There are three strength classes 5, 12.5 and 22.5. The 12.5 class may be supplied without the incorporation of an air entraining admixture, this is indicated by the letter "X" after the strength grade. The 22.5 strength class is not permitted to incorporate an air entraining admixture. Masonry cements are only available in standard strength classes, no sub classes are permitted by the standard.

Types of Cement

CEM I 42.5 N (Portland Cement)

This is the basic cement and is commonly used for general construction work. This cement is frequently combined with ground granulated blastfurnace slag or pulverized fuel ash (see the following sections).

CEM I 42.5 R and 52.5 N (Portland Cement)

This cement is normally made by grinding the same clinker as CEM I 42.5 N to a greater fineness: in order to prevent a more rapid set occurring than for CEM I 42.5 N. extra
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gypsum is usually added at the grinding stage. CEM I 42.5 R or 52.5 N is used where there is a requirement for early strength, for example precast applications.

Sulfate Resisting Portland Cement (CEM I + SR) BS 4027

To produce this cement iron oxide is added to the raw feed to the kiln which results in the production of a material low in tricalcium aluminate (C₃A). This is the compound that reacts with sulfates to potentially result in sulfate attack which may lead to the disintegration of the hardened mortar. The increased iron oxide content gives sulfate resisting Portland cement a darker colour than plain Portland Cement. Sulfate resisting Portland cement is often ground finer than CEM I Class (42.5 N) in order to compensate for the reduced early strength caused by its low C₃A content.

Masonry Cement (BS 5224)

Masonry cement was developed in the United States in the 1930's and is made by mixing Portland cement with up to approximately 60% of a filler such as ground chalk and incorporating a plasticiser/air entraining additive. This cement is weaker in strength than normal Portland cement, but has improved plasticity and water retention.

CEM II/A-L (Portland Limestone Cement)

This cement is produced by blending or intergrinding 6-20% of ground limestone with Portland cement. It is also possible to produce this material in the concrete mixer by mixing 6-20% of limestone fines, conforming to BS 7979, with Portland cement.

White Cement (CEM I)

This is a cement made from especially pure non-iron containing raw materials (e.g. China clay and white limestone) in order that the tetracalcium aluminoferrite (C₄AF) content is very low. It is normally made in a separate kiln and is therefore more expensive than standard Portland cement. Currently, this cement is only available in the UK as strength class 52.5 N.

Ground granulated blastfurnace slag (ggbs) - (BS 6699)

Ggbs is a by-product of the iron/steel manufacturing industry. The molten slag from the production of iron in a blastfurnace is rapidly cooled by high pressure water jets which subjects the slag to instantaneous solidification in the form of granules, these are then dried and ground to a similar fineness to CEM I Class (42.5 N) in a tube mill. Ggbs is off-white in colour. It may be described as a latent hydraulic material which means it will gain strength on its own, but very slowly.

Pozzolanic materials (including pfa)

Pozzolanic materials may be divided into two categories, natural pozzolanas and artificial pozzolanas. Natural pozzolanas include volcanic ashes such as those found around Pozzouli near to Mount Vesuvius, hence the name. Artificial pozzolanas include pulverized fuel ash, crushed burnt bricks and tiles.
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The Romans used to add volcanic ash to lime as they found that it created a stronger matrix. In some parts of Europe naturally occurring pozzolanas are still used. A pozzolana is mainly composed of compounds of silica, alumina and iron oxide, when mixed with a highly alkaline material, (such as cement) hydraulic properties are developed.

Pulverized fuel ash (pfa) is an artificial pozzolana which is the residue obtained from the combustion of pulverized coal collected from the flue gases in electrostatic precipitators at coal fired power stations. Normally, only the ash from base load power stations is of high enough quality for use in mortar or concrete, as a variable power generation cycle leads to unburnt carbon in the ash. The ash collected from the power stations may be further classified using air separators to remove certain size fractions. Pfa particles are spherical in shape and are generally as fine or finer than CEM I Class (42.5 N). Pfa is similar in colour to plain Portland cement and the technical requirements it is required to conform to, are listed in BS 3892.

Lime

Introduction

The ancient Greeks and Romans produced mortar by burning limestone and slaking (mixing with water) the resultant product with water and, then mixing it with sand.

When limestone (calcium carbonate) is heated to a high temperature or calcined the resultant product is quicklime. (The correct technical name is calcium oxide):

\[
\begin{align*}
\text{CaCO}_3 & \quad + \quad \rightarrow \quad \text{CaO} & \quad + & \quad \text{CO}_2 \\
\text{Limestone} & \quad \text{Heat} & \quad \text{Quicklime} & \quad \text{Carbon dioxide} \\
\text{Chalk} & \quad 850^\circ\text{C} & \quad & \\
\text{Marble} & \quad & \quad & \\
\end{align*}
\]

The calcination process was traditionally undertaken in small mixed feed kilns and examples of the remains of these may still be seen around the country. Chemical analysis of historic mortars indicates that many of these contain inclusions of lime that have remained unmixed and unslaked during mortar production. Currently the calcination of limestone is generally undertaken in shaft or rotary kilns.

Lime was traditionally classified as hydraulic or non-hydraulic. Hydraulic limes possess the ability to set under water. Current British Standards no longer use the terminology hydraulic or non-hydraulic in the classification of lime. The addition of water to quicklime results in a great deal of heat being given off and the formation of calcium hydroxide.

\[
\begin{align*}
\text{CaO} & \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{Ca(OH)}_2 & \quad + & \quad \text{Heat} \\
\text{Quicklime} & \quad \text{Water} & \quad \text{Calcium hydroxide} & \\
\end{align*}
\]

Traditionally, an excess of water was added to quicklime and the material allowed to soak for several weeks or even months in pits (the process called slaking). As time
Cementitious Materials

progressed the process was refined and after the addition of water the mixture was passed over a screen to remove particles which were reacting slowly. The mixture was then left to mature for about a month prior to use. The inefficiency of this process could lead to the expansion of some of the unslaked particles resulting in popping and pitting of lime based plasters. Expansion of the mortar could also take place, a phenomenon known as blowing. The slaking of quicklime has largely been superceded by modern methods of producing hydrated lime.

Hydraulic limes

These are produced by burning limestone (calcium carbonate) containing quantities of impurities such as silica, alumina and iron. The carbon dioxide is driven off at a temperature in excess of 850° C and the resultant product is calcium oxide with calcium silicates (which gives this material its hydraulic properties). The material is sometimes called quicklime.

Hydraulic limes made from limestones’ containing quantities of silica, alumina and iron are called natural hydraulic limes. Artificial hydraulic limes are produced by blending powdered hydrated limes with pozzolan material and/or cement.

Traditionally, hydraulic limes were classified as eminently hydraulic, moderately hydraulic and feebly hydraulic. Eminently hydraulic lime was sometimes called Roman lime.

Non-Hydraulic limes

These are materials with a high calcium content and only minor amounts of silica, alumina and/or iron. Limestones which have a high content of magnesium may also be classified as non hydraulic.

Hydrated lime

The addition of a carefully controlled quantity of water to quicklime produces a dry powder that is called hydrated lime, a process that is generally undertaken in a hydrating plant. When quicklime and water are combined, the product may be dry hydrate, lime putty or milk of lime, dependent on the increasing amount of water added.

To produce dry hydrate only the precise amount of water to complete the hydration reaction is required.

Lime putty is produced by the controlled addition of water to quicklime to produce a paste like consistency. Alternatively, milk of lime (which is not used in mortar production without further processing) can be allowed to settle out and the excess water removed. The properties of lime putties improve with age and they are frequently left to mature for some time.

Definitions

Calcium limes (CL): limes mainly consisting of calcium oxide or calcium hydroxide without any additions of hydraulic or pozzolanic materials.
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Dolimitic limes (DL): limes mainly consisting of calcium oxide and magnesium oxide or calcium hydroxide and magnesium hydroxide without any additions of hydraulic or pozzolanic materials.

Hydraulic limes (HL): limes mainly consisting of calcium hydroxide, calcium silicates and calcium aluminates produced by mixing of suitable materials. They have the property of setting and hardening under water. Atmospheric carbon dioxide contributes to the hardening process.

Natural hydraulic limes (NHL): limes produced by burning of more or less argillaceous or siliceous limestones with reduction to powder by slaking with or without grinding. All NHL have the property of setting and hardening under water. Atmospheric carbon dioxide contributes to the hardening process.

Classification

The 1995 edition of BS 890 (Specification for Building limes) introduced a new classification system for limes based on the calcium and magnesium oxide contents. These are shown in following table:

<table>
<thead>
<tr>
<th>Type of building lime</th>
<th>CaO +MgO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL 90</td>
<td>≥85</td>
<td>≤6</td>
</tr>
<tr>
<td>CL 80</td>
<td>≥75</td>
<td>≤6</td>
</tr>
<tr>
<td>CL 70</td>
<td>≥65</td>
<td>≤6</td>
</tr>
<tr>
<td>DL 85</td>
<td>≥80</td>
<td>≥27 ≤45</td>
</tr>
<tr>
<td>DL 80</td>
<td>≥75</td>
<td>≥4 ≤45</td>
</tr>
</tbody>
</table>

Table 1: Chemical properties of lime

Limes which contain ≥4 % magnesium oxide (MgO) are referred to as dolimitic Limes.

The European Standard BS EN 459-1 (Building lime: Definitions, specifications and conformity criteria uses a similar classification (Table 2) but also includes three categories of hydraulic lime. This standard will ultimately replace BS 890.
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<table>
<thead>
<tr>
<th><strong>Designation</strong></th>
<th><strong>Notation</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium lime 90</td>
<td>CL 90</td>
</tr>
<tr>
<td>Calcium lime 80</td>
<td>CL 80</td>
</tr>
<tr>
<td>Calcium lime 70</td>
<td>CL 70</td>
</tr>
<tr>
<td>Dolomitic limes 85</td>
<td>DL85</td>
</tr>
<tr>
<td>Dolomitic limes 80</td>
<td>DL 80</td>
</tr>
<tr>
<td>Hydraulic lime 2</td>
<td>HL 2</td>
</tr>
<tr>
<td>Hydraulic lime 3.5</td>
<td>HL 3.5</td>
</tr>
<tr>
<td>Hydraulic lime 5</td>
<td>HL 5</td>
</tr>
<tr>
<td>Natural hydraulic lime 2</td>
<td>NHL 2</td>
</tr>
<tr>
<td>Natural hydraulic lime 3.5</td>
<td>NHL 3.5</td>
</tr>
<tr>
<td>Natural hydraulic lime 5</td>
<td>NHL 5</td>
</tr>
</tbody>
</table>

Table 2: BS EN 459-1 Classification of building limes

Cement lime and combinations

There are a number of cements and combinations, which can be used in mortar, render, screed and concrete. While there are a considerable number of types of cement, many mortar plants have only limited silos and typically may stock:

CEM I Class (42.5 N), Ground granulated blastfurnace slag (ggbs) (BS 6699)

or

CEM I Class (42.5 N), Pulverized fuel ash (pfa) (BS 3892 Part 1) and lime

However for plants with several silos it may be possible to stock a combination of the above.

In some areas it is possible to purchase Portland slag cement (CEM II/A-S or CEM II/B-S), Blastfurnace cement (CEM III/A), Portland fly ash cement (CEM II/A-V or CEM II/B-V) or Pozzolanic cement (CEM IV/B) direct from a manufacturer, but it is more usual to produce these cements in the plant mixer or truck mixer by batching the constituent materials from separate silos.

CEM I Class (42.5 N) and ggbs are batched to give CIIA-S - 6-20% ggbs
CEM I Class (42.5 N) and ggbs are batched to give CIIB-S - 21-35% ggbs
CEM I Class (42.5 N) and ggbs are batched to give CIII/A - 36-65% ggbs
CEM I Class (42.5 N) and ggbs are batched to give CIIB - 66-80% ggbs
CEM I Class (42.5 N) and pfa are batched to give CIIA-V - 6-20% pfa
CEM I Class (42.5 N) and pfa are batched to give CIIB-V - 21-35% pfa
CEM I Class (42.5 N) and pfa are batched to give CIVB-V - 36-55% pfa
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Applications

Sulfate resisting Portland cement may be used where there is a likelihood of sulfate attack, in some work where sufficient quantities of sulfates are present. CIIA-S or CIIB-S are most commonly used for all types of construction work: CEM I may also be used.

Masonry cement may also be used for general masonry construction, but it has no particular sulfate resisting properties.

Safety

Care must always be taken when handling cementitious products due to their alkaline nature. Although they normally have no harmful effect on dry skin, they may cause irritation when mixed with water.

When working with wet mortar, waterproof or other suitable protective clothing should be worn.

Precautions should be taken to avoid dry cement entering the eyes, mouth and nose when mixing mortar. If wet cement or lime enters the eye it should be immediately washed out thoroughly with clean water and medical treatment should be sought without delay. Wet mortar on the skin should be washed off immediately.

Repeated skin contact with wet cementitious products over a period may cause irritant contact dermatitis in some people. The abrasiveness of the particles of cement and fine aggregate in mortar can contribute to this effect.
## Self assessment questions

<table>
<thead>
<tr>
<th></th>
<th>Question</th>
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<tbody>
<tr>
<td>1</td>
<td>What are the basic raw materials from which Portland cement is manufactured?</td>
</tr>
<tr>
<td>2</td>
<td>What is added to Portland cement to produce masonry cement?</td>
</tr>
<tr>
<td>3</td>
<td>What compound is absent from white cement?</td>
</tr>
<tr>
<td>4</td>
<td>What process is ggbs a by-product from?</td>
</tr>
<tr>
<td>5</td>
<td>What is the difference between hydrated and hydraulic lime?</td>
</tr>
<tr>
<td>6</td>
<td>What are hydraulic materials?</td>
</tr>
<tr>
<td>7</td>
<td>How do lime based materials gain their strength?</td>
</tr>
<tr>
<td>8</td>
<td>What is the effect of grinding cement more finely?</td>
</tr>
<tr>
<td>9</td>
<td>How much gypsum is added to cement clinker at the grinding stage?</td>
</tr>
<tr>
<td>10</td>
<td>Who obtained a patent for the production of Portland cement in 1824?</td>
</tr>
</tbody>
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Answers to self assessment questions

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1</td>
<td>A source of calcium carbonate (chalk or limestone) and a source of Silica (clay or shale).</td>
</tr>
<tr>
<td>2</td>
<td>A filler such as ground chalk and a plasticiser / air entrainer.</td>
</tr>
<tr>
<td>3</td>
<td>Iron bearing materials.</td>
</tr>
<tr>
<td>4</td>
<td>The production of iron from iron ore.</td>
</tr>
<tr>
<td>5</td>
<td>Hydraulic lime sets by reaction with water, hydrated lime does not.</td>
</tr>
<tr>
<td>6</td>
<td>Materials that have the ability to set under water.</td>
</tr>
<tr>
<td>7</td>
<td>Lime based materials gain their strength by the absorption of carbon dioxide from the air and converting the calcium oxide to calcium carbonate.</td>
</tr>
<tr>
<td>8</td>
<td>The cement has the ability to gain strength more quickly.</td>
</tr>
<tr>
<td>9</td>
<td>3-5% gypsum is added to cement clinker at the grinding stage.</td>
</tr>
<tr>
<td>10</td>
<td>Joseph Aspin.</td>
</tr>
</tbody>
</table>
EXPERTS IN MORTAR

CEMEX Mortar is available in ready to use or dry silo options providing the perfect solution for every situation. Our experts can advise on conformity to standards as well as strengths, colour and working with different brick and block options. At our centrally based research and development centre the team can support you further with special mix designs, durability and colour specification. All CEMEX Mortars conform to British and European standards and are factory produced for consistency and reliability.

For more information contact our Mortar Enquiry Line
Tel: 0800 667 827
Email: gb-enquiries@cemex.com

Or visit our website at www.cemex.co.uk/mortar