High alumina cement

Cement is the binder in concrete. Almost all the cements used in the Netherlands are based on Portland cement clinker. The most important are blast furnace cement, Portland cement and Portland fly ash cement. There are also other types of cement, for example high alumina cement. Concrete made using this cement has a number of specific properties. By using this cement it is possible to obtain concrete with a very high initial strength or very good refractory properties. This concrete is also resistant to attack by sulphates and weak acids. During the nineteen-seventies it was discovered that concrete made using high alumina cement could lose a substantial part of its strength and durability with time. This resulted in significant damage in a number of cases. In a number of countries the use of high alumina cement in structural applications was subsequently banned or subjected to very stringent conditions. As a result of this, high alumina cement was consequently only used for special applications. This issue of BETONIEK looks at high alumina cement’s history, production, composition and specific properties in relation to concrete technology and it gives guidelines for proper application.

High alumina cement is not a recent development. It was discovered in France as long ago as 1865 that fused and crushed mixtures of alumina and lime have hydraulic properties. Twenty-three years later a patent was issued in the United Kingdom for limestone bauxite cement. The limestone produces lime and the bauxite yields alumina. However, it was not until the beginning of the twentieth century that high alumina cement could be manufactured on an industrial scale. The first commercial producer was Lafarge, which started production in 1908. The cement has a number of advantages compared with Portland cement. The initial strength after one day is higher than that of Portland cement after 28 days. Concrete made from this cement is highly resistant to attack by sulphates. At the time, high alumina cement was set to take the world by storm. Manufacturing was started up all over the world in a very short time. The only disadvantage appeared to be the price!
Production and chemical composition

Almost all the manufacturing plants used the Lafarge process (Figure 1) known as ‘Ciment Fondue’. A mixture of limestone and bauxite is heated in an oven until it melts. The molten material is tapped off and poured into steel moulds. As it cools, the liquid turns into blocks of high alumina cement clinker. These are broken into coarse pieces and then ground to fine particles in a cement mill. A setting regulator is not added during the grinding stage. Another, less common, method is to sinter the raw materials in a rotary oven.

Fig. 1. Reverberatory oven for the production of high alumina cement clinker (Ciment Fondue)

High alumina cement clinker is made up of the same basic components as Portland cement clinker, i.e.: lime, silica, alumina and iron oxide. However, the ratio of the components is quite different from Portland cement clinker. The chemical composition is determined by the ratio of limestone to bauxite in the mixture. The iron oxide content of the bauxite also plays a major role. The refractory properties and strength development depend on the alumina content. The higher the iron oxide content, the darker the colour.

Cement chemistry

We shall begin with a quick look at the chemistry. In cement chemistry the chemical formulas are always abbreviated:

<table>
<thead>
<tr>
<th>name</th>
<th>formula</th>
<th>abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>alumina</td>
<td>Al₂O₃</td>
<td>A</td>
</tr>
<tr>
<td>lime</td>
<td>CaO</td>
<td>C</td>
</tr>
<tr>
<td>iron oxide</td>
<td>Fe₂O₃</td>
<td>F</td>
</tr>
<tr>
<td>silica</td>
<td>SiO₂</td>
<td>S</td>
</tr>
</tbody>
</table>

Abbreviations are useful because they enable us to describe complicated compounds more simply, for example 12CaO. 7Al₂O₃ is abbreviated to C₁₂A₇.

Types of high alumina cement

The properties of high alumina cement are determined by the alumina content. Broadly speaking there are three different types. The most frequently used cements have 40% to 50% alumina. Cements with a higher alumina content are used for very specific applications. The brand name is invariably followed by the alumina content. This gives an indication of the properties of the cement. The higher the alumina content, the more rapid the hardening and the better the refractory properties. An overview is given in the table below.

<table>
<thead>
<tr>
<th>Type</th>
<th>A (%)</th>
<th>C (%)</th>
<th>F (%)</th>
<th>S (%)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAC 40</td>
<td>37-42</td>
<td>36-4</td>
<td>11-17</td>
<td>3-8</td>
<td>darkgrey</td>
</tr>
<tr>
<td>HAC 50</td>
<td>49-52</td>
<td>39-42</td>
<td>1-1.5</td>
<td>5-8</td>
<td>lightgrey</td>
</tr>
<tr>
<td>HAC 70-80</td>
<td>68-80</td>
<td>17-2</td>
<td>0-0.5</td>
<td>0-0.5</td>
<td>white</td>
</tr>
</tbody>
</table>

After the melting and cooling stages, the basic components form hydraulic compounds, which are also referred to as ‘clinker minerals’. These are CA, (CA₂ for for HAC 70-80%) C₁₂A₇, C₂AS, C₆fA₄S and C₄AF. The clinker mineral C₄AF is also found in Portland cement clinker, but the other minerals are very different.
Clinker minerals in high alumina cement and their properties

CA  Monocalciumaluminate is the main ingredient in high alumina cement. It gives the cement its specific properties, i.e. the slow setting and the very rapid hardening.

$\text{C}_{12}\text{A}_7$  is present in the cement in small percentages. It sets rapidly but it makes no contribution to the strength. Higher percentages of $\text{C}_{12}\text{A}_7$ can overwhelm the slow setting behaviour of the CA.

C\textsubscript{2}AS  Gehlenit is present in small percentages. The setting is slow and it only contributes to the strength after a considerable period.

C\textsubscript{6}FA\textsubscript{4}S  Pleochrit is present in small percentages. The setting is slow and it barely contributes to the strength.

C\textsubscript{4}AF  Tetracalciumaluminoferrite is the second most important component of high alumina cement. In spite of this it makes no contribution to the setting and the strength development.

Properties of high alumina cement

Hydration

Hydration is the reaction between cement and water. In the case of high alumina cement, this reaction proceeds very differently than in cement based on Portland cement clinker. In the latter category, hydration is a relatively slow process. Depending on the type of cement, strength class and curing conditions, only approximately 60-80% of the cement has reacted after 28 days. After 28 days the reaction continues slowly but steadily.

When high alumina cement and water are mixed together, the calcium aluminate compounds dissolve within minutes. A small quantity of heat is released in the process. There is then a quiet period of two to three hours, called the dormant period. During the next 24 hours almost all the water reacts with the cement, whereby a large quantity of heat is generated in a short space of time. A well-known experiment is to mix high alumina cement and water in a plastic cup. Initially nothing happens, but once the reaction becomes established the cup becomes too hot to hold and it melts.

Measurements have shown that the complete hydration of 100 kg of high alumina cement requires approximately 80 kg of water. The complete hydration of the same quantity of Portland cement requires some 40 kg of water. High alumina cement can therefore bind much more water than Portland cement.

The temperature at which hydrates are formed is important in the hydration of high alumina cement. Different hydration products are created, i.e. $\text{CAH}_{10}$, $\text{C}_2\text{AH}_8$ and $\text{C}_3\text{AH}_6$, depending on the temperature at which the process takes place (see box on formation of hydration products).

The formation of hydration products at different temperatures

\begin{align*}
T < 20 ^\circ \text{C} & \quad \text{CA} + 10\text{H} \Rightarrow \text{CAH}_{10} \\
20 ^\circ \text{C} < T < 60 ^\circ \text{C} & \quad 2\text{CA} + 11\text{H} \Rightarrow \text{C}_2\text{AH}_8 + \text{AH}_3 \\
T > 60 ^\circ \text{C} & \quad 3\text{CA} + 12\text{H} \Rightarrow \text{C}_3\text{AH}_6 + 2\text{AH}_3
\end{align*}

Conversion

Most hydration products are formed within 24 hours. The result is a strong and very dense solid cementitious matrix. However, there is one problem. The cement hydrates $\text{CAH}_{10}$ and $\text{C}_2\text{AH}_8$ that are formed are not stable (metastable) at temperatures above 20 °C. In due course
they are converted into C\textsubscript{3}AH\textsubscript{6}. In the Dutch climate we have to assume that this conversion always takes place. The higher the temperature, the faster the conversion. During the conversion process the existing cement hydrates CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} release water, as a result of which more and more voids in the cement material become filled with water. The porosity and the permeability of cement material consequently increase substantially. The upshot is that the strength and durability decrease significantly.

**Conversion at temperatures above 20 °C**

\[3 \times \text{CAH}_{10} \rightarrow \text{C}_3\text{AH}_6 + 2 \times \text{AH}_3 + 18\text{H}\]

\[3 \times \text{C}_2\text{AH}_8 \rightarrow 2 \times \text{C}_3\text{AH}_6 + \text{AH}_3 + 9\text{H}\]

New reaction products are formed upon conversion to C\textsubscript{3}AH\textsubscript{6} and water is released. The porosity and the permeability of cement material consequently increase substantially.

**Strength development**

Because the hydration proceeds so rapidly, a high initial strength is achieved very rapidly. The greatest increase in strength takes place between three and nine hours after mixing. During this period the strength can increase by more than 30 N/mm\textsuperscript{2} within an hour. There is consequently no difficulty in achieving a strength of more than 45 N/mm\textsuperscript{2} within nine hours. If the temperature remains below 20 °C, the strength increases still further. If conversion occurs at temperatures above 20 °C, however, in due course the strength decreases. Above 38 °C the strength drops very rapidly (Figure 2). This has to be taken into account in structural applications.

**Durability**

Only a negligible quantity of calcium hydroxide is formed during the hydration of high alumina cement. This is markedly different from the behaviour of cements based on Portland clinker. Concrete and mortar made from high alumina cement is therefore more resistant to attack from weak acids and pure water. This applies down to pH 4. The difference soon disappears in the case of attack by stronger acids, which attack high alumina cement as easily as other cements.

Concrete and mortar made by using high alumina cement are very resistant to attack by sulphates. An important requirement for this is that no conversion occurs. It is during this process that other hydrates are formed that are less resistant to sulphates. As a result of the significantly increased porosity, the sulphates can easily penetrate and form ettringite. The formation of ettringite is accompanied by swelling caused by water absorption. This results in the concrete being forced apart.

The concrete and the mortar are not resistant to sodium and potassium hydroxides. They dissolve the hydrates that have been formed.

**Heat treatment**

Conversion leads to lower strength and reduced durability. We can limit the conversion by allowing the concrete to harden at higher temperatures. The stable C\textsubscript{3}AH\textsubscript{6} is formed straight away above a temperature of 60 °C. These temperatures can be reached by steam heating the concrete for the first 24 hours. The strength after 24 hours will be lower than that obtained when hardening at lower temperatures. The hydrates that are formed, on the other hand, are much more stable.

**Refractory properties**

High alumina cement concrete with the right composition has excellent refractory properties. In the first instance it might seem very strange that a concrete that loses its strength and dur-
bility at higher temperatures possesses outstanding refractory properties. This can be explained as follows. The strength decreases during heating as a result of slow and gradual evaporation of the chemically bound water (Figure 3). However, the concrete does not disintegrate, as would concrete based on Portland cement. It can consequently continue to perform its protective role.

The properties change dramatically above 1000 °C because ceramic bondings are formed.

Fig. 3. The effect of the temperature on the compressive strength of high alumina cement concrete.

This process is comparable with firing clay. The compressive strength increases again back to the original value or even higher. The tensile strength of the new material that has been created is higher than that of the starting material. The material retains its new properties if it is cooled down gradually. If the temperature is increased even more and the melting point is exceeded, the material will become liquid. This results in the loss of the strength and the refractory properties.

The refractory properties are determined by the alumina content of the cement and a correct choice of aggregate. The refractory properties of the cement are directly proportional to the alumina content. The refractory properties of the concrete, however, are not only dependent on the choice of cement. The right aggregate has to be selected to go with the cement.

Mixing high alumina cement and Portland cement

The mixing of high alumina cement and Portland cement is prohibited in virtually all concrete technology books. Nevertheless, a mixture of the cements has some very interesting properties. A disadvantage is that it is difficult to predict what the properties will be.

If high alumina cement is mixed with Ca(OH)₂, quick setting is obtained. Ca(OH)₂ is also formed during the hydration of cements based on Portland cement clinker.

Refractory properties

Melting point of high alumina cement concrete in °C

<table>
<thead>
<tr>
<th>Aggregate</th>
<th>Type of high alumina cement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40% Al₂O₃</td>
</tr>
<tr>
<td>basalt</td>
<td>1180</td>
</tr>
<tr>
<td>chamotte</td>
<td>1400</td>
</tr>
<tr>
<td>aluminium clinker</td>
<td>1450</td>
</tr>
<tr>
<td>chamotte</td>
<td>1480</td>
</tr>
<tr>
<td>brown corundum</td>
<td>1675</td>
</tr>
<tr>
<td>magnesite</td>
<td>–</td>
</tr>
<tr>
<td>white corundum</td>
<td>–</td>
</tr>
<tr>
<td>silicon carbide</td>
<td>–</td>
</tr>
</tbody>
</table>

Initial setting of mixtures of Portland cement and high alumina cement

When 100 kg of Portland cement reacts completely with water, 30 kg of Ca(OH)₂ is formed. If high alumina cement and Portland cement are mixed together, a binding agent with a very short setting time can be produced. If high alumina cement is added to Portland cement, there is a decrease in the setting time (Figure 4). The other side of the graph reveals the same picture. Adding Portland cement also results in a shorter setting time. Mixtures containing between 30% and 75% high alumina cement have a setting time of less than three minutes.
This would appear to be a good mechanism for reducing the setting time and increasing the initial strength. Unfortunately there are two constraints. The reduction in the setting time and the higher initial strength are accompanied by a drop in the final strength. A shorter setting time results in lower strength (Figure 5). Furthermore, the equilibrium of the chemical reaction is so sensitive that different batches of cement from the same source can lead to major differences in the final strength. The mixing of high alumina and Portland cements is therefore a matter for specialized firms and it is undertaken on an industrial scale. The mixtures are predominantly Portland cement with a small amount of high alumina cement. This is because of the higher price of high alumina cement. The skill is to find the right compromise between the reduction in the setting time and an acceptable loss of strength.

**Water requirement**

The water requirement of high alumina cement is lower than that of Portland cement. The actual water requirement will always have to be established on the basis of suitability tests. The mortar is stable for half an hour after mixing. After this there will be bleeding despite the low water content.

**Additives**

Generally speaking we have to assume that the additives used in combination with cements based on Portland cement clinker will react differently when used with high alumina cement. When using additives it is necessary to establish contact with the additive supplier. The folders produced by these suppliers are written for applications involving the use of Portland or blast furnace cement. Every concrete technologist knows that chlorides accelerate the hydration of a Portland cement in the initial phase. It is therefore an accelerator. This is not the case with high alumina cement. Here chlorides are used as a retarder. The mechanism becomes even more complex if we add CaCl₂. An accelerator and retarder at the same time. Citric acid is used as a plasticizer and retarder. These additives therefore perform very differently from what we expect on the basis of our experience with Portland cement. We have already addressed other substances that are frequently used in combination with high alumina cement, i.e. Ca(OH)₂ and Portland cement.

**Experience**

High alumina cement has been used in concrete since the nineteen-twenties because of its rapid strength development and durability, with success in many cases. For example, the bridge in Fringingshoe in Essex, UK (built in 1920) is still performing completely satisfactorily. The fact that the strength of concrete made using high alumina cement does not increase with time at high temperatures and air humidity but decrea
ses instead was first reported in 1929. Six years later it was demonstrated that the loss of strength occurs because the hydrates formed are not stable at temperatures above 20 °C. It was not until the nineteen-fifties that the whole mechanism was understood and given the name 'conversion'. The consequence of the new insights was that a water/cement ratio of 0.50 was recommended for reinforced concrete. Since the nineteen-fifties high alumina cement has also been used in prestressed concrete (prestressing with adhesion). A water/cement ratio of 0.40 was recommended in this case. Because of the high initial strength, prestressing could be carried out every day after 18 hours (remember that in those days CEM I 52.5 R had not yet appeared!). All went well until 1973. In 1973 and 1974 in the United Kingdom three roofs made from prestressed concrete beams collapsed. This led to a ban in the United Kingdom on the use of high alumina cement in structural applications. All buildings in which high alumina cement had been used came under suspicion. It was established afterwards that gross errors had been made during the manufacturing of the prestressed beams. It is possible to prestress the concrete within 18 hours even when using higher water/cement ratios. In almost all reported cases of damage the water/cement ratio was found to be above 0.50 and the covering of the prestressing reinforcement was found to be too small. At around this time a number of cases of damage were also discovered in Spain. Here it was established that a water/cement ratio of 0.6 to 0.7 has been used. The conversion process had made the concrete become so porous that water and air rusted the reinforcement. The damage occurred because the design rules were not adhered to. The damage had already been done!

Standards and guidelines

The new Dutch cement standard NEN 3550:1995 defines the requirements for cement based on Portland cement clinker. Many new types of cement were introduced in this standard. However, high alumina cement disappeared from the standard. There is currently no standard in the Netherlands for high alumina cement. A new European standard is being worked on.

Better understanding has been acquired during the last few decades. This understanding is based on the fact that 60-70 kg of water is necessary for the complete hydration of 100 kg of high alumina cement. Complete conversion can be avoided by maximizing the water/cement ratio at 0.4. The hydrate water that has already been formed is released upon conversion. Cement that has not yet been hydrated, which is always present at this low water/cement ratio, reacts with the water being released. The voids that are created are filled by new hydrates. This averts the danger of loss of strength and a decline in the durability (Figure 6). A cement content of 400 kg/m³ is maintained as a lower limit as an extra precaution.

Fig. 6. Strength development of high alumina cement when adhering to the guideline of water/cement ratio < 0.4 and cement content: > 400 kg/m³. Point A depends on the temperature attained after several days. At low temperatures (10 °C), it takes years to reach point A. If the temperature rises above 38 °C, the strength rapidly drops to point B. From this point the water being released reacts with the unhydrated cement. As a result of this the strength and durability increase again.
Applications

The most important properties of concrete and mortar based on high alumina cement are:
• very rapid hardening;
• good refractory properties;
• excellent resistance to sulphates;
• resistance to weak acids (pH > 4);
• highly abrasion resistance;
• can be processed at temperatures down to -10 °C.

High alumina cement sometimes has to be mixed with other raw materials in order to make the best possible use of some of its properties. For example, a mixture of high alumina cement and Portland cement produces a quick-setting quick-hardening repair mortar.

Conclusion

High alumina cement has many facets. It can really only be used if the very specific properties of this cement are needed. If used in the proper way, durable and strong concrete can be made using high alumina cement.

Literature

• Czernin, Dipl.Ing. Wolfgang ‘Cementchemie voor de bouwwereld’, Verkoopassociatie Nederlands Cement, ENCI-CEMIJ-ROBUR, Amsterdam 1968;
• Stiglitz, P. "Die Verwendung von Tonerdezement im Bauwesen, das Problem der schädlichen Veränderungen ist gelöst. Lafarge, z.j."