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THE USE OF THERMOANALYTICAL TECHNIQUES FOR THE DETECTION OF CHEMICAL ATTACK ON HIGH ALUMINA CEMENT CONCRETE*

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ABSTRACT

Rapidly converted high alumina cement concrete may be attacked by sulphates to form ettringite and by chlorides to form a complex calcium chloroaluminate hydrate; the reaction products may be positively identified by thermoanalytical techniques. All high alumina cement concretes may be disruptively attacked by CO_2 in the presence of soluble Na and K; unfortunately, the products of this reaction, AH_3** and $CaCO_3$, and the absence of C_3AH_6 are similar to the products of beneficial carbonation in the absence of soluble Na and K. The two types of carbonation may be distinguished by analysing the cement for Na and K.

INTRODUCTION

High alumina cement (HAC) concrete is usually considered to be resistant to chemical attack, but under some circumstances, it may be attacked by sulphates and chlorides and by CO_2 in the presence of alkali metal ions Na and K. High alumina cement undergoes a chemical change with time when the metastable calcium aluminate hydrates CAH_{10} and C_2AH_8 convert to the more stable compounds C_3AH_6 and AH_3. Rapid conversion increases the porosity[1] and so the permeability and vulnerability to chemical attack. For unconverted HAC pastes, the density is 2.11 and for converted pastes 2.64 which is equivalent to a volume decrease of 20%. With the increase in permeability of HAC on rapid conversion, HAC concretes will become vulnerable to chemical attack and so sulphates and chlorides in solution will disrupt the concrete.

Acids and CO_2 will attack any HAC, both unconverted and converted. CO_2 alone will produce a slow surface reaction with a possible increase in strength[2]; however, CO_2 in the presence of soluble sodium and potassium ions will decompose the cement hydrate minerals in the concrete usually with a disruptive effect. HAC concretes are more resistant than Portland cement concretes to the action of water

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** Cement chemists' shorthand notation: C = CaO, A = Al_2O_3, H = H_2O.

containing free carbonic acids and to weak solutions of mineral acids, but appear to be more vulnerable to strong solutions of acids.

Attack by sulphate solutions produces the mineral ettringite, approximate composition $C_3A\cdot 3CaSO_4\cdot 32H_2O$; attack by chloride solutions produces $C_3A\cdot CaCl_2\cdot aq$, while attack by CO_2 in the presence of Na and K ions decomposes the C_3AH_6 to AH_3 and $CaCO_3$. All of these minerals may be readily identified by DTA techniques, although there may be some confusion if building plaster, gypsum, contaminates the sample.

In DTA, the peak temperature increases with the amount of material in a mixture; the larger the quantity the higher the temperature. Over a limited range, the peak temperature, T, is related to the mass of the mineral present, m, by the equation

$$T = k \ln m + a$$

where k and a are constants depending on the apparatus and the material. Midgley[3] and Midgley and Rosaman[4] have used this method to identify the complex calcium aluminate salt hydrates in Portland cement pastes and the method is appropriate for the identification of phases in HAC concretes. To define the temperature of the thermal change, a normalised peak temperature is used. This is the temperature of the peak given by a fixed mass of sample. However, since the peak height for equivalent crystallinity 4d grain size is directly related to the mass of the sample, it was found more convenient to use as the normalised peak temperature (NPkT), the temperature of the peak which occurs when a sample gives a peak height equivalent to a difference temperature of 1 °C.

SULPHATE ATTACK

Ettringite has a strong endothermic peak at about 100 °C although the peak position will vary with composition. Midgley and Rosaman[4] showed that the peak temperature is lowered with the substitution of Al^{3+} by Fe^{3+} and raised by replacement of SO_4^{2-} by OH^-. The plot relating peak height to peak temperature for various quantities of synthetic $C_3A\cdot 3CaSO_4\cdot 32H_2O$ is given in Fig. 1; this gives a NPkT of 92 °C. Gypsum, $CaSO_4\cdot 2H_2O$, is also given and it has an NPkT of 132 °C. It will be seen that both ettringite and gypsum may have peak temperatures of 120 °C, but the peak for ettringite would be large and for the gypsum small.

CHLORIDE ATTACK

HAC concrete may be attacked disruptively by chloride solutions to form the complex calcium aluminate chloride hydrate, $C_3A\cdot CaCl_2\cdot aq$. Figure 1 gives the plot of peak temperature vs. peak height for various masses of synthetic $C_3A\cdot CaCl_2\cdot aq$, which results in a NPkT of 161 °C.

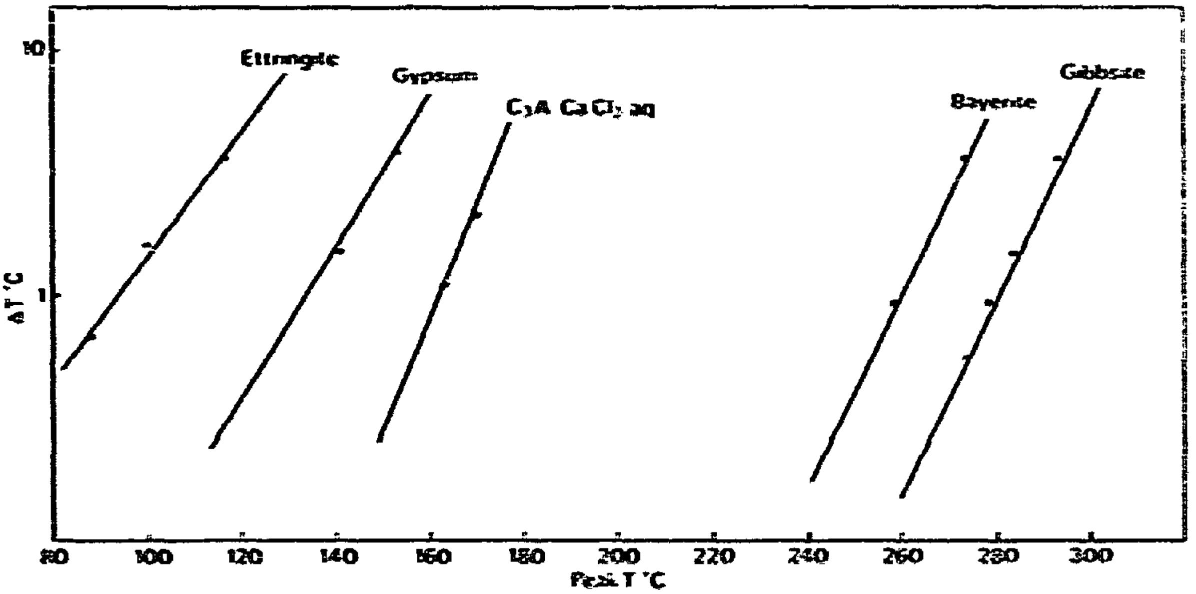

Fig. 1. Peak temperature vs. peak height.

CARBON DIOXIDE ATTACK IN THE PRESENCE OF SODIUM AND POTASSIUM

Carbon dioxide in the presence of sodium and potassium ions will decompose both CAH_{10} and C_3AH_6. The reactions may be represented by the following equations[1].

$2\,KOH + CO_2 = K_2CO_3 + H_2O$
$K_2CO_3 + CaO{\cdot}Al_2O_3{\cdot}10H_2O = CaCO_3 + K_2O{\cdot}Al_2O_3 + 10\,H_2O$
$K_2O{\cdot}Al_2O_3 + 4\,H_2O = 2\,KOH + Al_2O_3{\cdot}3H_2O$
$2\,KOH + CO_2 = K_2CO_3 + H_2O$
$K_2CO_3 + 3\,CaO{\cdot}Al_2O_3{\cdot}6H_2O = 3\,CaCO_3 + K_2O{\cdot}Al_2O_3 + 4\,KOH + 4\,H_2O$
$K_2O{\cdot}Al_2O_3 + 4\,H_2O = 2\,KOH + Al_2O_3{\cdot}3H_2O$

Na will react in a similar manner.

It will be seen that alkali hydroxide can react with atmospheric carbon dioxide to form K_2CO_3. This decomposes the calcium aluminate hydrates into $CaCO_3$ and alkali aluminate which will react with water to form alkali hydroxide and $Al_2O_3{\cdot}3H_2O$. It will be appreciated that the KOH is used up in the first reaction but comes available for carbonation to form K_2CO_3 and is thus available for further reaction. This form of attack, incorrectly known as alkaline hydrolysis, will manifest itself by the reduction in CAH_{10} and C_3AH_6 and an increase in both AH_3 and $CaCO_3$. However, this change in phase composition may also be caused by direct atmospheric carbonation which has been shown by Raask[2] to be beneficial. Thermal analysis may be used to detect this form of chemical change since γ-AH_3 has a strong endotherm with a NPkT of 280 °C (Fig. 1). C_3AH_6 has a NPkT at 300 °C and $CaCO_3$ at about 850 °C. So, if carbonation of HAC has taken place, there will be only a single peak due to AH_3 in the region 280–300 °C, no C_3AH_6 being detected, and there will be a large peak due to $CaCO_3$. To distinguish between disruptive carbonation (in the presence of alkali metal ions) and beneficial atmospheric carbonation, it is necessary to determine the quantities of alkali metals present in the HAC concrete. Analysis of 35 HACs manufactured in the UK since 1945 showed that they had equivalent alkalis (Na_2O + 0.658 K_2O) of 0.136 with a standard deviation of 0.052. At 99.5% confidence limits, HAC will not contain more than 0.236% combined alkalis. HAC contains 40.0% Al_2O_3 so that if the alkali content of the concrete is greater than 0.006 of the soluble Al_2O_3, then there has been added alkali and deleterious carbonation. So, to detect the so-called alkaline hydrolysis of the HAC concrete, the DTA thermogram should show only a single peak due to AH_3 and a large peak due to $CaCO_3$ and on chemical analysis the equivalent alkalis (Na_2O + 0.658 K_2O) should be greater than 1/175 of the acid-soluble Al_2O_3.

During investigations of samples of HAC concrete which have suffered alkaline hydrolysis, it was noted that the NPkT for the AH_3 tended to be around 266 °C, while the NPkT for γ-AH_3 (Gibbsite) was 280 °C and for α-AH_3 (Bayerite) 260° (Fig. 1). X-Ray diffraction (XRD) of samples of HAC which have suffered alkaline hydrolysis suggested that the AH_3 was present as nordstrandite, a polytype of AH_3, as well as Gibbsite. However, other samples of HAC which have not suffered alkaline hydrolysis and were shown by XRD to contain nordstrandite had a NPkT of 280 °C which would suggest γ-AH_3.

From this confusion the only conclusion is that it is not possible to identify the polymorphous polytype by thermal analysis alone.

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