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Effect of ettringite morphology on DEF-related expansion

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ABSTRACT

In this study, time dependent ettringite formation in heat-cured mortars has been investigated. In order to clarify the effect of formation place and morphology of ettringite on expansion, secondary electron images of cracked surfaces of mortars at three ages were analysed by SEM–EDS. Also, the X-ray microtomography analysis has been performed to observe the crack formation. The expansive role of delayed formed ettringite was related with its time dependent morphology as a function of formation place. From these observations, mechanism of ettringite reformation after heat curing has been proposed. Alumina rich species were the primary sources of ettringite formation as the starting nuclei. At later ages, if S and Al sources are readily available, the mentioned alumina rich nuclei will grow up and build ball ettringite. At long term, ball type ettringites (non-expansive) converted to massive type (expansive). These conversions can only take places if the form of available space is narrow (preformed micro-cracks). Massive ettringites exert pressure in these narrow spaces and cause expansion of mortar. If the form of the available space is spherical (entrapped air voids) ball ettringites preserve their initial form and do not cause any expansion.

1. Introduction

In the late 1980s, Heinz and Ludwig published a series of papers on expansion of laboratory and field mortars and concretes that were exposed to elevated temperatures and subsequently cured at room temperature under moist conditions [1]. Since then, hundreds of papers were published based on both laboratory studies to elucidate the mechanisms involved and on damaged concrete structures to correlate the experimental findings with the field [2–7]. From these literature, sensitivity of concrete to steam curing seems to be related to these phenomena: (a) decomposition or non-formation of ettringite due to high-temperature; (b) adsorption of the released sulfate by C–S–H or formation of monosulfoaluminate; (c) possible formation of initial micro-cracks due to thermal expansion; (d) release of sulfate from C–S–H upon cooling and subsequent ambient temperature (moist curing); (e) subsequent formation of micro-cracks as a result of drying shrinkage; (f) formation of ettringite nuclei in the pre-existing cracks or tiny micropores, and (g) growth of the nuclei resulting in expansion of paste.

There are two different hypotheses about expansion mechanisms of delayed ettringite formation (DEF): the uniform expansion of paste and the crystalline pressure of ettringite [4,8,9]. However, the crystal growth pressure hypothesis appears to be rather less convincing than the paste expansion hypothesis [7]. Furthermore, the paste expansion hypothesis is most strongly supported by the fact that neat cement paste also suffers from DEF-related expansion, which clearly demonstrates that the presence of aggregate particles is not a necessary condition for the expansion to occur. Odler and Chen [10,11] observed considerable expansion in neat Portland cement pastes approximately one year after high-temperature curing. Similarly, Yang et al. [12] reported that a neat cement paste expanded after 2.5 years, while the same cement mixed with siliceous sand started to expand in less than 100 days.

The above mentioned literature reviews repeatedly cited the significance of microstructure formation in the expansion mechanism. The microstructure and pore structure govern various physical properties, such as strength, permeability, connectivity, and diffusivity, and thus control pore solution transport in the system. There have been indications that these transport properties are important factors in the DEF-related expansion, however, these are not well established. Thus, the majority of studies focused only on the chemical aspects of DEF. In contrast, very little has been reported on the influences of physical properties of the system, and their relationships to the chemical reactions. Thus, there is a lack of information on the physical parameters that has left many uncertainties in understanding the DEF mechanism [7].

Most of the available microscopic information in literature has been obtained using light optical microscopy and scanning electron microscopy (SEM) in back-scattered electron (BSE) mode including microanalytical studies [13]. Reported microscopic observations of concrete damage include [1]:

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1. Expansion of the cement paste as revealed by formation of partial or complete rims (gaps, bands, circumferential cracks), up to about 25–30 micrometers wide, around the aggregate particles (e.g. Johansen et al. [14]);
2. partial or complete filling of these gaps by secondary ettringite formation;
3. formation of "nests" of ettringite in the cement paste (e.g. Marusin [15]);
4. formation of two-tone C–S–H features with values chemical compositions also known as inner and outer C–S–H (e.g. Scrivener [13]);
5. microcracking of the paste;
6. microanalytical studies on the composition of hydration products, (e.g. Scrivener and Taylor [16]; Famy [17]).

Microstructural observations were seldom related with the morphology of ettringite structure as a function of time and place of formation [8,18]. According to Famy et al. [19], expansion is attributed to the formation of microcrystals of ettringite in tiny places containing monosulfoaluminates, when sulfate is released from C–S–H. Besides its amount, the morphology of ettringite is also an important factor to influence its expansive effect. Secondary electron images of cracked surfaces were rarely employed. However, the secondary electron images can be valuable tools in qualitative determination of time dependent development of crystal structures on weak sections of mortars (pores and cracked surfaces).

The aim of this study is to investigate the microstructure of heat cured cement mortars (potentially susceptible to DEF by composition) and to find a relationship between expansion and ettringite morphology as a function of time and place of ettringite formation. The physical characterization of morphology of delayed formed ettringite has become possible by employment of secondary electron images.

2. Experimental

2.1. Materials

Cement characteristics that promote the early strength, in particular high fineness and high SO_3 content usually increases the DEF susceptibility of heat-cured mortars [20]. For this reason, special DEF susceptible cement with 4.5% of SO_3 has been prepared in the laboratory. A Blaine value of 535 m^2/kg has been achieved by extra grinding. Compressive strengths of standard mortar samples prepared with this cement were 21.1, 50.2 and 64.8 MPa at 2, 7 and 28 days, respectively. The Bogue compound composition of the cement was C_3S: 53.24%, C_2S: 11.75%, C_3A: 9.25% and C_4AF: 8.09%. This cement can be classified as high strength cement which is usually preferred by precast concrete producers.

Standard graded siliceous sand was used. Previous studies have revealed that natural siliceous sand is the most DEF susceptible sand due to its high thermal coefficient of expansion and low strength of interface with poor mechanical interlocking behaviour compared to crushed limestone sand [21,22]. SEM images demonstrating the improved interlocking mechanism of crushed limestone sand (Fig. 1a) compared to siliceous sand (Fig. 1b) are presented comparatively in Fig. 1.

2.2. Mortar preparation and curing procedures

Mortars were prepared at a constant water/cement ratio of 0.44 and sand/cement ratio of 2.5. Fresh mortars were tested by using a flow table conforming ASTM C230 [23] standard. The flow diameters of mortars were within the range of 128–135 mm. Mortars were cast in 25 × 25 × 285 mm prismatic moulds with stainless steel studs in their end faces. In order to investigate the DEF potential, half of the specimens were subjected to heat curing regime described by Grabowski et al. [24]. After a pre-curing period of 2 h at 20 °C, the temperature has been increased at a rate of 25 °C/h up to the required maximum temperature (85 °C) which has been kept constant for 4 h. Cooling rate was also 20 °C/h. All prisms were demoulded after 24 h. Duggan method describes series of wetting and drying periods after heat curing. After three days of waiting period in de-ionised water, specimens were subjected to three cycles of 1 day drying in an oven at 85 °C and 1 day wetting at 20 °C. The purpose of this additional process is to speed up the DEF. Any procedure that weakens the material will also lower its ability to resist expansion. Repeated heating and cooling may form microcracks due to thermal stresses. This will accelerate DEF, since water will penetrate in more easily and it will also weaken the paste-aggregate bonds [6,25]. Finally, the specimens were stored in water at 20 °C. The other half of the specimens were standard cured in water at 20 °C. Lengths of specimens were measured for a period of more than 2 years. The results recorded as the average of two mortar bar specimens.

2.3. Length change measurements

The length change of mortar prisms at a period of 800 days is presented in Fig. 2. As can be expected, there is a considerable difference between the expansion characteristics of heat cured and control mortars. All mortar prisms stored in water at 20 °C. The expansion of heat-cured mortars started immediately after heat curing (Fig. 2a). On the other hand, control mortars preserved their initial length and no considerable expansion was observed. In case of heat-cured mortars, the rate of acceleration increased before 90 days (Fig. 2b). After 90 days rate of acceleration started to decrease and expansions slow down between 90 days and 500 days. Beyond 500 days, length of specimens did not change. From these observations, the expansion history of mortar prisms can be divided into four critical time intervals: Initial or migration period (0–I: just after steam curing, up to 2 days-old), seeding and acceleration period (I–II: 2–90 days), deceleration period (II–III: 90–500 days), saturation period (III–∞: after 500 days). In order to investigate the influence of microstructural changes on expansion, samples were taken at three critical ages (at the beginning of acceleration period, in the middle of the acceleration period and from the end of the deceleration period). The possible reasons for the change of expansion rate at different time intervals will be discussed in the next section.

2.4. Microstructural investigations

2.4.1. Methodology

Cracked surfaces have been selected for investigations since during hydration of steam cured mortars most of the ettringite form in voids of varying size and shapes besides the micro-cracks in paste phase. A new product can only be formed in voids and/or cracks and they are the weakest link of a section which can appear after fracture. Fracturing of the specimen by hammer introduces additional cracks. Due to this fact, the fractured surfaces can not be used to study the crack patterns in the cement matrix or the cracking of the aggregate. In order to examine the crack pattern, X-ray microtomography (XMT) method has been used. Since, XMT is a non-destructive and versatile characterization technique for microstructural investigation of cement mortar and concrete, there is no need to make any sample preparation as in the case of polished surface investigations [26–28]. However, fractured surfaces are excellent for exhibiting ettringite crystalline structure in cracks, voids or at aggregate interface [29]. On the other hand, due