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Investigation of the microstructure and carbonation of C$\bar{S}$A-based concretes removed from service

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Abstract

The microstructure, mineralogy and depth of carbonation of two concrete samples, one removed from a normal strength crane column and the other from a high-strength pile, are reported. The normal strength C$\bar{S}$A cement concrete had a high w/c ratio; microstructural images show that clinker tends to hydrate almost completely. But for high-strength C$\bar{S}$A cement concretes, made with low w/c ratios, large amounts of partially hydrated clinker grains remain as a microaggregate.

C$\bar{S}$A cements and concretes are subject to carbonation in service conditions. The usual method of determining depth of carbonation, the phenolphthalein test, does not work with aged C$\bar{S}$A matrices. A new method, using infrared microscopy, has been used to determine carbonation depth of aging C$\bar{S}$A cement concrete. It has been shown that carbonation of a normal strength C$\bar{S}$A cement concrete exposed to open air for 16 years averages ~0.5 mm/year, and is thus comparable with reported rates of carbonation of OPC concretes. The high-strength C$\bar{S}$A concrete carbonated at a maximum rate of ~60 μm/year.

Keywords: Calcium sulfoaluminate cement; Carbonation; Infrared microscopy

1. Introduction

In the 1970s, research on the coexistence of calcium sulfoaluminate ($C_4A_3\bar{S}$) with other minerals resulted in the discovery of the practical value of those novel cement formulations [1]. A new type of cement based on $C_4A_3\bar{S}$, C_2S and ferrite, shorthand calcium sulfoaluminate, or C$\bar{S}$A cement, has been developed in China. Other types of clinker containing $C_4A_3\bar{S}$ are known, but we report on the Chinese product containing ca. 20–25% each of $C_4A_3\bar{S}$, belite, and ferrite. This clinker is normally interground with 10–15% gypsum.

In comparison with Portland cements, production of C$\bar{S}$A cements is small, ca. 1 million tonnes per year. But due to their balance of unique properties they are an alternative to Portland cements in some applications where the performance of Portland cement is insufficient. The unique properties of C$\bar{S}$A cements include rapid strength development even at low temperatures, good resistance to freezing during hydration and in service conditions, good corrosion resistance and excellent durability in aggressive water, e.g., sea water. However, structural uses of C$\bar{S}$A cements outside China are relatively uncommon and are largely confined to special cements used in non-structural applications.

C–S–H and ettringite are the main hydrates and strength-giving components of C$\bar{S}$A cements. Many researchers have expressed concern about the long-term stability and supposed rapid rate of carbonation of ettringite-based matrices [2–4]. Zhang et al. [5] reported results from an accelerated experiment on short-term C$\bar{S}$A-based concrete samples made in the laboratory, in which no significant

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differences in carbonation trends were found relative to equivalent Portland cement concretes. However, laboratory and field investigations often differ, and, in any event, it is difficult to establish a basis for equivalence between different cement types. No relevant literature has been found about microstructure and carbonation of $C\bar{S}A$-based concrete formulated with high $C_4A_3\bar{S}$-containing cements, and the resulting changes to the microstructure occurring under normal service conditions.

Phenolphthalein indicator is commonly used to determine the carbonation depth of Portland cement concrete. The method is also applicable to fresh high alumina cement (HAC) concretes to 2 years age, according to Dunster et al. [6]. However, they found that the visible indication is often indistinct and fades with time for more highly carbonated HAC concretes, both young and aged. Phenolphthalein is therefore not useful to determine carbonation depth in aged HAC concretes and the same was found to be true for aged $C\bar{S}A$ cement concretes. Obviously, another method is required to evaluate the carbonation of $C\bar{S}A$ cement concretes, particularly if it is also applicable to concretes made with limestone aggregates.

Depth of carbonation can also be determined by thermogravimetric analysis (TGA) using drill cuttings or diamond-sliced cores obtained at successively greater depths. Critical comparison of depths of carbonation determined by TGA and phenolphthalein reveals that the carbonation front in OPC is complex and often not sharp [7], and that direct comparison of carbonation depths is not straightforward. However, TGA is not portable and is unsuited for field investigations; moreover in the presence of carbonate aggregate, the paste fraction has to be handpicked under a binocular microscope prior to carbonate determination.

In this paper, research on samples removed from long-term service was made by SEM, XRD and IR micro-spectroscopy. The specimens were recovered from a normal strength crane column and a high-strength pile, believed to be typical of the range of uses of $C\bar{S}A$ cements. Application of infrared microscopy to determining depths of carbonation is a novel technique and is described in detail.

2. Sampling

2.1. Normal strength concrete sample from a crane column

Shijiazhuang (SJZ) Special Cement Plant, located in north China, has been producing $C\bar{S}A$ cements since 1974. Rapid-hardening $C\bar{S}A$ cement from this plant was used for concrete structures beginning around the end of the 1970s. The column described here was concreted during the cold winter of 1982 with hot mix water. The w/c ratio was relatively high, approximately ~0.55–0.60; 1% $NaNO_2$ was also added to the mix water as an anti-freeze. The rapid-hardening $C\bar{S}A$ cement content, formulated without limestone filler, was about 300–350 kg/m^3 and the 7-day compressive strength of the concrete was about 30 MPa. The column has been fully exposed to weathering in outdoor temperatures in the range ~−15 to +45 °C, enduring freeze–thaw, rain, etc. The concrete crane structure was in regular service when cored and showed no visual signs of deterioration.

The cross section of the column is about 40×40 cm. A cylindrical sample core was drilled from the crane column in September 1997. The specimen was then covered with adhesive duct tape, except for the top surface which had been exposed to air in course of service, and was thereafter stored at normal ambient temperature until examined in 2001.

2.2. High-strength concrete sample from a pile

This pile was trial-produced in June 1993 in Guangzhou (GZ), south China. The 3-day compressive strength of this concrete was required to reach 80 MPa. The objective of using $C\bar{S}A$ cement to produce this kind of pile was to eliminate the need for lengthy or complex curing. An iron-rich $C\bar{S}A$ clinker was used, produced in a special cement plant in south China and formulated without added gypsum. Medium sand with very low clay content and 5–20-mm crushed granite were used as aggregates; river water was used as mix water. In order to lower the w/c ratio and prolong setting time, superplasticiser and retarder were added to the fresh concrete mix: the cement content was 500 kg/m^3. The w/c ratio was normally controlled to ~0.30 but could be reduced to as low as ~0.26 because centrifugal casting was used. The production process of a cylindrical pile is as follows: initially fresh concrete is fed into the two halves of a clamped steel mould and prestress applied, followed by centrifugation, precuring, demoulding and secondary curing. The curing regime for $C\bar{S}A$ cement piling was to precure piles for 7–8 h prior to demoulding, followed by water curing at ambient temperature for 3 days, by which time compressive strengths exceeded 80 MPa. Secondary curing was uncontrolled. The temperature inside the pile during precuring reached ~50 °C. The $C\bar{S}A$ cement piles were stored outdoors for more than 1 year. Part of a pile produced in June, 1993 was cut off and transported to Beijing. It was kept outdoors unprotected from the weather until 1998, when a portion was sent to Aberdeen and examined in 2001. Visually, the pile was in perfect condition.

3. Experimental

3.1. Specimen preparation for SEM and XRD investigation

The specimens were prepared for backscattered electron (BSE) imaging by embedding the sample in epoxy resin blocks. The blocks were ground down using progressively finer grade abrasive papers and then polished to a surface roughness of <1 μm (using 6 μm diamond paste, followed by ¼ μm alumina paste as the polishing medium). The samples were coated with a thin layer of conductive carbon. Powdered