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An investigation of the hydration of calcium aluminate through ultrasonic wave propagation

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The hydration process of a high alumina cement was investigated through ultrasonic wave propagation techniques. A correlation between wave amplitude and velocity and breaking strength of the cement is demonstrated. The wave behaviour through hydrating cements was found to be a function of the cement-to-water ratio between values of 2 and 4. Changes in the temperature of the hydrating samples were found to exhibit a similar dependence.

1. Introduction

Interest in the hydration process of high alumina cements has been prompted by concern over the dependence of the strength of the hydrated cement on the degree of completion of the hydration process. Attempts aimed at following the progression of this process have commonly utilized destructive testing techniques. Microscopic, X-ray, and calorimetric techniques have been employed with various degrees of success. As anticipated, destructive testing techniques are unsuitable for practical application under most conditions of cement utilization. Ideally, therefore, a nondestructive technique (NDT) should provide for the continuous monitoring of the hydration process and, hence, those properties associated with it. While nondestructive testing methods have been utilized in concrete technology, they have been limited to the detection of flaws and cracks in the hardened product. Recently, however, evidence for the nondestructive monitoring of the hydration of Portland cement has been provided [1]. Although details of this work were not given, the research suggested the possibility of monitoring the course of solid state reactions acoustically. In an earlier investigation, this latter possibility had been verified for the solid state phase transitions in lead–zirconate–titanate ceramics [2].

The desirability of developing an NDT approach for the continuous monitoring of the hydration of cements is obvious. This work was initiated with the aim of providing an understanding of this approach and correlating the acoustic wave propagation properties with the physical and chemical changes in the cement. In this paper, wave velocity and amplitude are correlated with the physical changes accompanying hydration. In a subsequent paper [3] we present the results of an investigation of the chemical changes during the hydration of this high temperature cement.

2. Experimental materials and methods

2.1. Materials

The high purity calcium aluminate cement utilized in this study was made by Alcoa under the designation of CA-25. X-ray analysis of this cement, as-received, showed principally the presence of the phases α-Al_2O_3 and $CaO \cdot Al_2O_3$. (To simplify designations of phases, hereafter the notation adopted by the cement ceramists will be followed, i.e., C will refer to CaO, A will designate Al_2O_3,

and H will stand for H_2O.) In addition to CA and α-Al_2O_3, there was evidence for the existence of $C_{12}A_7$, and some unidentified phase(s). Quantitatively it is estimated that the unhydrated cement is made of about 70% α-alumina, 20% CA, and the remainder being $C_{12}A_7$ and the unknown phase. Detailed description of the observed X-ray peaks for the as-received cement is given in the subsequent paper [3].

For the ultrasonic experiments, 300 g of cement was thoroughly mixed with 100 ml of water at 297 K. To ensure uniformity of temperature for the mixing operation, the water was allowed to stand overnight at room temperature. Its temperature was measured prior to mixing with the cement. Within a maximum deviation of 1 K, the temperature of the water utilized in the hydration of all cement samples described in this paper was maintained at 297 K. Since the cement samples were stored under the same conditions, it is assumed that they were at this temperature before mixing. Mixing includes the addition of water to the cement and the stirring of these two phases for one minute with a wooden stirrer. While the majority of cement specimens studied in this work had a cement/water (C/W) ratio of 3 other cements were made with C/W values ranging from 2 to 4 by weight.

2.2. Methods

2.2.1. Ultrasonic monitoring of the cement hydration

The hydration process of the calcium aluminate cement was studied by means of an ultrasonic apparatus. Utilizing piezoelectric crystals of lead–zirconium titanates (PZT), an ultrasonic apparatus was set up with the following components: a pulse generator, input and output amplifiers, and an oscilloscope. The pulse generator provided signals at 30 kHz and a duration of 6 μsec.

The specimen cell has dimensions of 5.1 cm x 5.1 cm x 6.4 cm. The 5.1 cm x 5.1 cm sides were made of 0.64 cm thick plexiglas and the two ends and the bottom were made of 1.5 cm thick aluminium. Surrounded by a 2.5 cm layer of glass wool insulation, the cell was placed inside a box whose dimensions were 11.4 cm x 15.2 cm x 17.8 cm. In the original design of the cell the transducers were placed through the two ends of the cell. As the cement cured, however, shrinkage gave rise to poor contacts and hence diminished wave intensity through the cement. The cell bottom contained a circular hole through which one of the PZT transducers was inserted so as to be at the same level as the top of the aluminium plate. The other transducer was normally placed on top of the cement just after pouring it into the cell. Both transducers were covered with high vacuum grease to establish an interface between the cement mix and the transducer housing and material. This configuration was found necessary to avoid contact problems encountered in the early phases of these experiments.

The modification described above avoided this problem, at least with respect to one of the transducers. As for the top transducer, it was found necessary to re-establish contact at the end of the initial setting process. Details of this procedure are given in a later section.

Immediately after the cement was mixed, it was poured into the sample cell which had been previously prepared by greasing its sides and applying a 1.6 mm thick layer of Dow Corning high vacuum grease to the contact surfaces of the two transducers. Subsequent experimentation had shown silicone grease to be superior to the high vacuum grease initially utilized. Higher signal amplitudes were consistently obtained for the transmitted wave when this material was used as the wave coupling medium. A copper–constantan themocouple was immersed in the freshly mixed cement after being poured into the ultrasonic cell.

As the sample cured, shrinkage caused the displacement of the top transducer with respect to the sample, thus causing a significant decrease in the amplitude of the transmitted signal. To remedy this situation, a procedure was developed and practised throughout the phases of this work which followed the preliminary tests. The amplitude of the transmitted signal was monitored and when it became zero, the cement sample had hardened enough so as to be capable of manipulation without fear of changes in its integrity. The cement block was turned 90° and replaced in the ultrasonic cell. This procedure provided smooth surfaces to be again placed in contact with the crystals. The ultrasonic wave and the sample temperature were continuously monitored for a minimum duration of 12 h. Records of the pattern and intensity of the transmitted waves were photographically recorded at $\frac{1}{2}$-hour intervals. During the first phase of this research, monitoring of the transmitted ultrasonic wave was accomplished while the signal through the hydrating cement was

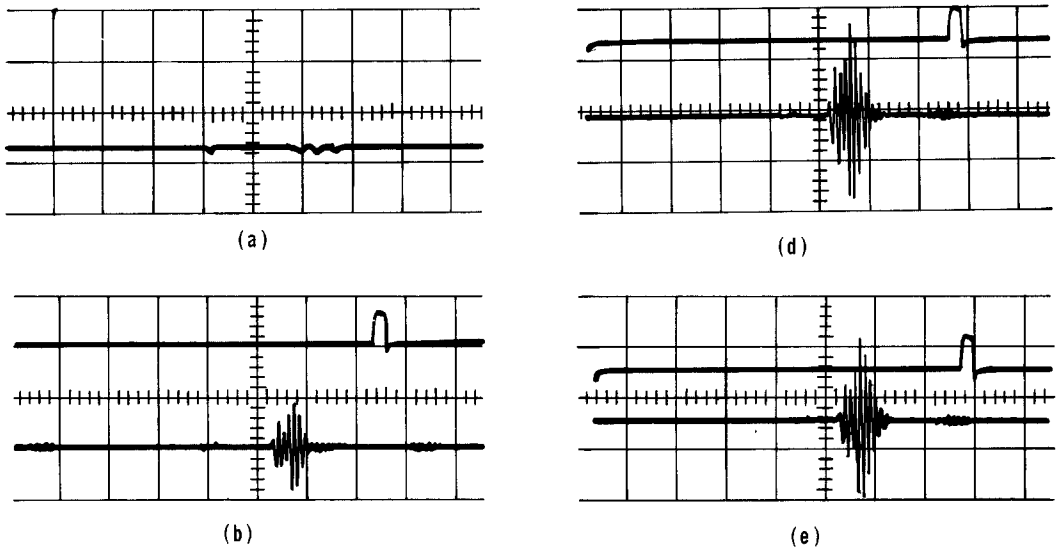

Figure 1 Changes in the intensity of the transmitted ultrasonic wave through a hydrating high alumina cement. The upper, input signal is shown for comparison. (a) Time: 1.5 h; scale: 0.02 V cm^{-1}; (b) 3 h; 0.05 V cm^{-1}; (c) 5 h; 0.05 V cm^{-1}; (d) 8 h, 0.1 V cm^{-1}; (e) 13 h, 0.5 V cm^{-1}.

left on continuously. It was later found that this procedure gave a drastically different time-dependence of the variation of the wave response during the hydration process. Details of this finding will be presented in Section 3. It is appropriate to mention here that the significant changes in the ultrasonic characteristics of this process occurred at earlier times when the transducers were left on than when they were turned off between readings. The apparent conclusion is that the transducers, when left on continuously, had generated a significant amount of heat which, in turn, influenced the solid state reaction being monitored. All subsequent studies on the hydration of the calcium aluminate cements were monitored nondestructively with the transducers turned on only while actual measurements were being made. At the end of a 12-h run, each sample was labelled and stored in the same laboratory environment for later examination.

2.2.2. Correlation of breaking strength with degree of hydration

Calcium aluminate specimens were made in accordance with procedures outlined earlier, however, the mixed cement was cast into standard 5.1 cm diameter, 10.2 cm high cardboard cylinders. Breaking strength of the resulting cements was obtained using a standard ASTM technique [4]. Strength measurements were made on samples with C/W value of 3, as well as values between 2 and 4. Measurements were normally made at 1-hour intervals between 4 and 144 h from the time of mixing, designated as zero time. No significant determinations could be made for cements which had cured less than about 4 h since the hydration process had not progressed sufficiently to allow the manipulation of the specimen. Typically mechanical properties were determined at 24-hour intervals after the first day.

3. Results

3.1. Ultrasonic investigation

Figs. 1a to e show the time dependence of the transmitted wave through hydrating calcium aluminate. For comparison, the input signal and its displacement from the output are also shown in these figures. A plot of the highest intensity of the output signal is shown in Fig. 2 as a function of hydration time for a cement with C/W = 3. Also shown in Fig. 2 is a curve depicting the temperature changes associated with this process. The rapid increase in temperature at 3 hours

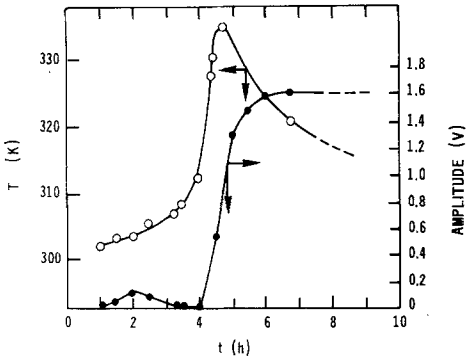

Figure 2 The time dependence of the amplitude of transmitted wave through a 3:1 cement during hydration. Continuous transducer mode.

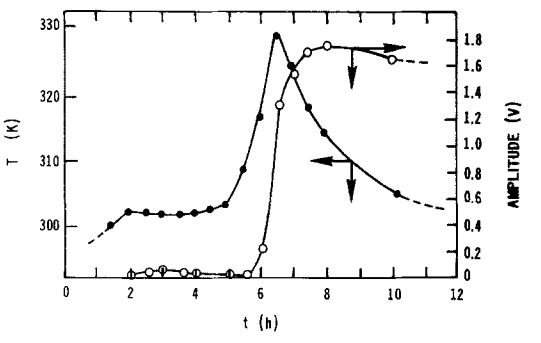

Figure 3 The time dependence of the amplitude of the ultrasonic wave through a hydrating 3:1 cement. Intermittent transducer mode.

precedes the sudden increase in the amplitude of the transmitted signal by 40 to 60 min. While not obvious in Fig. 2, a smaller, less significant peak in the temperature curve was observed to occur immediately after mixing the cement with water. No significant changes in the intensity curve were observed after the sudden increase occurring between 4 and 6 h. Transmitted wave patterns through samples which had been ageing for 24 h were nearly the same as those photographed at 8 h.

Subsequent experiments on the ultrasonic "signature" of the hydration process of calcium aluminates have shown a possible interference from the heat generated by the transducer crystals. As was pointed out previously, during the initial experiments, the transducers were left on for the 8 to 10 h duration of the experiments. When the crystals were turned off between actual measurements, the patterns generated were qualitatively similar but had distinct shifts on the time scale. The temperature peak, which had occurred at 5 h (Fig. 2) is observed now at 6.5 h as indicated by Fig. 3. Similarly the sharp increase in the intensity of the ultrasonic wave commenced at about 4 h when the transducers were left on continuously and at about 6 h when they were turned off between measurements. Another significant difference is found in the values of the maxima on the temperature and intensity curves of Figs. 2 and 3. By leaving the transducers on continuously, the highest measured temperature peak is 335 K which corresponded to a value of 329 K measured when the crystals were turned on intermittently. In contrast, a higher value for the intensity maximum is obtained for the case where the crystals were turned off between

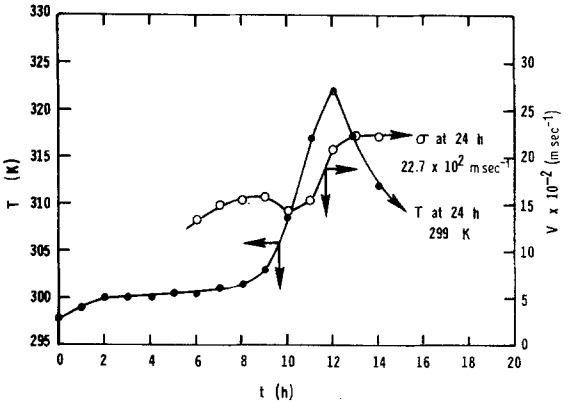

Figure 4 The variation of the velocity of the transmitted wave during the hydration process.

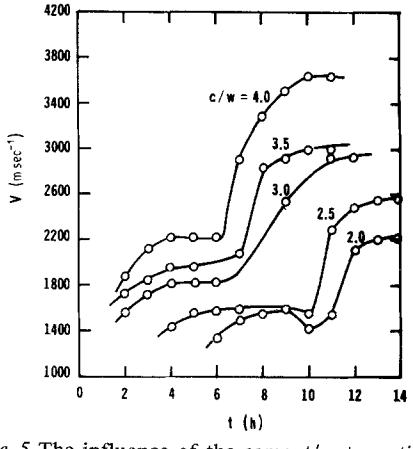

Figure 5 The influence of the cement/water ratio on the time dependency of the velocity of the ultrasonic wave during hydration.

readings (1.78 as opposed to 1.58 V).

When velocities of the waves transmitted through the hydrating cement are plotted as a function of time, a pattern typified by Fig. 4 results for cement with C/W = 2. Also shown

in Fig. 4 is the change of temperature with hydration time. Wave velocities for samples of varying C/W ratios are plotted as a function of time in Fig. 5.

3.2. Correlation of strength with ultrasonic changes and cement water ratios

Breaking strength as a function of time following the initiation of the hydration process is shown in Figs. 6 and 7 for a C/W value of 3. Corresponding to changes in the ultrasonic wave (Figs. 3 and 4), a rapid increase in the strength occurs between 6 and 8 h. The increase in strength continues at a reduced rate up to the longest duration examined, 5 days. The influence of the cement/water ratio on the behaviour of the ultrasonic wave through the hydrating cement was investigated. The dependence of the breaking strength of the cement on the cement/water ratio is shown in Fig. 8. The results presented in this figure are for samples which have been aged for 24 h.

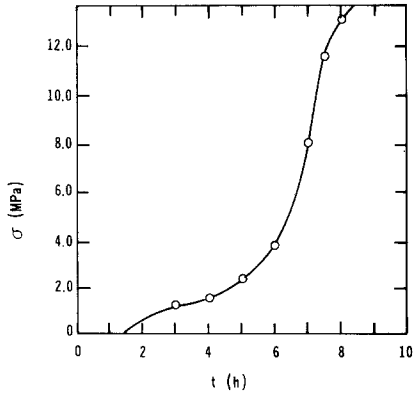

Figure 6 Changes in the compressive strength accompanying the hydration of a high alumina cement with C/W = 3.0.

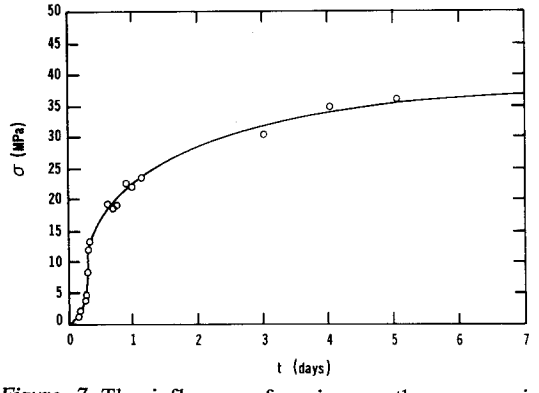

Figure 7 The influence of ageing on the compressive strength of high alumina cement. C/W = 3.0.

4. Discussion

The time dependence of the velocity of the ultrasonic wave through the hydrating cement gives a good correlation with changes in the strength of the sample. As shown in Figs. 3 and 6 a rapid increase in the wave intensity occurring at about 8 h on the time scale corresponds to the beginning of the sudden increase in the strength of the cement. The most rapid increase in strength takes place between about 9 and 12 h after the start of hydration. The breaking strength increased from about 2.07 MPa to 11.72 MPa over this three-hour period. In contrast to the ultrasonic pulse velocity the strength continues to increase beyond the twelve-hour time.

Examination of Fig. 4 reveals the existence of similar trends in each of the temperature and velocity curves. Both curves exhibit an initial increase followed by a relatively long period during which velocity and temperature show little change. In addition, there is a third region in which both properties undergo a rapid increase. At this point the similarities end and two distinct behaviours are observed for the temperature and velocity plots. In all of the specimens investigated the temperature peaks preceded the amplitude peaks by about one hour. In analogy to the colloidal theory advocated for the hydration of Portland cements [5], we propose a two-step mechanism for the hydration of the high alumina cements. Thus the first, less significant, temperature increase is believed to be associated with the initial step of hydration in which the formation of a new phase gives rise to the temperature peak. The second, more pronounced, peak in the temperature curve is believed to be the result of formation of a skeletal structure of the metastable

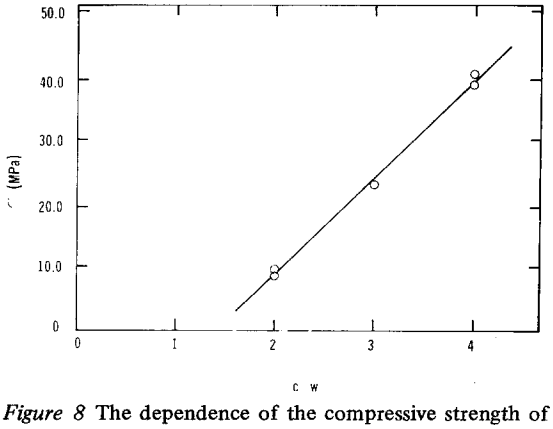

Figure 8 The dependence of the compressive strength of a cement aged for 24 h on the cement/water ratio.

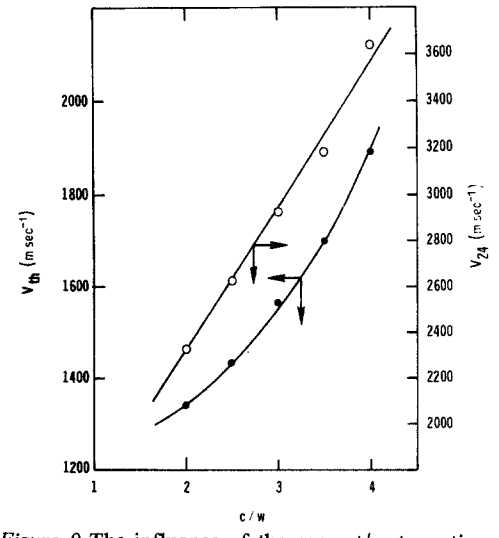

Figure 9 The influence of the cement/water ratio on the threshold velocity and the velocity at 24 h of the ultrasonic wave.

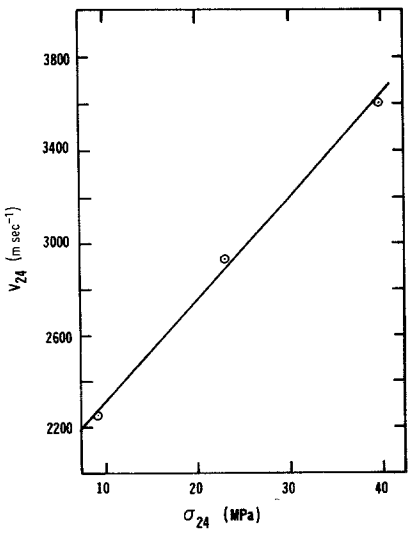

Figure 10 The relationship between strength and velocity at 24 h.

hexagonal phases of the cement. This, according to the theory, occurs after the initial phase has redissolved.

Corresponding changes in the velocity of the transmitted ultrasonic wave are explained in an analogous manner. Admittedly this theory is not universally accepted by those involved in Portland cement research. Furthermore, there is no conclusive chemical evidence of the existence of similar phase changes accompanying the hydration of high alumina cements. However, the results of the X-ray analyses presented and discussed in the following paper [3] give support to a mechanism similar to that outlined by the colloidal theory.

The threshold of detection of the transmitted wave and the calculated associated velocities, v_{th}, appear to be a function of the C/W ratio. Fig. 9 demonstrates this relationship for C/W values between 2 and 4. Although at considerably higher velocities, v_{24}, a similar relationship exists for cements which have been allowed to hydrate for 24 h, Fig. 9. These observations are consistent with strength determinations. Fig. 10 depicts the correlation between the transmitted velocities with the strength at 24 h. As expected a linear dependence is obtained. In contrast, the dependence of the maximum temperature on C/W is non-linear, exhibiting a maximum at C/W = 3 as shown in Fig. 11. In terms of proposed reaction paths for the hydration of calcium aluminate, CA, this C/W ratio represents an intermediate value between those theoretically required for the formation of the intermediate phase, C_2AH_6 and the final phase,

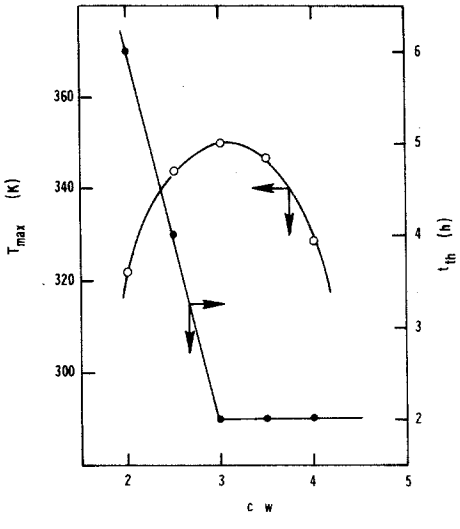

Figure 11 The variation of the maximum temperature and the threshold time with the cement/water ratio.

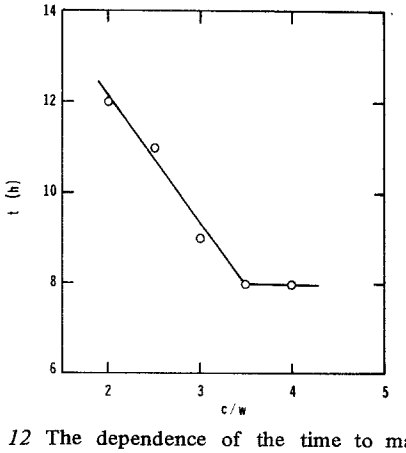

Figure 12 The dependence of the time to maximum temperature on the C/W ratio.

C_3AH_6. Theoretical C/W ratios for formation of these phases from CA are 2.19 and 4.39, respectively. Also shown in Fig. 11 is the dependence of the time before the appearance of the first signal, t_{th}, on the C/W ratio. The time decreases linearly to a C/W value of 3, then apparently remains constant beyond this ratio. A similar behaviour is obtained when the time needed to reach the maximum temperature is plotted as a function of the C/W ratio, Fig. 12. In this case, however, the point at which the time remains constant corresponds to a C/W value of 3.5.

It would be expected that the time needed for the appearance of the first wave signal through the hydrating cement would depend on the extent of the formation of a skeletal layer of the hydration product. In this respect, one expects a shorter time for cements with higher C/W ratios, in agreement with the present results. However, a lower limit is reached when the distance between the cement particles is no longer a factor in the kinetics of hydration.

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