JOURNAL OF MATERIALS SCIENCE 14 (1979) 647–652

Correlation of the phase transformation accompanying the hydration of calcium aluminate with ultrasonic wave behaviour

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Observations of changes in the amplitude and velocity of the ultrasonic wave transmitted through a hydrating high alumina cement were found to have no corresponding changes in X-ray phase analyses. A continuous X-ray scan of an hydrating sample showed no evidence for the completion of hydration. X-ray patterns from a sample aged for two months and from one aged for 24 hours were basically identical.

1. Introduction

In contrast to normal "high alumina" cements which are made by combining lime (usually from limestone) and bauxite, the "high purity" or "highly aluminous" cements are formed by substituting alumina for the bauxite. Table I shows a comparison between the various types of high alumina cements, including the high purity type [1, 2]. In addition to an increased Al_2O_3 content, these high purity cements have lower iron and silica impurity levels and thus are white in colour. The primary interest in this and other high alumina cements centres around their high temperature properties. With suitable aggregates, concretes of the high purity cements can withstand continuous exposure to temperatures in the neighbourhood of 2100 K.

Although the principal constituent of high alumina cements is calcium aluminate, CA, minor amounts of impurities often have a significant effect on the properties of the cement. Here again as in the previous paper [3], we follow the accepted notation where C, A and H refer to CaO, Al_2O_3, and H_2O, respectively. Fig. 1 shows the phases present in the $CaO–Al_2O_3$ (C–A) binary system [4]. Calcium monaluminate, CA, melts incongruently at ~ 1875 K and is reported to be monoclinic in structure. Upon hydration,

TABLE I Typical analyses of various high alumina cements [1]

Type	Source of alumina	Process of manufacture	% Al_2O_3	% Fe_2O_3	% SiO_2	% CaO	Colour
1	Red bauxite	Fusion	37–40	11–17	3–8	36–40	Grey to black
2	Red bauxite	Reductive fusion with removal of Fe metal	48–51	1–1.5	5–8	39–42	Light grey
3	White bauxite	Sintering Clinkering Fusion	51–60	1–2.5	3–6	30–40	Cream or light
4	Alumina	Sintering	72–80	0–0.5	0–0.5	17–27	White

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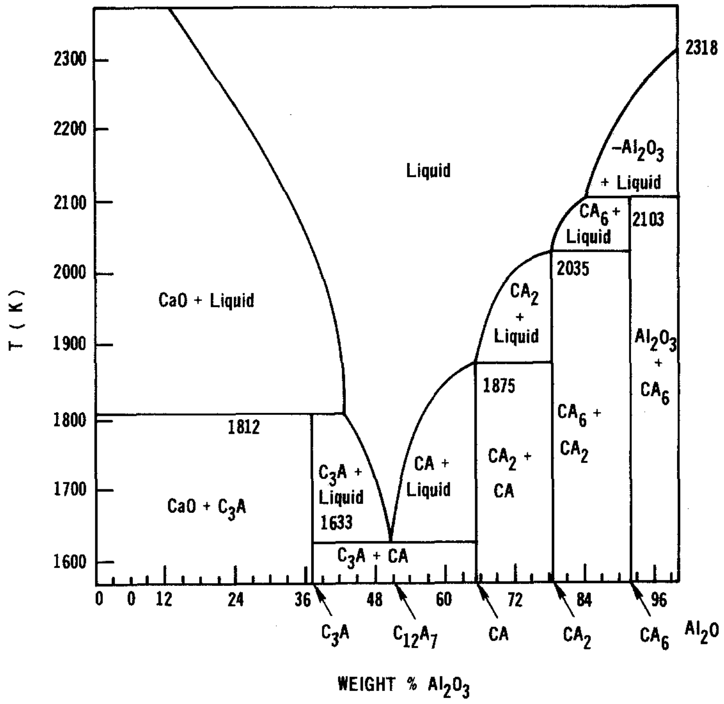


Figure 1 The phase diagram of the $CaO-Al_2O_3$ binary system.

significant chemical and structural changes occur with corresponding changes in the physical and mechanical properties. The process of hydration of CA is represented by the sequence of Fig. 2. The change from CA to C_2AH_8 can take place directly or via an intermediate step by first forming CAH_{10}. The final step is the change from C_2AH_8 to C_2AH_6. The hydration of CA to either CAH_{10} or C_2AH_8 is temperature dependent. The transformation of CA to CAH_{10} increases with increasing temperatures. At 288 K or below little if any any C_2AH_8 forms. It is reported that the critical temperature for the formation of C_2AH_8 from the hydration of pure CA is 296 K [5–7]. Regardless of the specific path of hydration, the intermediate hexagonal compounds (CAH_{10} and C_2AH_8) are metastable with respect to the cubic phase C_3AH_6. The rate of transformation of the metastable phases to the stable cubic phase is also temperature dependent. When high alumina cements are hydrated in the presence of air, the presence of a carbonato-aluminate, $C_3A\bar{C}H_{11}$, where $\bar{C}$ denotes $CaCoO_3$ is expected.

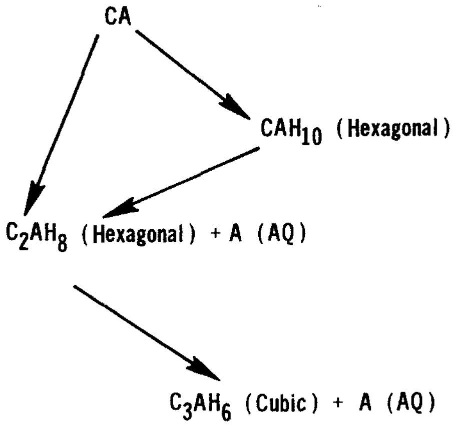


Figure 2 Schematic representation of the sequential steps in the hydration of calcium aluminate.

Interest in the hydration process of the 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. In the previous paper [3] we have reported the changes in the ultrasonic wave propagation behaviour through the calcium aluminate cement during the hydration process. In this paper we describe the results of X-ray determinations of the phase changes concomitant with the hydration process and the associated ultrasonic wave propagation.

2. Experimental materials and methods

Characterization of the high purity calcium aluminate cement utilized in this study were made through X-ray analysis. Results of this analysis, Fig. 3, showed CA and α-Al_2O_3 to be the most significant phases present. Of the minor peaks

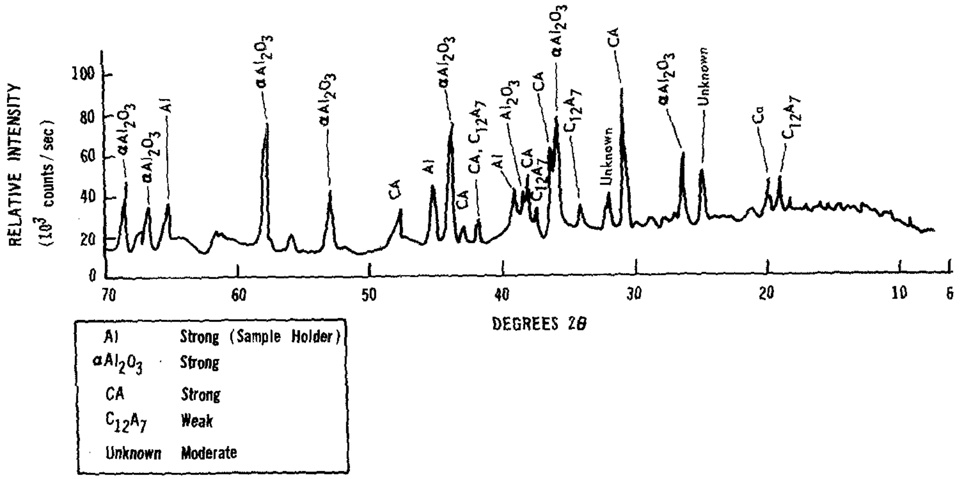


Figure 3 X-ray analysis of the as-received high alumina cement powder.

observed in this analysis those belonging to a $C_{12}A_7$ phase are discernible while others seem to be of unidentifiable origin. The strong peak related to Al is believed to originate from the sample holder.

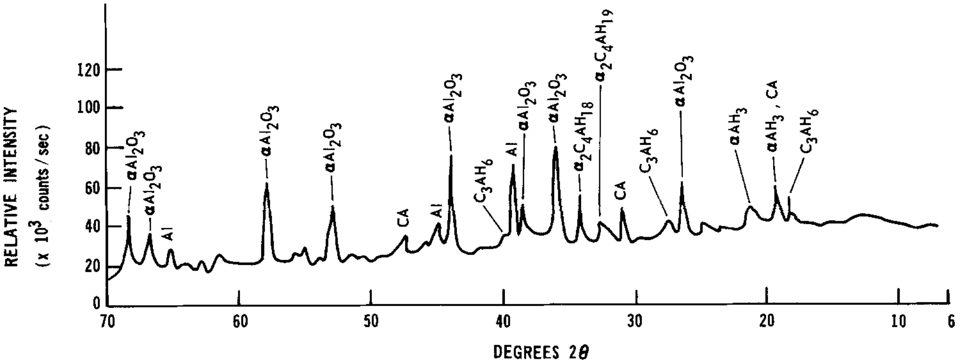
X-ray powder diffraction data were obtained using a Siemens (F-type) diffractometer equipped with a copper tube. For optimum peak resolution and intensity, tube and detector slits of 0.5° and 0.1 mm, were used, respectively. A nickel filter was utilized. Power settings during pattern determination were at 35 kV and 24 mA with a scanning rate of 2° of 2θ per minute. Diffraction patterns were registered on a strip chart recorder.

X-ray samples were prepared by breaking the cement blocks and extracting material from the centre. Each sample was mechanically ground for one to two minutes in a grinding machine and subsequently hand-ground to a fine consistency. Portions of this powder passing through a 200 mesh sieve were pressed against an aluminium sample holder to ensure a smooth, uniform surface for the X-ray examination. Following a determination of the powder's X-ray pattern, a calibration was made to correct for the chart recorder drift. Shifts in "*d*" values were obtained from a comparison of the actual and the measured values for the aluminium peaks (sample holder). Identification of existing compounds was based on the corrected "*d*" values in the scanning range 20 to 70 degrees of 2θ.

3. Results and discussion

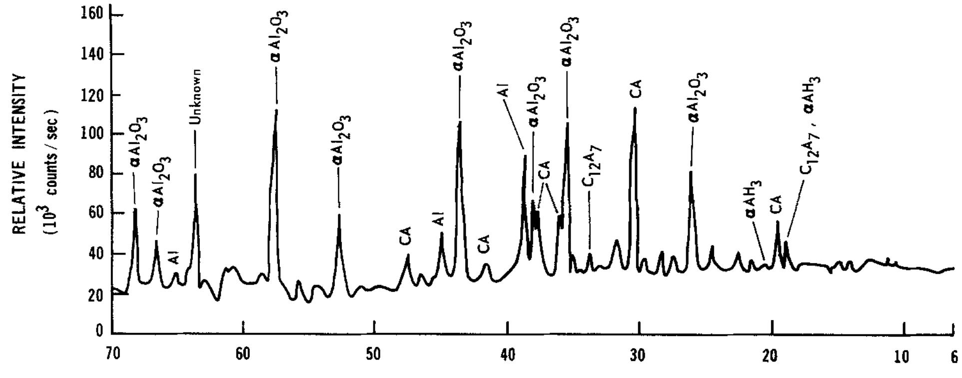
Our initial approach was to explain the observed changes in the amplitude of the transmitted ultrasonic signal with the phase changes associated with the hydration process of the cement. A cement sample with cement/water ratio (C/W) of 3 was made and placed in a specially designed plastic cell and exposed to X-radiation at 30-minute intervals. During exposure, the Bragg diffraction angle was scanned from 20 to 70 degrees (2θ). Lower values gave extensive background noise, making peak identification difficult and subject to great uncertainty. Results of these investigations which were conducted over a 12-hour period indicated that essentially no hydration had taken place, or at least none that could be ascertained by the X-ray analysis. It was thus decided to examine a cement block which had been mixed and aged for approximately 2 months. The X-ray data for this sample are indicated in Fig. 4. The results presented in this figure showed the presence of moderate lines for the hexagonal phase C_4AH_{19} and the cubic phase C_3AH_6. In addition, the presence of a moderate line for the alumina gel, αAH_3, was noted. The strong line for the Al_2O_3 phase, and the moderate peak intensity of calcium aluminate CA indicate that hydration was by no means complete.

Since the continuous X-ray monitoring experiment was apparently not successful, an alternative approach was attempted. Blocks of cement hydrated for 6 and 12 h were cut and an X-ray sample extracted from each. The results of the X-ray investigation on these samples are shown in Figs. 5 and 6. A strong peak in the 6-hour data could not be attributed to any of the possible or probable phases of the hydration process. The data showed a weak line for the phases $C_{12}A_7$ and



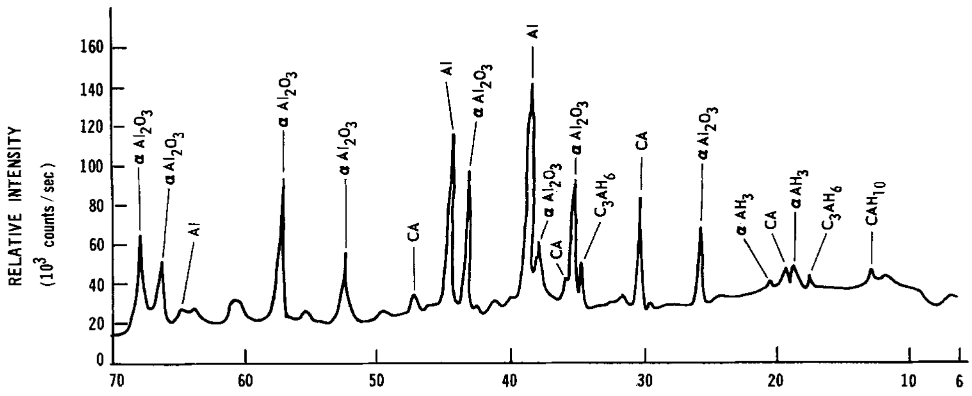
Al	Strong	$_2C_4AH_{19}$	Moderate
αAl_2O_3	Strong	C_3AH_6	Moderate
CA	Moderate	αAH_3	Moderate

Figure 4 X-ray diffraction pattern of a high alumina cement (C/W = 3.0) which had aged for 2 months.



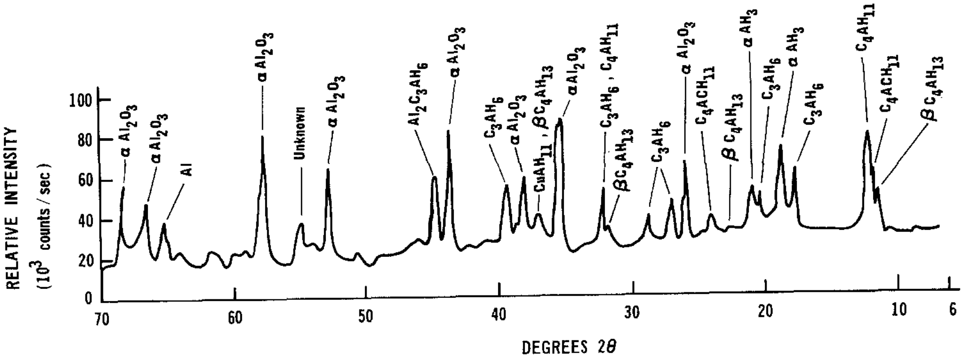
Al	Strong	$C_{12}A_7$	Weak
Al_2O_3	Strong	AH_3	Weak
CA	Strong	Unknown	Strong

Figure 5 The diffraction pattern of a high alumina cement after 6 h from the commencement of hydration.



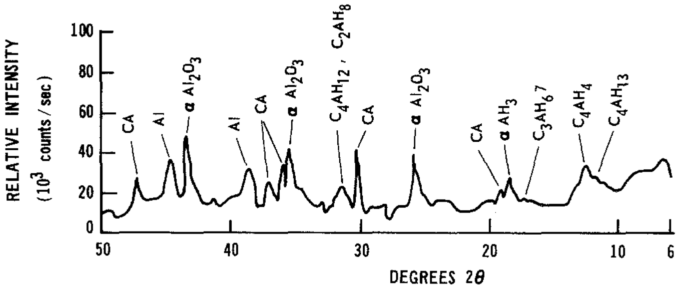
Al	Strong	C_3AH_6	Moderate
Al_2O_3	Strong	CAH_{10}	Weak
CA	Strong	AH_3	Moderate

Figure 6 The diffraction pattern of a high alumina cement allowed to hydrate for 12 h.



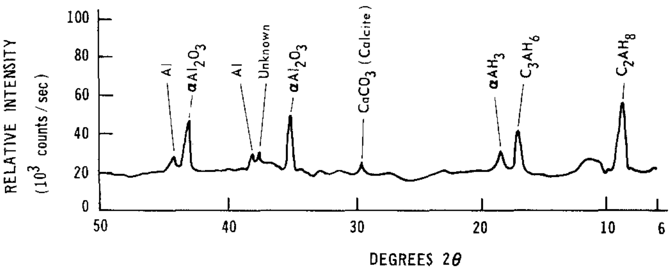
Al	Strong	βC_4AH_{13}	Weak
αAl_2O_3	Strong	C_4AH_{11}	Strong
αAH_3	Moderate	C_4ACH_{11}	Moderate
C_3AH_6	Moderate		

Figure 7 Diffraction pattern of a cement which was allowed to harden then was ground and rehydrated with excess water at 303 K.



αAH_3	Moderate
αAl_2O_3	Strong
CA	Strong
C_4AH_{11}	Moderate (broad peak)
C_4AH_{13}	Moderate
C_3AH_6	Very Weak
Al (from sample holder)	Moderate (broad peak)

Figure 8 X-ray pattern of a high alumina powder hydrated with excess water for 24 h at room temperature.



AH_3	Moderate	C_2AH_8	Strong
Al_2O_3	Strong	$CaCO_3$ (Calcite)	Weak
C_3AH_6	Moderate	Al (From Sample Holder)	Weak

Figure 9 X-ray diffraction pattern of a high alumina powder hydrated with excess water for 24 h at 314 K.

αAH_3. At 12 hours after the initial mixing of the cement and water, the results showed a moderate C_3AH_6 (cubic) and a weak CAH_{10} (hexagonal) lines. The line corresponding to the gel, αAH_3, is now much stronger. Again, the peaks corresponding to alumina and CA were relatively strong. Thus, while the changes in the intensity and velocity of the transmitted sound wave between 6 and 12 h of hydration were outstanding, X-ray indications of corresponding phase changes were remarkably weak.

The question of whether or not the sample studied thus far had indeed hydrated had to be answered by another series of experiments. A cement with $C/W = 3$ was mixed and allowed to set in the usual manner. It was then ground to 200 mesh particles and immersed in warm water (maintained at approximately 303 K) and kept under these conditions for 24 h. An X-ray sample obtained from the centre portion of the cement block gave the pattern shown in Fig. 7. A significantly large number of peaks is evident. Included among these are peaks of C_3AH_6, αAH_3, C_4ACH_{11}, C_4AH_{13}, and C_4AH_{11}. The most interesting observation, however, is the absence of any peaks for CA. This latter observation indicates the completion of the hydration process. Another series of experiments was carried out to further investigate the hydration process as affected by the presence of water. Calcium aluminate powder was added to an excessive amount of water and allowed to hydrate for 24 h. The water was held either at room temperature or at a higher value, 314 K. Under such experimental conditions, each powder particle is believed to be completely surrounded by water and thus the hydration process is not affected by the diffusion of water from the surface. Figs. 8 and 9 show the X-ray patterns obtained from samples which had been hydrated in this manner at room temperature and 314 K, respectively. At room temperature the hydration process appears to be incomplete as judged by the presence of strong CA and Al_2O_3 peaks and weak peaks for the hydration phases. At 314 K the indications are that the hydration process is at a higher degree of completion as evidenced by the absence of CA peaks and the relatively strong peaks for the hydration products.

The significant changes in the intensity and velocity of the wave through the cement during hydration [3] are not quantitatively matched by changes in the X-ray data. As indicated in an earlier section, only a slight evidence was observed for the formation of the hydrated compounds. Furthermore, the disappearance of the alumina lines did not occur unless the cement was hydrated with excessive amounts of water. These observations suggest two general possibilities. The first is that the cement at 24 h had not significantly hydrated. However, the X-ray patterns from a 2-month old cement gave essentially the same information as the 24-hour sample. Since it is highly unlikely that the hydration process takes a duration of this magnitude, it appears that the first explanation is not plausible. A second, more likely explanation, however, is that the products of hydration are predominantly amorphous in nature. Thus, in contrast to ultrasonic methods described in the previous paper [3], the present results indicate that ordinary X-ray techniques cannot be used as a means of monitoring the process of hydration of high alumina cements.

Acknowledgements

This work was made possible through a grant to one of the authors (ZAM) from the Kaiser Aluminum and Chemical Company. Helpful discussions with M. L. Van Dreser and J. Massaryk of Kaiser's Center for Technology contributed significantly to the success of this research. Finally, we wish to acknowledge the technical assistance of Tom Rach, then a graduate student at the University.

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Received 20 January and accepted 19 May 1978.