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PERFORMANCE OF HIGH-ALUMINA CEMENT CONCRETE STORED IN WATER AND DRY HEAT AT 25, 35 AND 50°C

D.H.H. QUON AND V.M. MALHOTRA

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PERFORMANCE OF HIGH-ALUMINA CEMENT CONCRETE STORED IN WATER AND DRY HEAT AT 25, 35 AND 50°C

by

D.H.H. Quon* and V.M. Malhotra**

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ABSTRACT

High-alumina cement, although not at present manufactured in Canada, is nevertheless frequently used in this country for special applications. Canadian Standards Association Committee A 23.1, Concrete Materials and Methods of Concrete Construction, in Appendix A of its 1977 edition has recommended against the use of this cement for structural purposes because of the recent structural failures associated with its use in England. This investigation is a continuation of the work undertaken in 1975 at CANMET and involves a study of the performance of high-alumina cement stored in water and dry heat at 25°, 35° and 50°C.

A series of 0.056-m^3 (2-ft^3) concrete mixes was made in the laboratory using crushed gravel and natural sand as coarse and fine aggregates respectively. Thirty 102 x 203-mm (4 x 8-in.) cylinders were cast from each mix. Following the initial moist-curing period of 24 hours at 18°C, one third of the cylinders were subjected to standard moist curing at 21°C, one third were cured in water at 25°C and one third were cured in dry heat at 25°C. A similar procedure was repeated for 35° and 50°C exposure conditions. The curing period varied from 1 day to 365 days for each exposure condition. At selected ages, the weights and pulse velocity of the cylinders were determined before the specimens were tested in compression. Small samples of mortar from the tested specimens were examined by X-ray diffraction (XRD) and differential thermal analysis (DTA) to determine the phase composition of the samples and hence to estimate the degree of conversion.

High-alumina cement concretes exposed to moist curing at 21°C show continuous gain in strength at least up to one

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year regardless of the water/cement ratio of the concrete. However at 25° and 35°C under both dry and humid conditions there is a loss in strength with age; the loss in strength increases with an increase in the water/cement ratio of the concrete. For continuous exposure at 50°C under both humid and dry conditions, the change in strength with age depends upon the water/cement ratio of the concrete. At a water/cement ratio 0.31 there is only an insignificant drop in strength at early ages, in spite of the high degree of conversion, following which the strength increases with age, reaching a value of 125 per cent of one-day strength at age 365 days. This is significant as it suggests a means by which very high strengths can be achieved and maintained at least up to one year.

The degree of conversion should not be used as a measure of compressive strength of high-alumina cement concrete because of lack of correlation between the two parameters.

LA PERFORMANCE DU BETON DE CIMENT A HAUTE TENEUR D'ALUMINE EMMAGASINE DANS L'EAU ET A LA CHALEUR SECHE DE 25, 35 ET 50°C

par

D.H.H. Quon* et V.M. Malhotra**

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RESUME

Quoique qu'il ne soit pas manufacturé au Canada en ce moment, le ciment à haute teneur d'alumine est néanmoins employé fréquemment dans notre pays dans le cas d'applications spéciales. Le Comité de l'Association canadienne de normalisation A23.1 sur les matériaux de béton et les méthodes de construction avec le béton ne recommande pas à l'annexe A de son édition 1977, l'usage de ce ciment pour la construction d'immeubles à cause de défaillances récentes survenues en Angleterre. Cette étude donne suite aux travaux effectués en 1975 par CANMET et comporte l'analyse de la performance du béton de ciment à haute teneur d'alumine emmagasiné dans l'eau et à la chaleur sèche de 25°, 35° et 50°C.

On a fait en laboratoire une série de mélanges de béton de 0.056 m^3 (2 pi^3) en employant du gravier concassé et du sable naturel servant respectivement d'aggrégats grossiers et fins. Trente cylindres de 102 par 203 mm (4 x 8 po) ont été coulés à partir de chacun des mélanges. Après avoir subi un traitement initial humide d'une durée de 24 heures à 18°C, le tiers des cylindres ont été soumis à un traitement humide normal à 21°C, le tiers ont été immergé dans l'eau à 25°C et l'autre tiers a subi un traitement à la chaleur sèche de 25°C. Un procédé semblable a été répété mais à des températures de 35° et 50°C. La durée du traitement a varié de 1 jour à 365 jours selon chacune des conditions d'exposition. A des temps voulus, le poids et la vélocité d'impulsion des cylindres ont été déterminés avant que les spécimens ne soient analysés en compression. De petits échantillons de mortier prélevés des spécimens analysés ont été examinés selon les méthodes de diffraction rayon-X et d'analyse thermique différentielle afin d'en déterminer la composition de phase des échantillons et estimer le degré de conversion.

La résistance des bétons de ciment à haute teneur d'alumine exposé au traitement humide à 21°C augmente continuellement au moins pendant un an indépendamment du taux eau/ciment

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du béton. Par contre à des température de 25° et de 35°C et selon des conditions sèches ou humides, ils perdront leur résistance avec le temps; cette perte de résistance augmente lorsque le taux eau/ciment de béton augmente. Lorsqu'ils sont exposés continuellement à une température de 50°C et à des conditions humides et sèches, le changement dans la résistance avec le temps varie selon le taux eau/ciment du béton. Lorsque celui-ci est de 0.31, il n'y a qu'une baisse négligeable de la résistance au début malgré le haut degré de conversion. Par la suite, la résistance augmente avec le temps et atteint 125% de la valeur de la résistance mesurée au premier jour lorsqu'il aura 365 jours. Cette analyse a démontré comment on peut atteindre et maintenir de grandes résistances pendant au moins un an.

Le degré de conversion ne devrait pas être employé comme mesure de résistance à la compression du béton de ciment à haut teneur d'alumine car il existe un manque de corrélation entre les deux paramètres.

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INTRODUCTION

In the period 1962 to 1963, investigations were conducted at CANMET (then Mines Branch) to study the effect of temperature, ranging from 100° to 1000°C, on the properties of concrete made with high-alumina cement[1,2,3]. In 1975 a further program was initiated to investigate the effect of near-ambient temperatures of 30°, 38° and 66°C on the compressive strength, pulse velocity, and conversion of high-alumina cement concrete[4].

The present investigation is a continuation of the work commenced in 1975 and deals with the performance of high-alumina cement concrete cured under standard moist room conditions as well as in water and in dry heat at 25°, 35° and 50°C. The research reported herein is one work element of a Project dealing with aggregates, cement and concrete, part of the Utilization Activity of CANMET's Minerals Research Program.

SCOPE OF INVESTIGATION

A series of nine 0.056-m^3 (2-ft^3) concrete mixes was prepared in the laboratory using crushed gravel and natural sand as coarse and fine aggregates respectively. Thirty 102 x 203-mm (4 x 8-in.) cylinders were cast from each mix. Following the initial moist curing for 24 hours at 18°C, the test specimens were treated as follows: one third were subjected to standard moist curing at 21°C, one third were cured at 25°, 30° and 50°C in water and the remaining one third were cured at 25°, 30° and 50°C under dry heat conditions. The curing age varied from 1 to 365 days. At selected ages, the weights, densities and pulse velocities of the cylinders were determined before they were tested in compression. Small samples of mortar from the tested specimens were subjected to X-ray diffraction (XRD) and differential thermal analysis (DTA) to identify the various hydrates and to determine the degree of conversion.

CONVERSION PHENOMENON AND DEGREE OF CONVERSION

The mineralogy of high-alumina cement and the practical limitations imposed by the phenomenon of conversion of the cementitious phases have been discussed elsewhere[5-9]. Notwithstanding this, it is stressed that the exact mechanism of the conversion is still not clear and needs further research. In brief, the high-alumina cement undergoes a change from the metastable compounds $CaO.Al_2O_3.10H_2O$ (CAH_{10}) and $2CaO.Al_2O_3.8H_2O$ (C_2AH_8) and alumina gel into the more stable compounds $3CaO.Al_2O_3.6H_2O$ (C_3AH_6) and $Al_2O_3.3H_2O$ (AH_3 or gibbsite).

The percentage of conversion (D_c), as a means of appraising the quality of high-alumina cement concrete, has been defined by Midgley[8,9] as:

$$D_c = \frac{\text{Weight of } AH_3}{\text{Weight of } AH_3 + \text{Weight of } CAH_{10}} \times 100 \qquad (1)$$

Generally, differential thermal analysis (DTA) has been used to study the degree of conversion. The peak heights of the DTA curve are usually interpreted to be a measure of the relative amounts of CAH_{10}, C_3AH_6 and AH_3.

MATERIALS USED

Cement

The cement used for this investigation was obtained from a commercial source. It was supplied in bags from a single lot. Upon receipt, the cement was stored in a dry room at a temperature of 21°C until required for use. The chemical composition of the cement is given in Table 1.

Aggregates

Minus 25-mm (1-in.) river gravel was used as the coarse aggregate and local natural sand as the fine aggregate. To ensure uniform grading in all mixes, the sand was separated into various size fractions that were then combined to give a specific grading.

The grading and physical properties of both the coarse and fine aggregates are given in Tables 2 and 3.

Air-Entrained Agent

No air-entraining agents were used in this investigation.

CONCRETE MIXES

A total of 12 concrete mixes were prepared in the laboratory between November 1, 1976 and February 2, 1977. A 0.067-m^3 (2.5-ft^3) laboratory counter-current mixer was used for preparing the concrete batches.

Mix Proportioning

Table 4 summarizes the proportioning of the concrete mixes. In all mixes, the room-dry coarse and fine aggregates were soaked in water for 24 hours prior to use, and the amount of mixing water was adjusted according to the water absorbed. A total of three mixes were made for each of four series having water/cement ratios of 0.31, 0.37, 0.47 and 0.60. The water content and the ratio of coarse to fine aggregate were kept constant for each series. During mixing, the temperature of the fresh concrete was maintained at 16 ± 2°C.

Properties of Fresh Concrete

The properties of the freshly mixed concrete, i.e., temperature, slump, unit weight and air content, are given in Table 4.

PREPARATION AND TESTING OF SPECIMENS

Preparation

Thirty 102 x 203-mm (4 x 8-in.) cylinders were cast from each mix. The cylinders were cast by filling steel moulds with two approximately equal layers, each layer being compacted on a vibrating table for 30 seconds. After casting, all the moulded specimens were covered with a glass plate, which in turn was covered with water-saturated burlap kept wet by a water spray, and were left in the casting room for 24 hours at 18 ± 2°C. Subsequently, all specimens were demoulded and density and pulse velocity measurements were taken immediately. Finally, three cylinders were capped with a high-strength capping compound and then tested in compression according to ASTM Standard C 39-72. Mortar from the tested specimens was separated from the aggregates by screening through a 200-mesh sieve. The minus 200-mesh material was characterized by X-ray diffraction and differential thermal analyses techniques. The remaining cylinders were then treated as follows:

Compression Testing

Series A - Mix No. 1

1. Nine of the cylinders were stored in a moist curing room maintained at 21 ± 3°C. At ages of 2, 7, 28 and 365 days, two of the cylinders were removed from the curing room and their densities and pulse velocities were determined. The cylinders were than capped and tested in compression in accordance with ASTM Standard C 39-72. Small samples were obtained from the tested specimens for material characterization using XRD and DTA techniques.
2. Nine of the cylinders were stored in a water bath at 25°C. At ages of 2, 7, 28 and 365 days, two cylinders

were removed from the water bath and cooled to room temperature; their densities and pulse velocities were then determined. The cylinders were finally tested in compression, and mortar from the specimens was used for material characterization.

3. Nine of the cylinders were stored in a cabinet maintained at 25°C (dry heat). At ages of 2, 7, 28 and 365 days, two of the cylinders were removed from the heating cabinet and cooled to room temperature; then their densities and pulse velocities were obtained. The cylinders were then tested in compression, and mortar from the specimens was used for material characterization.

Series A - Mix No. 2

The cylinders were treated in the same manner as Mix No. 1, except that the temperature of storage in both the water bath and heating cabinet was increased to 30°C.

Series A - Mix No. 3

The test specimens were treated as for Mix No. 1, except that the temperature of exposure in both the water bath and the heating cabinet was increased to 50°C.

Mix Series B, C and D

The test cylinders from the mixes of these series were treated in a manner identical to that employed for the specimens from the concrete mixes of Series A.

X-ray Diffraction Studies

Small samples of mortar from the broken test cylinders, obtained by screening through 200 mesh, were used for the XRD studies. All the X-ray photographs of the test samples were obtained with a Guinier-de Wolff focussing camera using Co K_{α} radiation. In the previous investigation[4], an attempt was made to measure the peak heights for the various hydrate phases from the X-ray photographs, using a microdensitometer. It was shown that this technique can only provide a qualitative estimate of the state of conversion of the high-alumina cement concrete. Hence, in the present investigation, the technique has been used only for qualitative estimates of conversion and for phase identification purposes.

Differential Thermal Analysis (DTA)

DTA has been found to be most useful both for phase identification and for estimating the degree of conversion of the high-alumina cement concrete. For these determinations, the cementitious fraction was separated from the aggregate fraction using a 200-mesh screen. One-gram aliquots of the cementitious component were used for DTA studies, conducted in air using a heating rate of 12°C per minute with alpha-alumina as the inert reference material. The sample was held in a nickel block and chromel-alumel thermocouples were used for both reference and differential temperature measurements, which were simultaneously recorded on a two-pen recorder, the former directly and the latter after amplification.

The technique for phase identification has been described in detail elsewhere[4]. The endothermic reactions recorded in the DTA curve at 120°, 160°, 195°, 290° and 300°C reflect the presence in the sample of alumina gel, CAH_{10}, C_2AH_8, C_3AH_6 and AH_3 (gibbsite) respectively. By measuring the peak height of the exothermic reactions from the DTA curve, it is possible to estimate the degree of conversion (D_C) by the technique described by Midgely[8,9]. In order to determine the degree of conversion as accurately as possible, the DTA apparatus was first calibrated by using materials having a known degree of conversion, which were obtained from the Building Research Establishment, U.K. Thereafter, the degree of conversion (D_C) of unknown samples was obtained by measuring the height of peaks recorded in DTA at 160°C (due to a phase change in CAH_{10}) and 300°C (due to phase change in AH_3) and employing a modified form of equation (1):

$$D_C = \frac{\text{Peak height of } AH_3 \text{ x } 100}{\text{Peak height of } AH_3 + \text{Peak height of } CAH_{10}} \text{ x } K \qquad (2)$$

where K is a calibration constant.

TEST RESULTS AND THEIR ANALYSIS

Three hundred and sixty 102 x 203-mm (4 x 8-in.) concrete cylinders were tested in this investigation. The densities, pulse velocities and compressive strengths of concretes stored under different environmental conditions are given in Tables 5, 6 and 7. The between-batch coefficients of variation of the test results of the four series of concrete mixes are given in Table 8. The relationships between water/cement ratio and compressive strength of the test cylinders are shown in Figures 1 to 5. Plots of the test results showing relationships between age and change in weight, compressive strength, and pulse velocity are shown in Figures 6 to 17. The relationships between age and degree of conversion at each temperature of exposure are shown in Figures 18 to 22.

A total of 156 samples of concrete were examined by the DTA technique. Figures 23 to 26 show typical DTA curves for the converted and unconverted high-alumina cement concretes of various water/cement ratios, stored under different environmental conditions, at the age of 7 days.

DISCUSSION OF RESULTS

Changes in Weight and Density of Test Specimens

The change in weight of test specimens under various storage conditions for concretes having different water/cement ratios are shown in Figures 6 to 9. At 365 days an increase in weight of 2 per cent or less is noted in all moist cured test specimens irrespective of the water/cement ratio.

The rate of weight gain, as well as its magnitude, is greater for test specimens stored in water, having lower water/cement ratios and exposed to higher temperatures. This confirms the results reported earlier[4], the rationale being that in richer mixes there is a larger volume of cement paste and when converted there is therefore a larger volume of pores, which in turn allows more water to be held. In general, the amount of water absorbed in the test specimens stored in water follows a similar trend to that of the specimens stored in the moist room.

The weight of test cylinders stored in dry heat at various temperatures decreases up to a maximum of 3.5 per cent for concrete having a water/cement ratio of 0.6. The weight loss increases with increasing temperature of storage as well as with increasing water/cement ratio. The decrease in weight is attributed to uncombined water being driven out by the drying process.

The densities of the test cylinders at various ages are given in Table 5. In most cases, a small but noticeable increase in density is observed at the age of 365 days. The desnity increase reflects the formation of the denser phases C_3AH_6 and AH_3 in the converted and partially converted high-alumina cement concrete.

Degree of Conversion and Associated Strength Loss

Moist Curing Regime

The degree of conversion data in Table 9 and Figures 18 to 21 show that, for test specimens stored under moist curing conditions at 21°C, the conversion had started after one day. This is so, even for concretes having low water/cement ratios. The values at one day vary from 19 per cent for concrete having a water/cement ratio of 0.37 to 36 per cent for concrete with a water/cement ratio of 0.47. The higher degree of conversion for concretes with a water/cement ratio 0.31 (Table 9) is unexplained. Apart from one instance where the degree of conversion reached 52 per cent at 365 days (for concrete with a water/cement ratio of 0.31), the degree of conversion does not change significantly with age up to 365 days. In spite of the high degrees of conversion reported above, there was no loss in strength (Table 6) nor decrease in pulse velocity (Table 7) of concretes associated with this conversion. This was true even for concretes having a water/cement ratio of 0.60. On the contrary, there was a gradual increase in strength with age, to values of 76.1 MPa (11,030 psi) and 60.8 MPa (8810 psi) at 365 days, for concretes with a water/cement ratio of 0.31 and 0.60 respectively. The test results at high water/cement ratios appear to be in contradiction with the data reported earlier[4] and that published by Teychenne[10], which showed significant strength losses with age when the water/cement ratio exceeded 0.45.

Curing Regime - in Water and in Dry Heat at 25°C

The exposure of test specimens to water and to dry heat at 25°C showed that, at ages up to 28 days, the degree of conversion was between 17 and 34 per cent (Figures 18 to 21). For concretes with a water/cement ratio of 0.31, there was a gradual increase in strength with age for exposure to dry heat at 25°C, the strength value at one year being 67.7 MPa (9820 psi). On exposure in water the strength increased with age up to 28 days but beyond that there was no significant change; the value at one year being 65.8 MPa (9570 psi).

Beyond 28 days, there was a sharp increase in the degree of conversion of all concretes stored both in water and in dry heat at 25°C regardless of the water/cement ratios. At one year, when the tests were discontinued, the conversion had reached between 59 and 65 per cent for dry heat exposure, and 59 and 77 per cent for test specimens stored in water (Table 9). There was no strength loss associated with this conversion for concretes having a water/cement ratio of 0.31. However, there was considerable strength loss for concretes having higher water/cement ratios. For example, at one year, the concrete cylinders with a water/cement ratio of 0.60 had decreased in strength to a value of about 68 per cent of the one-day strength, for test specimens stored in water. Furthermore the conversion trends in Figure 21 show that if the tests had been continued beyond 365 days, there would probably have been further increases in the degree of conversion of the high-alumina cement concrete and associated strength losses.

Curing Regime - in Water and in Dry Heat at 35°C

At ages up to 7 days, the degree of conversion was between 17 and 40 per cent for both conditions of exposure regardless of the water/cement ratio (Table 9). However, starting at 7 days there was a sharp increase in conversion that continued up to one year. At one year the degree of conversion was between 68 and 79 per cent regardless of the water/cement ratio and type of exposure.

The compressive strengths of the test cylinders generally reached maximum values at 7 days, following which they started to lose strength with minimum values being reached at one year. The maximum loss in strength for concretes having a water/cement ratio of 0.47 and continuously exposed in dry heat at 35°C occurred at one year, when the compressive strength was only 50.8 per cent of the one-day strength. The one-year strength values for concrete with a water/cement ratio of 0.60 were between 52.8 and 60 per cent of the one-day strengths. At this temperature of exposure, there was no strength recovery as was the case in the work reported earlier[(4)].

Curing Regime - in Water and in Dry Heat at 50°C

In this curing regime, concretes with low water/cement ratios show considerable conversion at 2 days, e.g., a value of 48 per cent is reached for concrete with a water/cement ratio of 0.31 for exposure to dry heat. The degree of conversion increases with age and at 28 days the conversion values vary from 60 per cent for concrete having a water/cement ratio of 0.37 to 80 per cent for concrete having a water/cement ratio of 0.47, for dry heat exposure. Beyond 28 days the conversion does not change significantly with age and remained at about 78 per cent, regardless of the water/cement ratio of concrete and the exposure conditions (Table 9).

The compressive strength reached a minimum value at either 2 days or 7 days. This is true for most of the concretes regardless of the water/cement ratio and exposure conditions. Following this, there was a sharp recovery in strength, particularly for concretes with a water/cement ratio of 0.31 and 0.37. The strengths of the concretes at one year, when tests were discontinued, were higher than the one-day strength. For example, for concrete having a water/cement ratio of 0.31 and exposed to dry heat, the compressive strength at one year was 77 MPa (11,190 psi) compared with a strength value of 57.1 MPa (8,280 psi) at one day.

For concrete with a water/cement ratio of 0.37, the strength recovery was not as marked but the one-year strength did exceed the one-day strength (Table 6).

For concretes with water/cement ratios of 0.47 and 0.60, the recovery was not significant and none of the test cylinders reached a strength comparable to the one-day values. In fact, for concrete test cylinders having a water/cement ratio of 0.60 and exposed to water at 50°C, there was a gradual loss in strength with age and a strength of 17.7 MPa (2,570 psi) was reached at one year compared to a one-day strength of 38.2 MPa (5,540 psi).

The above phenomenon of strength recovery following the initial decrease in strength associated with the conversion has also been reported by others[10,11,12] and may be explained according to a hypothesis advanced by Neville[5]. In the present investigation, strength recovery is not followed by loss in strength after 28 days, as was observed in the investigation reported in 1977[4]. This is significant because it confirms the data reported by others[5,12] that very high-strength high-alumina cement concrete can be developed and maintained for at least one year by exposing concretes with low water/cement ratios to above-ambient temperatures. Whether this is an economical way to make high-strength concrete is another question, the discussion of which is beyond the scope of the present report.

Pulse Velocity Measurements

The ultrasonic pulse velocity changes are given in Table 7 and Figures 14 to 17. The plots in Figures 14 to 17 follow the same general pattern as those for conversion (Figures 18 to 21).

The data in Table 7 indicate that pulse velocity is an excellent means of monitoring the progression and regression of strength in high-alumina cement concrete. However, it is stressed that pulse velocity measurements should not be used for estimating absolute values of strength of concrete because of poor correlations between these two parameters(3). This is well supported by data presented in Table 7.

Another interesting feature of the pulse velocity technique is that for each water/cement ratio there is a marked difference between the pulse velocities of cylinders stored in water at elevated temperature and those exposed to dry heat. The cylinders exposed to dry heat show relatively lower pulse velocities because, in addition to porosity caused by conversion, they contain microcracks caused by thermal stress. On the other hand, the high pulse velocity of cylinders stored in water at elevated temperatures is due to the fact that water fills the pores caused by the conversion thus resulting in shorter pulse travel time.

Differential Thermal Analysis (DTA)

DTA was used for the phase identification of high-alumina cement concrete having various water/cement ratios and stored under different environmental conditions.

Typical thermograms of the 7-day-old high-alumina cement concretes having water/cement ratios varying from 0.31 to 0.60 are shown in Figures 22 to 25. In some of these thermograms there are four strong and one weak endothermic peaks located at 120°, 160°, 195°, 290° and 300°C. The endothermic peaks at 120° and 160°C are ascribed to the removal of water from the alumina gel and the hydration of the high-alumina cement to form CAH_{10}. The weak endothermic peak at 195°C is ascribed to the presence of C_2AH_8 resulting from the conversion of CAH_{10}. The endothermic reactions at 295° and 300°C are due to the presence of gibbsite and C_3AH_6 resulting from the conversion of the alumina gel and CAH_{10}. It can be seen from Figures 22 to 25 that as the storage temperature increases there is a gradual decrease in the peak heights for the alumina gel and CAH_{10}, and a gradual increase in peak heights for the gibbsite and C_3AH_6, indicating a greater degree of conversion at higher temperature.

X-ray Diffraction Studies

Phase changes occurring during the conversion of components of high-alumina cement concrete can be detected by means of X-ray diffraction techniques. For the purpose of presentation in this report, the 0.513 nm diffraction peak height for C_3AH_6 was measured from a densitometer trace of the X-ray photographs for concretes stored for varying periods under different environmental conditions.

Figure 26 shows a typical plot of the change in peak height for C_3AH_6 for concrete with a water/cement ratio of 0.37 of different ages and storage environments.

It is recognized that there are difficulties in using XRD techniques for true quantitative analyses of the degree of conversion due to the poorly developed crystallinity of the various hydrates at earlier ages, and to interference by diffraction peaks resulting from the presence of fine aggregate minerals. However, it can be concluded that the C_3AH_6 peak height increases with increasing amount of that phase, although not necessarily in direct proportion. As further confirmation, the results shown in Figure 26 indicate that as the peak height, and hence the amount of C_3AH_6, increases, the compressive strength decreases.

CONCLUSIONS

High-alumina cement concretes exposed to moist curing conditions at 21°C show a continuous gain in strength at least up to one year, regardless of the water/cement ratio. The degree of conversion of about 20 per cent reached at early ages does not significantly change with age and there is no loss in strength associated with conversion.

High-alumina cement concretes cured at 25° and 35°C under both wet and dry conditions, in general, show loss in strength with age. This loss increases with an increase in the water/cement ratio. The degree of conversion also increases with age but is independent of the water/cement ratio of concrete.

For continuous exposure at 50°C under both humid and dry conditions the change in strength with age depends upon the water/cement ratio of the concrete. At a water/cement ratio of 0.31, there is only an insignificant drop in strength at early age in spite of a high degree of conversion, following which the strength increases with age to a value of 125 per cent of the one-day strength at one year. This is significant as it indicates a means by which very high strengths can be maintained in the high-alumina cement concrete at least up to one year. For a water/cement ratio of 0.37, the recovery in strength is not as marked as for a water/cement ratio of 0.31. At higher water/cement ratios, there is a significant loss in strength at one year.

The pulse velocity technique appears to be an excellent means of monitoring the long-term changes in compressive strength due to conversion of high-alumina cement concrete, especially for test specimens exposed to dry heat. However, its use to determine the absolute strength cannot be recommended.

The degree of conversion should not be used as a measure of compressive strength because of the lack of correlation between these two parameters for high-alumina cement concrete.

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TABLE 1

Chemical Composition of High-Alumina Cement

Oxide	Per Cent*
SiO_2	4.40
Al_2O_3	41.98
Fe_2O_3	12.62
CaO	36.96
MgO	0.83
SO_3	0.00
FeO	3.82
TiO_2	not reported

*Manufacturer's data.

TABLE 2

Grading of Aggregates

Coarse aggregate		Fine aggregate	
Sieve size	Cumulative percentage retained	Sieve size	Cumulative percentage retained
¾ in. (19 mm)	33.3	No. 4 (4.75 mm)	0
		No. 8 (2.38 mm)	10.0
⅜ in. (9.5 mm)	66.6	No. 16 (1.19 mm)	32.5
		No. 30 (600 μm)	57.5
No. 4 (4.75 mm)	100.0	No. 50 (300 μm)	80.0
		No. 100 (150 μm)	94.0
		Pan	100.0

TABLE 3

Physical Properties of Coarse and Fine Aggregates

	Gravel stone	Natural sand
Specific gravity	2.68	2.70
Absorption, %	0.40	0.50

TABLE 4

Mix Proportions and Properties of Fresh Concrete

Mix series	Mix no.	Mix Proportions		Properties of Fresh Concretes					
				Temperature °C	Slump		Unit weight		Entrapped air, per cent
		W/C*	A/C**		in.	cm	lb/ft^3	kg/m^3	
A	1	0.31	2.98	14.0	1.0	2.54	153.0	2450	1.7
	2	0.31	2.98	16.0	1.0	2.54	154.0	2467	1.8
	3	0.31	2.98	14.0	0.5	1.27	154.0	2467	1.7
B	4	0.37	4.28	16.0	2.7	6.89	155.0	2483	1.7
	5	0.37	4.28	12.0	1.1	2.79	154.0	2467	1.1
	6	0.37	4.28	13.0	3.5		154.0	2467	1.3
C	7	0.47	5.42	11.5	4.0	10.2	151.0	2419	1.5
	8	0.47	5.42	8.0	6.0	15.2	154.0	2467	0.9
	9	0.47	5.42	15.0	3.7	9.52	152.0	2435	1.5
D	10	0.60	7.02	8.0	2.2	5.7	152.0	2435	1.6
	11	0.60	7.01	13.0	2.2	5.7	151.0	2419	1.8
	12	0.60	7.02	10.0	2.0	5.0	151.0	2419	2.0

* Water/cement ratio (by weight).
**Aggregate/cement ratio (by weight).

TABLE 5

Density of Test Cylinders

W/C Ratio	Age, days	Curing conditions											
		A				B				C			
		Moist curing at 21°C		In water at 25°C		Moist curing at 21°C		In water at 35°C		Moist curing at 21°C		In water at 50°C	
		lb/ft³	Kg/m³	lb/ft³	Kg/m³	lb/ft³	Kg/m³	lb/ft³	Kg/m³	lb/ft³	Kg/m³	lb/ft³	Kg/m³
0.31	1	155.7	2493	--	--	156.1	2500	--	--	157.2	2518	--	--
	2	155.6	2492	155.8	2495	156.2	2502	155.9	2498	156.8	2512	157.9	2530
	7	156.4	2505	155.5	2491	155.3	2488	159.4	2553	160.9	2577	164.1	2628
	28	155.6	2492	155.9	2496	156.1	2500	155.8	2496	157.0	2515	156.8	2511
	365	158.4	2536	158.3	2534	158.7	2541	159.0	2545	159.6	2556	159.1	2549
0.37	1	155.4	2489	--	--	--	2487	--	--	155.1	2484	--	--
	2	155.5	2491	155.4	2489	155.3	2503	155.9	2497	155.7	2494	155.1	2484
	7	155.4	2489	155.3	2487	156.1	2500	156.5	2507	155.1	2485	155.5	2491
	28	155.1	2484	155.3	2488	156.2	2503	156.4	2505	155.4	2490	155.7	2494
	365	157.5	2522	156.9	2514	158.5	2538	158.7	2542	157.5	2522	157.6	2525
0.47	1	154.9	2482	--	--	155.0	2483	--	--	154.3	2472	--	--
	2	155.1	2484	155.8	2495	155.3	2487	154.4	2473	154.4	2473	154.9	2481
	7	155.1	2484	155.2	2486	154.8	2480	155.0	2483	154.3	2472	155.2	2485
	28	154.8	2480	155.5	2491	154.7	2477	154.9	2481	154.6	2477	155.3	2488
	365	157.2	2518	157.1	2517	156.8	2513	157.7	2526	157.1	2517	156.4	2506
0.60	1	157.3	2519	--	--	154.6	2477	--	--	154.2	2470	--	--
	2	154.4	2473	154.2	2469	154.4	2473	154.9	2481	154.8	2480	154.2	2469
	7	153.8	2464	154.3	2471	154.8	2479	154.2	2469	154.6	2476	154.9	2482
	28	154.0	2467	154.3	2472	154.8	2470	154.5	2475	154.5	2475	156.9	2513
	365	155.8	2496	155.0	2483	148.0	2370	151.8	2431	156.1	2500	155.7	2494

TABLE 6

Strength Development of Concretes

W/C* ratio	Age, days	Compressive strength																	
		A						B						C					
		Moist curing at 21°C		In dry heat at 25°C		In water at 25°C		Moist curing at 21°C		In dry heat at 35°C		In water at 35°C		Moist curing at 21°C		In dry heat at 50°C		In water at 50°C	
		psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa
0.31	1	8470	58.4	--	--	--	--	8880	61.2	--	--	--	--	8280	57.1	--	--	--	--
	2	8420	58.1	8940	61.6	8960	61.8	8990	61.9	9500	65.5	9470	65.3	9370	64.6	7720	53.2	8820	60.8
	7	9090	62.7	8870	61.2	9360	64.5	9510	65.6	10250	70.7	10140	70.0	10780	74.3	8101	55.9	7960	54.9
	28	10200	70.3	8180	56.4	9585	66.1	10320	71.2	6860	47.3	7440	51.3	10250	70.7	8420	58.1	8320	57.4
	365	11020	76.1	9810	67.6	9540	65.8	10440	72.0	8740	60.3	9220	63.6	10960	75.6	10620	73.2	11160	77.0
0.37	1	7270	50.1	--	--	--	--	7300	50.3	--	--	--	--	7260	50.1	--	--	--	--
	2	7882	54.3	8250	56.9	8130	56.1	7200	49.6	8110	55.9	8020	55.3	7390	51.0	7790	53.7	8910	61.4
	7	8300	57.2	7980	55.0	8520	58.7	7750	53.4	7680	53.0	7220	49.8	9340	64.4	4840	33.4	5860	40.4
	28	8820	60.8	8620	59.4	9450	65.1	9110	62.8	5200	35.8	6000	41.4	9590	66.1	7150	49.3	6670	46.0
	365	11820	81.5	7030	48.5	8640	59.6	9370	64.6	5930	40.9	7305	50.4	11101	76.5	7775	53.6	7030	48.5
0.47	1	6920	47.7	--	--	--	--	5960	41.1	--	--	--	--	6680	46.1	--	--	--	--
	2	6750	46.5	7680	53.0	6490	44.7	6080	41.9	7410	51.1	7120	49.1	6940	47.8	4340	29.9	4750	32.8
	7	8160	56.3	8550	58.9	8940	61.6	7670	52.9	8070	55.6	7870	54.3	6950	47.9	4390	30.3	3600	24.8
	28	9040	62.3	8470	58.4	9690	66.8	8340	57.5	5880	40.5	6790	46.8	9510	65.5	5540	38.2	4400	30.3
	365	8910	61.4	4980	34.3	6010	41.4	8540	58.9	4100	28.3	4500	31.0	9910	68.3	5535	38.2	4760	32.8
0.6	1	5740	39.6	--	--	--	--	5730	39.5	--	--	--	--	5540	38.2	--	--	--	--
	2	6140	42.3	6060	41.8	6040	41.6	5630	38.8	6570	45.3	6620	46.6	6330	43.6	6590	45.4	6770	45.9
	7	6350	43.8	7120	49.1	7186	49.5	6700	46.2	7370	50.8	7000	48.3	5900	40.7	2870	19.7	5800	39.9
	28	7360	50.7	7290	50.3	8240	56.8	7480	51.6	5180	35.7	6030	41.6	7520	51.8	4759	32.8	3286	22.7
	365	8810	60.7	5431	37.4	4140	28.5	8120	55.9	4440	30.6	3700	25.5	7560	52.1	4830	33.3	2570	17.7

*Water/cement ratio (by weight).

TABLE 7

Pulse Velocity of Cylinders

W/C* Ratio	Age, days	Pulse velocity																	
		A						B						C					
		Moist curing at 21°C		In dry heat at 25°C		In water at 25°C		Moist curing at 21°C		In dry heat at 35°C		In water at 35°C		Moist curing at 21°C		In dry heat at 50°C		In water at 50°C	
		ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec	ft/sec	m/sec
0.31	1	14206	4330	--	--	--	--	14088	4294	--	--	--	--	14039	4279	--	--	--	--
	2	13895	4235	14190	4325	13681	4170	14039	4279	14577	4443	13750	4191	14039	4279	14039	4279	14039	4279
	7	14039	4279	14341	4371	14278	4325	14039	4279	14656	4467	14190	4325	14341	4371	14039	4279	14341	4371
	28	13894	4235	14734	4492	13549	4130	14183	4323	14340	4371	14497	4419	14732	4490	14335	4369	15324	4670
	365	14948	4556	14572	4441	15326	4671	15240	4646	13950	4252	15576	4749	15326	4377	14200	4056	15913	4850
0.37	1	14341	4371	--	--	--	--	--	--	--	--	--	--	13288	4050	--	--	--	--
	2	14190	4325	14039	4279	14039	4279	13337	4065	13609	4148	13206	4025	13609	4148	14039	4279	13471	4106
	7	14341	4371	14498	4419	13494	4113	14380	4383	14114	4302	13471	4106	13609	4148	13078	3986	13402	4085
	28	14498	4419	14656	4467	14039	4279	14039	4279	13471	4106	13750	4191	14419	4395	13471	4106	13895	4235
	365	15968	4867	13891	4234	15239	4645	16647	5074	13203	4024	15415	4698	16162	4926	13675	4168	15066	4592
0.47	1	13563	4139	--	--	--	--	13471	4106	--	--	--	--	14039	4279	--	--	--	--
	2	13819	4212	14046	4281	14039	4279	13750	4191	13750	4191	12825	3909	14111	4301	13209	4026	13209	4025
	7	14262	4347	14341	4371	14341	4371	14039	4279	14039	4279	14111	4301	14502	4420	12950	3947	13543	4128
	28	15509	4727	14820	4517	14328	4672	15069	4593	13895	4235	15328	4672	15328	4672	13012	3966	13819	4212
	365	16162	4926	13201	4024	14733	4490	16260	4956	12122	3695	14898	4540	16300	4968	13176	4016	14415	4393
0.6	1	13524	4122	--	--	--	--	13845	4220	--	--	--	--	13662	4164	--	--	--	--
	2	13750	4191	13478	4108	14046	4281	14498	4419	14341	4371	14662	4469	--	--	--	--	--	--
	7	14187	4324	14341	4371	14820	4517	15240	4645	14656	4467	14662	4469	14498	4419	12825	3909	14984	4567
	28	14656	4467	14036	4278	15082	4597	15880	4840	14190	4325	15338	4672	15335	4674	12822	3908	13337	4065
	365	16161	4926	12995	3960	14381	4383	16481	5407	12662	3859	14847	4526	16268	4960	12681	3865	13918	4242

*Water/cement ratio (by weight).

TABLE 8

Between-Batch Coefficient of Variation for Strength Test Results

W/C	No. of batches	Average 28-day compressive strength, MPa	Standard deviation, MPa	Coefficient of variation, per cent
0.31	3	70.7	0.55	0.78
0.37	3	63.3	2.69	4.24
0.47	3	61.8	4.03	6.53
0.60	3	51.4	0.62	1.21

TABLE 9

Degree of Conversion of High-Alumina Cement Concrete

W/C*	Age, days	Conversion, per cent								
		A**	B	C	A	D	E	A	F	G
0.31	1	27	-	-	28	-	-	-	-	-
	2	32	34	25	34	29	30	32	48	38
	7	30	32	22	34	26	40	33	69	70
	28	25	32	27	35	67	65	40	72	70
	365	41	64	77	52	75	73	42	78	77
0.37	1	19	-	-	26	-	-	27	-	-
	2	18	18	18	23	27	28	20	23	20
	7	19	20	18	23	38	30	21	48	70
	28	18	24	23	25	49	64	16	60	78
	365	19	65	64	22	76	75	20	77	76
0.47	1	26	-	-	29	-	-	36	-	-
	2	26	25	25	24	18	18	30	44	45
	7	27	24	18	19	19	18	23	75	73
	28	24	21	23	20	30	29	27	80	74
	365	24	60	70	20	78	79	27	78	79
0.60	1	20	-	-	25	-	-	22	-	-
	2	19	19	19	23	17	18	20	21	18
	7	19	17	18	22	23	22	20	27	65
	28	19	21	18	21	34	40	19	68	69
	365	19	59	59	21	68	70	20	78	79

* Water/cement ratio by weight.

**A: Stored for 24 hours in moist air at 18°C, then in moist curing room at 21°C.

B: Stored for 24 hours in moist air at 18°C, then in water at 25°C.

C: Stored for 24 hours in moist air at 18°C, then in dry heat at 25°C.

D: Stored for 24 hours in moist air at 18°C, then in water at 35°C.

E: Stored for 24 hours in moist air at 18°C, then in dry heat at 35°C.

F: Stored for 24 hours in moist air at 18°C, then in water at 50°C.

G: Stored for 24 hours in moist air at 18°C, then in dry heat at 50°C.

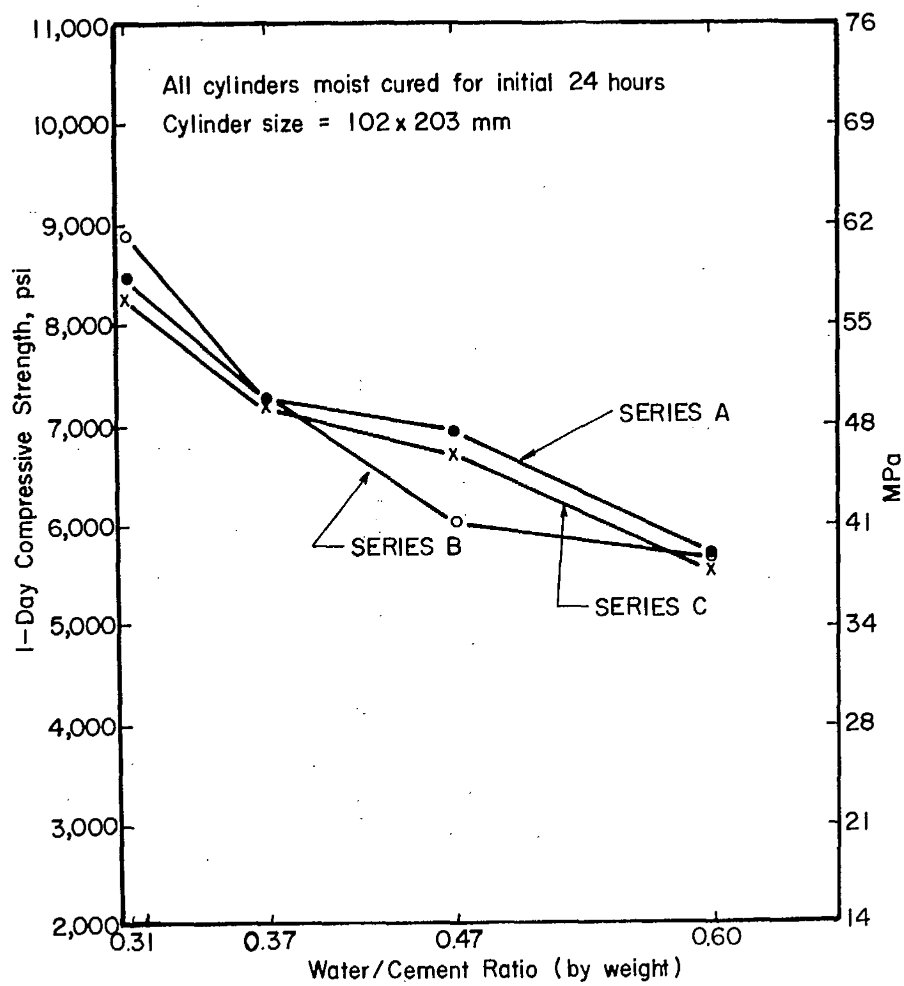

Figure 1. Relationship between water/cement ratio and compressive strength of high alumina cement concrete at one day.

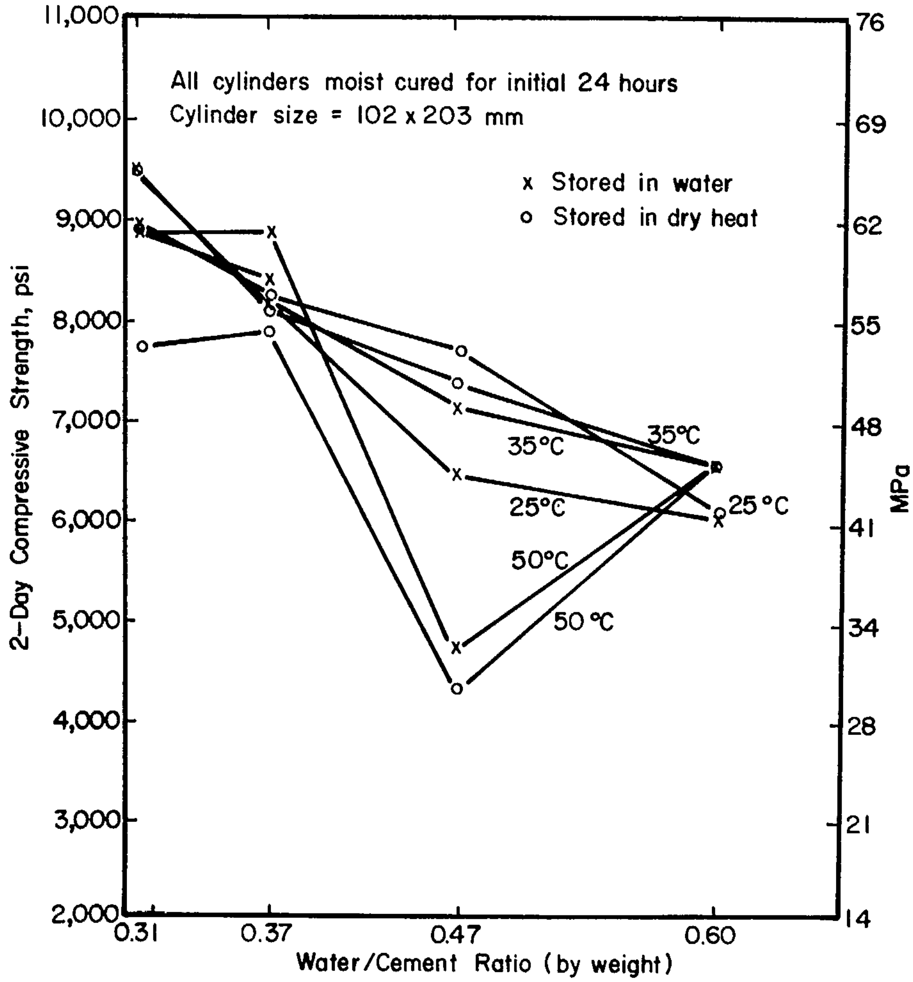

Figure 2. Relationship between water/cement ratio and compressive strength of high-alumina cement concrete at 2 days.

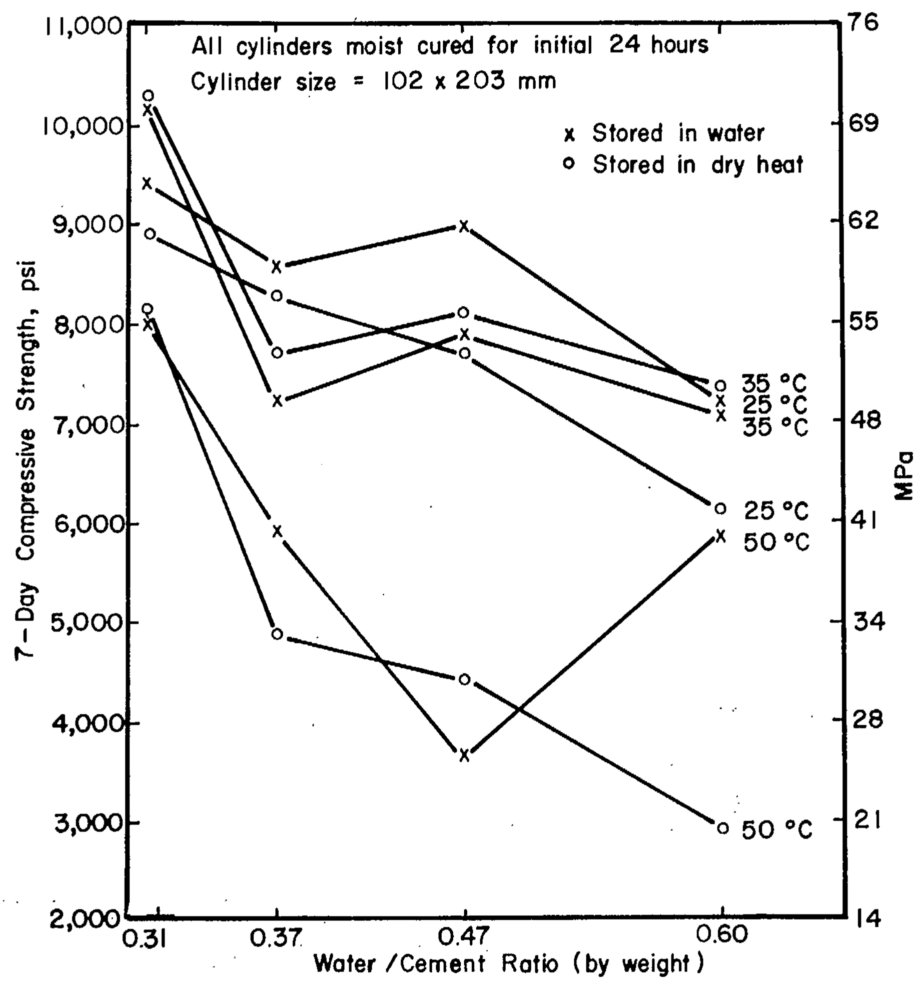

Figure 3. Relationship between water/cement ratio and compressive strength of high-alumina cement concrete at 7 days.

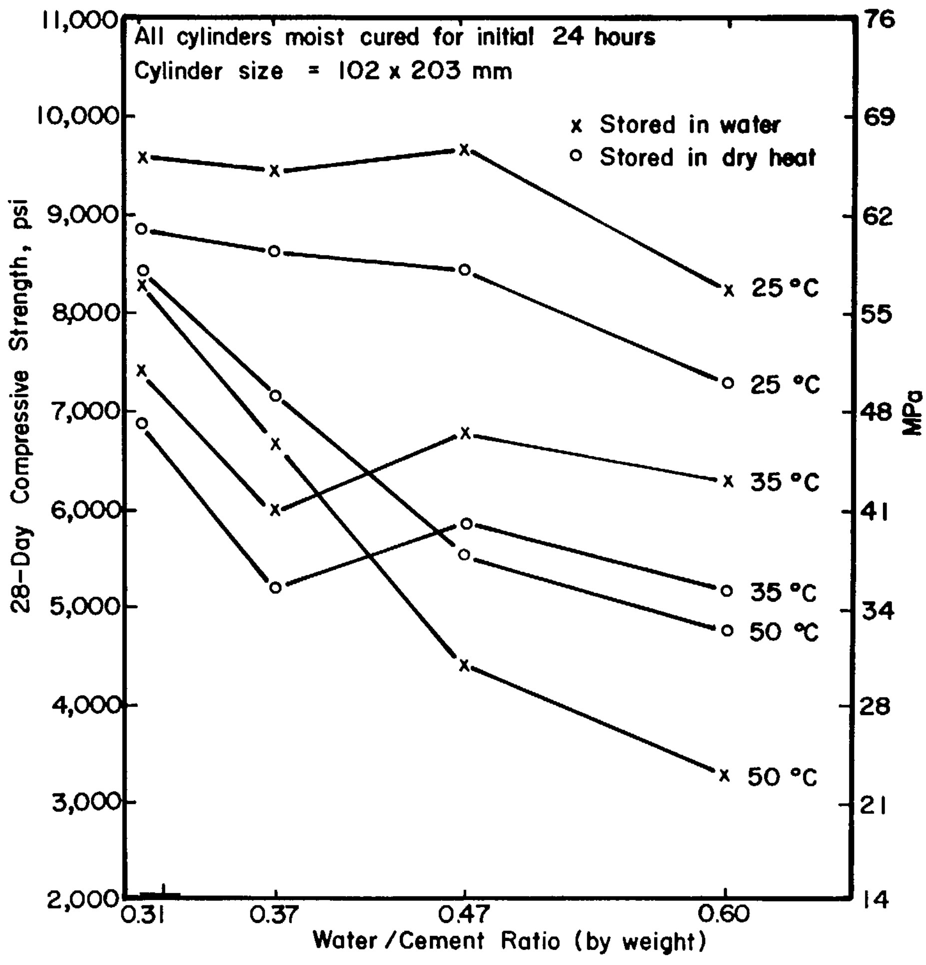

Figure 4. Relationship between water/cement ratio and compressive strength of high-alumina cement concrete at 28 days.

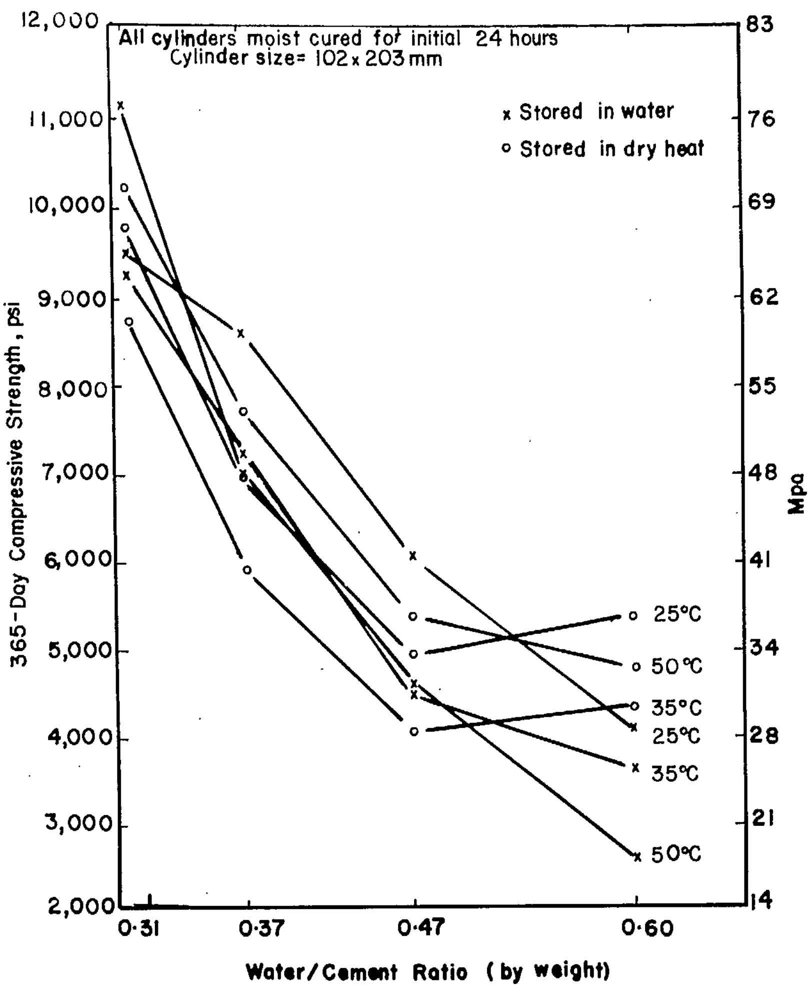

Figure 5. Relationship between water/cement ratio and compressive strength of high-alumina cement concrete at 365 days.

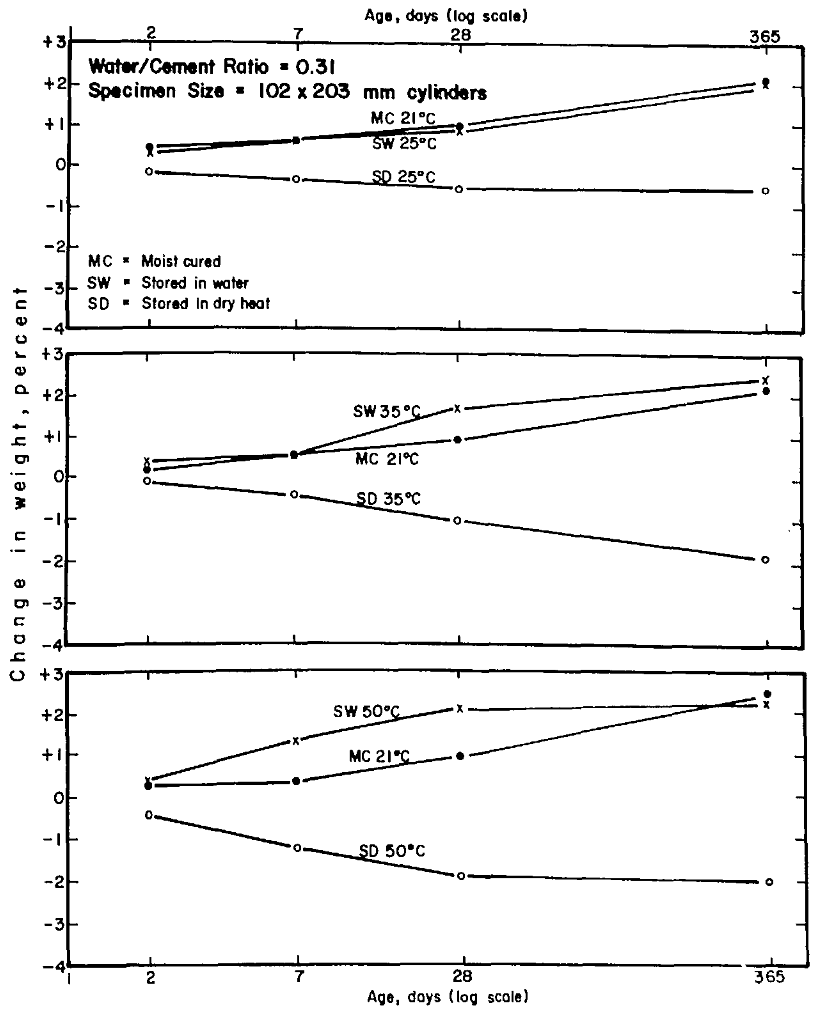

Figure 6. Relationship between age and change in weight of test cylinders - W/C = 0.31.

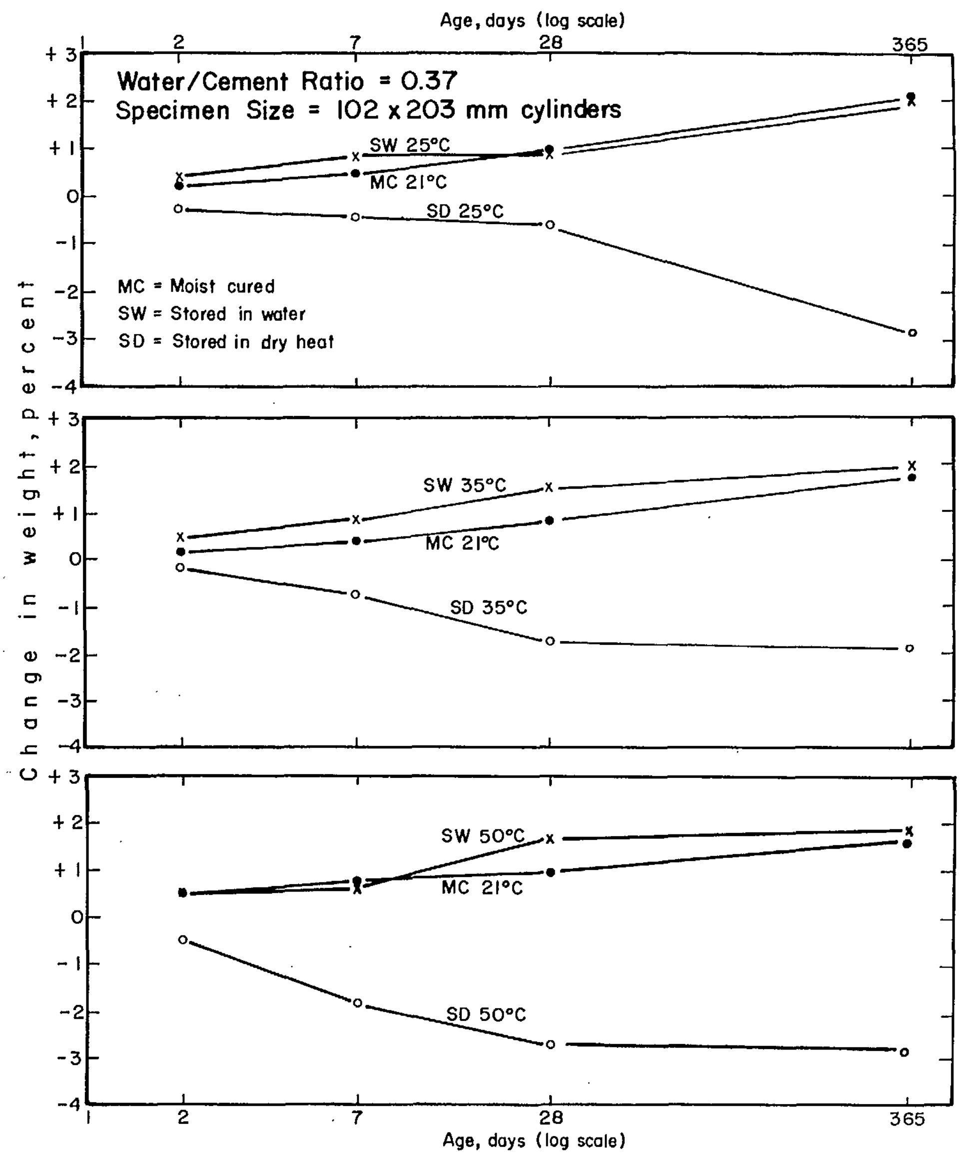

Figure 7. Relationship between age and change in weight of test cylinders - W/C = 0.37.

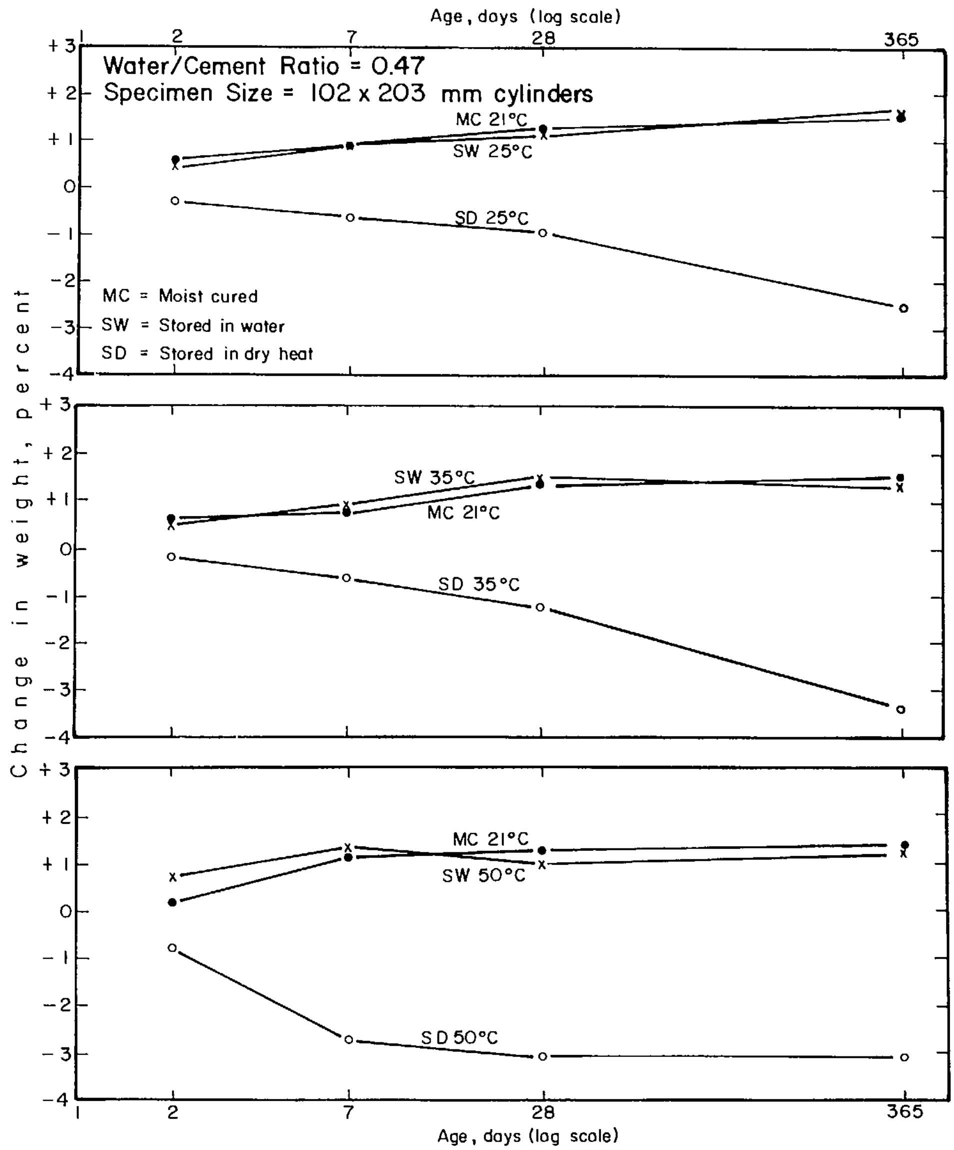

Figure 8. Relationship between age and change in weight of test cylinders - W/C = 0.47.

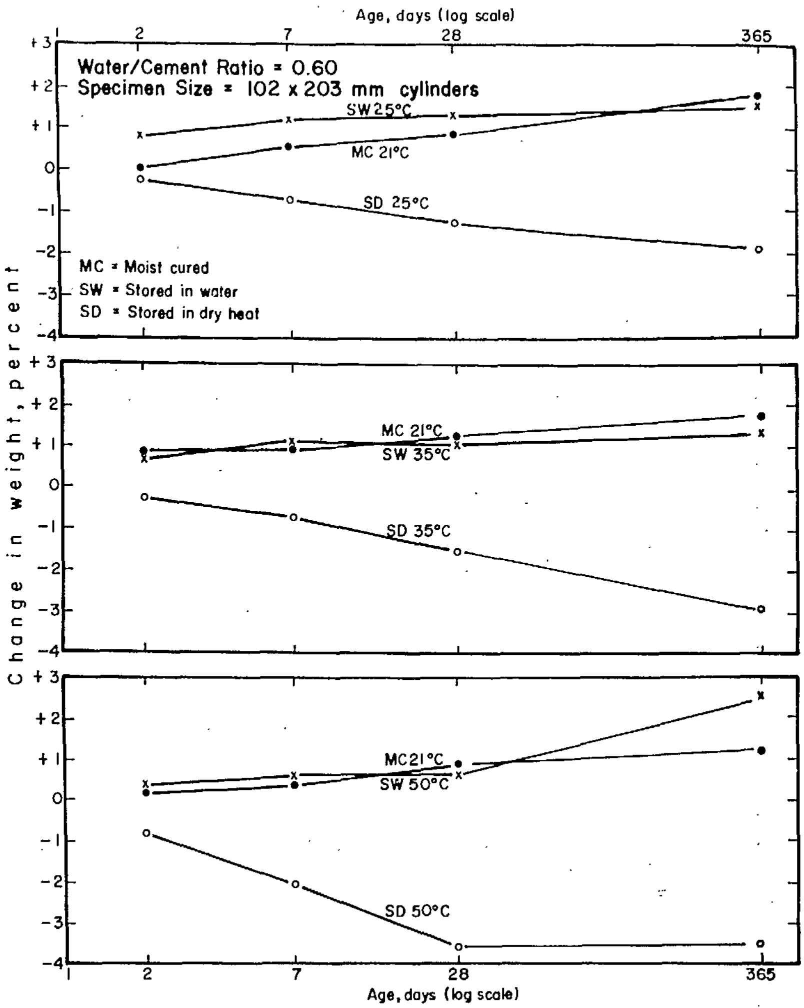

Figure 9. Relationship between age and change in weight of test cylinders - W/C = 0.60.

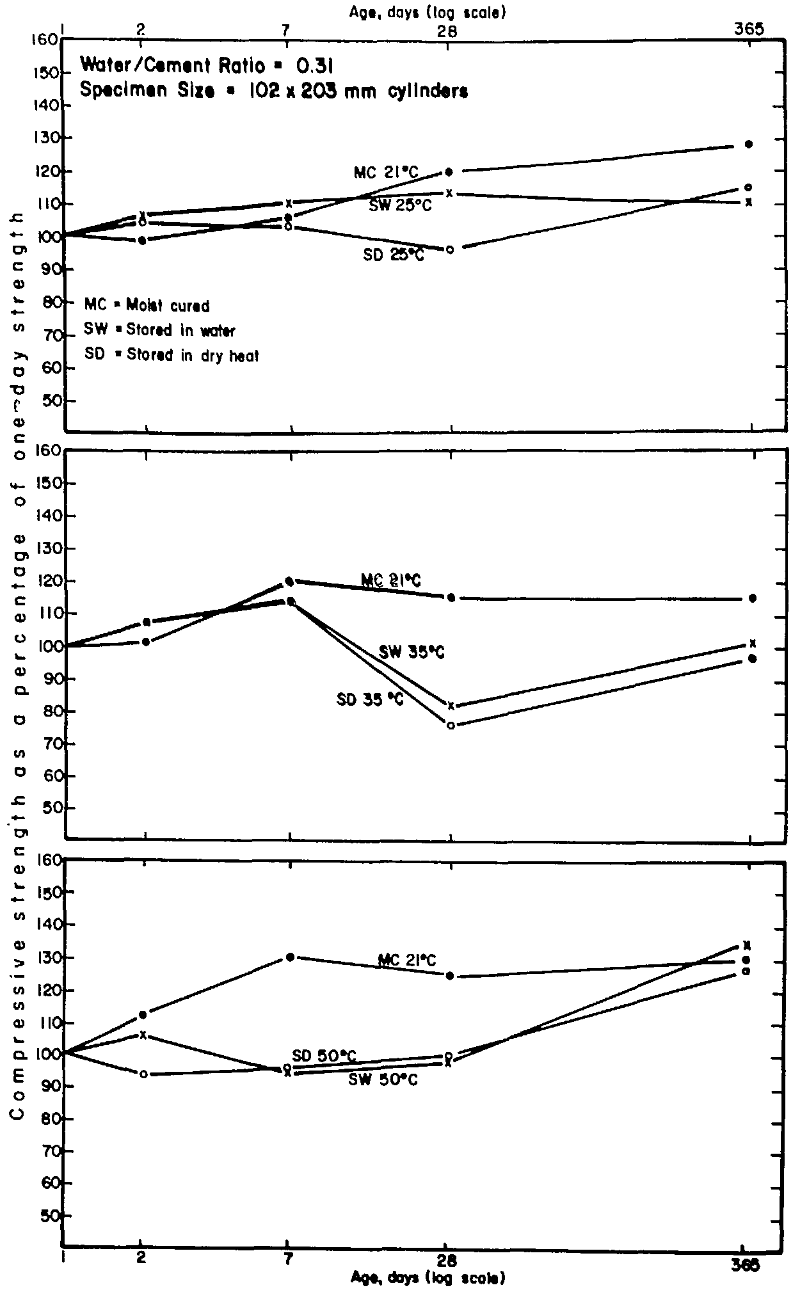

Figure 10. Relationship between age and compressive strength as a percentage of one-day strength - W/C = 0.31.

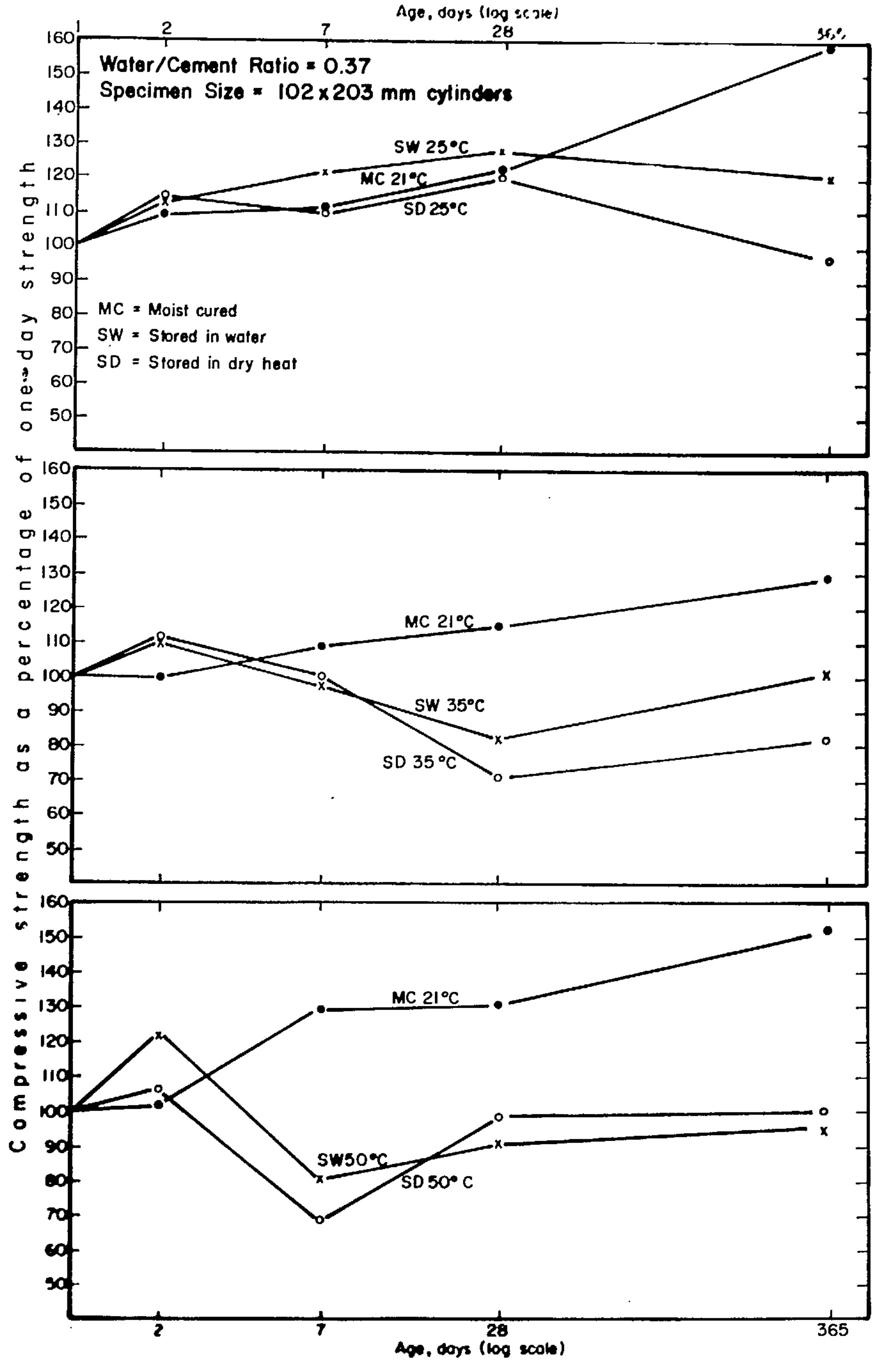

Figure 11. Relationship between age and compressive strength as a percentage of one-day strength - W/C = 0.37.

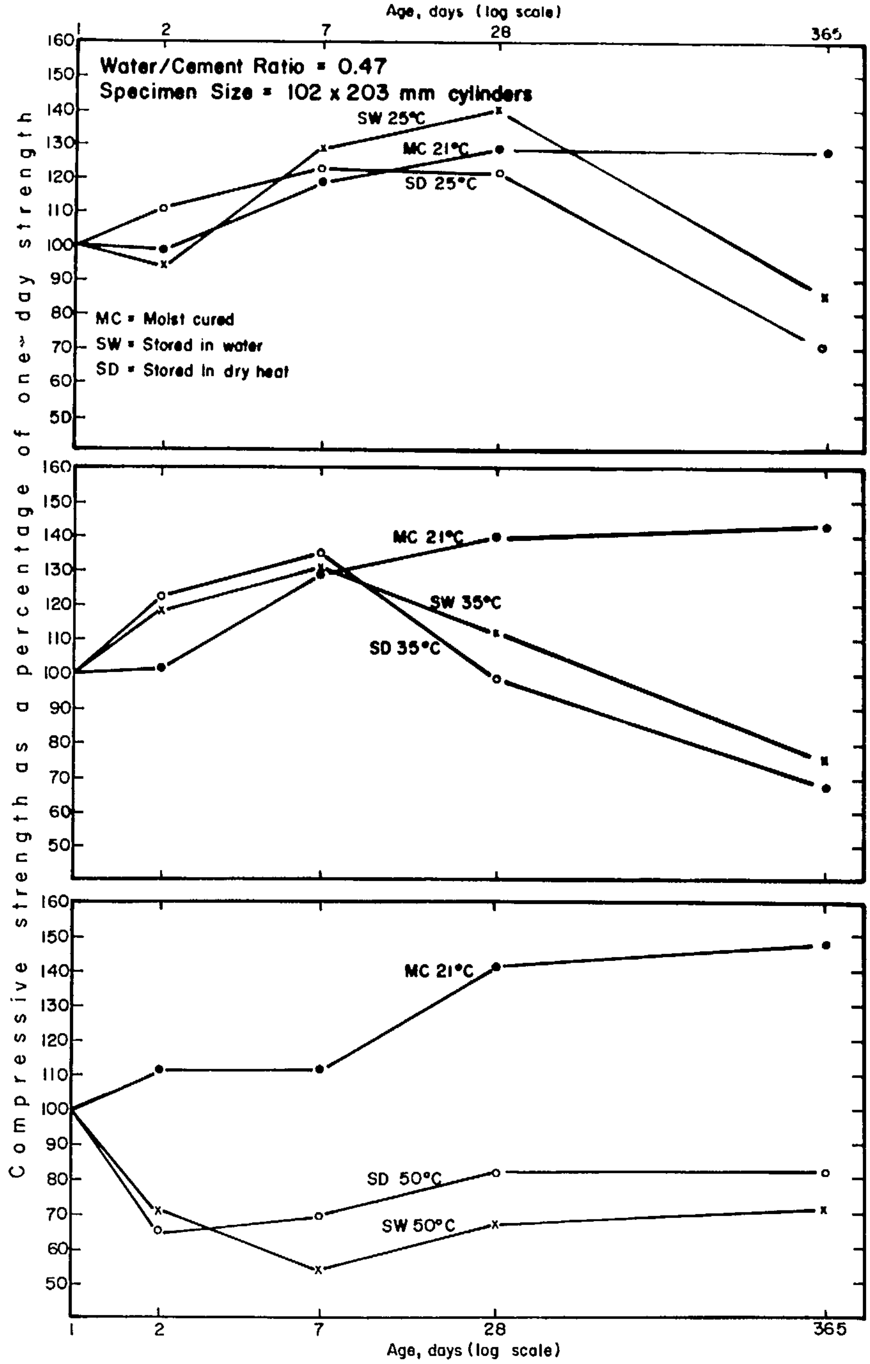

Figure 12. Relationship between age and compressive strength as a percentage of one-day strength - W/C = 0.47.

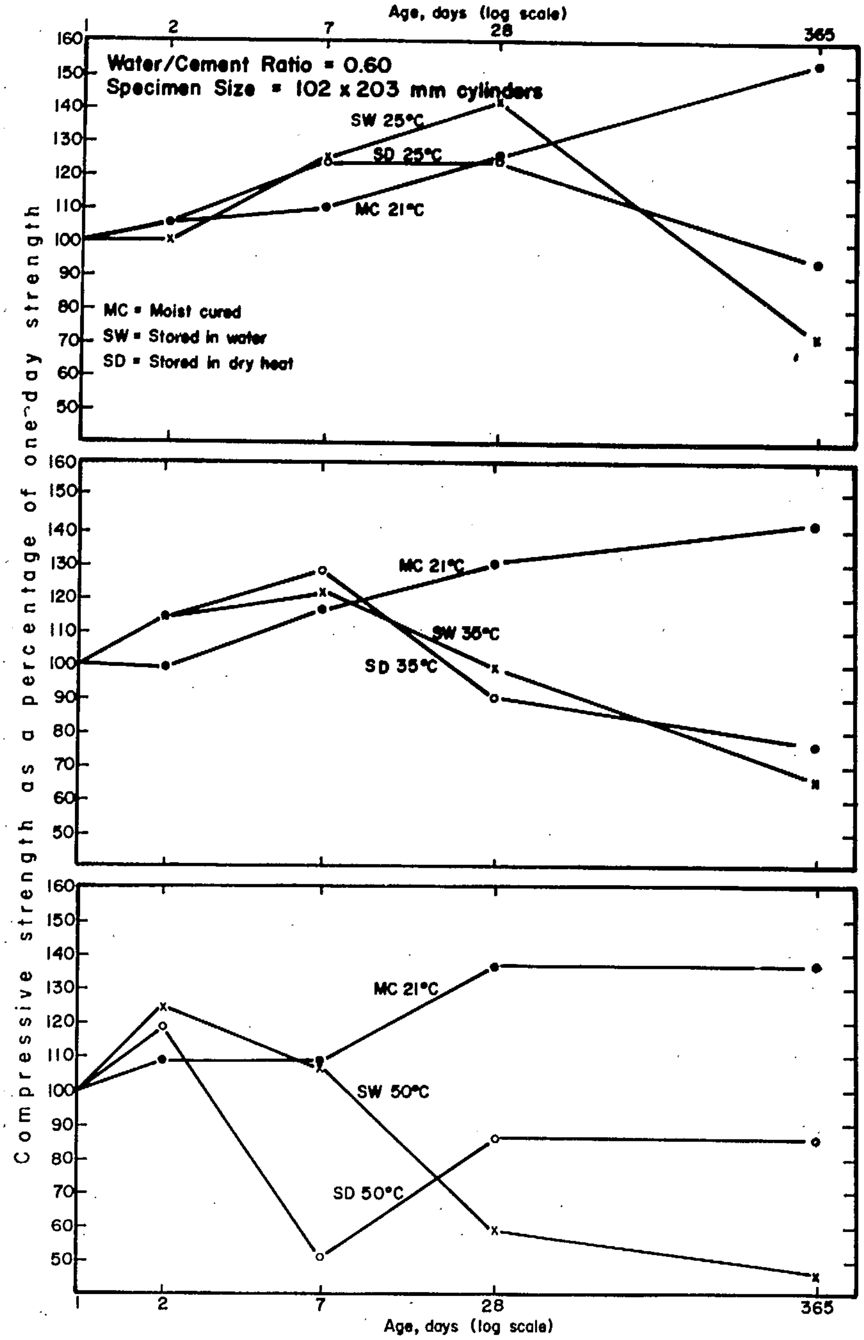

Figure 13. Relationship between age and compressive strength as a percentage of one-day strength - W/C = 0.60.

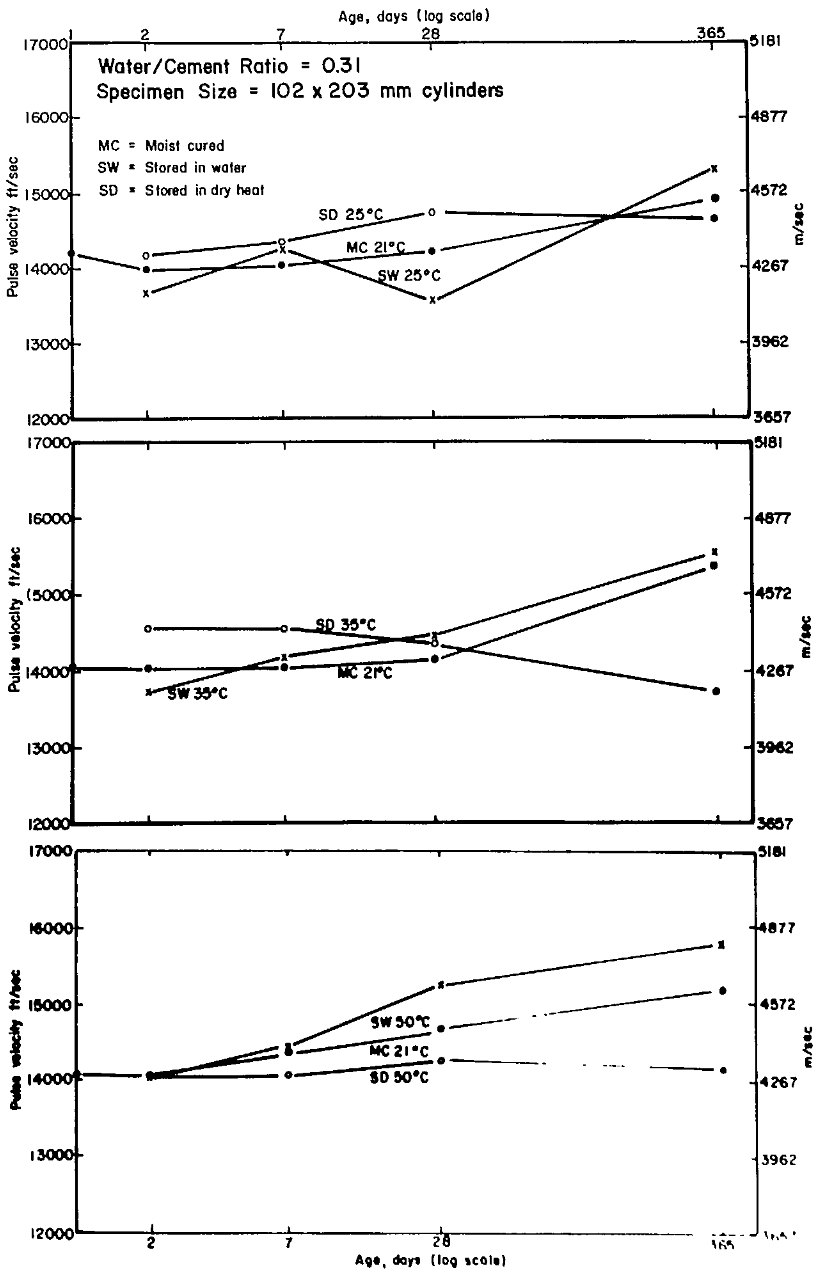

Figure 14. Relationship between age and pulse velocity of test cylinders - W/C = 0.31.

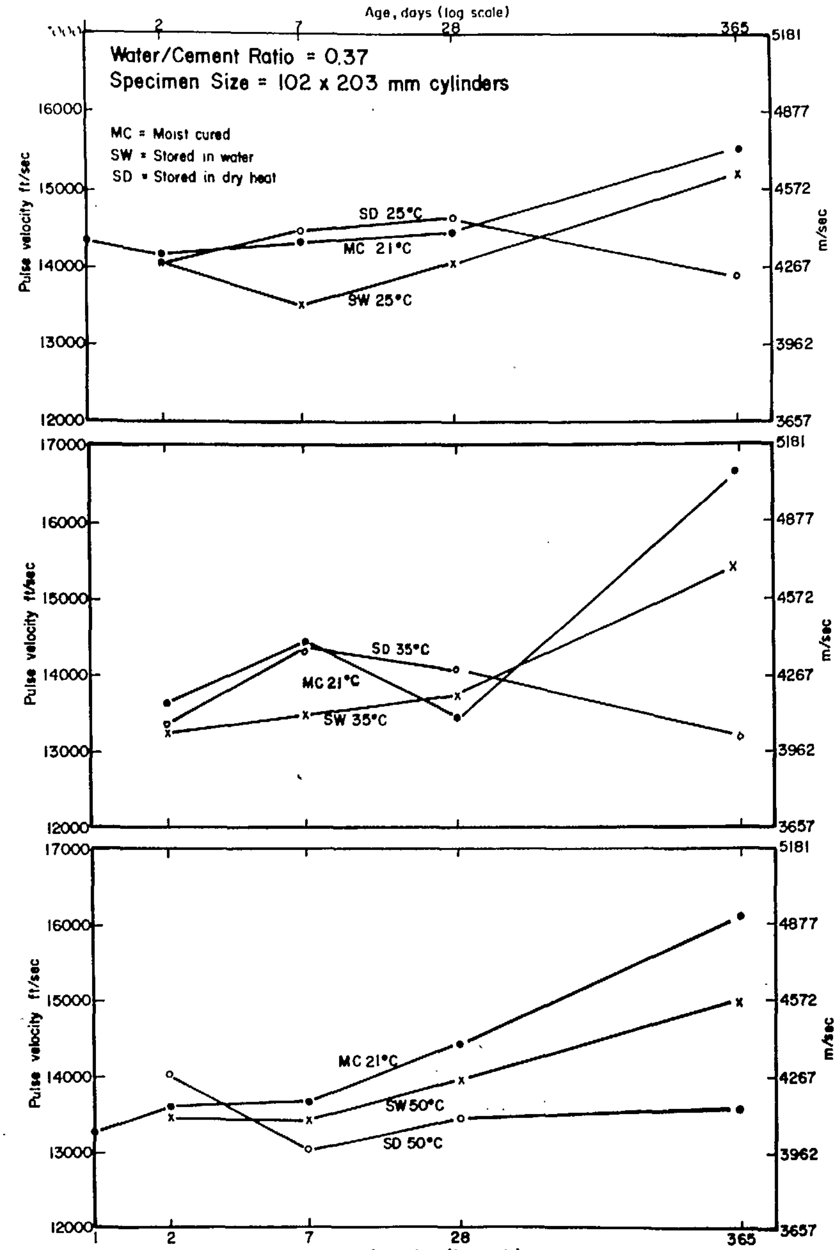

Figure 15. Relationship between age and pulse velocity of test cylinders - W/C = 0.37.

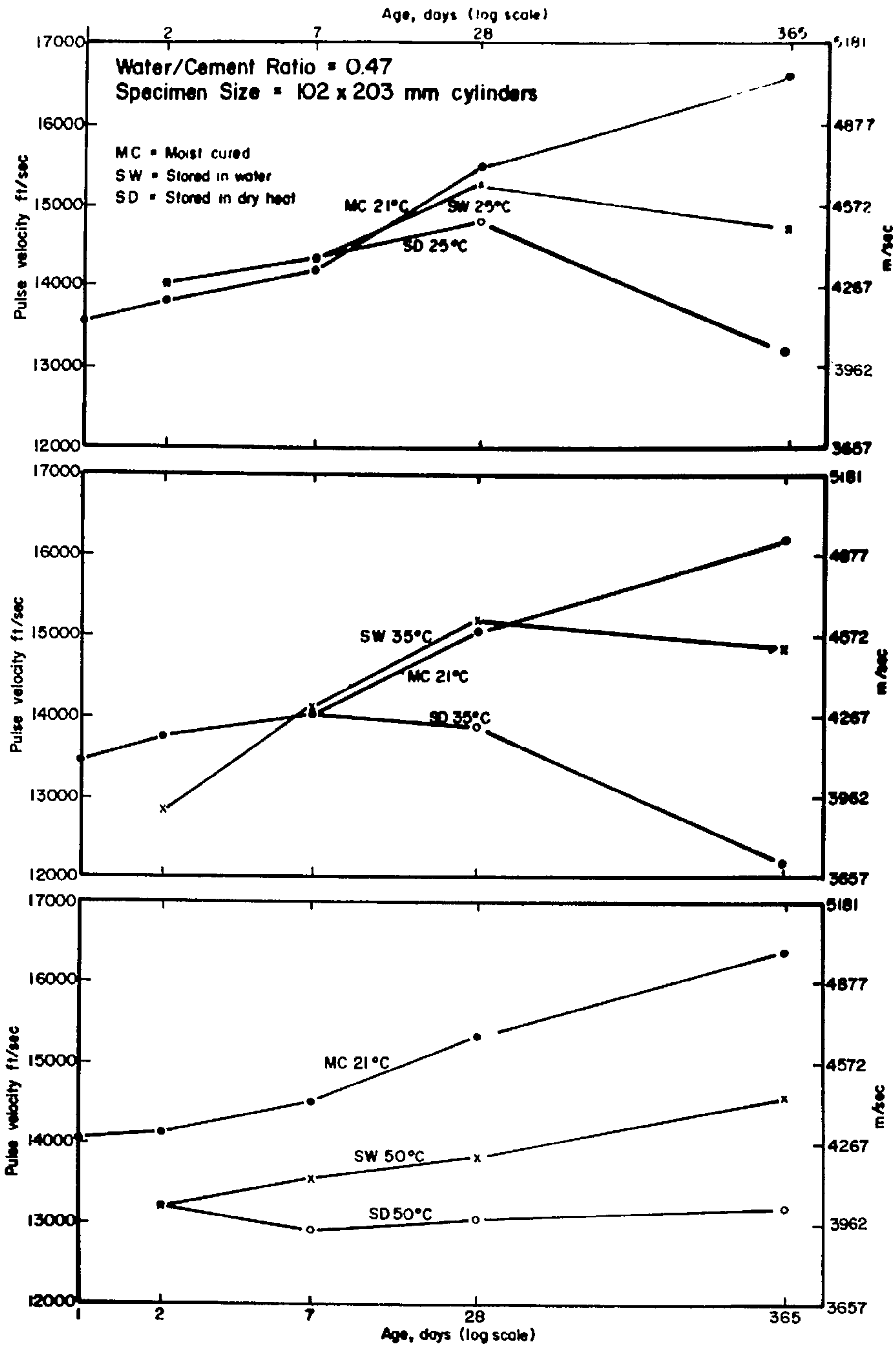

Figure 16. Relationship between age and pulse velocity of test cylinders - W/C = 0.47.

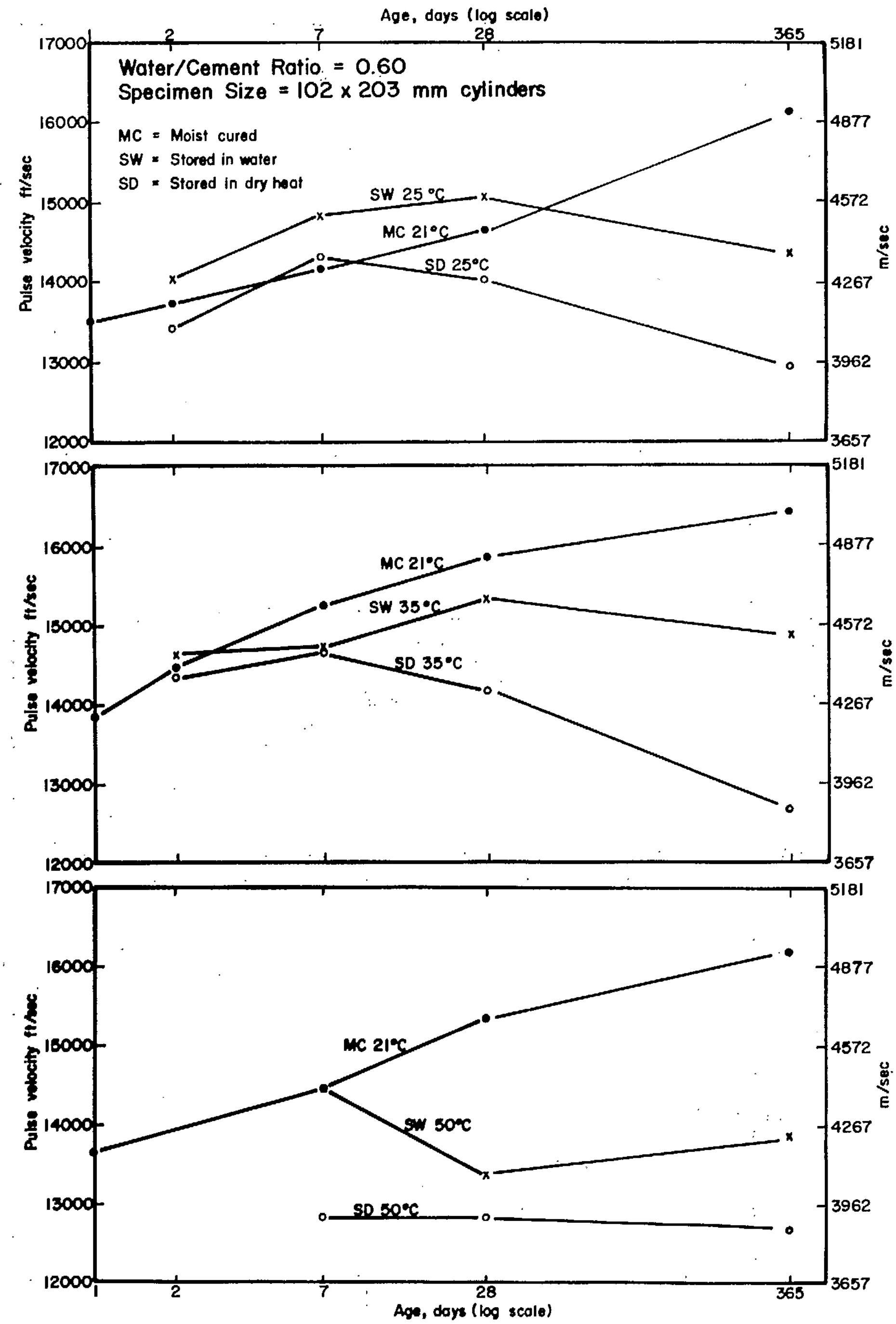

Figure 17. Relationship between age and pulse velocity of test cylinders - W/C = 0.60.

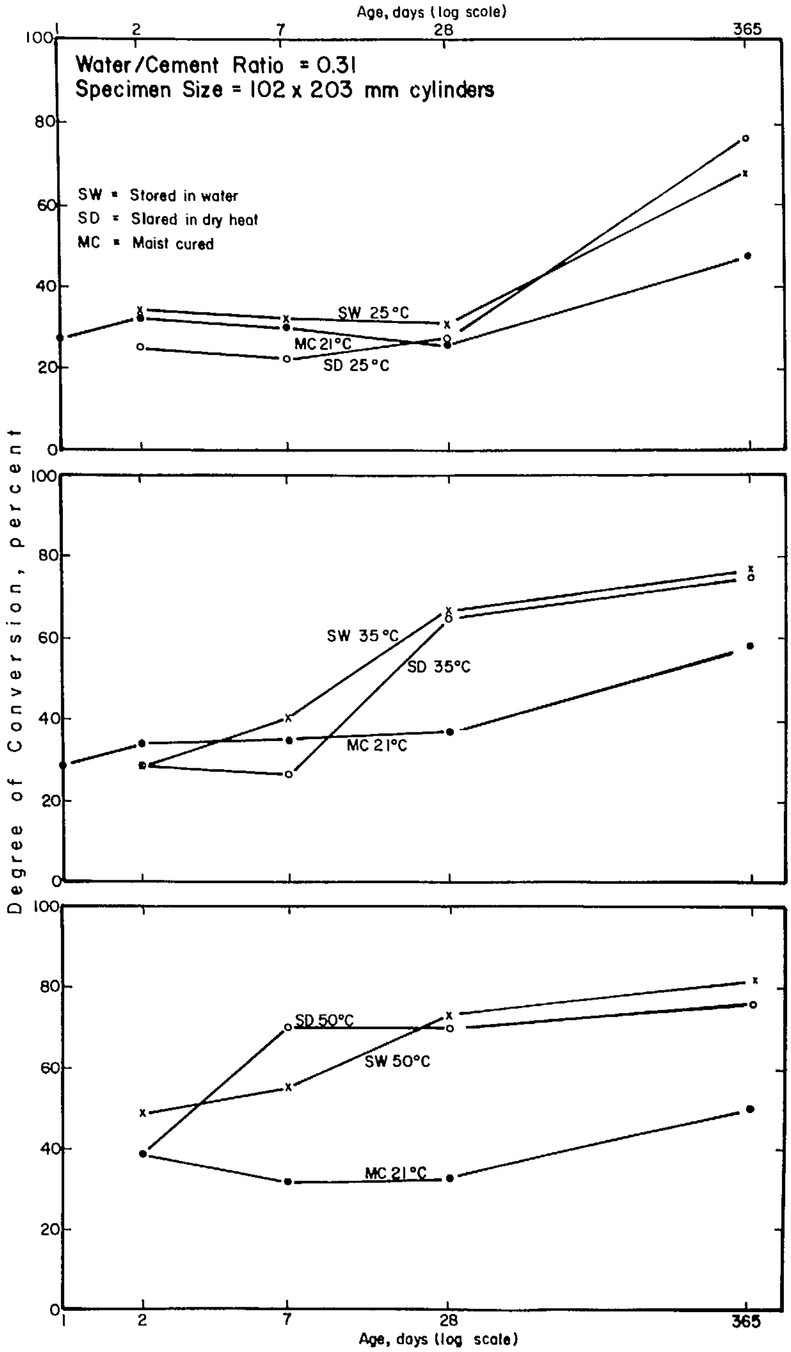

Figure 18. Relationship between age and degree of conversion - W/C = 0.31.

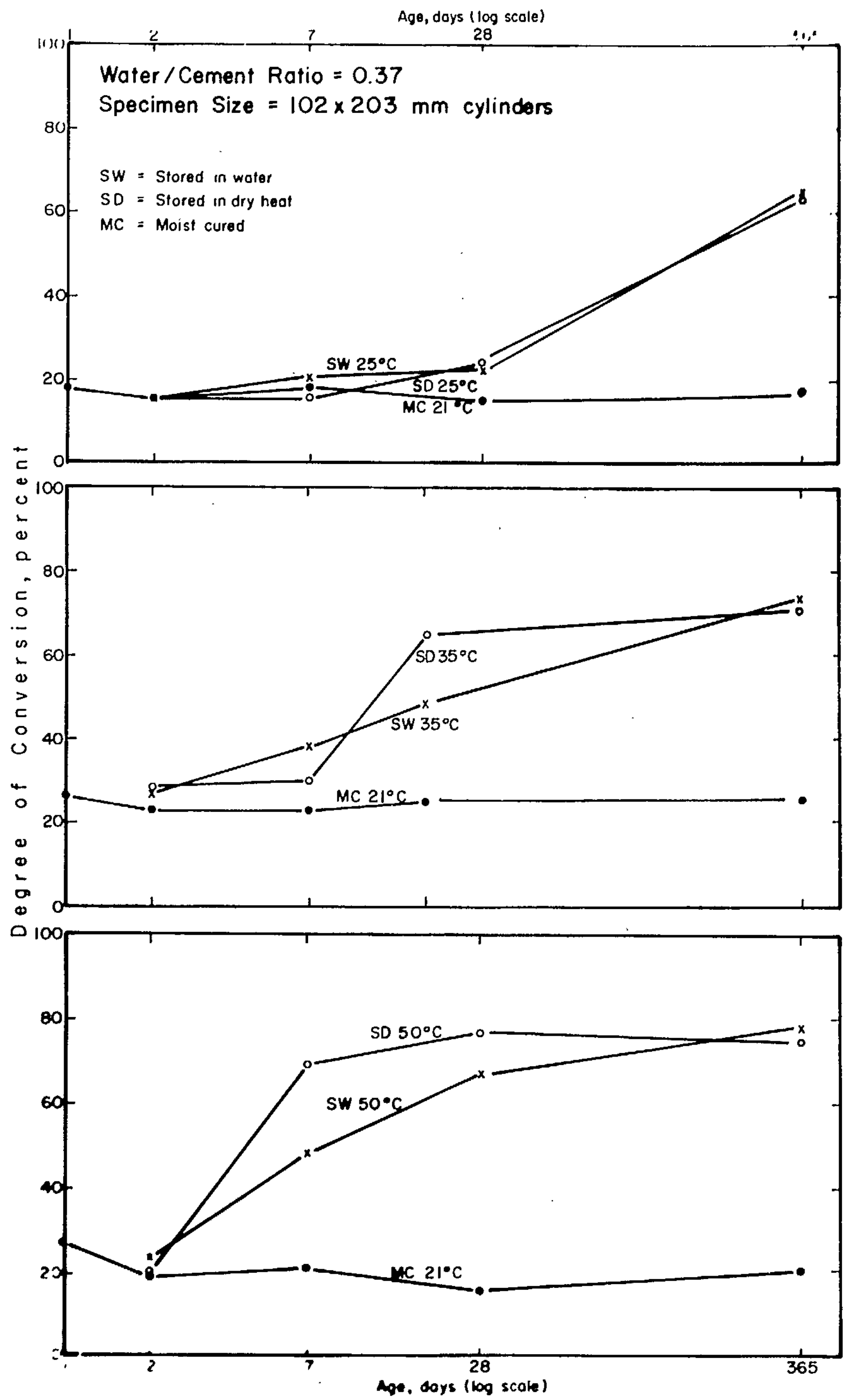

Figure 19. Relationship between age and degree of conversion - W/C = 0.37.

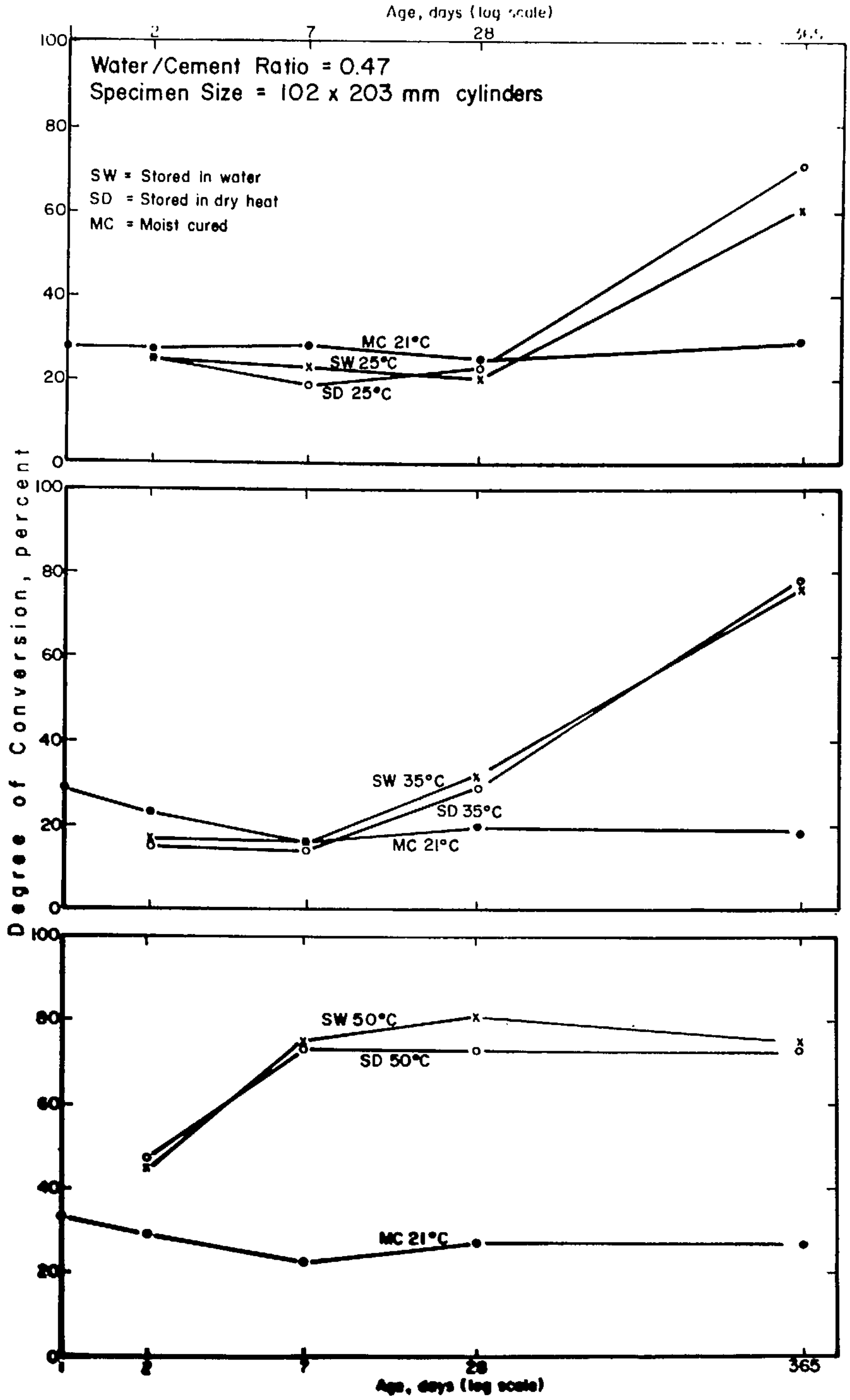

Figure 20. Relationship between age and degree of conversion - W/C = 0.47.

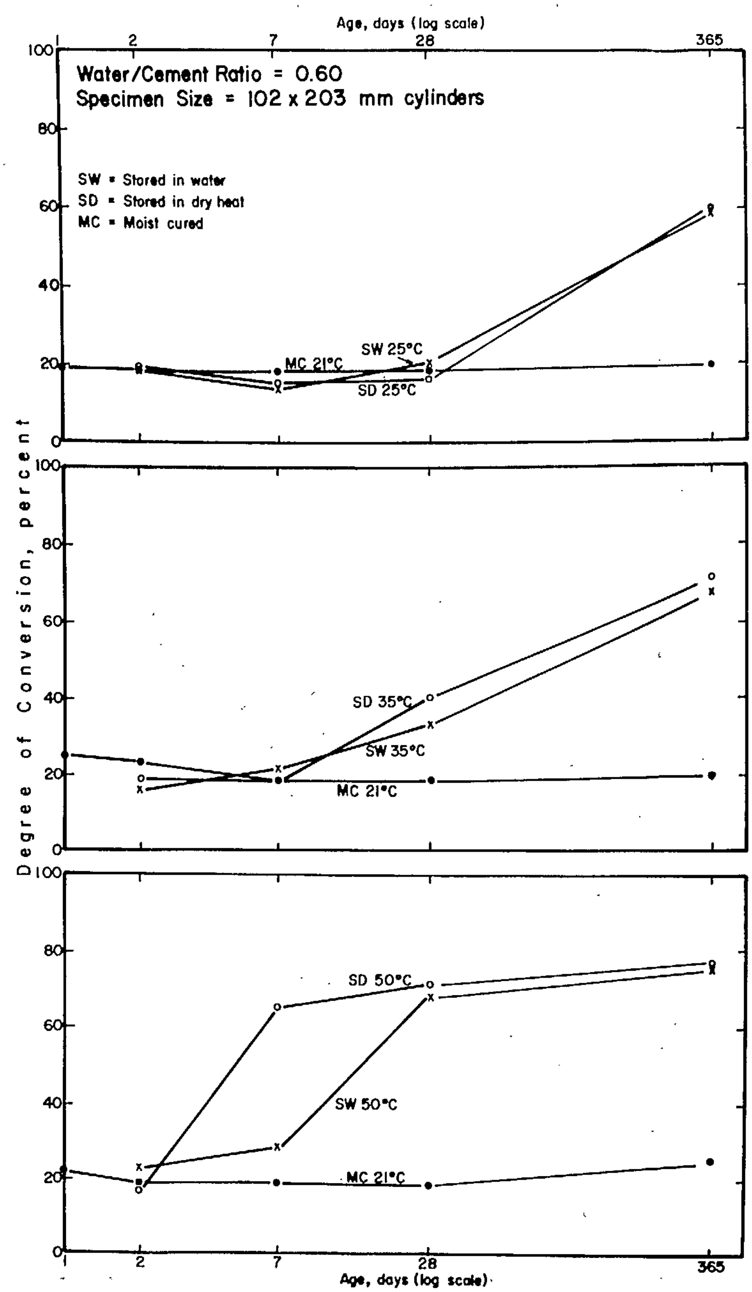

Figure 21. Relationship between age and degree of conversion - W/C = 0.60.

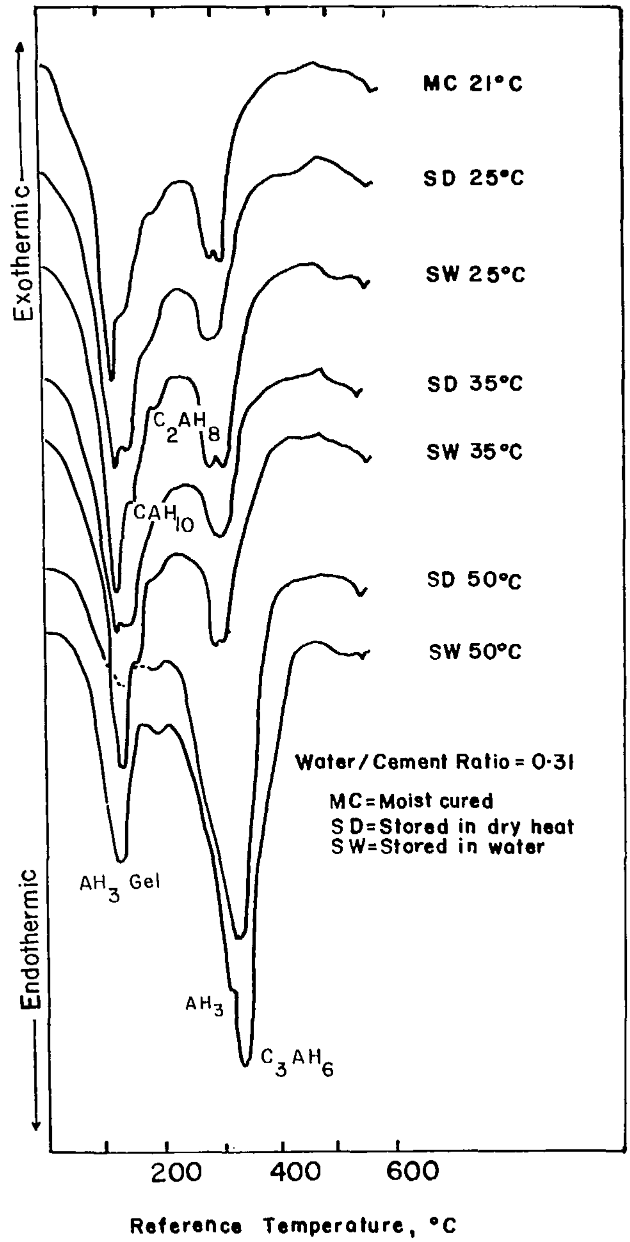

Figure 22. Thermograms of 7-day-old concrete - W/C = 0.31.

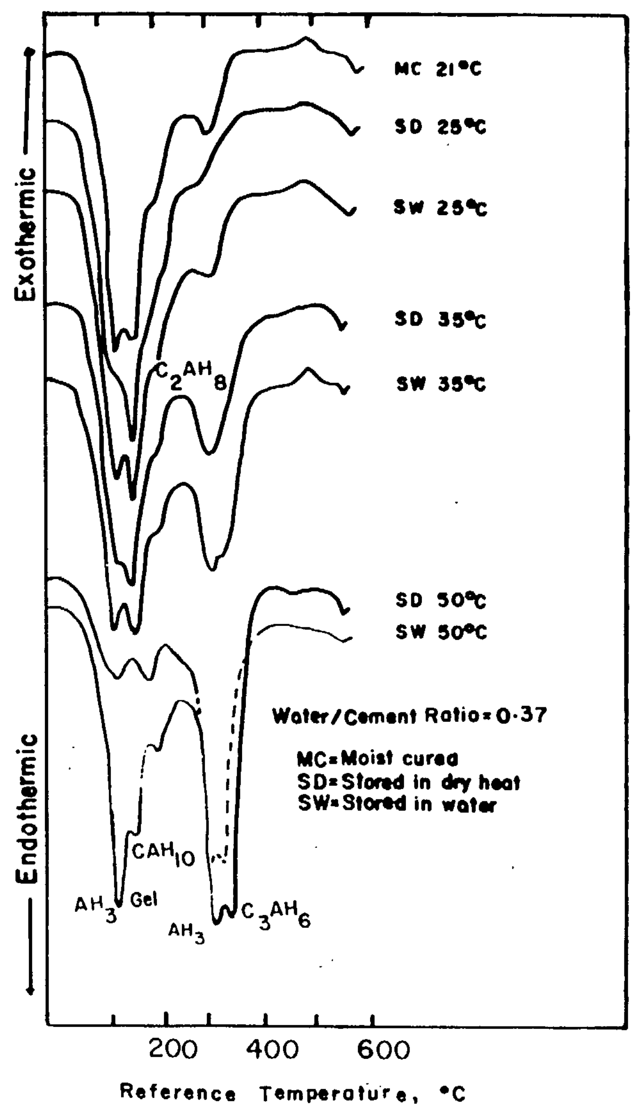

Figure 23. Thermograms of 7-day-old concrete - W/C = 0.37.

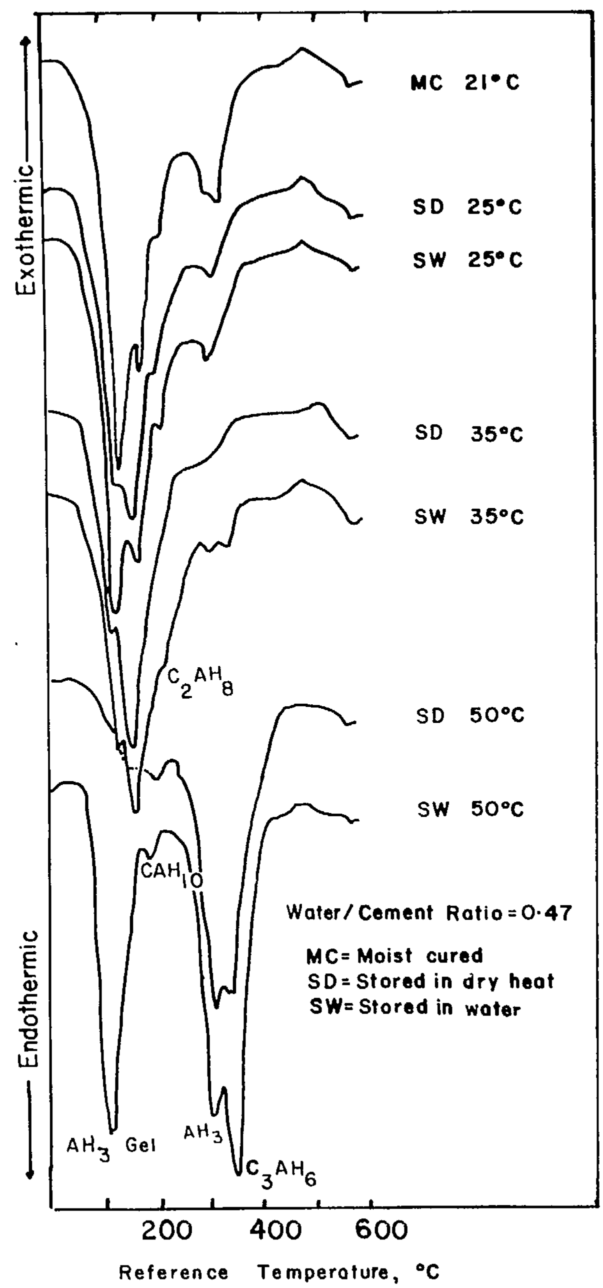

Figure 24. Thermograms of 7-day-old concrete - W/C = 0.47.

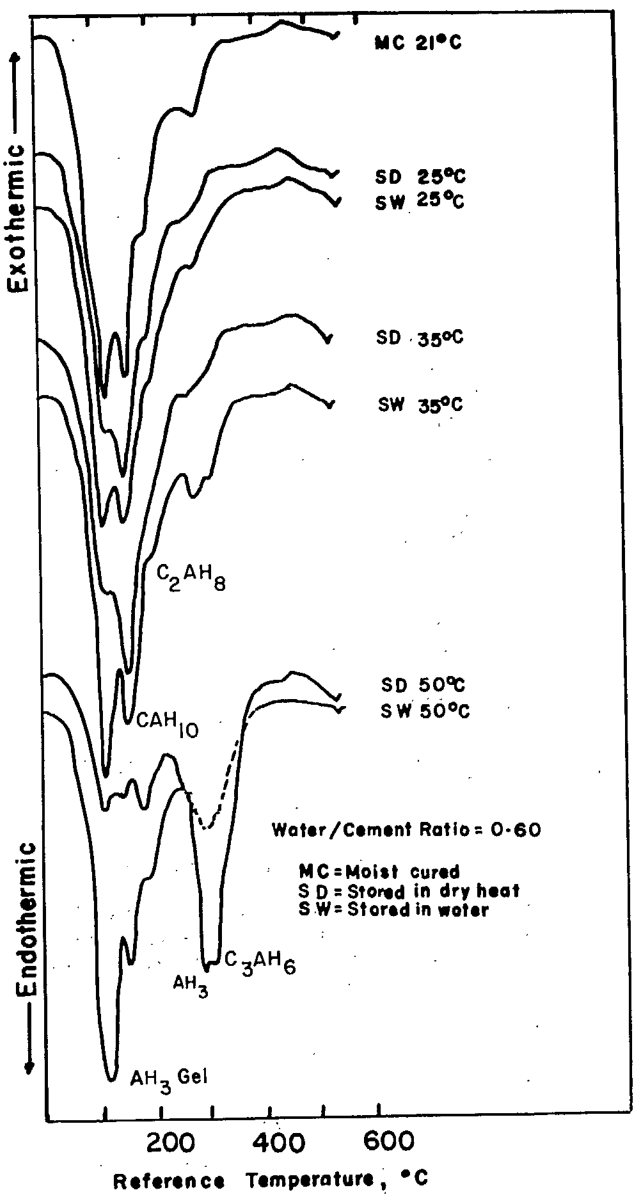

Figure 25. Thermograms of 7-day-old concrete W/C = 0.60.

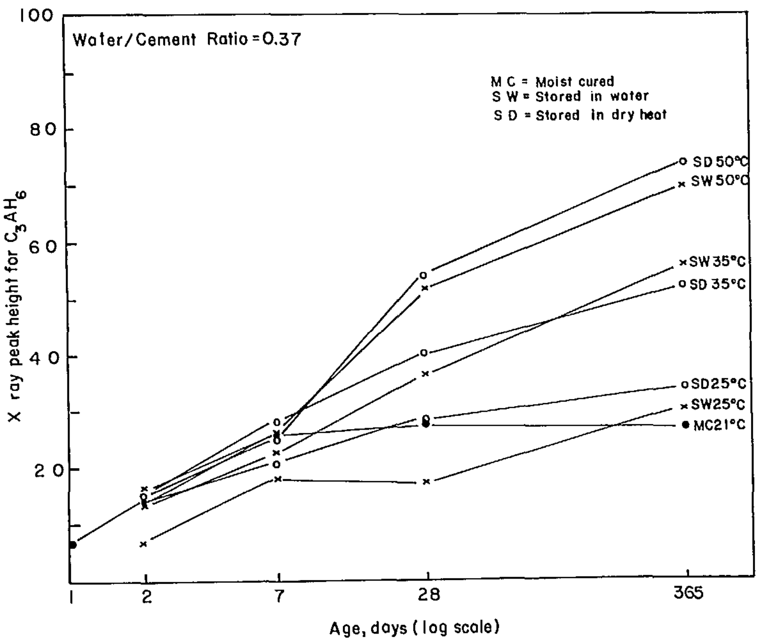

Figure 26. Height of the 0.513-nm X-ray diffraction peak of C_3AH_6 as a function of storage time.

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