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Hydratation et résistance du ciment portland pur

SOMMAIRE

La présente étude traite des relations existant entre certaines propriétés mécaniques du ciment portland et son degré d'hydratation. Le ciment a été hydraté à température ambiante dans des bouteilles de polyéthylène, pendant des durées diverses, à un rapport eau/ciment de 5. Des éprouvettes de ciment durci, pulvérisé et hydraté en proportions variées, ont été obtenues sous différentes compressions en vue de leur donner des porosités diverses et de déterminer ensuite leur module d'élasticité, leur résistance à la rupture et de leur dureté d'impression. L'étude confirme la relation entre les propriétés mécaniques et le degré d'hydratation et de porosité caractéristique des pâtes de ciment normalement hydratées. Les résultats de l'étude suggèrent l'emploi de cette technique comme moyen pratique d'évaluation des propriétés mécaniques de différents hydratants du ciment dans des conditions similaires ou différentes.

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Hydration and strength of neat Portland cement

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NATIONAL RESEARCH COUNCIL OF CANADA : DIVISION OF BUILDING RESEARCH*

SUMMARY

In order to examine the relationship between some of the mechanical properties and the degree of hydration of Portland cement, two different methods were used to prepare samples of hydrated cement paste. One method involved hydrating the cement in suspension for different lengths of time in rotating polyethylene bottles (water/cement ratio = 5). The dried powder was then compacted to different porosities. In the other method, the dry unhydrated cement was mixed with plastic beads in the ratio of 1:3 by weight and compacted at 10,000 lb/in² to give a porosity of about 38%, and then hydrated by immersion in water. These compacts, which were in the shape of discs of 1·25 in. diameter, were used to measure the modulus of elasticity, fracture strength and indentation hardness. This work indicated that these types of sample can be used to follow the characteristic change in mechanical properties with time and degree of hydration of the cement.

Introduction

The measurement of any mechanical property of hydrated cement that is indicative of strength is of great practical importance to the design engineer. It is equally important to the cement technologist responsible for control of production or to the chemist who may wish to evaluate changes in mechanical properties resulting from changes in composition or conditions of hydration.

Much previous work has concerned the development of strength in mortars or in concrete. Several workers[1,2] have observed the development of cement strength in mortars and estimated the extent of hydration from the changes in certain physical properties of cement during the hydration process. Werner and Giertz-Hedström[3] were, however, among the first to observe the dependence of strength upon the concentration of hydrated cement. Woods, Steinour and Starke[4], and Gonnerman[5] discovered that the rate of development of strength in mortars correlated with the rate of hydration of the cement, determined from its heat of hydration and composition. Dzulinsky[6] showed the rate of strength development to be a function of the volume of hydrated cement, and of the volume of evaporable water and air-filled space.

Powers and Brownyard[7] have shown experimentally that strength of cement paste is largely dependent upon the gel concentration in a given volume of paste; this is a function of the original water/cement ratio and of the degree of hydration. Shinohara[8] and Taplin[9] independently published works based upon similar ideas on the strength-hydration relationship.

All the above work has involved the hydration of cement in a confined space in a cast-in-situ environment, and where the structure thus formed both controls and is dependent upon the hydration reactions. It may be an advantage in some instances to hydrate the cement in suspension with water[10] in order to allow more complete hydration and avoid the primary influence of the structure in controlling the hydration reactions. Still another variation in the method of preparing the sample can involve the compaction of the dry unhydrated powder, which can be saturated with water for the hydration as has been done[11] for the measurement of length change during hydration of cement. The work described in this paper was designed to explore further the techniques developed at the Division of Building Research of the National Council of Canada[11-14] involving the measurement of physical and mechanical properties of compacts, which serve as models of the porous body. This paper describes the method of preparing and conditioning

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such test specimens, the measurement of modulus and hardness, and attempts to compare the results with compressive strengths of standard mortar cubes.

Experimental

MATERIALS

Two types of Portland cement, with the physical properties and chemical analysis found in Table 1, were used for this investigation. They differed essentially in the Blaine specific surface. This difference was a factor only in the tests involving compacts of unhydrated cement.

PROCEDURE

Bottle-hydrated compacts

Only the normal Portland cement was hydrated in rotating polyethylene bottles in suspension, with a water/cement ratio of 5, following the procedure described by Brunauer et al[10]. The time of hydration was varied from 1 to 28 days in order to obtain samples of different degrees of hydration. At the end of any hydration period, the cement slurry was quickly filtered by vacuum filtration and the hydration reaction was stopped by freezing and repeated washing with cold acetone. The filtered and washed samples of cement were then placed over magnesium perchlorate in vacuum desiccators and evacuated until no trace of free water could be detected by TGA.

TABLE 1: **Physical properties and chemical analyses of cements.** *

Description of test	Unit	Normal Portland cement	High-early-strength Portland cement
PHYSICAL TESTS			
Setting times:			
Initial	h : min	2 : 55	1 : 15
Final	h : min	5 : 20	3 : 00
Fineness, Blaine	cm^2/g	3,020	5,150
Autoclave expansion	%	0·25	0·16
Compressive strength:			
1 day	lb/in^2	—	3,070
3 day	lb/in^2	2,800	4,580
7 day	lb/in^2	3,880	—
28 day	lb/in^2	5,000	6,320
CHEMICAL ANALYSES			
Silica (SiO_2)	%	20·7	20·7
Alumina (Al_2O_3)	%	5·7	5·3
Iron oxide (Fe_2O_3)	%	2·8	2·3
Calcium oxide (CaO), total	%	63·4	63·5
Calcium oxide (CaO), free	%	0·67	0·99
Magnesium oxide (MgO)	%	3·0	3·0
Sulphur trioxide (SO_3)	%	2·4	3·2
Loss on ignition	%	0·73	1·1
Insoluble residue	%	0·33	0·51

*Provided by manufacturer

Compacts were made from dry powdered samples of hydrated cement according to the procedures described earlier[11-13]. All compacts were made 1·25 in. in diameter and 0·050 ± 0·0015 in. thick. Pressures of 20,000 to 100,000 lb/in^2 were used to compact the samples, which were prepared in gloved boxes controlled at 0% R.H. and free of CO_2.

The degree of hydration of the cement samples was determined by means of TGA and the weight loss between 115 and 550°C was used. Weight loss of 24% was assumed to be complete hydration.

The measurement of the modulus of elasticity and fracture strength was accomplished by the procedure described earlier[13]. Indentation hardness was measured with the Tukon Hardness Tester using the Knoop Indenter.

The porosity of the test compacts was calculated from their measured volumes and weights, and the specific gravity of unhydrated and completely hydrated cement of 3·15 and 2·60 respectively. The approximate specific gravities of the cements with different degrees of hydration were obtained from a graph plotted with these two values.

All compacts of bottle-hydrated cements were brought to equilibrium at 0% R.H. and investigated under the same conditions.

Compacts of unhydrated cement

Dry unhydrated Portland cement does not compact readily because of its low specific surface. An aid to compaction was provided by fine, inert plastic beads which also acted as a diluent to ensure more extensive hydration in the available pore spaces. The beads are polytertiary butyl styrene hydrocarbon (kerosene) gel, with a fineness of 1 to 150 microns, a specific gravity of 0·9481, and a melting point of about 200°C. The material is unreactive to acids or bases and is unaffected by temperatures up to 200°C. It was supplied by Dow Chemical Co.

The proportions used were 1 part of plastic beads to 3 parts of Portland cement by weight (a minimum amount required for making a good compact). The mixture was first homogenized manually in a small mortar and pestle for 15 min and then placed in a stoppered bottle and agitated for 15 min on a shaker. The homogenized powder was pressed to form 'compacts' 1·25 in. in diameter and 0·050 ± 0·003 in. thick following the same procedure as above. Compacting pressure of 10,000 lb/in^2 was used. The porosity of a test compact was calculated from the measured volume and weight. The specific gravity of the mixture was 2·6.

The test specimens (compacts) made from the two types of cement were placed on edge in a wire holder made of a stainless-steel spring acting as a spacer. These were then placed in a desiccator which was evacuated for 15 min. Boiled distilled water was then introduced so as to cover the sample completely during

the curing period. This method was considered to ensure uniform hydration throughout the sample. It also prevented contamination by CO^2. The curing was carried out at a temperature of 23 ± 2°C for 28 days. During this period the specimens were removed for testing at specified ages and immediately returned to the curing condition.

The increase in static modulus of elasticity of each compact was measured at curing ages of 6 hours, 1, 2, 5, 7 and 28 days. Modulus values were based upon the load-deflexion method developed in this laboratory and described previously.[13] Specimens were measured in a saturated, surface-dry condition.

Mortar cubes for standard compressive strength measurements were prepared from the same batches of cements used in the above tests, and tested in accordance with CSA Standard A5-1961 in the laboratory of a local cement plant.

Results and discussion

BOTTLE-HYDRATED CEMENT COMPACTS

The degree of hydration as a function of time for the process of bottle hydration is shown in Figure 1. This curve is characteristic of the hydration of Portland cement having a high water/cement ratio as shown by Taplin[9].

Figure 2 shows the relationship between porosity and compacting pressure for cement samples hydrated for 1, 3, 7 and 28 days. The semi-logarithmic relationship seems to hold reasonably well for each series of samples having the same degree of hydration. The slopes of these curves are different for each series because each contains different proportions of hydrated and unhydrated cement and the compaction characteristic is determined by the mixture. The particles or crystals of each constituent of the mixture differ in their resistance to deformation and fracture. The exponential relationship of porosity to compaction pressure has been observed in this laboratory for a number of powdered materials including plaster, lime, gypsum and calcium carbonate.

The experimental results presented in Figure 3 demonstrate the dependence of fracture strength, modulus of elasticity, and hardness upon porosity and degree of hydration. These results confirm and expand the findings previously reported[13,14]. The semi-logarithmic relationship of modulus of elasticity and fracture strength to porosity were found to apply to a number of porous materials[15,16]. It is reasonable to predict that differences in the hydration products would also be reflected in differences in these various relationships, thus providing a new 'tool' for evaluating differences in cements.

The hardness versus porosity relationship (Figure 3c) shows less dependence upon degree of hydration than the relationship for modulus or breaking strength. The explanation for this difference must be sought in

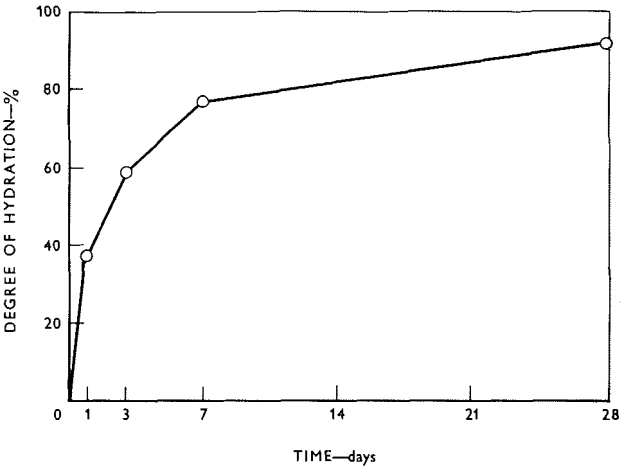

Figure 1: Degree of hydration as a function of time for bottle-hydrated cement.

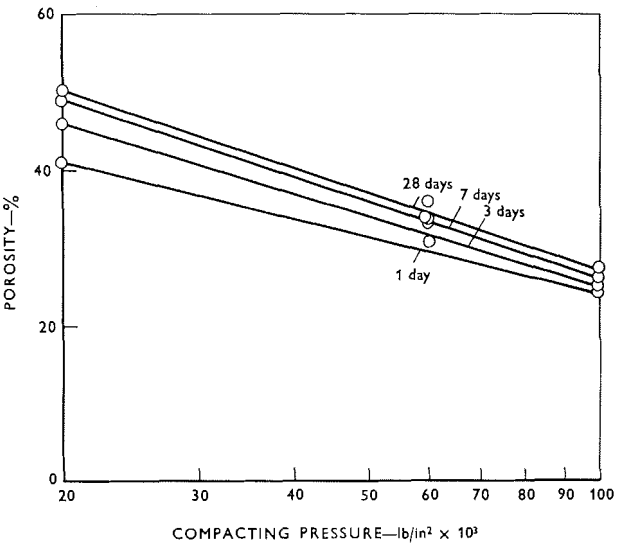

Figure 2: Compaction characteristics of bottle-hydrated cement for different periods of hydration.

the characteristics of the system and the nature of the hardness measurement. The partially hydrated cement consists of large particles of unhydrated cement surrounded by very small particles of hydrated material. The particles of unhydrated material are so large at the early stages of hydration that they can occupy a substantial part (as much as one-half or more) of the area of indentation and may have a disproportionate influence upon the resulting value, especially at low porosity. This is in contrast with their effect upon the modulus of elasticity or breaking strength, where the bulk property of the composite system is being measured.

Microhardness measurements may be very useful for special investigations in cement technology, as indicated by the present work and that of others[17].

To show the relationship between the various mechanical properties of hydrating cement samples of the same porosity and degree of hydration, the results

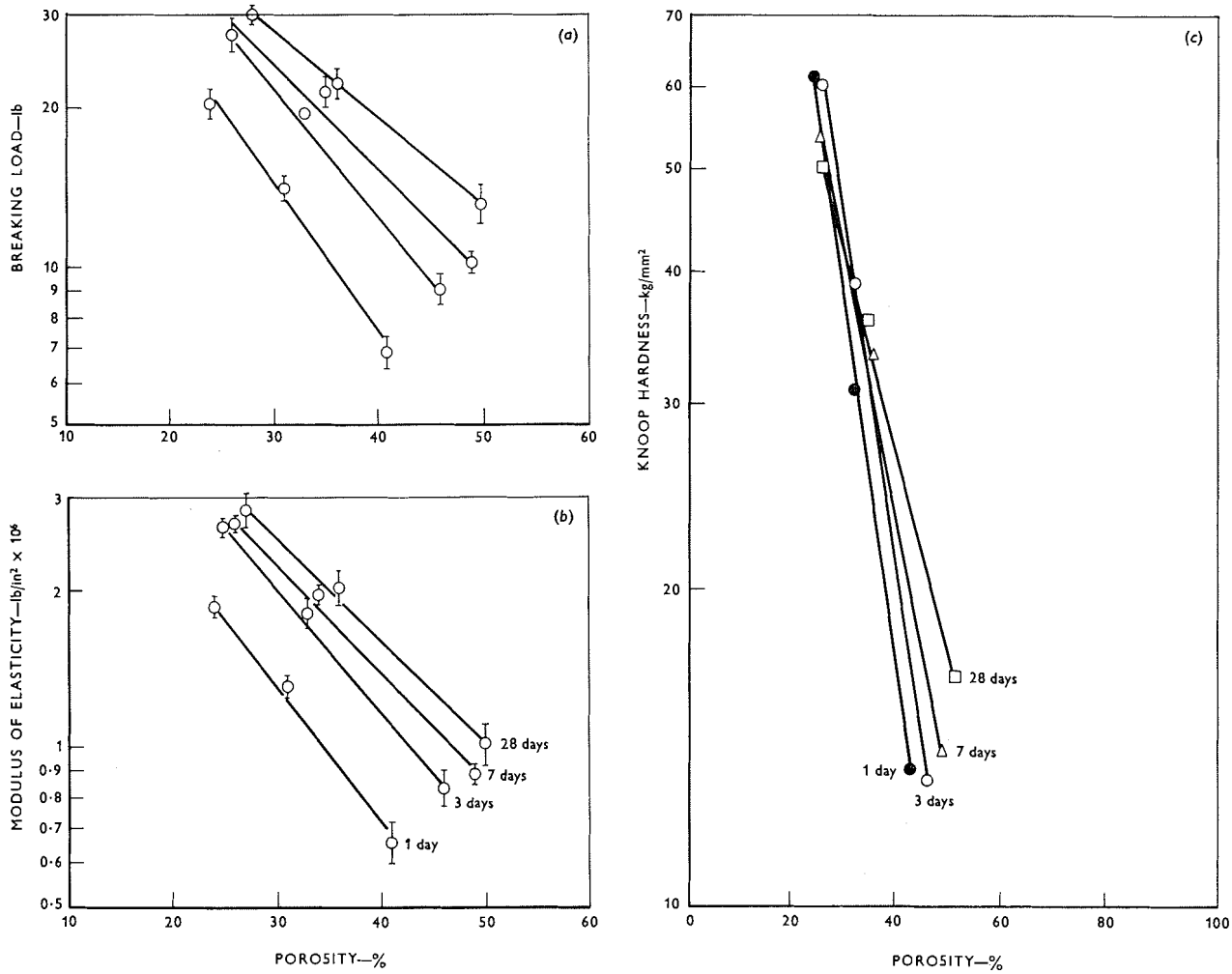

Figure 3: Plots of (a) breaking load, (b) modulus of elasticity and (c) hardness for compacts of bottle-hydrated cement as a function of porosity and different periods of hydration.

shown in Figures 1 and 3 are re-plotted in Figure 4. These plots are not linear and indicate that the rate of development of the mechanical properties may be decreasing as hydration proceeds for these types of sample.

Figure 5 shows the correlation of fracture strength, modulus of elasticity and microhardness, as determined on compacts at 40% porosity and 0% R.H, with the standard mortar cube compressive strength (the cube compressive strength test data was supplied by the Canada Cement Company) measured according to the standard ASTM method. The strength data were compared after 3, 7 and 28 days' curing. (It is assumed that the degree of hydration bore a constant relationship to that of the cement hydrating in the bottle.) It is significant that these correlations appear to be linear, suggesting that any of the measurements of mechanical properties on compacts would give a good indication of the development of strength with curing and might be substituted for the standard cube compressive strength.

COMPACTS OF UNHYDRATED CEMENT

A cement mix containing 25% by weight of plastic beads compacted at a pressure of 10,000 lb/in² represented a sample with a minimum of diluent to provide for good compaction (giving a strong sample) and retain adequate porosity (38·5%) to facilitate normal rate of hydration (with a water/cement ratio about 0·4). The volume ratio of plastic beads to cement was roughly 1:1.

The curves in Figure 6 show the percentage increase in modulus of compacts hydrating in water in comparison with the percentage increase in compressive strength of standard mortar cubes for corresponding time of curing. It is apparent that, for the high-early-strength Portland cement, good agreement is obtained. The agreement for normal Portland is not so good. The data for the above curves are based upon an average value obtained from 5 to 10 compacts for each age, i.e. 6 h, 1, 2, 3, 5, 7, 15 and 28 days. The spread from the mean ranged up to ±15%. It is obvious, however, that the test involving the measurement of

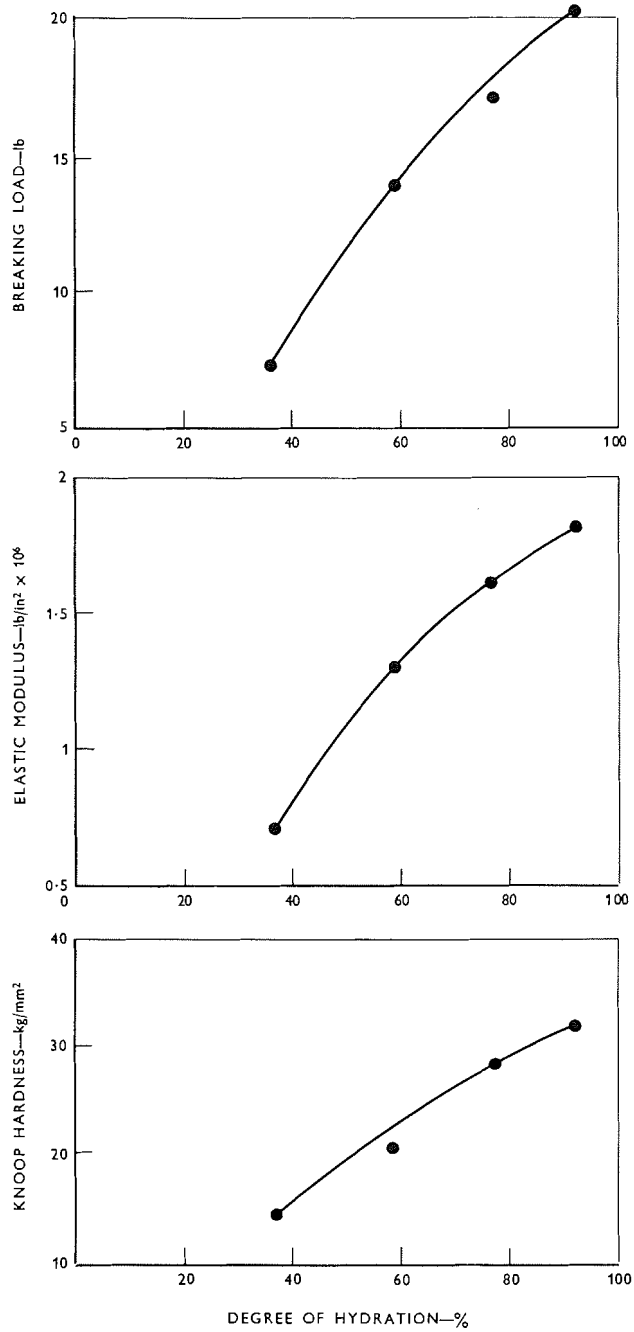

Figure 4: Breaking load, modulus of elasticity and hardness versus degree of hydration for compacts of bottle-hydrated cement. All compacts were made at constant porosity.

the increase in modulus of unhydrated compacts with plastic beads can be used to indicate the development of strength with time and to distinguish between different types of cement as does the standard cube test.

Because of the major differences between the compacts used for modulus measurement and the mortar cubes for compressive strength measurements, it cannot be argued that the similarity of the curves in

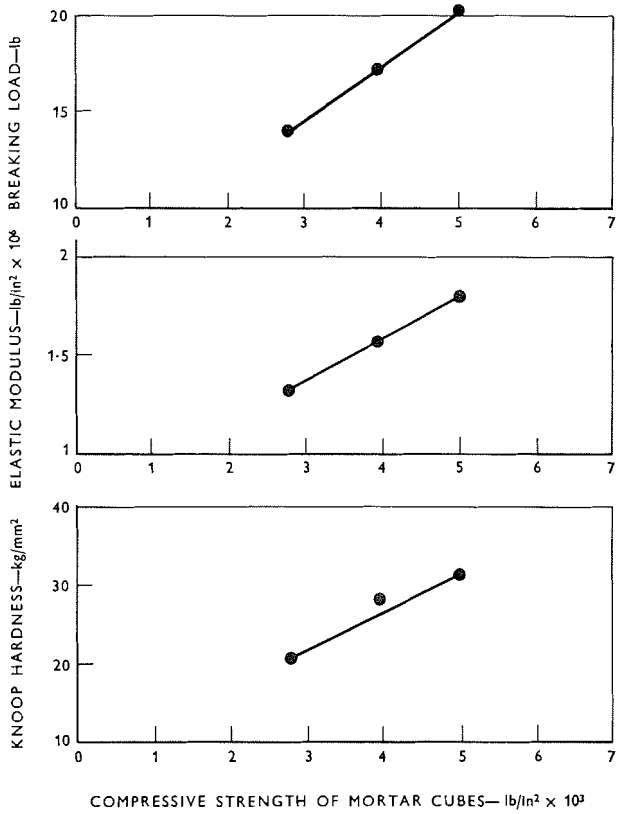

Figure 5: Comparison of mechanical properties of compacts of bottle-hydrated cement with compressive strength of standard mortar cubes at 3, 7 and 28 days' hydration.

Figure 6 necessarily implies that these results confirm the correlation between these parameters.

Conclusions

The results of this work further confirm the significance of the compacted cement system in comparison with normal in situ hydrated cement. The relationships of modulus of elasticity, breaking strength, and microhardness to porosity and to degree of hydration show the usefulness of these techniques. The fact that the mortar cube strength correlates reasonably well with the measured mechanical properties on compacts of bottle hydrated cement, as well as compacts of unhydrated cement cured in water, is significant.

It is expected that these techniques may provide a new 'tool' for evaluating significant changes in mechanical properties brought about by changes in the composition or conditions of hydration of the cement.

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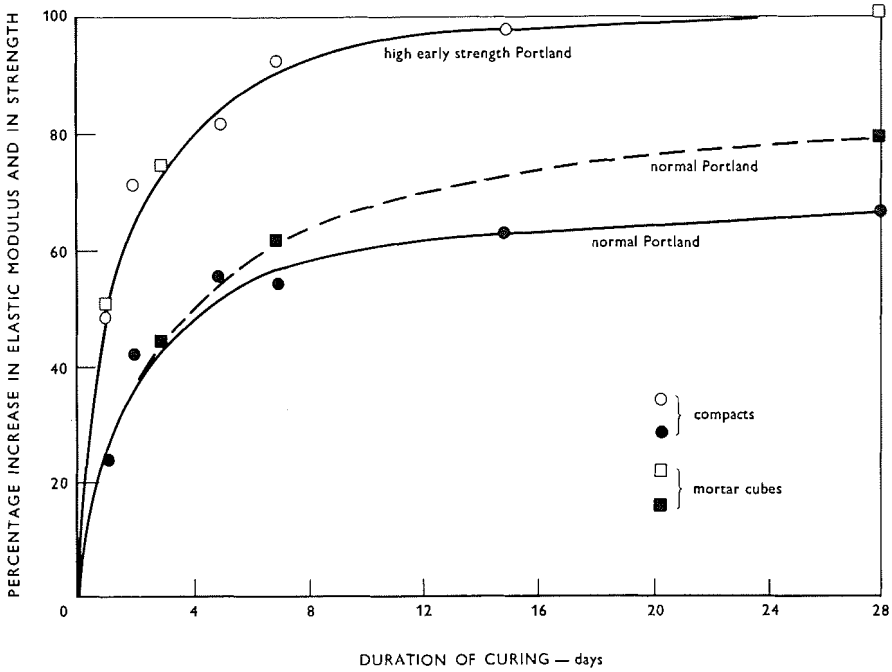

Figure 6: Percentage increase in elastic modulus of compacts and in compressive strength of mortar cubes with time of curing, based upon the 28 day value for the high-early-strength Portland cement.

Cement Company for supplying samples of cement and for providing analyses and test data.

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