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THE STRUCTURE OF CEMENT-STONE AND THE USE OF COMPACTS AS STRUCTURAL MODELS

BY

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I. SOROKA AND PETER J. SEREDA

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LA STRUCTURE DE LA PATE DE CIMENT DURCIE ET L'EMPLOI DES ECHANTILLONS COMPACTES COMME MODELES DE STRUCTURE

SOMMAIRE

Les auteurs ont étudié la relation entre la dureté, le module d'élasticité et la porosité de trois systèmes différents de ciment portland normal de type I, en vue d'obtenir des renseignements sur la structure de la pâte de ciment durcie, et plus particulièrement sur la nature de la liaison entre les particules et leurs effets sur les propriétés mécaniques. Cette étude permet également d'évaluer les possibilités d'emploi des échantillons compactés en recherche cimentière.

Les trois systèmes, appelés I, II et III, sont: pâtes de ciment (I) d'une porosité de 40% à 70% et une hydratation de 73% à 98% (rapport eau/ciment 0.40 à 1.20); pâtes de ciment compactées (II) de porosité 25% à 60%; et des échantillons compactés de ciment hydraté en bouteille (III) de porosité 20% à 55% et d'hydratation 0% à 90% (i.e. des échantillons compactés de ciment non-hydraté ont été inclus).

Les résultats d'essais ont généralement confirmé que la résistance de la pâte de ciment durcie découle principalement d'un type défini de liaison entre les particules. On a conclu que la liaison se fait par le contact de solide à solide qui résulte du rapprochement des surfaces et qu'elle est essentiellement la même dans les échantillons compactés que dans la pâte de ciment.

La concordance des valeurs obtenues pour les propriétés mécaniques des échantillons compactés et des pâtes laisse croire que les échantillons compactés qui servent de modèles à la pâte de ciment durcie constituent un outil fiable et prometteur en recherche cimentière.



Supplementary Paper III-34 The Structure of Cement-Stone and the Use of Compacts as Structural Models

I. Soroka* and Peter J. Sereda**

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Synopsis

The relation between hardness, modulus of elasticity and porosity was investigated in three different systems prepared from normal Type I portland cement. This study was undertaken to obtain some data on the structure of cement-stone, particularly with regard to the nature of the interparticle bonds and their effect on mechanical properties. The study also enabled the evaluation of the possible use of compacts in cement research.

The three cement systems, designated as I, II, and III, cement pastes (I) in which porosity varied from 40% to 70% and the degree of hydration from 73% to 98% (w/c ratio 0.40 to 1.20), compacted cement pastes (II) in which porosity varied within the range of 25% to 60%, and compacts of bottle hydrated cement (III) in which the porosity varied from 20% to 55% and the degree of hydration from 0% to 90% (i.e., unhydrated cement compacts were included).

Test results generally supported the concept that the strength of the cement-stone is mainly derived from a particular type of interparticle bond. It is concluded that this bond is a solid to solid contact resulting from the bringing together of surfaces, and that it is essentially the same in compacts as in cement paste.

The close agreement between values for mechanical properties of compacts as compared to paste suggests that compacts, used as a model of the cement-stone, are a promising and a reliable tool in cement research.

Introduction

It is generally accepted that the structure of cementstone*** is rather complex, and there are still quite a few aspects concerning its nature awaiting clarification. Although extensive data exist to indicate that the hydration products are essentially comprised of colloidal-sized particles having a great variety of microstructure, as shown by Grudemo (1), little is known about the nature of the bonds between these colloidal particles to account for the strength of the cementstone. Philleo in his review (2) discussed the various types of bonds and pointed out that limited swelling of the cement-stone in water has been considered as evidence for the existence of some chemical (primary) bonds between the gel particles but that the secondary bonds accounted for most of the strength of the cement paste. This conclusion was made on the grounds that adsorbed water was a constituent part of the bond, in order to account for some of the unusual physical and mechanical behaviour. Recent work at DBR (3-6), however, contradicts the above hypothesis.

It is recognized that the terms "chemical" and "secondary" bonds have been used in describing the structure of hydrated cement system without a strict definition of their meaning. This has led to considerable misunderstanding. It is believed that what was meant by the "chemical" bond between the particles was a solid to solid contact similar to that of a grain boundary in a polycrystalline material where some atoms approach the spacing and arrangement in the crystal. Such "chemical" bonds could be formed during a crystallization process accompanying a chemical reaction where the mobility of atoms allows for a regular arrangement resulting in an intergrowth of crystals. It follows that these bonds would be strong and, when broken, would not be remade in normal circumstances.

It is believed that the term "secondary" bonds as applied to the hydrated cement system arose out of the assumption that adsorbed water was a constitu-

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^{***}Cement-stone refers to the system of cement gel and the associated capillary space, and is an alternate name for the hardened cement paste.

ent part of the interparticle bond; hence the general term of van der Waals forces was considered appropriate.

Previous work in this laboratory has indicated that neither of these definitions would fit adequately the interparticle bonds in the hydrated cement system. It is suggested, therefore, that a different interparticle bond be postulated which would involve a solid to solid contact resulting from the bringing together of surfaces (by pressure or accommodation) forming a particle boundary having no regular atomic arrangement or spacing. Atoms at such a boundary would engage a varying proportion of the long range and the short range forces depending on the degree of disorder and the average spacing. It can be visualized that this interparticle bond can be broken and subsequently remade under appropriate loading conditions. This type of bond differs from the "chemical" bond defined above, which has a more regular atomic arrangement, and in which the spacing of the atoms may approach that of the lattice spacing in the crystal.

The vital question of the structural model for hy-

drated cement, therefore, has yet to be resolved, especially in regard to the nature of the particular interparticle bonds for which there is considerable evidence from the work at DBR involving compacts of hydrated cement. The present work was designed to shed some further light on the above questions of the structure of portland cement-stone.

In the first stage of the study, some mechanical properties of compacts and pastes were compared in a gypsum system, which is distinctly crystalline and where intergrowing of crystals is a distinct possibility. The results of this stage of the work were reported elsewhere (7), but the essential part is reproduced here to enable direct comparison of the gypsum system with the cement system.

In the second series of experiments reported here, essentially the same tests were carried out with Type I normal portland cement instead of gypsum. It was hoped that the comparison of results for the two systems (distinctly different in the degree of crystallinity) would reveal information about the nature of the bonds.

Experimental

In the tests described, the hardness and modulus of elasticity of portland cement pastes and of compacts with a wide range of porosities were compared. All specimens involved were flat, round plates 1.25 in. (approximately 32 mm) in diameter and 0.050 in. (approximately 1.25 mm) thick. Specimens of three different systems were prepared, all from the same brand of Type I normal portland cement.

Preparation of Specimens

System I—Cement Paste

The cement was mixed in vacuum with boiled distilled water to give cylinders measuring 1.25 in. in diameter and approximately 5 in. high. (For the chemical composition of the cement see reference (3), and for further details of mixing procedure see reference (8)). The water/cement ratio in the specimens varied from 0.40 to 1.20 resulting in pastes of seven different porosities ranging from approximately 40% to 70%(Table 1).

Specimens were demoulded after 48 hours and, to avoid carbonation, were wet-cured in tightly closed rubber bags. At the age of approximately 3 months the cylinders were taken out and sliced to give specimens having the required thickness of 0.050 in. Conditioning of specimens involved two stages; they were first allowed to dry at 30% R. H. and 22°C (saturated solution of CaCl₂), and then placed over a NaOH solution to reach equilibrium at 50% R. H. and 22°C both in a CO₂-free atmosphere.

The porosity of the samples was calculated from the weight, volume, and degree of hydration, taking the density of the unhydrated cement to be 3.15 g/cc and that of the hydration products to be 2.60 g/cc.

System II—Compacted Cement Paste

Some of the cement paste specimens (system I),

 Table 1. Summary of test data

 System I—Portland cement pastes and compacts

Designation	w/c ratio	Porosity, %	Hardness, kg per sq mm	Modulus of elasticity × 10 ⁴ , kg per sq cm	Degree of hydration, %
15	0.40	39.6	32.0	14.71	73.3
16	0.50	45.6	20.6	10.86	80.9
19	0.60	51.8	10.7	7.92	80.2
23	0.70	55.6	8.2	6.95	86.8
25	0.80	59.3	5.9	5.63	88.6
31	1.00	65.5	3.3	3.80	91.7
37	1.20	69.9	_	2.57	98.5

after being cured and sliced, were subjected to a compacting pressure in a closely fitting mould (0.003 in. nominal clearance). In each case the thickness of the sliced specimens was adjusted to yield the nominal thickness of 0.050 in. after compaction. Porosity was controlled by the amount of the applied pressure and ranged from approximately 25% to 60% (Table 2). When the initial porosity was known, porosity after compaction was determined simply from the change in the dimension of the specimens involved.

Compaction was affected when the paste specimens reached equilibrium at 30% R. H.; however, testing was carried out after they were conditioned at 50% R. H.

System III—Compacts of Bottle Hydrated Portland Cement

The hydrated cement was prepared by mixing 1:5

Table 2.	Summary of tes	t data		
System IICompacted	portland cement	pastes	and compacts	

Designation	Compacting pressure, kg per sq cm	Porosity, %	Hardness, kg per sq mm	Modulus of elasticity × 10-4, kg per sq cm
15	1,430	39.1	41.6	4.90
	2,860	36.6	51.2	14.76
	5,730	30.0	69.9	22.41
	11,460	24.9	85.6	26.84
16	1.140	45.1	25.4	9.28
	2,290	40.4	41.4	12.36
	4.580	33.3		19.78
	5,730	30.3	63.2	22.10
	11,460	24.8	87.1	26.90
19	1,140	49.4	23.9	7.89
	2,290	41.5	38.7	14.79
	4,300	34.0	_	20.57
	5,730	31.1	64.9	23.36
	11,460	25.8	80.4	24.34
23	1,140	50.2	<u> </u>	8.92
	1,430	47.3	26.0	10.82
	1,720	46.8		11.24
	2,290	40.4		14.20
	2,860	37.3	46.0	15.98
	5,730	29.1	67.6	23.49
	11,460	24.6	85.8	27.94
25	860	53.5	15.3	7.67
	1,140	51.0		7.42
	1,430	49.0		9.72
	1,720	47.7		10.40
	2,000	44.5	30.5	12.08
	2,290	43.3	56.6	13.39
	4,300	33.5	56.0	20.08
	5,730	29.0	<u>(0</u>)	25.05
	0,870	20.2	07.3	25.50
31	11,460	23.1	10.9	5 20
51	1 1 40	50.7	10.0	6.00
	1,140	33.3		9.56
	2,720	49.0	32.1	11.75
	2,270	10.9	52.1	16 29
	5 730	30.8	62.0	17.66
	11,460	25.6	79.5	25.92
37	570	59.4		4.72
	740	57.6	10.4	5.08
	860	54.7		6.67
	1 140	51.0		8.11
	1 430	48.9	20.8	9.20
	1.720	46.7		9.92
	3.440	37.9	45.9	16.35
	4,300	33.9		20.58
	5,730	31.0	66.9	27.24
	10.020	25.9		27.03
	11.460	25.2	77.9	26.99

mixtures of cement and water in tightly closed bottles which were mounted on a rotating disc. The mixing period varied between 24 hours and 28 months, resulting in products of different degrees of hydration within the range of approximately 35% to 90% (Table 3).

When mixing was completed, the hydrated cement was filtered, dried at 30 % R. H. over CaCl₂, and then screened through a 100-mesh sieve. The remaining fraction (mostly Ca(OH)₂ crystals) was ground and recombined with the sieved material. At this stage the powdered hydrated cement was used to produce the compacts by the method described elsewhere (3-5). Altogether, compacts of 5 different degrees of hydration were prepared within the porosity range of approximately 20% to 55% (Table 3). To complete the picture and to provide data for "zero" degree of hydration, compacts of unhydrated cement were also prepared in the porosity range of 18% to 31% (system IIIa-Table 4). As in system I (cement pastes) porosity was determined from the weight, volume and degree of hydration and using the density values mentioned previously. To conform with the

 Table 3. Summary of test data

 System III—Compacts of bottle hydrated portland cement

Designation	Mixing time	Degree of hydra- tion, %	Com- pacting pressure, kg per sq cm	Porosity, %	Hard- ness, kg per sq mm	Modulus of elasticity × 10-4, kg per sq cm
B1	l day	34.1	860 2,860 5,730	45.7 34.0 26.7	10.4 37.2 62.6	5.80 15.16 22.38
B 3	3 days	49.8	11,460 860 2,860 5,730	19.9 48.9 36.8 28.3	92.8 13.0 38.9 69.1	29.46 6.14 15.20 23.17
В7	7 days	63.8	11,460 860 2,860 5,730	21.3 47.9 35.5 30.6	99.0 16.0 40.4 50.1	30.84 6.73 16.31 20.50
B28	28 days	75.5	11,460 860 2,860 5,730	28.7 49.7 37.3 34.5	51.4 16.0 35.5 43.8	21.15 7.84 16.95 19.06
ВМ	28 months	90.7	11,460 860 2,860 5,730 8,020 11,460	33.9 54.8 41.0 31.5 26.6 23.2	9.1 30.8 52.4 70.5 81.7	4.08 11.57 19.22 25.75 27.16

 Table 4.

 System IIIa—Compacts of unhydrated portland cement

Compacting pressure, kg per sq cm	Porosity, %	Hardness, kg per sq mm	
1.430	31.1	19.6	
2.860	26.8	28.3	
5.730	22.4	50.8	
11,460	18.1	81.6	



Fig. 1. General view of testing layout

other systems, testing was carried out after specimens reached equilibrium at 50% R. H. and 22° C.

Testing Methods

All tests were carried out in a gloved box which was conditioned at 50% by means of a NaOH solution (Fig. 1). The following tests were conducted.

Hardness

Vickers hardness was determined with a Leitz Miniload hardness tester; the load was adjusted in each case to give indentation to a depth of 35 to 50μ . For each specimen tested, the hardness was taken as the average of 10 tests carried out along an arbitrary diameter at 0.1-in. spacing.

Young's modulus of elasticity was determined with an apparatus described elsewhere (5). Essentially the procedure involves the measuring of the deflection of a specimen when it is loaded at its centre and supported at three points located at the circumference of a circle 1 in. in diameter. Under such conditions, Young's modulus is related to centre-deflection as follows (9):

$$\mathrm{Def} = \beta \frac{\mathrm{P}a^2}{\mathrm{E}h^3}$$

where $\mathbf{P} =$ the applied load

a = radius of circle of support

E = Young's modulus of elasticity

- h = specimen thickness
- β = parameter related to Poisson's ratio (μ), number of supports (m) and the ratio (t) between the radius of circle of supports (a) and radius of specimen (c).

To determine the value of β in the above formula, it was assumed that the modulus of elasticity in compression is equal to the value determined from the deflection test. In turn, the modulus of elasticity in compression was determined on cylinders 1.25 in. $\times 2$ in. which were, in fact, the companion specimens of the cylinders used for preparing systems I and II.

The average of five tests was considered as Young's modulus for any given set of conditions.

Degree of hydration was determined by means of a thermo-balance test (TGA). The weight of the sample in a "dry state" was taken as the value recorded when no weight loss was observed (readings to the nearest milligram) with the oven temperature kept constant at 120°C. The amount of water required for complete hydration was considered to be 25.4% of the unhydrated cement weight. For each set of conditions, the degree of hydration was taken as the average of three or four such tests.

It is realized that the accuracy and reproducibility of the results of the above procedure are questionable to some extent. This, in fact, is somewhat indicated in the results reported in Tables 1 and 3. It can be seen that, contrary to what could have been expected, the degree of hydration in the paste with a w/c ratio of 1.20 was found to be higher than that observed in the cement which was bottle-hydrated for 28 months. It should be kept in mind, however, that for the purpose in hand, where the degree of hydration is used to calculate porosity, the use of a better established value is less critical than it perhaps would be under different conditions. Using, for instance, the formula suggested by Powers (10) it can be shown that a difference of 10% in the degree of hydration is associated only with approximately 3% variation in the porosity of denser pastes (w/c = 0.40) and 1%variation in high-porosity pastes (w/c = 1.20). It is, therefore, considered that possible errors of such order are not liable to affect materially the results and the use of the above procedure in no way limits the following conclusions.

Results and Discussion

In Figs. 2 and 3 respectively, hardness and modulus

of elasticity are plotted against porosity, together



Fig. 2. Modulus of elasticity vs. porosity for the cement systems

with the corresponding regression line. These lines were calculated to fit test data employing the least squares method and assuming a semi-logarithmic relation between the factors involved. It can be seen that for each of the systems prepared, (excluding the higher end of the porosity range), such an assumption resulted in fairly good agreement with the experimental data. It should be realized, however, that the exponential expression used here, although suggested and used by others (11, 12), is purely empirical and therefore does not necessarily represent the "true" relation between the factors involved. Moreover, it is possible to devise other expressions to fit the very same data. In the present study, however, where the main object is the comparative evaluation of the different cement systems, this aspect becomes of secondary importance. In fact, for the present purpose, any other expression which can be shown to represent the experimental data may be used with more or less the same degree of success.

The most significant result, as shown in Fig. 2, is that the modulus versus porosity relation was the same for the compacted cement paste as for the cement paste despite the fact that paste samples, having an original porosity in the range of 40 to 70% were compacted to porosities in the range of 25 to 60%. This is strong evidence for the absence of "chemical" bonds because it is unlikely that these would not be broken (if they were present) when the pore volume is reduced by one half during compaction. The fact that the values for the modulus of the compacts of bottle hydrated cement fit so closely to that of the paste and compacted paste lends further support to the idea that this system has none or very few "chemical" bonds.

The above results are in striking contrast with the results for the gypsum systems presented in Fig. 4 (reproduced from reference (7)) where "chemical"



Fig. 3. Hardness vs. porosity for the cement systems



Fig. 4. Modulus of elasticity vs. porosity for the gypsum systems

bonds can be identified. In this case the modulus for the in-situ hydrated gypsum was an order of magnitude greater than for the compacts at the same porosity.

The results of microhardness versus porosity presented in Fig. 3 lead to the same conclusions as the results for modulus; the "chemical" bonds, if present in the paste, play an insignificant role because paste and compacts give the same relation with porosity. It is surprising, however, that the compacted paste samples give higher values for hardness. This may be related to a surface effect in the case of these samples.

It is also evident from the data in Figs. 2 and 3 that the degree of hydration is a significant factor only when its value is below 50% as represented by system III (B1). All series of cement compacts (system III) made from material in which the degree of hydration exceeded 50% (B3, B7, B28 and BM-Table 3) are Highway Res. Bd., Spec. Rpt. 90, 175-185, (1966).

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