

Some Researches on the Physical Properties of Hardened Pastes of Portland Cements Containing Granulated Blast Furnace Slag

CESARE CESARENI and GIUSEPPE FRIGIONE
Cementerie del Tirreno, Naples, Italy

A portland cement clinker interground with 4 percent gypsum was blended, in different proportions, with a granulated blast furnace slag which had also been interground with 4 percent gypsum. The fineness of each the two products from which the blended cements were made was $3200 \text{ cm}^2/\text{g}$ Blaine, and the blends covered the range from 0 to 90 percent of the ground slag component in steps of 10 percent. Pastes of the blended cements with water/cement ratios of 0.22 and 0.50 were prepared. The following properties of the pastes stored at 25.0 C were studied: (a) the bleeding of the fresh pastes, (b) the nonevaporable water contents, (c) the specific surfaces as determined by water vapor adsorption, and (d) the capillary and gel pore volumes; each of the last three properties was determined at 7 days, 28 days and 18 months. The results showed that the specific surface area development was greatest for the blends containing about 50 percent of the ground slag component, though the nonevaporable water contents were approximately constant from 0 to 40 percent of the component, and fell sharply as the percentage was increased further. Possible interpretations of the results are discussed. It is concluded that at least for the particular slag and clinker studied, the properties of the blends containing up to about 50 percent of the slag component were similar to those of the portland cement component by itself.

•THIS paper is a contribution to the study of some basic physical properties of hardened pastes of cements containing granulated blast furnace slag. The study, which is the first part of a much wider program, is limited to experimental work on the behavior of a series of cements obtained from mixtures of a clinker sample and a slag sample over a ratio range of 90 to 10 percent, compared with cement obtained from clinker only.

The experiments were conducted using the methods developed for portland cement by Powers and various coworkers (1, 2, 3, 4).

The practical purpose of this work was to investigate similarities and differences, if any, in slag behavior in blast furnace cement as compared with portland cement, from the viewpoint of the hydrated paste properties. The results accruing from this first series of experiments hold good, of course, only for mixtures of components having the same characteristics. Before they can be generalized, they must be confirmed or otherwise by a full set of experiments, which we intend to conduct, on clinker and

slag having varying properties and mixtures where the gypsum percentage will also vary, since this material affects slag hydration very considerably.

The research did not cover all the many aspects of the physical properties of paste studied in the papers cited, but was confined to these basic properties: (a) sedimentation phenomena of fresh pastes; (b) determination of nonevaporable water at ambient temperature; (c) extent of surface area of hardened cement pastes; and (d) paste porosity.

In the conclusions, some interpretations of the physical structure of the paste will be given, based on the experimental data obtained in the tests regarding the points mentioned.

CHARACTERISTICS OF CEMENTS TESTED

The clinker and slag used in the experiments were ordinary commercial products. Table 1 lists the chemical analyses. The clinker is a dry-process rotary kiln product, while the slag originates from the basic-process blast furnace and was granulated in seawater directly in a pit near the furnace.

The various mixtures—10 in all—were blended in an appropriate mixer, the two main components having been ground in a laboratory mill with the addition of a fixed quantity of 4 percent gypsum, to a particle fineness characterized by a Blaine specific surface of 3200 cm²/g.

SEDIMENTATION TESTS ON FRESH PASTES

With regard to the properties of fresh cement pastes, our research was confined to a check on the sedimentation behavior of the various mixtures in order to determine the bleeding water, which is known to be a parameter that in turn conditions the subsequent texture of the paste in the hardening stage.

Two series of mixtures with a different water/cement ratio were studied. The series of lower water/cement ratio mixtures (W/C = 0.22) was obtained using the same method as suggested by ASTM C 191-58 to prepare pastes for use in the determination of setting time.

TABLE 1
CHEMICAL ANALYSES OF MATERIALS
AND POTENTIAL COMPOUND
COMPOSITION OF THE CLINKER

Analysis	Clinker	Slag
Loss on ign.	0.20	1.02
SiO ₂	22.89	28.38
Al ₂ O ₃	4.56	16.01
Fe ₂ O ₃	3.01	3.22
Total CaO	65.58	41.60
MgO	1.56	6.18
SO ₃	0.73	—
S (sulfur)	—	1.13
Mn ₃ O ₄	0.12	0.90
Na ₂	0.36	0.78
K ₂ O	0.96	0.60
Free CaO	0.60	—
C ₃ S	53.6	
C ₂ S	25.2	
C ₃ A	7.0	
C ₄ AF	9.2	
CaSO ₄	1.24	

The series of higher water/cement ratio mixtures (W/C = 0.50) was prepared using a Hobart mixer (Rotations per minute: 285 ± 10; revolutions per minute: 125 ± 10). The cement and water were mixed for two minutes, left standing for one minute, and then mixed for two more.

The method suggested by Powers (3) was followed for determination of bleed water quantities, but the water was collected to the end of separation.

The quantity of water accumulated at the surface determined by this method is given in Table 2. The various mixtures differ widely and these discrepancies call for more thorough investigation.

At a water/cement ratio of 0.22 there is practically no bleed water for mixtures up to a slag content of 40 percent; while the bleeding increases, first slowly and then more quickly, with the slag content, until it reaches a value of 0.02 for mixture 10, based on the weight of cement.

Qualitatively, the same trend is observed with mixtures having a water/cement ratio of 0.5, apart from the obvious fact that the richer clinker mixtures

TABLE 2
LOSS OF WATER DUE TO BLEEDING

Mix No.	Percent Slag	Paste W/C = 0.22		Paste W/C = 0.50	
		Loss of Water (g/g) of Orig. Cement	Loss of Water (g/g) of Orig. Cement	Na ₂ O (g/l)	K ₂ O (g/l)
1	0	—	0.075	5.48	19.26
2	10	—	0.070	4.95	18.00
3	20	—	0.072	4.46	14.76
4	30	—	0.078	4.27	13.06
5	40	0.001	0.086	4.00	11.20
6	50	0.002	0.093	3.82	8.93
7	60	0.003	0.104	3.52	6.90
8	70	0.005	0.114	3.32	5.20
9	80	0.012	0.137	3.50	3.70
10	90	0.020	0.155	2.00	1.85

also produce appreciable quantities of bleed water, with a minimum for mixture 2 (containing 10 percent slag).

Since the total quantity of water accumulated at the surface is obviously a function of both bleed velocity and the duration of sedimentation, it was decided to investigate which of these factors is mainly responsible for the differences noted in bleed water quantities.

The velocity of the process was measured with the method suggested by Powers (3). It was found that, at least for mixtures containing more than 40 percent slag (i. e., those evidencing more marked bleed water differences), the velocity increases with the higher slag content.

Despite the small differences—not more than 10 percent—found in the values of this parameter, we thought it of interest to ascertain which factors were mainly responsible for the variations.

Since the factors varying from mixture to mixture that might influence bleed velocity, according to the Kozeny-Carman equation adapted by Powers (1), are

- ρ_e = cement density,
- ρ_f = fluid density,
- η = fluid viscosity,
- ϵ = paste porosity, and
- W_i = immobile water factor,

the bleed water alkali content was determined to ascertain the effects of variations in alkali concentrations on ρ_f and η , while the other parameters can be determined from the density of the two solid components of the mixture and their respective contents.

The alkali content values in Table 2 show a fairly appreciable variation (where S is constant, while k_c is assumed as constant) sufficient to bear on the above quantities in a significant way. The alkali content clearly tends to decrease with the slag content, and relates fairly well with the quantity of soluble alkaline oxides in the clinker and slag. While the potassium oxide comes mostly from the clinker so that the quantity in solution is roughly proportional to the clinker content of the mixture, the sodium oxide in solution increases with the slag content (the slag contains quite large quantities of sodium chloride originating from seawater used for granulation).

For η the solution separated from mixture 1 differs from that separated from mixture 10 by about 6 percent; the corresponding variation in ρ_f is 2.5 percent.

On the basis of these premises the only unknown quantity left in the Kozeny-Carman equation is W_i . When the different values obtained for the variables were introduced, it was found that the trend of W_i decreases slightly with the slag content. Insofar as concerns sedimentation velocity, it can be concluded that slag and clinker give exactly the same performance. The slight variations in velocity are entirely explained by variations in the physical properties of the fluid and the specific gravity of the cement.

The light thus thrown on bleed velocity trends as a function of slag content, which does not suffice per se to explain the variations in total bleed water values, since these range between 0.07 and 0.155 (i. e., 120 percent variation) against a maximum velocity

variation of not more than 10 percent, as well as the fact that we noted only slight variations in W_i , indicate that the flocculation effect is the chief factor. This effect is probably less marked in higher slag mixtures, where the amount of hydrolytic lime from the clinker is quite small.

NONEVAPORABLE WATER (W_n/C)

Hardened paste characteristics were determined on specimen pastes obtained by the same procedure as used for fresh paste tests.

The specimens were left in the mold for 24 hours in a damp environment (relative humidity above 90 percent); after removal from the mold they were kept in water at constant temperature (20 ± 2 C) until the date when the various assays were performed.

Nonevaporable water at a temperature of $25 \text{ C} \mp 0.001$ was determined by the method described by Copeland and Hayes (2). The values are shown in Figures 1 and 2.

A first glance at these diagrams shows that for the first five mixtures, up to a slag content of 40 percent or less, the W_n/C value is almost constant. On closer examination, however, it will be seen that for a W/C ratio of 0.22 the W_n/C value for various curing periods rises as the slag content drops (always up to 40 percent), while with longer curing periods this decrease tends to be canceled out.

For paste with a W/C ratio of 0.50, from the first curing periods the W_n/C value remains constant, again for the first five mixtures. However, with this W/C ratio the hydration velocity is obviously higher than with a W/C ratio of 0.22.

Therefore, it is concluded that, up to a certain hydration limit, the velocity of this process is decidedly higher for clinker than for slag. Beyond this degree of hydration both velocities are probably equal, consequently the quantity W_n/C is the same both for clinker and slag.

The W_n/C values (Figs. 1 and 2), for mixtures containing from 50 to 90 percent clinker, show that these curves tend to drop sharply; actually, while the slope is only

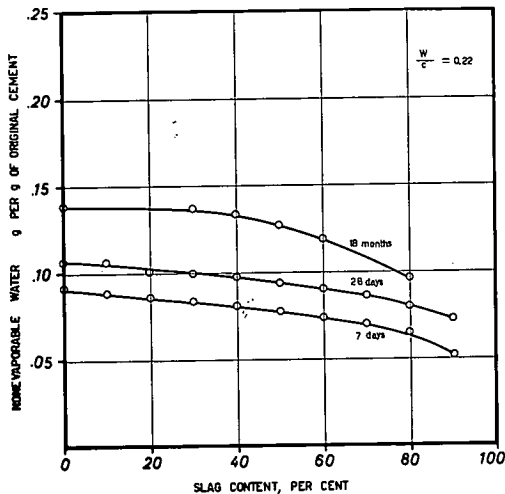


Figure 1. Nonevaporable water as a function of slag content of the cement, W/C ratio 0.22 by weight.

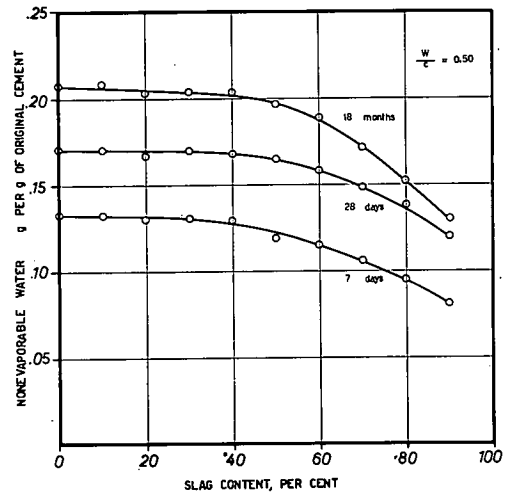


Figure 2. Nonevaporable water as a function of slag content of the cement; W/C ratio 0.50 by weight.

slight for mixtures with W/C of 0.22 after 7 days' curing, for mixtures with a much higher W/C ratio and the same curing period the slope is far steeper.

SPECIFIC SURFACE

Specific surface areas of hardened pastes were evaluated on the basis of water vapor adsorption measurements. Since our purpose was to make comparative measurements, it seems superfluous to debate whether results by this method are more or less reliable than those obtainable by nitrogen adsorption (5).

The quantity of water adsorbed at four different vapor pressures was estimated by measuring the weight increment of the various samples dried to the nonevaporable water state. The samples were placed in a water vapor adsorption apparatus, where the various relative vapor pressures were controlled by saturated solutions (4). From the adsorption data, we proceeded, applying equation BET (6, 1), to calculate V_m , a characteristic factor of the surface area with which it is directly proportional.

Values of this factor are given in Figures 3 and 4, where it can be seen that the total surface area presents a maximum for all mixtures. This maximum tallies with the mixture having equal slag and clinker content and has a tendency to increase as hydration proceeds. The curves suggest that the products of hydration of the slag are colloidal and contribute significantly to the total surface area. S was estimated on the basis of the numerical coefficient 3800 used by Brunauer, Kanthro and Copeland (7).

The variation in the K ratio between parameters V_m and W_n as a function of slag content appears of even greater interest. The value of K obtained by taking the mean of the ratios for the six different periods is given in Figure 5. The mean value was taken because, apart from slight deviations ascribable at least in part to experimental errors, K was found to be constant.

In practice, this statement may not be true in the first stages of hydration, since the hydration products might not be the same as during the later stages. Thus, in the first hours of hydration, the clinker reaction velocity is fairly high while that of the

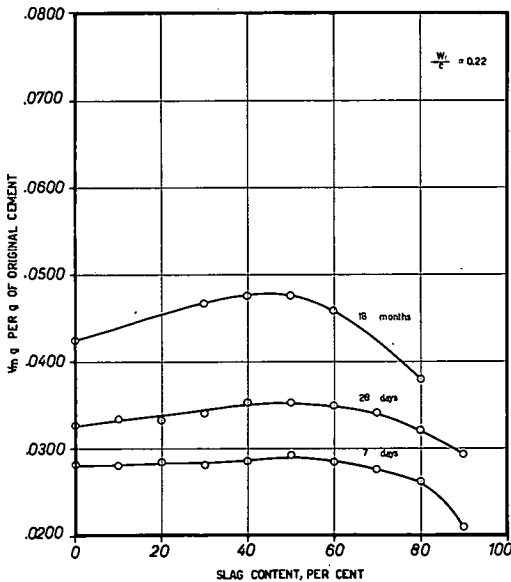


Figure 3. V_m and specific surface area S as a function of slag content of the cement; W/C ratio 0.22 by weight.

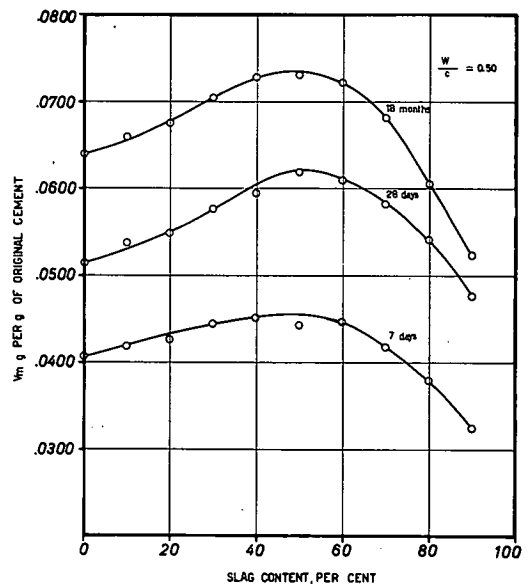


Figure 4. V_m and specific surface area S as a function of slag content of the cement; W/C ratio 0.50 by weight.

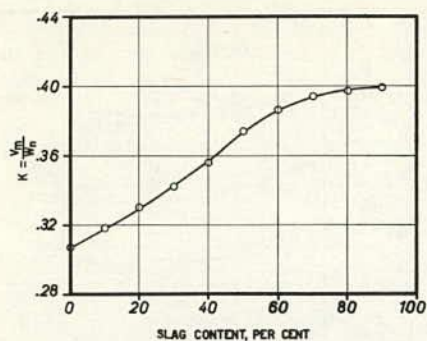


Figure 5. The relationship between V_m and non-evaporable water (W_n) as a function of slag content of the cement.

similar to those of clinker but in larger quantities (similarity is confined to the high surface area). This is probably due partly to the presence of less calcium hydroxide which, being coarsely crystalline, makes an almost negligible contribution to surface area development (1).

PASTE POROSITY

Paste porosity at various curing periods was calculated on the basis of evaporable water W_e values obtained by the Powers method (1).

Figures 7 and 8 show the volume of capillary pores of the different mixtures at various curing periods. There is a minimum quantity under all curing conditions and, for both water/cement ratios, tallying with slag content between 40 and 60 per cent; these minimum values are more clearly noticeable as hydration proceeds. It also appears that in mixtures with a low or medium slag content the reduction in capillary pore volume as a function of curing is more regular. For high slag mixtures this reduction seems to be more marked between 7 and 28 days, and is far less between 28 days and 18 months.

Figures 9 and 10 show the values of gel pore volumes of the various mixtures calculated on the basis of data reported by Copeland and Hayes (4). These curves run contrary to the capillary pore volume curves, with maximum values becoming more pronounced as curing proceeds around medium slag content (50 to 60 per cent).

Gel porosity is evidently linked with gel volume. This curve trend bears out the previous remarks on the surface area of pastes, i.e., slag, within certain limits, produces a greater surface area (and, possibly, a greater quantity of colloidal substances) as hydration proceeds.

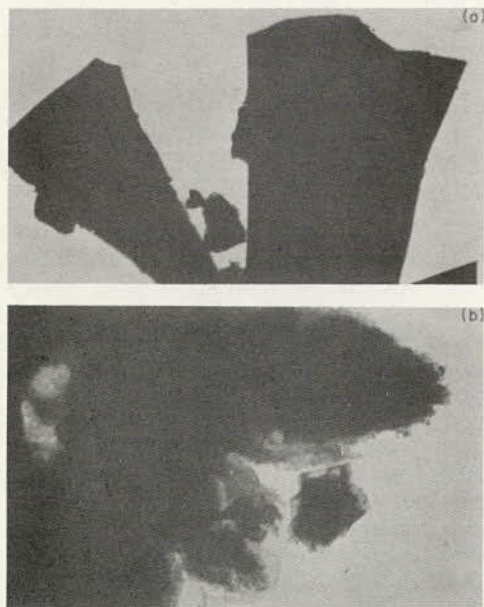


Figure 6. Portland blast furnace cement paste hydrated 1 hour (slag content 60%): (a) slag grains, and (b) clinker grains.

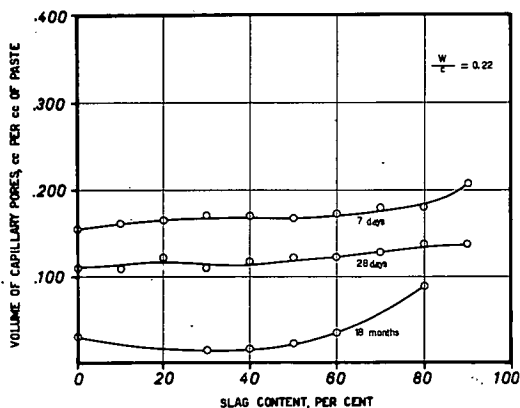


Figure 7. Volume of capillary pores as a function of slag content of the cement; W/C ratio 0.22 by weight.

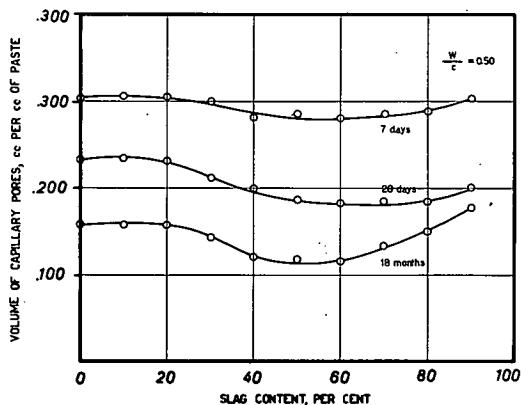


Figure 8. Volume of capillary pores as a function of slag content of the cement; W/C ratio 0.50 by weight.

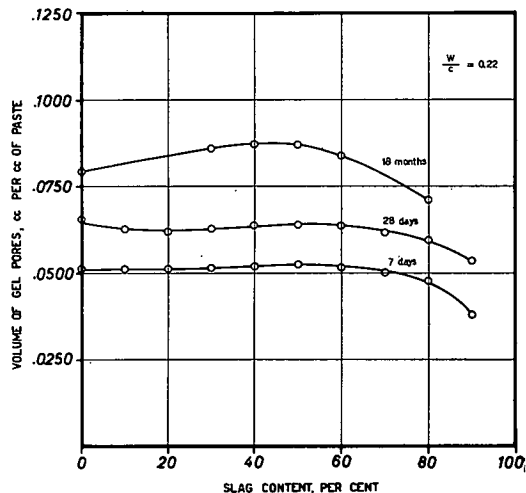


Figure 9. Volume of gel pores as a function of slag content of the cement; W/C ratio 0.22 by weight.

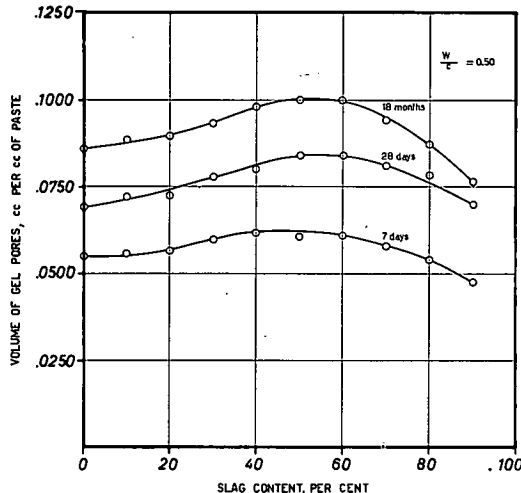


Figure 10. Volume of gel pores as a function of slag content of the cement; W/C ratio 0.50 by weight.

CONCLUSION

The conclusion to be drawn from our overall results seems that the slag tested in relation to the physical properties of the hardened paste behaves in exactly the same way as portland cement clinker. Up to 50 to 60 percent slag, no big differences are noticeable in any of the quantities characterizing the hydration process; moreover, some of these quantities evidence maxima or minima at slag levels between 50 and 60 percent, the latter percentage being typical of ordinary blast furnace cements.

This, of course, holds good particularly for mixtures where hydration appears to be more complete, since it was found that at the first curing periods and with a W/C ratio of 0.22, slag has a lower reaction velocity than clinker.

We have thus observed (Fig. 2) that nonevaporable water, starting from 28 days curing with a W/C of 0.50 (the main indication of the degree of hydration), is practically the same for all mixtures up to 50 percent slag.

We have also stressed the fact that pastes develop maximum surface areas (Figs. 3 and 4) at about the same slag percentage, while the same maximum is found in the volume of gel pores—a quantity closely related with the previous one. Capillary pore volumes, instead, are at a minimum for this mixture.

The properties of the paste, and hence of the concrete, which are adversely affected by an increase in the capillary pore volume (i. e., compressive strength, permeability, resistance to freeze and thaw) should therefore be improved by the presence of slag, at least within the limit of this composition. This is borne out by Figure 11, at least insofar as concerns compressive strength. Figure 11 gives compressive strength values obtained in tests conducted by the Cembureau-Rilem method.

It has been pointed out that above a 60 percent slag content the characteristic parameters of the process (especially the nonevaporable water) present values that gradually decrease as the slag content increases. It is conceivable that as slag hydration proceeds, microcrystalline hydration products are formed, liable to break down at relative vapor pressure 0.5 mm of Hg, so that lower values would be found when determining W_n/C .

Apart from the fact that if this were true there should be no reason why it should not apply to low slag mixtures also, an examination of Figure 12, showing quantities of water adsorbed by paste samples prepared with a W/C of 0.22 at various curing periods, rules out this assumption. It seems that the process slows down for high slag mixtures, as if the progress of the hydration process were for some reason disturbed. These adsorption tests were conducted on samples set on a vibrating table and with a practically constant water-cement ratio W_0/C —apart from small quantities of bleed water.

The samples were cured in water for up to 28 days, then in an ambient with relative humidity above 96 percent to avoid lime leaching. They were then removed from the curing chamber only for the time strictly necessary to weigh them at the various curing stages. It was noted that although the quantity of water adsorbed is constant at the outset, in case of prolonged curing high slag mixtures adsorb far less water than others, and this difference becomes more marked as curing proceeds.

The total water content of the hardened paste, W_t , can be determined (4) by

$$W_t = W_0 + 0.254 W_n$$

where W_0 is the original net (corrected for bleeding) water content of the fresh paste, and W_n is the nonevaporable water content of the hardened paste. Since the water adsorbed is equal to $W_t - W_0$, for constant values of W_0 the water adsorbed is proportional to W_n . It is therefore proven that the quantity of nonevaporable water in the high slag mixtures is really less than that of the other mixtures, and that the process

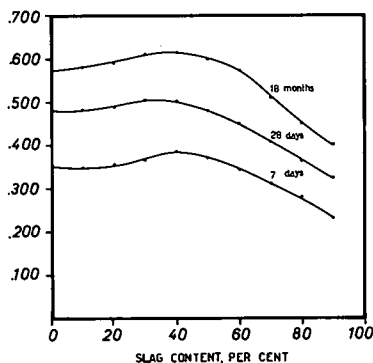


Figure 11. Effect of slag content on the development of compressive strength.

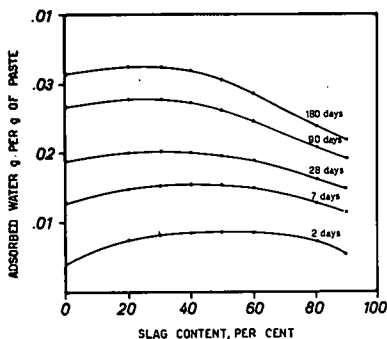


Figure 12. Relationship between slag content and water adsorbed.

of hydration is in effect actually slowed down. The causes of this slowing down in the reaction may be either physical or chemical.

As a physical cause one might suggest that the process is slowed down by the formation of a sheath consisting of extremely compact reaction products which enclose the slag grain and prevent water from penetrating to the core of the grain.

To test the acceptability of this hypothesis, and bearing in mind that some re-searchers had found the addition of gypsum to the various cements probably had a good effect on the speed of reaction (8, 9) assumedly influencing the structure, we conducted water adsorption-tests with increasing additions of gypsum to mixtures having various slag contents.

It would seem (Fig. 13) that for portland cement, at least with gypsum levels up to 4 to 6 percent, this assumption has been corroborated by our tests, in that the increase in water adsorbed accompanying the higher gypsum content points to a quicker reaction, possibly promoted by the greater ease with which the water passes through the already formed gel.

Conversely, the same thing does not occur with high slag cements (Figs. 14 and 15), where the higher gypsum content produces a drop in the adsorbed water, suggesting that the structure is already sufficiently open, even with the minimum gypsum content, and that chemical factors must play some part in slowing down hydration.

It is conceivable that above a given slag content the lime in the contact solution is not sufficient to complete the slag hydration reaction; the drop in lime is in turn to be ascribed to the pozzolanic action of the slag itself (10).

Another at least partial explanation of the reduced degree of hydration for the same curing period, observed in high slag pastes, might be the W_0/C ratio which is appreciably lower in these mixtures because of the more marked sedimentation in fresh pastes.

Obviously these conjectures must be borne out by research designed to determine—by providing conditions under which the slag can complete its reaction—the maximum end point of nonevaporable water W_n for high slag mixtures at a degree of hydration equal to I. It is along these lines that we intend to pursue our investigations on other slags with higher lime contents.

Even within the above limits and without claiming that the outcome of our tests can be considered of general application, we feel justified in concluding that the practical performance of cements containing 50 to 60 percent slag is similar to that of pure clinker products. They do evidence a slight lag in hydration in comparison with clinker cement, but if stored under appropriate curing conditions they produce more compact, more impervious and hence stronger material.

The above statement does not hold true for slag contents of about 75 to 80 percent in which the reaction develops very slowly. Nevertheless, the development of colloidal

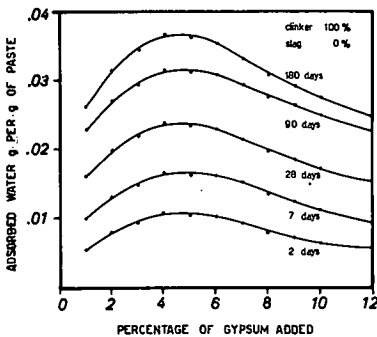


Figure 13. Relationship between gypsum added and water adsorbed in portland cement pastes.

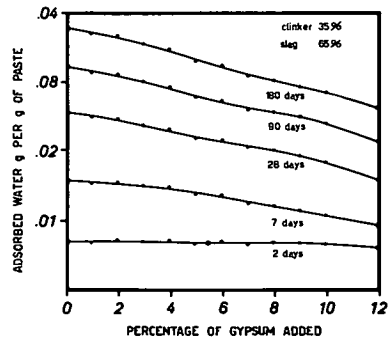


Figure 14. Relationship between gypsum added and water adsorbed in portland blast furnace cement pastes (slag content 65%).

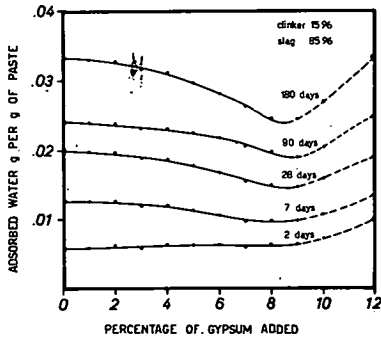


Figure 15. Relationship between gypsum added and water adsorbed in portland blast furnace cement pastes (slag content 85%).

substances, even with a limited degree of hydration, is sufficient to build up fair mechanical properties in these cements too, which are used mostly for special fields where the particular properties of slag (specifically chemical resistance and low heat of hydration) become of overriding importance.

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