# USE OF ADMIXTURES IN PRODUCTION OF LOW-POROSITY PASTES AND CONCRETES

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This paper reviews the results of studies on the development of a low-porosity, high-strength cement paste and concrete. The paste is made by mixing finely ground cement clinker, containing alkali or alkaline earth lignosulfonates, with 0.20 to 0.30 parts of water containing alkali carbonate. Concretes and mortars made with low-porosity cement paste have improved strength, dimensional stability, and other engineering properties.

•IT is commonly accepted that the water-cement ratio (w/c) of portland cement paste at a given temperature determines the porosity of the hardened paste (1, 2, 3, 4). A low w/c leads to low porosity, which, in turn, leads to greater strength and dimensional stability.

Theoretical and experimental work of Pickett (5), Helmuth and Turk (6), and others led to the conclusion that the drying shrinkage of cement paste and concrete diminishes linearly with the porosity of the paste. Thus, the two main engineering properties of concrete, namely strength and dimensional stability, can be improved by using a low w/c that results in low-porosity paste.

The previously mentioned results of experiments led to an interest in cement pastes and concretes having porosities as low as possible. Two different methods for obtaining low-porosity systems are currently under study. One method involves compaction of low w/c mixes as reported recently by Skalny and Bajza (7), Bajza (8), Lawrence (9), and Roy, Gouda, and Bobrowsky (10). The second method (11, 12, 13, 14, 15, 16, 17), discussed in this paper, makes possible a decrease in porosity by using a low w/c and by maintaining workability by the use of a suitable system of chemical additives.

## MATERIALS AND EXPERIMENTAL METHODS

All of the results were obtained on commercially available, grouped types 1 and 2 portland cement clinkers. $K_2CO_3$ was used to replace gypsum as set regulator, and a Ca-lignosulfonate has been used as a water reducer. Various grinding aids have been used as a means for obtaining Blaine surface areas above 6000 $cm^2/g$.

During the investigations, the properties of both fresh and hardened cement pastes and concretes have been studied. These include consistency, strengths, volume changes, rates of hydration, density, pore volume and surface area distributions, and absorption and environmental resistance. Details of experimental methods used are given elsewhere (13, 14, 15).

## HYDRATION OF LOW-POROSITY PASTES

### Effect of Experimental Parameters on Degree of Hydration

Degree of hydration x is defined by the equation

$$x = \frac{w_n}{w_n^o} \tag{1}$$

where $w_n^\circ$ is the nonevaporable water at complete hydration, and $w_n$ is the nonevaporable water at any given age of the D-dried paste per gram of unhydrated cement. Because the clinker minerals present in cement hydrate at different rates (18), the degree of hydration of cement as a whole does have questionable scientific meaning, mainly at early stages of hydration. However, from the practical point of view, the strength and volume changes of cement pastes and concretes are determined by the degree of hydration of the paste. Therefore, the assumption was made that all the unhydrated compounds present in the paste after 1 day of hydration continue to hydrate at equal fractional rates. If we accept the view that the rate-controlling step in this stage of the hydration reaction is the diffusion of particles through the coating of hydrates formed on the unhydrated clinker particles, the use of equation 1 is justified.

The following effects on the degree of hydration of low-porosity pastes have been studied: type of cement and grinding aid, temperature, $w/c$, and fineness of cement.

Grinding aids strongly influence the rate of hydration mainly at early stages, as can be seen in Figure 1 [pastes are hydrated at 77 F (25 C) and $w/c = 0.2$]. Of the four sets of type 2 pastes, two hydrate much faster than the two others. After 1 day, there is a sixfold difference between the pastes TMN 2 and REAX-70 2 (1 and 2 characterize the type of clinker used). The degree of hydration of the DEC 1 paste is only about one-third that of the DEC 2 paste after 1 day, but the difference can be attributed to different levels of lignosulfonate (1 versus 0.5 percent).

The fact that the induction or dormant period (as measured by degree of hydration) does not begin at zero time shows that, in addition to the grinding aid and lignosulfonate, the preventing coating (believed to cause the decrease in reaction rate in the dormant period) contains some hydration products. Actually, cement pastes not containing admixtures also exhibit a dormant period. The dormant periods of REAX-70 2 and DEC 2 pastes are very different from those of TMN 2 and AR-100 2 pastes. It seems that the last two form a coating much less pervious to water than the first two. In fact, no dormant period appears in Figure 1 for the REAX 2 and DEC 2 pastes; thus, if there is any dormant period at all, it is shorter than 1 hour.

The effect of temperature on the rate of hydration is shown in Figure 2 [pastes are hydrated at 41, 77, and 122 F (5, 25, and 50 C) from 1 to 180 days; $w/c = 0.2$]. As in other chemical reactions, the rate of hydration increases at early stages of hydration as temperature increases, and the rate decreases as the ultimate degree of hydration is approached. The induction period at 41 F (5 C) lasts for at least 3 days, but it has not been detected at the two higher temperatures.

The effect of $w/c$ on the degree of hydration is shown in Figure 3 [pastes are hydrated at 77 F (25 C) from 1 to 90 days; $w/c = 0.2$ and $0.3$]. At all ages, the degrees of hydration of the pastes made with $w/c = 0.30$ are greater than those of the pastes made with $w/c = 0.20$. The higher $w/c$ produces pastes of higher total porosity; this results in the accommodation of larger quantities of hydration products.

The effect of cement fineness on the degree of hydration was studied on types 1 and 2 clinkers ground to low and high surface areas with 0.5 percent diethylcarbonate (DEC) as a grinding aid. The levels of $K_2CO_3$ and lignosulfonate, the $w/c$, and the temperature were kept constant. The low-surface area type 2 cement had a long dormant period (at the end of 1 day, the degree of hydration was still only 15.8 percent), but the high-surface area cement was hydrated to 44.9 percent. Subsequently the gap continued to become narrower; at 14 days, the values of x were 68.3 and 70.3 percent; thus, the degree of hydration of the low-surface-area cement almost reached that of the high-surface-area cement.

The influence of the surface of the cement was much greater for the type 1 pastes than for the type 2 pastes. When the same amount (1 percent) of lignosulfonate was used for the high- and low-surface-area type 1 cement, the degree of hydration of the low-surface-area cement even after 14 days was only 23.0 percent, but the value of x for the high-surface cement was 61.8 percent.

## Mechanism of Hydration Process

The hydration of low-porosity cement pastes may be divided into three stages. After water gels in contact with cement grains, a fast hydration starts that may be called the predormant period. Soon, however, the early hydration products plus the grinding aids and the calcium lignosulfonate form an almost impervious coating on the grains, and the hydration becomes very slow. This is the dormant or induction period that starts at about 10 to 15 percent hydration and ends at about 15 to 20 percent hydration. The beginning and the duration of the induction period strongly depend on the temperature and the amount of lignosulfonate used.

During the induction stage, there is a slow reaction. Because the hydration products have larger volumes than unhydrated cement, pressure caused by newly formed hydration products may build up under the coating. This results in eventual breakup of the coating. After this happens, water again has direct access to the unhydrated grains, and the reaction speeds up. Hydration products now accumulate in the pore system, and, after the degree of hydration reaches about 30 percent, diffusion through the hydration products becomes the rate-controlling step, and the rate of hydration gradually slows down again. This is the third stage in the hydration process, and it continues until the ultimate degree of hydration is reached.

It is uncertain whether the diffusion of water through the hydration products to the unhydrated grains or whether the diffusion of the hydrated ions from the surfaces of the unhydrated grains, through the hydration products, and to water-filled pores (in which they can precipitate and form new hydration products) is the slowest and therefore rate-determining step. For convenience it was assumed that the slow step is the diffusion of water to the unhydrated grains.

The formation of the hydration products is accompanied by the formation of very small pores, called gel pores. As the hydration progresses, these pores become narrower, and the path through which molecules or ions must diffuse becomes longer. Thus, diffusion becomes slower as the amount of hydration products increases. Because the clinker minerals hydrate at different rates (as mentioned previously), only the third stage of hydration was found amenable to discussion of the kinetics in quantitative terms.

Analysis of the process has shown that, in addition to the amount of unhydrated cement in the paste and hydration products formed and the original w/c, the rate of hydration is a function of the volume of the hydration products at equal degrees of hydration. This volume, in turn, depends on the composition of cement present in the paste. The results indicate that the retardation of the rate of hydration is becoming increasingly greater as the pore space becomes more and more filled by newly formed hydration products. These products cause even greater retardation of the diffusion of water to the unhydrated grains.

For example, DEC 1 pastes, hydrated at the same temperature and with the same w/c, hydrated more slowly than DEC 2 pastes. On the basis of the compositions of the two clinkers, one would expect only a slight difference, if any, in the hydration rates at the beginning of the third stage.

It seems, therefore, that the double amount of lignosulfonate in the type 1 cement has a considerable effect not only on the early stages of hydration (e.g., Figure 1) but even in the beginning of the third stage.

The difference between the ultimate degree of hydration of these two pastes (75.4 percent for DEC 2 versus 69 percent for DEC 1) may also be due partly to the same cause. The double amount of lignosulfonate in the DEC 1 pastes may make the hydration products less pervious to water; thus, a negligible hydration rate may be reached when the amount of hydration products in the pore system of the paste is smaller than that in the DEC 2 paste. As discussed earlier, however, the volume of the hydration products, at equal values of x, in the type 1 pastes was 5 percent greater than that of the type 2 pastes, and this may explain the differences found in the rate of hydration.

The apparent energy of activation can be evaluated without reference to any mechanism if the rate of hydration is known at, at least, two different temperature levels and if the rate of the reverse reaction is negligible compared with the rate of the forward

reaction. This is certainly true for the hydration of portland cement. If a single step in a complex process is the rate-controlling step, the rate of reaction can be expressed as the product of the function of the temperature only and the function of the composition variables only. The apparent energies of activation (an indication of relative energy barriers) were evaluated for DEC 1, DEC 2, and REAX-70 2 pastes, with w/c = 0.20, by using the equation

$$\frac{d\ell n \left[ -\dfrac{d(100 - x)}{dt} \right]}{d(1/T)} = \frac{d\ell n k(T)}{d(1/T)} \tag{2}$$

DEC 1 pastes gave excellent straight lines. Figure 4 shows this as an Arrehenius plot of log R versus 1/T, where R is the rate and T is the absolute temperature. The points were obtained from three DEC 1 pastes, each with a 40 percent degree of hydration at 41, 77, and 122 F (5, 25, and 50 C). The slope multiplied by 2.303 gave an apparent energy of activation of 4,700 cal (19.7 MJ), rounded to the nearest 100 cal (418 kJ), for 40 percent hydration. The apparent energies of activation for 50 and 60 percent hydration were 6,300 and 7,700 cal (26.4 and 32.2 MJ) respectively. The increases in apparent energies of activation with progressing hydration indicate that the energy barrier to diffusion becomes greater as the hydration products keep on accumulating in the pore system. One possible reason for this is the formation of more constructed entrances of the ink-bottle pores, i.e., pores with wide bodies and narrow entrances.

The 122 F (50 C) curve for REAX-70 2 was out of line with the others; consequently, only the 41 and 77 F (5 and 25 C) curves could be used for the calculation of the energies of activation. The values for 40, 50, and 60 percent hydration were 9,000, 10,600, and 11,200 cal (37.7, 44.4, and 46.9 MJ) respectively. The trend with progressing hydration was the same as that for DEC 1, but the values were much higher.

The DEC 2 pastes did not give good straight lines. Nevertheless, it is worth noting that the apparent energies of activation for DEC 2 at 40 and 50 percent hydration were 10,800 and 9,000 cal (45.2 and 37.7 MJ) respectively. These are almost exactly the reverse of the values given above for REAX-70 2. Thus, in spite of the questionable results, it can be concluded that the apparent energies of activation for REAX-70 2 and DEC 2 were about equal and were higher than the values obtained for DEC 1. Apparently, for some reason, the energy barrier is higher for the type 2 pastes than for the type 1 pastes.

### Action of Admixtures

The effect of $K_2CO_3$ on the setting time and strength development of cement mortars was studied by Niël ([20]). He concluded that $K_2CO_3$ affects the early hydration process through an interaction with the $C_3A$ and gypsum in the cement. In that the materials system used in this study did not contain gypsum, the results obtained by Niël are only partly applicable to the present work. However, in agreement with our results, Niël found that $K_2CO_3$, up to a certain level, improves workability, prolongs setting times, and increases early strength.

The interaction of $K_2CO_3$ with $C_3S$ was studied by several authors ([15, 21, 22]). It was shown that, in the absence of retarding admixtures (such as lignosulfonates), $K_2CO_3$ accelerates the hydration of $C_3S$. It causes changes in the compositions of liquid phase and in the composition and microstructure of hydrates formed. Presence of $K_2CO_3$ causes complicated heat effects in the first hour of hydration; the mechanism of these effects is not known as yet.

Based on theoretical considerations and limited amount of experiments, Brunauer et al. ([13]) suggested a probable mechanism for the effect of the additives and admixtures on the hydration of low-porosity cements. The effect of $K_2CO_3$ in the low-porosity

pastes is similar in part to the effect of gypsum in normal cement pastes. In place of the sulfoaluminate, the carbonate ions form a carboaluminate, which is partly responsible for the retardation of the fast set. However, the 0.5 percent $K_2CO_3$ used in the present work is not sufficient to convert the $C_3A$ into carboaluminate even in the type 2 cement, which contains only 1.4 percent $C_3A$. Besides the retarding action of $Ca(OH)_2$ and of the carbonate ion, it is the coating formed by the grinding aid and calcium lignosulfonate that probably makes an important contribution to the prevention of flash setting.

$K_2CO_3$ has two other effects besides the formation of carboaluminate. Alkalies increase the rate of hydration of cement. The potassium part of $K_2CO_3$ forms KOH. This decreases the solubility of $Ca(OH)_2$. Thus, the carbonate ion acts as a retarder, but the potassium part of the compound acts as an accelerator.

The third effect of $K_2CO_3$ is connected with the calcium lignosulfonate additive. The lignosulfonate ion is adsorbed on the cement grains. The unhydrated grain surfaces are predominately composed of oxide ions; it is possible, therefore, that calcium and lignosulfonate ions are jointly adsorbed or are adsorbed as molecules. Nevertheless, this is not necessarily true. Kane, La Mer, and Linfor (22) have shown that large negative ions may be adsorbed even on negatively charged surfaces because the attractive van der Waal's forces may overcome the electrostatic propulsion.

The mechanism of the joint action of $K_2CO_3$ and lignosulfonate is probably the following. Without the presence of $K_2CO_3$, the calcium lignosulfonate would quickly precipitate out of the solution because there are enough calcium ions in the aqueous phase of hydrating cement to exceed its solubility product. However, the $K_2CO_3$ produces $OH^-$ ions, which diminish the concentration of the $Ca^{++}$ ions in the solution; therefore, the lignosulfonate is not precipitated. This gives the lignosulfonate ions a chance to be adsorbed on the grains of the cement.

## PROPERTIES OF LOW-POROSITY CEMENT PASTES

### Workability and Setting Time

Because of the low w/c and the absence of gypsum in the low-porosity cement, special emphasis was given to the question of setting time and consistency. An arbitrary empirical scale was adopted for the consistency, and a paste flowing into a mold with no other help than gravity was considered to be of ideal consistency. As expected, the setting times and the consistency of the pastes depend on several factors, such as surface area of cement, type and amount of additives, temperature of curing, and type of cement. From the investigations, several conclusions were made:

1. The same quantities of different grinding aids, under otherwise constant conditions, have different effects on the consistency and setting time,
2. The grinding aid determines the consistency and setting times in conjunction with the other additives,
3. Increasing the $K_2CO_3$ and lignosulfonate content above certain value does not necessarily improve the properties of paste, and
4. For different clinkers, different amounts of grinding aid, $K_2CO_3$, and lignosulfonate give the optimal consistency.

It is believed that, for different applications of low-porosity concrete, cements giving desirable workabilities and setting times can be produced.

### Porosity and Pore Structure

In the study of total surface areas, total pore volumes, and the pore volume and surface area distributions of low-porosity pastes, nitrogen and water vapor were used as adsorbates. One clinker type, two different grinding aids, two w/c, and three

temperatures were the variables.

It was found that the nitrogen molecules were unable to penetrate not only into the micropores (widths < 20 Å) but even into many wider pores in spite of the fact that the diameter of a nitrogen molecule is only 3.5 Å. This is explained by the presence of ink-bottle pores. As the hydration progresses, a part of the wide pores is converted into micropores. After 1 day, about one-half of the surface of the pastes is located in the micropores; the fraction increases to about three-fourths after 28 days. The grinding aid has an important effect on the pore volume and surface distribution. With REAX-70 2 as grinding aid, a larger fraction of the pore volume of the pastes is in micropores and a smaller fraction is in wide pores than with DEC as grinding aid.

Some differences in the strength of low-porosity pastes can be explained by the differences in the pore-volume distribution. This factor was found to be complementary to the degree of hydration and total porosity.


## Compressive Strength

The strength of hardened portland cement paste is usually correlated with degree of hydration and total porosity. As hydration progresses, the total porosity decreases because the hydration products occupy a greater volume than the unhydrated cement. Consequently, a part of the hydration products deposit in the pores. Thus, the two effects work in the same direction. The compressive strength results show good correlations with degree of hydration and with total porosity. Figure 5 shows the early strength development of DEC 1 and TMN 1 pastes, hydrated at 77 F (25 C) from 1 to 72 hours, with w/c = 0.2. The dormant period of the DEC 1 pastes is about 1 day, after which the strength increases sharply. The dormant period for strength development is not the same as for the degree of hydration because strength development is not a function of the degree of hydration only.

The dormant period of the TMN 1 pastes is only about 15 hours; thus, the difference of the 1-day strengths between DEC 1 and TMN 1 is very great. Obviously TMN, together with the lignosulfonate and the hydration products, forms a coating that is more pervious to water than that formed by DEC.

The early strength development of the type 2 pastes is shown in Figure 6 [pastes are hydrated at 77 F (25 C) from 1 to 72 hours; w/c = 0.2]. Compressive strength and degree of hydration at 1 day are very low for TMN 2 and AR-100 2, and they are high for REAX-70 2 and DEC 2. However, a new factor appears here. On the basis of degree of hydration and porosity, the REAX-70 2 pastes should have slightly higher compressive strengths than the DEC 1 and 2 pastes, but, both at 1 day and 3 days, they are about 4,000 psi (27.6 MPa) lower than those of the DEC 1 and 2 pastes. Thus, there must be at least one other factor, besides degree of hydration and porosity, that has an influence on strength. It was found to be the pore volume distribution.

Grinding aids probably have some effect on the final strength, but, if so, the effect is not very great. The final strengths of the pastes made from types 1 and 2 cement and ground with the same grinding aids were found to be nearly equal.

The temperature dependence of the compressive strength was investigated for the DEC 1, DEC 2, and REAX-70 2 pastes. The strength gain is enhanced by increasing the temperature. The dormant periods at 41 F (5 C) are much longer than at 77 F (25 C). At every age, the strength is higher at higher temperatures. For example, the final strength of the DEC 1 paste at 122 F (50 C) measured after 90 days of hydration is 40,000 psi (275.8 MPa). At the same age, the 77 F (25 C) paste has a compressive strength of 34,600 psi (238.6 MPa). For the 41 and 77 F (5 and 25 C) pastes, strengths were measured at 180 days; they are 27,000 and 36,400 psi (186.2 and 238.6 MPa) respectively. It is not likely that the strengths of the 122 F (50 C) pastes would have increased significantly after 90 days, nor is it likely that the strengths at 77 F (25 C) would have increased significantly after 180 days. The strengths at 41 F (5 C) would probably have increased after 180 days, but it is very unlikely that they would have reached an ultimate strength as high as those for the 77 F (25 C) pastes. Thus, the ultimate strength appears to increase significantly as temperature increases.

**Figure 1. Degree of hydration versus time of four sets of type 2 and one set of type 1 pastes from 1 hour to 7 days.**
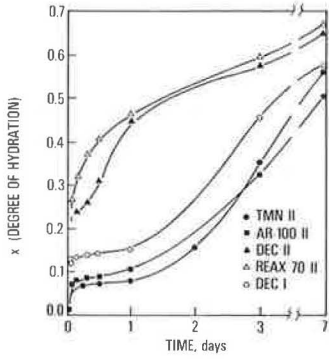


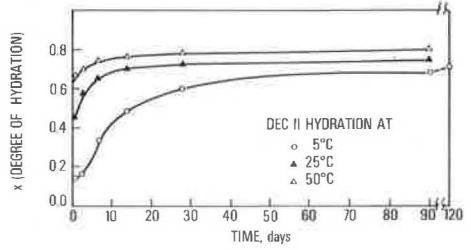**Figure 2. Degree of hydration versus time of DEC 2 pastes.**



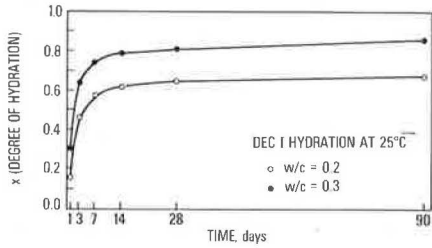**Figure 3. Degree of hydration versus time of DEC 1 pastes.**
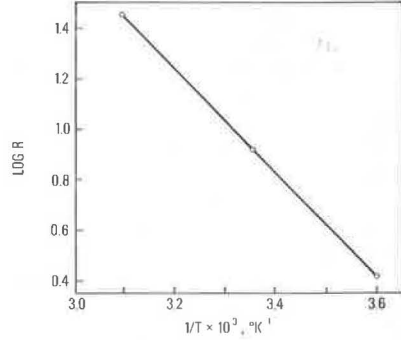


**Figure 4. Arrehenius plot of log R versus 1/T.**



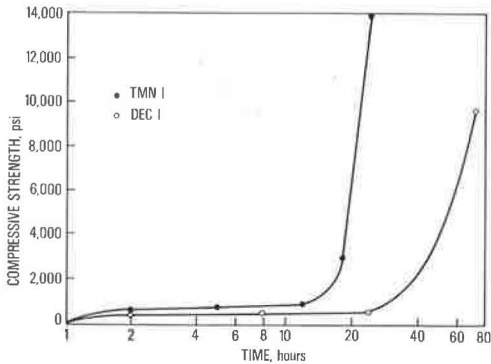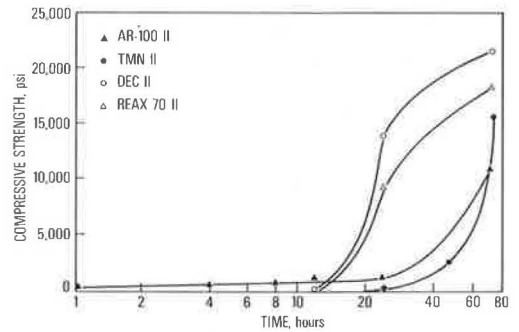**Figure 5. Compressive strength versus time of DEC 1 and TMN 1 pastes.**



**Figure 6. Compressive strength versus time of four sets of type 2 pastes.**

Similar results were obtained for the other pastes.

The dormant period of the DEC 1 pastes made with w/c = 0.3 is about the same as that of the pastes made with w/c = 0.2; it is about 1 day. At 3 days, the paste with the higher w/c appears to have somewhat higher strength, though this may be within the experimental error. From then on, the pastes with the lower w/c increase in strength much faster than the others. The strengths of the pastes with w/c = 0.3 level off after 28 days; the 29, 90, and 180-day strengths are all approximately 25,000 psi (172.4 MPa). Thus, as expected, the final strength is much lower than that of the paste with w/c = 0.2. The pastes with the higher w/c have a higher degree of hydration, but this is greatly overcompensated by the much higher porosity of these pastes. The porosities at 90 days of the pastes with w/c = 0.2 and 0.3 are 17.2 and 27.7 percent of the paste volume respectively.

The DEC 2 pastes gave somewhat different results. The dormant period of the pastes with w/c = 0.2 is very short; therefore, at the age of 1 day the paste already has a strength of 14,000 psi (96.5 MPa). The dormant period of the paste with w/c = 0.3 is much longer; therefore, at 1 day the strength is almost nil. Because of this, the strengths of the pastes with w/c = 0.3 are lower at all ages. The final strength of the paste with w/c = 0.3, measured at 90 days, is 29,000 psi (199.9 MPa). At the same age, the paste with w/c = 0.2 has a strength of 35,200 psi (242.7 MPa). The difference is again due to the difference in porosity.

The effect of the surface area of the cement on compressive strength was investigated for the DEC 1 and DEC 2 pastes at 77 F (25 C), from 1 day to 28 days in which w/c = 0.2. The dormant period of the DEC 1 pastes of the high-surface cement (7600 $cm^2$/g) is 1 day; that of the pastes of the low-surface cement (4300 $cm^2$/g) is 3 days. It is clear that the coating on the low-surface cement grains is much thicker.

The DEC 2 pastes of the high-surface cement (8400 $cm^2$/g) have a very short dormant period; those of the low-surface cement (4000 $cm^2$/g) have a dormant period of 2 days. The 28-day strength of the paste of the high-surface cement is 27,000 psi (186.2 MPa); that of the low-surface cement is only 3,000 psi (20.7 MPa) lower. However, the strength values of the pastes of the low-surface cement appear to flatten out and may not be much higher at later ages; however, there is a greater further increase in the strengths of the pastes of the high-surface cement.

As mentioned previously, there must be at least one other factor besides degree of hydration and total porosity that has a significant influence on compressive strength. A possible explanation of the strength differences may be found in the pore volume distribution. Further studies are needed to substantiate this claim.

## Dimensional Changes

Two different dimensional changes were studied in this project: the expansion of the fresh cement paste and the drying shrinkage of hardened cement paste. The expansion was calculated, but the drying shrinkage was obtained experimentally.

The expansions of the pastes were calculated from the equation

$$\text{Exp} = 100(v_p - v_{p\ theor})/v_{p\ theor} \tag{3}$$

where $v_p$ is the actual volume of the paste produced by the hydration of 1 g of cement, and $v_{p\ theor}$ is the volume of the paste without expansion. Two opposing factors influence this expansion. The hydration products have greater volume than the unhydrated cement, and, because the pore space in this paste is limited by the low w/c, the accumulation of the hydration products builds up an internal pressure that tends to enlarge the paste, thus increasing the pore volume available for further hydration. This internal pressure is resisted by the increasing strength of the paste. After the paste reaches certain strength, it also acquires a stable volume. The above hypothesis explains the fact that the expansion of a paste depends on the initial w/c. The greater

this ratio is, the greater the available internal pore space and the smaller internal pressure will be. Consequently, greatest expansion values are expected, and were found, in low-porosity pastes studied.

The work on drying shrinkage showed

1. Type 2 pastes exhibited considerably less shrinkage after 1 day of curing than the type 1 pastes, but after 28 days of curing the differences were slight;
2. Shrinkage differences due to different grinding aids were slight;
3. After 28 days of curing, pastes of clinkers ground to specific surfaces of about 6500 $cm^2/g$ showed less shrinkage than those of clinkers ground to specific surfaces of about 7500 $cm^2/g$ or greater; and
4. The low-porosity pastes showed one-third to one-half as large length changes as pastes made from the same cement with w/c = 0.4 and one-fourth to one-third as large as those made with w/c = 0.6. Therefore, volume changes can be greatly reduced by using low-porosity cement pastes.

## PROPERTIES OF LOW-POROSITY CONCRETES

It has been shown previously that the engineering properties of low-porosity cement pastes are influenced by variables such as cement composition and surface area, w/c, type and amount of additives, and temperature of curing. Properties of low-porosity concretes are also influenced by variables such as the type, composition, and grada-tion of sand and aggregate. The concrete studies were related mainly to workability and strength development problems.

### Workability

It was soon realized that a combination of admixtures that gives excellent properties to a fresh and hardened cement paste is not necessarily the best combination for use in concrete. The concentrations of Ca-lignosulfonate and $K_2CO_3$ had to be increased from 0.5 to 0.65 and from 0.5 to 1.00 percent respectively to obtain workable mixes. These are typical values; the optimum concentrations depend on the grinding aid used. Even at the mentioned levels of admixtures, the setting time was shorter than that of normal concretes having the same slump.

Figure 7 shows the effect of the w/c on workability, as measured by the Vebe con-sistometer for three Blaine cement surface areas. The 6000-$cm^2/g$ cement at 32 sec of vibration, which is the upper limit of extremely dry concrete according to standards, yielded a concrete with approximately $1\frac{1}{2}$-in. (3.8-cm) slump. Vibration times for concretes with w/c < 0.3 were excessively long, sometimes as long as 3 min. The workability problem has not been conquered because comparatively long vibrating times are required to compact the concrete.

### Strengths

In spite of some problems with the workability of low-porosity concretes, specimens with a w/c as low as 0.26 were cast. Contrary to the early strength development in cement pastes, that of moist-cured concrete was strongly retarded by the admixtures present. Steam curing had to be used to obtain very high early strengths. The differ-ence between paste strengths and concrete strengths may be explained by a weaker bond, caused by the admixtures used, between the aggregate and cement paste at early stages of hydration.

Concretes made of cements ground to three Blaine surface areas were steam cured for various lengths of time. Some results are shown in Figure 8. All 6 by 12-in. (15.2 by 30.5-cm) specimens had preset times of 1 hour and a 40 F (4.4 C)/hour tem-perature rise to 150 F (65.6 C), at which they were soaked for various times. When

Figure 7. Workability versus water-cement ratio for concretes made with cements having different Blaine surface areas.
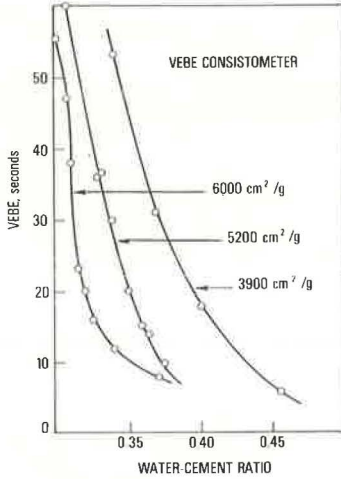


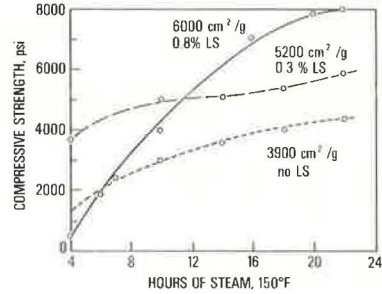Figure 8. Compressive strengths of concretes made with cements of different surface areas.



Table 1. Strengths of concretes made with Blaine and control cement samples.

| Sample | Steam Temperature (F) | Curing Time (hours) | Modulus of Rupture[a] (psi) | | | Compressive Strength[b] (psi) | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1-Day | 7-Day | 28-Day | 1-Day | 7-Day | 28-Day |
| Blaine | 130 | 4 | 759 | 933 | 1,148 | 6,213 | 10,800 | 13,033 |
| | 130 | 20 | 1,082 | 1,060 | 1,466 | 10,364 | 12,600 | 14,190 |
| | 150 | 15 | 1,075 | 1,180 | 1,543 | 12,675 | 14,813 | 14,300 |
| | 150 | 20 | 1,008 | 1,208 | 1,306 | 10,808 | 11,780 | 14,525 |
| | 170 | 4 | 1,010 | 1,020 | 1,163 | 9,482 | 11,838 | 14,734 |
| | 170 | 10 | 953 | 1,090 | 1,350 | 11,766 | 12,875 | 13,000 |
| Control | 130 | 4 | 661 | | 980 | 3,725 | | 6,175 |
| | 130 | 20 | 848 | | 1,022 | 5,904 | | 7,500 |
| | 150 | 15 | 724 | | 1,036 | 4,450 | | 6,713 |
| | 170 | 4 | 744 | | 882 | 3,875 | | 6,875 |
| | 170 | 20 | 760 | | 946 | 5,520 | | 7,720 |

Note: Cement: aggregate = 1:5 and sand:rock = 2:3. 1 F = 1.8 (C) + 32. 1 psi = 6.9 kPa.
[a]For 2 by 2 by 12-in. (5.1 by 5.1 by 30.5-cm) beams.     [b]For 2 by 2-in. (5.1 by 5.1-cm) cubes.

they were removed, they were allowed to cool for 1 hour and then tested. All batches were made with a 1:5 cement-aggregate ratio, and different levels of the Ca-lignosulfonate admixture were used, depending on the cement fineness. The 3900-$cm^2$/g system had a typical rise. The 5200-$cm^2$/g system was slightly retarded but then rapidly gained strength. The 6000-$cm^2$/g system was retarded for almost 4 hours, but the strength rise was very sharp to an eventual 8,000-psi (55.2-MPa) strength after 22 hours of steaming.

A comparison of some typical concretes prepared with both a normal type 2 cement and a 6000-$cm^2$/g Blaine special cement made from the same type 2 clinker is given in Table 1. All 6000-$cm^2$/g Blaine cement samples were prepared by using w/c = 0.26; 0.5 percent Ca-lignosulfonate and 0.9 percent $K_2CO_3$ by weight of cement were added. The 3000-$cm^2$/g control samples made with w/c = 0.41 had a 1-in. (2.5-cm) slump. In all cases, saturated surface dry aggregate was used. All samples had preset time of 1 hour. On an average, 100 percent higher compressive strength and 30 percent higher moduli of rupture were obtained for samples made from the 6000-$cm^2$/g cement.

## Other Properties

Shrinkage tests included both steam-cured and moist-cured samples. Steam curing was performed at 150 F (65.6 C) for 15 hours and at 130 F (54.4 C) and 170 F (76.7 C) for 4 hours. Without exception, all samples had lower shrinkage than the limit given by Structural Engineers Association of California [0.032 percent for 4 by 4 by 12-in. (10.2 by 10.2 by 30.5-cm) specimens; 0.415 percent for 3 by 3 by 12-in. (7.6 by 7.6 by 30.5-cm) specimens], and a majority of the samples had lower shrinkage than the control samples made from type 2 cement. Because of the limited amount of tests and samples, no quantitative conclusions similar to those given by Brunauer, Skalny, and Yudenfreund (12) can be given at this time.

The beams for freeze-thaw resistance were made by using the mix design and mixing conditions that gave the highest 28-day compressive strengths. Two different steam-curing temperatures and periods were used. Low-w/c concrete performed much better than the controls, as would be expected because of its higher density. At 100 cycles, all beams appeared to be unaffected. At 135 cycles some beams had begun to develop small cracks along the upper surface, but no scaling was yet visible. The affected specimens were those that had the longer steam-curing periods (15 hours), both at 130 F (54.4 C) and 170 F (76.7 C). No air-entraining agents were used.

## SUMMARY

The results show that it is possible to prepare workable cement paste and concrete mixes at lower than usual w/c and that these ratios at the same time will give higher early and ultimate strength and better dimensional stability. However, the technical problems connected with larger scale production of low-w/c concretes are far from being solved. The mechanisms of the interaction of the different admixtures used with the clinker minerals, both individually and in the presence of others, should be investigated more thoroughly. The presence of sand and aggregate in concrete mixes adds to the long list of variables.

The combination of admixtures used in this study is not optimal, and admixture systems giving better workability and strength should be available in the future; however, these were not available when this study was initiated.

## ACKNOWLEDGMENT

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