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BACKSCATTERED ELECTRON IMAGING OF CEMENT PASTES CURED AT ELEVATED TEMPERATURES

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ABSTRACT

The microstructure of cement pastes containing 5% silica fume or 30% ground granulated blast furnace slag was investigated in comparison with plain portland cement pastes. The pastes were cured at constant temperatures of 23°C and 70°C to degrees of hydration of 30 and 70% as indicated by the nonevaporable water content. Backscattered electron images indicate that in general, elevated temperature curing results in a coarser, more continuous pore structure. Both silica fume and slag are effective in reducing the size and continuity of the pores. These results are consistent with measurements of the rate of diffusion of chloride ions through comparable concretes subjected to the same curing conditions.

Introduction

In concrete practice, elevated temperatures occur as a result of hot weather, accumulated heat of hydration, and/or steam curing to accelerate the strength gain. Kjellsen, Detwiler, and Gjørv (1) studied the influence of curing temperature on the microstructure of plain portland cement paste and found that low curing temperatures resulted in uniformly distributed hydration products and fine, self-contained pores. Elevated temperatures, however, resulted in nonuniformly distributed hydration products and coarse, interconnected pores. Tests of chloride ion penetrability on portland cement concrete by the same authors (2) confirmed their hypothesis that the more open pore structure resulting from elevated curing temperatures would adversely affect the resistance of the concrete to the ingress of harmful species. They suggested that the use of slag, silica fume and/or fly ash might mitigate the effects of elevated temperature curing. Detwiler, Fapohunda and Natale (3) tested this hypothesis and found that both slag and silica fume were beneficial in reducing the rate of diffusion of chloride ions through concrete. Campbell and Detwiler (4) found that by optimizing the dosages of slag and silica fume, they were able to reduce the charge passed in six hours by 0.45 w/s steam cured concretes from above 10,000 coulombs for the control to 200 coulombs for concretes containing slag and silica fume.

The main objective of this study was to investigate the effect of silica fume or blast furnace slag on the microstructure of portland cement pastes cured at elevated temperatures. The results are then

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used to interpret the diffusivity of comparable concretes cured at the same temperatures. Since both the combinations of cementitious materials and the curing temperature affect the rate of hydration, comparisons are based on the degree of hydration rather than the age of the pastes.

Experimental Procedure

Cement pastes with 5% silica fume or 30% blast furnace slag by mass were compared with control pastes made from 100% portland cement. A water/solid material ratio (w/s) of 0.5 was used for all pastes. No chemical admixtures were used in this study. The physical and chemical characteristics of the materials are as described in the table below.

Characteristics of Cementitious Materials Used

Compound	Cement	Silica fume	Slag
SiO_2,%	21.86	93.21	37
Al_2O_3,%	4.24	0.82	9.69
Fe_2O_3,%	3.09	0.06	0.24
CaO, %	62.25	0.00	35.94
MgO, %	3.12	0.46	13.93
Na_2O,%	0.23	0.09	0.38
K_2O,%	0.42	1.17	0.48
SO_3,%	2.56	0.43	3.98
LOI, %	3.06	2.56	0.00
Fineness, m^2/kg	403	23,000	400
Relative density	3.12	2.22	2.92

The pastes were mixed in a high-speed blender with water. A vacuum was applied during mixing to eliminate air bubbles from the paste. Prior to mixing the pastes to be cured at 70°C, the mixing water, mould and blender bowl were warmed to about 35°C. This temperature was selected as a compromise between 20°C, which might cause problems with cracking due to thermal shock when the specimens were introduced into the curing chamber, and 70°C, which would cause the specimens to stiffen too quickly. After casting, the specimens were immediately placed in the appropriate curing temperature environment. They were rotated for the first four hours to prevent segregation.

The degree of hydration was determined from the non-evaporable water content. Non-evaporable water contents for bottle-hydrated samples of the same materials at approximately 100% hydration had been previously determined by Hooton (5). The degree of hydration for each specimen was determined by the ratio of its non-evaporable water content to that of the comparable "100% hydrated" paste. This method assumes that the ratio of non-evaporable water to the degree of hydration of the pastes is constant and is not influenced by temperature within the range used. The amount of non-evaporable water was determined by the total mass loss in the paste on heating from 105°C to 1055°C. Loss on ignition due to the volatile material present in the original materials was also taken into account.

After curing to the desired degrees of hydration (30% and 70%) the specimens were immersed in iso-propanol to dehydrate. They were cut using a low-speed diamond saw and impregnated with epoxy before grinding and polishing. No water was used in the preparation of the specimens. Cao (6) describes the procedures of the SEM sample preparation in more detail. The samples were coated with carbon before examination. In the microscopy study, a magnification of 500X was selected and 20 fields were qualitatively examined for each specimen. A voltage of 15 kV and working distance of 15 mm were used for this work.

Results and Discussion

Portland Cement Paste

30% Hydration

Figure 1 shows a portland cement paste hydrated at 23°C to a degree of hydration of about 30%. A number of thin plates of $Ca(OH)_2$ can be observed. A thin rim of C-S-H has already formed mainly on the small cement grains (bright white), indicating that the small grains are more active due to their larger specific surface. More massive $Ca(OH)_2$ crystals (light grey) in the centre of the micrograph were also formed, beginning to fill in the pore space (black area). The paste has an open, porous structure.

The microstructure of the paste cured at 70°C to approximately the same degree of hydration is shown in Figure 2. The thin plate formations characteristic of the paste hydrated at 23°C cannot be seen here. Instead, the $Ca(OH)_2$ has formed in clumps. In the middle left of the photograph is a hollow grain with a visible remnant of anhydrous material (Hadley grain). On the lower right side, there are a number of completely empty pores of similar size. The unhydrated remnant grains may have been plucked from the specimen surface during polishing. The structure of the matrix looks more densely packed. It appears that the reaction products, to a large extent, have formed through-solution and precipitated in the open space. In comparison with the paste cured at 23°C, the paste cured at 70°C has a more scattered distribution of $Ca(OH)_2$, probably due to the lower solubility of $Ca(OH)_2$ at the higher temperature.

70% Hydration

Figure 3 shows a portland cement paste cured at 23°C to approximately 70% hydration. The microstructure is characterized by well-developed C-S-H shells surrounding the cement grains and massive formations of $Ca(OH)_2$. The matrix structure is obviously much more densified and the pore structure appears more discontinuous than that of the paste at 30% hydration.

Figure 4 shows a comparable paste cured at 70°C to the same degree of hydration. The microstructure of this paste is characterized by a large number of big Hadley grains which make the structure appear extremely porous, even more porous than that at 30% hydration (Figure 2). The hydration shells are well developed at this stage as well. A grain with an annular ring can be seen in the upper right quadrant. The grain appears to have been consumed and replaced by inner product. This particular grain serves as evidence that both outer and inner products have been formed at the later stage of hydration. It is possible that the remnant unhydrated cement grain was plucked out during the preparation of the specimen.

Silica Fume Cement Pastes

30% Hydration

The microstructure of the silica fume cement paste cured at 23°C was found to be uniformly developed in the intergranular space, as shown in Figure 5. More hydrates have formed in the matrix area than around the cement grains. Small formations of $Ca(OH)_2$ can be seen. Compared with the paste without silica fume at the same maturity and curing temperature (Figure 1), there are few plate-like formations of $Ca(OH)_2$ in the silica fume cement paste. The Hadley grains are more prevalent than in the portland cement paste. The silica fume cement paste has a much less porous matrix structure than does the comparable portland cement paste. The absence of large calcium hydroxide formations in the silica fume cement paste indicates that silica fume has the effect of refining the structure of the hydrated paste. This is likely due to both nucleation and filler effects. Grain refinement has the effect of densifying the microstructure of the paste as Mehta (7) has observed.

Figure 6 shows a comparable paste cured at 70°C to 30% hydration. A noticeable difference from the paste cured at 23°C is that the $Ca(OH)_2$ formations are less clustered. While the distribution of hydration products is still relatively uniform, there appear to be more large, continuous pores between the cement grains.

In general, at 30% hydration the pastes containing silica fume have a denser microstructure than the pastes without silica fume. The curing temperature appears to have influence on the microstructure of the silica fume cement paste than on that of the portland cement paste at this stage.

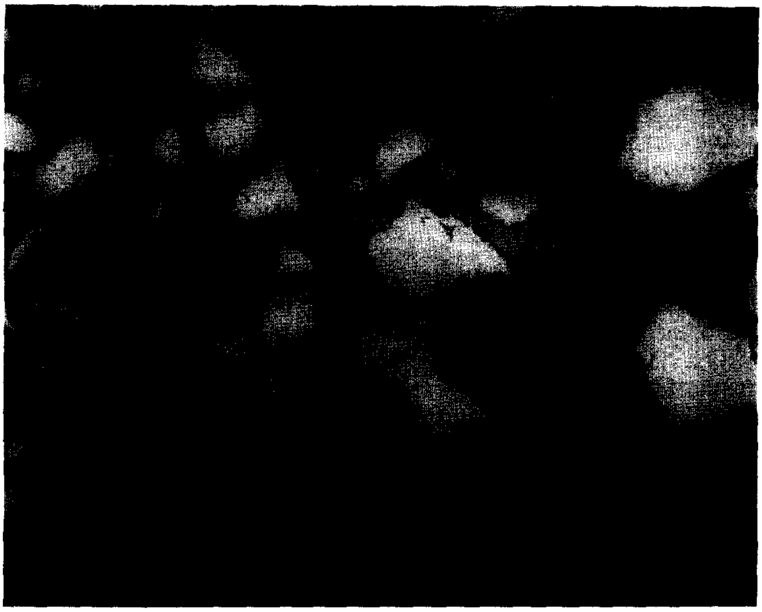

FIG. 1

Portland cement paste (w/c = 0.50) hydrated at 23°C to a degree of hydration of 30%.

FIG. 2

Portland cement paste hydrated at 70°C to a degree of hydration of 30%.

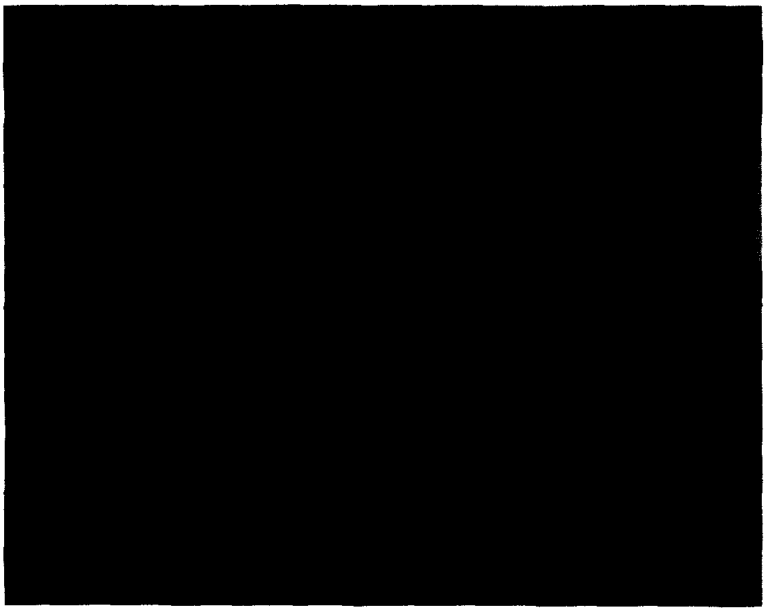

FIG. 3

Portland cement paste hydrated at 23°C to a degree of hydration of 70%.

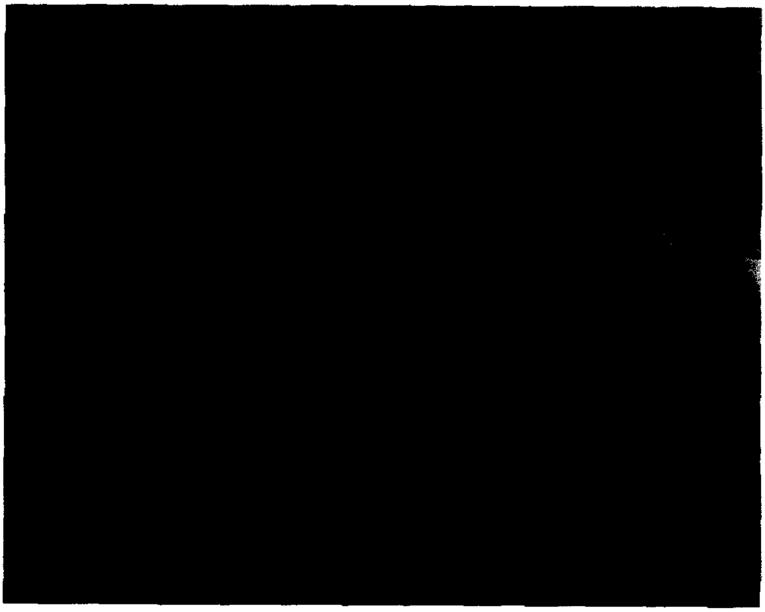

FIG. 4

Portland cement paste hydrated at 70°C to a degree of hydration of 70%.

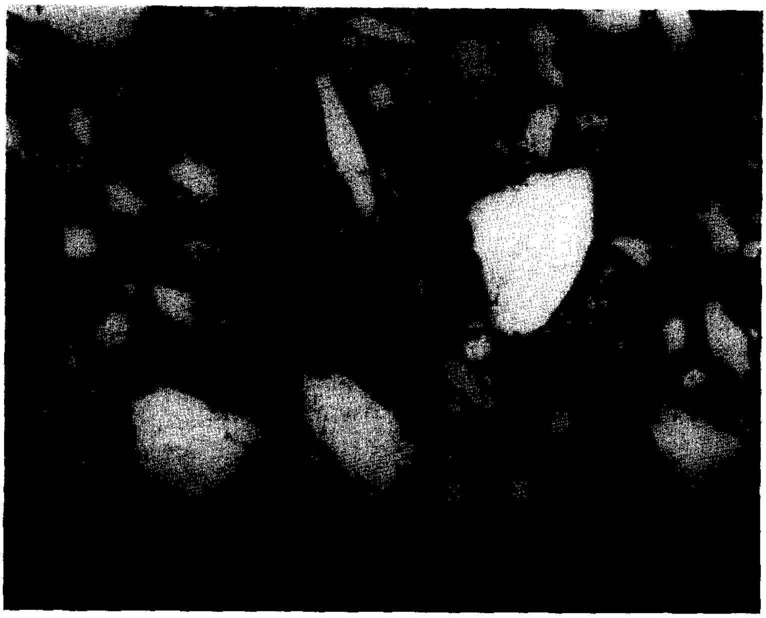

FIG.5

Cement paste containing 5% silica fume (substitution by mass) hydrated at 23°C to a degree of hydration of 30%.

FIG. 6

Cement paste containing 5% silica fume (substitution by mass) hydrated at 70°C to a degree of hydration of 30%.

70% Hydration

The presence of Hadley grains is most noticeable in the paste cured at 23°C as depicted in Figure 7. Some of these Hadley grains contain remnant unhydrated cement grains. It is possible that some completely empty pores are artifacts of the sample preparation process. A shell of relatively dense hydration products is well developed at 70% hydration. Massive formations of $Ca(OH)_2$ were developed as hydration progressed from 30% to 70%. This observation indicates that the addition of 5% silica fume did not have much influence on the growth of $Ca(OH)_2$ in the paste cured at 23°C.

A large number of Hadley grains is observed in the silica fume cement paste cured to approximately 70% hydration at 70°C (Figure 8). Shells formed by the inner and outer hydrates are clearly observable in this paste. A remarkable reduction in terms of both the size and the quantity of $Ca(OH)_2$ is noticeable, which is probably attributable to the high temperature curing and the presence of silica fume. The microstructure of the silica fume cement paste cured at 70°C appears more porous than that cured at 23°C. The $Ca(OH)_2$ content appears to be lower in the paste cured at 70°C than in that cured at 23°C.

The silica fume cement paste has a denser matrix and more discontinuous pore structure than the portland cement paste (Figure 4). No remarkable difference in the amount of $Ca(OH)_2$ can be found between the two comparable pastes. However, the $Ca(OH)_2$ appears to be more dispersed in the silica fume paste, suggesting that at a dosage of 5% silica fume has more influence on the microstructure of the paste through the physical mechanisms of nucleation and/or the filler effect than the chemical mechanism of the pozzolanic reaction.

Slag Cement Pastes

30% Hydration

Figure 9 shows the microstructure of a cement paste containing 30% slag cured to a degree of hydration of 30% at 23°C. A number of almost completely empty pores with thin white rims can be seen. The cement grains appear either to have dissolved to a great extent or to have been plucked out during polishing of the specimens, leaving either a completely hollow space with a thin white rim or a very porous layer around the boundary of the cement grains. The slag does not appear to have reacted, suggesting that only the cement contributes to the maturity of the paste at this stage of hydration. The $Ca(OH)_2$ in the paste has an elongated form. The paste has an open, porous microstructure.

Thin fibrillar hydrates form a remarkable microstructure in the paste cured at 70°C as shown in Figure 10. It seems that at the same degree of hydration (30%) the hydrates of cement grains in slag cement paste grow better at 70°C than at 23°C, in contrast to what was found in the ordinary portland cement paste. The fibrillar structure of the hydrates appears uniformly distributed, resulting in a denser structure. However, the pore structure still appears highly connected. In addition, some of the slag particles have an indistinct boundary. It is difficult to resolve whether this is due to the formation of pozzolanic hydrates or the hydrates of cement on the slag grains. The $Ca(OH)_2$ is more uniformly distributed in this paste. Very little hydrate has precipitated on the surfaces of cement particles. This indicates that the dissolved species have a high mobility in the paste. This is probably attributable to a high water/cement ratio (or interpreted as a high effective water content). This effect lowers the concentration of ions in the fluid for the same dissolved amount, facilitating ion migration.

70% Hydration

A distinct hollow rim around the slag particles was an outstanding microstructural feature in the slag cement pastes cured to 70% hydration at both 23°C and 70°C, as shown in Figures 11 and 12, respectively. X-ray elemental analysis showed extremely high concentrations of Mg and Al in this area. This phenomenon has been reported by a number of researchers. Tanaka [8] explains that Ca and Si, the majority of the slag composition, have greatly dissolved, or diffused away, leaving a skeletal surface with less mobile Mg and Al elements. According to his hypothesis, the apparently separated area is a very porous layer. Some small slag particles appear to have fully reacted, leaving isolated voids.

FIG. 7

Cement paste containing 5% silica fume (substitution by mass) hydrated at 23°C to a degree of hydration of 70%.

FIG. 8

Cement paste containing 5% silica fume (substitution by mass) hydrated at 70°C to a degree of hydration of 70%.

FIG. 9

Cement paste containing 30% ground granulated blast furnace slag (substitution by mass) hydrated at 23°C to a degree of hydration of 30%.

FIG. 10

Cement paste containing 30% ground granulated blast furnace slag (substitution by mass) hydrated at 70°C to a degree of hydration of 30%.

FIG. 11

Cement paste containing 30% ground granulated blast furnace slag (substitution by mass) hydrated at 23°C to a degree of hydration of 70%.

FIG. 12

Cement paste containing 30% ground granulated blast furnace slag (substitution by mass) hydrated at 70°C to a degree of hydration of 70%.

There are no distinct local hydrates on the outer portion of the hollow ring. This is probably due to the low density of pozzolanic products and the low degree of the secondary reaction. With an increase in curing temperature, an increased thickness of the "gap" is observed (Figure 12), indicating that the reactivity of the slag was increased by the elevated curing temperature. A coarser matrix structure of the pastes resulting from a higher curing temperature is observed. A refinement in the size of the $Ca(OH)_2$ deposits in the paste is noticeable with an increased curing temperature. However, there is no apparent change in the quantity.

In comparison with the paste without slag at the same degree of hydration, the slag cement paste cured at 23°C has a denser microstructure. Comparison of the specimens cured at 70°C shows that the slag cement paste appears to have a more discontinuous pore structure.

Implications for Durability

The durability of concrete depends largely on the permeability, which in turn depends on the continuity of the pore structure. Detwiler et al. (3) report the results of a study of concretes made using materials similar to those used here and cured to a degree of hydration of 70% under comparable conditions. They determined the rate of chloride ion diffusion through these concretes. Their findings are broadly consistent with the observations of the microstructure reported in this paper. In all cases, an increase in the curing temperature from 23°C to 70°C resulted in a substantial increase in the diffusivity of chloride ions through the concrete. For any curing temperature, the substitution of either 5% silica fume or 30% slag for an equal mass of cement significantly reduced the rate of chloride ion diffusion through the concrete. The dosages of 5% for silica fume and 30% for slag were about equally effective in reducing the rate of diffusion in concrete cured at 70°C.

Conclusions

1. In general, an elevated curing temperature results in a coarser, more continuous pore structure for cement hydrated to a given degree of hydration.

2. However, slag cement pastes at 30% hydration appeared to benefit from elevated curing temperature, in contrast to portland cement and silica fume cement pastes.

3. The slag was found to react mainly after 30% hydration of the paste. The voids left by the reacted slag particles resulted in a very porous phase. However, these pores are not likely to contribute to the permeability of the paste because they are isolated from the other pores.

4. In the specimens hydrated at 23°C, the $Ca(OH)_2$ was uniformly distributed in the silica fume cement paste while in the slag cement paste the $Ca(OH)_2$ had more elongated crystalline forms. Elevated temperature curing resulted in smaller, more numerous deposits of $Ca(OH)_2$.

5. Hadley grains were a distinct feature of the microstructure of all of the pastes at 70% hydration. The morphology largely reflects the temperature and extent of hydration. Inner hydration products which were formed through the diffusion mechanism were observed mainly in the mature pastes cured at 70°C.

6. In general, the microstructure of pastes cured at 70°C were found to be more porous and less uniform than that of pastes cured at 23°C regardless of the composition of the cement pastes. The presence of the additives, particularly silica fume, had a pronounced effect in refining the pore structure and homogenizing the distribution of the hydrates. These findings are consistent with measurements of chloride diffusion in comparable concretes.

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