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PORE SIZE DISTRIBUTION OF OPC & SRPC MORTARS IN PRESENCE OF CHLORIDES

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ABSTRACT

The pore structure of chloride-free ordinary portland cement(OPC) and sulphate resistant portland cement(SRPC) mortars are compared with the corresponding mortars with NaCl and $CaCl_2$ added during mixing. In both OPC and SRPC mortars the addition of chlorides reduced the total accessible pore volumes compared to the corresponding chloride-free mortars. Also, in the presence of chlorides, the number of coarse pores were increased. These changes in the pore structure are believed to be due to dense calcium silicate hydrate(C-S-H) gel morphology formed in the presence of chlorides. The SRPC showed greater changes in pore structures than the OPC with equivalent amounts of chlorides added. This may be due to the lower chloride binding capacity of the SRPC and hence the higher availability of free chlorides to modify the gel morphology.

Introduction

The pore structure is an important physical parameter controlling the susceptibility of reinforced steel to corrosion. For example, the permeability of concrete increases with an increase in number of pores with diameters greater than 150 nm(1). The modifications in pore structure of hardened cement paste due to the factors such as counter diffusion of Cl^- and OH^- ions and the changes in C-S-H morphology have been documented in the literature(2,3)

Kondo et al.(2), identified $Ca(OH)_2$ crystals on the surface of the hydrated cement when the Cl^- ions from the aqueous $CaCl_2$ diffuse through hardened cement paste. This, according to them, is due to the counter diffusion of Cl^- and OH^- ions between the solution and the cement paste. Such counter diffusion was also thought to occur in the case of chlorides derived from NaCl and KCl. The diffusion coefficients for the cations are less than that for the associated chloride ions. This is due to the fact that the hydrated cement behaves as an electro-positive semi-permeable membrane(4). The counter diffusion of Cl^- and OH^- similar to an ion exchange process in the hardened cement paste will cause dissolution of $Ca(OH)_2$ in the hardened cement paste, thus coarsening the pore structure. However, the leaching of $Ca(OH)_2$ should be greater with Cl^- derived from $CaCl_2$ compared to NaCl, thereby increasing the coarseness of the hardened cement paste. This is due to the higher diffusion coefficient for the Cl^- ion derived from $CaCl_2$ compared to that from NaCl(2,5).

A few investigations have been reported in the literature on chlorides added during mixing as either NaCl or $CaCl_2$ and their role in modifying the pore structure of the cement paste. For example, using mercury porosimetry, Young(3) found increased pore volumes for the fine pores when 1% $CaCl_2$ was admixed to tri-calcium silicate(C_3S) compared to the chloride-free C_3S. The change in the pore size distribution with $CaCl_2$ addition was attributed to the change in morphology of the C-S-H gel. Gouda et al.(6), based on adsorption studies, also found increased pore volumes above 2.5 nm hydraulic radius with 2% $CaCl_2$ addition to the OPC paste. While Hansson et al.(7) again using mercury porosimetry, showed higher intrusion volumes with $CaCl_2$ and NaCl additions, particularly for the pores around 100 nm radius, compared to the chloride-free mortar. However, both Gouda et al., and Hansson et al., have not proposed any mechanism for these changes in pore structure.

In the present investigation, the pore size distribution for the OPC and SRPC mortar is examined in the presence of the chloride ions added during mixing as NaCl and $CaCl_2$. An attempt is made to explain the mechanism responsible for the modified pore structure.

Experimental

Cylindrical mortar specimens(3.9 cm in diameter and 5 cm in height) were cast in plastic bottles. The mortar was hand mixed in small container. Chloride was added to the mortar at the time of mixing as NaCl and $CaCl_2$ salt dissolved in the mix water. The sealed plastic bottles were stored in laboratory for curing. Table 1 summarises the mortar mix design used in the production of mortar specimens. The SRPC used in the present investigation is a low C_3A cement conforming to BS 4027(8) and OPC used conforms to BS 12(9). After demoulding, small fragments of mortar weighing approximately 2.5 g were chiselled from the core of the central third of the specimen. These mortar fragments were then heated in a oven to 105 °C to constant weight.

Table.1. Mortar Mix Design Used in the Production of Mortar Specimens

Mortar specimen type	Wt of cement g	Wt of sand g	W/C ratio	% Cl^- by wt of cement	Conc of Cl^- in mix water M
OPC	24	95.8	0.7(16.8)**	0	0
OPC+NaCl	24	95.8	0.7(16.8)	1.75(0.693)*	0.705
OPC+$CaCl_2$	24	95.8	0.7(16.8)	1.75(0.657)	0.705
SRPC	24	96.1	0.7(16.8)	0	0
SRPC++NaCl	24	96.1	0.7(16.8)	1.75(0.693)	0.705
SRPC+$CaCl_2$	24	96.1	0.7(16.8)	1.75(0.657)	0.705

* Indicates the actual amount of NaCl/ $CaCl_2$ added to the mix water in g.

**Indicates the actual amount of H_2O added to the mix water in cc.

The pore size distribution studies were carried out on a Micromeritics Pore Sizer(Model 9310). The contact angle used in the Washburn equation was 117° as the mortar sample was oven dried(10). The pores were assumed to be circular in cross section and hence the shape factor was chosen to be 4.

The pore size distribution studies were carried out on the chloride-free OPC and the SRPC mortars hydrated for 33 days. These pore size distributions were compared with the OPC and SRPC mortars containing 1.75% Cl^- by weight of cement as either NaCl or $CaCl_2$ hydrated as far as possible to the same degree as the chloride-free mortar. The OPC mortar with NaCl and $CaCl_2$ additions were hydrated for 30 days whilst, the SRPC mortar with NaCl was hydrated for 30 days and that with $CaCl_2$ was hydrated for 16 days. These times were decided upon using measurements of the evaporable water as a gauge of the degree of hydration. Table 2 gives the evaporable water contents for the OPC and SRPC mortar specimens at the various days of hydration.

Table 2. Evaporable Water Contents for the OPC and SRPC Mortars Secimens at Different Periods of Hydration.

Mortar specimen type	%Cl^- by wt of cement	Evaporable water contents in g		
		16 days	30 days	33 days
OPC	0	----	----	13.31
OPC+NaCl	1.75	----	13.33	13.24
OPC+$CaCl_2$	1.75	----	13.35	13.28
SRPC	0	----	----	14.19
SRPC+NaCl	1.75	----	14.24	14.14
SRPC+$CaCl_2$	1.75	14.10	----	13.54

Results

Pore size distribution for OPC mortars

The cumulative pore volume versus pore diameter plots for the OPC mortars containing 0% Cl^- and 1.75% Cl^- by weight of cement added as NaCl and $CaCl_2$ are given in Figure 1.

In Figure 1, the steep portion of the curve corresponds to the geometrically continuous pore system(capillaries) in the hydrated cement(10). It is evident from Figure 1 that the chloride-free OPC mortar had a larger volume of geometrically continuous pores compared to the mortars with 1.75% Cl^- added as NaCl and $CaCl_2$. This implies that the addition of Cl^- as NaCl and $CaCl_2$ to the mortar reduced the accessible pore volume compared to the chloride-free mortar. The minimum effective neck diameter or the threshold diameter was around 1100 nm for all the above cumulative pore volume curves.

In the present investigation, the differential pore volume plot such as dV/d(logD) versus the pore diameter(on log scale) is used to estimate the pore volume contribution arising from individual pore diameters.

Figure 2 shows the differential pore volume plots for the chloride-free mortar and for the mortar with 1.75% Cl⁻ by weight of cement as NaCl and $CaCl_2$. The mortar admixed with $CaCl_2$ showed higher differential pore volumes for the finer pores accompanied with lower differential pore volumes for the coarse pores compared to the chloride-free mortar. This indicates the presence of fewer pores in the fine pore range and a larger number of pores in the coarse pore range for the

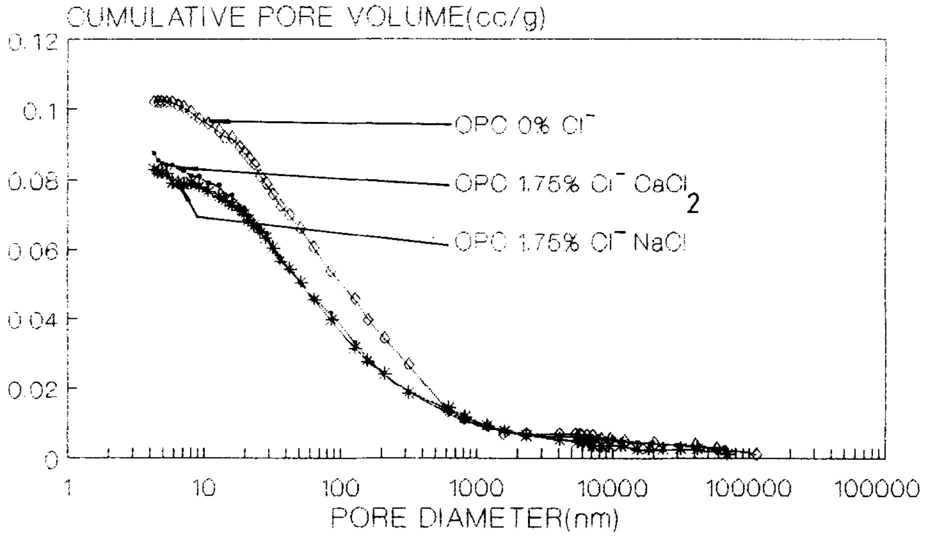

FIG. 1

Cumulative pore volume curve for the OPC mortar.

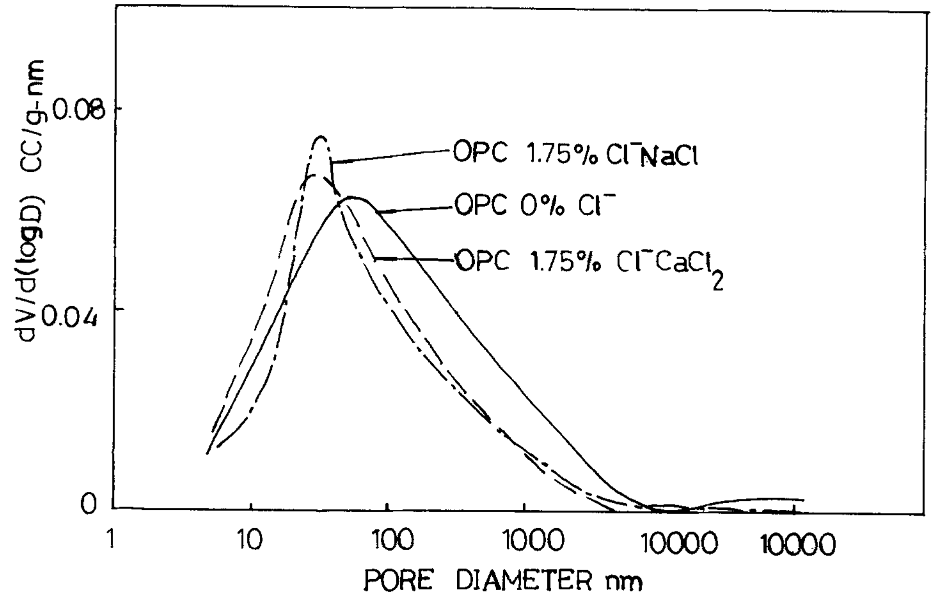

FIG. 2

Differential pore volume curve for the OPC mortar.

chloride-free mortar compared to the mortar admixed with $CaCl_2$. Similar results were observed by Gouda et al.(6) in the adsorption studies with OPC admixed with 2% $CaCl_2$.

The mortar containing chloride as NaCl also showed a reduction in differential pore volumes for the coarse pores compared to the chloride-free mortar. It also showed higher pore volumes for pores with diameters around 30 nm.

Thus, the pore size distribution in presence of chloride changed from wider to narrow distribution with a shift in mean pore diameter towards the finer diameter.

Pore size distribution for SRPC mortars.

Figure 3 shows the cumulative pore volume versus the pore diameter plots for the SRPC mortars containing 0% Cl^- added as NaCl and $CaCl_2$ by weight of cement. From the Figure 3 it appears that the chloride-free SRPC mortar exhibited a bimodal pore distribution. This may be due to the hydration properties associated with the SRPC mortars. For the SRPC mortar made with NaCl and $CaCl_2$ the accessible pore volumes were less than the chloride-free mortar. It is also clear that in the presence of chloride as NaCl and $CaCl_2$ the majority of the pore volume was contributed by the finer pores(<100 nm in diameter).

By comparing Figures 1 and 3 it is evident that for the same duration of hydration(33 days) and water-cement ratio (0.7) the SRPC mortar has slightly higher accessible pore volume than the OPC and the difference arises from the coarse pores.

Figure 4 shows the dV/d(logD) versus pore diameter plots for 0% Cl^- and 1.75% Cl^- by weight of cement added as $CaCl_2$ and NaCl. In comparison with the chloride-free mortar, the mortar admixed with $CaCl_2$ showed distinctively higher differential pore volumes for the finer pore diameters accompanied with a reduction in differential pore volume for the coarse pore diameters. This result appears to have a significant practical implication in the hydrated cement from the corrosion stand point, because it would indicate an increase in number of finer pores and thereby increasing the degree of accessibility for the ions.

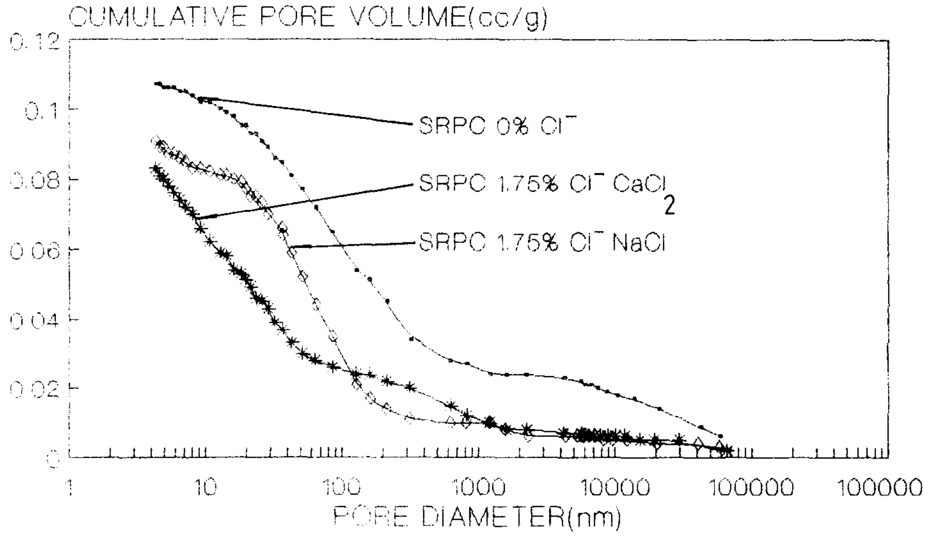

FIG. 3

Cumulative pore volume curve for the SRPC mortar.

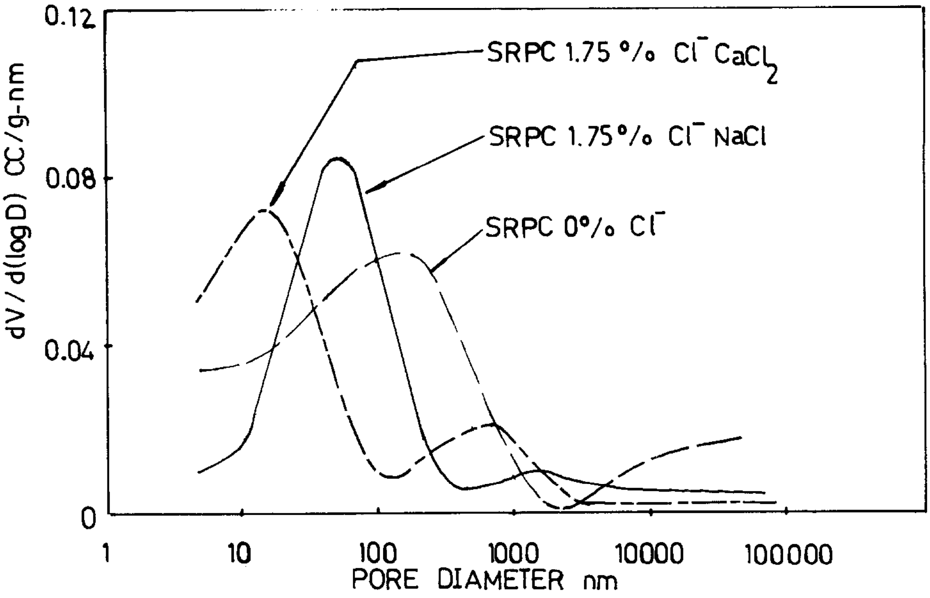

FIG. 4

Differential pore volume curve for the SRPC mortar

Alternatively, the NaCl also reduced the differential pore volumes, particularly for the coarse pore sizes, however, the number of finer pores were increased compared to the chloride-free mortar.

Thus, the addition of chlorides changed the pore size distribution from wider to narrower distribution and the mean pore diameter was shifted towards the finer pore diameter, although the mortar with $CaCl_2$ showed a very small differential pore volume for the coarse pores.

Discussion

Since modifications in the pore structure of both OPC and SRPC has taken place in the presence of NaCl and $CaCl_2$ it is obvious that the NaCl or $CaCl_2$ or their compounds are responsible for these changes. The different possibilities for these changes are examined below.

The chlorides in hydrated cement paste are found in different forms. Part of the added Cl^- is bound with the cement as chloro-complexes, $C_3A(F).CaCl_2.10H_2O$, and the balance existing in the pore solution as free-chloride or possibiy in the form of a chemisorbed layer on the surface of the C-S-H gel(11). Lambert et al.(12), in their recent investigation with synthetic grade C_3S, found the quantity of chloride ions bound with the C-S-H gel to be insignificant. Thus, the possibility of chemisorption of the chloride ions on the surface of the C-S-H gel which modifies the pore size distribution seems remote.

A decrease in the degree of accessible pore volume in the presence of NaCl and $CaCl_2$ is associated with an increase in the number of finer pores, and a decrease in the number of coarse pores. This suggests that chloro-complexes may have formed in the coarse capillaries thereby reducing their diameter. The essential condition for the above argument is that the C-S-H morphology in both the chloride-free and in the samples made with NaCl and $CaCl_2$ should be identical. However, the C-S-H gel in the presence of NaCl and $CaCl_2$ became modified to a different morphology in both OPC and SRPC indicating an altogether different pore structure. Hence, the changes in the pore structure cannot be explained based on the mechanism of deposition of chloro-complexes in the coarse capillaries. However, this mechanism is applicable provided the C-S-H morphology does not change with the chloride addition.

The chloride-free OPC and SRPC contained fibrous or needle shaped C-S-H. Figure 5 shows the SEM micrograph of the C-S-H gel for the chloride-free OPC mortar. From the Figure 5 it can be seen that considerable pore space(void space) exists between the radiating needles. These pore spaces between the needles are expected to contribute a large fraction to the total accessible pore volume. This explains the large accessible pore volumes observed for the chloride-free OPC and SRPC mortars compared to the mortars with chlorides.

FIG. 5.

SEM micrograph showing the fibrous C-S-H gel.

FIG. 6

SEM micrograph showing the dense C-S-H morphology.

For both the OPC and SRPC mortars in the presence of $CaCl_2$ and NaCl the C-S-H morphology is modified to a more dense structure. Figure 6 and 7 show SEM micrographs illustrating the dense morphology for the OPC containing 1.75% Cl^- added as $CaCl_2$. Even at a higher magnification these did not show the large void spaces found in the chloride-free gel. Thus, with dense gel, the number of accessible pores were reduced in comparison with the chloride-free mortar, the chloride containing mortar also exhibit an increase in the number of finer pores as already shown by the differential pore volume plots. This indicates that the dense C-S-H gel is less porous compared to the fibrous gel and has an inherently higher percentage of finer pores. Although the pore size variation is wider for the dense C-S-H gel the mean pore diameter is small compared to the fibrous C-S-H gel. Young(3) also reported a change in morphology accompanied with a change in pore structure. But they reported a lace-like morphology with $CaCl_2$ addition to the C_3S paste.

FIG. 7

SEM micrograph showing the dense C-S-H morphology.

For both cements, the addition of $CaCl_2$ caused comparatively greater changes than with an almost equivalent quantity of NaCl(equivalent in Cl^- content). This may be due to a more effective modification of the originally fibrous C-S-H to a denser morphology in both the cements in the presence of $CaCl_2$. Also, the more significant changes in pore structure observed for the SRPC mortars compared to the OPC mortar with identical quantities of chloride is due to the low chloride binding capacity of the SRPC(13). This means that more free-chlorides are available in SRPC to modify the C-S-H to a dense morphology. Thus, the results obtained by the mercury porosimetry are explained by the changes in the C-S-H morphology of the cements.

Conclusions

The following conclusions are drawn from the present investigation.

1. The addition of NaCl and $CaCl_2$ to the mix decreased the accessible pore volumes for both the OPC and SRPC mortars compared to the chloride-free mortar.

2. The addition of NaCl and $CaCl_2$ to the OPC and SRPC mix increased the pore volumes for the finer pores and decreased the number of coarse pores. This is due to the change in the morphology of C-S-H gel from a fibrous to a dense morphology.

3. More significant changes in pore structure were observed for the SRPC mortar than the OPC in the presence of equivalent amounts of chlorides. This may be due to the presence of higher free-chlorides in SRPC to modify the gel morphology.

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