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CEMENT PASTES OF LOW WATER TO SOLID RATIO: AN INVESTIGATION OF THE POROSITY CHARACTERISTICS UNDER THE INFLUENCE OF A SUPERPLASTICIZER AND SILICA FUME

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ABSTRACT

Porosity was investigated in cement pastes with a water to solid ratio of 0.28 and cured at normal temperature. Samples with and without superplasticizer admixture were prepared using an ordinary portland cement in which 0-5-10 and 15 per cent of weight was replaced by condensed silica fume (CSF). Solvent exchange treatment and vacuum drying of samples were carried out before the use of the mercury intrusion technique. Capillary water suction (CWS) and the pore sizes distribution (PSD) were determined after various hydration times ranging from 1 day to 3 years. PSD of all CSF-containing composites showed a majority of pores with radii below 15 nm even after 1 day of hydration. In some pastes after 250 days of water curing a re-increase of median pore size was observed. Changes of the CWS and PSD parameters indicated the superplasticizer action on the formation of pore structure of cement stones. This action was also confirmed by measurements of the temperature of hydrating pastes.

INTRODUCTION

The porosity and pore structure of cement pastes are of the greatest importance for the performance of hydrated cement based composites. Decreases in the porosity and the permeability of hardened composites depend on the water content /1-2/. A reduced water-binder ratio is obligatory in creating cement based composites of low-porosity /3-5/. Many such cement composites incorporate condensed silica fume.

If the initial w/c ratios are significantly lower than the value 0.38 - according to Powers the value for OPC paste at which cement can be fully hydrated- a part of binder particles remains unhydrated in the mature paste /6,7/. Unreacted binder particles were also considered as "internal filler" /8/.

The cement matrix may exhibit aging effects, or environmental reactions or both. Because of that and based on some research results (for example ref./9,11/) there is still concern regarding the presence of unhydrated binder particles in low porosity composites which may influence their thermodynamic stability or durability.

The present paper will deal with the formation of the pore structure of OPC and OPC-CSF pastes (w/s=0.28) with respect to the role of a superplasticizer and CSF. Testing of samples after long-term water curing was also scheduled. This work is part of a research project whose results concerning hydration kinetics and polymerization of silicate anions were published earlier /12,13/.

EXPERIMENTAL

Research was carried out using an ordinary portland cement (OPC, Type I ASTM), condensed silica fume (CSF) a by-product of ferrosilicon alloy production, a superplasticizer (HRWR, ASTM C-494) of melamine-formaldehyde type (solution with 20 % of dry substances) and distilled water. The OPC had a density of 3.12 kg/dm^3, a Blaine value of 271 m^2/kg, and the following oxide composition : SiO_2=20.90 % , Al_2O_3=5.65 %, Fe_2O_3=2.69 %, CaO_{tot}=63.21 %, MgO=2.15 %, Na_2O=0.34 %, K_2O=0.68 %,loss on ignition (Loi)=1.00 % and insoluble residue=0.60 %.

CSF (SiO_2 content of 86.92 % and bulk density of 0.20 kg/dm^3) was from the same stock as described in Ref /13/. The basic parameter fixed in all pastes tested was a water to solid ratio of 0.28. The testing was carried out at room temperature.

Four pastes were made in series without superplasticizer using OPC and by replacing the OPC with the following weight portions of CSF: 0% (paste PC), 5% (paste 5P), 10% (paste 10P) and 15% (paste 15P). In the superplasticized series of four pastes containing an equivalent amount of CSF (paste with "s"-index:PC^s,5P^s,10P^s and 15P^s), the dosage of liquid superplasticizer was always 4% per weight of OPC+CSF. The materials were weighed and mixed for 3 minutes in a "Toni-Technik" cement mixer. Immediately after setting the pastes were immersed in water for further hydration at 20°C.

In addition, new portions of the pastes were prepared for the measurement of the temperature increase during their hydration.

Capillary water suction (CWS)

Capillary water suction by a shallow immersion test was carried out on samples hydrated for 1, 3 and 28 days. The specimens had a suction area of 4x16 cm and a thickness of about 1.8 cm. They were made by cutting a normal cement prism of 4x4x16 cm into two equal halves. The specimens were cured in water until the ages stated above and after cutting they were transferred to drying for 48 hours at 105-110 degree Celsius. The samples were cooled in a dessicator and weighed before putting in water. The test was conducted in an environment of 21-22°C and relative humidity 60-65 % by bringing one face of a dry sample in contact with the surface of water in a container and measuring the increase in sample weight with time up to 5 hours. After that the specimens were fully immersed in water for the additional 24 hours and absorbed water determined.

Pore size distribution (PSD)

The pore size distribution (PSD) of hardened cement pastes was determined by mercury intrusion porosimetry (MIP) which produce a record of pore entry sizes. The pressure was increased up to 200 MPa. After curing in water for the time of 1, 7, 28, 250 days and 3 years the slices (at each age 4 slices) of about 6 mm were cut from the paste specimens having initially a size of 4x4x16 cm. The first outside slices were rejected because of the carbonation. The other slices were subjected to a solvent replacement treatment. They were placed in dioxane for 7 days, afterwards in water-free ethanol for 7 days and finally dried at 20 degree celsius for 48 hours under vacuum. The slices of 2x3 cm were analyzed using a MIP equipment of a type "Carlo Erba 2000 WS" (Milano,Italy) coupled with a computer. Values of 0.480 N/m and 141 degree respectively were used for the surface tension of mercury and for the wetting angle. A commercial software of a type "Milestone 200" evaluated the intrusion curves by implementing the correction factors for hydrostatic mercury pressure, the compressibility value of sample container filled only with the mercury and the value for pore shape (for circular cross section of pores the value of 4,0 was used - for comparing see ref./14/) .

Temperature increase of hydrating pastes

The temperature increase of hydrating pastes was measured by direct reading on thermometers having a precision of 1/10 Celsius degree.
All materials, the mixing bowls and the paddles were adjusted to proper temperature before mixing of each individual cement paste. Each fresh sample mass amounted to 440 grams was placed into thin plastic beakers (with a diameter of 65 mm). The thermometers were placed and fixed into the center of each plastic beakers . Surrounding temperature was maintained between 21-22 degree Celsius. All eight paste composites were tested simultaneously during the first 20 hours of hydration by recording of the temperature at every 15 minutes.

RESULTS AND DISCUSSION

In this work the capillary porosity of tested pastes was characterized by the rate of capillary water suction determined on previous dried samples. The capillary suction rate, similar as the resistance to water penetration /15/, depends on the structure of the capillary space of the hydrated samples. The loss of weight by drying of hydrated and water-saturated pastes was used in evaluation of CWS results. The loss of weight and thus also the CWS parameters of hydrated samples are sensible effective by the applied drying regime /16/ which may make the results difficult to interpret. This problem is made somewhat easier by comparing the changes in the pore structure between the different paste compositions. According to the results shown in Table 1 the total porosity (including capillary space) of an individual paste decreased by increasing the curing time to 28 days. This was an expected consequence of the filling up of the interparticular space in the hydrating pastes with the new hydrating products.
In the pastes containing CSF an increase in the curing time provides a greater probability of discontinuous porosity /17/. At the same time capillaries of smaller radius could be formed. Smaller

TABLE 1
Weight Loss of Water-Saturated Cement Pastes of w/s=0.28
During 48 Hours of Drying at 105-110°C.

Sample	PC	5P	10P	15P	PC^S	$5P^S$	$10P^S$	$15P^S$
CSF(%)	0	5	10	15	0	5	10	15
Weight loss (%)								
1 day	19.3	19.7	19.0	17.7	19.2	19.8	19.7	19.3
3 days	18.4	18.6	17.7	17.2	17.7	18.4	17.5	17.8
28 days	17.3	17.8	17.1	16.9	17.0	17.3	17.0	17.1

capillaries have a higher suction power /18/. Both processes overlapped and the resulting consequences determined as the capillary suction rate are presented in FIG 1-3. The capillary suction rate was computed by dividing the weight of absorbed water of the paste during a chosen time by its total weight loss (given in Table 1) for its corresponding age.

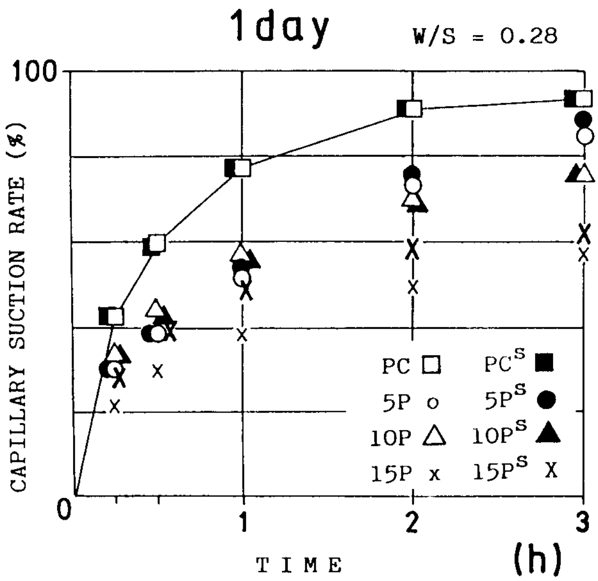

FIG 1

Capillary suction rate at 1 day age.

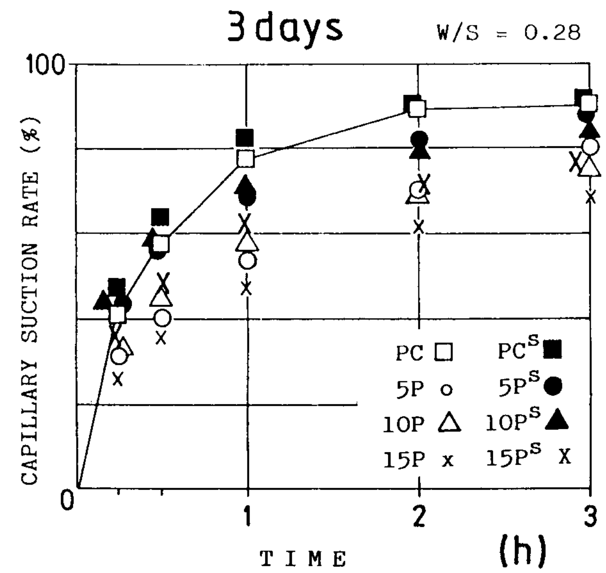

FIG 2

Capillary suction rate at 3 days age.

Longer hydrated OPC-CSF pastes with HRWR admixture showed a higher initial rate of capillary water suction but reduced total capillary suction. Higher initial rate is most obviously by CWS-results of superplasticized paste with 10 % CSF determined after 15 minutes immersion in water:

Capillary suction rate (%) after 15 min.

Paste age 1 day	PC=42%	1OP=33%	PC^s=43%	$1OP^s$=33%
Paste age 28 days	PC=37%	1OP=29%	PC^s=39%	$1OP^s$=39%
	-5%	-4%	-4%	+6%

Therefore it may be concluded that by increasing the curing time of CSF-blends, reduced

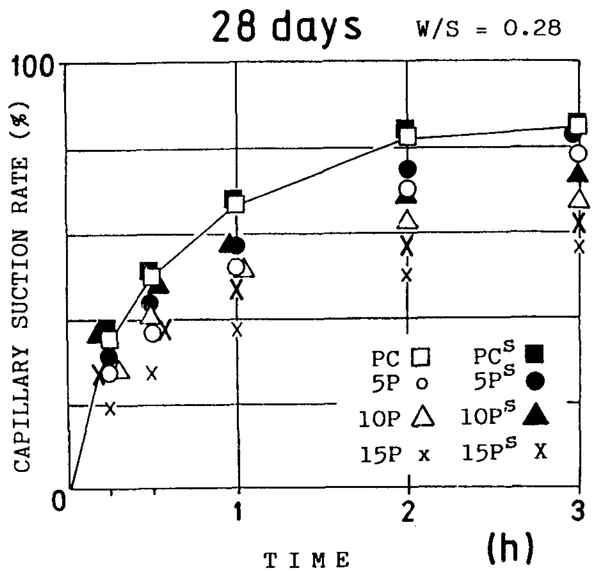

Fig 3

Capillary suction rate at 28 days age.

capillary porosity with a higher proportion of smaller capillaries in their structure will be formed.

The influence of CSF and the consequences of HRWR action on the structure of hardened pastes of low water content are also reflected on the results of PSD obtained by MIP (FIG 4-8). The results shown in FIG 4-8 agree with the findings generally accepted that the blending of CSF with Portland cement leads to a modified structure of a finer size distribution than neat pastes. At a certain age (28 and 250 days) the total intruded volume determined by MIP was slightly higher in the blend with the smaller amount of

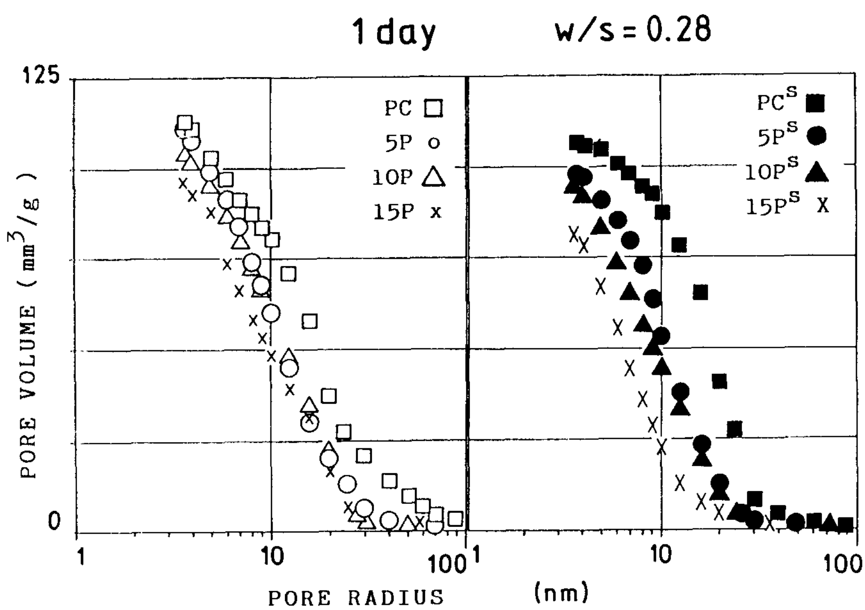

FIG 4: Cumulative pore size distribution at 1 day age.

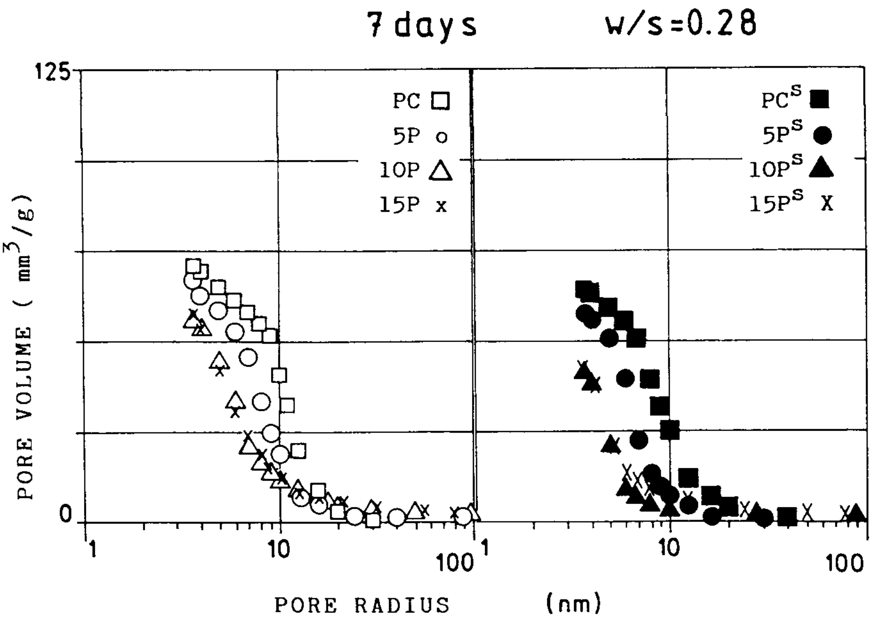

FIG 5: Cumulative pore size distribution at 7 days age.

CSF (5%) than in the pure OPC paste. Similar results in some research were explained by the greater volume of small pores /19,20/. The median pore size, defined as described by Kumar and Roy /21/, of all CSF-containing pastes was smaller than 15 nm even after one day of hydration (Fig 4). This value (related to the intruded pore volume) would somewhat change if higher MIP pressure could be applied because the mercury is forced

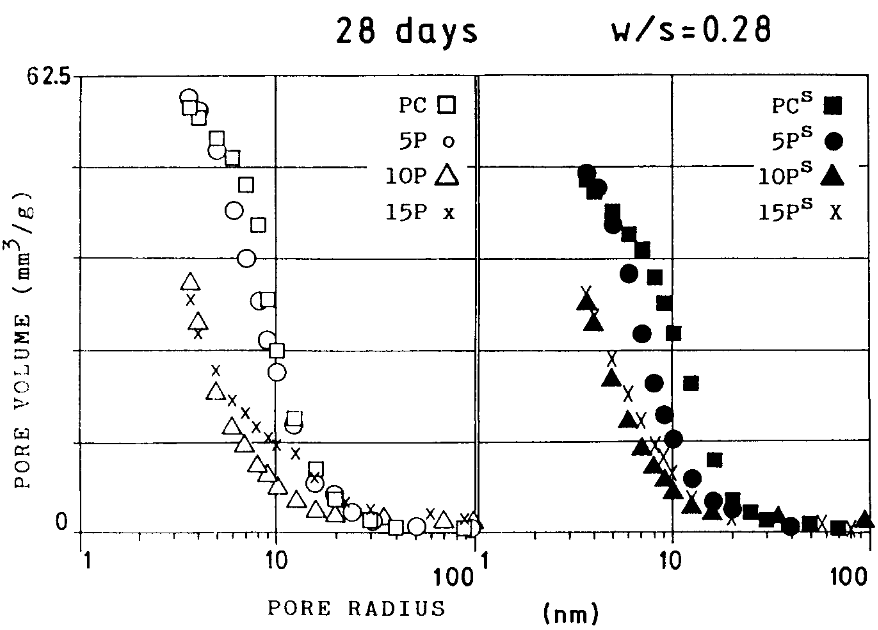

FIG 6: Cumulative pore size distribution at 28 days age.

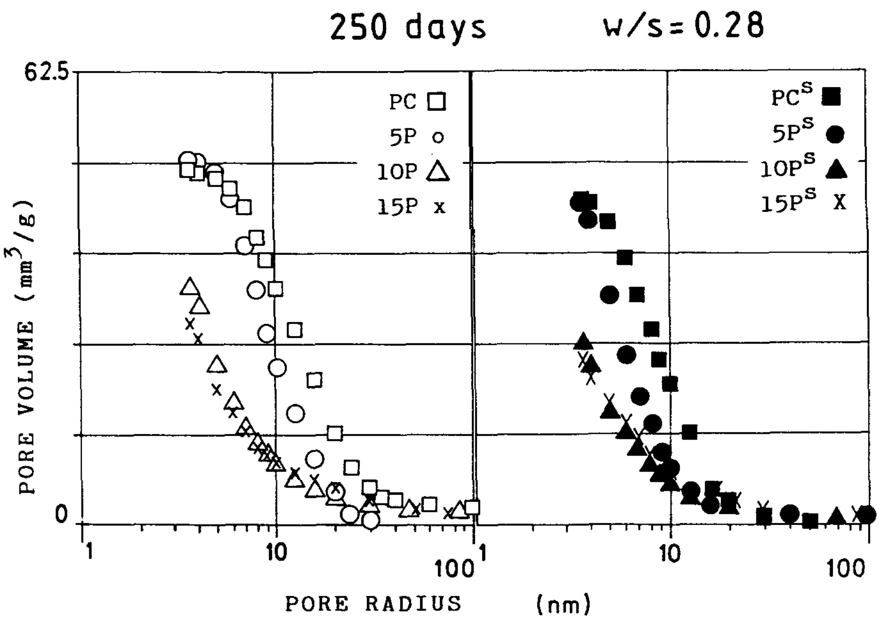

FIG 7: Cumulative pore size distribution at 250 days age.

into porous sample with increasing pressure (Washburn equation). At 200 MPa some of the smallest pores remain unincluded in PSD.

The median pore size changes as a function of curing time may also be related to the water mobility restriction of different paste compositions. Increasing curing time up to 28 days (FIG 4-6) led to a decrease in the mean pore sizes. But at the age of 250 days a

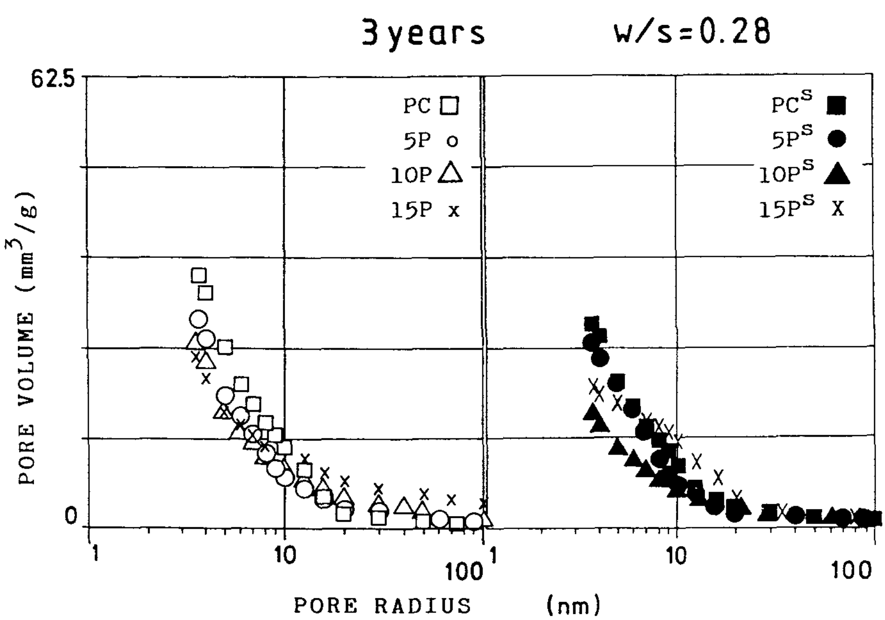

FIG 8: Cumulative pore size distribution at 3 years age.

TABLE 2
Changes of the median pore size (at 50 % of intruded pore volume /22/) by aging of the cement pastes of w/s=0.28

Sample	PC	SP	10P	15P	PC^s	$5P^s$	$10P^s$	$15P^s$
CSF (%)	0	5	10	15	0	5	10	15
Pore radius (nm)								
1 day	15.7	10.7	10.9	10.0	16.5	10.5	9.5	7.5
28 days	9.5	8.4	5.4	7.3	11.4	7.3	6.0	6.8
3 years	7.0	6.3	6.0	7.4	7.0	6.8	6.9	10.9

re-increase of that radius was observed. The median pore size re-increase, as shown in table 2, was most clearly detected at the age of 3 years in the superplasticized paste with 15 % CSF. Such re-increase of the median pore size between 6 months and one year was observed by curing the pastes at elevated temperatures and at higher w/c ratios /22/.

Given the principles of the mechanism used in /23/ the re-increase of median pore size in the pastes with low water content may be explained as follows: As free water in the hydrating mixes runs out, and if practically no water is provided externally due to very restricted water mobility in the dense composite, a cement paste tends to self-desiccate, and for continuing hydration only the water contained in the gel pores would be available. Using the water from the gel pores may cause restructuring of pore sizes which would also change the median pore size.

When comparing MIP data in FIG 5-7 attention should be paid to the PSD of the pastes containing 10 and 15 % of CSF, i.e. to the pastes with a higher small particles content. The distribution of pore sizes in these pastes was apparently different than the PSD of other pastes (without CSF or with 5% CSF only). Moreover, the PSD of both pastes signed 10P and 15P are also similar to each other. These facts lead again to the conclusion that the pore structure formation in the pastes of low water content was strongly influenced by the availability and the mobility of water. Lending support to this opinion were the changes in the PSD results in all pastes with HRWR admixture which occur to a greater extent than in the pastes without HRWR. Previous investigations of the same paste compositions have shown /12,13/ that the improved dispersion of solid particles by the action of HRWR was the principal advantage in the whole process of hydration in the CSF-blends of low water content. According to the PSD parameters obtained the same is true of the formation of the pore structure.

It is well known the cement hydration process characterizes also the specific surfaces of the hydration products developed. This products build up the pore structure. There is a causal dependence between specific surface of hydration products and the specific surface of the pores and the pore volume. Thus, the ratio between the cumulative pore volume and the specific surface of the pores could indicate the hydration activity of cement paste. This presents Fig 9. Already at the age of 28 days, the ratio between the cumulative pore volume and specific pore surface of the pastes with 15 % of CSF showed minimal change despite the HRWR admixture. At the same age the ratios of both pastes with 15% CSF were higher than the ratios of the pastes with 10 % CSF. Both of these results prove that the conversion rate of hydrating particles was strongly reduced. Hydration was reduced most probably due to the water mobility restriction in the dense composite. A similar decrease in the hydration product's specific surface by increasing the curing time was observed also in DSP composites /24/. The ratios shown in Fig 9, which

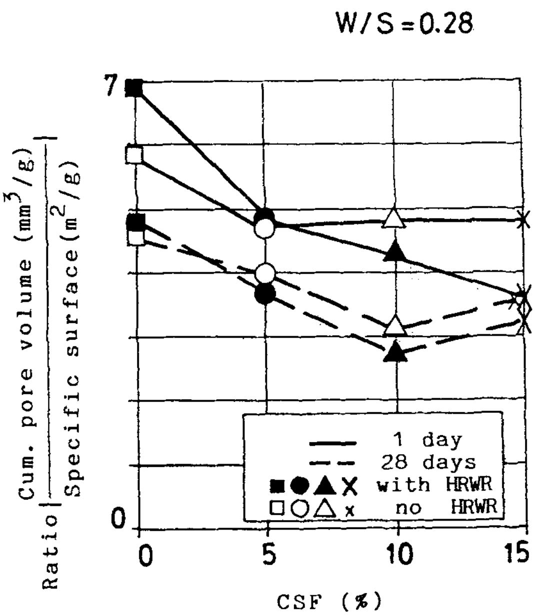

FIG 9:

Changes of the ratio (cumulative pore volume/specific surface) after 1 and 28 days in the cement pastes of w/s=0.28 with different CSF content.

are analog to the hydraulic ratio as described by Feldman /25/, were computed using data after evaluation of the MIP curves using the commercial software "Mileston 200".

The influence of a superplasticizer and the effects of the dispersity of solid binder particles when preparing the PC pastes with the CSF addition and low water content were additionally confirmed by the measurement of temperature increase during the first 20 hours of paste hydration (Figure 10). The minimum or the maximum of temperatures reached in hydrating superplasticized mixes can be related to the improved dispersity of

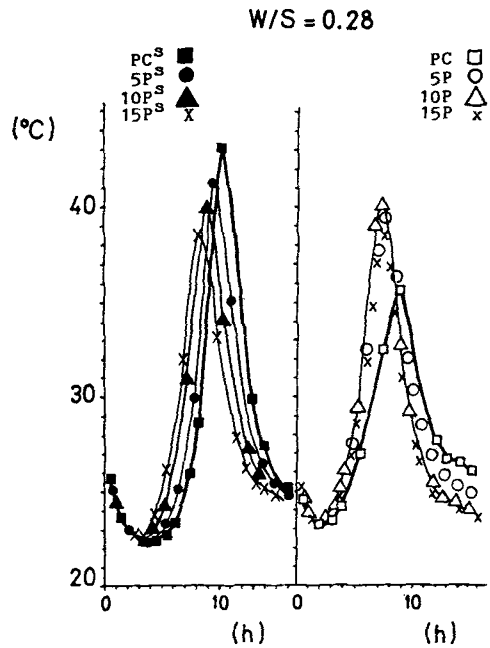

FIG 10:

Temperature increase in hydrating cement pastes of w/s=0.28 which contain 0-5-10 and 15 % CSF (sample sign: PC,5P, 10P and 15P respectively-mixes with HRWR admixture are additionally marked with "s" index.

solid particles due to the action of HRWR. The highest temperature was detected in the HRWR-containing pure OPC paste (sign PC^s in FIG 10) whose particles were best dispersed because the HRWR-dosage was kept constant (4%) in all superplasticized mixes and anhydrous OPC particles had the smallest specific surface. The relationship between the HRWR dosage and the specific surface of the anhydrous particles of CSF-blends has been extensively elaborated in a previous paper /26/. Besides, the pure OPC paste had the greatest content of clinker minerals which are responsible for the evolution of most of the total hydration heat. On the other side, in hydrating pastes without HRWR, ie. in the paste without improved dispersion of solid particles, the restricted mobility of water caused a reduction of hydration rate so that all the temperatures of those pastes were lower than the temperatures of the comparative pastes with HRWR admixture.

Finally, among the pastes without superplasticizer admixture the known CSF-accelerating effect during early hydration of alite and C_3A caused CSF-containing blends to have temperature maxima higher than the pure PC paste.

CONCLUSIONS

- By increasing the curing time in the OPC and OPC-CSF pastes of low water content the capillary porosity decreased. At the same time capillaries of smaller radius characterized by higher suction power were formed. The admixture of HRWR was beneficial for the formation of small capillaries in the pastes of low water content, particularly in the OPC-CSF blends.

- In all CSF-containing pastes of w/s=0.28 a distribution of pore sizes was found in which the majority had pores of a radius smaller than 15 nm even after one day of hydration. At 28 days age the refinement of the pore sixes progressed further. Later,after 250 days of curing in water a re-increase of the median pore size in some pastes was observed. The most obvious re-increase of the median pore size was detected at the age of 3 years in the blend with 15 % of CSF and HRWR admixture.

- After a relatively short curing time changes in all structural parameters determined were increasingly reduced by progressive hydration. One of the main influences seems to be the strong restriction of water mobility by the densifying of the low water composite structure. In the pastes without HRWR and by increasing the CSF-content in the pastes this restriction appeared sooner and was more pronounced.

- Paste temperature measurements confirmed that the presence of HRWR was of principal advantage in the hydration process in the pastes of low water content. The highest temperature was measured in the superplasticized pure OPC paste where the solid particles were best dispersed. The highest clinker content in pure OPC paste also influenced the temperature level of the paste. The results of temperature increases of hydrating pastes are congruent to the results and changes in the other tested parameters.

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