

TEMPERATURE DEPENDENCY OF THE HYDRATION OF DENSE CEMENT PASTE SYSTEMS CONTAINING MICRO SILICA AND FLY ASH



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ABSTRACT

The effect of curing temperatures of 5, 25 and 50°C on sealed cured cement paste samples containing between 7.5 and 25 % pozzolanic filler in the form of fly ash and micro silica at a water/powder ratio of app. 0.23 has been studied. The results indicate that the main effect of elevating the curing temperature is densification or crystallization of the hydrates, liberating significant amounts of surface adsorbed water and increasing the amount of chemically bound water.

Key words: Hydration, Temperature, Cement paste, Pozzolans.

1. INTRODUCTION

It is well documented that the amount of chemically bound water and the compressive strength of a Portland cement system decreases, when the curing temperature is increased beyond the usually applied reference temperature of 20°C^{1,2,3,4,5}. At least this is the case in the normally used range of water/cement ratios (above 0.35 to 0.50^{1,2,3,4,5}). There is some difference of opinion as to whether the addition of pozzolanic fillers like fly ash influences this tendency. Some observe an increase in strength at elevated curing temperatures when more than 10 % of fly ash is added², some a decrease for an addition as high as 30 %⁴. The degree of hydration however is reported to increase as a function of temperature, even at a water/cement ratio of 0.56⁶.

The reason for the reduced strength at higher curing temperatures is believed to be the rapid formation of dense inner product hydrate layers on the surface of the cement grain, resulting in a reduced hydration rate⁴ and an increased porosity. Micro cracks caused by thermal stresses and similar phenomenon may weaken the matrix further.

In denser systems with lower water/cement ratios, the effect of temperature is not as well documented. Some investigations on neat cement pastes have been conducted, suggesting that the main effect of increased curing temperature is visible through a densification of the inner product hydrates⁷ and a corresponding increase in general porosity⁸. However, the low water/cement ratio systems are rarely applied using only neat cement pastes, rather they incorporate significant amounts of pozzolanic fillers such as fly ash and micro silica.

As part of an industrial Ph.D. study⁹, the relation between curing temperature and chemically bound water content (often used as indicator for the degree of hydration and therefore as indicative for compressive strength) in dense cement pastes containing significant amounts of fly ash and micro silica, was established.

2. MATERIALS AND METHODS

The investigation was conducted on cement paste samples in a sealed cured state (no moisture transfer with the surroundings and therefore allowed to self-desiccate). The mix designs for the mixes are shown in Table 2, and the Bogue composition of the used cements is shown in Table 1. Elkem micro silica and Danaske fly ash were used. As superplasticizer, Glenium 51 was used (in solution, 35 % solids). Normal tap water was used.

Table 1: Chemical composition of the used cement types (Bogue). Both cements were ground to a Blaine fines of app. 400 m²/kg in the laboratory.

Cement type	C ₃ S [%]	C ₂ S [%]	C ₃ A [%]	C ₄ AF [%]	Total [%]
"W": White cement	61.7	24.9	4.5	0.9	92.0
"M": Mineralised cement	63.0	10.0	8.0	11.0	92.0

Table 2: Mix designs for the investigated cement pastes. "W" in the beginning of the mix name symbolises white cement and "M" mineralized cement. "f" indicates percentage of fly ash, "s" percentage of micro silica. All percentages of dry powder weight.

Mix	Cement [%]	Fly ash [%]	Micro silica [%]
W-f5-s2.5	92.5	5.0	2.5
M-f5-s2.5	92.5	5.0	2.5
W-f15-s2.5	82.5	15.0	2.5
M-f15-s2.5	82.5	15.0	2.5
W-f5-s10	85.0	5.0	10.0
M-f5-s10	85.0	5.0	10.0
W-f15-s10	75.0	15.0	10.0
M-f15-s10	75.0	15.0	10.0

The mixes consisted of 500 g of powder (cement, fly ash and silica), and 100 g of water (water/powder-ratio 0.20). The super plasticizer was added to the mix without correction for water content (dosages ranging from 2 to 4 % by weight), and the materials contained some water, resulting in slightly varying water/powder ratios around 0.23. The cement pastes were first mixed under vacuum, and then cast and cured in sealed polypropylene micro tubes containing app. 2 ml. of cement paste.

The cured samples were dried to weight constant in a vacuum oven (CO₂-free drying) to establish the content of evaporable water, and subsequently burned at 975°C to weight constant to establish the amount of non-evaporable or chemically bound water. Six samples were cast for each mix/temperature/maturity combination and the average results used.

Since the reaction rate of cement is highly temperature dependent, it is necessary to compare the evaporable and non-evaporable water contents as a function of accumulated maturity M_θ , relative to the fixed temperature, θ , in order to compare the results obtained at different curing temperatures. Thus, the accumulated maturity of the samples is compared to what would have been achieved by curing the samples at 25°C, presuming constant activation energy of 33.5 kJ/mol (corresponding to ordinary Portland cement¹⁰), according to the Arrhenius function¹¹. The curing time expressed in maturity hours is henceforth denominated $\tau(M_{25})$. The samples were allowed to cure to $\tau(M_{25})$: 3, 6, 20, 54, 168 and 672 hours (from 0.125 to 28 days) at 5°C, 25°C and 50°C. Selected samples were investigated using Scanning Electron Microscopy (SEM) to determine differences in physical structure as a result of the different curing temperatures.

3. RESULTS

An example of the results is shown in Figure 1. The obtained water phase distribution at 28 days for the investigated mixes are presented in Table 3.

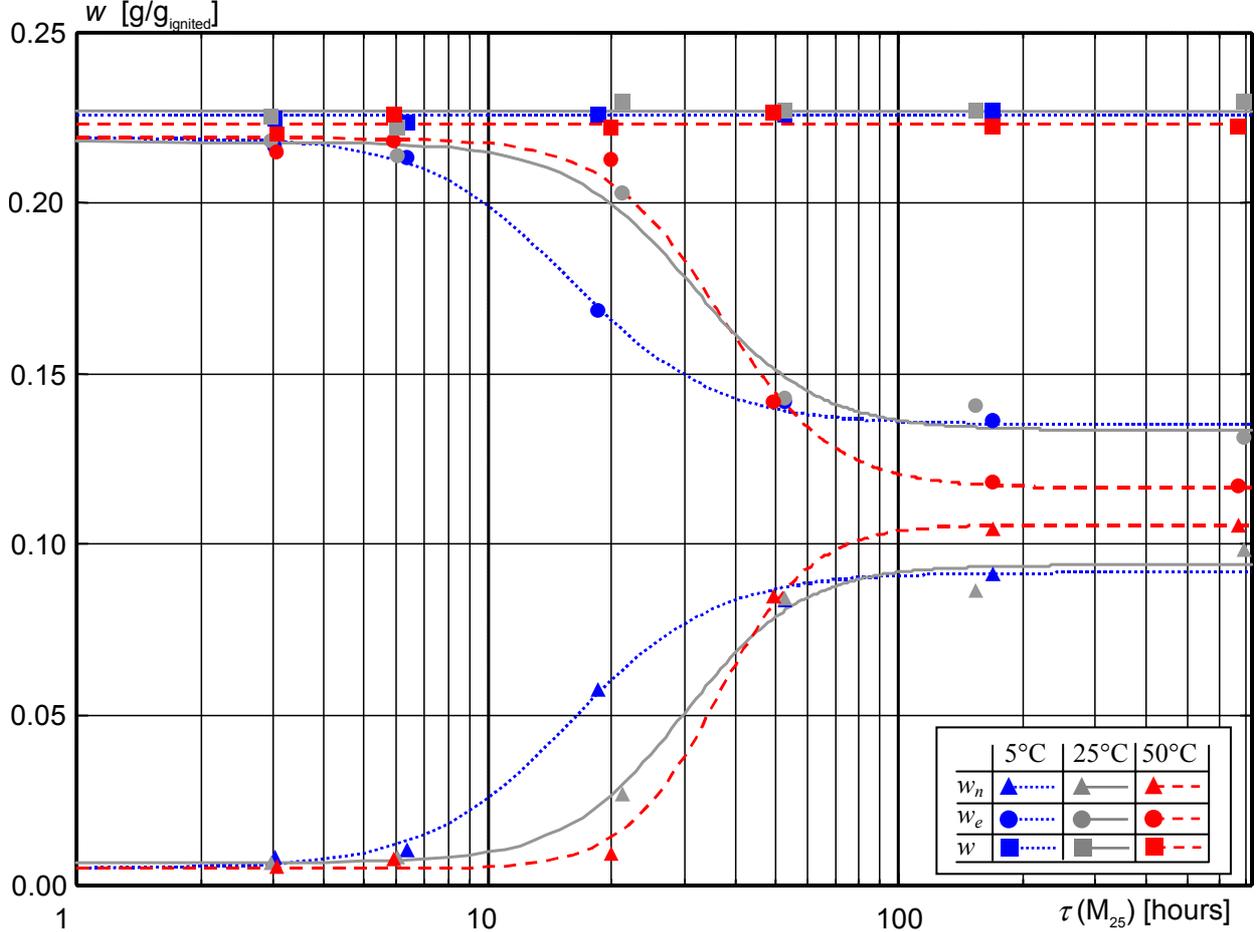


Figure 1: Water phase distribution development up to 28 days for cement paste W-f5-s2.5 cured in a sealed cured state at 5°C, 25°C and 50°C. w_n is the chemically bound water, w_e evaporable or physically bound water and w is total water content.

Table 3: Water phase distribution at 28 days M_{25} for the investigated cement pastes. All values are in gram water per gram ignited powder weight. w_n is the chemically bound water, w_e evaporable or physically bound water and w/p is total water content per gram powder.

Sample	5°C			25°C			50°C		
	w_n [g/g]	w_e [g/g]	w/p [g/g]	w_n [g/g]	w_e [g/g]	w/p [g/g]	w_n [g/g]	w_e [g/g]	w/p [g/g]
W-f5-s2.5	0.0947	0.1324	0.2271	0.0984	0.1312	0.2296	0.1056	0.1172	0.2228
M-f5-s2.5	0.0945	0.1381	0.2326	0.0899	0.1431	0.2330	0.1116	0.1078	0.2194
W-f15-s2.5	0.0859	0.1342	0.2201	0.0907	0.1364	0.2271	0.0971	0.1247	0.2218
M-f15-s2.5	0.0899	0.1385	0.2284	0.0887	0.1388	0.2275	0.1021	0.1216	0.2237
W-f5-s10	0.1004	0.1448	0.2452	0.1015	0.1461	0.2476	0.1039	0.1440	0.2479
M-f5-s10	0.0944	0.1492	0.2436	0.0954	0.1499	0.2453	0.0973	0.1417	0.2390
W-f15-s10	0.0945	0.1485	0.2430	0.0927	0.1555	0.2482	0.0931	0.1487	0.2418
M-f15-s10	0.0985	0.1498	0.2483	0.0970	0.1486	0.2456	0.0919	0.1454	0.2373
Average	0.0941	0.1419	0.2360	0.0943	0.1437	0.2380	0.1003	0.1314	0.2317

The apparent difference in the course of hydration between the curing temperatures in Figure 1 is mainly due to differences between presumed and actual temperature of the samples during the first few hours of curing. The samples were all mixed at 20°C, and it took one to two hours before the samples attained their intended curing temperatures at 5°C and 50°C. Hence the calculated maturities used for the plot deviates from the actually attained. Forthwith only the water phase distribution at 28 days is considered.

4. DISCUSSION

From Figure 1 and Table 3 it is evident that there is little difference between 5°C and 25°C on the final hydration ratio of the cement paste. A curing temperature of 50°C increases the amount of chemically bound water at the expense of physically bound water – additional strength giving hydrates are formed – contrary to the usual assumption regarding the effect of curing at elevated temperature described in section 1.

These tendencies are common to all samples, although not equally pronounced. To illustrate the effect of curing temperature, the amount of chemically bound water in g pr. g cement at 28 days M_{25} is presented in Figure 2. The water/cement ratios for the samples are calculated directly by disregarding the filler content in the mixtures.

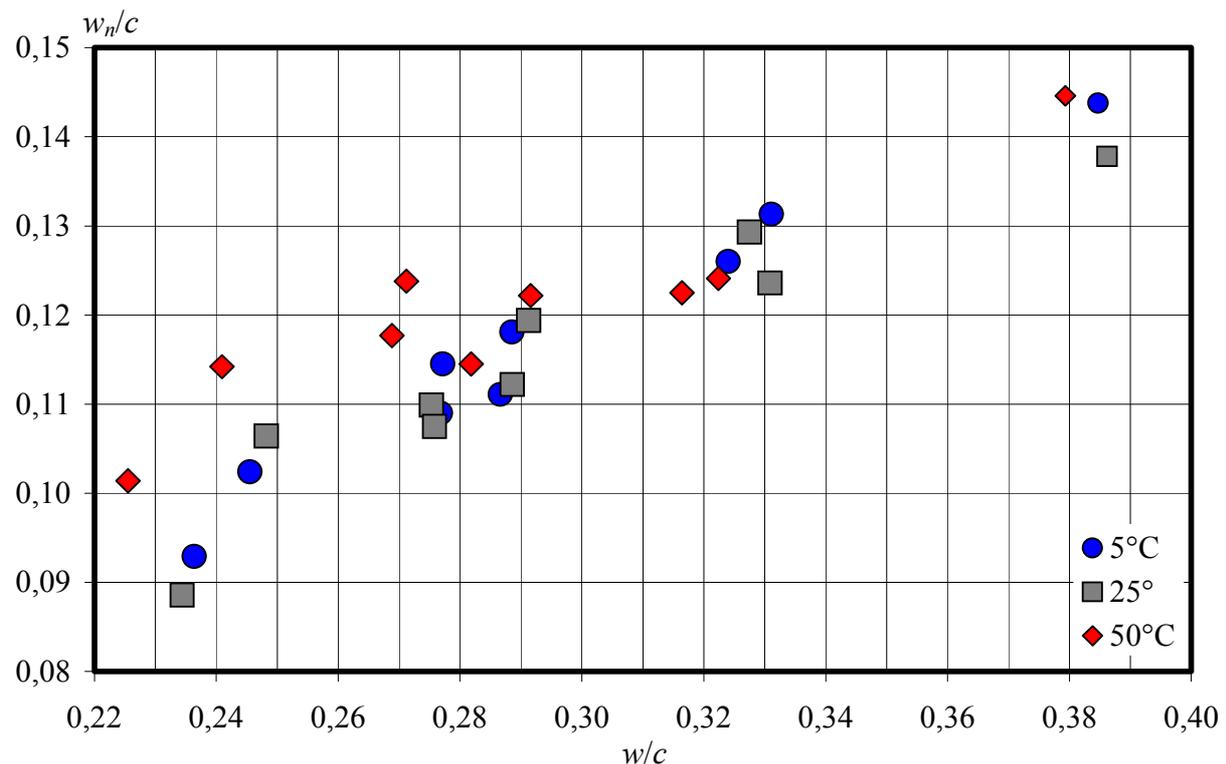


Figure 2: Relation between water/cement ratio and chemically bound water pr. g cement at 28 days M_{25} . The contents of pozzolanic filler in the pastes vary from 7.5 to 25 percent by weight.

For comparison, the expected chemically bound water contents at complete hydration of cement ranges from app. 0.21 to 0.23 g/g cement^{12,13,14}. By calculation, the specific theoretical values for the used temperatures were 0.2103 g/g at 5°C, 0.2134 g/g at 25°C and 0.2094 g/g at 50°C¹⁴. The calculated lower content of chemically bound water at 50°C is a result of the differences in equilibrium temperatures at which different CSH hydrates are stable¹⁵. At low temperatures all

normally found hydrates are stable (or rather meta-stable). At higher temperatures however, the hydrates containing a significant number of water molecules destabilize and may release water. Hence at different temperatures, different hydrates are thermodynamically meta-stable. At low temperatures, the usually assumed average chemically bound water content for the hydrates of 0.23 g/g may well be valid in a system containing sufficient water. However, when the temperature is increased, the meta-stable hydrates will – on average – contain less water, reducing the value to less than 0.23 g/g.

The difference between the observed chemically bound water content around 0.11 g/g cement compared to the usual 0.21 to 0.23 g/g cement at complete hydration, is mainly attributable to the low initial water cement content (below 0.38), making complete hydration impossible. But the addition of pozzolanic fillers, especially micro silica also influences the ratio:

Since pozzolanic hydration reactions cause no significant change of water phase distribution^{15,16}, the effect of pozzolanic reaction is to bind a large fraction of the accessible water originally in the mix by surface adsorption. Hence the effect of the pozzolans on the water phase distribution is to decrease the *available* water/cement ratio. So although the presence of filler in the system initially increases the water/cement ratio, the ultimate effect is to decrease the amount of water available for cement hydration. The mechanism is schematically illustrated in Figure 3.

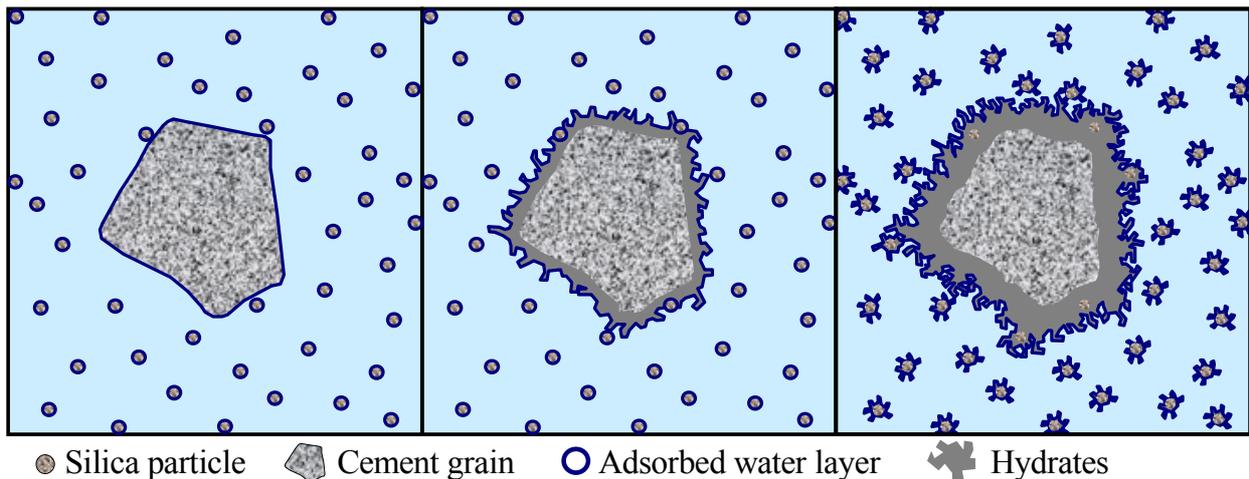


Figure 3: Progressive surface adsorption. Immediately after water addition (left) the cement and silica particles are suspended in water and bind little water physically. Next, cement hydration begins, increasing the surface area and the amount of physically bound water (middle). Finally, the pozzolanic particles react with calcium hydroxide from the cement reactions and the cement hydration continues, both increasing the physical binding of water (right).

Thus, in addition to the temperature effect, the self-desiccation of the cement paste system, accelerated by the physical binding of water on the surfaces formed by pozzolanic reactions, may result in a further redistribution of water within the system. The thermodynamic activity is lowered due to the self-desiccation, forcing some of the more water-containing hydrates to release some of their crystal (or chemically bound) water to the surroundings, where some reacts with unhydrated cement, and some is adsorbed onto the formed surfaces.

To summarize, the attainable chemically bound water content pr. g cement in a dense cement paste containing pozzolanic fillers at increased curing temperatures should be the result of two parallel processes: The water-rich hydrates becomes less stable due to increased temperature,

and, the lowered activity of the physically bound water in the system due to self-desiccation accelerates the release of chemically bound water from the hydrates.

How does the above mentioned correlate to the fact that the observations from the measurements indicate an *increase* in chemically bound water in the samples cured at 50°C compared to those cured at 5°C and 25°C, and not a decrease?

Two mechanisms are believed responsible:

A: Some of the water liberated from the hydrates at higher temperatures react to form more hydrates, compensating somewhat for the reduced w_n/c ratio by increasing the amount of reacted cement. This only *reduces* the loss of chemically bound water pr. g. cement compared to normal temperature cured materials, since it also results in the formation of new surfaces.

B: The structure of the hydrates formed at higher temperatures is more crystalline than hydrates formed at lower temperatures (meaning denser, with less surface area). The reduced surface area liberates a significant quantity of otherwise physically bound water for further hydration. This mechanism would also explain the difference between "low" and "normal" water cement ratio systems: In the "normal" range, the liberation of physically bound water is insignificant to the hydration since there is already sufficient free water for complete hydration of the cement. Hence no extra hydration takes place, and the reduced w_n/c ratio and the "blocking effect"⁴ governs the final amount of chemically bound water. This mechanism is believed to be the main reason for the observed increase in chemically bound water content at increased curing temperature for the considered cement paste systems.

The conclusion is supported by SEM results, see Figure 4 and 5, showing a significant densification of the hydrates when the temperature is increased, also observed previously⁷.

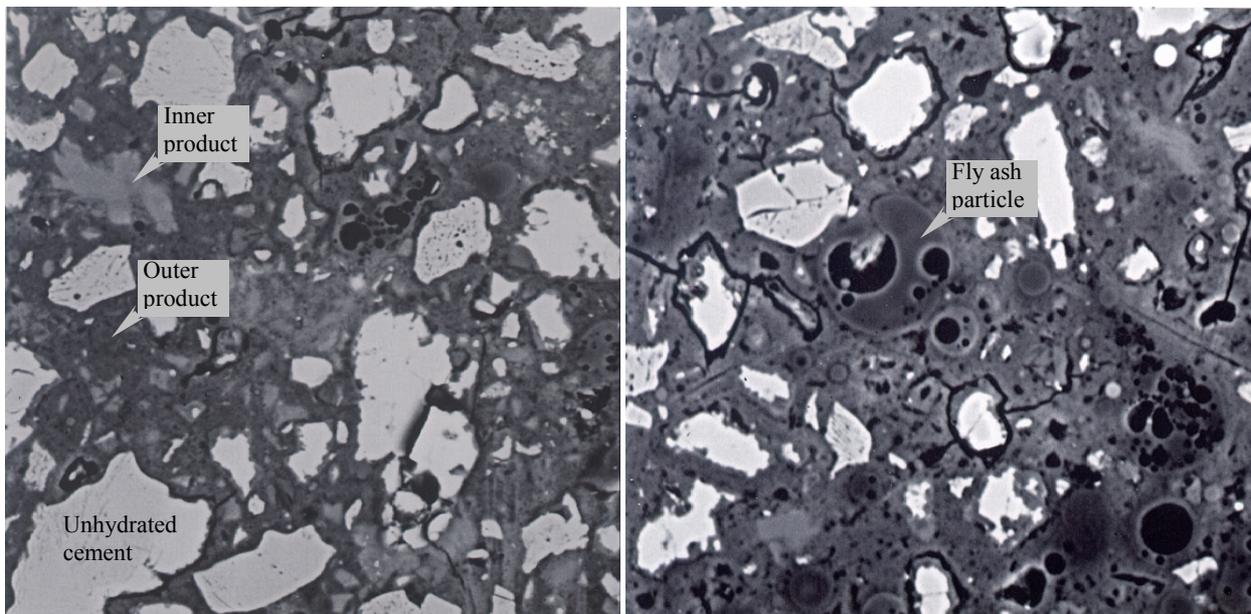


Figure 4: SEM BSE images of cement paste microstructure at 5°C. W-f5-s2.5 left and W-f15-s10 right. The images are 100 μm wide (original magnification 1000 \times)

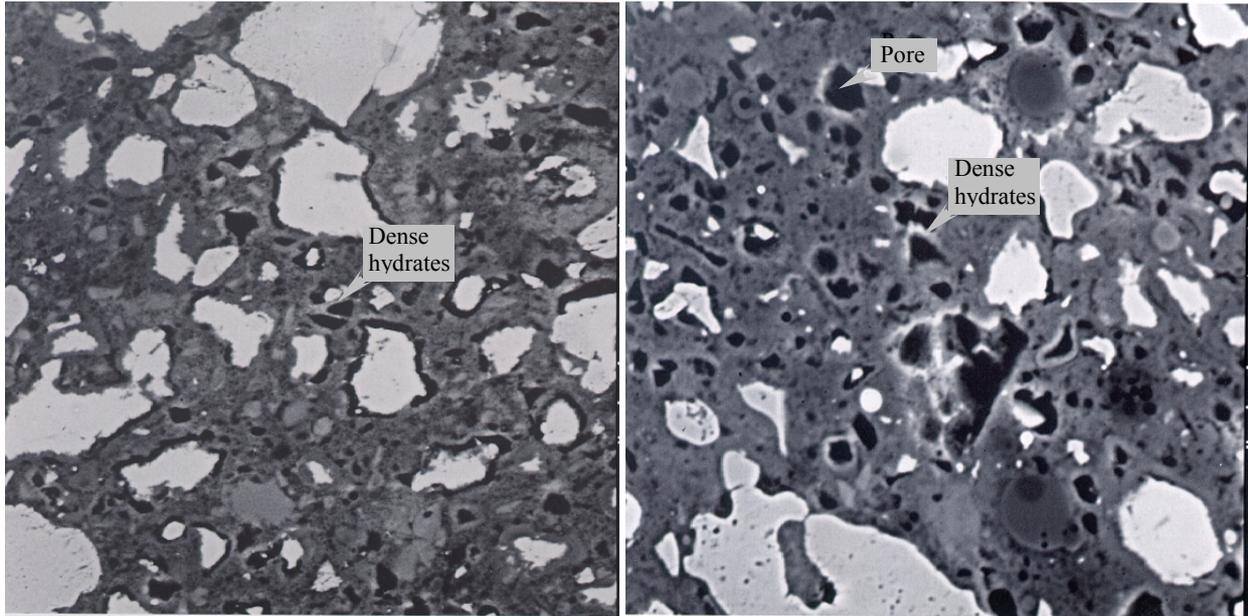


Figure 5: SEM BSE images of cement paste microstructure at 50°C. W-f5-2.5 left and W-f15-s10 right. The images are 100 μm wide (original magnification 1000×)

5. CONCLUSION

It has been demonstrated that the amount of chemically bound water increases with curing temperature for a sealed cured cement paste system containing moderate amounts of pozzolanic fillers at *sufficiently low* water/cement ratios.

This is believed to be the direct result of a more crystalline structure of hydrates formed at higher temperatures, reducing the amount of surface adsorbed water in the system: In the low water/cement ratio system, the available amount of water is limited and the system is self desiccated. The reduced physical adsorption increases the amount of water available to hydration.

This increase in available water counters the effect of reduced w_n/c ratio of the hydrates at higher temperature, and the retaining of water by physical binding on the surfaces of hydrates formed by pozzolanic reactions.

Within the considered composition and curing temperature range the net result of these mechanisms ranges from an increase in chemically bound water content with increased curing temperature at *low to moderate* pozzolanic filler contents (especially micro silica contents appears significant) to a negligible effect at *high* filler contents.

This increase in chemically bound water (and thus formed hydrates) due to the above mentioned mechanisms may be the cause for the increased compressive strengths at increased curing temperatures observed in some low water content systems.

6. ACKNOWLEDGEMENTS

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