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INVESTIGATIONS ON THE AGING OF HYDRATED TRICALCIUM SILICATE AND PORTLAND CEMENT PASTES

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ABSTRACT

Pure tricalcium silicate and portland cement pastes made with variable water solid ratios were cured at 20 °C for 1 to 24 months. It was found that even after the hydration reaction had been terminated the pastes exhibited gradual changes in their specific surface area as determined by N_2 and H_2O adsorption and in pore size distribution as determined by Hg porosimetry.

INTRODUCTION

On contact with water, clinker minerals present in portland cement hydrate, yielding a variety of hydration products. The hydration process stops when the whole amount of cement is hydrated, or when the amount of available water is consumed, or if the hydrates already formed prevent the migration of water to the surface of the residual non-hydrated material. It is conceivable that further changes in the structure of the present hydrates may take place even after the hydration process had been terminated. We will call changes of this kind, which take place without any further uptake of water, aging of the paste. In previous work Rodgers et.al. [1] studied pure tricalcium silicate pastes cured up to 20 years and found a progressing [SiO_4] polycondensation with increasing curing time. In our work we studied the structure of pure tricalcium silicate and ordinary portland cement pastes cured for different periods of time. The aim of the work was to explore, whether any structural changes are taking place in the pastes in a period at which the hydration process has been already terminated and the material is stored in a completely hydrated state.

EXPERIMENTAL

The following materials were used in the experiments:

Pure tricalcium silicate (abbr. C_3S) with a specific surface area of 370 m^2/kg (Blaine).

A portland cement of the oxidic composition CaO: 65.2%, SiO_2: 20.8%, Al_2O_3: 5.72%, Fe_2O_3: 2.25%, MgO:1.18%, SO_3: 3.00%, Na_2O: 0.48%, K_2O: 0.78% and TiO_2:0.25% with a fineness of 468 m^2/kg (Blaine).

Pastes prepared from both materials with variable water-solid ratios were placed into a series of glass jars. Each jar was closed with a plastic top and additionally sealed into polyethylene bags to prevent water loss and carbonation. The samples were stored at 20 ± 2 °C for periods between one and 24 months. After that the hydration was stopped and the free water removed by d-drying.

In samples produced this way the presence of non-hydrated material was determined by X-ray diffraction. The thermal decomposition and the free lime content was studied by differential thermal analysis (DTA) and thermogravimetry (TG). The amount of combined water was determined as the loss on ignition at 1000 °C. The specific surface area was measured by water vapor and nitrogen adsorption.

The pore size distribution was determined by Hg porosimetry. From the obtained data the specific surface area was calculated assuming a cylindrical cross section of the pores.

RESULTS

X-ray diffraction

In XRD-studies only very small peaks belonging to C_3S were found in C_3S pastes hydrated for one month. In samples cured 3 months and longer non-hydrated C_3S was not detectable by X-ray diffraction.

Also in portland cement pastes made with water-solid ratios of 0.60 and 1.00 all peaks belonging to non-hydrated cement phases disappeared within three months of curing. Contrary to that, in the paste made with w/s = 0.30 small amounts of non-hydrated material were still detectable even after 24 months of hydration, however, the intensity of the pertinent peaks remained unchanged after three months, indicating a stopping of the hydration at that time.

Combined water and free lime

Table I summarizes the combined water and free lime values found. The latter ones represent the averages of results found by DTA and TG.

It appears that the combined water content did not vary significantly in samples hydrated 3 months and longer. Among PC-pastes the final value, i.e. that after 24 months of curing, was lower in the sample made with w/s = 0.30 than in those made with w/s = 0.60 and 1.00, apparently due to its incomplete hydration.

Also the free calcium hydroxide content did not vary significantly in samples cured for different lengths of time. The only exception was the PC-paste with w/s = 0.30 in which a moderate increase of the free lime content was found. The final calcium hydroxide values differed in different pastes. They were higher in C_3S than in PC pastes and increased with increasing water-solid ratio.

The obtained combined water and free calcium hydroxide values are in line with the XRD results found, indicating the completion or termination of the hydration process within less than three months of curing.

The performed DTA and TG investigations revealed also that the shapes of the obtained curves did not change distinctly between 3 and 24 months of curing.

Specific surface area

The found specific surface area values are summarized in Table II. In line with previous observations the values found by nitrogen adsorption were significantly lower than the corresponding water adsorption results, however, the ratio S_{N2}/S_{H2O} varied greatly in different pastes and after different curing times.

TABLE I

Combined water and free $Ca(OH)_2$ contents

binder	w/s	hy. time (months)	$H_2O_{comb.}$ (%)	f.$Ca(OH)_2$ (%)
C_3S	0.5	1	22.1	26.5
		3	22.1	28.9
		6	25.2	28.7
		12	25.9	29.6
		18	25.1	29.1
		24	24.6	28.9
C_3S	1.0	1	22.2	33.0
		3	25.3	33.5
		6	26.8	33.3
		12	26.0	34.4
		18	26.0	34.4
		24	25.3	34.2
PC	0.3	1	18.1	9.4
		3	18.4	10.8
		6	20.3	10.3
		12	20.8	12.3
		18	20.3	12.0
		24	20.0	11.8
PC	0.6	1	27.2	18.3
		3	29.5	18.2
		6	28.3	20.5
		12	29.7	19.6
		18	29.2	19.2
		24	28.5	19.5
PC	1.0	1	29.3	20.2
		3	29.7	20.1
		6	30.6	22.6
		12	30.9	21.6
		18	30.3	21.7
		24	29.4	21.0

The S_{H2O} values generally increased with progressing curing time. At equal curing times the values found in C_3S pastes were generally higher than those of portland cement, inspite of a higher amount of portlandite present whose specific surface area is very low. The lower values found in cement pastes with w/s = 0.30 are apparently due to a incomplete hydration of this material.

The BET_{N2} values remained constant in the PC paste with w/s = 0.30 and increased with

TABLE II

Specific surface area determined by water vapor and nitrogen adsorption

binder	w/s	hydr. time (months)	S_{N2} (m^2/g)	S_{H2O} (m^2/g)
C_3S	0.5	1	6.6	85.0
		3	14.7	101.0
		6	17.9	99.7
		12	38.2	121.9
		18	48.2	129.2
		24	55.5	158.3
C_3S	1.0	1	6.8	85.2
		3	12.0	110.9
		6	15.7	112.5
		12	59.4	131.0
		18	80.9	134.3
		24	117.0	150.7
PC	0.3	1	5.4	63.0
		3	5.5	69.7
		6	4.7	70.7
		12	4.8	87.3
		18	5.1	93.6
		24	5.0	106.5
PC	0.6	1	15.7	87.5
		3	17.0	89.5
		6	21.1	105.4
		12	20.0	118.9
		18	20.4	118.5
		24	20.9	134.1
PC	1.0	1	18.5	65.9
		3	22.3	104.1
		6	30.9	106.7
		12	35.7	115.5
		18	34.7	114.6
		24	34.5	122.8

progressing curing time in those with higher water-solid ratios. At each curing time the specific surface area increased with increasing water-solid ratio. The values found in C_3S-pastes increased even more than those in PC-pastes. At shorter curing times they were lower than similar values found in PC pastes, whereas after 12 months they became significantly greater.

Pore size distribution

The data obtained are summarized in table III. It appears that the volume accessible to Hg at 2000 atm (P) declined between 2 and 24 months of curing, implying an increase of the volume of very fine pores (r < 4 nm) not accessible to mercury. Among pores accessible to Hg the fraction of pores with r < 100 nm increased whereas that with larger radii declined. The medium radius of the pores accessible to Hg declined as well. These findings imply an overall refinement of the pore system in the course of curing.

The specific surface area values determined from Hg porosimetry data were between those found by nitrogen and water adsorption. They increased distinctly with increasing water-solid ratio but changed little between 2 and 24 months of curing.

TABLE III

Specific surface area and pore size distribution determined by Hg porosimetry

binder	w/s	hy. time (months)	S_{Hg} (m^2/g)	P (ml/ml)	$P_{<100nm}/P$	$P_{>100nm}/P$	$r_{50\%}$ (nm)
C_3S	0.50	2	42.7	0.366	0.516	0.484	87.1
		18		0.266	0.677	0.323	45.7
		24	55.1	0.148	0.696	0.304	15.2
PC	0.30	2	25.8	0.235	0.638	0.362	48.4
		18		0.210	0.667	0.333	47.2
		24	24.1	0.135	0.696	0.304	43.0
PC	0.60	2	43.5	0.349	0.728	0.272	55.3
		18		0.303	0.719	0.281	44.9
		24	53.5	0.184	0.859	0.141	18.6
PC	1.00	2	82.0	0.558	0.656	0.344	63.6
		18		0.522	0.851	0.149	37.6
		24	93.1	0.526	0.856	0.144	25.3

CONCLUSION

Our results suggest the existence of further structural changes in pure tricalcium silicate and portland cement pastes in a stage at which the hydration process had been terminated due to either a completed hydration or a too low starting water-solid ratio. These changes include a gradual increase of the specific surface area as measured both by nitrogen and water vapor adsorption and changes in pore size distribution as determined by mercury porosimetry. These results were obtained from pastes prepared with variable water-solid ratios, cured between 1 and 24 months at 20±2 °C in a sealed state and d-dried prior to testing. The origin of these changes is not obvious at this time. A comparison of pastes made with different water-solid ratios revealed the existence of differences in the specific surface areas determined at equal curing times, as well as in the amount of liberated calcium hydroxide, and thus, in the stoichiometry of the formed CSH phase.

REFERENCES

[1] S.A. Rodgers, G.W. Groves, N.J. Clayden and C.M. Dobsons: A study of tricalcium silicate hydration from very early to very late stages. Mat. Res. Soc. Symp. Proc. 85, 13-20 (1986).