THE HYDROXIDE-SULPHATE ION EQUILIBRIUM IN CEMENT PASTE PORE SOLUTIONS AND ITS SIGNIFICANCE TO THE THEORY OF AAR IN CONCRETE

Roland Herr and Wolfgang Wieker
Centre of Inorganic Polymeres, Berlin

The main chemical reactions going on during hydration of Portland cements are reflected by OH^-- and SO_4^{2-}-ion concentrations in the cement paste pore solutions. Long-term heat treatment of 5 Portland cements indicates a significant shift of the OH^-/SO_4^{2-}-ion equilibrium for the disadvantage of OH^--ions. The decrease of OH^--ion concentration is the clearer the larger the alkali content of the cement and the higher the temperatures are. On the basis of this finding the lag effect of AAR expansion at elevated temperatures can be chemically explained.

INTRODUCTION

In the theory of alkali-aggregate reaction exists a considerable deficiency regarding the explaination of temperature effect on mortar and concrete expansion above 40 °C and humidity saturation. With increasing temperatures the expansion rate is initially proportional to temperature, but falls off more rapidely at higher temperatures (Locher (1), Diamond (2)). In principle, Diamond et al (2) recognized two distinct stages of AAR

Stage I	Attack of aggregate by hydroxide ions and production of gel
Stage II	Sorption of pore fluid by reaction products, leading to concrete distress.

Under room temperature conditions and slightly elevated temperatures up to 40 °C the trend of expansion follows the proportions of alkalis dissoluted in the cement paste pore fluid and the temperature applied. A precondition for expansion is that a certain OH ion concentration is exceeded. Diamond (3) proposed an OH ion threshold concentration of 250 mMoles OH/l; Herr and Wieker (4) found a threshold value of about 500 mMoles OH/l related to 1 mm/m maximum expansion of mortar bars containing 20 mass-% borosilicate glass as alkali sensitive aggregate in the mortar sand.

Heat treatment of mortar bars above 40 °C exhibits in expansion measurements a lag effect which is the higher the higher the temperature is. French (5) and Jones and Poole (6) supposed from this finding that the AAR mechanism of Stage I is not a purely chemical, and must involve a physical component.

In the last few years we performed investigations of cement paste pore solutions squeezed out of short-term thermally cured Portland cement pastes in order to make a contribution for explaining the chemical reasons of subsequent Ettringite formation in steam cured concrete (Herr et al (7), Wieker and Herr (8), Herr and Wieker (9)). We monitored a significant increase of sulphate ion concentration in the cement paste pore fluid. The increase is the stronger the higher the alkali content and the SO_3/Al_2O_3 molar ratio of the cement and the sharper the heat treatment conditions are. After the end of a short-term thermal curing of cement pastes (relevance to concrete unit prefabrication) in a hydration period over months a decrease of the sulphate ion concentration was measured, accompanied by a molar 1 : 1 proportional increase of the hydroxide ion concentration - a chemical equilibrium process closely connected with its thermal equilibrium conditions. The OH/SO_4 ion equilibrium is the reflection of the chemical and thermal stability of calciumsulphoaluminate hydrates, e.g. Ettringite and can be described by the following equation

$$3\,CaO\cdot Al_2O_3\cdot 6H_2O + 2\,Ca(OH)_2 + CaSO_4\cdot 2H_2O + 2(K;Na)_2SO_4 + 24\,H_2O$$

$$\xrightleftharpoons[40...100\ ^{o}C]{20...40\ ^{o}C} 3\,CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O + 4\,(K;Na)OH \qquad (eq.\ 1)$$

Consequently the question rose whether - if the high temperature level is maintained over a long-term period - a further and clearer change in the OH/SO_4 ratio occurs which is characterized by an additionally reduced hydroxide ion concentration level.

The discussion on the OH ion threshold concentration has shown that the alkaline attack to aggregates strongly depends on the OH ion concentration in the pore fluid. We supposed the shift of the OH/SO_4 ion equilibrium could be a chemical reason on the AAR expansion lag effect at elevated temperatures. This paper deals with the results of our long-term hydration studies of cement pastes and their pore solutions and compares these results with that of mortar bar expansion measurements performed under the same hydration conditions.

EXPERIMENTAL

In our investigations 5 commercial Portland cements were used. They were selected according to their total alkali contents which range from 0.40 to 1.19 Na_2O-eq. %. The sulphate content of the cements was considered too, but we could not find cements which have in addition constant SO_3 concentrations. The chemical compositions of the cements are shown in table 1.

For preparing cement pastes all cements were mixed with distilled water in plastic bottles using a constant water-cement-ratio 0.50. The bottles were tightly closed and additionally - in order to prevent any loss of water during the long-term heat treatment - stored in sealed glass containers above a water layer. After mixing the samples were prestored for 2 hours at room temperature and than exposed to hydration temperatures of 20, 40, 50 and 60 °C. After a hydration period of 1, 7, 28, 90 and 180 days the hardened cement pastes were squeezed with a maximum compressive stress of 320 MPa in each case. The analysis of the pore fluids was performed by acidimetric titration and by ion chromatography.

TABLE 1 - Chemical composition of the Portland cements, mass-%

PC-type PC-No. oxides	PC 35 F*) 1	PC 45*) 2	PC 45 F 3	PC 55 4	PC 45 5
SiO_2	19.72	21.39	20.31	20.04	20.01
Al_2O_3	4.65	5.39	4.51	4.66	5.80
Fe_2O_3	2.92	2.10	3.14	2.57	2.28
CaO	64.51	64.06	63.96	63.74	61.70
MgO	1.09	1.58	2.75	3.52	3.30
K_2O	0.54	0.59	1.00	1.25	1.42
Na_2O	0.05	0.19	0.11	0.20	0.26
SO_3	3.25	3.30	3.33	3.93	3.33
L.O.I.	2.93	1.14	0.31	n.d.	n.d.
CO_2	1.72	0.15	n.d.	n.d.	n.d.
Na_2O-eq.	0.403	0.578	0.768	1.023	1.194
SO_3/Al_2O_3 **)	0.89	0.78	0.94	1.07	0.73

*) low alkali cements; **) molar ratio; n.d. not detected

For investigating the AAR expansion effect in dependence on cement type and hydration temperature flat mortar prisms of 2 x 4 x 16 cm using a mixture proportion cement : aggregate sand : water 1 : 2.5 : 0.50 were cast. 20 mass-% of the aggregate quartz sand within the fractions 0.16 - 0.50, 0.50 - 1.00 and 1.00 - 2.0 mm was replaced by crushed and sieved borosilicate glass (analogous Pyrex) with the same grain size distribution. The mortar was compacted by vibration, and the prisms were demolded after 1 day room temperature hydration. They were stored in a upright standing way in sealed copper containers on a perforated slab of plastics above a water layer. To avoid leaching of the prisms by condensed water the lids of the containers were covered by a polystyren thermal insulation. The expansion measurements were performed initially in a distance of few days, later in a distance of 10 to 20 days over a period of 60 weeks.

RESULTS AND DISCUSSION

Results of pore solution analysis. In principle, the cation and anion concentrations in the cement paste pore fluids are well balanced. By reasons of the clearness of our graphs we have represented in the figures 1, 2 abd 3 the OH and SO_4 anion concentrations only.

Fig. 1 demonstrates that low alkali Portland cement (Na_2O-eq.

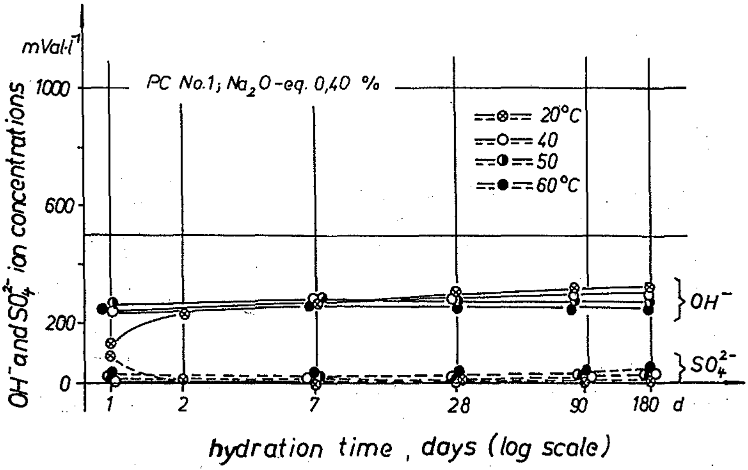

Fig. 1: Hydroxide and sulphate ion concentrations in the cement paste pore solutions versus hydration time and temperatures of low alkali Portland cement.

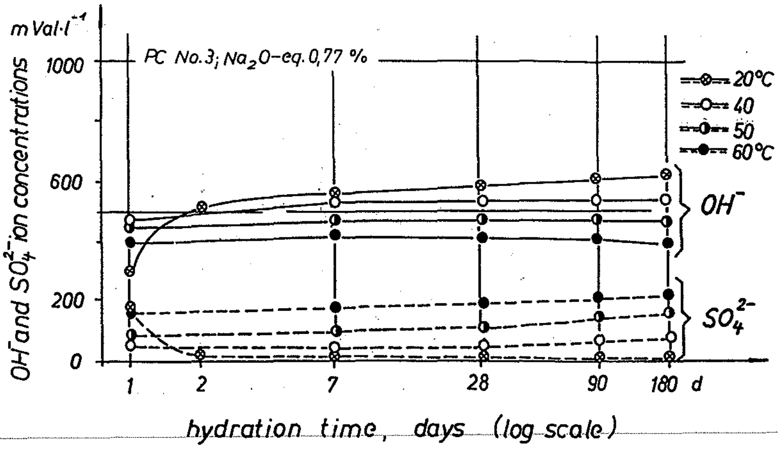

Fig. 2: Hydroxide and sulphate ion concentrations in the cement paste pore solutions versus hydration time and temperatures of medium alkali Portland cement.

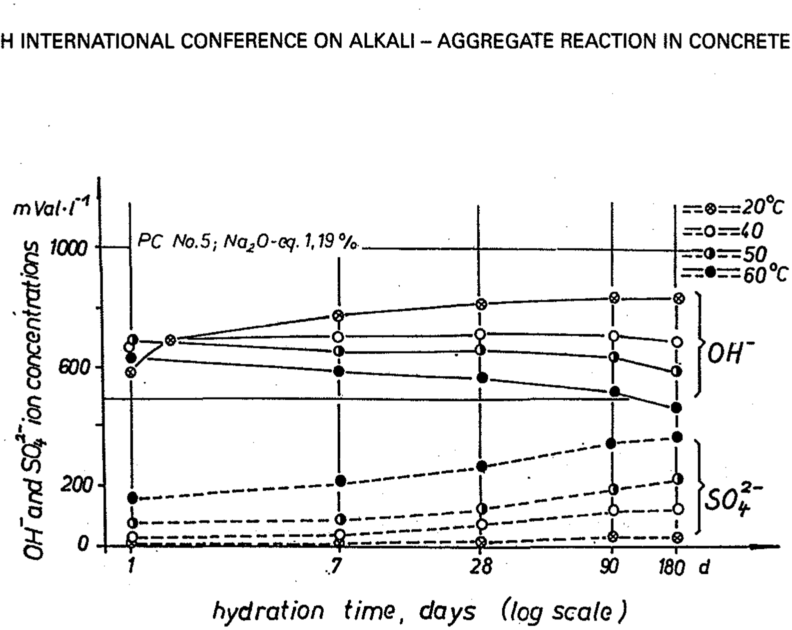

Fig. 3: Hydroxide and sulphate ion concentrations in the cement paste pore solutions versus hydration time and temperatures of high alkali Portland cement.

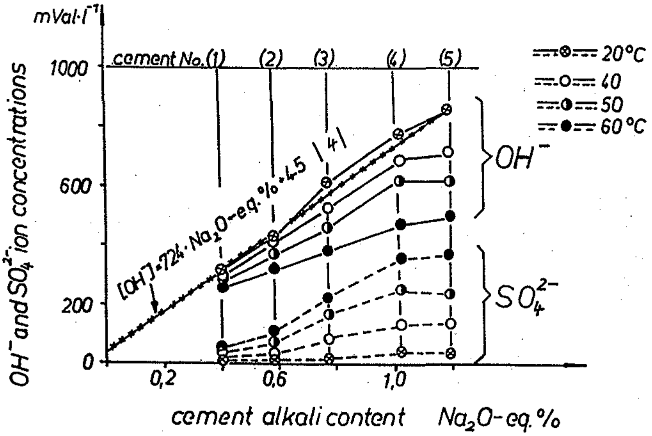

Fig. 4: Hydroxide and sulphate ion concentrations in the cement paste pore solutions after a hydration time of 180 days versus the total alkali content of the unhydrated Portland cements.

0.40 %) develops a relatively low alkalinity level of about 300 mMoles OH/l. The sulphate binding to calciumsulphoaluminate hydrates seems to be influenced in a small rate only. The SO_4 ion concentrations remain on a low level over the whole range of temperatures. Consequently, temperature changes from 20 to 60 °C have a modest effect on the shift of OH/SO_4 ion concentrations. This result was confirmed by the results of X-ray analysis related to Ettringite (Aft-) and Monosulphate (Afm-) phases in the thermally treated cement pastes. Under these low alkali conditions both Aft- and Afm-phases show a good thermal stability.

Fig. 2 shows the results of the anion analysis of the pore fluid of medium alkali (Na_2O-eq. 0.77 %) Portland cement. The shift of OH/SO_4 ion concentrations for the benefit of SO_4 ion is clearly visible. With increasing hydration temperatures from 20 to 60 °C the OH ion concentration drops from about 600 to 400 mMoles/l related to a hydration time of 180 days. The deminishing of 200 mMoles OH/l (200 mVal/l) is accompanied by an increase of the SO_4 ion concentration of 200 mVal SO_4/l (100 mMoles/l). This result is in correspondence with our X-ray investigations of the cement stone with regard to Aft- and Afm-phases. With increasing hydration temperature and time the intensity of both Ettringite and Monosulphate peaks became continously weaker.

Fig. 3 demonstrates the pore solution anion concentrations of the high alkali (Na_2O-eq. 1.19 %) Portland cement. The shift of the OH/SO_4 ion concentration is very clearly visible. With increasing hydration temperatures from 20 to 60 °C the OH ion concentration is deminished from 825 to about 490 mMoles OH/l after 180 days of hydration. The difference of 335 mMoles OH/l is balanced by an increase of the sulphate ion concentration from 30 to 369 mVal SO_4/l. Investigations of the cement stone by X-ray signalized a bad permanence of both Aft- and Afm-phases above 40 °C and long-term hydration conditions.

In fig. 4 are comprimized the results of hydroxide and sulphate ion concentration measurements in the pore fluids of all 5 cements after a hydration time of 180 days. The results are plotted versus the alkali content of the unhydrated cements. It is to be seen that the slope of the OH ion concentration curves is the less the larger the total alkali content and the higher the applied temperatures are. Furthermore, in reverse to the OH ion curves the slope of the sulphate ion curves is the larger the higher the total alkali content and the higher the temperatures are.
The relationship between OH ion concentrations of the pore fluids and the sodium equivalent (Na_2O-eq. = Na_2O % + 0.658 K_2O %) of the cements can be approximately described by linear functions. In dependence of the temperatures we get four equations (table 2). The equation from table 2 which is valid for 20 °C hydration processes is in a good accordance with our previously established equation (Herr and Wieker (4)):

$$Y = 724\,X + 45 \qquad \text{(eq. 6)}$$

Y = OH^- ion concentration mMoles OH^-/l

X = Portland cement Na_2O-equivalent content %

TABLE 2 - Equations for the calculation of equilibrium OH^- ion concentrations in cement paste pore fluids in dependence on the alkali content of unhydrated cement and hydration temperature (valid for water-cement ratio 0.50 and 180 days hydration time).

heat treatment temperature °C	equation	No. of equation
20	$Y = 708.5\ X + 41.5$	(eq.2)
40	$Y = 550.2\ X + 89.1$	(eq.3)
50	$Y = 462.1\ X + 85.6$	(eq.4)
60	$Y = 318.4\ X + 127.6$	(eq.5)

Legend: Y = OH^- ion concentration in mMoles/l
X = Portland cement Na_2O-eqivalent content %

The equation 2 of table 2 also is in good accordance with an equation calculated on the basis of an international data collection published by Diamond (10):

$$Y = 699\ X + 17 \qquad \text{(eq. 7)}$$

The symbols used have the same meaning like that in table 2. All 20 °C-equations are valid for water-cement ratios of cement pastes and mortars 0.50 and a duration of hydration of at least 30 days.

Doubtless, the linear relationships related to the equations No. 3, 4 and 5 have to be established more precisely especially for cement alkali contents larger than 1.0 Na_2O-eq. %, but in principle our investigations have proved the shift of the OH/SO_4 ion equilibrium in cement paste pore solutions for the disadvantage of OH ion with increasing alkali content of the cement used and the hydration temperatures applied. The OH ion concentration values after a hydration time of 180 days are scheduled in table 3. There they are compared with the results of the mortar bar expansion measurements.

Results of mortar bar expansion measurements. The results of the mortar bar expansion tests are shown in the fig. 5, 6 and 7 and are related to the Portland cements No. 1, 3 and 5. The expansion behaviour of the mortars was measured over a storage time of at least 400 days. In principle, low, medium and high alkali Portland cements demonstrate quite different expansion effects of the borosilicate glass containing mortars.

Fig. 5 shows as expected a very small maximum expansion of the low alkali (Na_2O-eq. 0.40 %) Portland cement mortar less than 0.2 mm/m within 400 days storage time. The influence of the temperatures from 20 to 60 °C remains very moderate.

Fig. 6 is valid for the medium alkali (Na_2O-eq. 0.77 %) Portland cement mortar and demonstrates a typical AAR expansion lag effect at storage temperatures larger than 40 °C. The expansion maximum with about 3.3 mm/m is reached at 40 °C storage of the mortar. Above 40 °C, at 50 and 60 °C storage temperatures the expansion

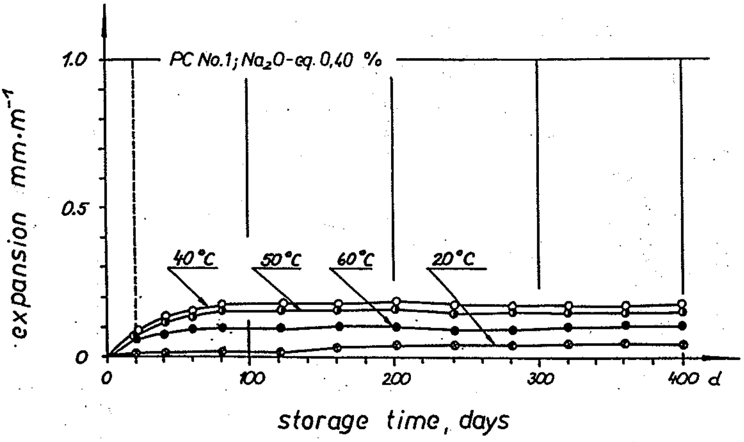

Fig. 5: Expansion of mortar bars made with low alkali Portland cement versus the mortar storage time at 20, 40, 50 and 60 °C.

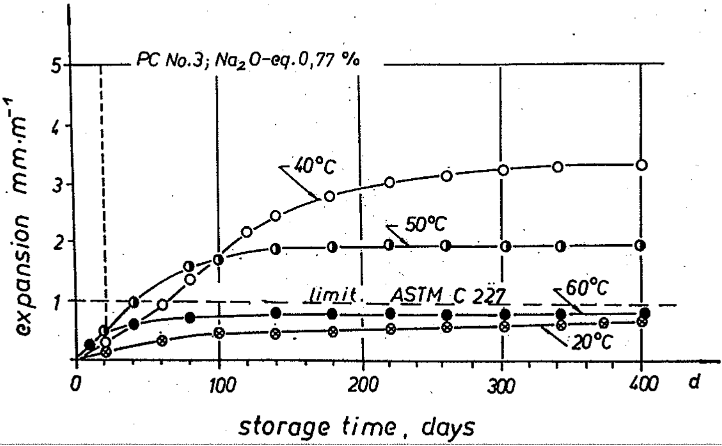

Fig. 6: Expansion of mortar bars made with medium alkali Portland cement versus the mortar storage time at 20, 40, 50 and 60 °C.

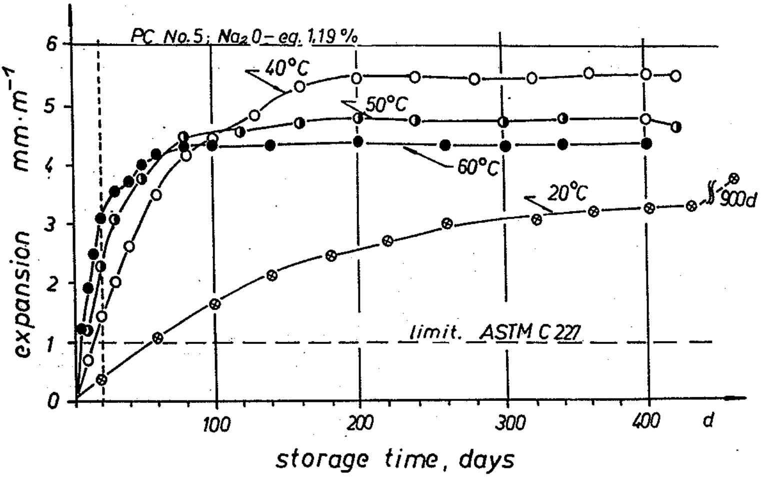

Fig. 7: Expansion of mortar bars made with high alkali Portland cement versus the mortar storage time at 20, 40, 50 and 60 °C.

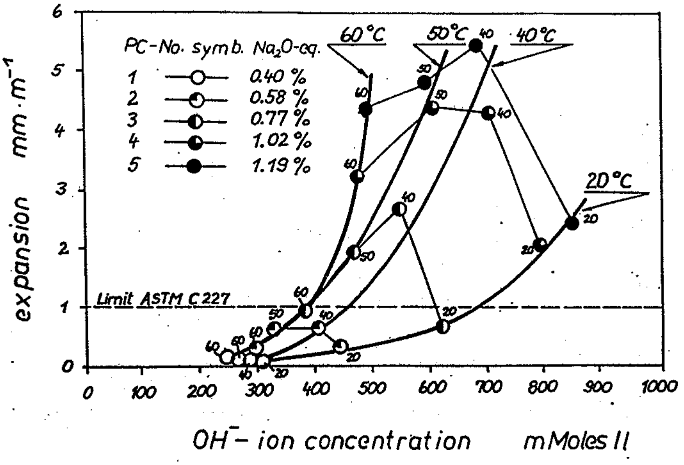

Fig. 8: Expansion of mortar bars versus the hydroxide ion concentration in the cement paste pore solution at 20, 40, 50 and 60 °C after a hydration/expansion time of 180 days.

maxima are deminished. The 60 °C expansion level is about 0.90 mm/m and as low as that of the 20 °C expansion curve after a storage time of 400 days.
Fig. 7 demonstrates an AAR expansion lag effect too but in the case of the high alkali (Na_2O-eq. 1.19 %) Portland cement mortar the deminishing of the maximum expansion level with about 5.6 mm/m at 40 °C to 4.3 mm/m at 60 °C is less than in the case of medium alkali cement mortar (fig. 6).

In general, the expansion curves can be sub-divided into two ranges. The first range characterizes the early stage of expansion which includes the period from the beginning of the experiment until about 20 days. In that period the expansion curves are characterized by a more or less linear slope. The slope is the steeper the larger the alkali content of the cements and the higher the storage temperatures are. The second range of expansion curves can be described by a transition to an expansion equilibrium. We think this range is more important for explaining the relationship between cement paste alkalinity level, temperature and expansion potential. Therefore we took the expansion readings after a storage time of 180 days and compared them with the OH ion concentrations in the cement paste pore fluids. The values were scheduled in table 3.

TABLE 3 - Comparison of hydroxide ion concentrations in the pore solutions of thermally cured Portland cement pastes and mortar bar expansion values after a hydration time of 180 days (all pastes and mortars were prepared with water-cement ratio 0.50).

PC-No.	Na_2O-eq. %	temperature °C	OH-conc. mMoles/l	expansion mm/m
1	0.40	20	310	0.04
		40	286	0.10
		50	272	0.16
		60	255	0.17
2	0.58	20	440	0.36
		40	401	0.74
		50	322	0.68
		60	294	0.30
3	0.77	20	623	0.60
		40	541	2.87
		50	465	1.95
		60	391	0.85
4	1.02	20	791	2.05
		40	716	4.25
		50	605	4.35
		60	473	3.28
5	1.19	20	850	2.45
		40	681	5.45
		50	594	4.85
		60	486	4.30

The data from table 3 are graphically represented in fig. 8. It is to be seen that the higher the hydration respectively the storage temperatures of the cement pastes and mortars are the more effective is the alkaline attack of hydroxide ions to Pyrex glass as model for alkali sensitive aggregates. At elevated temperatures small increases in the OH ion concentration cause strong expansion effects.

CONCLUSIONS

The AAR expansion lag effect at elevated temperatures higher than 40 °C can be explained as a superposition effect of two counteracting factors. On the one hand the reaction rate is deminished by the OH/SO_4 ion concentration shift resulting in an OH ion decrease at elevated temperatures, on the other hand the reaction rate is increased according to the kinetic theory with increasing temperatures. The shift of the OH/SO_4 ion concentration is strongly influenced by the alkali content of the cement used. Ultimately, the OH/SO_4 ion shift is closely connected with the chemical and thermal stability of calciumsulphoaluminate hydrates (Aft- and Afm-phases) which itself strongly depends on the cement alkali content, the molar SO_3/Al_2O_3 ratio and the temperature. Therefore, in all test procedures for testing aggregates, glasses, glassfibres etc. in contact with cement at elevated temperatures the specific properties of cement, i.e. alkali, sulphate and Al_2O_3 contents have to be taken into consideration. As shown from the expansion experiments an ignorance of cement properties may result in wrong conclusions with respect to alkali sensitivity of aggregates.

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