ASR in Concrete with Supplementary Cementitious Materials Effect of Pore Solution Composition on Damage

K. Schmidt, H. Hilbig, D. Heinz
Centre for Building Materials, Technical University Munich, Germany

The necessary technological measures to avoid the damaging alkali-silica reaction (ASR) in concrete have not yet been completely clarified and are still the subject of intense discussion. The effectiveness of latent hydraulic or pozzolanic supplementary cementitious materials (SCM) such as ground granulated blast furnace slag or pulverised fuel fly ash in preventing ASR damage has been a subject of investigation for many years. The beneficial effect of such materials is attributed primarily to the reduction of the concentration of alkali and hydroxyl ions in the pore solution. In principle, SCM may be regarded as working in a passive and an active manner. The passive effect is based on the dilution of the alkali concentration of the pore solution and the reduction of the effective alkali content of concrete when cement is replaced by SCM. It is assumed that SCM introduce at most small quantities of alkalis into the concrete. The passive effect is attributed particularly to ground granulated blast furnace slag /1/. The active effect is explained by the removal of alkalis from the pore solution by binding in the reaction products of the SCM. This effect is attributed to pulverised fuel ash /2/. It has, however, not been satisfactorily explained how fly ash is able to reduce the alkali content of the pore solution despite an overall increase in total alkali content of the concrete and whether the binding of alkalis is durable. In addition, SCM produce in the long-term a denser and stronger microstructure, slowing down ion transport which also affects ASR susceptibility.

In the present contribution, results are presented on the effect of ground granulated blast furnace slag and pulverised fuel ash on the chemical composition of the pore solution of concretes made with greywacke as reactive aggregate. Possible reasons for the active effect of fly ash over and above dilution are discussed.

The composition of the pore solution with regard to a correlation with expansion and crack formation was investigated. In addition, the effect of pore solution composition on the chemical and structural composition of the ASR gel was considered.

The results were produced in a research project on the avoidance of alkali reactions by fly ash funded by the German Federation of Industrial Research Associations "Otto von Guericke" e.V. (AiF) /3/.

1   Concrete Compositions and Materials

A total of 30 different concrete compositions with precambrian greywacke as reactive aggregate were produced in the laboratory. The binder contents were 400 or 500 kg/m^3 with w/b ratios of 0.45 and 0.5,

respectively. The grading curve of the aggregate was A16/B16 as defined in DIN 1045. Greywacke was used for the 2/16 mm fraction making 70% of the total aggregate content. The cement was replaced by weight with different amounts of SCM keeping the w/b ratio constant. Starting from mixes with pure Portland cement, the mass ratio of binder paste to greywacke was kept constant by adjusting the amount of 0/2 mm inert quartz sand.

The Portland cements CEM I 32.5 R (Z1 to Z4) possessed alkali equivalents Na_2O_e between 0.6 and 1.2 wt.%, Tab. 1. The cements CEM II/A-S, CEM III/A and CEM III/B, all strength class 32.5, contained 13, 42 and 72 wt.% ground granulated blast furnace slag (GGBS), respectively. They originated from the same plant as the Portland cement Z1 with an alkali equivalent of 1.21 wt.%. The fly ashes chosen (F1 to F3) covered the range of fineness and alkali content of regular German fly ash, Tab. 2. The finely ground limestone (GL) served as an inert SCM for comparison.

Tab. 1: Alkali equivalents of the cements used

Cement:	Z1	Z2	Z3	Z4	Z1 (GGBS13)	Z1 (GGBS42)	Z1 (GGBS72)
	CEM I				CEM II/AS	CEM III/A	CEM III/B
Na_2O_e [wt.%]	1.21	1.02	0.76	0.65	1.09	1.00	0.78

Tab. 2: Properties of greywacke and binder materials

Oxide [wt.%]	Aggregate and binder materials								
	Grey-wacke	Z1	Z1 GGBS13	Z1 GGBS42	Z1 GGBS72	GL	F1	F2	F3
CaO	1.1	60.8	57.7	53.3	47.1	--	3.6	2.6	4.7
SiO_2	67.1	19.7	22.1	25.8	29.5	--	47.8	50.3	46.2
Al_2O_3	16.5	5.04	5.96	7.45	9.39	--	26.6	28.0	24.9
Fe_2O_3	4.94	3.48	2.95	2.17	1.33	--	9.1	4.7	4.6
Na_2O	2.78	0.27	0.27	0.29	0.30	0.13	1.36	1.09	0.37
K_2O	3.04	1.43	1.24	1.08	0.73	0.12	3.41	4.04	1.10
Na_2O_e	4.78	1.21	1.09	1.00	0.78	0.21	3.61	3.75	1.09
fineness [wt.% > 45µm]							21.4	1.0	18.1
Activity index 90d [%] /7/							98	114	104
Glass content[1] [wt.%]							80	85	67

[1] XRD with Rietveld analysis

2 Investigations

In order to investigate expansion and cracking behaviour, prisms and cubes measuring 500×100×100 mm^3 and 300×300×300 mm^3 were stored after demoulding in a fog chamber at 40°C and a relative humidity near 100% as specified by Part 3 of the Alkali Guideline published by the German Commission for Reinforced Concrete (DAfStb) /4/. Pore solutions were extracted under pressure from additional concrete specimens after storage at 40°C in tight polyethylene containers to prevent moisture exchange with the environment. The chemical analysis of the pore solutions was

performed using optical emission spectroscopy with inductively coupled plasma. The OH⁻ concentrations were determined by titration. In addition, binder pastes were mixed with compositions corresponding to those of a number of selected concrete compositions for the measurement of the degree of hydration as well as the mean chain length and Si/Al ratio of C-S-H using ^{29}Si MAS-NMR. The pastes were also stored in polyethylene containers at 40°C. ASR gels were taken from ASR damaged concrete specimens after approximately 2 years storage. The specimens were fractured and ASR gel, which had accumulated in air voids, extracted. The gel was analysed using both ^{29}Si and ^{27}Al MAS NMR to obtain information on gel structure for the different binder compositions, see /5/ and /6/ for details. In addition, infrared absorption spectra were recorded in a number of cases.

3   Results and Discussion

In the following, the specimens are characterised and discussed in terms of the total alkali content in concrete N due to Portland cement only, i.e. a possible alkali contribution from SCM is omitted. The different effect of SCM on the chemical composition of the pore solution is considered with regard to expansion and cracking caused by chemical attack on the reactive aggregate. Other factors, such as changes in porosity and strength of the microstructure, are not considered in this article.

3.1   Expansion and Cracking of Concrete

Fig. 1 shows the expansion of concrete prisms of different composition during storage in a fog chamber at 40°C. The concrete specimens made using pure Portland cement without SCM behave similarly with regard to the beginning and degree of ASR damage; the variation of alkali content N between 4.1 and 6.1 kg/m^3 (w/c ratios 0.45 and 0.5, respectively) does not affect the damage process. Compared with pure Portland cement, the use of 13% GGBS (N = 4.2 kg/m^3), 20% ground limestone (N = 3.9 kg/m^3) or 30% ground limestone (N = 3.4 kg/m³) postpones the induction period from 2 months, for pure Portland cement, to 4, 6 and 12 months for the SCM concretes, respectively.
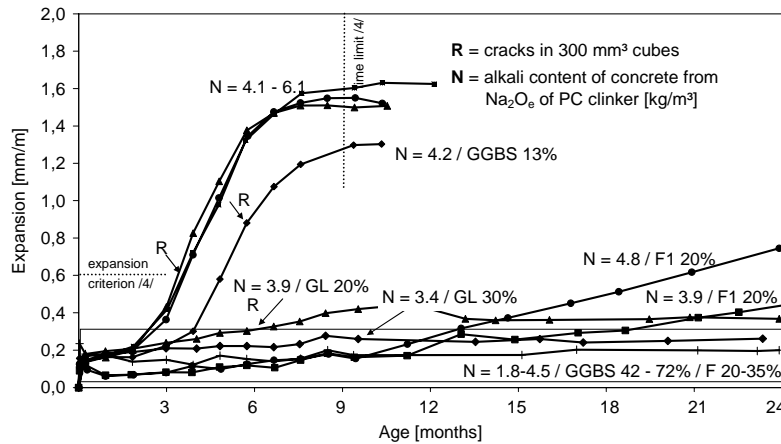
Fig. 1: Expansion of concrete prisms 100×100×500 mm^3 with different binder compositions during storage in a fog chamber at 40°C

In the case of the concretes made with 20% and 30% ground limestone, the expansion was small (0.4 mm/m) or near the base value (0.25 mm/m) caused by temperature and moisture variations. However, large cracks opening to widths of 1.2 and 1.1 mm, respectively, formed in the cubes. Irrespective of the type of fly ash, the Portland cement oxide composition and the amount of replaced cement (20 to 35%), concretes made with fly ash did not exhibit expansion due to ASR after 9 months (evaluation period according to the DAfStb Alkali Guideline - Part 3 /4/). At the current storage time of 24 months a steady increase in expansion is observed only for concretes with 20% fly ash F1 with alkali contents of N = 4.8 and 3.9 kg/m³. The expansion began after 10 and 14 months and is currently 0.75 and 0.45 mm/m, respectively. Up to now no cracks have formed in the cubes. The specimens with 20% fly ash F2 and F3 (N = 3.9 kg/m^3) show no signs of ASR damage which, apparently, is due to the higher fineness and lower alkali content of these fly ashes.

Up to now, concretes made with pure Portland cement with alkali contents of N = 2.6 and 3.0 kg/m³ as well as concretes with high GGBS contents (42 and 72%) and 25 to 35% fly ash F1 (N = 1.8 to 4.5 kg/m^3) have shown no signs of ASR damage. At present, it is not possible to estimate the applicability of these results to equivalent concrete specimens currently being exposed to natural climatic conditions. Nevertheless, when considering that the beginning of damage is 14 months for concretes made with fly ash F1 as opposed to 6 months for concretes made with 20% ground limestone, although in both cases N = 3.9 kg/m^3, it is clear that fly ash plays an active part in avoiding ASR damage.

3.2   Composition of the C-S-H Phases

Tab. 3 contains the results of the NMR investigations on the different binder pastes. At the age of investigation (180 days) it was found that 50% of fly ash F1 and 75% of the GGBS had reacted. Compared with

pure Portland cement paste, the replacement of cement Z1 by fly ash F1 or GGBS results in similar C-S-H phases, but with longer chain lengths and lower Si/Al ratios.

Tab. 3: Degree of hydration of binder paste, mean chain length (CL) and Si/Al ratio of C-S-H phases based on NMR investigations

Binder	Degree of hydration[1]				CL	Si/Al
	total	Z1	F1	GGBS		
	mol % Si	mol % Si	mol % Si	mol % Si		
Z1	92	92	-	-	4.6	14.0
Z1 + 30% F1	64	74	54	-	8.2	6.3
Z1 + 72% GGBS	74	77	-	73	7.4	5.7

[1]   Degree of hydration as in terms of reacted silicon for binder composition or individual components

3.3   Composition of the Pore Solution

3.3.1   Alkali and OH^- Concentrations

Figs. 2 and 3 show the effect of the type and quantity of SCM on the alkali and OH^- concentration of extracted pore solution for concretes with 400 kg/m^3 binder and a w/b ratio of 0.45 at an age of 90 days. The cement Z1 with a Na_2O_e of 1.21 wt.% was used. The straight lines in the figures correspond to concentrations calculated for theoretical dilution due to cement replacement starting from the concrete made without SCM. Points which lie above, on, or below these lines arise from the release, dilution or binding of alkalis by the SCM, respectively. In the case of the GGBS and ground limestone, the replacement of cement clinker led to a proportional reduction in the concentration of alkalis and OH^- ions. In contrast to this, fly ash - especially F3 - resulted in concentrations below the values expected for dilution. After 90 days, the finer fly ash F2 produced a significant reduction of alkalinity (70 mmol/l) compared with the coarser fly ash F1 - although the alkali contents are both near 3.7 wt.%. After 28 days the concentrations for these two fly ashes were similar. This effect can be explained by the stronger pozzolanic reaction of the finer fly ash and also confirms the ability of fly ash to bind alkalis in the reaction products. Over the range of binder compositions with 10 and 35 wt.% fly ash F1, which has a high alkali content, the total alkali concentration ($Na^+ + K^+$) is lowered by 60 mmol/l below the theoretical value for dilution. The concretes made with the low-alkali fly ash F3 have by far the lowest concentration of ions in the pore solution. In this case, a reduction of alkali concentration by about 200 mmol/l below the dilution value is achieved by cement replacements of 20 and 30%. The pH value is reduced by about 0.2. It is concluded that the capacity of fly ash for binding alkalis supplied by the Portland cement decreases as the alkali content of the fly ash increases. It is expected that above a certain fly ash alkali content, fly ash will supply alkali ions to the pore

solution. Apparently, this limit is not exceeded by fly ashes fulfilling DIN EN 450 /7/.
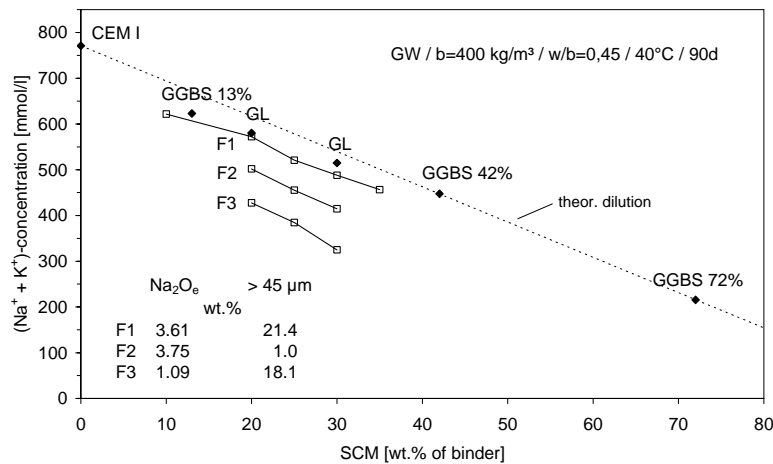

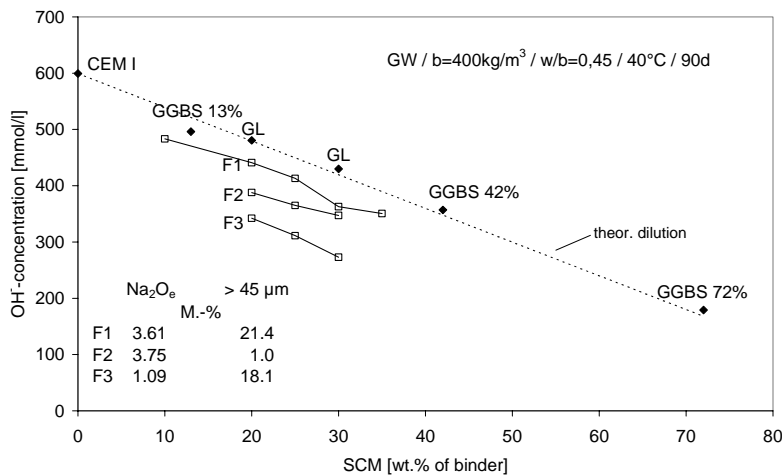Fig. 2: Effect of SCM on the total alkali concentration of the pore solution

Fig. 3: Effect of SCM on the OH⁻ concentration of the pore solution

3.3.2 Effect of OH⁻ Concentration on the Beginning of Damage

Fig. 4 compares the behaviour of all the concretes during storage in the fog chamber (40°C / 100 %RH) with regard to the effect of SCM on the OH⁻ concentration of the pore solution measured at an age of 28 days. The open symbols are placed at the present age of the concretes which up to now have shown no signs of damage. The full symbols are placed at the time when either cracking started or the expansion exceeded 0.4 mm/m. It is striking that, despite similar OH⁻ concentrations (520 mmol/l), the duration of the induction phase of concretes with 13% GGBS and 20% ground limestone is longer than that of the Portland cement concretes which exhibit damage after 3 months. The behaviour of the former concretes cannot be explained by

6

a reduction in OH⁻ concentration, but must be affected by other factors such as changes in porosity or strength. Based on the present results with greywacke, it is concluded that ASR damage can be avoided in the long-term when an OH⁻ concentration of 400 mmol/l, corresponding to the concrete with Portland cement, N = 3.0 kg/m³, in Fig. 4, is not exceeded. This would mean that the two concretes with 420 mmol/l (open squares in Fig. 4) made with 20% F2 (N= 3.9 kg/m³) and 25% F1 (N = 4.5 kg/m³), which up to now show no indications of damage, should have been damaged by ASR. This cannot be explained solely by the OH⁻ concentration of the pore solution of these concretes. The higher effectiveness of fly ash F2 in lowering the OH⁻ concentration compared with F1 (see Fig. 3) can be explained, as already mentioned, by the stronger pozzolanic reaction due to the higher fineness of fly ash F2.
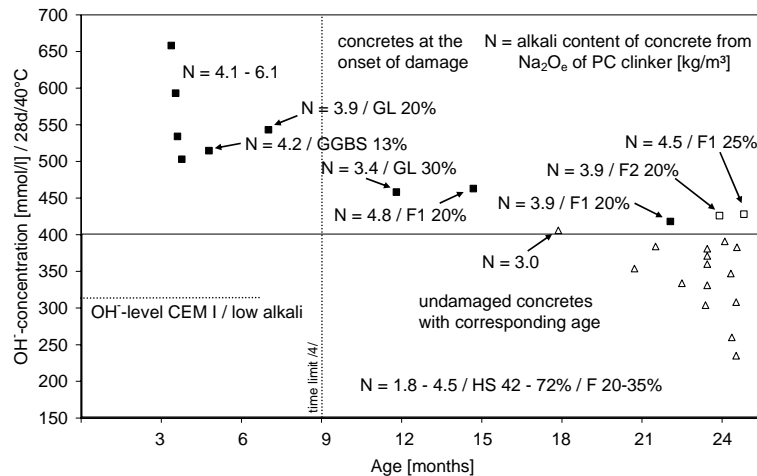
Fig. 4: Comparison of OH⁻ concentration at an age of 28 days with time to onset of damage or current age.

3.3.3 Aluminium Concentration

Apparently, fly ash not only affects the concentration of alkalis, but also aluminium in the pore solution; moreover to a greater degree than GGBS, Fig. 5. Compared with concrete made with pure Portland cement, the use of fly ash ($Al_2O_3 \approx 25$ wt.%) leads to an increase in aluminium concentration by a factor of as much as 4. By contrast, the use of GGBS ($Al_2O_3 \approx 10$ wt.%) leads to a reduction in aluminium concentration corresponding to dilution. This result is surprising since the Al_2O_3 contents of concretes made with fly ash or GGBS both cover the same range (10 and 30 kg/m³).
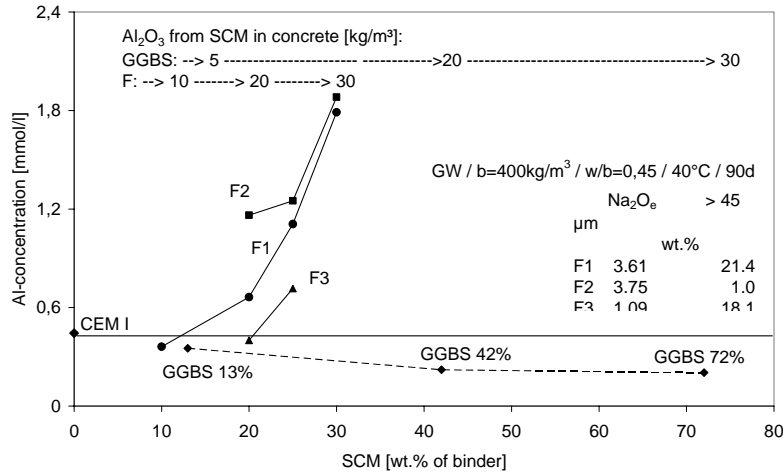
Fig. 5: Effect of fly ash and GGBS on the aluminium concentration of the extracted pore solution

At present, it is not possible to understand why fly ash F3 supplies less aluminium to the pore solution although the aluminium contents of the three fly ashes are similar. This may be caused by (a) the smaller glass content of F3 (67%) compared with F1 and F2 (80%) or (b) the low alkali content of F3 (1.1%). Compared with fly ash F1, the higher degree of hydration of the finer fly ash F2 apparently causes more aluminium to enter the pore solution. The ability of the aluminium rich fly ashes to bind considerable quantities of alkalis is attributed to the additional formation of C-A-S-H phases /8/. This could be verified by the present NMR investigations. The ions Na^+ or K^+ supply the necessary charge compensation when Al is substituted for Si in the silicate hydrates /9/. If apart from the aluminium that is needed for the formation of C-A-S-H phases, excess aluminium is able to enter the pore solution then non-swelling alumino silicates could form via the silanol groups formed by the alkali silica reaction. Thus damage due to ASR would be prevented. In /10/ it is argued that this effect lowers the susceptibility of concrete made with greywacke to ASR damage because, along with silicon, aluminium is dissolved out of this material. The same effect could be achieved by an additional supply of aluminium from fly ash. Fig. 6 attempts to find a relationship between the strength of attack (OH^-), the inhibiting effect of aluminium and the total alkali content of the concrete derived from Portland cement. Even at higher alkali contents a low OH^-/Al ratio can ensure that no ASR damage occurs or that it is inhibited over a long period of time.
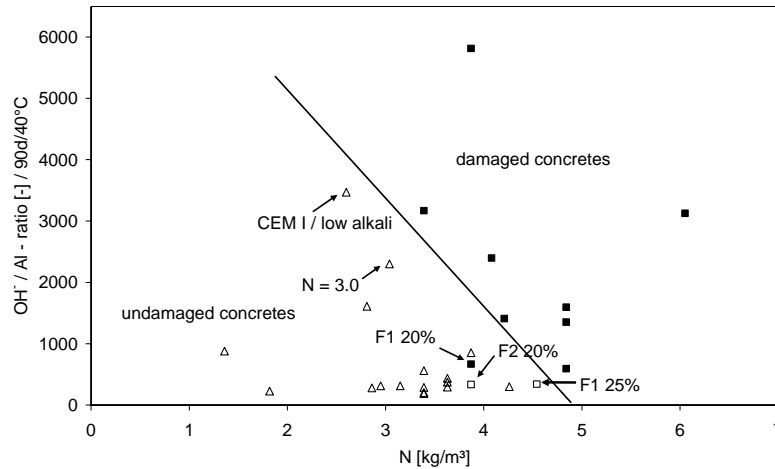
Fig. 6: Effect of OH⁻/Al ratio at an age of 90 days on a damaging ASR with respect to the total alkali content of concrete from Portland cement N

The effect of aluminium may explain why ASR damage has not, at present, occurred for the concretes with 20% F2 (N = 3.9 kg/m^3) and 25% F1 (N = 4.5 kg/m^3) after 24 months despite their high 28d OH⁻ concentration (420 mmol/l), open squares in Fig. 4. Nevertheless, the reduction of the alkali concentration is still the main factor to be considered with regard to avoiding ASR damage.

3.4   Composition of ASR Gels

The values obtained for the chemical composition of ASR gels extracted from damaged specimens are listed in Tab. 5. Whereas the gels from the pure Portland cement concrete and the concrete with 13% GGBS are very similar, the gel from the concrete with ground limestone contains distinctly more CaO. It seems that binder paste containing ground limestone is able to supply additional calcium to the chemical reactions forming the gel.

Tab. 5: Chemical composition of ASR gels

	Binder								
SCM	Z1	GG BS	GL	F1	SCM	Z1	GG BS	GL	F1
wt.%	0	13	20	20	wt.%	0	13	20	20
	Content in wt.%				Content in mmol/g				
SiO$_2$	47.6	48.3	41.5	43.5	Si	7.92	8.05	6.90	7.24
CaO	9.6	8.9	19.2	7.8	Ca	1.71	1.58	3.43	1.39
Na$_2$O	3.7	4.1	2.3	3.7	Na	1.20	1.31	0.76	1.19
K$_2$O	13.9	14.0	9.5	16.7	K	2.96	2.98	2.01	3.53
Al$_2$O$_3$	0.10	0.10	0.24	0.44	Al	0.02	0.02	0.05	0.09
H$_2$O	24.6	24.3	26.1	27.0	H$_2$O	13.7	13.5	14.5	15.0

The gel taken from the concrete with 20% fly ash F1 possesses a higher aluminium content compared with the other concretes. The

stoichiometric composition of the gels correspond, with the exception of the concrete with ground limestone, to silicate layers of plate-like morphology $(Si_2O_5^{2-})_n$. Certain amount of Ca^{2+}, Na^+ and K^+ are incorporated to neutralise charge. The morphology is confirmed by the ^{29}Si NMR Spectra where a number of peaks can be attributed to a Q^3 environment, -87 ppm to -98 ppm; see Tab. 6 and Fig. 7. Since the stoichiometry requires the presence of Si-OH units, it is unlikely that the signal at -87 ppm is due to Q^2 sites. Equivalent absorption peaks were not present in the corresponding infrared spectra. Distinct Q^1 and Q^2 peaks exist in the NMR spectrum for the gel taken from the concrete prepared with ground limestone indicating the formation of C-S-H together with the ASR gel. This behaviour has also been observed by Hou et al. /13/ for synthetic gels with similar (Na+K)/Si and Ca/Si ratios. Owing to the small amounts of Al in the gels, a distinct signal could only be resolved in the ^{27}Al NMR spectrum for gel taken from concrete with 20 wt.% fly ash F1, Fig. 8. Its chemical shift of 58 ppm points to an AlO site with four-fold coordination and surrounded by 4 Si atoms $(Q^4(4Si))$ as is the case for alumino silicates.
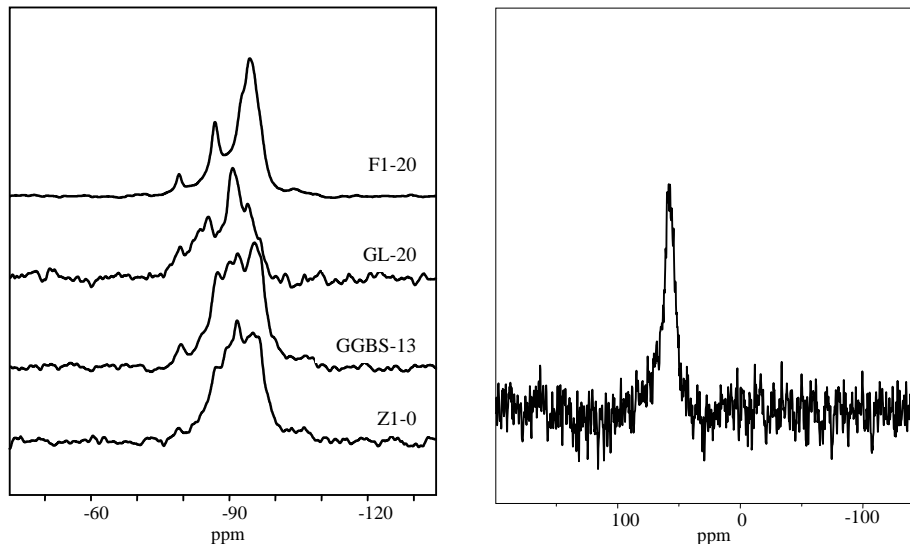

Fig. 7: ^{29}Si-MAS NMR spectra for the gels

Fig. 8: ^{27}Al-MAS NMR spectrum for gel with 20% F1

Since alumino silicates do not swell, it can be assumed that they will remain at their formation location and thus, in contrast to gels containing layer silicates, will not be forced into the pore system by the action of swelling. This would explain why the gel taken from the air voids in concrete made with 20% fly ash F1 did not contain a high amount of aluminium, i.e. the gel was composed of layer-like silicates without aluminium. Apparently, the amount of aluminium in this binder was not high enough to prevent the formation of gel with swelling potential and thus ASR damage.

Tab. 6: ^{29}Si MAS NMR spectra - deconvolution results for the gels

Binder	Q^1		Q^2		Q^3	
	Chem. shift [ppm]	Proportion [%]	Chem. shift [ppm]	Proportion [%]	Chem. shift [ppm]	Proportion [%]
Portland cement Z1	- 78.9	0.8	- 84.5	4.9	- 86.9	7.5
					- 89.6	23,6
					- 91.8	8.6
					- 94.8	49.8
					- 96.6	4.8
13% GGBS	- 79.2	2.7	- 83.7	2.8	- 87.0	16.9
					- 89.6	17.5
					- 91.7	11.6
					- 95.2	46.0
					- 96.7	2.6
20% GL	- 79.0	6.8	- 82.6	9.4	- 90.4	32.5
			- 85.3	21.7	- 91.9	9.5
					- 94.2	16.0
					- 96.4	4.1
20% F1	- 78.9	3.4	- 83.8	3.7	- 86.7	16.0
					- 89.5	6.9
					- 92.4	18.0
					- 94.5	40.5
					- 96.2	11.5

4. Conclusions

The alkali silica reaction is affected by the different chemical properties of the pore solution where the dominating factor is the alkali concentration. As well as being part of the swelling gel of layer silicates formed by ASR, the alkalis increase the pH of the pore solution enhancing the chemical attack on the aggregate. The use of the supplementary cementitious materials fly ash and ground granulated blast furnace slag results in the dilution of alkali concentration thus reducing the susceptibility of concrete to ASR damage. The pozzolanic reaction of fly ash consumes OH$^-$ and forms aluminium containing C-A-S-H phases which are able to bind alkalis; thus reducing the susceptibility of concrete to ASR. As opposed to ground granulated blast furnace slag, fly ash increases the aluminium concentration of the pore solution significantly. Instead of swelling silicate gel, non-swelling alumino silicates may be formed which do not damage concrete. Although the alumino silicates remain at their formation location, small amounts of alumino silicates were found in the gels analysed.
Thus even at relatively high total alkali contents, concretes made with sufficient amount of fly ash exhibit no ASR damage.

5. Acknowledgements

References

/1/ Tätigkeitsbericht VDZ e.V.; 2001 / 2003; S. 97-99

/2/ E. Schäfer: Effect of the reactions of the main cement components on the alkali composition of the pore solution of hardened cement paste, Clausthal, Fakultät für Bergbau, Hüttenwesen und Maschinenwesen der Technischen Universität Clausthal, PhD thesis 2004, in German

/3/ Research project "Avoidance of ASR by using fly ash", AiF Nr. 13605, VGB Nr. 245, cbm Centre for Building Materials, TU Munich F10.001/02, 2006, in German

/4/ DAfStb Guide line: Preventative measures against damaging alkali reactions in concrete (Alkali guide line); part 3: concrete aggregate from precambrian greywacke or other alkali sensitive minerals ; version May 2001, in German

/5/ H. Hilbig, F.H. Köhler, P. Schießl: Hydratation von Hochleistungs-feinkornbetonen, NMR-spektroskopische Untersuchungen, 15. Internationale Baustofftagung ibausil, Tagungsband, 2003, Weimar, 1-0489 – 1-0496

/6/ A. Buchwald, H. Hilbig, Ch. Kaps: Alkali-aktivated metakaolin-slag blends – performance and structure in dependence of their composition, J. Mat. Sci., DOI: 10.1007/S10853-006-0525-6

/7/ DIN EN 450-1: 2005. Fly ash for concrete - part 1: definitions, requirements and conformity criteria

/8/ H.F.W. Taylor, K. Mohan, G.K. Moir: Analytical Study of Pure and Extended Portland Cement Pastes, Part I: Pure Portland Cement Pastes; Part II: Fly Ash and Slag Cement Pastes, J. Am. Ceram. Soc. 68 [12] (1985) 680-690

/9/ Sung-Yoon Hong, F. P. Glasser: Alkali sorption by C-S-H and C-A-S-H gels. Part II. Role of alumina, Cem. Concr. Res. 32 (2002) 1101-1111

/10/ K.-J. Hünger, S. Hill: Accelerated test for alkali sensitivity of aggregate under practice conditions; BFT 7, 2005, S. 36-47, in German

/11/ X. Hou, R.J. Kirkpatrick, L.J. Struble, P.J.M. Monteiro: Structural Investigations of Alkali Silicate Gels; J. Am. Ceram. Soc. 88 [4] (2005) 943-949