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LETTER

The effect of activator concentration on reaction degree and structure formation of alkali-activated ground granulated blast furnace slag

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Blast furnace slag is an industrial by-product that can be alkali-activated to yield adhesive and cementitious compounds, whose production is less energy-intensive and CO_2 emission less than in ordinary Portland cement manufacture. The reaction products of alkali-activated blast furnace slag have been widely investigated. They are similar to calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH) of Portland cements apart from incorporated tetrahedral aluminium into the dreierketten structure of the CSH [1] and hydrotalcite if the slag contains magnesium [2, 3]. Considering different activation concentrations, Song and co-workers [4] determined in calorimetric investigations a faster hydration when more NaOH is present. The microstructure observed using ESEM was not affected.

In this work the effect of the activator concentration on the reaction degree and the structure formation of an alkali-activated slag were investigated using ^{27}Al and ^{29}Si NMR spectroscopy.

As can seen in the chemical phase composition in Fig. 1 as well as 73 wt% glass, the slag used in this work contained crystalline calcium silicate phases and a considerable amount of calcite addition. Almost certainly some Portland cement and limestone were added in the grinding process of the slag.

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Different concentrations of NaOH (between 3.4% and 13.6% by weight of slag) were used in the alkali activation, the water to solid ratio was always 0.33. Samples measuring $1 \times 1 \times 6$ cm^3 were prepared and kept in the moulds at 40 °C for one day. After demoulding the samples were stored in closed boxes over water at room temperature.

The present discussion bases on the results of ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy (NMR), which is the most suitable method for quantification of the silicate phases in these amorphous systems. The NMR spectra were recorded according to the procedure and the parameters described elsewhere [5]. The signal patterns of the spectra were deconvoluted with the Bruker WINNMR software using Lorentz shape function.

The signals measured with ^{29}Si NMR spectroscopy are due to the following Si sites: Silicon tetrahedra, which are bonded in silicate chains can either be situated at the chain ends (Q_1; signal at –78 ppm ± 2 ppm) or in the middle (Q_2, signal at –85 ppm ± 2 ppm). If aluminium is incorporated into the silicate chain as a bridging tetrahedron an additional peak is seen at –82 ppm ± 2 ppm (Q_2(1Al)) [6, 7].

Figure 2 shows the ^{29}Si NMR spectrum of the raw material as well as the spectra of the alkali-activated materials.

The spectrum of the slag contains one broad peak centred around –74 ppm. The alkali-activated slag samples contain unreacted slag (broad peak at –74 ppm) and a reaction product that can be seen as three overlapping peaks in the range between –75 and –87 ppm.

The ^{27}Al NMR spectrum of a slag binder should show four coordinated aluminium created by the

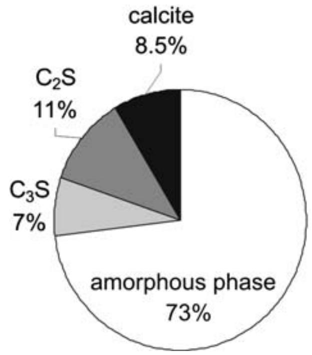

Fig. 1 Mineral composition of the slag used

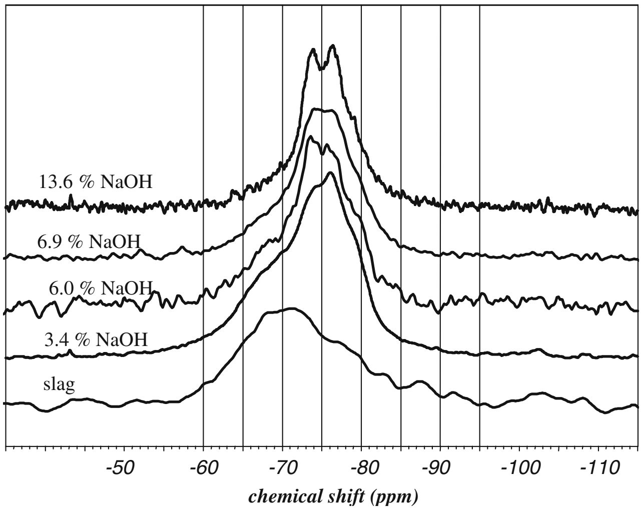

Fig. 2 ^{29}Si MAS NMR spectra of the raw material and the alkali-activated slags

aluminate tetrahedra incorporated in the silicate chains of the CSH phases [8] as well as six coordinated aluminium from magnesium or calcium aluminate hydrate phases [2]. Fig. 3 shows the ^{27}Al NMR spectrum of the raw material as well as the spectra of the alkali-activated materials. The spectrum of the slag shows several broad strongly overlapping peaks according to varying environments of four, five and six coordinated aluminium. The alkali-activated slag samples consist of unreacted slag indicated by the asymmetric shape of the tetrahedral aluminium that overlaps the peak of tetrahedral aluminium inside the CSH phases (around 70 ppm). Additionally reaction product with six coordinated aluminium is formed indicated by the sharp peaks at about 10 ppm. In view of the results of X-ray diffraction investigations [5] this signal can be attributed to the hydrotalcite phase. The superposition of the signals of the six coordinated aluminium of the unreacted slag (question mark in Fig. 5) and the hydrotalcite prevent quantification of this phase. CAH

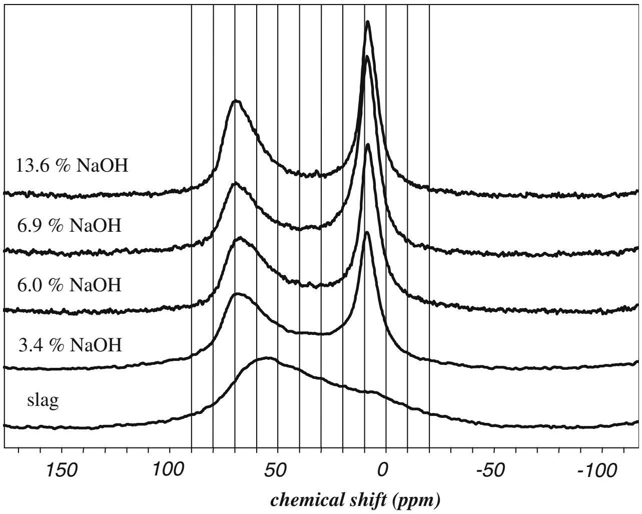

Fig. 3 ^{27}Al NMR spectra of the raw material and alkali-activated slags

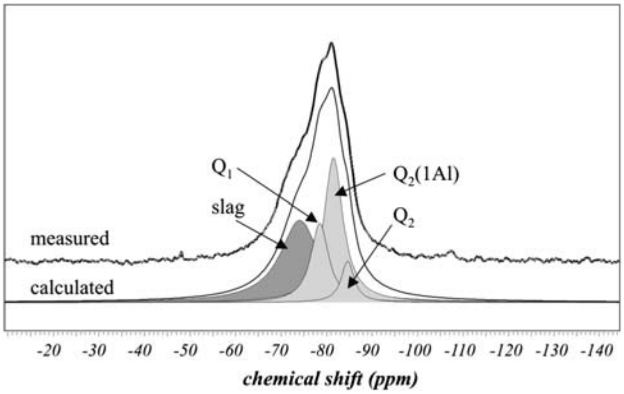

Fig. 4 ^{29}Si NMR spectrum and interpretation of the alkali-activated slag with 3.4 mol% NaOH

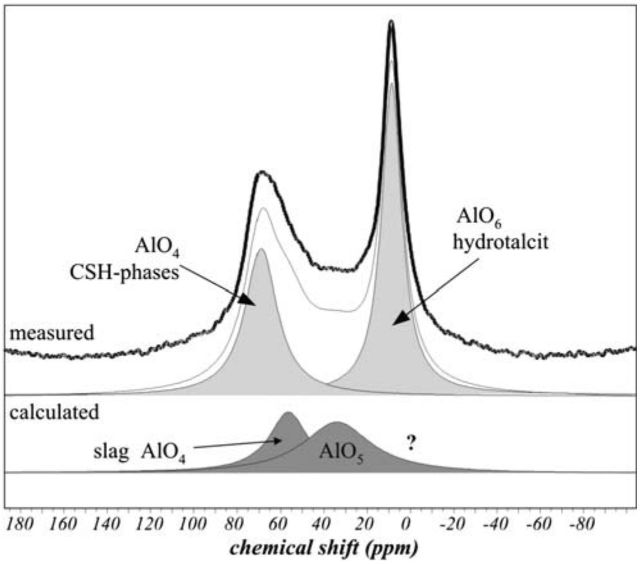

Fig. 5 ^{27}Al NMR spectrum and interpretation of the alkali-activated slag with 3.4 mol% NaOH; “?” = expected AlO_6

Table 1 Results of ^{29}Si NMR spectroscopy

Position G_i/mol%Si	S–74 ppm	Q_1–79 ppm in CSH	Q_2(1Al) –81 ppm in CSH	Q_2–85 ppm in CSH
Slag	100	–	–	–
3.4% NaOH	35.7	30.4	21.8	12.1
6.0% NaOH	25.9	36.7	23.6	13.8
6.9% NaOH	21.2	36.7	26.7	15.5
13.6% NaOH	11.0	39.9	30.9	18.2

Table 2 Results of ^{27}Al NMR spectroscopy

Position G_i/mol%Al	AlO_4		AlO_5 30 ppm in slag	AlO_6 10 ppm in slag or hydrotalcit
	68 ppm in CSH	56 ppm in slag		
Slag	–	52.2	37.3	10.4
3.4% NaOH	27.7	13.0	19.1	40.2
6.0% NaOH	29.8	10.7	10.1	49.4
6.9% NaOH	25.1	9.3	10.3	55.3
13.6% NaOH	37.3	9.0	5.6	48.1

Phases, which should also show a signal in this region, were not determined in the X-ray diffraction investigations.

The ^{29}Si NMR spectra have been deconvoluted according to following regime: Firstly, the spectrum of the raw material was interpreted. The peak position and its width were found. Secondly, the spectra of the alkali-activated binders were interpreted by using the fixed peak position and width to fit the peak intensity for the unreacted material. The peaks of the reaction product were fitted using the Si sites as described above. The values of peak position, width and intensity were determined using the deconvolution software.

Examples of the deconvolution and the interpretation are shown in Figs. 4 and 5.

The intensity of the single peaks has been used to calculate the amount G_{Qi} of the different chemical environments of silicon and aluminium (Tables 1 and 2).

Due to the large mount of unreacted raw material the question of the reaction degree (RD) arises. The reaction degree RD can be calculated from the ^{29}Si NMR by using the amount of the reaction products:

$$\mathrm{RD}\,(^{29}\mathrm{Si}) = \sum_{i=1}^{3} G_{\mathrm{Q_i}}$$

Basing on the quantification of each signal the average chain length (CL) and the molar silicon to aluminium ratio of the CSH phases ($\mathrm{Si/Al_{CSH}}$) can be calculated [7]:

$$\overline{\mathrm{CL}} = \frac{G_{\mathrm{Q_1}} + \frac{3}{2}G_{\mathrm{Q_2(1Al)}} + G_{\mathrm{Q_2}}}{\frac{1}{2}G_{\mathrm{Q_1}}}$$

$$\mathrm{Si/Al_{CSH}} = \frac{G_{\mathrm{Q_1}} + G_{\mathrm{Q_2(1Al)}} + G_{\mathrm{Q_2}}}{12G_{\mathrm{Q_2(1Al)}}}$$

The results are given in Table 3.

Table 3 Reaction degree (RD), average chain length (CL) and Si/Al ratio, calculation from ^{29}Si NMR spectroscopy

	RD	CL	Si/Al
3.4% NaOH	0.64	5.0	5.9
6.0% NaOH	0.76	5.1	5.6
6.9% NaOH	0.79	5.0	5.9
13.6% NaOH	0.89	5.2	5.8

The alkali-activated slags reacted to form CSH phases (with incorporated aluminium), shown by the Q_1 and Q_2 sites in the ^{29}Si NMR spectrum and four coordinated aluminium in the ^{27}Al NMR spectrum. Hydrotalcite formed shown by six coordinated aluminium in the ^{27}Al NMR spectrum and verified by X-ray diffraction spectra.

Both the average chain length and the Si/Al ratio of the CSH phases remain unaffected by the change in alkaline concentration in the range studied. Chains with an average length of 5 tetrahedrons, where mostly the middle tetrahedron contains Al, were always determined. As opposed to this, the reaction degree was enhanced by a higher concentration of NaOH (Fig. 6).

It is concluded that the alkali activation is not a catalytic activation, but is necessary for dissolving the glassy structure of the slag. Thus the reaction degree is dependent on the quantity of dissolved glass and not on the amount of water. The alkaline solubility must be

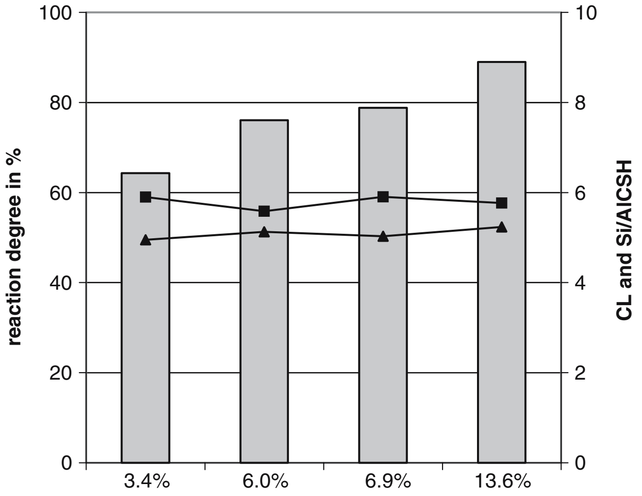

Fig. 6 Dependence of reaction degree (columns), average chain length (■) and Si/Al ratio (▲) on the alkali activation

similar for the Al and the Si phases, since the different activation has no effect on the Si/Al ratio in the hydration products.

The alkali activated hydration reaction is comparable to a classic polymerisation reaction. More activation leads to more monomers in solution. The faster hydration observed in calorimetric investigations [4] is due to the larger number of polymerising units. At the end of the reaction, if all dissolved educts have been consumed, the resulting reaction products have the same average chain length and Si/Al ratio. This indicates that the reaction kinetics of the condensation is unaffected by the activation.

References

1. Schilling PJ, Butler LG, Roy A, Eaton HC (1994) J Am Cer Soc 77:2363
2. Richardson IG, Groves GW (1992) J Mater Sci 27:6204
3. Wang S-D, Scrivener KL (1995) Cem Concr Res 25:561
4. Song S, Sohn D, Jennings HM, Mason TO (2000) J Mater Sci 35:249
5. Buchwald A, Hilbig H, Kaps Ch J Mater Sci (in press)
6. Andersen MD, Jakobsen HJ (2003) J Skibsted Inorg Chem 42:2280
7. Engelhardt G, Michel D (1987) High-resolution solid-state nmr of silicates and zeolites, John Wiley and Son, Chichester
8. Wang S-D, Scrivener KL (2003) Cem Concr Res 33:769