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Investigations on alkali-silica reaction products using Raman spectroscopy

Miriam E. Krüger [(1)], Volker Thome [(2)], Harald Hilbig , Melanie Kaliwoda [(3)], Detlef Heinz

[(1)] Centre for Building Materials (cbm), Technical University of Munich, Munich, Germany, miriam.krueger@tum.de

[(2)] Fraunhofer Institute for Building Physics (IBP), Valley, Germany, volker.thome@ibp.fraunhofer.de

[(3)] Mineralogical State Collection of SNSB, Munich, Germany, kaliwoda@snsb.de

1. INTRODUCTION

The Alkali-silica reaction (ASR) is one of the main causes of concrete deterioration. During ASR, alkali-reactive siliceous aggregates react with the alkalis in the pore solution of concrete to form an expansive alkali-silica reaction gel (ASR gel). Due to its hygroscopic behaviour, the ASR gel absorbs water and swells, resulting in a pressure that often forms a typical crack network and severely affects the durability of the concrete. The study focus on the effects of different compositions on the structure of synthetic ASR gels. Raman spectroscopic measurements were performed on synthetic ASR gels with different compositions, i.e. Na/Si and Ca/Si molar ratios. Raman spectra were analysed using PeakFit software and compared with data from the literature and the specID and MSC-RD internal databases. Band assignments were validated by comparing the results with ^{29}Si NMR spectroscopic measurements.

2. MATERIALS & METHODS

The ASR gels were synthesized from the following starting materials: $Ca(OH)_2$, colloidal SiO_2, deionized water and NaOH or KOH pellets. The NaOH or KOH was dissolved in the deionized water and the colloidal SiO_2 and $Ca(OH)_2$ were then added. The Na/Si molar ratio of the three sodium silica gels was 0.3, 0.6 and 1.2 (sample name: NS0.3, NS0.6, NS1.2). The sodium-calcium silica gels were synthesized with a Na/Si molar ratio of 0.3 respectively 0.7 and a Ca/Si molar ratio of 0.22 respectively 0.46 (NSC0.3_0.22, NSC0.7_0.46). The potassium silica gel was synthesized with a K/Si molar ratio of 0.3 (KS0.3). The six blends were prepared at room temperature in polyethylene bottles and stored for three weeks in an overhead pan shaker. After mixing, a portion of the liquid was removed and dried in a vacuum desiccator for seven days and analysed by ICP-OES.

The analytical measurements were carried out with a Raman spectrometer Senterra I from Bruker equipped with an Olympus BX 51 confocal polarizing microscope. The samples were measured using frequency doubled Nd: YAG laser with a wavelength of 532 nm, a maximum laser power of 10 – 20 mW and 20x objective lens. The measurements were performed with a spectral resolution of 9 - 13 cm^{-1} and in a spectral range of 50 - 4000 cm^{-1}. Raman spectra were evaluated using the program Peakfit (version 4). The ^{29}Si NMR experiments were performed with a Bruker Avance 300 spectrometer (magnetic field strength 7.0455 T, resonance frequency for ^{29}Si: 59.63 MHz) in MAS mode (magic angle spinning) using the single pulse technique (90° pulse). The samples were placed in 4 mm zirconia rotors and spun with 8 kHz. About 5000 scans were recorded for each spectrum with a repetition time of 45 s. The shifts were set relative to the external standard tetramethylsilane. The signal patterns of the spectra were deconvoluted with Bruker WINNMR software.

3. RESULTS AND DISCUSSION

The ^{29}Si NMR spectrum of the potassium silica gel (KS0.3) is shown in Figure 1 a). Four main peaks are apparent and are identified as different tetrahedral Q^n environments for Si in silicates. The Gaussian distributions are centred about **-80 ppm, -88 ppm, -97 ppm** and **-107 ppm** and are attributed to Q^1, Q^2, Q^3 and Q^4 sites, respectively (1). The fitted relative integral intensities for the curves are about 49 % for Q^3, 19 % for Q^2, 16 % for Q^4 and 4 % for Q^1. Figure 1 b) shows the Raman spectra for sodium silica gels with different Na/Si molar ratios. The Raman spectroscopic investigations on synthetic ASR gels reveal a shift of prominent peak position depending on the Na/Si and Ca/Si molar ratios. The experiments with sodium silicate gels exhibit shift of the low frequency band from **530 cm^{-1}** (Q^3) to **600 cm^{-1}** (Q^2) with

increasing Na/Si molar ratio (2). Moreover, the results show that increasing the Na/Si molar ratio leads to more non-bridging oxygen atoms in the structure and therefore a reduction in the degree of cross-linking. The Q^3 peak position of the sodium silicate gels (Na/Si ratios 0.2 - 0.8) in the Raman spectra (**520 - 565 cm^{-1}**) can be used to estimate the Na/Si molar ratio of the gel.

Figure 1 c) shows the Raman spectra of the sodium-calcium silica gels in comparision with the spectrum of a C-S-H phase (Ca/Si molar ratio of 0.8). The graph shows that the low frequency band of the sodium/calcium silica gels shifts towards higher wavenumbers and, with increasing Ca/Si molar ratios, becomes more and more like that of C-S-H phases (3).

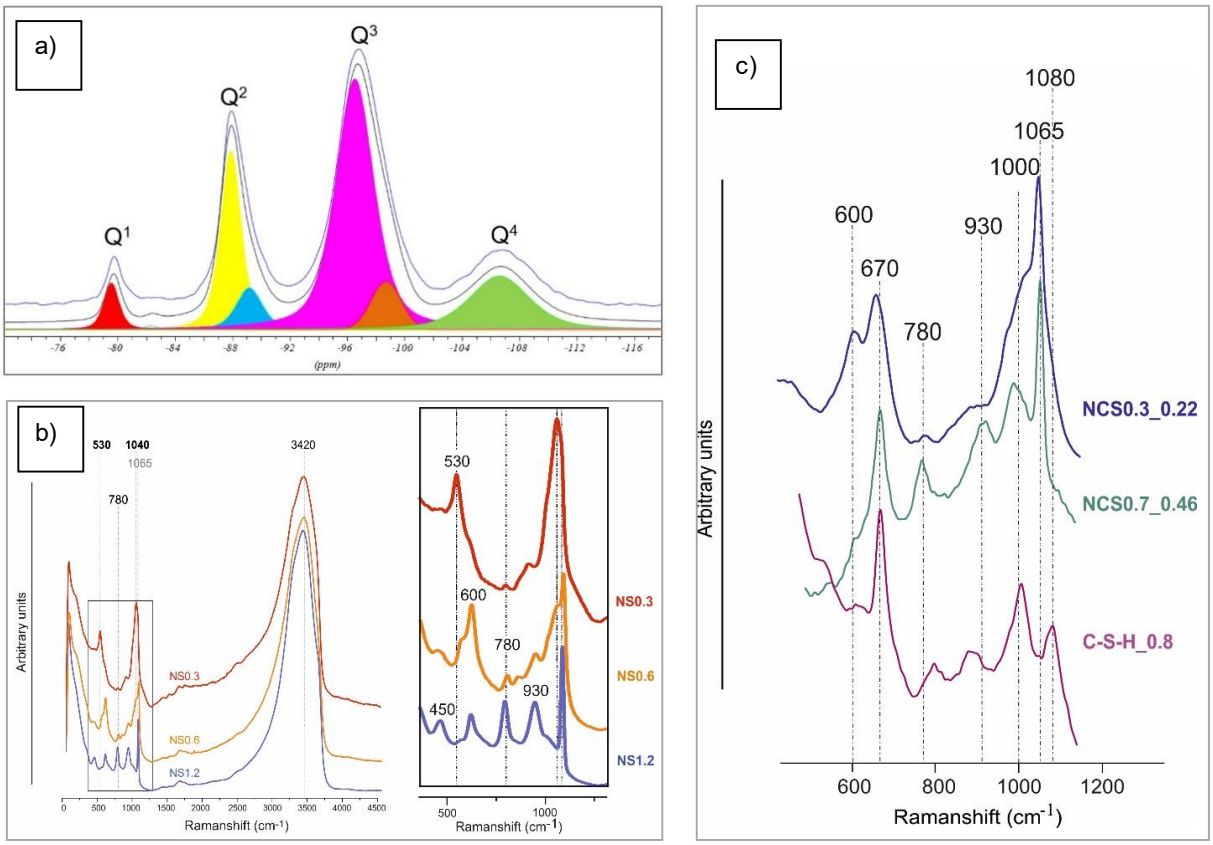

Figure 1: a) ^{29}Si NMR spectrum of the potassium silica gel (K/Si molar ratio = 0.3).
b) Characteristic vibration bands of the sodium silica gels with different Na/Si molar ratios.
c) Characteristic vibration band of the sodium-calcium silica gels in comparison with C-S-H_0.8.

4. CONCLUSION & REFERENCES

Raman spectroscopy is a useful analytical method to gain insight into the Q species in ASR gel structure. The systematic analysis of synthetic ASR gels provides new information about the role of alkalis in the structure of ASR gels.

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