QUANTITATIVE ANALYSIS OF THE STRENGTH GENERATING C-S-H-PHASE IN CONCRETE BY IR-SPECTROSCOPY

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Abstract.
The C-S-H-phase is the most important strength generating phase in concrete and other cementitious materials. The analysis of C-S-H is therefore an important instrument of innovations in the field of concrete and its durability and sustainability. The quantification and insights in C-S-H are hindered by the predominantly amorphous structure of C-S-H. Only the time consuming and expensive solid state nuclear magnetic resonance spectroscopy (NMR) gives a chance to get results, but is restricted to model substances. A new technique, based on the cheap and widespread infrared-spectroscopy (IR) was developed. The quantitative analysis is based on the silicon content in the different structural units of C-S-H and a calibration with natural and synthetic materials with known silicon content in these units. The technique allows to investigate specimens from real structures. Specimens with quartz or limestone aggregate can be analyzed directly. In other cases the aggregates must be separated, for example with heavy liquid separation. Tests with different mortars showed a good correspondence of measured and expected values of C-S-H concentration.

Keywords: Calcium-Silicate-Hydrate (C-S-H), quantitative analysis, spectroscopy.

1. Introduction

Undoubtedly the C-S-H-phase is one of the most important chemical substances in the world. It is generated by the hydration of C_3S and C_2S, puzzolanic reactions and reactions of latent hydraulic components. It is the strength building phase in most cementitious material. If researchers want to improve mineral building materials, and as a consequence improve sustainability of such materials, it is therefore of great importance to quantitatively analyze C-S-H and its variable, actual structure. Also in the case of corrosion and durability investigations, where the C-S-H is attacked and the concentration is decreased, it will be very helpful to quantitatively analyze C-S-H. Still by the extensive amorphous character of C-S-H in X-ray diffraction experiments and other possible amorphous components in the material it is not possible to quantitatively analyze C-S-H at the moment in a general manner. Only model substances can be analyzed quantitatively, for example hydrated alite or hydrated white cement with ^{29}Si magic angle spinning solid state nuclear magnetic resonance, which is a very expensive and time consuming technique. Also special systems can be analyzed with quantitative X-ray diffraction by calculating the C-S-H from the changes of the crystalline species. Up to now it is not possible to take a specimen from a real structure and make a quantitative analysis (QXRD). This was the motivation for the development of the method.

2. Basic information

The method is based on Attenuated Total Reflection (ATR) Fourier Transform (FT) Infrared Spectroscopy (IR), with a single reflection diamond ATR. The generated evanescent wave at the interface is attenuated by the absorption in the specimen, based on the excitation of vibrations in functional groups with a change of the dipole moment. Nearly no scattering effects are generated by this technique and the penetration of the evanescent wave into the specimen is less than 5 microns. A quantitative analysis with the ATR-technique is based on Lambert-Beers law, like in transmission. That means the absorbance is directly proportional to the concentration, except very high concentrations [1]. To our experience it is necessary to dilute the calibration substances at least to 50 % to make sure that the calibration curve is in the linear range.

The basic structure of C-S-H consists of short chains of SiO_4-tetrahedrons. The so called Q^1 structural units are the ends of the chains, the Q^2 structural units are in the middle. The chain length is connected with the ratio Q^1/Q^2. Infrared spectroscopy produces direct signals from C-S-H, generated by the

Q^1 and Q^2 structural units. They can be used to develop a method for the quantitative analysis of C-S-H. The bands are weak and broad and there are overlapping signals from other phases. And, of course, a quantitative analysis needs a calibration. These difficulties must be overcome.

For the development of the method different portland cements, blastfurnace slags, flyashes, silica fume, lime stone powders, quartz powder, hydrated lime, mixtures of these components, and hydrated mortars made of these components were used. The components were characterized by polarized light microscopy, X-ray diffraction, X-ray fluorescence and infrared spectroscopy.

The measurements were performed with a Perkin Elmer Spectrum Two with Universal Attenuated Total Reflectance Accessory and the Perkin Elmer software Spectrum. Peak fitting was performed with the program PeakFit of Systat Software, Erkrath, Germany.

3. Method for the quantitative analysis of C-S-H in cementitious materials by ATR-IR-spectroscopy

A detailed inspection instruction is available from the corresponding author (in German).

1. At first a qualitative phase analysis of the specimen is needed. Due to the overlapping of peaks, it is important to know the phase assemblage in the sample.

2. The specimen is crushed to a grain size of some millimeters and dried. The drying must be restricted to a minimum of 11 % r.h., because a stronger drying can affect the C-S-H phase. Then the specimen has to be ground to a powder. With an ATR crystal area of four square millimeters it is necessary to grind to a grain size of about thirty to forty micrometers to get sufficient grain statistics of several thousand grains. Dry grinding is possible, but it is necessary to avoid temperatures above 70 °C. The powder must kept dry and without carbonation.

3. Other minerals than quartz and calcite in the aggregates must be separated from the specimen, because of possible peak overlapping. This separation starts with a careful crushing in step 2, where big aggregates can be separated by hand. The further separation of aggregates can be done with heavy liquid separation with diiodomethane/acetone mixture with a density of 2.4 g/cm³. [2] The separation must be done quantitatively. This technique does not affect the infrared spectra of C-S-H. The very common minerals quartz and calcite need not to be separated. Therefore it is possible to produce laboratory concrete specimens, which can be analyzed without a heavy liquid separation. The aggregates from concrete specimens from buildings must be separated normally, because of the many different aggregate types inside.

4. The method needs an internal standard to correct differences between the density of the specimens on the ATR-crystal and changes in the intensity of the light source of the spectrometer. The scattering of the C-S-H signals is decreased by working with a relative absorbance. We found potassium ferricyanide, $K_3[Fe(CN)_6]$ to be sufficient as an internal standard for this method. It must be grinded wet in water free ethanol to a grain size of about 20 micrometers without remarkable increase of temperature. Any contact with acid, chromium trioxide, oxidizing agents, fluorine, ammonia, nitrates and nitrites must be avoided. Because of its solubility in water it is usable only with dry specimens. The standard shows two peaks at 2117 and 2120 cm⁻¹ and a weak band at 500 cm⁻¹. It must be kept dry and guarded from light.

5. The specimen and the internal standard are mixed in a 60 to 40 relation by weight. This mixing must be done wet in a little amount of ethanol, to get a homogenous mixture. The precision of weighting is critical. Ethanol must completely evaporate before the measurement.

6. The specimen, mixed with the internal standard is measured with a resolution of 2 cm⁻¹. The ATR crystal must be completely covered with powder and the pressure on the powder must be controlled so that the spectrum is not changed with increasing pressure. At least 5 measurements of the material are recommended.

7. The spectrum is converted into absorbance, and an ATR correction is performed, assuming ideal contact of powder to the crystal. The ATR correction is a mathematical transformation, converting the spectrum into a spectrum comparable with a transmission spectrum.

8. Now it is necessary to eliminate interfering signals from other phases, known by step 1. Interfering signals can be separated within the necessary peak fit (see the following step). But in the case of components with very broad IR-signals, for example flyash or blastfurnace slag, it is helpful to subtract a typical spectrum of such a component, measured with the same conditions. Often it is not possible or recommended to subtract all of the intensities of the interfering substances. The residual intensities will be eliminated by the peak fit, remembering the peaks of the interfering substances.

9. In the next step a peak fit in the area of the C-S-H peaks and of the internal standard is performed. During this peak fit, also the remaining interfering signals from other phases and the background must be considered. We prefer a linear background between 1850 and 2250 cm⁻¹ for the internal standard, and a background with logarithm function
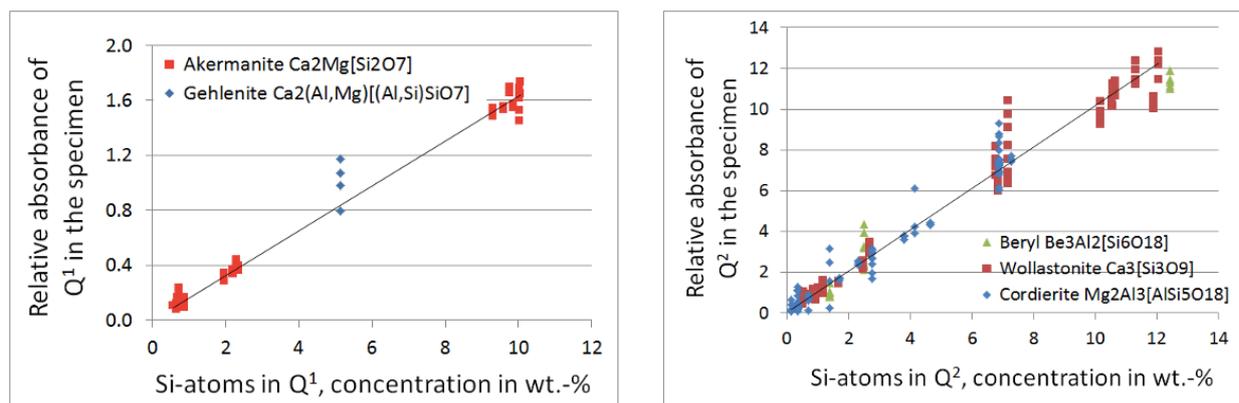
FIGURE 1. Calibration curves for the Q^1 (left) and Q^2 (right) structural units in C-S-H.

in the range of the C-S-H bands, leaned on the minimum points in this range. It is absolutely necessary to restrict the peaks to that, existing in the different phases of the specimen. It is necessary to make this fit with experience on the technique, knowledge of the phases in the specimen and their typical peaks. The absorbance is measured as peak area (Voigt-function).

10. Then, with the absorbance A_Q of the Q^1 and Q^2 signals of C-S-H and the absorbance of the internal standard A_I, a relative absorbance $A_{rel} = A_Q/A_I$ of Q^1 and Q^2 is calculated.

11. With the help of calibration functions the relative absorbance is changed into a concentration of silicon in the Q^1 and Q^2 structural elements of C-S-H in the specimen.

4. CALIBRATION WITH CRYSTALLINE SUBSTANCES

Unfortunately there is no C-S-H standard existing, were the concentration of Si in the Q^1 and Q^2 structural elements is known. Therefore we tried to use minerals containing Q^1 or Q^2 structural elements as calibration substances to develop the calibration curves for C-S-H. For the calibration of the silicon in the Q^2 structural units we used the natural minerals cordierite, wollastonite and beryl. For the calibration of the silicon in the Q^1 structural units the synthesized minerals åkermanite and gehlenite were used. All calibration standards were characterized by X-ray fluorescence, X-ray powder diffraction and IR-spectroscopy. The calibration substances were diluted with fly ash, blastfurnace slag, lime powder, unhydrated portland cement, hydrated lime and silica fume to get specimens with different content of Q^1 resp. Q^2 groups. These specimens were measured and the data processed as described in chapter 3. Because of the lack of space no more details of this calibration can be presented here.

Figure 1 shows the calibration curves for silicon in the Q^1 and the Q^2 structural units in C-S-H with the data of all calibration substances, diluted by different substances common in cementitious materials, named at the beginning of this chapter, and analyzed by three different people. These calibration curves refer to dry specimens. It can be seen in these diagrams, that although very different calibration substances were used, with different dilution components, and different people performing these measurements, they all fit to the same calibration curves, within an expectable scatter.

5. CALIBRATION USING IN ADDITION FULLY HYDRATED ACTIVATED ALITE

Plausibility tests were performed by analyzing fully hydrated activated alite, different hydrated binders, and mortars (with binder enrichment) with well-known composition. Using the calibration described in chapter 4 the tests systematically result in too high total silicon concentrations in the specimens. So the calibration and the results were checked very carefully again. In addition the measured chain lengths are in the range of data reported in the literature, based on ^{29}Si MAS NMR measurements. This indicates that the measured Q^1/Q^2-ratio is correct, assuming that the NMR-data are right. So it seems that the calibration of the Q^1/Q^2-ratio by measuring crystalline minerals is possible. But the total Si-content must be calibrated with C-S-H specimens with a known Si-content. We used therefore fully hydrated activated alite, described in chapter 6 for the calibration of the total Si content in C-S-H. With this technique we got the following calibration functions.

$$c_{\text{Si in } Q^1} = A_{\text{rel, } Q^1} \big/ (0.163 + 0.122) \qquad (1)$$

$$c_{\text{Si in } Q^2} = A_{\text{rel, } Q^2} \big/ (1.017 + 0.763) \qquad (2)$$

- c_{Si} concentration of Si in the Q^1 or Q^2 structural units of C-S-H respectively

- A_{rel} relative absorbance of the Q^1 or Q^2 peaks respectively, described in chapter 3

Age	24 hours	7 days	6 months
wt.-% Si in Q^2 in specimen	3.4 ± 0.2	4.0 ± 0.2	3.9 ± 0.2
wt.-% Si in Q^1 in specimen	2.0 ± 0.1	2.1 ± 0.2	1.9 ± 0.2
Sum of two lines above	5.4 ± 0.3	6.1 ± 0.3	5.8 ± 0.4
Mean chain length	5.4 ± 0.2	5.8 ± 0.4	6.1 ± 0.3

TABLE 1. Plausibility tests with fully hydrated activated alite.

Age	24 hours	7 days	6 months
Measured weight percent C-S-H (as C1.7SH2.6)	34.8 ± 1.2	36.4 ± 0.1	37.4 ± 1.0
Measured weight percent portlandite	20.7 ± 0.4	20.5 ± 0.5	20.0 ± 0.5

TABLE 2. XRD measurements with fully hydrated activated alite.

The first numeric value in the equations originates from the calibration with the crystalline substances (see chapter 4). The second numeric value originates from the correction of the total Si-content, measured with fully hydrated activated alite. The measurement of the same hydrated cement stone in different laboratories showed, that it will be necessary to make an instrument specific calibration. It is one result of the research that this calibration can be reduced to a one-point-calibration of the second numeric value in equations (1) and (2), together with the proof that without C-S-H in unhydrated cementitious binder the measured absorbance of Q^1 and Q^2 signals will be zero. The authors can deliver fully hydrated activated alite to perform such a calibration.

The typical quantitation limit of silicon in the Q^1 or Q^2 structural unit of 0.3 wt.-% for a number of measurements of 5 and a significance level of 5 % in most cases is sufficient not only for hydrated binders, but also for mortar and concrete. Otherwise an enrichment of the binder and/or an increased number of measurements are necessary.

6. PLAUSIBILITY TESTS WITH FULLY HYDRATED ALITE

Activated alite (71.7 wt.-% CaO, 25.9 wt.-% SiO_2, 1.8 wt.-% MgO, 0.6 wt.-% Al_2O_3) was hydrated with a water cement ratio of 1.1 at 23 °C in closed containers without moisture loss or uptake from the environment. The total concentration of silicon in this system is very well known. It amounts to 5.72 wt.-%. XRD measurements after 24 h reaction time with water showed no C_3S anymore. All of the silicon must therefore be incorporated in the reaction product C-S-H. But the detailed structure of the C-S-H is unknown and a function of age. The hydrated system was analyzed by ATR FT IR spectroscopy after 24 h, 7 days and 6 months reaction time. Differing from the method described in chapter 3 the specimen was not dried until the mixing with the internal standard. Additional measurements with thermal analysis proofed, that the moisture loss until mixing with the internal standard was maximum 0.9 wt.-%, increasing the sil-

icon content in the system to maximum 5.76 wt.-%. Additional water loss after the mixing with the internal standard do not affect the analysis results. The results are shown in Table 1. It is visible, that the mean chain length is slightly increasing with time. The mean chain length is near chain lengths based on NMR-data in the scientific literature [3–6]. The total silicon in C-S-H of course is near the theoretical value of 5.72 wt.-%, because the specimens were used for the calibration of this parameter.

In addition the material was analyzed independently by X-ray diffraction with the method of Bergold et al. [7] at the same time. Assuming a C-S-H composition of C1.7SH2.6, 41.2 wt.-% C-S-H and 20.1 wt.-% portlandite can be expected. The results of the measurements are shown in Table 2. It can be seen, that the C-S-H content is lower than the expected one. This was also the result of Bergold et al. [7] and is an indication that a part of the C-S-H is totally X-ray amorphous. This may be the dimer molecules. The XRD detectable amount of C-S-H is increasing with time.

Figure 2 shows the spectrum of the fully hydrated activated alite with age 6 months in the range of the Si-O stretching vibrations in C-S-H. It shows 4 peaks resulting from the Q^2 structural unit at 910, 954, 995 and 1064 cm^{-1}. At the age of 7 and 1 days only the two strongest peaks in the middle can be observed. The Q^1 structural unit shows two peaks at 793 and 820 cm^{-1}. At 1 day only the strongest peak above 800 cm^{-1} can be observed. At 7 days the weak splitting is observable. The full spectrum additionally contains the common bands resulting from portlandite, the internal standard, water, carbonate, a peak at 1325 cm^{-1} perhaps a Si-OH bending vibration in C-S-H [8], a weak peak at 655 cm^{-1} and several peaks in the area 450 - 545 cm^{-1}, perhaps resulting from deformations of the tetrahedrons or the tetrahedron chain.
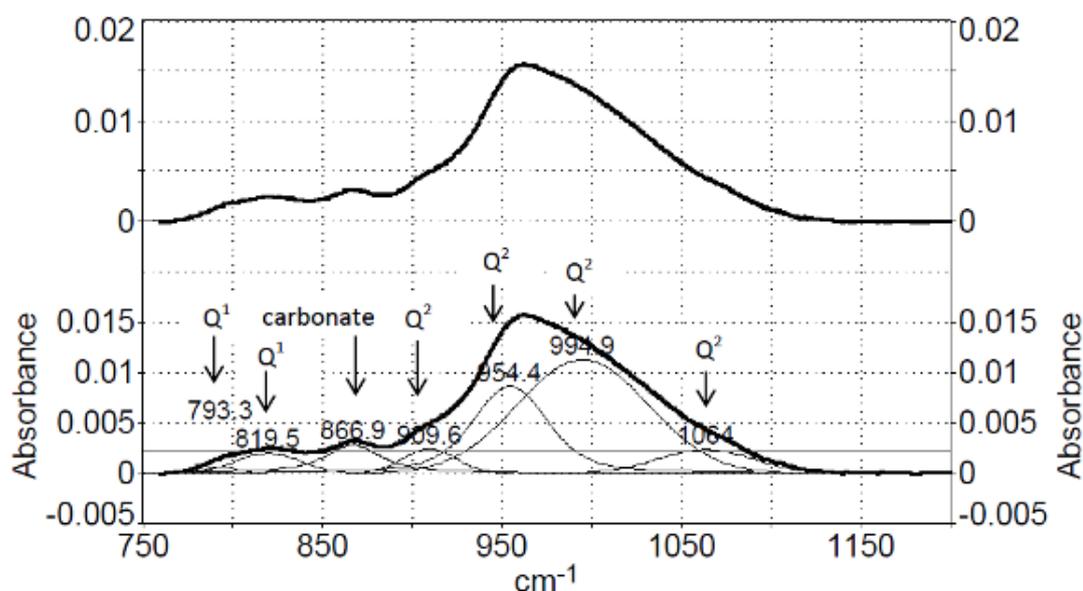
FIGURE 2. ATR IR spectrum of fully hydrated activated alite with age 6 months in the range of the most important bands of C-S-H including the peak fit. Background (logarithm function) subtracted before, leaned on the minima at the end of the displayed range. Note that the signal of the Q^1 structural element seems to be more sharp and restricted to lower wave numbers than in the case of a commercial cement stone (see Figure 3).

Cement	CEM I 42,5 R	CEM I 42,5 R-SR 0	CEM I 52,5 R	CEM I 52,5 R	CEM I 52,5 R
Cement g	680	680	780	325	590
Water g	237.82	267.72	232.88	194.7	353.44
Silica fume Elkem 940 U g	−	−	−	−	65.52
Water-cement ratio	0.35	0.4	0.3	0.6	0.6
Water-binder ratio	−	−	−	−	0.54
Degree of hydration C_3S %	81.3	93.7	73.7	99.4	95.6
Degree of hydration C_2S %	18.9	35.5	7.8	43.9	35.0
wt.-% Si in Q^2 in specimen	3.6 ± 0.2	3.8 ± 0.2	3.7 ± 0.2	4.6 ± 0.4	5.5 ± 0.4
wt.-% Si in Q^1 in specimen	1.8 ± 0.3	1.3 ± 0.2	1.9 ± 0.2	1.9 ± 0.2	2.4 ± 0.2
Sum of two lines above	5.4 ± 0.3	5.1 ± 0.3	5.6 ± 0.2	6.5 ± 0.3	7.9 ± 0.5
Expected value (see text)	5.3	6.4	4.9	7.4	10.0
Mean chain length (calc.)	6.0 ± 0.6	7.9 ± 1.1	6.0 ± 0.6	6.9 ± 0.6	6.6 ± 0.4

TABLE 3. Plausibility tests with hydrated binders.

7. PLAUSIBILITY TESTS WITH HYDRATED BINDERS AND MORTARS

Using the phase analysis of the cements measured by the Rietveld method, the degree of hydration of C_2S and C_3S measured by the G-factor method [9], an assumed degree of hydration of 100 % for silica fume, the composition of the mixtures, and the drying conditions, the amount of silicon in the Q^1 and Q^2 structural elements of C-S-H was calculated in weight percent of the specimens and compared with the experimentally determined value for several hydrated binders. All specimens were stored in closed containers at $23 \pm 2\,^\circ$C and above 95 % r.h. until drying. The age before drying was at least 84 days. Peaks at about 850 and 900 cm^{-1} were treated as residual cement phases in this case. Table 3 summarizes the tests and their results.

It can be seen, that the maximum deviation from the expected total silicon content of the specimens C-S-H is about 20 %. Positive and negative deviations could be observed. The specimen with the w/c-ratio 0.6 contents more C-S-H as the specimen with the same cement and the w/c-ratio 0.3, as a result of the higher degrees of hydration. The increase of C-S-H content by the addition of silica fume is very well visible. The mean chain length of the hydrated binders amounts to 6.0 - 7.9 and is near chain lengths based on NMR-data in the scientific literature [3–6].

In the same way the amount of silicon in C-S-H of several hydrated mortar binders was analyzed. In this case, the total water content of the specimens was determined by thermal analysis as loss on ignition. After production all mortar specimens were

Aggregate type	Granite, sand	Basalt, sand	Limestone, sand	Quartz sand
Granite, basalt, limestone g	962.42	962.42	962.42	0
Sand, mainly quartz g	641.62	641.62	641.62	1738.07
Cement type	CEM I 52,5 R	CEM I 52,5 R	CEM I 52,5 R	CEM I 52,5 R
Cement g	535	535	535	580
Water-cement ratio	0.5	0.5	0.5	0.55
Heavy liquid separation	Yes	Yes	Yes	No
Degree of hydration C_3S %	100	100	100	100
Degree of hydration C_2S %	98.1	98.7	97.2	100
Residual phases of aggregate wt.-%	Quartz 1.8	Quartz 1.8	Calcite 10.4 Quartz 1.3	Quartz 12.4
wt.-% Si in Q^2 in specimen	3.3 ± 0.3	3.3 ± 0.3	2.9 ± 0.1	3.8 ± 0.1
wt.-% Si in Q^1 in specimen	2.5 ± 0.3	2.3 ± 0.3	2.0 ± 0.1	2.0 ± 0.3
Sum of two lines above	5.8 ± 0.6	5.6 ± 0.4	4.9 ± 0.2	5.8 ± 0.3
Expected value (see text)	7.6	7.7	6.9	6.9
Mean chain length (calc.)	4.6 ± 0.2	4.9 ± 0.4	4.8 ± 0.1	5.8 ± 0.6

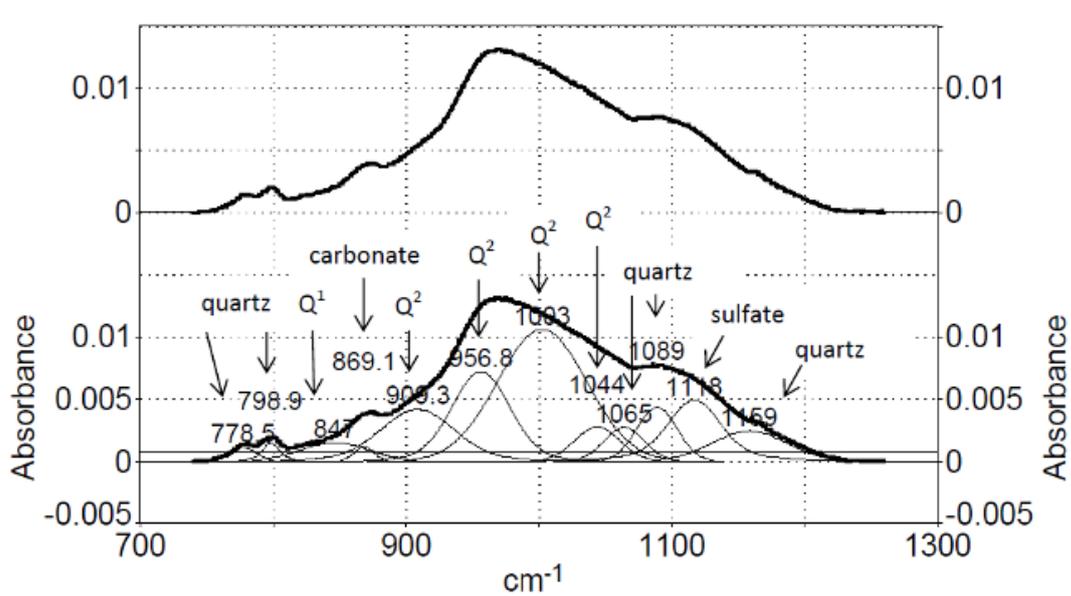TABLE 4. Plausibility tests with binders of hydrated mortars.

FIGURE 3. ATR-IR spectrum including the peak fit of a mortar with quartz aggregate and enrichment of the binder by grinding and sieving, showing the peaks of the Q^1 and the Q^2 structural units in the C-S-H. Background (logarithm function) subtracted before, leaned on the minima at the end of the displayed range.

stored in closed containers at $23 \pm 2\,°C$ and above 95 % r.h. until drying. The age before drying was at least 1.5 years (mortar with only quartz: about 0.5 years). The aggregates of the mortar specimens were then removed by two steps: 1) repeated grinding and sieving, removing the coarse grains, 2) heavy liquid separation of the fines with diiodomethane/acetone mixture with a density of 2.4 g/cm³ (only mortars with basalt, granite and limestone). Table 4 summarizes the tests and their results. All specimens contain a small amount of residual quartz, probably from the quartz sand. The mortar with only quartz aggregate contains a much higher value, because a heavy liquid separation was not performed in this case. All specimens contain about 0.5 wt.-% calcite, probably by carbonation. The specimen with limestone aggregate

contains a much higher value. This indicates that the limestone aggregate cannot be removed well by the heavy liquid separation. But quartz and calcite can be treated during the evaluation of the spectra. No typical minerals from the basalt and the granite could be observed after heavy liquid separation.

Astonishing is the very high degree of hydration of the C_2S. This cannot be an effect of the heavy liquid separation, because also the mortar with quartz and without heavy liquid separation has a degree of hydration of 100 %. Figure 3 shows the peak fit of a specimen with quartz sand. Because of the high degree of hydration no residual cement phases were considered. In this case all measured Si-contents in the specimens C-S-H are lower than the expected values, and the deviation is greater (maximum 29 %).

Because of the broader Q^1-peak used in these peak fits (compare Figure 2 and Figure 3), the calculated mean chain length is smaller than in the alite and the hydrated binder evaluation.

8. CONCLUSIONS

It can be concluded, that ATR-infrared spectroscopy is a very helpful and powerful technique, also in a quantitative manner. Infrared spectroscopy is used for the analysis of cementitious materials for a long time, but its potential is not exhausted. Also amorphous species are producing signals that can be observed directly. This feature was used to develop a quantitative analysis method for the structurally only weakly ordered C-S-H in cementitious materials. With this technique it is possible to analyze specimens from real life, not only model materials. Cementitious materials with quartz or calcite aggregates can be analyzed directly, although an enrichment of the binder will facilitate the analysis. Other aggregates must be separated, for example with the help of heavy liquid separation. In addition infrared spectroscopy is a very fast and cheap technique that is common in most laboratories, active in the field of construction chemistry. The described method measures the silicon content in the Q^1 and Q^2 structural units in the C-S-H. Crystalline minerals containing Q^1 or Q^2 structural units were used to calibrate the Q^1/Q^2 ratio. But it was not possible to use these crystalline materials for the total silicon content as well. The total silicon content was calibrated with the help of an activated fully hydrated alite with very well known silicon content in the C-S-H phase.

Plausibility tests on different hydrated binders and the binder in mortars showed that the total silicon content in C-S-H, measured with the method, is in the range of the expected values, but deviations of up to 30 percent could be observed. In particular the measurement of the small Q^1 absorbance is difficult. In addition also the ratio Q^1/Q^2 is measurable and therefore the chain length, which is in the range of literature data based on NMR.

In spite of these difficulties researchers and manufacturers have the chance to analyze the concentration and the internal structure of C-S-H as a function of relevant parameters with this method. Not only the success of improvements of the time dependent C-S-H quantity and structure, but also the effects of other measures on C-S-H and the results of decomposition of C-S-H by chemical attack can be investigated.

In the future it will be helpful to investigate how aluminium and alkalies in C-S-H will affect the IR-spectra of C-S-H and the method. In addition it is necessary to find an alternative internal standard, that is not soluble in ethanol and water, has a good grindability and chemical stability, is not toxic and does not overlap with the interesting peaks. Further activity should pay attention also on the calibration substance and the removal of interfering aggregates.

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