

SURFACE COATING OF SILICEOUS PARTS OF AGGREGATE GRAINS BY ALUMINA CONTAINING SCM'S IN ALKALINE SOLUTIONS

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Abstract

It is well known that SCMs containing alumina can prevent the damaging alkali silica reaction in concrete. This paper deals with the direct interactions between aggregate grain surfaces (quartzitic rock material Q1) and the dissolved amounts of SCMs (metakaolin, aluminum hydroxide). Investigations have confirmed that the presence of such SCMs can strongly decrease the silica release from aggregates in comparison to solubility experiments without SCM addition. The reason for this effect is the formation of a thin alumina containing layer (some nanometers thick) on the grain surfaces. The existence of this layer could be determined by XPS. Only this method provides data of the strongly increased alumina concentration in a thin surface area and also of the layer thickness in dependence on reaction parameters. Dissolution experiments of grains coated with such layer demonstrate the effectiveness of this process and can give a further contribution for understanding the preventing mechanisms of SCMs.

Keywords: Alumina containing SCMs, inhibition, surface coating, alumina silicate layer, XPS method

1 INTRODUCTION

The alkali-silica reaction (ASR) between the alkaline pore solution and the aggregates is one of the most investigated degradation reactions in concrete. It is well known that the hydroxide ion concentration in the pore solution and the alkali sensitivity of the aggregate play an important role for the formation of swelling alkali silicate gels which leads to concrete cracking. Because alkali resistant aggregates and cements with low alkali contents are not available in all regions of concrete producing countries, the ASR is mainly prevented by reducing the pH value of the pore solution. The reduction of the pH value of pore solution can be achieved by using SCMs which was reviewed by Thomas [1] and Lothenbach et al. [2] in 2011. The composition and structure of SCMs can vary in wide ranges and determine their effectiveness to prevent concerning the ASR. But the drop of the pH value [3-5] in the liquid phase of the concrete is not the only effect caused by the SCMs. It is known that the whole hydration reaction of the binder is influenced. For example if the binder contains microsilica (MS) the hydration is faster [6, 7]. Furthermore the structure of the solid hydration products changes to higher condensed silicate anions [8] and additional CSH phases are formed by the reaction of the SCM with calcium hydroxide [9]. If the SCMs contain alkali soluble aluminum compounds additional effects are observed, for example the further connection of the CSAH phases formed through the influence of the aluminum [10] and higher Al concentrations in the pore solution [4]. This means, such SCMs, for example metakaolin, are very effective and ensure the long term durability of concrete [5]. While most of the positive effects of using SCMs in concrete are connected with the interaction between the cement stone and the SCM, there is a gap in knowledge about the interaction between the SCM and the aggregates. So it is known from Fournier et al. [11] that the expansion of concretes which contain SCMs with identical composition depends on the aggregate type. Recently, Chappex and Scrivener [12, 13] have shown that aluminum containing SCMs seem to influence the dissolution of the aggregate but it is unknown in which extent this process proceeds. Own results [14] dealing with the characterization of the alkali sensitivity of aggregates by dissolution experiments are the basis for these investigations. Kronemann [15, 16] and Huenger et.al. [17] could show in their works that changes on the surface areas of aggregate grains occur in the presence of aluminum containing SCMs. But they couldn't find reasons for this effect either. The aim of this paper is to investigate the dissolution processes of a special prepared quartzitic aggregate (Q1) without and with SCMs of two different types in alkaline solution in order to determine the influence of aluminum on the effectiveness of the respective SCM. In a second step different analytical methods (FTIR, XRD-GID, XPS) were used to investigate and to characterize the surface areas of such quartzite samples.

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2 MATERIALS AND METHODS

2.1 General

For all experiments a medium reactive aggregate (quartzitic rock Q1) was used. It was combined with two different types of SCMs, metakaolin and aluminum hydroxide ($\text{Al}(\text{OH})_3$). Already Bickmore et.al. [18] have examined the influence of aluminum hydroxide on the dissolution rate of quartz. In order to determine the influence of aluminum containing SCMs on the ASR, two kinds of experiments were performed. In a first step the solubility of silicon and aluminum of the aggregate and the pure SCMs in alkaline solution were determined. Next also the interaction in the mixtures between aggregate and SCM was tracked by solubility experiments.

The structure analytical part consists of FTIR, XRD-GID and XPS investigations. Especially the surface areas of polished aggregate grains of Q1 before and after storage in alkaline solutions were analyzed. The investigations were performed without and with SCM addition in order to specify the changes in the chemical, mineralogical and structural composition of the surfaces.

2.2 Materials

The aggregate used for the investigations is a medium reactive rock material quartzite (Q1). It was used because of its absolutely high quartz content of more than 98 wt%, the rest is muscovite, a mica mineral (1 - 1.5 wt%), which also contains aluminum in its structure too, but the amount of Al in the surface area of the grains is very small. This fact is important because nothing should interfere with the detection of aluminum on the surface of the rock material. For all experiments the original grain size 8-16 mm in diameter was used but special prepared for each method. For the XRD-GID and FTIR- investigations the grains were embedded in a resin, and the surfaces of the so prepared samples Q1 were polished. For the solubility experiments and the XPS investigations so-called thick section samples, with a thickness of approx. 2 mm, were produced. The results are disc-shaped samples. The SCMs are mainly amorphous. Their mineralogical composition is listed in Table 1. The solution for the solubility experiments has a concentration of 0.1 mol KOH/L prepared from the analytical grade substance and demineralized water. 200 mL of this solution was used, the special prepared thick sections were stored inside and 0.25 g of each SCM was added.

2.3 Methods for analysis

General

A wide range of investigation methods were used to determine changes in the composition of the alkaline solution and in the surface compositions of Q1 samples. Solubility experiments of special prepared samples were made to describe the dissolution process of Q1 under different storage conditions.

The main part of used methods should be able to characterize the surface compositions and structures of Q1 samples.

Dissolution experiments and chemical analysis of the solution by ICP-OES

For dissolution experiments thick sections were produced with a thickness of approx. 2 mm and a diameter according to the original grain size of the aggregate Q1 (8 - 16 mm – see Figure 1). Such prepared samples were stored in an alkaline solution (0.1 M KOH solution) at 80 °C for 14 days by varying the added kind of SCM. An analogous experimental series was performed by changing the storage time (from 7 to 20 days). At certain days 3 ml of the solution was taken and analysed by using the ICP-OES method. In this solution the concentration of Si and Al were determined, calculated as SiO_2 and Al_2O_3 values under consideration of different dilution factors and registered as a function of time. The results are dissolution curves of Q1 samples under different storage conditions.

ATR-FTIR

The ATR-FTIR spectroscopy (attenuated total reflection spectroscopy) is a special method of the IR spectroscopy to investigate layered surface areas of solid materials. The spectra here were measured at the contact area between the ATR crystal (here ZnSe) and the different sample surfaces of Q1. Very important for an evaluation is the knowledge of the penetration depth of the IR-beam. Based on the data used (wavelength = 10 μm , refraction index $n_{\text{ZnSe}}=2.4$, refraction index $n_{\text{quartzite}}=1.4$ and incidence angle $\theta = 45^\circ$) a depth d_p of approx. 1 μm can be calculated, based on the equation (1).

$$d_p = \frac{\lambda}{2\pi \sqrt{n_1^2 \sin^2(\theta) - n_2^2}}$$

equation (1).

X-ray diffraction - Grating Incidence Diffraction (XRD-GID)

To characterize the surface composition by structural analytical method XRD-GID measurements were performed. GID stands for grating incidence diffraction, and it is a typical mineralogical method to identify surfaces. The incidence X-ray beam is fixed at small angles (0.5°, 0.25° and even 0.1°) while the reflection beam is detected at a range of 4 – 60° 2 θ . Using this method a thin area on the surface of polished samples can be determined and the mineralogical composition of crystalline structures can be characterized. Polished plane samples embedded in a resin were put in a specimen holder following the procedure described in [19]. Operating conditions of the Seifert X-ray diffractometer XRD 3000 TT were set to 40 kV and 30 mA. Diffractograms were recorded from 4-60 °2 θ , in 0.05 °2 θ increments with 5 s counting time per increment. Important here is the penetration depth d , which can be calculated by using Fe-filtered CoK α radiation of wavelength $\lambda = 1.7903 \text{ \AA}$, an incidence angle ω of 0.1°, $2\theta = 30^\circ$ and an absorption of 90 % of approx. 100 - 120 nm by using equation (2).

$$A(d) = 1 - e^{-\mu \cdot d \left(\frac{1}{\sin \omega} + \frac{1}{\sin(2\theta - \omega)} \right)}$$

equation (2).

X-ray photoelectron spectroscopy, XPS

XPS is a method to determine the chemical composition of solid state materials especially of their surfaces. The method is based on the fact that X-rays with different energies are produced by electromagnetic excitation. Operating conditions of the device XPS Quantum 2000, Physical Instruments were set to AlK α radiation (1486.7 eV) with a beam energy of 10 - 15 kV and a filament current of 10 - 30 mA in a CAE/NORMAL/CRR modus. The result are overview spectra of elements containing in a surface area of approx. 1 mm² for each sample. Another result is a depth profile of different elements (here mainly important Si and Al) in dependence on the sputtering time. To assign the sputtering time with a depth value the calibration with quartz was performed which means that 1 min sputtering time is equal to 1 nm ablation depth.

3 RESULTS

Photographs of the sample surfaces are shown in Figure 1. It can be seen that after alkali attack (stored 14 days in KOH solution at 80 °C) the surface shows changes in its structure and reflection behaviour. Samples which are stored in aluminum containing alkaline solutions do not indicate any visible changes.

The diagrams in Figures 2, 3 and 4 show the solubility results of samples determined under different conditions. Figure 2 contains the solubility curves of the starting materials Q1, Al(OH)₃ and metakaolin in 0.1 M KOH solution at 80°C. It can be seen, that Q1 releases SiO₂ only in the alkaline solution (after 14 days 75.7 mg/L), Al(OH)₃ only Al₂O₃, as expected (after 14 days 652 mg/L) and metakaolin, as expected, both SiO₂ and Al₂O₃ in a relation of approx. 1 (SiO₂/Al₂O₃ = 355/334 mg/L). In Figure 3 solubility curves of Q1 samples with presence of SCMs are shown. The data contain a superposition of the solubility of Q1 material and the SCMs added. Because of this fact the real measured solubility of the pure SCMs must be eliminated. The results can be seen in the two diagrams in Figure 4. With presence of SCM materials the silica release of the rock material Q1 is approx. zero in both cases. The solubility of the pure SCMs only can be determined and exactly this can be demonstrated by subtraction of the measured curves from the graphs of the starting material.

Further dissolution experiments in pure KOH solution were performed with the samples Q1 which were covered with dissolved SCM parts to demonstrate the effectiveness of SCMs on the solubility of aggregate grains after coating. The results are summarized in Figure 5. As can be seen in the three diagrams the solubility of uncovered sample Q1 increases further and reaches a value of 92.9 mg/L. Differences can be determined between the covered samples and the uncovered ones. The sample with Al(OH)₃ coating releases 60.7 mg/L silica into the alkaline KOH solution (in comparison to the starting material it is a reduction of 20 %), the sample with metakaolin covering releases 56.6 mg/L silica (a reduction of 25 %) after 14 days of storage.

Further important investigations were made to characterize the surface of the samples after alkali attack in presence of SCMs in comparison to the starting material. Figure 6 demonstrates results of the ATR-FTIR investigations. The curve above in the picture shows the spectra of the starting material, the curve below after alkali attack and with presence of metakaolin. The differences between both samples are marginal, the vibrational band at 1159 cm⁻¹ shifted appears to 1164 cm⁻¹ and additionally a signal can be measured at 1140 cm⁻¹. All other bands can be associated to quartz.

XRD-GID investigations were also made to characterize the surface structure in a more detailed way. Figure 7 documents the results. Such investigations were performed under conditions of different incidence angles, with similar results. There are no significant changes in peak angles, only the intensities decrease with presence of metakaolin in the alkaline solution and maybe on the surface of the sample.

A very important method to analyse the formation of a layer structure is the XPS method. This method allows to measure atom concentrations of elements in a very thin surface area. Under consideration of the sputtering time and the calibration with quartz, depth profiles can be determined to find evidences for a formation of an Al containing layer on the surface. Two different investigations were made: at first the formation of a layer in dependence on SCMs used ($\text{Al}(\text{OH})_3$ and metakaolin) after a setting time of 14 days in comparison to the starting material, and second in dependence on the setting time (from 7 - 20 days). Table 2 contains the results of both series. Very important is that in both cases the starting materials have no Al concentrations. With presence of Al containing SCMs the Al concentration increases and reaches values of approx. 3-8 at%. As it can be seen in Figure 8 the Al concentration increases according to the raise of the storage time (from 7-14-20 days) and also in dependence on the SCM material chosen. Here metakaolin delivers a higher amount of Al in the top layer of the Q1 rock material than $\text{Al}(\text{OH})_3$.

Further XPS investigations allow to determine depth profiles of the top area of the samples. Figure 9 demonstrates the results. It can be seen that the starting material provides a uniform and proportional increase of the Si and Al concentration in dependence on the sputtering time. With presence of metakaolin the depth profile has changed. Si starts with a value of about 50 % at the surface and increases slowly until to a depth of 10 nm, Al reaches a maximum at approx.. 1 nm and decreases then very slowly also to a depth of approx. 10 nm. The sputtering time was calibrated by using a quartz standard what means that 1 min sputter time is equal to 1 nm ablation depth. Maybe this is a first direct proof for the idea that a very thin layer has been formed on the siliceous parts of aggregate grains consisted of Al and Si. K may bound as an alumino silicate structure.

4 DISCUSSION

A lot of investigations were performed to characterize surface changes of siliceous parts of aggregate grains with presence of aluminum containing SCMs which are at the same time in the alkaline solution. A simple visual proof is that an alkali attack by using KOH solution provides a clearly visible change of the surface structure. With presence of aluminum containing SCMs, here metakaolin and even $\text{Al}(\text{OH})_3$, which is not a SCM in a strict sense, no visible changes in the surface area of the Q1 samples can be observed. This result is well known, because Chappex and Kronemann have reported already on this fact.

A further indirect proof for the influence of the surface structure by aluminum containing SCMs is the changed dissolution behavior of samples Q1. By addition of SCMs into the alkaline solution the solubility has changed dramatically. It can be clearly said, that if aluminum containing SCMs are present in an alkaline solution under chosen conditions the silica release is strongly reduced or even stopped. In such an alkaline solution the solubility of the SCM materials can be measured only. The Q1 rock material does not provide any contribution to the silica concentration in the alkaline solution.

But the further investigations show, that it is very difficult to give a direct proof for the existence of a layer or another structural change of the surfaces of Q1 samples. ATR-FTIR measurements show that certain Si-O-Si bonds of quartz have changed with presence of metakaolin in the alkaline solution. Some bonds have shifted but a clearly detectable signal, which can be assigned to an alumino silicate surface structure, cannot be measured. One possible reason for this might be the interaction/penetration depth of the IR beam and the solid, which is with approx.. 1 μm very large.

XRD-GID measurements normally provide a very good result to characterize thin surface structures. Of course such structures should be crystalline. In our case, XRD-GID measurements indicate no changes in d-values, even in dependence on incidence angle. The intensity of quartz peaks only decrease if the angle also decreases which can be clearly explained by a smaller irradiated volume in the surface area. Again, the penetration depth of the X-ray beam can be estimated to approx. 70 - 80 nm. In comparison to the FTIR depth this is much smaller but obviously not enough to find advices for an alumino silicate layer on the surface of siliceous rocks.

Only the XPS method allows to measure compositions in a very thin area on the surface of the Q1 rock material. Depth profile measurements can be performed in very small steps in a range of 1 nm. By using this method differences in the surface composition can be determined, especially the Al content in an immediate surface area depends on the storage time and the kind of SCM used. In comparison to the Al concentration of the initial material which is close to zero it is possible to find Al concentrations of approx. 3 - 8 at%. Normally pure quartzite contains no Al. The samples used here are not pure, they contain about 1 - 1.5 wt% muscovite, but this quantity of muscovite couldn't cause the detected increase of Al. An indication that small amounts of Al are inside of the Q1 sample is shown in the left diagram of Figure 9. In dependence

on the sputtering time both the Si and the Al concentration increase. On the surface both values are zero because of the carbon effect and increase proportionally. Note that these are relative values, the absolute concentration of Al is very small. But in the diagram right of Figure 9 the measure values have changed. It must be summarized that on the surfaces of Q1 rock material Al has enriched. Additionally the presence of potassium in this area is an indirect evidence that the coated surface area has an alumino silicate structure because of the necessary charge compensation in alumino silicates by alkalis.

Additional depth profile measurements allow the conclusion that, if such a layer exists indeed, it can be only some nanometers thick. Exactly this fact can probably explain that other methods used here (ATR-FTIR, XRD-GID) are not able to determine changes in surface characteristics because of their very large penetration depth.

Summarizing all information and results it must be clearly said that

- an effect on the solubility behavior of aggregate grains (Q1) with presence of aluminum containing SCMs can be determined,
- Al has accumulated on the surface area of siliceous parts of aggregate grains,
- the penetration depth at which chemical and structural changes can be measured in comparison to the inner parts of the quartzite rock must be very small (a few nanometers only),
- it could be an alumino silicate layer because of the high potassium concentration in this area.

But it must be mentioned too, that

- a direct proof for the existence of an alumino silicate layer on the surface of siliceous parts of aggregate grains cannot be clearly provided. A high resolution XPS measurement on the surfaces of samples investigated was not possible until now.

5 CONCLUSIONS

A special prepared quartzitic rock material – medium alkali reactive - was used to investigate the influence of SCMs ($\text{Al}(\text{OH})_3$ and metakaolin) on the dissolution behavior in alkaline solutions. Different structural methods were performed to find reasons for the interactions between SCMs and the quartz surfaces.

Solubility investigations by ICP-OES:

With presence of both $\text{Al}(\text{OH})_3$ and metakaolin in each case, together with the rock samples in an alkaline solution, the solubility of SiO_2 can be strongly reduced, and it is close to zero. The solubility of the pure SCMs can be measured only. This is a strong proof for the inhibitory effect of aluminum containing SCMs. This result is supported by dissolution experiments with coated samples. A decrease of the solubility of such prepared samples under pure alkali influence can be measured.

FTIR spectroscopy:

Quartz bands only can be determined at the Q1 surfaces, maybe one or two vibrational bands added with presence of Al, but they cannot be assigned to a mineral listed in a date base. The penetration depth of this method is approx. 1 μm and this might be too large to measure any effects.

XRD-GID measurements:

Also by using this method to investigate the composition of surfaces quartz can be only analyzed. In dependence on the incidence angle the intensities of the quartz peaks decrease but no other peaks can be detected. The penetration depth of this method depends on the wavelength of the X-Rays and the incidence angle and is here approx. 70 to 80 nm, usually sufficient for the detection of new structures formed.

XPS-method:

This method used here is obviously the only method to find evidences for an aluminum enrichment on the surface areas of the quartzite samples. Is the Al concentration in the starting material under 1 at%, with presence of aluminum containing SCMs the Al content increases on values of approx. 3-8 at%, which means three to eight times higher. Depth profile investigations can be carefully discussed in such a way that probably Al is concentrated until a depth of a few nanometers, maybe 5 - 8 nm, in maximum 10 nm. Maybe the high potassium concentration by using metakaolin (see Table 2) can be an indirect evidence that the surface layer on Q1 samples has an alumino silicate structure. Because of the charge compensation potassium can be incorporated there.

The results of the XPS method can reveal the disadvantages of the other characterization methods used here. Obviously the penetration depths are too large to find differences between covered and uncovered samples.

Further investigations have to be done to find more clear evidences for the existence and the structure of this layer on the surface of siliceous rock materials, which are used as an aggregate in concrete.

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TABLE 1: Mineralogical compositions of SCMs used (in wt%).

Phase	Metakaolin	Al(OH) ₃
Amorphous	68.1	81.7
Boehmite	1.6	17.2
Kaolinite	25.1	-
Quartz	5.1	-

TABLE 2: Atom concentrations of different samples measured by XPS method.

series 1 XPS in dependence on SCM		O1s	Al2p	Si2p	K2p
	starting material	93.28	0	6.72	0
	coated with Al(OH) ₃	70.01	3.10	25.45	1.44
	coated with MK	66.06	7.73	17.63	8.58
series 2 in dependence on time	starting material	71.83	0.71	27.44	0
	7 days	68.85	4.68	21.78	4.67
	20 days	72.10	5.04	21.03	1.83

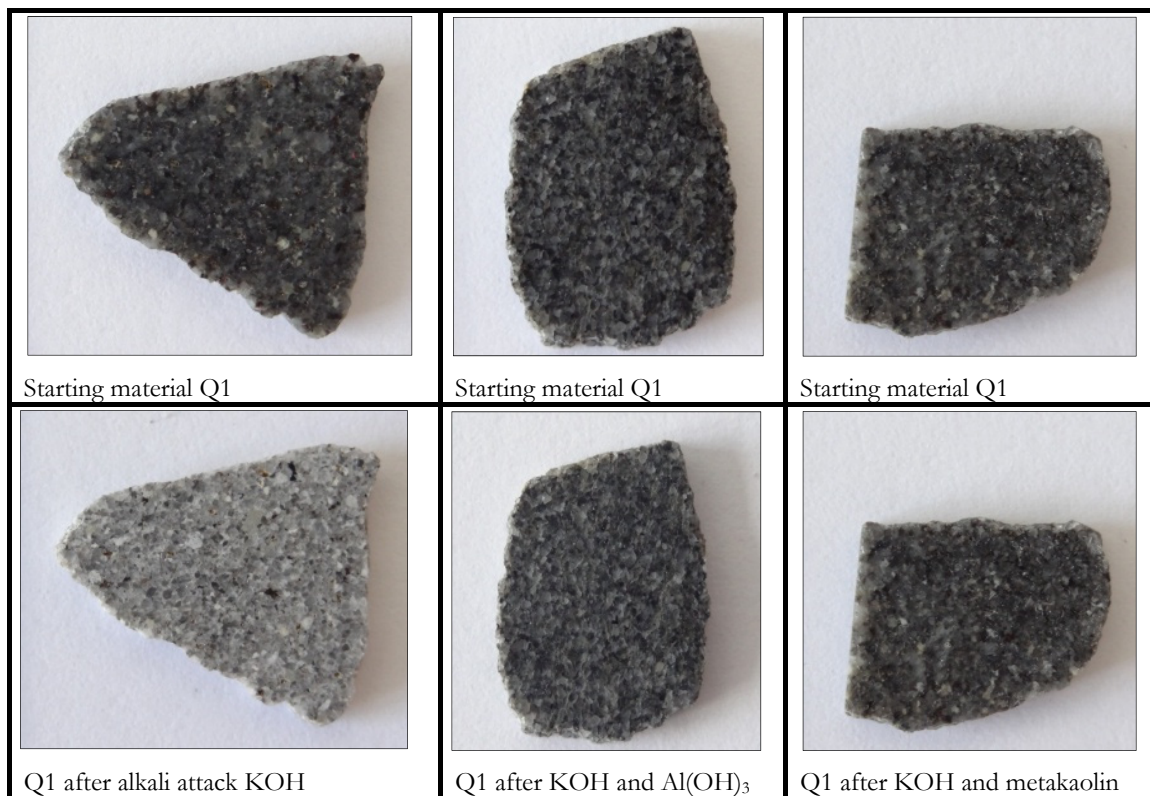


FIGURE 1: Photographs of investigated samples, column 1: after KOH attack; column 2: after alkali attack and Al(OH)₃ addition; column 3: after alkali attack and metakaolin addition.

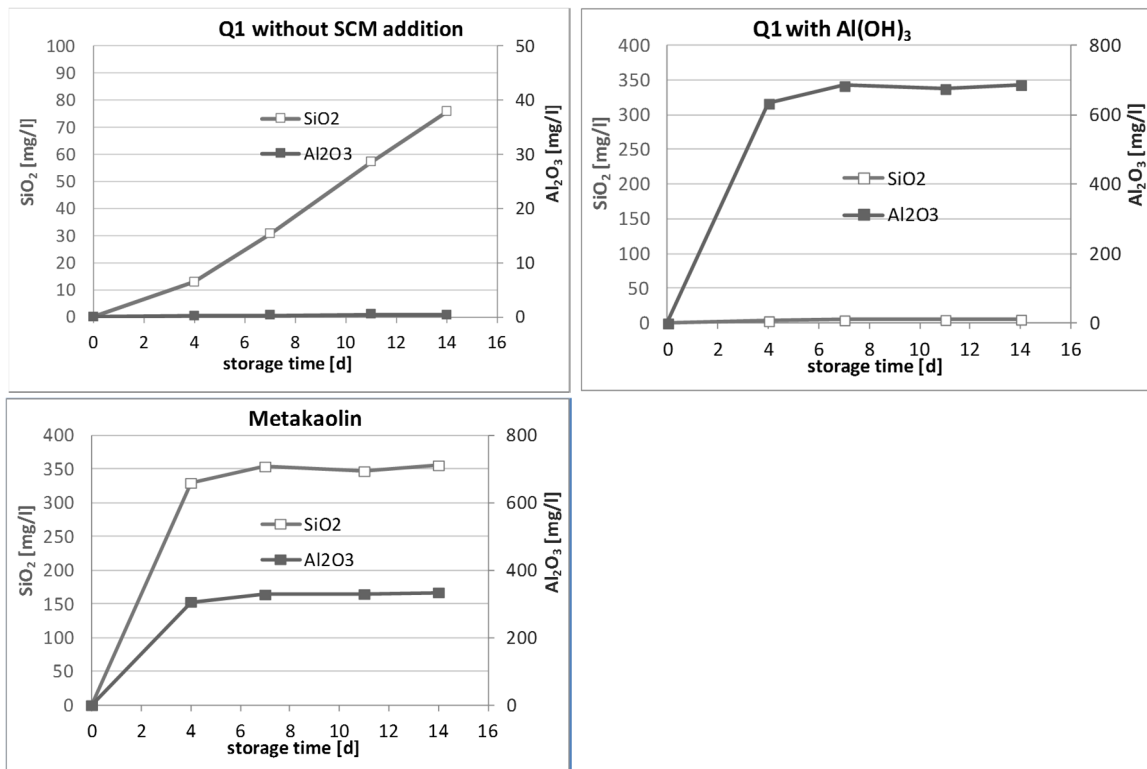


FIGURE 2: solubility curves of samples investigated - starting materials.

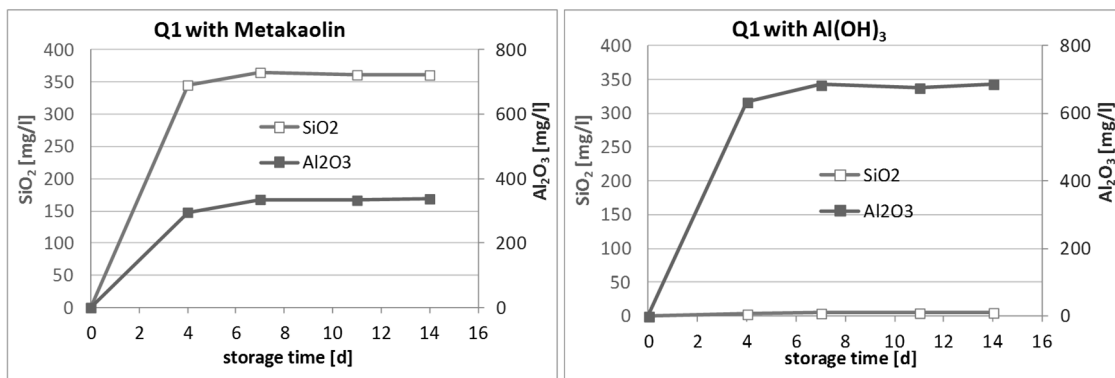


FIGURE 3: solubility curves of samples Q1 - after alkali attack and SCM addition.

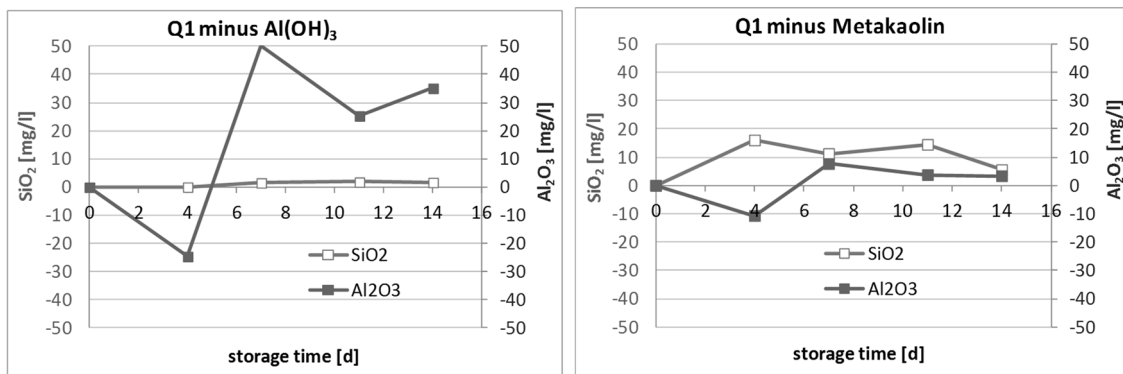


FIGURE 4: calculated solubility curves (difference curves) of samples Q1.

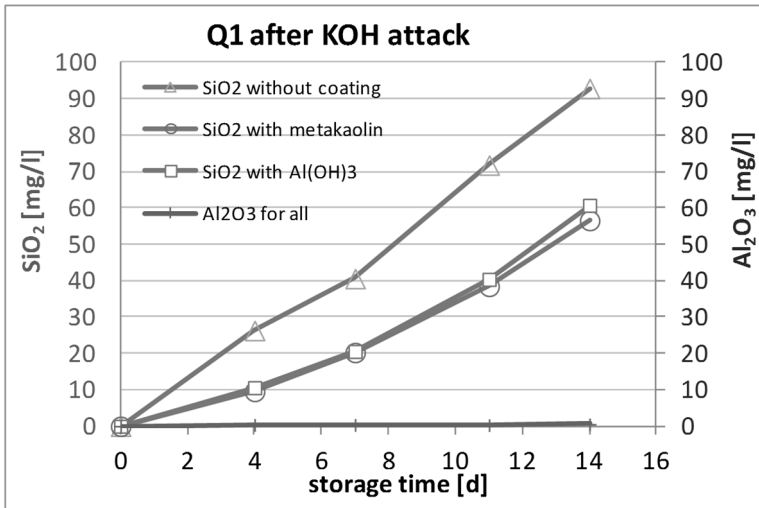


FIGURE 5: solubility curves of uncoated and coated samples in alkaline KOH solution.

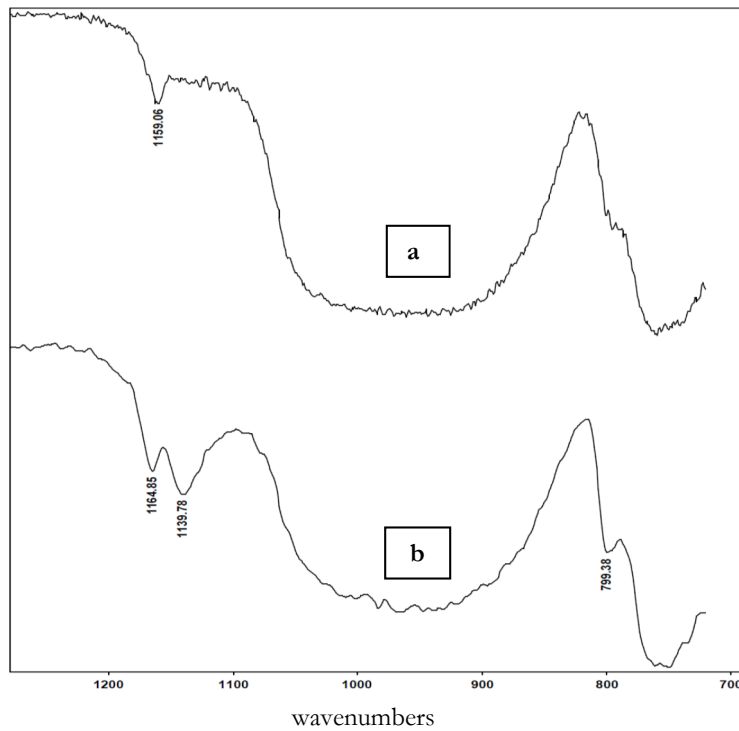


FIGURE 6: ATR-FTIR spectra of Q1 samples, Q1 starting material (a) and coated with metakaolin (b), differences are discussed in the text.

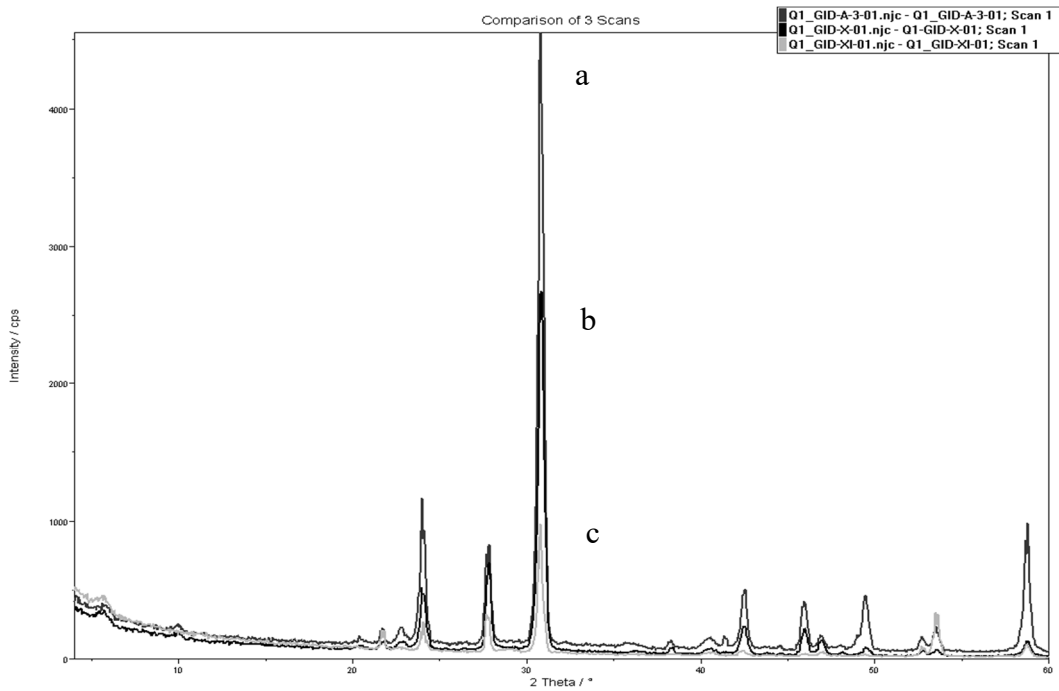


FIGURE 7: XRD pattern of sample Q1 in comparison between starting material (a) and metakaolin addition (b, c) after 7 and 20 days.

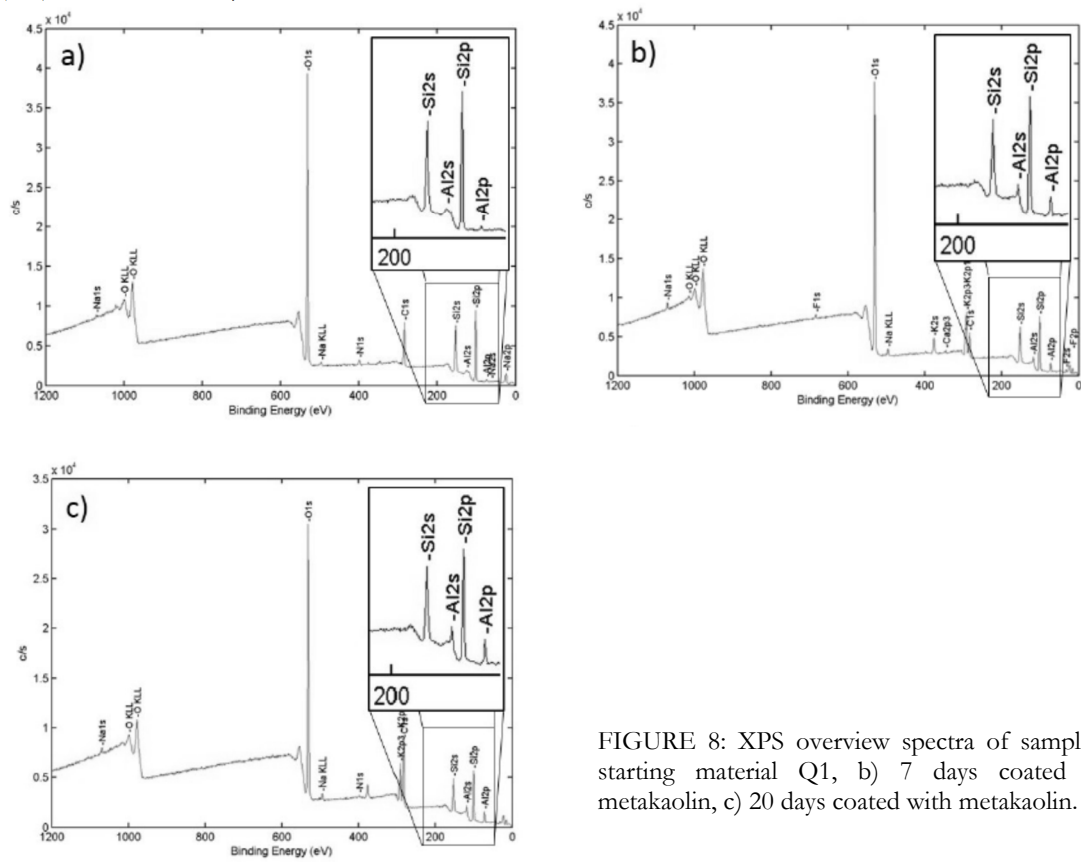


FIGURE 8: XPS overview spectra of samples a) starting material Q1, b) 7 days coated with metakaolin, c) 20 days coated with metakaolin.

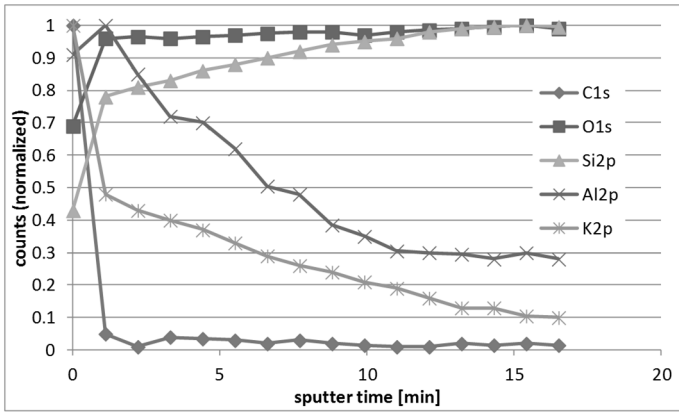
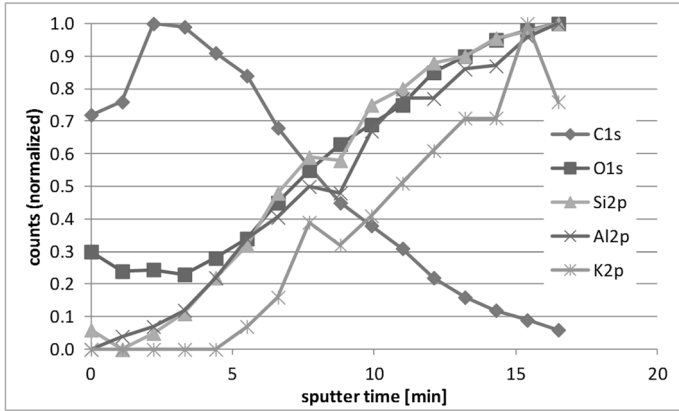


FIGURE 9: depth profiles of measured samples by XPS method, above starting material Q1, below coated with metakaolin for 14 days, sputter time calibrated by quartz means that 1 min is equal to 1 nm.