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Cement and Concrete Research 37 (2007) 1193 – 1205

Cement and Concrete Research

The contribution of quartz and the role of aluminum for understanding the AAR with greywacke

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Received 23 October 2006; accepted 25 May 2007

Abstract

Precambrian Greywacke from Lower Lusatia (Germany) has been well known as an alkali sensitive aggregate for several years. It can cause considerable damages in concrete buildings due to an Alkali–Aggregate-Reaction. The investigations are focused on quartz as the main releaser of silica, its characterization and its behavior in an alkaline solution. But there are no relations between quartz properties and the alkali sensitivities of greywacke samples. To understand this fact the role of aluminum which greywacke releases in different amounts into the alkaline solution too must be considered. Aluminum affects the silica concentration by three different mechanisms. The result is always a decrease of the silica concentration in the solution caused by an alumino silicate formation. The silica bound by alumino silicate structures can be quantified by ^{27}Al–NMR-spectroscopy. The expansions of concrete samples can now be described much well as a function of a so called "free" silica. Based on this results a direct test method for the assessment of the alkali sensitivity of greywackes could be created and suggestions for an inhibition can be given.

Keywords: Kinetics; TEM; Grain size distribution; Alkali–aggregate reaction; Alumino silicate formation

1. Introduction

Many authors who publish investigations on AAR of poly mineral rocks deal with the silica releasing in general but especially with the characterization of quartz crystals the different rocks consisted of because the quartz grains are suspected to be the releaser of a damaging alkali reaction in concrete. Gogte [1] already suggested of the "straineffects" of the containing quartz crystals to determine the alkali reactivity of different poly mineral rocks. To quantify the observed crystal defects Dolar-Mantuani [2] took the angle of the undulatory extinction in strained quartz crystals as a criteria for indentifying potentially alkali-reactive rocks. Many rocks e. g. the quartz grains inside the rocks were characterised by using this method. Many investigations were made but the validity as a reliable criteria was doubted.

Grattan-Bellew [3] recommended using the existence of micro crystalline quartz as criteria for the alkali sensitivity of poly mineral rocks. By using the TEM (transmission electron microscope)-method on different rocks Zhang et al. [4] could confirm that a relationship between both the alkali reactivity on the one hand and the high grain boundary areas of little quartz crystallites and their density of dislocations on the other hand exist. Investigations on alkali sensitive greywackes under TEM by Blackwell and Pettifer [5] also showed that the micro crystalline quartz which was found as a matrix mineral of these rocks had a high density of dislocations.

Kerrick and Hooton [6] and Shayan [7] realized polarized microscopic investigations and also concrete expansion test at metamorphic rocks and could show that not only the micro crystalline quartz which was formed by a recrystallization process but also texture properties of the rocks influence the alkali sensitivity.

Thomson and Grattan-Bellew [8] demonstrated a very interesting way to investigate the mineral constituents of poly mineral rocks. They separated the rocks in to the mineral constituents by using the magnetic field technique, enriched the different minerals in certain fractions and determined the contribution of the so accumulated mineral fractions to the reactivity of the whole rock. It could be shown that the mineral fractions consisted of a mixture of quartz–mica–chlorite and the

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doi:10.1016/j.cemconres.2007.05.009

fraction consisted of micro crystalline quartz crystals (so called sub crystals) expanded strongest also in comparison to the whole rock. The also enriched feldspar fraction had the lowest expansion values. These results and additionally the determination of dislocations along the grain boundaries of quartz under TEM showed that the micro crystalline quartz with its sub crystallites is responsible for the alkali reactivity but not the adulatory extinction of quartz grains. Thomson and Grattan-Bellew did not find any relation between the quartz crystallinity index measured by XRD and the reactivity.

Also Wigum [9] realized different investigations on poly mineral rocks. The grain size and the content of quartz of the investigated rocks were measured. These data served to calculate the average surface area of quartz of the rocks. The amount of micro crystalline quartz could be estimated by comparison of the quartz content measured by DTA and XRD because micro crystalline quartz can not be determined by DTA. The grain sizes, the calculated grain surface areas and often also the amount of micro crystalline quartz gave a good correlation to the concrete expansion test values. Wigum also found out that a relation between the concrete expansion values and the crystallinity index of quartz was very unsteady.

In sedimentary and metamorphic rocks Wakizaka [10] found a correlation between the concrete expansion values and the dissolved silica concentrations in the alkaline solution. The last one depends on the amount and the crystallinity of quartz constituents of the rocks.

Newest investigations by Broekmans [11] confirm results that quartz crystals can have CI_{XRD}-values of <1 to 10 and even higher. But these investigations show that it is unclear which crystal structural features that affect the solubility of quartz influence the CI_{XRD}-value too.

Another possibility to explain the importance of quartz for understanding the alkali reactivity of certain poly mineral rocks is to have a view to the solubility data of different minerals which the rocks can consist of. In comparison to other minerals of poly mineral rocks quartz has the highest solubility rate in an alkaline solution, e.g. the stability of quartz is lowest in a pH-range of about 12 and higher.

In the literature ([12–17]) different solubilities can be found on the one hand based on the stoichiometrical and also on the non stoichiometrical dissolutions of minerals. In the first case the dissolution process of the whole mineral was measured, the other one describes the dissolution process of certain ions, which the mineral consisted of. These differentiation is unreasonable because quartz consists of SiO_2 only but the differentiation can be important to investigate micas and feldspares especially to determine the dissolution rates in dependence of the pH-value and the grain size of the minerals.

Fig. 1 shows a summary of data from the literature. The separate points in the diagram represent the logarithm of dissolution rates measured by different authors. By using a simple law ($r = k_{OH} * [H^+]^n$) the solubility rates can be described in dependence on the pH-value. The result of this calculation is marked on as straight lines in the diagram. These values were measured on minerals with analogous grain sizes.

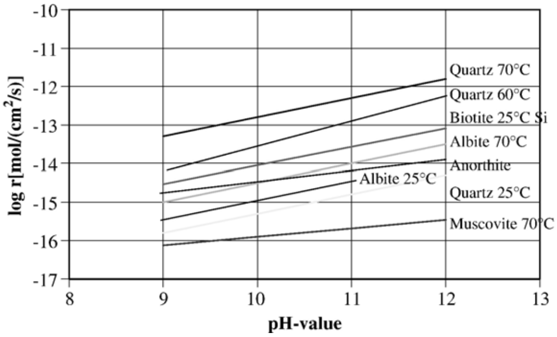

Fig. 1. Dissolution rates *r* of different minerals at different temperatures in dependence on the pH-value (data from the literature [12–17]).

As you can see in the diagram at a temperature of about 25 °C the solubility of quartz is in the same range as the solubility of other minerals. At a temperature of about 70 °C the solubility increases very strongly and now it lays about 10^2 times higher. It can also be seen that the mineral muscovite has the lowest solubility rate of all minerals investigated even at temperatures of about 70 °C. Any exact datas at a pH-range of about 13 or higher could not found in the literature. But both the investigations of the solubilities of minerals and the direct observations under a TEM (see data in [3–5]) show that the quartz should be the silica provider of a poly mineral rock and it should be also the main silica provider of precambrian greywackes.

Newest investigations in Germany (Huenger [18,19]) demonstrate a new direction to find reasons for different AAR reactivities of poly mineral rocks. Because of the fact that greywacke releases not only silica but also aluminum into the alkaline solution it should exist interactions between silica and aluminum. Silica releasing constituents (mainly quartz what corresponds with data from the literature) and aluminum releasing constituents could be found in precambrian greywackes from Lower Lusatia (Germany). Reactions and interaction mechanisms were postulated and first results were presented at the 12th ICAAR Conference in Beijing in 2004 [20]. This paper contains further proofs for the postulated mechanisms and gives first results for practical uses in the field of advanced concrete technology.

2. Materials and methods

2.1. Chemical and structural analysis

To determine what amount of silica and aluminum can minerals release into the alkaline solution dissolution experiments using mineral constituents accumulated through magnetic separation after crushing into pieces smaller than 20 μm were performed. The separated solutions were investigated by chemical analysis with ICP–OES and the whole solutions by ^{27}Al–NMR spectroscopy. Also, expansion tests of mortar bars and concrete samples were carried out. To get information about the mineralogical composition of both the whole greywacke and the greywacke constituents accumulated XRD-analyses were carried out first.

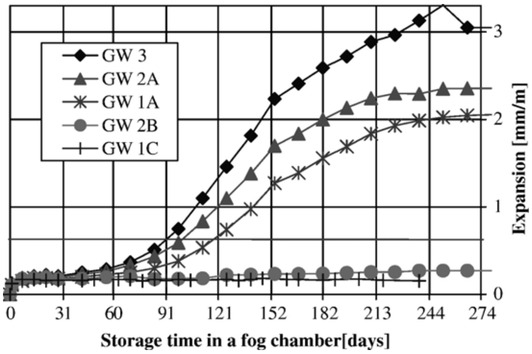

Fig. 2. Expansions of greywacke samples gathered from different areas of a quarry (test due to the alkali guideline of the DAfStb, part 3).

2.2. Situation in a quarry

Because of the fact that greywacke is a sedimentary rock which was additionally altered by a metamorphous process it can be assumed that differences between greywacke samples exist in a quarry. These differences can be found certainly in the reactivity or better the sensitivity of the samples. To make sure to investigate always the same samples certain areas of a quarry have to be defined. Fig. 2 shows the results of a concrete prism test due to the alkali guideline of the German Committee of Structural Concrete (DAfStb) [21] which has been valid since 1997. Concrete prisms (10*10*50 cm^3) with a special mixture of highly alkaline cement and aggregates (the grain sizes are 2–8 mm and 8–16 mm of the sensitive test material; the sand fraction 0–2 mm consist of a non sensitive material) are deposited under certain conditions (40 °C, R.H. 100%). The test takes 9 months.

In the last years until now greywacke samples of three quarries have investigated. Many quarry areas have determined and for this paper five quarry areas were chosen. Two samples (GW2B, GW1C) do not show any expansions except the normal expansions which were caused by the influences of higher temperature und higher moisture. But three samples show intensified expansion values (GW3, GW2A, and GW1A) in this order. The area of the quarry of sample GW3 is a little bit inhomogenous regarding the alkali reactivity what means that the expansion curve measured at the first time to determine the alkali reactivity class is differently from the curve measured once again at later times to confirm the results (see also Fig. 19).

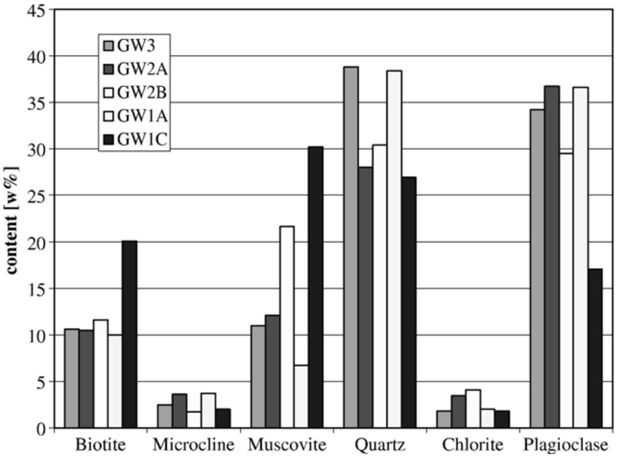

Fig. 3. Mineral composition of greywacke samples investigated.

2.3. Mineralogical composition of investigated rocks

The mineralogical composition of the greywackes was determined by using XRD coupled with a Rietveld analysing program called Autoquan (Seifert Analytical X-ray). To avoid mistakes caused by a texture preparation the pulverized samples were mixed with cork powder. In Fig. 3 the results are summarized.

It can be certified that there is not any relation between the sensitivity of greywacke samples and the quartz content. GW3 and GW1A (both sensitive greywackes) have the highest quartz contents of all samples investigated but GW2A (also a highly sensitive greywacke) has almost the same content as GW1C (this is a non sensitive one) and the quartz content of GW2B (also a non sensitive one) lies in the middle. There are large differences in the muscovite content as shown also in Fig. 3. Both the non sensitive greywackes GW2B and GW1C have the highest mica content of all greywackes. The sensitive greywackes have only the half of the muscovite amount.

2.4. Separating and accumulating of quartz and other greywacke constituents

The XRD-investigations mentioned above were made at the whole greywacke samples. But greywacke is a poly mineral rock consisted of many minerals. Quartz is one of them and a greywacke normally contains about 30 to 35%. To enrich the quartz content and to guarantee that mainly quartz is the silica provider into an alkaline solution a separation and accumulation process was used (see Fig. 4) to divide greywacke rocks in different fraction (Weidmueller [22], Huenger [23]).

After breaking, grinding and sieving to a grain size of about 20 μm or smaller the so formed powder was transformed in a suspension by water addition. This suspension was given on a shaking table to separate the non-magnetic layer silicates (e.g. muscovite) from the rest fraction. This rest fraction consists of a magnetic (mF) and a non-magnetic fraction (nmF) which can be

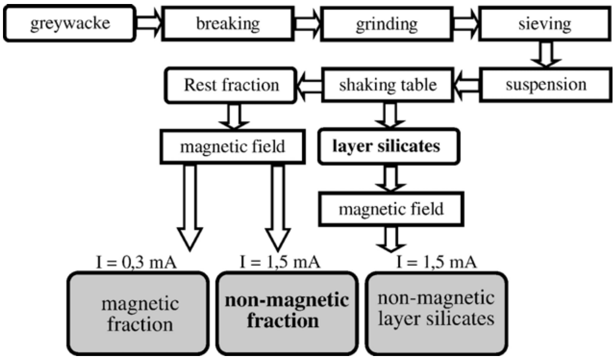

Fig. 4. Scheme for sharing in different greywacke constituents (Weidmueller [22]).

separated by a magnetic field. The accumulating effect of this process can be seen in Table 1. The enriching process was very successful. The nmF-fractions of GW3 and GW2B consist now of more than 70% quartz. The magnetic fraction contains layer silicates (biotite, phengite) and another phase described later in the text.

3. Results to the contribution of quartz

3.1. Characterization of quartz

In the first part of this paper the contribution of quartz to a damaging alkali reaction is discussed because the question is very interesting: How can the quartz crystals be characterised furthermore? To answer this question from all samples three samples are chosen. That means the following investigations are made with GW3, GW2A as a sensitive rock and GW2B as a non sensitive rock material.

The BSE-mode (back scattered electron-mode) of a SEM allows to determine grain sizes and grain size contents of certain minerals of greywackes. The grain boundaries were indicated. The areas could be countered by using the image analysing program KS400 Rel. 2.0 of the Fa. KONTRON ELEKTRONIK under different magnifications in dependence on the grain sizes (see Fig. 5, GW2A as an example). Also the fine grained greywacke GW2B could be investigated by using this method. The results can be seen in Fig. 6. This figure represents the summary frequency of areas in [%] in dependence on certain grain size classes.

The average grain size of quartz grains of GW2B is about 7 µm, the $d_{50\%}$-value of GW3 is about 23 µm and the value of GW2A is about 14 µm. But it can also be seen that in GW2B a high content of very small quartz grains exists with grain sizes of about 1 µm or smaller. In opposite the grain sizes of quartz grains of GW2A and of GW3 too are bigger and start at about 5 to 6 µm. Especially in GW3 there are many quartz grains with a size of 100 µm and higher.

3.2. To the crystallinity index of quartz crystals

On three greywacke sample also crystallinity indices were determined before, during and after alkali attack. The principle bases on Murata [24].

Table 1
Quantitative mineral composition of the magnetic (mF) and the non-magnetic fraction (nmF) of GW3 and GW2B determined by XRD

Weight%	GW3		GW2B	
	mF	nmF	mF	nmF
Biotite	22.1	0.2	21.6	0.4
Chlorite	4.5	0.0	10.2	0.0
Plagioclase	25.6	16.1	24.9	22.2
Microcline	1.9	2.3	4.0	0.8
Muscovite	13.4	3.1	15.9	3.1
Quartz	28.4	**74.7**	17.7	**71.9**
Σ	95.9	96.4	94.3	98.4

Data in bold indicate the accumulation effect of quartz by using the special enriching method (see Section 2.4).

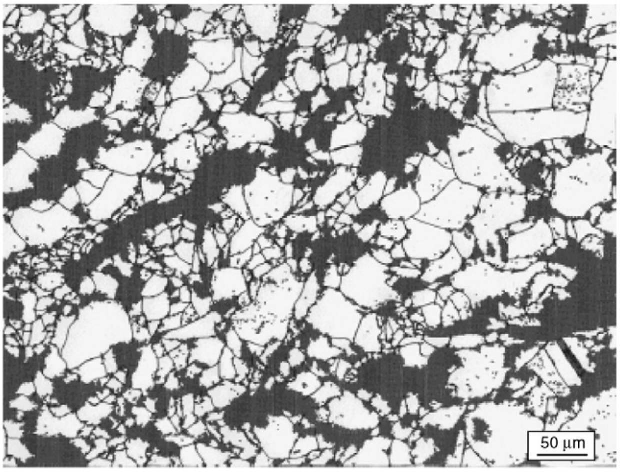

Fig. 5. Copying of the grain boundaries "by hand" to determine the grain sizes (here quartz of sample GW2A).

3.2.1. Crystallinity indices on original quartz

First the crystallinity indices are lower than 10 in generally (the value 10 stands for pure crystalline quartz). That means that in the investigated greywackes quartz crystals exist with a certain density of dislocations or other defects. But this is more or less the same in all three greywacke samples. Furthermore it can be found that there is no relation between the CI-value and the sensitivity. GW2A, a sensitive one, has the lowest CI-value (7.1) of all but the CI-value of GW3 and GW2B are in the same range of about 7.7. These investigations confirm results which are described recently in the literature (Broekmans [11]).

The values mentioned above demonstrate the original situation of greywacke samples. In the following part investigation results are summarized which were got during and after alkali attack.

3.2.2. Changes of the crystallinity index of quartz crystals after alkali attack

Fig. 7 demonstrates the results of the CI-values during and after alkali attack (0.1 m KOH). In general it can be said that an increasing of the CI-value is connected with a dissolution process of destroyed and strained quartz particles on the surface.

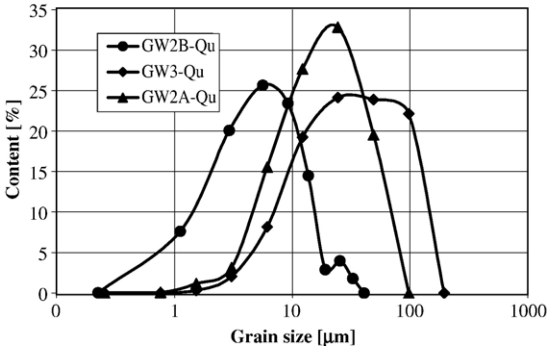

Fig. 6. Grain size distribution of quartz inside of greywackes GW3, GW2A and GW2B (the *y*-axis represents the summary frequency of countered areas in percent).

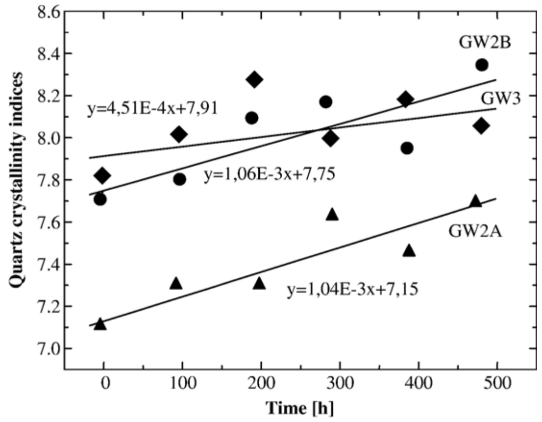

Fig. 7. Changes of the crystallinity indices of quartz at 25 °C ($c = 0.1$ m KOH) in dependence on the storage time.

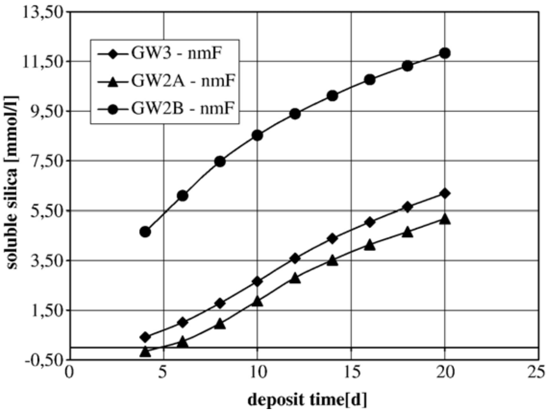

Fig. 8. Summary curve of silica which comes from the quartz fractions of greywackes investigated.

That means that especially in the samples GW2A and GW2B such areas have to exist. As you can see in the Fig. 7 both samples have the same rise (the △CI-value is about 0.6) but the curves are parallel shifted because of the different starting points. In opposite to this the GW3 shows other behaviour that means the rise of the curve is lower (the △CI-value here is 0.3 only).

Transformed to the problem of the silica releasing process of quartz it can be summarized:

The greywacke sample GW3 consists of quartz crystals which have a relatively low content of strained areas and dislocations inside the grains (GW3 has the highest CI-value at the origin). And the low rise of the CI-curve in dependence of time additionally demonstrates that there is also a low amount of dislocations or other strained areas on the surfaces. Also the grain sizes of quartz of GW3 are the highest of the three investigated greywackes. If the silica releasing rate depends on such structural and geometrical features GW3 should release a very low amount of silica into the alkaline solution. But GW3 is the most sensitive one.

The greywacke sample GW2B consists of quartz crystals too which have a low content of strained areas and dislocations inside the grains (it is in the same range as GW3). But the high rise of the CI-curve in dependence of time demonstrates that the dislocations are concentrated on the surface of the quartz grains. The grain sizes of quartz of GW2B are the lowest. In comparison to GW3 the releasing rate of silica should be higher than of GW3 especially at the beginning of the alkali attack.

Because of the medium grain sizes the behaviour of GW2A should be between GW3 and GW2B. Based on the crystallinity index evolution it should have an analogous behaviour as GW2B. But GW2A is a sensitive one too.

3.3. *Silica releasing rate of separated quartz grains from greywackes*

The nmF-fraction or better the quartz fraction was put into an alkaline solution (the chosen concentration of the solution was 0.1 mol/l KOH at 20 °C) and the silica concentrations were measured by ICP-OES. The summary results of the measured silica concentrations are demonstrated in Fig. 8.

Summary results mean that the actual concentrations measured every 2 days are added (summary curve). Because of the small sizes of the grains (less micro meters) of the nmF-fraction the releasing process took place very fast and was investigated for 20 days only. Every 2 days from the fourth day to the twentieth day the actual silica concentrations in the solutions were determined. It can be seen in the figure that the prediction which were given as a result of the CI-values discussion and the grain size parameters comes true. The silica concentrations of GW2B are higher than the concentrations of GW3 and also of GW2A. But it shall be repeated: the GW2B is a non sensitive greywacke and the others are sensitive ones. That is the reason for using the name sensitive and not alkali reactive. In the sense of a chemical reaction all investigated greywackes are reactive because all greywackes provide silica into the alkaline solution, even the GW2B and this greywacke even in the highest amount.

In Fig. 9 the dissolution rates calculated of the three investigated greywacke samples are marked as a straight line too. The rate [mmol/l/d] for the first 10 days is calculated here in a

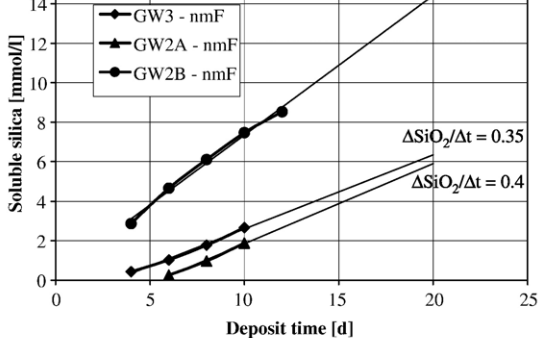

Fig. 9. Soluble silica amount during the first 10 days including the dissolution rates of quartz of the greywackes ($\triangle(\mathrm{SiO_2})/\triangle t$-values in [mmol/l/d]).

simple way by calculation of the quotient $\triangle(SiO_2)/\triangle t$. The calculated values are marked in the diagram. The rate *r* (GW2B) is about three times higher than the rate *r* (GW3) or *r* (GW2A). Is there any relation to the specific surface of the quartz grains of greywackes? The specific surface can be calculated from the grain sizes and the grain size distributions as you can see in Fig. 6. Based on these data (without any calculation scheme) the following specific surface values can be given: GW2B = about 1000 cm^2/g, GW3 = about 300 cm^2/g and GW2A = about 400 cm^2/g. Therefore also the specific surface of quartz grains of GW2B is three times higher than in the other greywacke samples. The dissolution rates r_{GW} depend directly on the surfaces of quartz grains in greywackes. From the equation (Parkhurst and Appelo, [25], Merkel and Planer-Friedrich [26])

$$R_K = r_K{*}A_0/V{*}(m_k/m_{0k})^n, \tag{1}$$

with:

r_K	Specific rate of a mineral (e.g. quartz) [mol/m^2/s]
A_0	Initial surface of a mineral [m^2]
V	Amount of solution [kg]
m_{0k}	Initial amount of a mineral [mol]
m_k	Amount of a mineral at time *t*
n	Factor for regarding the changes of A_0/V (most 2/3)

follows that the dissolution rate R_K depends directly on the surface or the quotient between A_0/V. And exactly this is what we can find here at the beginning of the alkali attack during the first 10 days and this is a confirmation of the chemical kinetics theory.

How is the situation at the second 10 days that means at the end of the dissolution reaction investigated? At the end of the dissolution reaction the rates of all investigated greywacke samples are the same. That means the high starting dissolution rate of GW2B does not continue and adapts to the other samples. But especially this shows that GW2B releases the same amount of silica into the alkaline solution as the other samples at later times.

The investigation results on quartz discussed here confirm that quartz is the main provider of silica and quartz shows dissolution behaviour due to the theory of the chemical kinetics. Using a special separation and enriching method differences of the dissolution behaviour of quartz as a constituent of rocks can be measured and it can be found that a good correlation exists between the dissolution process in fact and a theoretically initial dissolution rate which directly depends on the grain size distribution of quartz crystals in the rock.

It is also possible to investigate the quartz dissolution process by determination of the crystallinity index of quartz especially its changes during alkali attack. But it can be found that there is no relation between both the CI-value at the origin and the dissolution rate of quartz. There is also no relation between both the changes of the CI-value during alkali attack and the measured dissolution rate of quartz. That means that it is not possible to use both the original index and also the index which is determined during alkali attack to predict the sensitivity of precambrian greywackes. The reason therefore is that the crystallinity index is a value which described a volume property but the dissolution process of quartz mainly takes place on the surface of the quartz grains only.

But there is an important problem. Based on these conclusions the sample GW2B also has to be a sensitive greywacke, maybe the most sensitive greywacke sample of all samples investigated here. But this cannot be observed.

Therefore additional basic mechanisms for understanding the alkali sensitivity of greywackes must be valid.

4. The role of aluminum

4.1. Aluminum releasing constituents

Recently Huenger [23] has reported on this part of investigations. Our original aim of this part was to look for other silica releasing components in the greywacke rocks (amorphous silica ?) and to find answers for the question: Where does the alumina come from? These investigations lead to a surprising result. We found a new phase that has been unknown until now. Fig. 10 shows the structure of the greywacke sample GW2B. The large crystals with longish shape are biotite crystals. The grains at nearby the biotite crystals represent quartz crystals which show deformations caused by the electron beam shot. But the structures inside the circle are very interesting. These structures connect biotite crystals with other constituents of the greywackes. It is possible to measure *d*-values by using the electron diffraction. The measured pattern of this unknown phase must be calibrated by measuring *d*-values of a well known phase. A well known phase e. g. is quartz. The small

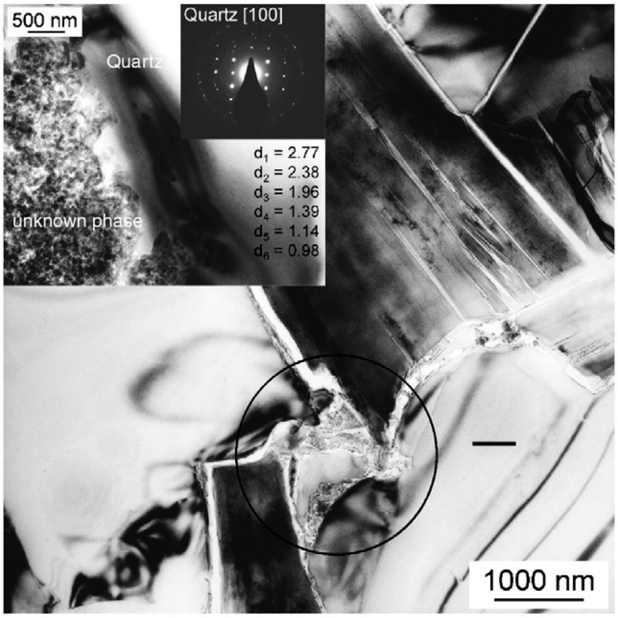

Fig. 10. Structure of GW2B under a TEM including the newly detected phase (this phase can be characterized as γ-Al_2O_3).

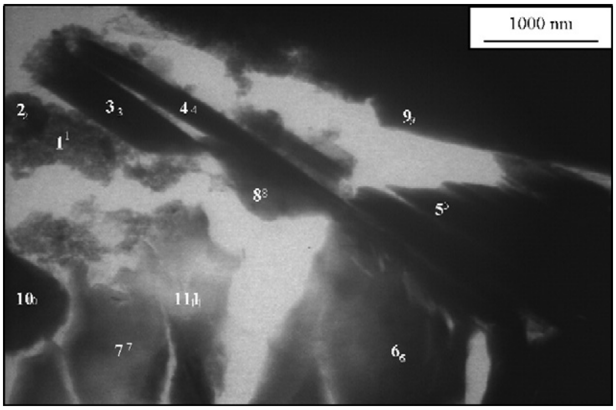

Fig. 11. TEM- micrograph after alkali attack, white areas represent dissolved phases, assignment of the measured points: biotite: 3, 4, 10, muscovite: 7, 8, 11, γ-Al_2O_3: 1, 2.

picture in Fig. 10 represents another area of the nanocrystalline phase, where a quartz crystal is nearby. The *d*-values displayed in the small picture right were calculated by using the well known pattern of a quartz crystal orientated in [100]-direction.

And especially this small picture left shows another fact. The grain size of this unknown phase is very small (about 20 to 30 nm). Because of the small sizes and the crystallinity (*d*-values can be measured!) it can be said that this phase has nano crystalline properties. It can be characterized as a nano crystalline phase. The composition could be determined by using element detection analysis under TEM. Such nano crystalline phase (we found it in different samples) consists of aluminum oxide because Al and O only can be detected. And if we summarize all information on this phase we can suggest that it must be γ-Al_2O_3. It is a primary mineral originally contained in the aggregate. It can be said that γ-Al_2O_3 is a relic of the laterite formation of our greywackes 550 to 600 million years ago.

Summarized it can be said that not only quartz is dissolved by the alkali attack but also other greywacke constituents which provide aluminum into the alkaline solution. Therefore in a poly mineral rock we have to decide in silica releasing and in aluminum releasing components. Al-releasing constituents in greywackes are very small biotite and muscovite crystals and additional a newly detected phase in our greywackes with a nano crystalline structure. It is γ-Al_2O_3 and has because of its crystallite size a very high releasing rate of aluminum into the alkaline solution. The dissolution processes take place at very small areas of greywacke grains as you can see in Fig. 11.

The TEM-micrograph shows dissolved areas after alkali attack (here 1.0 m KOH). The white areas represent dissolved phases where the thin carbon sheet remains only. But the surrounding areas can be investigated to determine the chemical composition and these results allow conclusions to the dissolved phases. The assignment of the measured points to certain phases is given in the figure too. These investigations confirm that not only silica but also aluminum is released into the alkaline solution. Now the question is in which kind does this aluminum affect the silica releasing process?

4.2. Mechanisms of affecting silica release

The aluminum released into the solution influences the silica concentration by different mechanisms. It can be postulated that the following mechanisms take place:

a) An aluminum adsorption process on the silica surface (quartz).
b) An alumino silicate formation process on the silica surface and in the solution.
c) and later, a zeolite precipitation process.

How can these assumptions be proved?

4.2.1. Aluminum adsorption process

The mechanism a) can only be confirmed by a mathematical way. A direct observation of aluminum sheets or aluminum clusters on the surface of quartz grains has not succeeded until now. The calculation bases on a method by Labrid [27] in which he described the dissolution process of quartz in alkaline solutions with or without aluminum. Labrid used this method to explain changes of quartz containing sand by presence of soluble aluminum. Huenger [23] transformed this method to the question of greywacke AAR. The equation system has the following form:

$$r = -\frac{dQtz}{dt} = K_1 \cdot \frac{\left(1 - \frac{\mathrm{si}}{k_0}\right)}{\left(1 + k_s\mathrm{si} + k_a\mathrm{al} + k_z\mathrm{alsi}^2\right)} \qquad (2)$$

$$\frac{dc_{\mathrm{si}}}{dt} + \frac{dq_{\mathrm{si}}}{dt} + \frac{2dc_z}{dt} + \frac{dq_z}{dt} - r = 0$$

with:

r	Reaction rate of the quartz dissolution
si	Concentration of silica [$Si(OH)_4$] in the solution
al	Concentration of aluminum [$Al(OH)_4^-$] in the solution
K_1	Constant of the starting reaction
k_o, k_s, k_a, k_z	Equilibration constants of parts of the reactions
q	Concentration of silica at the surface

The constants k_0 and k_s describe the equilibrium between the quartz grain surface and the concentration of silica monomers in a surrounding solution. But there are two additional terms in this equation system. The second term k_a describes the silica

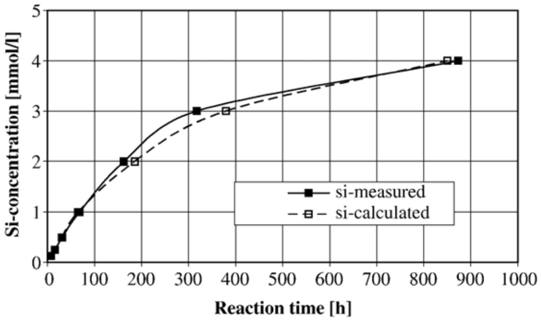

Fig. 12. Measured and calculated silica concentrations by using equation system 1 (after LABRID).

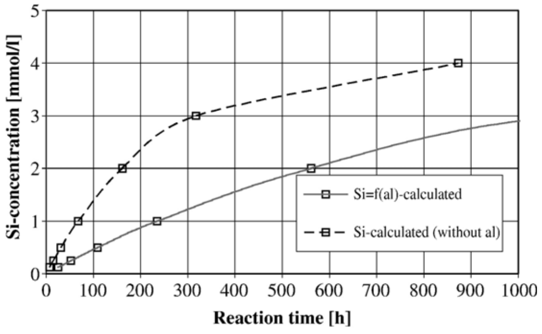

Fig. 13. Calculated silica concentration without and with aluminum.

releasing process affected by soluble aluminum which is in the solution and the third term k_z stands for the influence of a zeolite formation.

If the constants k_a and k_z are zero and therefore the concentrations c_z and q_z in Eq. (2), part 2 are also zero (i.e. no aluminium is in the solution and therefore a zeolite formation is not possible) the equation system can be reduced to a simple system. It describes the quartz dissolution without any influences of other ions.

The result of such a calculation is seen in Fig. 12. But if the term k_a is not zero the equation system describes the dissolution process of quartz grains affected by soluble aluminum in an additional way. The result of this calculation is demonstrated in Fig. 13. There it can be found that the concentration of silica considering a soluble aluminum content in the solution is lower as without.

The controlling mechanism part a) leads to a decrease of the silica concentration in the alkaline solution.

Aluminosilicate formation process to prove mechanism b) On this it was already reported (Huenger [20]). A short summary should be given here. Fig. 14 shows the results of the ^{27}Al–NMR-spectroscopy method of the solution of the sample GW2B. By using a Lorentz line distribution the measured curve (marked in the figure) can be separated in three parts. And after this fitting process (this was the real sequence of evaluation of the results) each line can be assigned to a certain aluminosilicate or to a pure $Al(OH)_4$-complex. This assignment is seen in the figure. The areas under the calculated curves can be quantified and an average Al:Si-ratio can be given. It is about 1:1.5 what means that one aluminum ion can bind one or two siliceous ions in alumino silicate structures of a highly alkaline solution. In the meantime further ^{27}Al–NMR-investigation in alkaline greywacke solutions were made and the first results can be confirmed in a qualitative and quantitative way. These data are the basic for an important practical use (see there).

Investigations under TEM show that the alumina releasing components of greywackes are the nanocrystalline phase consisted of γ-Al_2O_3 and very small mica minerals. That means, of course, that not only aluminum but also silica is released into the alkaline solution by muscovite and biotite because of their chemical composition. The Al:Si-ratio of pure muscovite is 1:1, if we take all aluminum (tetrahedral and octahedral coordinated structures) together, it is 1:3, if we take the alumino silicate structure parts of muscovite only. The ratio of biotite is about 1:3 (theoretically). But the measured average Al:Si-ratio by using ^{27}Al–NMR-method is 1:1.5 and lays between. It can be assumed that mica minerals are dissolved completely (e. g. stoichiometrically), but an additional supplier of alumina must exist. This is obviously the nanocrystalline phase. Therefore the results must be discussed in such a way that quartz and also mica minerals provide silica but the mica minerals and the nanocrystalline phase must release aluminum into the alkaline solution. The consequences on a mineralogical point of view are demonstrated in part 4.3.

4.2.2. Zeolite precipitation

XRD-investigations after alkali attack under extreme conditions 80 °C and 1 m NaOH solution (under normal conditions mineral changes could not be found) confirm a zeolite formation inside the greywacke grains (deposit time 850 h). It could be identified as the zeolite Na–P2. Not the fact of the formation but the amount of the zeolite is interesting because there is an inverse relation between the silica releasing rate of greywackes and the amount of zeolite formed. Fig. 15 contains the results. GW3 has the highest silica releasing rate and the smallest zeolite amount. GW2B shows an inverted behavior that means a high zeolite content is coupled with a low releasing rate. And the GW2A is as so often in the middle. These results also agree very good with the theory of the controlling mechanism part c).

Summarizing this part of investigations it can be said that the postulated three mechanisms really take place in greywackes

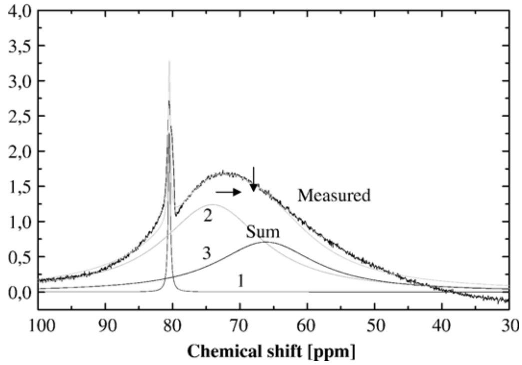

Fig. 14. Measured ^{27}Al–NMR-spectra and fit by a Lorentz line distribution line 1 = $Al(OH)_4^-$; line 2 = $Al(OH)_3(OSi)^-$; line 3 = $Al(OH)_2(OSi)_2^-$.

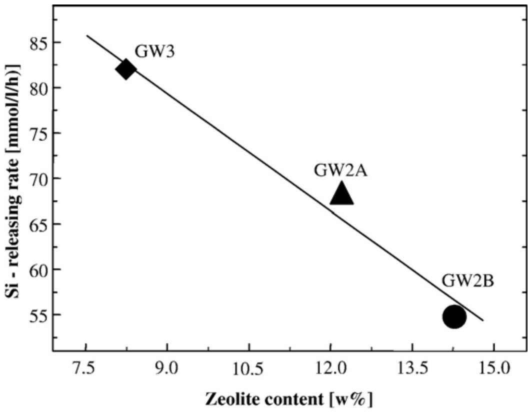

Fig. 15. Zeolite content vs. silica releasing rate with an inverse relation.

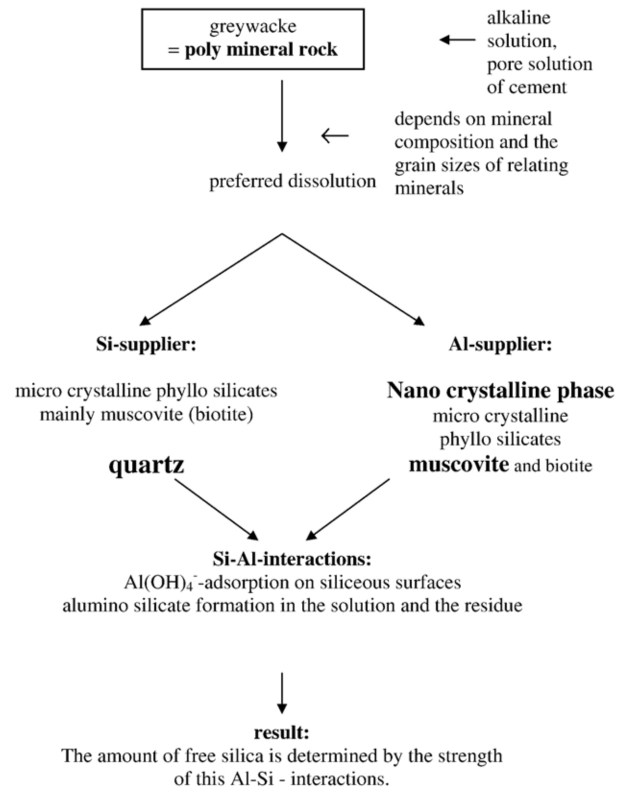

Fig. 16. Reaction scheme of an alkali reaction with precambrian greywacke.

and lead to a decrease of silica which comes from the quartz grains inside of greywackes.

4.3. Reaction mechanisms

To describe the reaction mechanisms between a highly alkaline solution and the poly mineral rock greywacke the following scheme can be given (see Fig. 16):

Based on this scheme the Si–Al-interactions mentioned above lead to a formation of free silica under certain conditions. It depends on the chemistry and mineralogy of the aggregate. It can be summarized that both the microcrystalline quartz as the mainly silica supplier and the nano crystalline phase and muscovite as the mainly aluminum suppliers react with the alkaline solution to form a zeolite Na–P2 as a result of a pozzolanic reaction. In dependence on the amount of the silica and alumina supplier in the aggregates, their grain sizes and their crystallinity free or better surplus silica can be released. And exactly this free silica can lead to an deleterious alkali–silica reaction and forms an ASR gel.

Different reactions can be discussed:

1) When muscovite is present in excess of microcrystalline quartz, free alumina is formed in addition to zeolite:

$$\begin{aligned}&2\ \mathrm{SiO_2}\ \text{(microcrystalline quartz)}\\&+3\ (\mathrm{K_2O^*3Al_2O_3^*6SiO_2^*2H_2O})\ \text{(muscovite)}\\&+0\ \mathrm{Al_2O_3}\ \text{(example without the nanocrystalline phase)}\\&+12\ \mathrm{NaOH}\\&+17\ \mathrm{H_2O}\rightarrow 2\ (\mathrm{3Na_2O^*3Al_2O_3^*10SiO_2^*13H_2O})\\&\times(\text{Na–P2}-\text{zeolite})+3\ \mathrm{Al_2O_3}+6\ \mathrm{KOH}.\end{aligned}$$

If free alumina is added or already exists in the aggregates (nanocrystalline phase) zeolite will form easier than in this case. But the amount of bound silica by forming this zeolite is strongly increased as the next formulae shows:

$$\begin{aligned}&14\ \mathrm{SiO_2}\ \text{(microcrystalline quartz)}\\&+(\mathrm{K_2O^*3Al_2O_3^*6SiO_2^*2H_2O})\ \text{(muscovite)}\\&+3\ \mathrm{Al_2O_3}\ \text{(nanocrystalline phase)}+12\ \mathrm{NaOH}\\&+12\ \mathrm{H_2O}\rightarrow 2\ (\mathrm{3Na_2O^*3Al_2O_3^*10SiO_2^*13H_2O})\\&\times(\text{Na–P2}-\text{zeolite})+2\ \mathrm{KOH}.\end{aligned}$$

This behaviour can be observed obviosly in sample GW2B.

2) When muscovite is contained in an equilibrated content with microcrystalline quartz, pozzolanic reaction takes place to form a zeolite (the nanocrystalline phase is not needed):

$$\begin{aligned}&4\ \mathrm{SiO_2}\ \text{(microcrystalline quartz)}\\&+(\mathrm{K_2O^*3Al_2O_3^*6SiO_2^*2H_2O})\ \text{(muscovite)}+6\ \mathrm{NaOH}\\&+9\ \mathrm{H_2O}\rightarrow \mathrm{3Na_2O^*3Al_2O_3^*10SiO_2^*13H_2O}\\&\times(\text{Na–P2}-\text{zeolite})+2\ \mathrm{KOH}.\end{aligned}$$

3) When muscovite is deficient relative to microcrystalline quartz, free silica is formed, which further produce ASR gel and expansion of concrete (this formula may be most important and should be valid for samples GW3 and GW2A):

$$\begin{aligned}&10\ \mathrm{SiO_2}\ \text{(microcrystalline quartz)}\\&+(\mathrm{K_2O^*3Al_2O_3^*6SiO_2^*2H_2O})\ \text{(muscovite)}+6\ \mathrm{NaOH}\\&+9\ \mathrm{H_2O}\rightarrow \mathrm{3Na_2O^*3Al_2O_3^*10SiO_2^*13H_2O}\\&\times(\text{Na–P2}-\text{zeolite})+4\ \mathrm{SiO_2}\ \text{(free silica)}+2\ \mathrm{KOH}.\end{aligned}$$

5. Conclusions for a practical use

Based on these mechanisms of controlling the silica releasing process from greywackes of course it was looked for a practical use. In the field of recent advances in concrete technology two directions are seen:

- Development of a test method directly at the aggregate grains (without any mortar bar or concrete prism tests).
- Inhibition of the AAR by addition of special aluminum containing substances to the concrete mixture.

This part of investigations was made originally to confirm the found mechanism on the concrete field. Microscopical investigations by using SEM coupled with a special EDX-linescan analysis show that leaching processes of silica, but especially of aluminum (GW2B) occur on the surface of greywacke grains used as an aggregate in concrete. The observed structures are similar to an reaction rim on the surfaces of aggregate grains. But the formation of zeolites or other alumino silicate structures could not be determined. ^{27}Al–NMR-investigations using cement slurries as an highly alkaline solution were not sucessfully too. Also the use of a saturated calciumhydroxide solution only leads to a substantial decrease of the alumina and silica concentrations in the solution and exploitable results could not be measured. One possible conclusion is that the AAR of such rock materials occurs inside of greywacke grains, e. g. in cracks, which are observed in damaged concretes in a large number. The alkali containing solution only get inside such cracks by a diffusion process through a CSH-barrier and can react there with greywacke constituents (Powers and Steinour [28]). To proof this conclusion relations between chemical values and concrete expansions were searched.

5.1. A test method directly at the aggregate grains

The companies' need a method for testing aggregates which provides results very fast but also very sure. The concrete prism test in Germany as a part of the alkali guideline of the German Committee of Structural Concrete (DAfStb) takes 9 months and that is too long for a practical use.

5.1.1. The aluminum–silica-ratio

Due to the ^{27}Al–NMR-investigation it could be determined by a quantitative description of many NMR-diagrams measured that the ratio between aluminum and silica bound is almost in the same range and lies between 1:1.3 and 1:1.5. Converted in an oxide composition the Al_2O_3:SiO_2-ratio is from 1:1.4 to 1:1.6. That means by knowledge of the solve aluminum oxide concentration in the alkaline solution the amount of bound silica can be calculated. The scheme in Fig. 17 shows the principle. The whole silica ($SiO_{2\mathrm{whole}}$) was determined by a photometrical, alumina ($Al_2O_{3\mathrm{whole}}$) by a complexometrical analysis, both according to a typical cement analysis procedure. To be on the "sure site" the Al_2O_3:SiO_2-ratio was fixed at a value of 1:1.4 (lowest level). There are cases where the aluminum binds the whole silica by forming aluminosilicate structures but there are also cases where a certain silica amount remains. This silica dissolved without any influence of aluminum can be indicated as "surplus" or "free" silica. But only this "free" silica can lead to a damage of greywacke grains in concrete because the aluminosilicate structures do not cause swelling. The result of such a calculation is given in Fig. 18 for GW3 and GW2B (Hill [29]).

The chemical test considering the silica bound by aluminum is a direct method but it is not fast yet. Are there any possibilities to accelerate the deposit time?

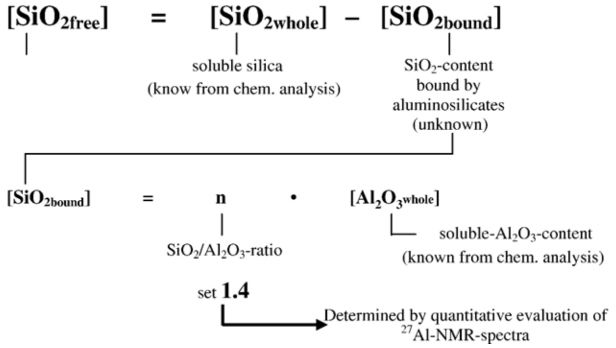

Fig. 17. Scheme of the calculation of "free" silica.

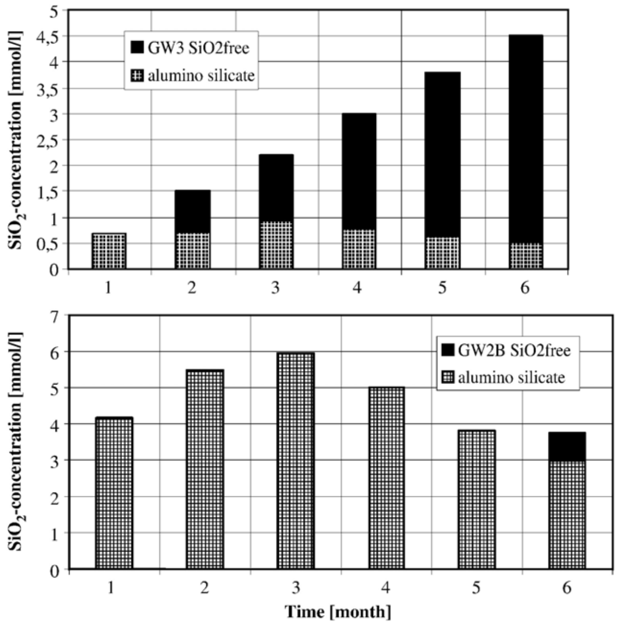

Fig. 18. The amount of free silica and of aluminosilicate structures at GW3 and GW2B as a dependence of time (concrete conditions, no accelerated conditions).

5.1.2. An accelerated chemical test method

Due to the theory of the chemical reaction kinetics an acceleration of a chemical reaction is possible by increasing the temperature, the pH-value of the alkaline solution and/or by decreasing the grain sizes of the aggregates. But the question is: Under which conditions are the relations between aluminum and bound silica valid yet? To answer this question the concentrations were varied between 0.1 mol/l and 2 mol/l KOH

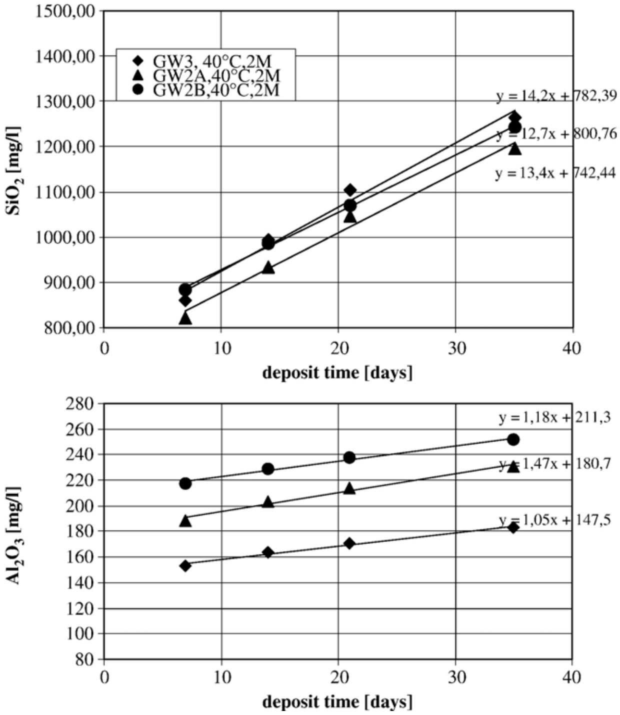

Fig. 19. Measured silica and alumina concentrations at accelerated conditions (40 °C, 2 mol/l NaOH).

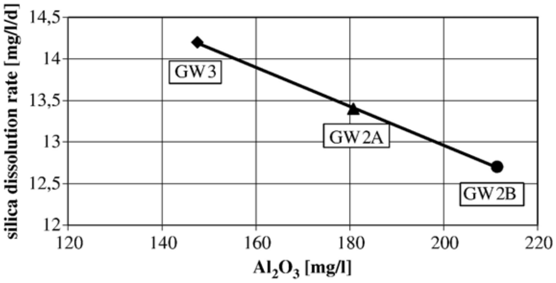

Fig. 20. Initial alumina concentration vs. silica releasing rate at the accelerated conditions 40 °C, 2 mol/l NaOH.

solution, the temperatures of the solution were between 20 °C and 80 °C and the grain sizes were between 0.020 mm to 8 mm. The measured chemical concentrations and relations are demonstrated in Fig. 19. The upper part of this figure contains the silica dissolution, the part below the alumina dissolution of the three investigated greywacke samples GW3, GW2A and GW2B under the conditions 40 °C and 2 mol/l NaOH solution.

Of course the silica concentrations are higher than the alumina concentrations. While the silica concentrations are very similar of all investigated samples there are differences between the three investigated samples especially in the alumina concentrations. The alumina concentration of the solution of sample GW2B is the highest one of all investigated greywackes followed by the sample GW2A and then sample GW3. The equations, which describe the silica and alumina dissolution, are given in this figure too. These equations consist of two parts: the first part is the rise of the equation (these values represent the dissolution rates), the second part is the intersection with the *y*-axes (and these values stand for the initial releasing amount). The relation between the silica dissolution rates and the initial alumina amount is shown in Fig. 20. There is an inverse linear relation what confirms that under this conditions a controlling influence of the silica release by alumina occurs.

It was found that the same inverse relation between the initial Al-concentration in the alkaline solution and the silica releasing rate exist at certain condition:

Highly concentrated alkaline solution (2 M) and moderate temperature (40 °C) or moderately concentrated alkaline solution (0.1 M) and high temperature (80 °C). But the diagram in Fig. 20 shows the results only of 2 mol/l/40 °C conditions. Under these chosen conditions the alkali ion Na or K do not play so an important role. Further investigations indicated that under extreme conditions (high temperature and high pH-value) the found relations are not valid.

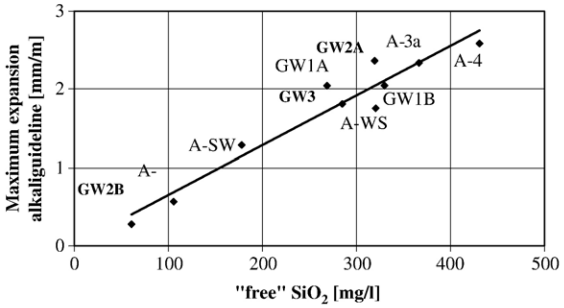

Fig. 21. “Free” silica vs. maximum expansion value of concrete prisms — straight line as an important proof for the rightness of the mechanism.

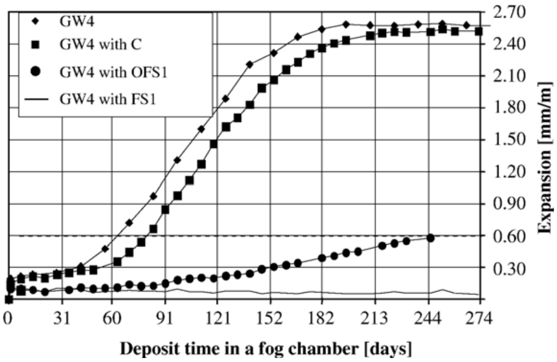

Fig. 22. Concrete expansion tests of a highly sensitive sample without and with an addition of different aluminium containing admixtures.

That means a controlling mechanism of the silica release by aluminum takes place not only under “concrete conditions” but also under accelerated conditions and this fact is the basic for a chemical test method directly on greywacke grains. The test conditions are: 0.1 mol/l KOH-solution, 80 °C and 14 days deposit time. The maximum of the silica and aluminum dissolution rate is between 0.25 mm to 2 mm, therefore the following grain size fractions were chosen: 0.25–0.5 mm, 1–2 mm and 4–8 mm. The results of using this method are demonstrated in Fig. 21 (Hill and Huenger [30]). In this diagram the maximum expansion values due to the concrete prism test after 9 months versus the free silica value after 14 days deposition in a 0.1 m and 80 °C hot alkaline solution are marked in. Each point represents a greywacke sample. The straight line with a certainty of more than 90% shows not only that a chemical test is available now. This diagram is an important proof that the relations between aluminum and silica and the role of aluminum for the controlling mechanisms of the silica releasing rate are right.

In the meantime further investigations to test other aggregates consisted of poly mineral rocks were carried out and it seems that the results can be transferred.

5.2. The role of aluminum for inhibition the AAR with greywacke and other aggregates

A short overview should be given which chances exist to use this found mechanism for an inhibition of an AAR. Huenger

Table 2
Characterization of dusts used

Oxide	Chemical analysis			Phase	Mineralogical composition		
	FS 1	OFS	C		FS 1	OFS	C
Na_2O	0.62	0	0	Amorphous	79.8	47.7	0
Al_2O_3	49.84	60.45	98.11	Corundum	13.7	31	94.1
SiO_2	43.12	32.91	1.58	Quartz	2.4	3.2	0.6
K_2O	0.78	2.36	0.09	γ-Al_2O_3	2.2	13.9	3.2
Fe_2O_3	4.64	4.08	0.3				

Table 3
Soluble amount of silica and alumina after 14 days deposition in a 0.1 mol/l KOH-solution (conditions according to the newly developed chemical test)

Soluble amount of	FS 1		OFS 1		EK	
	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3
[mg/l]	169.13	760.86	274.13	404.57	33.00	55.07

[14] reported on a self inhibition mechanism of greywackes where the inhibited aluminum comes from inside the grains. But what happens if highly aluminum containing dusts or other admixtures are put to a concrete mixture? The first results are shown in Fig. 22. The curves demonstrated in this figure represent: GW4 (greywacke 4) — expansion curve of a highly sensitive greywacke (the sensitivity of this material according to results of the concrete prism test is higher than GW3 and GW2A, it is the most sensitive one at this time in our region); GW4+C — addition of corundum dust (content of 60 kg/m^3 concrete) and GW4+OFS1 and GW4+FS1 respectively — two kinds of other highly aluminum containing byproducts (also 60 kg/m^3).

The chemical and mineralogical compositions of these byproducts are summarized in Table 2, the soluble silica and alumina amounts contain Table 3. Corundum dust with grain sizes between 10 µm to 100 µm does not affect the expansion as expected because the corundum dust releases a very small amount of alumina into the alkaline solution. But the other admixtures have a great influence on the sensitivity. Between FS1 and OFS 1 differences exist in the composition, in the grain sizes and maybe also in the structure of the aluminum providing constituents. The releasing rates and the amount of soluble aluminum are differently between both the FS1 and the OFS1 admixture, as you can see in Table 3.

In the meantime further investigations using such special dusts were carried out and it seems that the damaging potential of aggregates can be controlled in a very good way. In the laboratory damages of concrete samples produced with FS1 have not been observed until now. Some of the samples have deposited in the fog chamber (extreme conditions) for several years without any damages.

A very positive effect on the durability of concrete can be found. But the mechanisms are surely not so simple. Probably the inhibition depends on two parts: an alumino silicate formation to bind silica and additionally an alkali fixing in such formed structures. Therefore the investigations must go on in this direction.

6. Summarizing conclusions

The aim of this work is to discuss a new mechanism to understand the AAR of poly mineral rocks especially of Greywackes. It can be confirmed that quartz is the main releaser of silica into the alkaline solution. But there are no relations between different quartz characteristics (grain size, specific surface, crystallinity) and the alkali sensitivity of Greywackes.

Greywackes release not only silica but also other ions especially aluminum ions into the highly alkaline solution. Aluminum comes from very small mica crystalls and a newly detected γ–Al_2O_3-phase and both silica and aluminum can be located in the alkaline solution. The investigations show that aluminum controls the silica releasing process by mainly three mechanisms discussed in the paper. The result of these interactions can be summarized as alumino silicate formation processes which take part on the surfaces of quartz grains, in the solution and inside the greywacke structures.

One part of the released silica amount is bound by aluminum and forms alumino silicates the other part exists as so called "free" silica. And this free silica only can react with alkalis and swell and therefore it can lead to expansions of concrete structures. Based on this mechanism a chemical test method directly at greywacke grains was developed which allows to classify greywacke samples to alkali sensitivity classes in a very good way and additionally in a very short period of time.

References

[1] B.S. Gogte, An evaluation of some common Indian rocks with special reference to alkali–aggregate reactions, Engineering Geology 7 (1973) 135–153.
[2] L.M.M. Dolar-Mantuani, Undulatory extinction in quartz used for indentifying potentially alkali-reactive rocks, in: R.E. Oberholster (Ed.), Proc. of the 5th Int. Conf. on AAR in Concrete, Cape Town, 1981, pp. 1–12.
[3] P.E. Grattan-Bellew, Microcrystalline quartz, adulatory extinction and the alkali-silica reaction, in: A.B. Poole (Ed.), Proc. of the 9th Int. Conf. on AAR in Concrete, London, vol. 1, 1992, pp. 383–394.
[4] X. Zhang, B.Q. Blackwell, G.W. Groves, The microstructures of reactive aggregates, British Ceramic. Transactions and Journal 89 (1990) 89–92.
[5] B.Q. Blackwell, K. Pettifer, Alkali-reactivity of greywacke aggregates in Maentwrog Dam (North Wales), Magazine of Concrete Research 44 (161) (1992) 255–264.
[6] D.M. Kerrick, R.D. Hooton, ASR of concrete aggregate quarried from a fault zone: Results and petrographic interpretation of accelerated mortar bar tests, Cement and Concrete Research 22 (1992) 949–960.
[7] A. Shayan, Alkali reactivity of deformed granitic rocks: a case study, Cement and Concrete Research 23 (1993) 1229–1236.
[8] M.L. Thomson, P.E. Grattan-Bellew, Anatomy of a porphyro-blastic schist: alkali-silica reactivity, Engineering Geology 35 (1993) 81–91.
[9] B.J. Wigum, Examination of micro structural features of Norwegian cataclastic rocks and their use for predicting alkali-reactivity in concrete, Engineering Geology 40 (1995) 195–214.
[10] Y. Wakizaka, Alkali-silica reactivity of Japanese rocks, Engineering Geology 56 (2000) 211–221.
[11] Maarten A.T.M. Broekmans, The crystallinity index of quartz by XRD, its susceptibility for ASR and a brief methological review, in: Mingshu Tang, Min Deng (Eds.), Proc. of the 12th Int. Conf. on AAR in Concrete, Beijing, vol. 1, 2004, pp. 60–68.
[12] P.V. Brady, J.V. Walther, Controls on silicate dissolution rates in neutral and basic pH solutions at 25 °C, Geochimica et Cosmochimica Acta 53 (1989) 2823–2830.
[13] P.V. Brady, J.V. Walther, Kinetics of quartz dissolution at low temperatures, Chemical Geology 82 (1990) 253–264.
[14] K.G. Knauss, T.J. Wolery, Dependence of albite dissolution kinetics on pH and time at 25 °C and 70 °C, Geochimica et Cosmochimica Acta 50 (1986) 2481–2497.
[15] K.G. Knauss, T.J. Wolery, The dissolution kinetics of quartz as a function of pH and time at 70 °C, Geochimica et Cosmochimica Acta 52 (1988) 43–53.
[16] K.G. Knauss, T.J. Wolery, Muscovite dissolution kinetics as a function of pH and time at 70 °C, Geochimica et Cosmochimica Acta 53 (1989) 1493–1501.

[17] M. Malmstroem, S. Banwart, Biotit dissolution at 25 °C: The pH dependence of dissolution rate and stoichiometry, Geochimica et Cosmochimica Acta 61 (1997) 2779–2799.

[18] K.-J. Huenger, S. Hill, H. Wollgam, Grauwacken aus der Lausitz und ihre Ver-änderungen im alkalischen Milieu von Beton, Forum der Forschung 11 (2000) 96–100.

[19] K.-J. Huenger, H. Weidmüller, S. Hill, P. Schreiter, Mögliche Kieselsäurelieferanten aus der Grauwacke für eine schädigende Alkalireaktion, in: J. Stark (Ed.), Proc. of the 15th Int. Baustofftagung, Ibausil, Weimar, vol. 2, 2003, pp. 2–0735–2-0744.

[20] K.-J. Huenger, S. Hill, H. Weidmüller, The Self-inhibition mechanism of certain greywackes, in: Mingshu Tang, Min Deng (Eds.), Proc. of the 12th Int. Conf. on AAR in Concrete, Beijing, vol. 1, 2004, pp. 125–134.

[21] DAfStb-Richtlinie, Vorbeugende Massnahmen gegen schädigende Alkalireaktion im Beton (Alkali-Guideline), Beuth-Verlag, Berlin, 2001 issue 2001-05.

[22] H. Weidmueller, Löse-und Stabilitätsuntersuchungen von Mineralbestandteilen präkambrischer Grauwacken im alkalischen Milieu, Diss., Leipzig, 2003.

[23] K.-J. Huenger, Zum Reaktionsmechanismus präkambrischer Grauwacken aus der Lausitz bei ihrer Verwendung als Gesteinskörnung im Beton,ISBN 3-8322-4670-3, Shaker Verlag, Aachen, 2005.

[24] K.J. Murata, M.B. Norman, An index of crystallinity for quartz, American Journal of Science 276 (1976) 1120–1130.

[25] D.L. Parkhurst, C.A.J. Appelo, User's Guide to PHREEQC (Version 2) – a computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical calculations, U.S. Goelogical Survey, Earth Science Information Centre, Denver, CO., 1999.

[26] B.J. Merkel, B. Planer-Friedrich, Grundwasserchemie, Springer Verla, Berlin Heidelberg, 2002.

[27] J. Labrid, Modelling of high pH sandstone dissolution, The Journal of Canadian Petroleum Technology 6 (1991) 67–74.

[28] T.C. Powers, H.H. Steinour, An interpretation of some published researches on the alkali–aggregate reaction:Part 1: the chemical reactions and mechanism of expansion, ACI Journal 26 (1955) 497–516; Part 2: a hypothesis concerning safe and unsafe reactions with reactive silica in concrete, ACI Journal 26 (1955) 785–812.

[29] S. Hill, Zur direkten Beurteilung der Alkaliempfindlichkeit präkambrischer Grau-wacken aus der Lausitz anhand deren Kieselsäure-und Aluminiumlöseverhaltens, Diss., Cottbus, 2004.

[30] S. Hill, K.-J. Hünger, Direct assessment of the alkali sensitivity of Precambrian Greywacke from Lausitz, Cement International 1 (2005) 104–119.