

INTERACTIONS OF CHEMICAL AND PHYSICAL PARAMETERS OF AGGREGATE GRAINS FOR A BETTER UNDERSTANDING OF ALKALI-SILICA-REACTION

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Abstract

Mortar bar and concrete prism tests are the most commonly used methods for the evaluation of alkali-silica reactivity (ASR). Despite their widespread use, both methods have significant drawbacks. The largest issue is that neither test is a direct measurement of the aggregate. Matrix effects from the mortar or concrete, or variations in the individual non-aggregate materials can influence the outcome.

This paper describes fundamental results as the basis for the chemical and physical test method (BTU-SP test) directly carried out at aggregate grains. Additional methods (BET, microscopy) confirm that not only the aluminate from the aggregate controls the silica release but also the pore structure inside of rocks (i.e. voids, cracks) buffer the swelling potential of the formed alkali-silica gel. As a result a reaction model describing the interactions of chemical and physical parameters in 4 phases has been developed for an alkali-silica reaction.

Keywords: BTU-SP test, 4 phases model, silica release, open porosity, alumino silicate formation

1 INTRODUCTION

Although substantial research of alkali-silica reaction has been done world wide for over 80 years, a general valid and applicable test method has not been developed. Most methods to determine the alkali-silica reaction (ASR) sensitivity of an aggregate lack a necessary efficiency or reliability. Mortar bar and concrete prism tests are the most commonly used methods for the evaluation of alkali-silica reactivity. Despite their widespread use, both methods have significant drawbacks. The mortar bar test is prone to false positives, often resulting in rejecting aggregates that otherwise show no evidence of ASR in field concrete. While the concrete prism test typically yields more realistic results, the testing protocol requires at least 1 year, and often up to 2 years, to evaluate ASR potential in an aggregate or specific concrete mixture. Another issue is that neither test is a direct assessment of the aggregate. Matrix effects from the mortar or concrete or variations in the individual non-aggregate materials can influence the outcome. Other influences include the broad variety of chemical and mineralogical composition of the aggregates itself.

The most up to date procedures for the ASR assessment of aggregates now include both prescriptive and performance based approaches [1],[2]. The decision schemes have a combination of different test procedures which usually start with a petrographic analysis followed by the common accelerated mortar and

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concrete test methods. The major issue for the identification of suspicious aggregates by petrography is the difficulty of the procedure, which can only be done by experienced experts. In addition the petrographic assessment can only point to possible reactive phases and minerals within an aggregate source but is not able to determine the actual degree of reactivity. This can become disadvantageous when further preventive measurements are considered due to the lack of innocuous aggregate alternatives. Field studies of in-service concrete with the assessed aggregates are also recommended as one of the initial steps, but due to concerns of material variability (even within the same quarry) not widely accepted.

Since the BTU-SP Test was proposed [3] further studies have led to an improvement of the test method to better distinguish reactive, non-reactive and moderate-slow reactive aggregates. These developments are due to a better understanding of the underlying ASR mechanism. The reaction can be explained in 4 phases using the chemical and physical properties of the aggregate, which ultimately leads to the determination of an aggregate reactivity. Using these refined techniques, a new model describing the interactions of chemical and physical parameters for an alkali-silica reaction has been developed.

This paper deals with the transfer of this new knowledge obtained by further studies to develop a model to better describe the ASR mechanisms. The following questions were the motivations in initiating a closer aggregate assessment in regards to an alkali-silica reaction:

- The pores in aggregates can offer a buffer space for the reaction product (silica gel). Can this explain the difficulties of the common mortar test methods to assess the aggregates correctly?
- How does a higher pore volume (open porosity) which also increases the reactive surface affect the solution kinetics of the silica and alumina?
- Is it possible to calculate a pore volume utilization rate based on the chemical values of the alumina silicates and the physical values of the aggregate porosity?
- Are there relations between the utilization rate of the pore volume with silica gel and the expansion values of concrete prisms?
- How can a new reaction model best describe the internal processes that lead to a deleterious ASR?

2 MATERIALS AND METHODS

2.1 General

Based on successful research with a chemical test method for aggregates in combination with assessment of physical aggregate properties (porosity), a new direct test method (BTU-SP Test) was proposed at the latest ICAAR 2008 in Trondheim, Norway [4]. The chemical part is based on an alumina-silicate formation process which reduces the reactive amount of free soluble silica. Only this excessive “free silica” can react with alkalis to form a swelling gel reaction product. The open porosity as the second parameter describes a physical mechanism, in which this accessible pore volume represents a buffer area wherein silica or other reaction products can be deposited. Ultimately a new characteristic value was developed to characterize the reactivity of aggregate samples, called “ s_{PASR} ”.

The past and present aim was and is the development of a direct method to assess the aggregate sensitivity for an alkali-silica reaction without being influenced by other material parameters of concrete or mortar bar structures. Knowing and understanding the interactions of chemical and physical parameters of aggregates will ultimately lead to a better understanding of an alkali-silica-reaction. All procedures herein described are either chemical or physical methods directly carried out at the aggregate grains.

The additional calculations for the pore volume utilization rate are based on values from published papers and research studies conducted at the Brandenburg University of Technology Cottbus, Germany. An important step to combine the chemical and the physical value of aggregate grains is the knowledge of the molar volume of the alkali-silica gel. There are several methods available to determine this value. First, small

tablets with different $\text{Na}_2\text{O}/\text{SiO}_2$ compositions (1/4 and 1/5) were made. Under defined conditions (23°C, ~100% R.H.) these synthetic gel tablets swell. The free swelling can be measured with an extensometer and the maximum volume is determined. With these data the molar gel volume could be calculated with a range between 200 and 250 cm^3/mole [5]. This self determined value is about ten times higher than the known 21.5 cm^3/mole [6].

2.2 Materials and mixture proportions

The tested aggregates are: Precambrian greywackes (15 sources), carbon-devonian greywackes (6 sources), rhyolites (6 sources) and gravel (17 sources). The gravel materials are petrographical diversified containing a variety of different constituents. Besides the quartzous rock material other constituents include greywackes, rhyolite or limestone.

2.3 Methods for assessment and analysis

General

The new chemical and physical test method BTU-SP (Brandenburg University of Technology – solution and porosity) and the concrete prism test are the basis for the discussion. All samples have been analyzed accordingly and the classification into reactive or non-reactive is based on the results of these tests. Furthermore the specific surface area of selected aggregates was determined and then used for the solution kinetic assessment.

Open porosity

The sample material was first reduced by manual splitting to ~1 kg and thoroughly washed to clean the aggregates from any fine dust particles. For the ease of use the simple pycnometer method of DIN 1097-6:2000 [7] was applied and the measured values adapted for the equation of DIN EN 1936:2006 [8] to calculate the open porosity value.

Chemical analysis and alumina-silicate calculation

The sample aggregate was first comminuted in a jaw crusher and then sieved into three fractions of 0.25 to 0.5 mm, 1 to 2 mm and 4 to 8 mm, consecutively washed and oven dried before all three test fractions were put into a highly alkaline solution (0.1 mole/l KOH, 80 °C). The whole silica (indicated as SiO_2 or $\text{SiO}_{2\text{whole}}$) was determined by a photometrical analysis, alumina (Al_2O_3 or $\text{Al}_{2\text{O}_{3\text{whole}}}$) by a complexometric one. Both procedures are typical cement analyses. Alternatively Inductively Coupled Plasma (ICP) analysis can also be used. The final value of “free silica” can be calculated as follows: $\text{SiO}_{2\text{free}} = \text{SiO}_{2\text{whole}} - 1.4 \times \text{Al}_2\text{O}_3$. The shown figures display the average concentration values for all three fractions. It should be noted that the aggregates were not divided into different rock constituents, as e.g. described by WIGUM [9] who took the petrographical method AAR-1 according to RILEM recommendations into account. The reason is that the whole rock is used as an aggregate and therefore the whole rock material is put into the test solution.

Specific surface (BET analysis)

The BET (Brunauer, Emmett and Teller) [10] Theory is commonly used to evaluate the gas adsorption data and generate a Specific Surface Area result expressed in units of area per mass of sample (m^2/g). Prior to analysis, the sample must be preconditioned to remove physically bonded impurities from the surface of the sample. This can be accomplished by applying elevated temperature to the sample in conjunction with vacuum or continuously flowing inert gas. Thus prepared samples were analyzed with the static pressure (Volumetric) method using nitrogen. The measurement process must be carefully controlled

and monitored in order to generate the most accurate and repeatable results. Therefore the liquid level should be maintained at least 50 mm above the sample and constant within 1mm. The instrument (Quantachrome Nova) was calibrated using a helium gas at testing temperature.

3 RESULTS

Defined with the physical test parameter of the BTU-SP test method, Figure 1 shows the results of the open porosity for the aggregates in comparison to their respective expansion value determined with the German concrete prism test [11]. The classification into reactive or non-reactive is based on the expansion (threshold = 0.6 mm/m) of the concrete prism after 9-month storage in a fog chamber. There is a clear trend of high porosity with low concrete expansion values to increasing expansions with decreasing open porosities. Therefore none of the tested aggregates showed both values (high concrete expansion and high porosity) simultaneously. These observations were independent of the aggregate type and source.

As a next step the values for the dissolved silica and alumina in the alkaline solution (indicated as SiO_2 and Al_2O_3) were compared to the specific surface area of their respective aggregates (Figure 2). The classification into reactive or non-reactive again is based on the results of the concrete prism test. Some of the reactive aggregates show very high measured silica values at the lower end of the specific surface area ($>600\text{mg/l}$ at around $1.0\text{ m}^2/\text{g}$). But most of the plotted SiO_2 values are within a bandwidth of 200-400 mg/l independently of the specific surface area. The observations were different for the varying aluminium concentrations. With increasing specific surface area the solubility of the alumina increases as well. While the reactive aggregates are concentrated at the low end with lower values of specific surface and aluminium concentration, the non reactive aggregates can be found on the higher levels of specific surface area and alumina concentrations.

To determine possible affects on the solution kinetics, the individual measured values for the silica and alumina concentrations were plotted over the course of the solution test method duration (14 days). Figure 3 shows the curves for the silica concentrations with their respective specific surface value. Most of the displayed curves are within the same range regardless of their specific area value. On the other hand, the aluminium concentrations (Figure 4) indicate that with higher specific surface (which is also true for the non reactive samples) the solubility for Al_2O_3 increases as well.

In addition to the kinetics the pore volume utilization rate should be determined. This can be done by calculating the gel volume from the “free silica” value as well as the pore volume from the measured open porosity. Results for a slow or late reactive aggregate are plotted in Figure 5. It is clear that the gel volume curve approximates the pore volume shown as a constant threshold line. Figure 6 shows more examples of reactive and non reactive aggregates with their gel volume in comparison to the available pore volume calculated from the open porosity. It can be stated that for innocuous aggregates the volume of the gel product stays below the pore volume while for reactive aggregates the threshold is exceeded. Although it must be noted that this calculation was not absolutely unambiguous and sometimes underestimated the gel volume for certain reactive aggregates with high pore volumes.

4 DISCUSSION

4.1 Aggregate porosity

Only from the aggregate surface accessible pore volume (open porosity) is considered a possible silica-gel buffer within an aggregate grain. As Figure 1 shows, there seems to be a correlation between the open porosity and the concrete prism test expansion. For all tested aggregates the concrete prism test expansions increase when their corresponding open porosity value is lower. This is true for all types of aggregates although the porosity threshold at which critical expansions (above limit) occur might slightly differ. More

dense aggregates (e.g. greywacke) seem to have a critical open porosity of 2%Vol. while more porous aggregates like rhyolites or even some gravels need 3%Vol. or more to prevent deleterious expansions. In general it can be concluded that the aggregates open porosity as a value of the accessible pore volume has an influence on the overall outcome of the concrete prism expansion. This indicates that the open pore volume of an aggregate acts as a buffer for the developing silica-gel. However, when crushing the aggregates to test them accordingly with accelerated mortar bars tests, this correlation could be debilitated. Due to the mechanical processing porous structures of the aggregates could be broken up or small voids be filled while the overall chemical and mineralogical constituents of the material remain unchanged. That would also explain why mortar bar tests (e.g. ASTM C1260) [12] in general are more likely to give false positives when compared with the concrete prism test where the aggregates in contrast are not physically damaged.

4.2 Solubility of silica and alumina subject to the specific surface

Former studies suggest [13] that many aggregates release not only silica but also alumina into the alkaline solution. The maxima of the silica and the alumina releasing rates were found at the same time but in different time periods. In some cases the whole released alumina is consumed by forming aluminosilicate structures during the first period of time, and excessive silica remains to form an alkali silica gel. This behaviour is characteristic for reactive samples and can be found with many materials studied. These reactive samples, e. g. greywackes, porphyry rocks, granodiorites and gravel materials that do not only contain quartz, release silica and alumina into the highly alkaline solution. In case of non-reactive samples enough alumina is supplied to bind silica over the whole period of the silica release.

Since the accessible pore volume of an aggregate apparently plays a key factor in determination of aggregate reactivity, the effect of the specific surface on the solubility kinetics of silica and alumina needs to be addressed. Theoretically with a higher reactive surface the amount of soluble silica could increase as well, which eventually would transform into more silica gel and offset the positive buffer effect from the aggregate pore volume. As shown in Figure 2, most of the tested aggregates have a constant silica release value. Except for some very high values, most samples release between 200-400 mg/l SiO₂ into solution regardless of the aggregate type. It is also independent from whether an aggregate is innocuous or reactive. There is clearly no indication that with higher specific surface and therefore more reactive area the silica release increases. This could mean that the silica is preferentially dissolved and the solubility more likely depends on other factors e.g. structure of the SiO₂ or the degree of crystallinity of the quartz. For the aluminium, the solubility depends on the specific surface. All non-reactive aggregates have higher specific surface values and also show for almost all samples higher aluminium concentrations. Therefore with a higher specific surface the Al₂O₃ solubility increases. As for the solubility kinetics, shown in Figures 3 and 4, the found correlations are confirmed. The silica release rate shows no dependence of the specific surface while the aluminium dissolves more and faster if the specific surface is higher.

4.3 Pore volume utilization

One of the possible applications for the demonstrated correlations between chemical ("free silica") and physical (open porosity) aggregate parameters is the calculation of an actual gel and pore volume. When both values are compared to each other it could be determined whether a swelling silica gel has enough space within the aggregate voids (non-reactive aggregate) or the gel volume exceeds the actual pore volume (reactive). Figure 5 shows the results of this comparison for a so called slow/late reactive aggregate, which had a slow and late expansion growth during the concrete prism test and eventually exceeded the limit. Similar results for reactive aggregates where the gel volume exceeds the pore volume and vice versa for non-reactive samples are shown in Figure 6. The herein presented samples were all verified with the concrete

prism test. However, for some of the tested reactive aggregates the calculated gel volume did not always exceed the pore volume. This may be due to a more diversified void system within the single aggregate grain which needs further research in regards to e.g. the pore distribution. Also the gel volume calculation itself with the stated molar volume of $255 \text{ cm}^3/\text{mol}$ should be taken as an initial value for further research.

5 CONCLUSIONS

A theoretical approach with alkali silica-gel and pore volume could be transferred into a practical application to determine the aggregate sensitivity for a deleterious ASR. Based on the present results and correlations of “free silica” as chemical and open porosity as a physical aggregate factor the following ASR model can be proposed. The reaction process can be divided into 4 basic phases. During the initial phase (1), also described by Sprung and Sylla [14] an alkali-silica gel develops on the surface of the aggregate, which is not stable in the presents of Calcium ions and transforms into a non swelling alkali-calcium-silica hydrate. A further enrichment will ultimately lead to a semi-permeable membrane to form around the rock which can only be passed through by alkali ions and water. In the next phase (2), the alkali ions reach the interior reactive surface of the aggregate pores and the dissolution of silica and alumina will take place. This will in the case of a reactive aggregate lead to the formation of a swelling alkali-silica gel. The role of the calcium ions however is controversial, but the author believes that due to their slower mobility calcium will not play a substantial role in this reaction initially. In phase three (3), the formed alkali-silica gel will further accumulate water and therefore swell. This reaction will proceed as long as enough dissolved silica and water are available. The swelling gel will eventually fill out the entire voids inside the rock while the semi-permeable membrane around the rock prevents the gel to disperse into the surrounding cement paste. During the last stage (4), the gel has completely filled out the void or crack and increases the pressure within the rock after some initial compaction processes. The pressure eventually exceeds the critical rock strength, and as a result tears the rock and cement paste apart. Time and magnitude of the cracking mainly depend on the amount of gel, available pore volume, aggregate strength as well as type and amount of the aggregate constituents.

This mechanism could also be proven by microscopical investigations of damaged concretes in the field. In one case the inspected concrete indicated that aggregates which are potentially reactive rhyolites were used. The micrograph showed a part of such an aggregate grain with microcracks inside the grain. There was no continuation of the cracks outside the grain into the cement matrix. However inside one crack a gel like substance could be found. At first the cracks are obviously the open pores of our model and are then filled out by gel. This inhibits the damaging effect of the gel although in this dense concrete structure little amounts of gel should have been sufficient to damage the concrete. In summary it can be said:

- The presented 4 phases model can be used to further explain the chemical and physical correlation found with the accelerated test directly carried out at aggregate grains (BTU-SP test).
- The pore volume of an aggregate grain acts as a buffer for the developing silica-gel and can be quantified with the open porosity.
- When crushing the aggregates to test them accordingly with accelerated mortar bar tests this correlation could be debilitated due to the mechanical processing. That would explain why mortar bar tests are more likely to give false positives.
- Chemical evaluations show that silica is preferentially dissolved and the solubility more likely depends on other factors e.g. structure of the SiO_2 or the degree of crystallinity of the quartz.
- For the alumina, the solubility depends on the specific surface. Therefore with a higher specific surface the Al_2O_3 solubility increases.
- As for the solubility kinetics, the silica release rate shows no dependence of the specific surface while the aluminium dissolves more and faster if the specific surface is higher.

- Based on the alumino-silicate formation process which reduces the amount of the whole silica a negative effect of higher pore volume and therefore possible higher silica release can be refuted
- For the first time aggregate pore volume utilization with alkali-silica gel can be calculated based on the found molar gel volume of 250 cm³/mol. Although further research in this field is needed.

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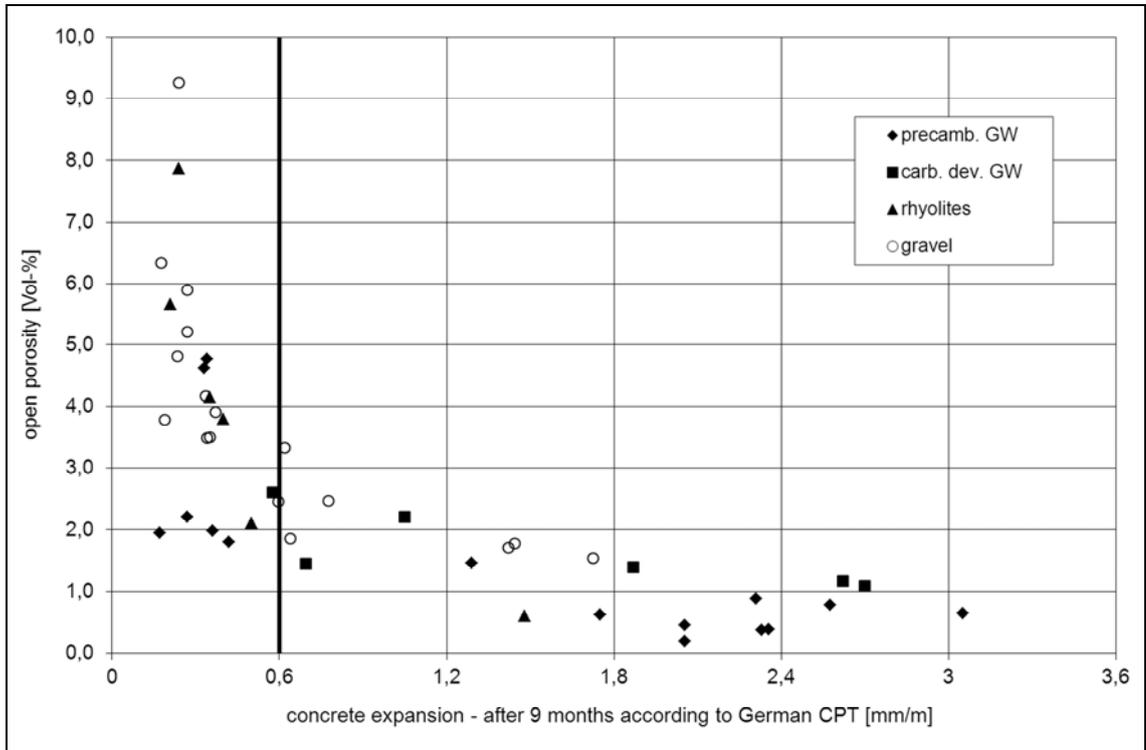


Figure 1: Relation between concrete expansion values and open porosity of aggregates

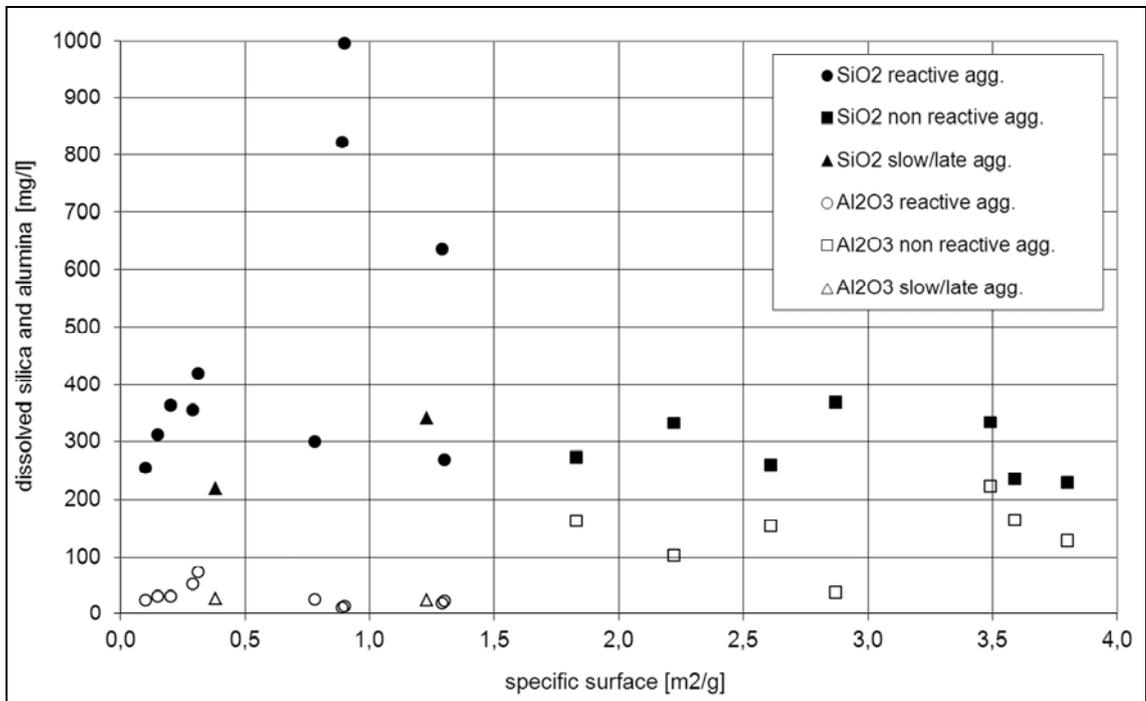


Figure 2: BET - specific surface with max. SiO₂ and max. Al₂O₃-concentrations

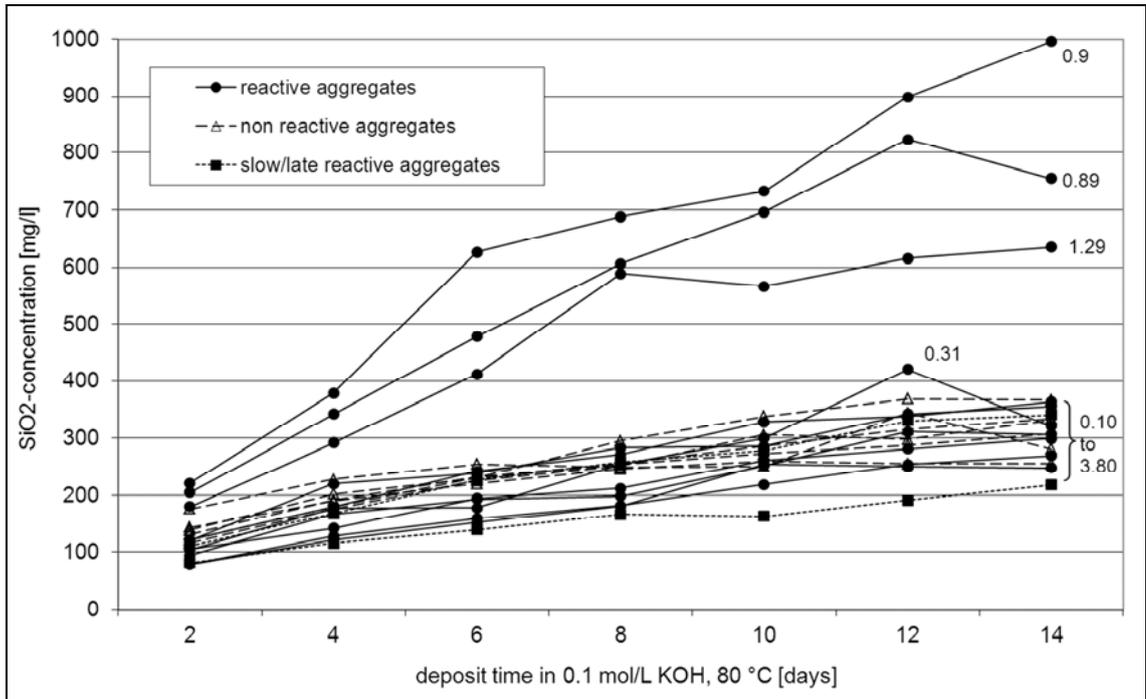


Figure 3: BET - specific surface and SiO₂-releasing rate

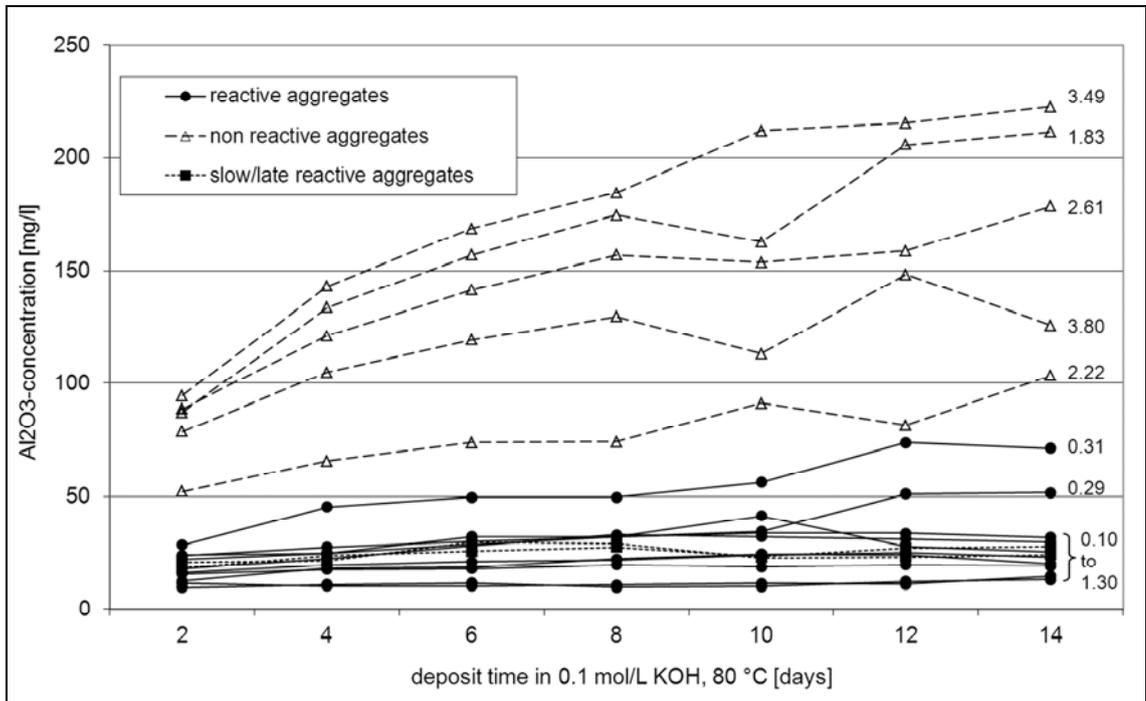


Figure 4: BET - specific surface and Al₂O₃-releasing rate

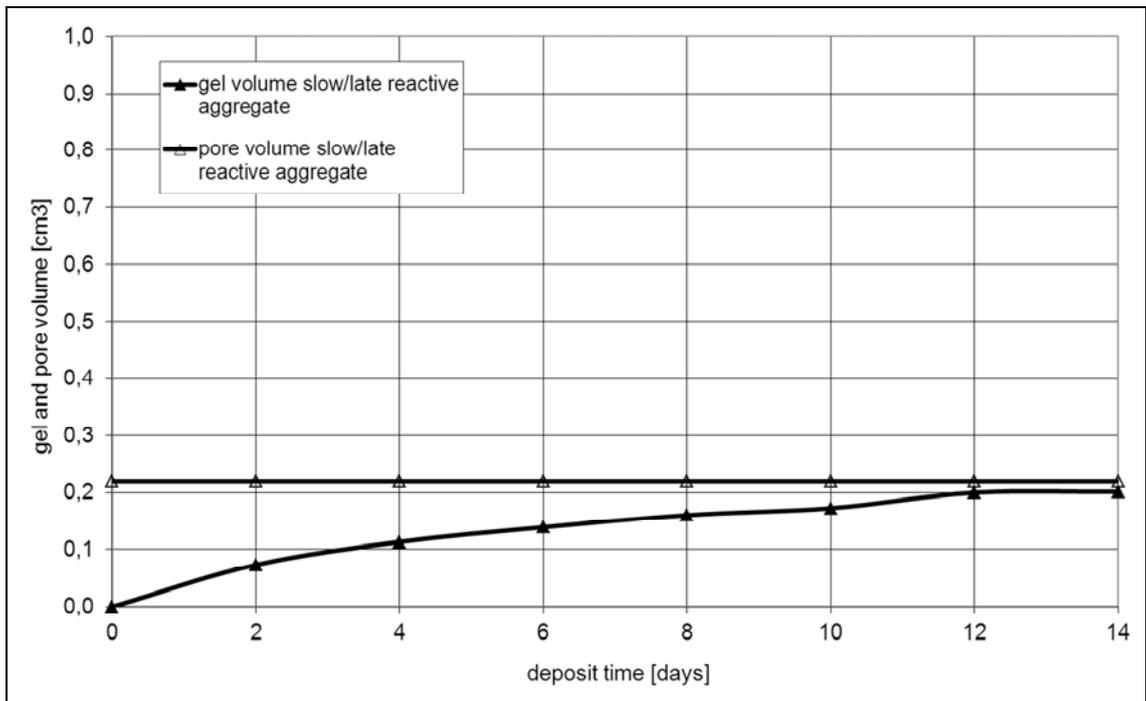


Figure 5: Relation of silica gel volume and pore volume for a slow-late aggregate

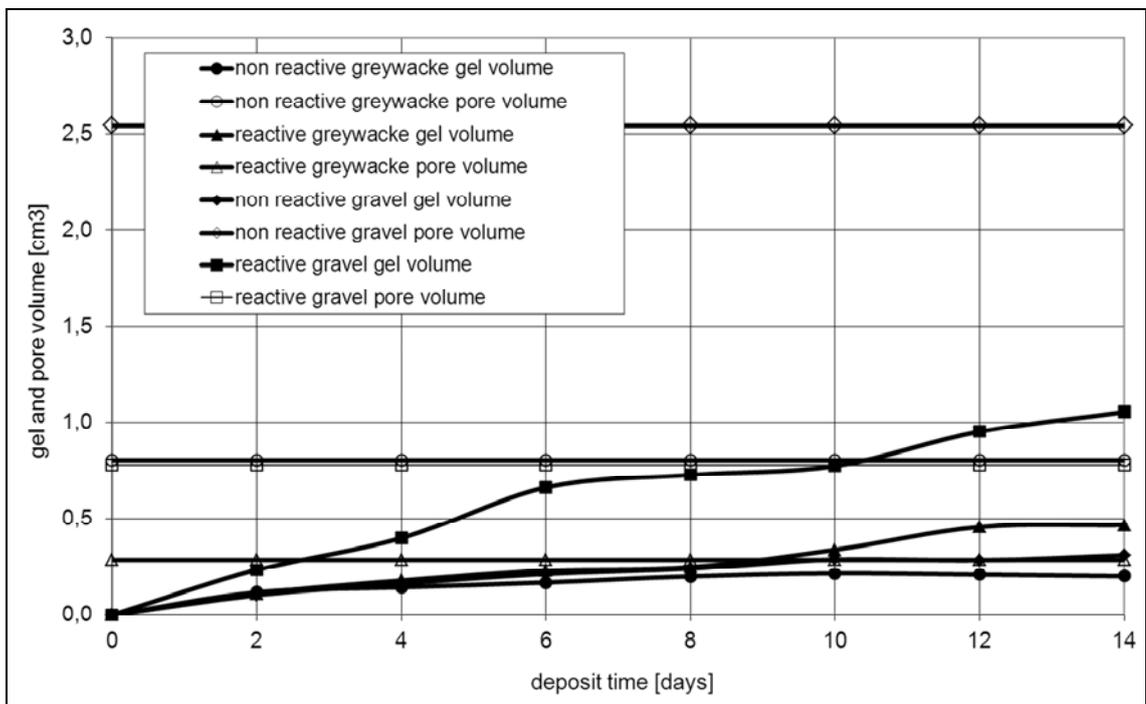


Figure 6: Relation of silica gel volume and pore volume for reactive and non-reactive aggregates