# AN ACCELERATED CHEMICAL TEST METHOD FOR ASR CARRIED OUT DIRECTLY AT AGGREGATE GRAINS

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#### Abstract

Worldwide, there are several methods to test aggregates on ASR. The new German alkali guideline, published in 2007, contains a concrete prism test and two accelerated mortar bar tests. This paper describes a chemical test method directly carried out at aggregate grains.

Studies on ASR with Precambrian Greywackes showed that the soluble aluminium also released from the aggregate grains controls the releasing rate of silica by forming alumino-silicate structures. Further studies with other aggregate materials confirm such processes, too. Even the average alumino-silicate binding factor of 1.4 is similar. The remaining quantity of silica is the so-called free silica, and this silica can only cause damage. In most cases, there is a good correlation between this "free silica" value and the concrete expansion. Exceptions of the rule can be explained by considering the open porosity of these rocks. A graphical relation between the open porosity and the "effective free silica" is given that suits better for the classification of aggregates within a period of up to 14 days.

Keywords: Direct chemical test, aggregate, alumino silicate formation, silica release, open porosity

### 1 INTRODUCTION

In 1997(adapted in 2001 and 2007), the German Committee of Structural Concrete (DAfStb) published a new alkali guideline [1] which, for the first time, included a special concrete prism test described in Part 3 of this guideline (the issues published before only contained Part 1 and Part 2). At that time, the reason for the establishment of this guideline was that there are aggregate materials in Germany (used in concrete structures and causing damage), which could not be tested by using the normal test method (storage in a sodium hydroxide solution at 80°C for 1 day, and determination of the mass loss after deposition - a method according to ASTM C289).

Since 1997 much experience in using this concrete test method has been collected, but the conclusions are that the test takes too long (about 9 months, sometimes even longer, if the aggregate is a slow/late material), and therefore this test is not suitable for practical use in production control. After 9 months of storage time, the expansion values of many aggregate samples are very different. There are non-reactive samples (over the whole period of time, the curve is below the boundary value of 0.6mm/m) as well as highly reactive samples with expansion values of about 2.5 mm/m and higher, but there are also aggregates with a middle to low reactivity. And, in addition, there are aggregates which do not react during the test period of 9 months but only later (after 10, 12 or sometimes 15 months). All these measured values confirm the need to look for other test methods that are faster, better and cheaper than the concrete prism test.

All over the world, there are a lot of test methods, either by measuring expansions of concrete prisms and mortar bars or using chemical methods carried out directly at the grains. Worldwide, the accelerated mortar bar test (AMBT) originally proposed by OBERHOLSTER&DAVIS in 1986 [2] is probably the most widely used method for testing the alkali reactivity of aggregate. The RILEM AAR-2 ultra accelerated mortar bar test [3] is based on this method. Another important test method is the concrete prism test (CPT) performed at 38 °C and 100 % (relative humidity of air). This concrete prism test is described in the RILEM AAR-3 recommendations [4]. In 2004, Lu Du et.al. [5] reported on the experience gained with both test methods. They asserted that, in a lot of cases, there are no significant correlations between both the AMBT- and CPT-test results. Another problem is the duration of the test, the concrete prism test in particular. The long period of time from about 9

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months to one year very strongly limits the use of such a method in the quality control process. Chemical tests (e.g. ASTM C289) show analogous results [6]. Particularly the test duration is very short (one to three days) but a classification and an exact ranking of aggregate materials is very often impossible, too.

In Germany, special mortar bar tests for ASR have been developed for several years, too. Based on the NBRI/RILEM-test, a so-called DAfStb-test (reference test) has been modified [7]. The differences to the NBRI-test are in the use of other grain sizes and the storage time of 13 days, but the test conditions are the same (80°C, deposit in a 4 wt% sodium hydroxide solution). The boundary value of expansion of the mortar bars is at 1mm/m.

Another mortar bar test is the method by PHILIPP [8], which is performed at 70°C, and the composition and the storage also differ from the DAfStb-test. The mortar bars are stored above water, and the alkali level is reached by adding sodium hydroxide into the hydration water. In this test the boundary value of expansion is 2mm/m, and the maximum storage time is 21 days. The third mortar bar test was developed by STARK (alternative test) and is based on the PHILIPP-test. The one and only difference to this test is the measurement temperature. While PHILIPP measures expansion values at 70°C, STARK determines values at 20 °C (therefore the prisms are cooled under defined conditions). The result of this procedure is that the storage time increases up to 28 days and the boundary value of expansion goes down to 1.5 mm/m. The new alkali guideline in Germany, published in 2007, contains a concrete prism test and the two mortar bar tests (reference and alternative test) mentioned above.

But the main problem in using all these mortar bar test methods, in comparison to the concrete prism test, is that the results are not clear. The German experience agrees with the international one. Very often, the tests work in one direction only what means that, if the limit is not reached, the aggregate can be classified as non-reactive, but if the limit is exceeded no classification is possible. In these cases the concrete prism test with its long duration has to be performed. This is not a solution for practical use. Besides, both tests, according to our studies, performed with the same material, provide different results (up to 30%).

### 2 MATERIALS AND METHODS

### 2.1 General

For several years, another approach has been chosen by HILL [9], HILL & HÜNGER [10] and HÜNGER [11, [12]. The past and present aim was and is the development of a method which can be used directly at aggregate grains without being influenced by the concrete or mortar bar structures. Based on the studies with Precambrian greywackes performed from 2000 to 2005, a chemical ASR-test for Precambrian greywackes could be developed. This test is a result of the latest knowledge about reaction mechanisms of such poly-mineral rocks. It could be shown that not only silica but also other constituents, especially alumina, are released from greywackes into the highly alkaline solution. Highlight of this research work was the proof that the released alumina can control the silica releasing process by forming alumino-silicate structures with a defined aluminium/silicon ions ratio. Therefore the amount of alumino-silicate in an alkaline solution can be calculated if the whole silica and alumina concentrations in the alkaline solution are known. The calculation scheme is demonstrated in Figure 7 of this paper. A new characteristic value could be found to characterize the reactivity of greywacke samples, called the "free silica" [SiO2<sub>free</sub>].

The result of these studies with Precambrian greywackes [13] is that there is a direct linear relation between these new chemical values of free silica and the expansion values of concrete samples after 9-month storage in a fog chamber. Furthermore, the advantage is that this chemical test takes 14 days only and requires smaller quantities of aggregates.

This paper deals with the transfer of exactly this knowledge obtained by studying Precambrian greywackes to other rock materials. The following questions should be answered:

- If silica and alumina are released by the aggregate materials, do the same controlling mechanisms of alumina affect the release of silica?

- Are there analogous relations between the chemical criterion "free silica value" and the expansion values of concrete prisms?

- If not, what additional mechanisms must be considered?

#### 2.2 Materials and methods for assessment and analysis

Table 1 gives an overview of the samples studied. The list contains Precambrian greywackes (16 rocks), Carbon-devonian greywackes (6 rocks divided into 11 grain size fractions), rhyolites (7 rocks with 12 fractions) and 18 gravels consisting of 42 fractions. The gravel materials do not only

contain quartzous rock material but also other constituents (greywackes, rhyolite, limestone). The number of rocks differs from the number of fractions because two or sometimes three grain sizes of each rock material have been studied. The table contains the methods also used to characterize reactivity. The chemical test BTU (BTU stands for Brandenburg University of Technology) and the concrete prism test are the basis for our discussion. All the samples have been analyzed by using these tests. The mortar bar tests were carried out with selected aggregate materials.

# 3 RESULTS OF THE CHEMICAL ANALYSIS OF THE SOLUTION

Based on our chemical test method (test BTU), Figures 1 and 2 show the results of determining the silica and alumina concentrations in the alkaline solution. The whole silica (indicated as  $SiO_2$  or  $SiO_{2whole}$ ) was determined by a photometrical analysis, alumina ( $Al_2O_3$  or  $Al_2O_{3whole}$ ) by a complexometric one. Both procedures are typical cement analyses. The classification into reactive or non-reactive is based on the results of the concrete prism test.

Figures 1 and 2 represent the curves of measured silica and alumina concentrations in a highly alkaline solution (0.1 mole/l KOH, 80 °C). The test grain sizes are 0.25 to 0.5 mm, 1 to 2 mm and 4 to 8 mm, which means that three test fractions were put into an alkaline solution. The figures demonstrate the average concentration values of all fractions. Figure 1 shows the typical curves of reactive aggregates. Figure 2 contains the same relations, but for non-reactive materials.

We do not divide the rocks into different rock constituents, as e.g. described by WIGUM [14] who took the petrographical method AAR-1 according 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.

As you can see in Figures 1 and 2, each rock material (reactive or non-reactive, even gravels) more or less releases silica into the alkaline solution. Independent of the rock material studied, it can be found that the alumina concentrations in the alkaline solution of non-reactive samples are higher. Other results, e.g. expansion values of concrete prisms produced with such an aggregate, and mortar bar test results are described in the following text and figures.

#### 4 **DISCUSSION**

### 4.1 Solubility kinetics

The first step is to transfer the reaction mechanism found on Precambrian greywackes to other rock materials. Based on this data measured (in the meantime a lot of studies have been performed), the releasing rates of silica and alumina ( $rSiO_2 = \Delta[SiO_2]/\Delta t$ , as well as for  $Al_2O_3$ ) were calculated. The results are demonstrated in Figures 3 and 4.

As you can see in Figure 3 (reactive rocks), all samples show a very similar behaviour of two reaction periods. The first period is from zero to about 6 or 8 days, the second one from 8 to 14 days. In the first period, both the releasing rates of silica and alumina are similar but the maximum values are different. They start at zero, reach a maximum after two days and go down after 6 or 8 days. Exactly at that time at the end of this first period, the releasing rate of alumina is zero, what means that no alumina is released further into the alkaline solution. But exactly at this time too, the releasing rate of silica rises again to a second maximum after about 12 days. After 14 days, the silica rate is zero again and the maximum silica concentration in the solution has been reached.

This behaviour is characteristic for reactive samples and can be found with many rock 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. Figure 4 shows the results for non-reactive samples. It is impossible to divide the reaction process, because this process takes about 12 or 14 days and is characterized by a very similar behaviour of both the silica and the alumina release. The maximum peak of both curves is achieved exactly at the same time, but the maximum values are different. In comparison to Figure 3, the releasing rates of alumina of non-reactive samples are about 4 times higher than the rate of alumina of the reactive ones. The differences between reactive and non-reactive samples continue in such way that at 12 days or later the alumina releasing rate decreases while the silica rate remains zero, what means that no second

maximum was found here. An exception is the sample "rhyolite wer". This material will play an important role in a latter part of this paper. In summing up it can be demonstrated that many rocks release silica but also alumina into the alkaling solution.

alkaline solution. The maxima of the silica and the alumina releasing rates can be found at the same time but in different periods. Therefore it can be assumed that in cases of reactive samples, the whole released alumina is consumed by forming alumino-silicate structures during the first period of time, and silica remains to form an alkali silica gel. In the other case, enough alumina is supplied to bind silica (non-reactive samples) over the whole period of the silica release.

# 4.2 Role of alumina for silica release

Former studies on Precambrian greywackes showed that there is an inverse relation between the silica releasing rate and the alumina concentrations or the alumina releasing rate in the solution. But in the studies described they occurred at powder samples only. The question that arises is: Do analogous relations exist under accelerated conditions and in using other grains sizes? Figure 5 demonstrates that the silica releasing rate obviously depends on the initial alumina concentration in the solution in an inverse way.

As one can see in Figure 5, this inverse relation depends on the rock material used as an aggregate in concrete. Depending on the rock material, there are different slopes but the linear relation remains the same. Precambrian greywackes, rhyolites and gravel aggregate show the same line with a very similar slope, carbon-devonian greywackes show an evidently irregular correlation.

# 4.3 The amount of free silica

To confirm the binding factor of 1.4 determined with Precambrian greywackes, the ratio between  $Al_2O_3$  and  $SiO_2$  was calculated at all types of rock materials studied (see Figure 6). The diagram shows that below a black line that demonstrates this postulated ratio of 1.4, no concentrations could be measured. This means, if alumina is released by a rock material, a minimum amount of silica already exists in the alkaline solution at the same time. And this can only mean that alumino-silicate structures have been formed in the highly alkaline solution under these conditions which are destroyed by a chemical analysis. Without NMR studies, this is an indirect proof to fix the binding factor for all other types of rock at 1.4 too. Literature also proves that structures with such a ratio between alumina and silica are very stable [15]. Based on this mechanism, different cases can be discussed.

1) The rock material releases enough alumina. In that case, the silica releasing rate reaches the value zero, and all released silica was bound by alumina. This mechanism occurs in none-reactive polymineral aggregate.

2) The rock material releases alumina too, but the amount is not sufficient enough. As mentioned above, in this case, the same mechanism occurs during the first period. But a certain amount of free silica remains in the alkaline solution. The whole amount of free silica is collected by adding the silica from the first period (silica which cannot be bound by alumina) and the silica of the second period.

The exact quantity of this free silica can be calculated using the scheme in Figure 7.

#### 5 CONCLUSIONS

# 5.1 Correlation between free silica and concrete expansion

Figure 8 shows the values calculated for certain rock materials. The basis for this calculation is the maximum values of both silica and alumina concentrations in the solution. Some aggregates show a very high amount of whole silica and little of whole alumina, while others have nearly the same amount of whole silica and whole alumina. Most values of whole silica are above 200 mg/l which is a lot higher than our boundary line of 100 mg/l free silica [10] for Precambrian greywackes. This shows that the whole silica value is not qualified to determine or classify rock materials. As to the consideration of alumina only and the calculation of the free silica value we get satisfied results. Rocks with a high amount of whole alumina binding the released silica have a smaller value of free silica. In some cases, this free silica value is lower than 100 mg/l and should result in a non-reactive rock material.

Based on the previous results of free silica we put these values in a chart showing the concrete expansions determined at concrete prism in a fog chamber according to the alkali guideline. Figure 9 demonstrates the main categories of these rocks. The relation between concrete prism expansion and free silica values seems to be dependent on the rock material.

As you can see in Figure 9, we can divide the aggregate samples into two groups. The first one is the aggregates of Precambrian greywackes, rhyolites and gravels with a strong rising exponential curve. The second one is the carbon-devonian greywackes with a gently inclining exponential curve. Obviously such greywackes show another behaviour, and this is a result which was already found in determining the correlation between the alumina content in the solution and the silica releasing rate (see Figure 6).

Attention should be paid to the two sample values that differ from the exponential curve marked in the figure. The point on the right (a rhyolite rock) does not seem to be compatible with our discussed curve and, as mentioned before, according to Figure 6, the silica rate increases at later times again (this is the sample "rhy wer"). On the other hand, the concrete prism test carried out according to the German alkali guideline shows that this sample is not reactive. The point on the left and perhaps some other rocks studied in the future do not seem to be exactly compatible to this exponential curve and, according to the alkali guideline, not to be reactive. What could this mean?

# 5.2 Porosity as an additionally considerable value of rock material

A possible second mechanism could be the accumulation of dissolved silica inside of rock structures. Such structures could be pores or cracks inside of rocks. Obviously, the limit at which aggregates react sensitively or not depends on the value of the open porosity. Especially the open porosity varies from rock to rock, whereas the whole porosity remains more or less constant.

The open porosity of the aggregate was determined by using the pycnometer method from DIN 1097-6:2000 [16]. The calculation has been adapted to DIN EN 1936:2006 [17]. For the ease of use we applied the simple pycnometer method and transformed the determined values into the equation of DIN EN 1936:2006. Furthermore, we calculated the free silica value of all these rocks with our BTU-test method. And last but not least, we determined the concrete expansion values (concrete made of these aggregate) after storage in a fog chamber for a period of 9 months and more. This was necessary in order to be able to compare every result with Part 3 of the alkali guideline. And a correlation between open porosity, free silica value and concrete expansion could be found. The result is shown in Figure 10.

The result is a more or less uniform distribution of points. It looks like a cloud of points. Based on our experience on concrete expansion values this chart can be divided into three parts. We have a concentration of values between 100 and 400 mg/l free silica and up to 6.0Vol% porosity (area B). Furthermore, there is a concentration of values below 100 mg/l free silica with an open porosity range from 1 up to 11% (area A) and over 400 mg/l free silica with an open porosity range between 1 to 3% (area C). For rocks with a free silica value above 400mg/l, we know that the concrete prism test, according to the guideline in Germany, shows the result "reactive". These are carbon-devonian greywackes and some gravel from the Upper Rhine. From our chemical BTU-test method based on Precambrian greywackes we get the boundary value of reactivity for aggregate materials of less than 100 mg/l free silica. Thus every single rock below this value should be non-reactive, too. All concrete results confirm this classification.

But what about the values between 100 and 400 mg/l free silica? Therefore, according to the Alkali guideline Part 3, we again compared the points in the chart with our expansion results of the concrete prism test. And it seems to be that the reactivity depends on the porosity in a direct way. Then, especially in this area "B" on the x-axis, it is possible to find two fields within this cloud. A straight line can be drawn with a certain slope. Points, values or samples which are located below the line are all reactive (area B2). The other samples the points of which are above this line are all non-reactive (area B1). And samples the points of which are located directly on the line or nearby are slow/late-rocks.

Summarizing the results discussed here it can be said that:

- An accelerated test directly carried out at aggregate grains could be developed.
- The test consists of a chemical part and, if required, a physical porosity part.
- The first one is based on an alumino-silicate formation process which reduces the amount of the whole silica that comes from the aggregate grains to a value called "free silica".
- This "free silica" can only react with alkalis to form swelling reaction products.
- The second part (porosity) can be described as a physical or mechanical mechanism, which means that the pore volume, especially the open pore volume, represents a buffer area in which silica or other reaction products can be deposited.
- And especially this physical mechanism allows us to characterise the free silica value between 100 to 400mg/l in an exact way. Therefore the name "effective free silica" was chosen.
- Based on this physical mechanism, the special expansion curves of the so-called slow/late aggregate can be described in a better way.

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kind of rocks	amount of aggregate	Test methods			
		concrete prism test fog chamber	mortar bar test DAfStb	mortar bar test PHILIPP	chemical test BTU
Precambrian greywackes	16 fractions of 16 rocks	every aggregate	selected aggregate	selected aggregate	every aggregate
Carbon devonian greywackes	11 fractions of 6 rocks	every aggregate	selected aggregate	selected aggregate	every aggregate
rhyolites	13 fractions of 7 rocks	every aggregate	selected aggregate	selected aggregate	every aggregate
gravels	42 fractions of 18 rocks	every aggregate	selected aggregate	selected aggregate	every aggregate



Figure 1: Soluble amount of silica and alumina of reactive samples. (pkGW - precambrian greywacke; kdGW – carbon-devonian greywacke; Rhy – rhyolite; Gv – quarzitic gravel with other components (greywackes, rhyolite); Gd – granodiorite).



Figure 2: Soluble amount of silica and alumina of non reactive samples.



Figure 3: Releasing rates of silica and alumina of reactive rock materials.



Figure 4: Releasing rates of silica and alumina of non reactive rock materials.



Figure 5: Relation between initial (2 days) alumina concentration in solution and the silica releasing rate of the first period of time of certain rock materials (grain sizes according to the BTU-test method).



Figure 6: SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> -ratio of all types of investigated rock materials.



Figure 7: Calculation scheme of free silica amount based on the determination of silica and alumina concentrations in the solution.



Figure 8: Maximum amount of whole silica and alumina determined within 14 days and resulting free silica of certain rock materials.



Figure 9: Relation between concrete expansion values according to the alkali guideline and free silica.



Figure 10: Relation between open porosity values and the maximum free silica within 14 days.