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# DETERMINATION OF THE REACTIVITY AND THE AMORPHOUS COMPONENT FOR OPALSANDSTONES BY THE RIETVELD METHOD

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## ABSTRACT

The amorphous component of opalsandstone - the cause for the AAR in Germany - consists of siliceous material (siliceous sponges). According to literature, the bulk density of opalsandstones varies between 1.2 and 2.4 g/cm³. The amorphous content of different opalsandstones was calculated by the Rietveld method. The NBRI-test was used for measuring the level and velocity of the AAR for the different opalsandstones.

Our intention was to verify whether a varying amorphous content or another property is the reason for a different expansion rate during AAR.

The results of the NBRI-test show that the higher the bulk density of opalsandstones the stronger the long-term AAR. The velocity of the reaction decreases with increasing bulk density.

The amorphous content, evaluated by the Rietveld method, is nearly the same in all opalsandstones. The only difference is the porestructure. It was shown in thin sections that the AAR starts inside the aggregates. If the developing alkali-silica gel does not find any more space in the pores of the aggregate, it will start to build up a pressure outside the aggregates.

Keywords: Rietveld method, opalsandstone, amorphous content, porestructure, NBRI

## INTRODUCTION

The Rietveld method is the best method to quantify components of an aggregate by x-ray powder diffraction. Even the amorphous component is detectable.

All other methods do not have the crystallographic basis for an evaluation. It was the intention to check if a different amorphous content of an alkali-reactive aggregate could be the reason for a different expansion behaviour in concrete.

In northern Germany the opalsandstone is the aggregate with the strongest alkali-silica reaction. But the degree of the alkali-silica reaction differs depending on the apparent density. The amorphous component of opalsandstone - the cause for the AAR - consists of siliceous material (siliceous sponges). Hence it is important for a further understanding of the alkali-silica reaction to evaluate, if variations in the amount of reactive (amorphous) material is the main component for a changing reactivity.

## DESCRIPTION OF THE RIETVELD METHOD

The Rietveld method is a method to evaluate x-ray powder diffraction patterns. It is used for refinement of crystal structures and for calculating the quantitative compounds of a sample. The method was developed by Hugo Rietveld and was published in 1969 (Rietveld 1969). Due to the fast development of computers, calculation with comfortable Rietveld programs is now possible on modern PC's.

The Rietveld method is comparing of a theoretical diffraction pattern based on the crystallographic properties of each single phase and the measured diffraction pattern. It does not use integrated powder diffraction intensities, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram (Young 1992). The advantage is the ability to calculate different phases in a sample even if problematic peak overlappings occur. This method will only work correctly if all phases of the sample are identified.

For calculating the amorphous component a further component of known quantity (e.g. 10%) has to be added and homogenised with the sample. If after evaluating, the added component shows for example 15 %. The calculated, added component has to be set back to 10 % by dividing. The portion of the other components have to be divided by the same quotient. The remainder will be the amorphous content.

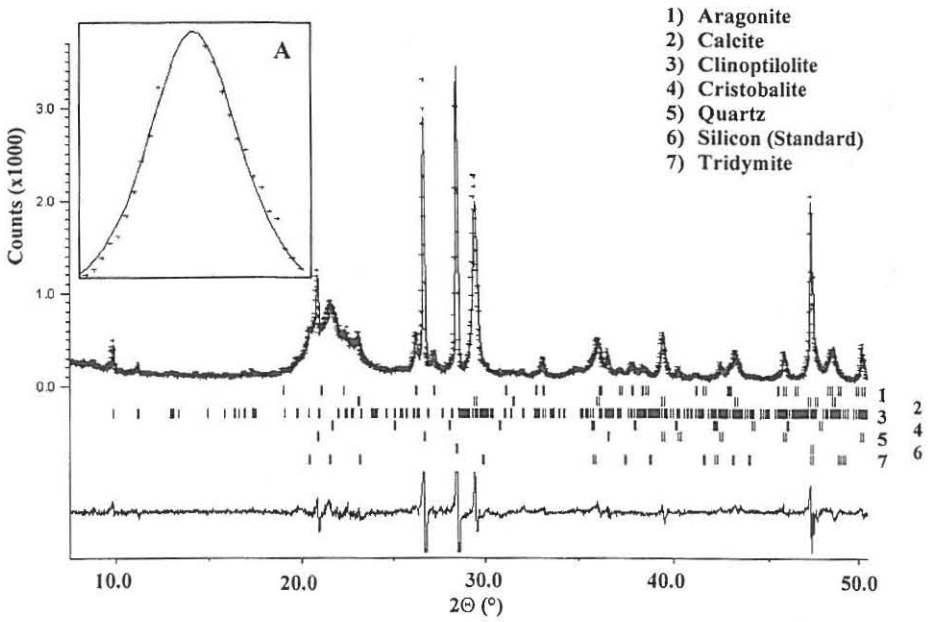


Fig. 1: Typical powder diffraction diagram of an opalsandstone. The thin line shows the theoretical, the crosses the measured diagram (see enlargement A). The lowest line indicates the difference between these diagrams. The short black lines represent the peak position of the different components.

**Description of the Aggregate and Measurement Procedure**

The opalsandstones mainly consists of quartz, calcium carbonate and siliceous sponges. These sponges show - beside their amorphous $SiO_2$ - low cristobalite and low tridymite. Hence the name opal ct is used for them.

The opalsandstones were transported from Scandinavia to the northern part of Germany by the last ice ages. This is the reason for the occurrence in nearly every gravel pit in this area. For concrete production the opalsandstones removed by density seperation due to their low density (1.2 – 2.4 g/cm³). Only aggregates with a higher density are used in concrete.

Some scientists (Bettermann 1973, and Lenzner 1981) assume that the opalsandstones with a high bulk density show no expanding reaction and that opalsandstones with a medium bulk density show the highest expanding reaction.

For scrutinising this statement we have collected opalsandstones in 4 different gravel pits, several hundred each. The bulk density was determined and classified in bulk density ranges. These groups were both examined with the NBRI-test and measured by the x-ray powder diffraction. The opalsandstones were also studied under the microscope (thin sections).

## RESULTS

The measurement of the bulk density showed a gap between 2.1 and 2.25 g/cm³ in which no opalsandstones occur. All "opalsandstones" exeeding 2.25 g/cm³ do not show any expansion on the NBRI test and do not have any silicious sponges in thin sections. These aggregates were identified as common green sandstones.

The results of the expansion test are shown in Fig. 2. The higher the bulk density, the higher the expansion. In the first few days the velocity of expanding increased with decreasing density. This changed dramatically after 4 to 5 days.

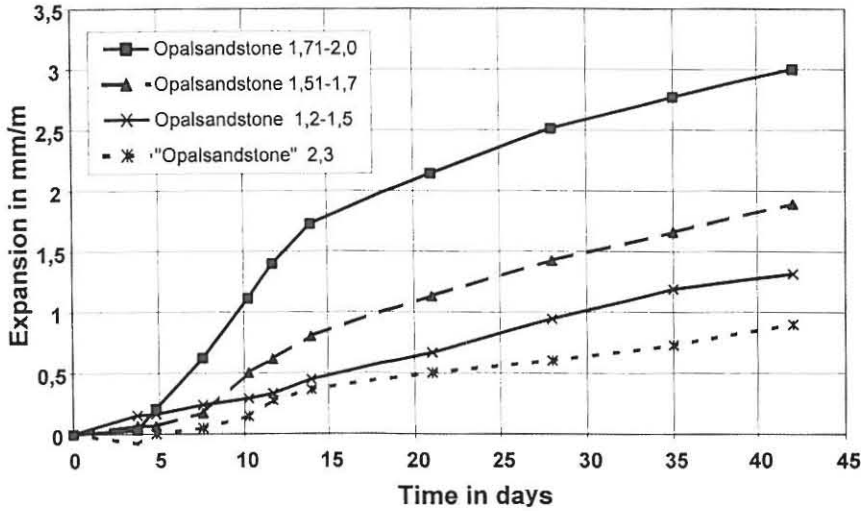


Fig. 2: Results of the NBRI test with opalsandstone. Each graph is a mean value of 3 NBRI tests. The numbers in the legend show the bulk density ranges.

### Rietveld Analysis

The amorphous component and the content of cristobalite and tridymite were evaluated with the Rietveld method. These are the reactive components of the opalsandstone. Fig. 3 shows the reactive components of two different samples of opalsandstones evaluated with the Rietveld method. Although the content of individual reactive minerals varies, the total reactive component content is situated in the same range.

The samples that were tested by the NBRI-test were also evaluated. This test shows that the reactive component of all opalsandstones is nearly similar. The difference of the bulk density does not have a great influence on the mass of the reactive component.

To compare the results of the powder diffraction, pulverised opalsandstone were dissolved in NaOH-solution. After 24 h the suspensions were filtered and the weight difference between the original sample and the insoluble (non-reactive) part were measured. The Si-concentration of the solution were also measured.

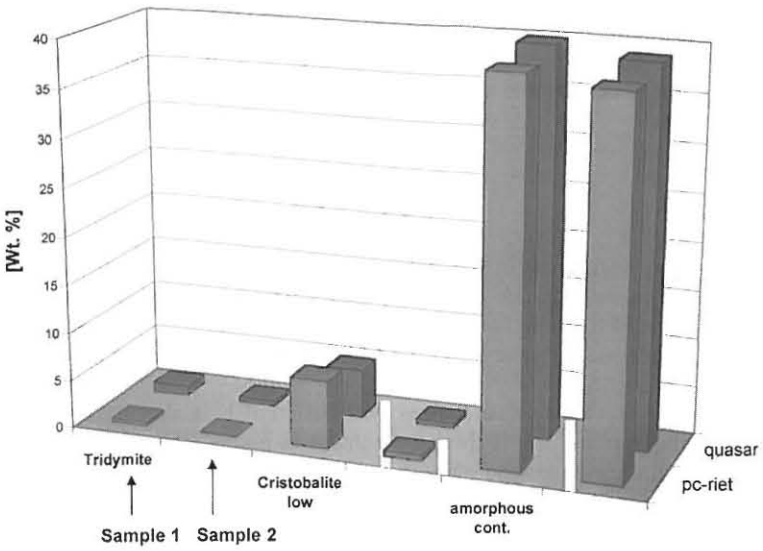


Fig. 3: Two samples of different opalsandstones. These samples were evaluated with two different rietveld programs (Quasar, PC-riet) (Eickemeier 1997). It can be seen that the samples have a similar amorphous content.

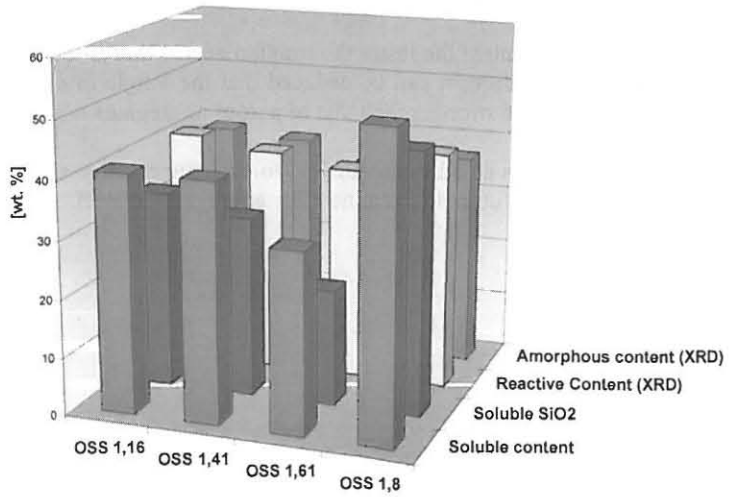


Fig. 4: Comparison of the amorphous and the reactive (opal ct) content evaluated by the rietveld method. The soluble $SiO_2$ indicates the content of dissolved silica in a solution of 1 m NaOH. The soluble content describes the weight loss of the sample after dissolution in NaOH solution.

The results are shown in Fig. 4. It can be seen that the results of all measurement methods are of the same order of magnitude. The sample with the median bulk density of 1.61 g/cm³ has a smaller soluble content due to formation of alkali silica gel during the dissolution.

## CONCLUSIONS

Due to only slight variations in the content of reactive components in opalsandstone aggregates, it has to be assumed that there is another reason for the difference in the expansion behaviour. All other characteristics of the opalsandstones were similar. The only exception is the porestructure. The lower the bulk density the higher the pore volume.

Thin sections of reacted opalsandstones with different bulk density reveal a different distribution of alkali-silica gel. If the pore content is higher, the gel is more dispersed. Opalsandstones with only a low porosity show almost no gel in the aggregate. These have only a reaction rim visible, and the amount of gel-produced is less, but the expansionrate is high.

It seems that the gel fills the aggregate pores and develops less pressure if space is available. If aggregates show less pore content less gel is needed to develop expansion (pressure).

This can be seen best by comparing the expansion behavior and the gel production of an opalsandstone with a defined pore content and a reactive granitic aggregate (Fig. 5).

The higher the pore content the faster the reaction occurs due to the larger surface of the reactive aggregate. Therefore, it can be deduced that the longterm expansion of compact reactive aggregates will be stronger than that of porous aggregates.

The Rietveld method is an adequate method to evaluate reactive aggregates and should be used more often in the future to examine other aggregates as well.

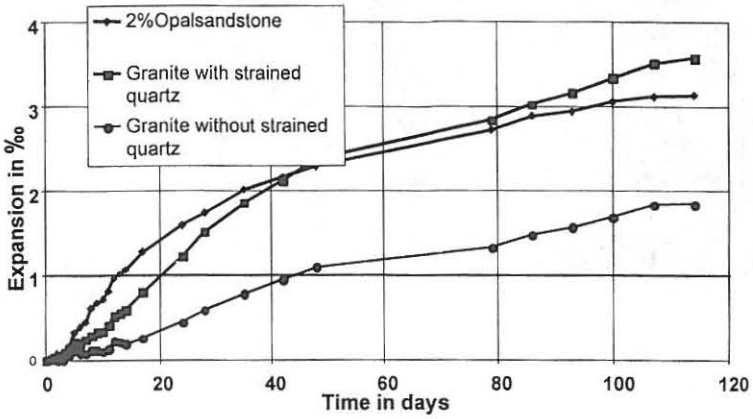


Fig. 5: Comparison of a reactive porous aggregate and a dense reactive aggregate measured with the NBRI-test. The velocity of the expansion of the porous aggregate is higher but the AAR of the dense aggregate is stronger. The Granite without strained quartz indicates a non deleteriously expansive aggregate.

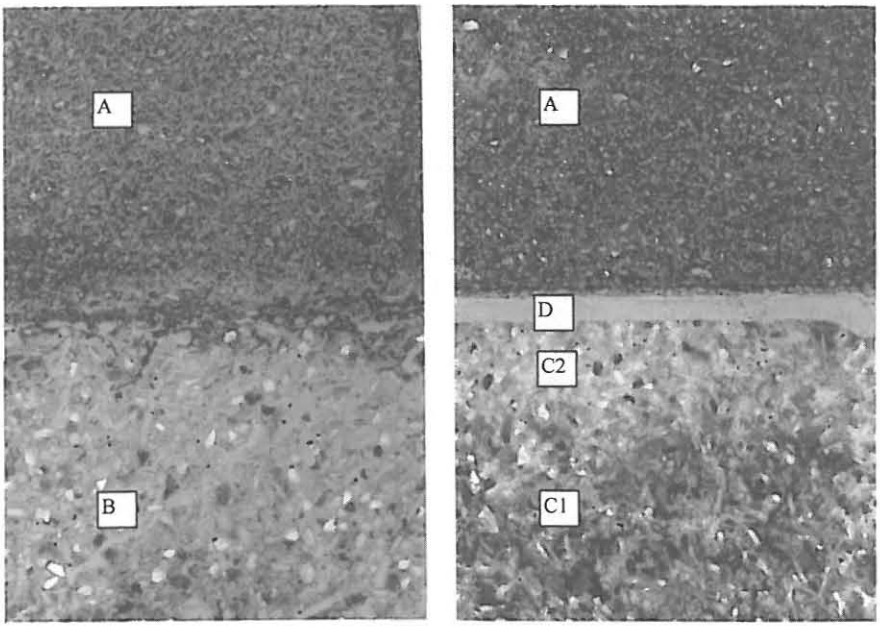


Fig. 6: Comparison of a porous and a nearly dense reacted opalsandstone in cementstone. A = cementstone , B = opalsandstone with low density, C = opalsandstone with high density (C1 = unreacted, C2 = reacted), D = Crack without Gel. The size is 2.4 mm.

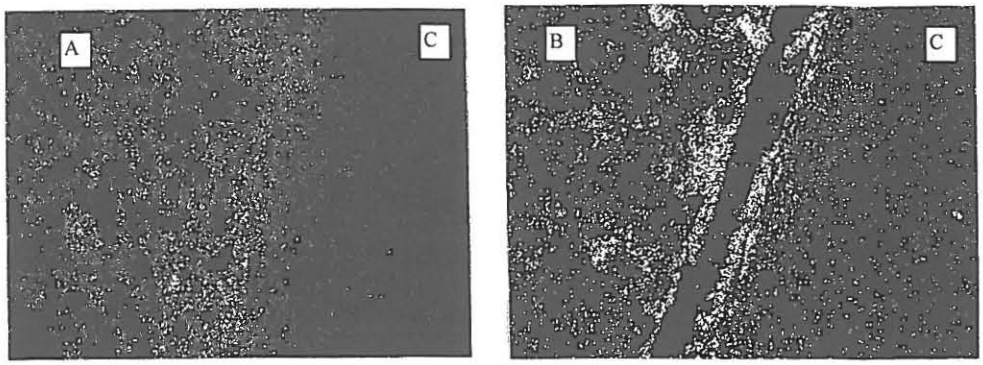


Fig. 7: Potassium mapping with an electron microprobe of the same samples.
A = opalsandstone with low density, B = opalsandstone with high density,
C = cementstone. On the left picture, the potassium bearing gel is uniform distributed in the opalsandstone. On the right picture the potassium bearing gel is enriched on the border cementstone – opalsandstone.

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