

CONCRETE DAMAGE CAUSED BY GREYWACKE REACTIONS - AN AAR?

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ABSTRACT

This paper discusses a damage mechanism in concrete produced with greywacke as an aggregate. The macroscopical phenomenon is characterized by network-like rifts on the surface of the concrete analogous to a well-known ASR. However, the special feature is that the greywacke grains damaged do not swell (e.g. like an opal containing sandstone), but they cleave. On each cleaving plane of the greywacke grain and also in pores near damaged greywacke grains a characteristic white substance is formed. This substance can be described as a strongly disordered layer silicate analogous to stilpnomelan (a transition mineral between hydrobiotite and montmorillonite). It can be argued that this silicate is probably a final product of a "weathering" process of plagioclases and micas inside the greywacke matrix. Most important is that greywacke itself can obviously provide all constituents of the damage reaction, what can be shown by specific concrete analysing methods. If this mechanism takes place in such a way it is different from other processes described in the literature as AAR until now. *Keywords: aggregate reaction, cleaving, greywacke, layer silicate formation, weathering*

INTRODUCTION

In the sixties it was reported for the first time in Germany on damage at concrete buildings in which alkali ions of the cement used and aggregates with a high content of amorphous silica were involved. In a short time these processes were identified as a so-called Alkali-Silica-Reaction (ASR). In the meantime the reactions between cement components (alkali) and aggregates which form a concrete damaging alkali silicate, the conditions for the course of these reactions and the macroscopical phenomena of the damage are well-known (Dahms, 1994).

FEATURES OF THE CURRENT DAMAGE

In the area of Lower Lusatia in the eastern part of Germany in the last few years some cases of damage at concrete buildings (dams, roads) have been observed which do not match any classical alkali silica reaction described before and which have been well-known in Germany until now. According to this "classical" ASR the macroscopical phenomenon of the damaged concrete building is characterized by a network-like rift structure (see Fig. 1). But substantial differences to a "classical" ASR are:

- The concrete aggregates damaged are greywacke grains. Greywacke is sedimentary rock with crystalline mineral components.
- The age of this rock is about 600 million years (the amorphous substances formed a long time ago have recrystallized).
- Only some parts of the concrete building are damaged although the "same" greywacke aggregates were used in the whole building.

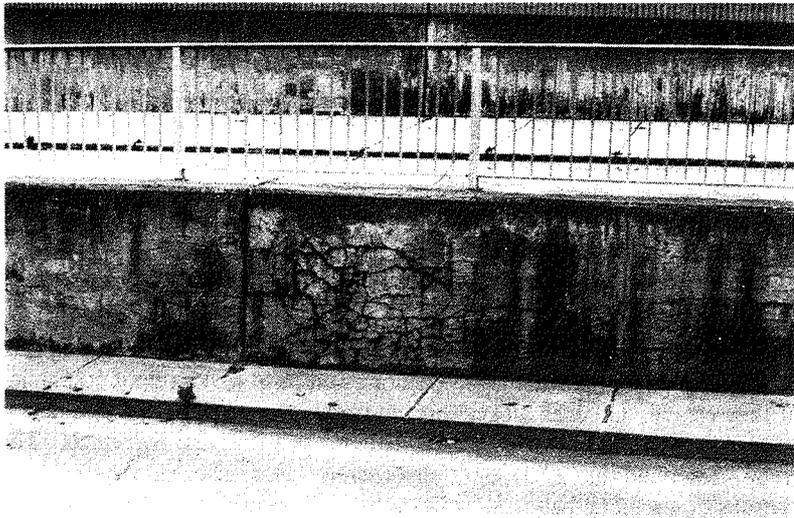


Fig. 1: Typical damage of the concrete

- Damage was also observed at low concentrations of alkali ions in the cement of the concrete.
- The aggregates damaged cleave. A swelling process on the surface of the aggregate grains was not observed.
- On **each** cleaving plane of the greywacke grains a characteristic white substance, formed as a seam, can be seen (see Fig.2).



Fig. 2: Typical structure on the cleaving plane of a greywacke grain

- Pores in the near of the damaged greywacke grains are also filled with a white substance. But this substance cannot be identified as Ettringite.
- The riftzone on the surface of the concrete is characterized by dirty brown crusts.
- Inside the greywacke aggregates rifts can be seen which do not have any continuation in the surrounding hardened cement.

Drilling sample investigations show that the destruction of the concrete is primarily a result of the damage of the greywacke grains. The damage mechanism can only be explained by investigation of the changes inside the greywacke grains and also by determination of the chemical composition and the structure of the white substance on the cleaving planes of the greywacke grains.

INVESTIGATIONS

Chemical analysis of the concrete

Several buildings were investigated (concrete wall, concrete road, dam) and from every building some drilling samples were gathered with the aim to determine the chemical composition of the concrete. The investigations were carried out according to two schemes:

- analysis of the whole drilling sample or the whole concrete respectively, and
- analysis of the concrete after sorting out the greywacke grains damaged.

Table 1: Results of the chemical concrete analysis

Constituents (wt %)	a) The whole concrete		b) Concrete without greywacke	
	Crushed sample	Cement and soluble constituents of greywacke	Crushed sample	Oxide content of the pure cement
Loss of mass after heating	4.79		7.19	
Insoluble	71.60		65.83	
Soluble constituents		(values in parenthesis see text)		
SiO ₂	5.05	21.39 (29.17)	5.82	21.57
Fe ₂ O ₃	3.15	13.34 (18.19)	1.65	6.12
Al ₂ O ₃	2.65	11.22 (15.30)	1.99	7.38
CaO	10.41	44.09 (60.23)	16.25	60.23
MgO	0.87	3.68 (5.02)	0.65	2.41
SO ₃	0.58	2.46 (3.35)	0.81	3.00
Chloride	0.025	0.106 (0.15)	0.013	0.048
K ₂ O	0.49	2.08 (2.84)	0.15	0.56
Na ₂ O	0.07	0.30 (0.41)	0.03	0.11
Na ₂ O-eq.	0.39	1.65 (2.25)	0.13	0.48

This approach was necessary because it was not possible to get sufficient and useful information from the concrete analysis made according to scheme a) about the kind of the cement used, the alkali content and the content of the other oxides. A typical result of the chemical concrete analysis which represents the drilling sample investigated is shown in Table 1.

Analogous differences (more or less for the individual constituents) between both kinds of investigation shown in the table can be found out also by investigations of the other samples. Normal concrete does not show such differences. In order to discuss the results of Table 1 it can be seen that the whole concrete (scheme a) has a high alkali content, a high content of iron and aluminium oxide, but a very low content of calcium oxide. In contrast to this the concrete without greywacke grains (scheme b) has the same composition as a typical Portland cement with a low alkali content. This can not be because it is the same drilling sample.

These differences are important. The one and only conclusion from this is:

Certain constituents of greywacke were dissolved during the life of the building caused by the permanent influence of the largely basic environment of the concrete.

Where can these ions or oxides come from?

Greywacke used here as an aggregate consists of quartz, feldspars (plagioclases), micas (muscovite, biotite, sericite) and pyrite. Caused by the longterm permanent influence of the largely basic environment of the concrete it can be assumed that the ions come from micas and feldspars (SiO_2 , Fe_2O_3 , Al_2O_3 , MgO , alkali ions) as well as pyrite (Fe_2O_3). Investigations of basaltic rock (Goguel, 1995) to determine the alkali solubility confirm this assumption.

Since the ions or oxides cannot be removed inside the closed system of the concrete and calcium oxide exists as supplementary oxide caused by the surrounding porewater of the hydrated cement, a new formation of minerals takes place inside or in the near of greywacke grains damaged. The results of these new formations of minerals are obviously the white substances which were found on the cleaving planes of the greywacke grains and also in the pores of the hardened cement stone.

Using a Leica scanning electron microscope (SEM) coupled with a Link energy dispersive X-Ray spectrometer (EDX) the chemical composition of the white substance located on the cleaving planes was measured. In the second column of Table 2 the results calculated as oxides are listed. These values are compared with the oxide composition dissolved from the greywacke (third column of Table 2). The calculation of these values based on the assumption that CaO does not exist as a soluble constituent of greywacke minerals. In the absence of limestone this proved to be a tenable assumption.

Considering the relations of the CaO contents determined by scheme a) and b) factor 1.36 results (the equation for this is: $60.23/44.09=1.36$, see values in Table 1). The oxide concentration values of the whole concrete analysis were multiplied by this factor (except the CaO value) and the results are already shown in Table 1 as values in parenthesis. If you subtract the concentration values of the pure cement from the values in parenthesis you can get the concentrations of the constituents of greywacke which are available for the new formation reactions of minerals.

Tab.2: Comparison of the EDX-results of the white substance with the soluble constituents of greywacke

Constituents	Oxide composition of the white substance inside greywacke grains (using EDX-detection) (wt %)	Oxide contents which are available from greywacke (for calculation see in the text) **
SiO ₂	50.1	7.8
Fe ₂ O ₃	7.8	12.1
Al ₂ O ₃	5.4	7.8
CaO	7.6	0.0
K ₂ O	12.7	2.2
Na ₂ O	4.8	0.3
TiO ₂	1.4	not investigated

** These values are the soluble content of 100g greywacke grains.

In Table 2 only the concentration ratios of the oxides can be compared, but not the absolute values. Very interesting is that the potassium oxide/silicium oxide-ratio is the same (about 0.3) measured according to both analysing schemes. The pore solution of the surrounding hardened cement paste consisting of Ca(OH)₂ yields the missing content of calcium oxide. The oversupply of iron oxide can obviously be found in the dirty brown crust on the surface of the concrete. This crust consists of iron oxide or iron hydroxide. The oversupply of aluminium oxide determined by the chemical investigation of the concrete cannot be explained at this time because in such high concentrations aluminium could not be found in the white substance on the cleaving planes of the greywacke grains and also not in the pores of the cement stone by using the EDX method. But also ettringite, the compound which can bind a high amount of aluminium, could not be proved in the pores of the hardened cement or could only be proved in traces.

Structure investigations

X-ray analytical investigations show that both the substance of the cleaving planes and the substance inside the pores of the cement stone are the same. Fig. 3 shows a typical X-ray diffractometer pattern of a sample of the white substance. Obviously, this is at least a partially crystalline material which differs to a high degree from the amorphous alkali silicates found in Germany until now.

At the moment an identification of the white substances based only on the X-ray analytical or the EDX-investigation results is not possible.

Therefore we tried to convert the chemical composition results measured by using the EDX detection into a structure formula. These results are listed in Table 3.

The result of this calculation can be interpreted as an anion complex with the formula [Al_{0.4}Si_{3.6}O₁₀]^{-4.4}. This is a typical structure of a three-layer silicate. The numbers of oxygen atoms (13.5) resulting from the calculation (see Table 3) can spread over the tetrahedral layer of this silicate (here 10), the octahedral layer as hydroxide and the interstratified layer as water molecules. The cations Ca²⁺, K⁺, Na⁺, Fe^{2+/3+} and Ti⁴⁺ compensate the charges in the octahedral layer and also in the interstratified layer of this layer silicate.

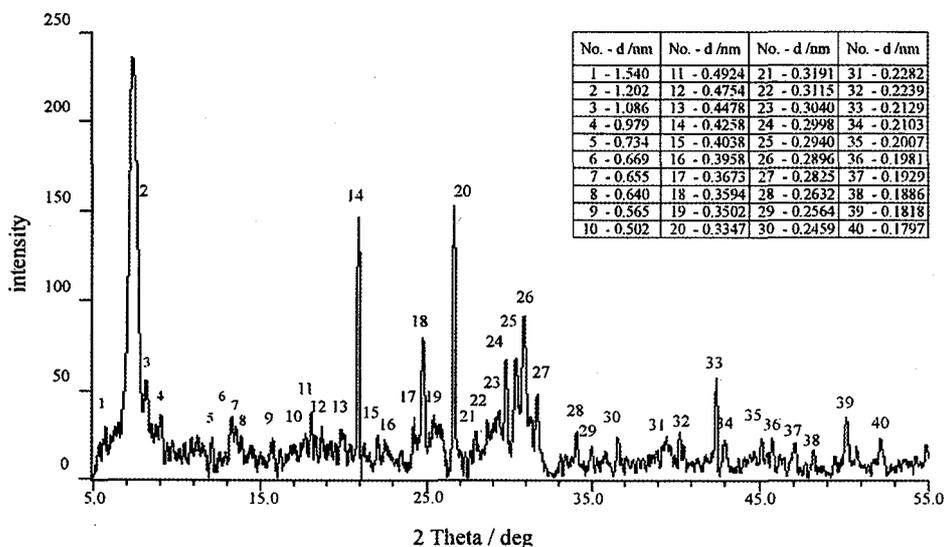


Fig. 3.: X-ray diffractometer pattern and d-values of the white substance of the cleaving planes transmission geometry - capillary technique (radiation: Cu K α)

Tab. 3: Calculation of a possible silicate structure based on the EDX results

Constituents	(Wt %)	(Mol)	Calculated to oxygen atoms	12	Calculated to oxygen atoms	13.5
Calcium	5.4	0.14	0.54		0.6	
Potassium	9.7	0.25	0.97		1.1	
Silicium	23.4	0.84	3.25		3.6	
Aluminium	2.5	0.1	0.39		0.4	
Sodium	3.9	0.17	0.65		0.8	
Iron	4.8	0.09	0.35		0.5	
Sulphur	0.0	0.0	0.0		0.0	
Titanium	0.8	0.02	0.08		0.1	
Oxygen	49.5	3.1	12		13.5 (10+3.5)	

But Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TG) investigations show that the distribution of the oxygen atoms given below is not quite correct (Hünger et al. 1994). There is only one mol hydroxide in the octahedral layer, i.e. there is obviously a deficit in this layer. The rest of the oxygen (2.5 mol) can be assigned to the water of the interstratified layer.

EVALUATION OF THE RESULTS

- The white substances can be described as predominantly crystalline silicates with a layer structure. The basal spacing of the layers measured by the X-ray diffraction method is about 1.20 nm.
- The distance of the element layers is variable (between 1.17 to 1.24 nm) and depends on the alkali content (especially potassium), the alkali/silicium-ratio, the calcium content and water.
- The following formula summarises all information on this silicate obtained until now:



This formula shows that the white substance can be a three layer silicate, but with a high deficit in the octahedral layer. The alkali and calcium ions (calcium is also bound as carbonate) are concentrated in the interstratified layer. The composition and the stability of the octahedral layer is not clear yet. Eventually the oversupply of aluminium determined by the chemical analysis of the concrete could compensate the deficit in the octahedral layer.

Other identifications of silicates given in the literature, e.g. as zeolite (Cole et al. 1981), as okenite (Cole & Lancucki. 1983) or as tobermorite gel (Davies & Oberholster. 1988), are more difficult because of the measured chemical relations. The Ca/Si ratio (=1/6) and the Al/Si relation (=1/9) measured here do not match the chemical composition of tobermorite or zeolithe. It is also important that the swelling process of the mineral observed here requires a specially crystalline silicate structure.

What can be the origin of this silicate? An analogous mineral could not be found in greywacke grains.

POSSIBLE REACTION MECHANISM - "WEATHERING" OF FELDSPARS AND MICAS

Based on the structure of the new mineral formation mentioned above the so-called greywacke reaction can be a "weathering" process. The origin can be the plagioclases containing a high amount of alkali ions and the mica minerals biotite and sericite. The final product would be the three-layer silicate found as a white substance on the cleaving planes of the greywacke grains and also the white substance inside the pores of the cement stone. Important for this mechanism are the other solubility conditions in the basic environment, the grain sizes of the constituents of the greywacke matrix consisting of feldspars and micas and certain petrographical features of this sedimentary rock.

This "weathering" hypothesis is supported by the accumulation of alkali ions, aluminium, silicium, iron and titanium inside the white substances. These ions or constituents can only come from the greywacke minerals themselves. A direct proof for this are the differences measured between the chemical composition of the whole concrete and the chemical composition of the concrete without greywacke. These differences are obviously caused by the solubility process of certain greywacke minerals.

The iron ions Fe^{2+} (there is enough in the Lusatian greywacke minerals biotite and pyrite) in the octahedral layer but also the aluminium ions control the silicate formation process in such a way that the formation of layer silicates especially of three-layer

silicates is possible. This layer silicate is disordered (it seems to be a crystal with a high deficit in the octahedral layer). In the interstratified layer of this mineral alkali and earth alkali ions and water can be intercalated.

Based on this "weathering" mechanism a characterization of the white substance as a disordered mineral analogous to stilpnomelane offers good correspondence with the measured pattern (see Powder Diffraction File of the International Centre for Diffraction Data, PDF# 17-505 or 25-174). Stilpnomelane is a strongly destructed transition mineral between hydrobiotite and montmorillonite and it is a layer silicate.

CONCLUSIONS

The damaging process of concretes produced with greywacke aggregates must be a very complex mechanism because of the many crystalline minerals inside the greywacke grains.

The permanent pore solution containing $\text{Ca}(\text{OH})_2$ can react with several mineral components of greywacke. After 15 to 20 years this leads to a release of certain ions from the greywacke grains. Controlled by iron (Fe^{2+}) and aluminium ions an at least partially crystalline layer silicate with a predominantly smectite analogous structure is formed. The mineral identification is difficult, but it might be a mineral analogous to stilpnomelane which is strongly disordered in the octahedral layer. But only a three-layer silicate structure can explain the swelling process observed. Under certain petrographical conditions the swelling process of this silicate leads to a cleaving of greywacke grains and thus to damage of the concrete.

Concrete damage caused by greywacke reactions - an AAR?

Our investigations have shown that **greywacke itself** used as an aggregate in concretes **can provide all constituents** which are necessary for the damaging process. These are the reactive silicate and aluminate components, but also the alkali ions. The cement provides only the CaO caused by the permanent $\text{Ca}(\text{OH})_2$ solution. The one and only reactant that has to come from outside is the permanent humidity.

Therefore it would be only an aggregate reaction (maybe a specific greywacke reaction).

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