# CONTRIBUTION TO THE CHEMICAL REACTION MECHANISM OF THE ALKALI-AGGREGATE-REACTION

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ABSTRACT:

With respect to the mechanism of the alkali-silica reaction we investigated the reaction of the δ $Na_2Si_2O_5$, as a possible intermediate compound in the reaction between NaOH and SiO_2 at room temperature under different water vapor conditions.   Starting with relative humidities higher than 20 % the primarily dry mixture reacts according to the following equation to kanemite with silicate layer structure.

$$\delta\ Na_2Si_2O_5 + 2\ SiO_2 \xrightarrow{\ H_2O\ } 2\ NaHSi_2O_5 \cdot 3\ H_2O \quad \text{(kanemite)}$$
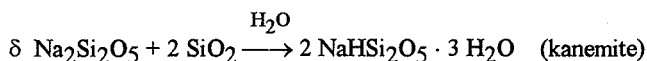
This reaction is connected with a volume increase as a result of the insertion of H_2O molecules between the silicate layers like in clay minerals. The near similarity of the above reaction to the alkali-silica reaction is supported by the fact that in both cases the expansion can be avoided by an admixture of lithiumhydroxide. Addition of $Ca(OH)_2$ results in an nearly unchanged volume increase and probably in a partial substitution of protons and sodium- cations by calcium ions in the kanemite structure.

KEYWORDS: *Alkali-aggregate-reaction, alkali-layer-silicate, reaction mechanism*

INTRODUCTION

Since Stanton 1940 observed the destructive effect of the formation of an alkali containing silica-gel in concretes several efforts were made to get a deeper insight into the mechanism of this concrete damaging process.   It is well established (Powers & Steinour. 1955) in the meantime that the source of this crack forming in concrete is the result of a reaction of alkali hydroxides with reactive silica by which an alkali-silicate gel of unknown constitution is formed. In the presence of moisture this gel adsorbes water and swells by which a stress is generated in the concrete leading to crack formation and an expansion of concrete constructions. According to a Danish group (Johansen *et al.* 1993) the stress formation is especially located in vains and cracks present in the aggregate minerals which are filled by an alkali-calcium silicate hydrate gel.   The chemical composition of such gels isolated from concrete constructions varies very much with respect to alkali / calcium as well as the alkali / calcium to SiO_2 ratio. In a very recent paper (Scrivener. 1994) on the alkali-silica reaction in a monolithic opal it was shown that even in the same gel filling the crack the alkali / calcium ratio is high at the crack front while the calcium content increases with the distance from the front.

In accordance with some other publications (Wang & Gilott. 1991) this effect is explained by the assumption of an ion exchange between the alkali silica gel and the C S H -phases. There is no broad knowledge about the structure of the alkali-silica gels because mostly they are amorphous and in the rare cases in which X-ray reflections can be seen it was not possible to assign them to known crystalline substances. The only structural information of the alkali-silica gels came from ^{29}Si-NMR-measurements

(Xiang-Dong et al. 1993). These show that the gels contain SiO_4 tetrahedra which are connected with two (Q^2), three (Q^3) and four (Q^4) other SiO_4 tetrahedra via $\equiv Si - O - Si \equiv$ bonds. Among these different SiO_4-tetrahedra mostly those dominate which are bound to three further tetrahedra. This means that the gels should contain predominantly alkali silicate-layer structures. Therefore we looked for crystalline sodium silicates with silicate-layer structures to investigate their formation conditions in concretes their swelling behaviour under moist conditions and their ion exchange with $Ca(OH)_2$, to get a deeper insight into the chemical mechanism of the alkali silica reaction. Sodium-layersilicates are investigated with increasing interest in the last decade and the following compounds are described in the literature (Beneke et al. 1995).

$Na_2Si_2O_5$ ($\alpha, \beta, \delta, \gamma$ -Modification)	$Na_2Si_8O_{18} \cdot 10.2\ H_2O$	Octasilicate
$NaHSi_2O_5 \cdot 3\ H_2O$ Kanemite	$Na_2Si_{14}O_{29} \cdot 11\ H_2O$	Magadiite
$Na_2Si_4O_9 \cdot 5\ H_2O$ Makatite	$Na_2Si_{22}O_{45} \cdot 10\ H_2O$	Kenyaite

Theoretically all of them could be end- or intermedium products of the alkali-silica reaction. Because the Na_2O / SiO_2 ratio in the alkali-silica gels are mainly found (Knudsen. 1975) to be between 0,2 and 0,5, we have investigated at first the compounds $Na_2Si_2O_5$ and $NaHSi_2O_5 \cdot 3\ H_2O$ (kanemite).

EXPERIMENTAL

As starting materials we used α, β and δ $Na_2Si_2O_5$ which are prepared by heating corresponding mixtures of Na_2CO_3 and SiO_2 and curing the resulting melts at definite temperatures (α:~750°C, β:~600°C, 20 h, δ:~640°C, 40 h).

The kanemite was sythesized according to a recent patent of the Hoechst AG (Tapper et al.1994) by treating a mixture of silica gel together with δ $Na_2Si_2O_5$ under moist conditions in the temperature range of 20°C - 60°C.
Expansion measurements were performed on pressed tablets in an apparatus sketched in *Figure 1.* combined with LVDT.
Structural changes as consequence of swelling processes were investigated by X-ray methods or ^{29}Si and ^{1}H-MAS-NMR measurements.
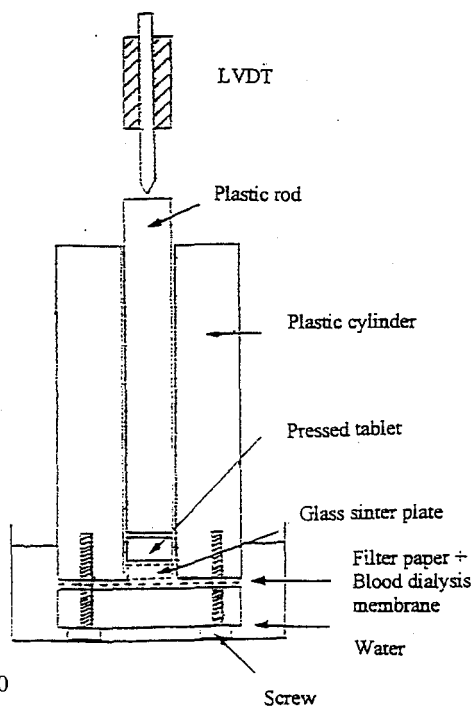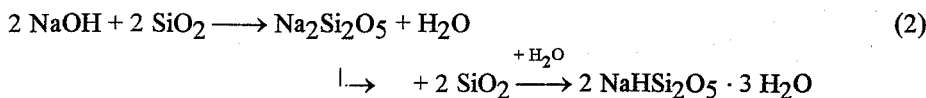

LVDT

Plastic rod

Plastic cylinder

Pressed tablet

Glass sinter plate

Filter paper +
Blood dialysis
membrane

Water

Screw

Figure 1 Devise for measuring the expansion

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RESULTS

When tablets of α, β or δ $Na_2Si_2O_5$ are installed into the apparatus shown in Figure *1* a slow uptake of water vapour as well as fluid water results only in the first minutes in a very small expansion ~0.5% but afterwards a relative strong shrinkage ~2.5% can be observed which results from the formation of a glassy viscous mass. These results show that the sodium layersilicates $Na_2Si_2O_5$ in the α, β and δ modification itself are not able to swell to such an extent that it can become harmful with respect to expansion reactions. Therefore we concentrated our investigations especially on the kanemite $NaHSi_2O_5 \cdot 3\,H_2O$ because, as already mentioned, the preparation of this compound from a mixture of δ $Na_2Si_2O_5$ and reactive silica at room temperature has a certain similarity to the alkali-silica reaction, which is normally described by the reaction

$$NaOH + SiO_2 \longrightarrow \text{alkali-silica gel.} \tag{1}$$

But the above reaction does not proceed directly from the starting materials to the alkali-silicate gel but goes continuously to sodiumsilicates of higher and higher SiO_2 content. Therefore one can formulate this reaction with $Na_2Si_2O_5$ as an intermediate compound.

$$2\,NaOH + 2\,SiO_2 \longrightarrow Na_2Si_2O_5 + H_2O \tag{2}$$
$$\overset{+\,H_2O}{\underset{}{\longmapsto \quad + 2\,SiO_2 \longrightarrow 2\,NaHSi_2O_5 \cdot 3\,H_2O}}$$

The second step in this reaction sequence is the reaction (equation 2) for the formation of kanemite. That this reaction is possible at room temperatur is shown in the following X-ray-diagrams *(Figure 2)* which we got in dependence the reaction time from a dry mixture of δ $Na_2Si_2O_5$ with a precipitated silica gel to which a very small amount of water ~7 M %, so that the mixture still seems to be dry, was added.
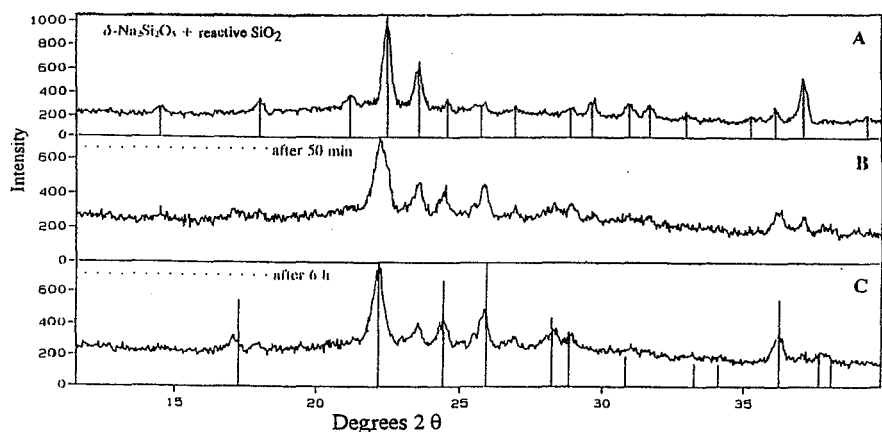

Fig. 2 X-ray powder diffraction diagrams from starting mixture of δ $Na_2Si_2O_5$ + SiO_2 (A); mixture after 50 min (B), mixture after 6 h (C). The line diagrams indicate the diffraction pattern of pure δ $Na_2Si_2O_5$ (A) and $NaHSi_2O_5 \cdot 3\,H_2O$ (kanemite) (C).

The intensity of the reflections of crystalline δ $Na_2Si_2O_5$ decreases with increasing reaction time, while those of the kanemite increase at the same time, so that after 6 hours pure kanemite is formed.

Even though no X-ray structure determination of this compound exists today it is clear from ^{29}Si and ^{1}H-MAS-NMR investigations (Wieker *et al.* 1995) that it is formed by preservation of the silicate layerstructure of the $Na_2Si_2O_5$ but in which one half of the SiO_4-tetrahedra carries Si-OH groups while at the other half the negative charges of the $\equiv SiO^-$ groups are compensated by Na^+-ions corresponding to the formula $(NaHSi_2O_5 \cdot 3\ H_2O)_x$. The 3 water molecules per Si_2O_5 unit are bound between the silicate layers. Under relatively mild thermal conditions the water content can be reduced to 1 respectively 0.30 H_2O per Si_2O_5. By this dehydration the silicate layer structure itself remains practically unchanged. Only the distance between the layers is reduced from 10.3 Å to 7.37 Å respectively 6.35 Å. Under normal water vapor pressure at room temperature the 1 and 0.3 H_2O containing compounds rehydrate to kanemite with 3 H_2O / Si_2O_5.

If one compares the molar volumes of $Na_2Si_2O_5$ with those of $NaHSi_2O_5 \cdot 3\ H_2O$ (kanemite) and its dehydration products $NaHSi_2O_5 \cdot 1\ H_2O$ and $NaHSi_2O_5 \cdot 0.3\ H_2O$ one can see *(Table 1)* that there is only a small volume increase going from the $\delta\ Na_2Si_2O_5$ to the monohydrat but that there is a strong growth of the molar volume (46.9 %) connected with the formation of the kanemite. Therefore we made measurement of the volume changes during the reaction of $\delta\ Na_2Si_2O_5$ with reactive SiO_2.

Table 1 *Mol volumes of $\delta\ Na_2Si_2O_5$, kanemite and its dehydration products.*

compounds	mol volume (cm³/mol)
$\delta\ Na_2Si_2O_5$	73.0
$NaHSi_2O_5 \cdot 3\ H_2O$ (kanemite)	107.3 "
$NaHSi_2O_5 \cdot 1\ H_2O$	79.2 "
$NaHSi_2O_5 \cdot 0.3\ H_2O$	~76 "

- Expansion measurements

In these investigations we used pressed tablets from mixtures of $\delta\ Na_2Si_2O_5$ and silica gel in a molar ratio of 1 : 2 according to:

$$Na_2Si_2O_5 + 2\ SiO_2 \xrightarrow{\ H_2O\ } 2\ NaHSi_2O_5 \cdot 3\ H_2O \qquad (3)$$
$$\text{kanemite}$$
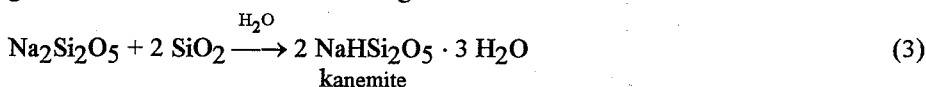
The water was supplied along a hard filter paper which was covered by a polymer membrane and a disk of a G 1 (with big pores) glass filter plate on which the tablets were situated. By this arrangement the water uptake of the tablet is possible mainly via the absorption of water vapour. This is necessary because a too quick uptake of water results in the formation of a very viscous mass, sometimes even connected with a shrinkage instead of the expected expansion.

Figure.3 shows the results of these expansion measurements. It demonstrates that the reaction of $\alpha\ Na_2Si_2O_5$ with SiO_2 results only in a relatively low expansion in contrast to the $\delta\ Na_2Si_2O_5$ which gives under the same reaction conditions an expansion of nearly 37 % of the height of the inserted tablet. It was surprising that this expansion was reached already after one day. X-ray investigations of the reaction product showed that the basal reflections of kanemite at 10.3 Å can be detected already after such a short reaction period.
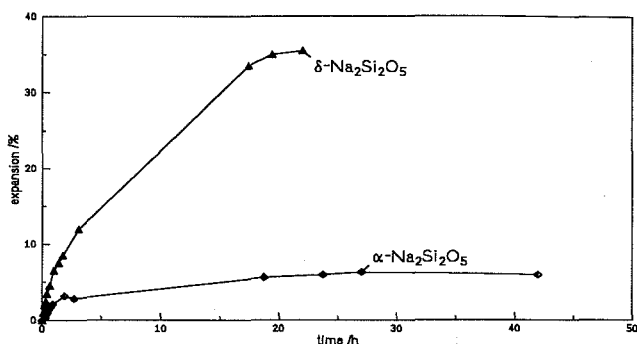
Figure 3 Expansion of mixtures of α and δ $Na_2Si_2O_5$ with reactive SiO_2

To demonstrate that the observed expansions are mainly connected with the formation of kanemite with ~3 H_2O per mol we dehydrated this compound to the 1 and 0.3 H_2O per mol $NaHSi_2O_5$ and studied the volume changes connected with their rehydration to the trihydrate. The results in *Figure. 4* show that the monohydrate gives an expansion but it is much lower (~8 %) than the formation of the trihydrate from $Na_2Si_2O_5$ and SiO_2 mixtures. The expansion during the rehydration of the 0.3 hydrate is much higher (~20 %) but does not reach that of the kanemite $\cdot$ 3 H_2O formation.

These results correspond with the calculated molar volumes *(Table. 1)*.

The fact that the layer structure remains unchanged during the de- and rehydration shows that the expansion is caused by an uptake of water molecules between the silicate layers. This is connected with an increase of the distance between the layers from 6.35 Å in the 0.3 hydrate, 7.37 Å in the monohydrat and 10.3 Å in the trihydrate as demonstrated by X-ray diffraction investigations.
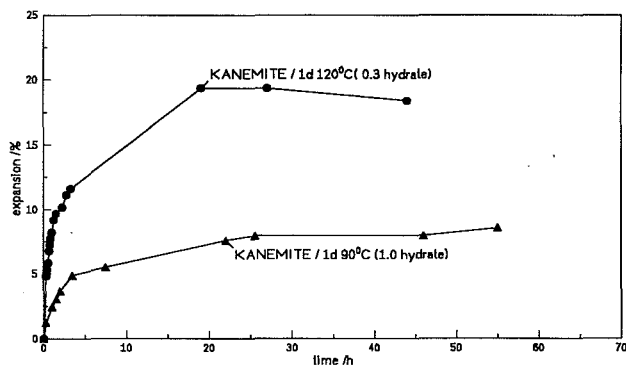

Figure 4 Expansion of partially dehydrated kanemite

Therefore we assume that the swelling-process caused by the alkali-silica reaction is very similar to that of clay minerals, which are also built up by silicate layers, in the presence of water.

To demonstrate the very near relationship between the alkali-silica reaction and the reaction of $Na_2Si_2O_5$ and SiO_2, we investigated the influence of some admixtures on this reaction. As admixtures those substances were selected which are known to influence the expansion caused by the alkali-silica reactions i.e. LiOH, $Ca(OH)_2$.

- Addition of LiOH:

From the literature (Sakaguchi *et al*. 1986) it is well known that in concretes expansions resulting from alkali-silica reactions can be depressed by an admixture of LiOH. Therefore we added a small amount of LiOH (100 mg) to an 1:2 molar mixture of δ $Na_2Si_2O_5$ and SiO_2 (970 mg) pressed it to a tablet and observed the changes of its height as described before. The results *(Figure 5)* show very clearly that no expansion but a small shrikage occurs. This means that Li^+-ions have the same effect on the expansion in the reaction of δ $Na_2Si_2O_5$ with SiO_2 as on the alkali-silica-reaction in concretes. In both cases it is not quite clear why the Li^+-ions prevent the swelling. But we assume that the high positive fieldstrength of the Li^+-ion acts like a clamp between the negatively charged silicate layers so that water molecules are not able to enlarge the distance of the silicate layers and to enter the space between them and cause an expansion.

- Addition of Ca(OH)$_2$:

The influence of $Ca(OH)_2$ on the reaction of δ $Na_2Si_2O_5$ with SiO_2 was of interest because most samples of alkali-silica-gels from damaged concrete structures contain a more or less amount of Ca-ions and it is not totally clear if they have an influence on the expansion process or not.

Therefore we prepared tablets from mixtures of δ $Na_2Si_2O_5$ with SiO_2 and different amounts of $Ca(OH)_2$ and investigated their expansion in the presence of water vapor.
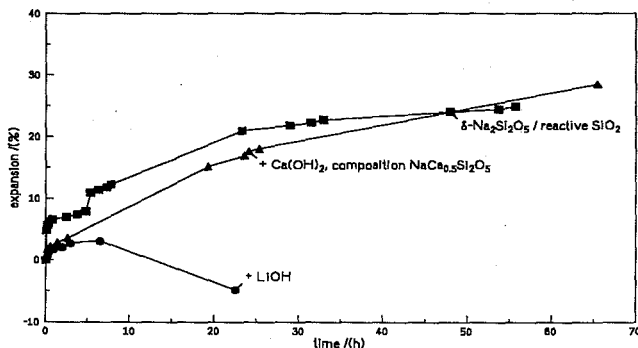

Figure 5 *Expansion of mixtures of δ $Na_2Si_2O_5 + SiO_2$ pur and with admixtures of Ca(OH)$_2$ and LiOH*

The results are shown in *Figure 5* for a sample in which the $Ca(OH)_2$ content of the reaction mixture of δ $Na_2Si_2O_5$ and $Ca(OH)_2$ was adjusted to an amount, that the over all mol ratio of Na_2O : SiO_2 : CaO was 1 : 4 : 1. The resulting expansion in the presence of water vapor is nearly the same as in the $Ca(OH)_2$-free system. This means that Ca-ions do not hinder the expansion reaction. The chemical reaction in this system is not clear in the moment. But we know by X-ray investigations of the reaction product, that kanemite is formed and that no crystalline $Ca(OH)_2$ is detectable. In further investigations we hope to get more information on the structure of this reactionproduct and on the role of Ca-ions in the alkali-silica-reaction.

- Dependence of the reaction of δ $Na_2Si_2O_5$ with SiO_2 the relative humidity:

During the investigations mentioned above we recognized that the velocity of the reaction between δ $Na_2Si_2O_5$ and SiO_2 and the expansion connected with it strongly depends on the water vapor partial pressure. Therefore we studied this reaction under

different humidity conditions at 20°C. Dry mixtures of δ $Na_2Si_2O_5$ and SiO_2 in the mol ratio 1 : 2 were stored in a desiccator over salt solutions with different water vapor pressures. The progress of the reaction was detected by the gravimetric water uptake and X-ray powder pattern. *Figure 6* shows that we used four different relative humidities (r.h.) at 8, 47, 95, 97 % (mean values) which we changed always after some days, depending on the rate of the water uptake (stepwise curve). The measured curve indicates that up till to a r.h. of ~20 % only a very small uptake of water occurs but that from 20 % up till 75 % r.h. there is a steep increase. Afterwards there is only a very slow uptake. If one calculates from the amount of $Na_2Si_2O_5$ and SiO_2 used in the experiment and the water uptake the number of water molecules Y per formula unit of the formed kanemite one sees, that 3 H_2O per $NaHSi_2O_5$ were reached shortly before the steep increase in the water uptake goes over in a slower one. But the *Figure 6* shows also that 5 to 6 H_2O molecules per formula unit can be taken up by the reaction product. The X-ray pattern of the reaction products shows that at low water vapor pressures no reaction occurs. The first formation of kanemite can be observed when the water uptake increases drastically between ~20 % - 75 % rel. humidity at 20°C. That means that only a relatively thin water layer must be pesent at the surface of the starting materials so that an effective mass transport can occur in this reaction.
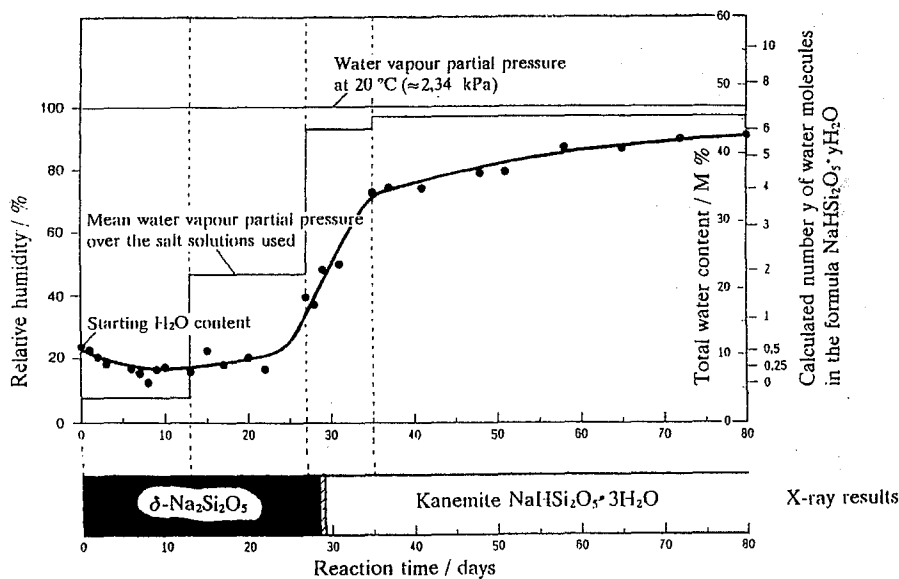

Figure 6 Formation of kanemite from δ $Na_2Si_2O_5$ and reactive SiO_2 (mol ratio 1 : 2) in dependence of the relative humidity at 20°C.

COMPARSION OF THE KANEMITE FORMATION WITH THE ALKALI - SILICA - REACTION

The results reported above provide a number of close similarities to the alkali-silica-reaction and it seems to us that the reaction of δ $Na_2Si_2O_5$ with reactive SiO_2 is a suitable model to understand which chemical reactions are really going on in the alkali-silica-reaction because of the following facts:
- alkali-silicates primarily formed in the reaction of NaOH and SiO_2 react at low water vapor partial pressure with further SiO_2 to the kanemite with a silicate layerstructure connected with a relatively strong volume expansion.

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- The kanemite formed during the expansion is a silicate with layerstructure. That corresponds with results of NMR measurements from alkali-silicate gels taken from damaged concrete strutures.
- Li-ions are able to hinder respectively to avoid the expansion in both cases.
- Ca-ions do not hinder the alkali-silica-reaction as well in concretes as in the kanemite formation.
- The typical interference at 10.3 Å in X-ray diffraction pattern of kanemite can be very often observed in those of alkali-silica gels from damaged concrete structures, which are published in the literature (Oberholster. 1983).

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