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# SOME EXPERIENCES IN CHEMICAL MODELLING OF THE ALKALI-SILICA REACTION

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# ABSTRACT

Using the reaction of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with SiO<sub>2</sub> and SiO<sub>2</sub> containing minerals in the presence of small amounts of water as a model reaction for the ASR it is shown that layer silicates are formed which cause expansions. The degree of the expansions depends on the reactivity of the SiO<sub>2</sub> in the samples and the relative humidity under which pressed tablets of these compounds are stored. The expansion increases with increasing the relative humidity up to ~ 80 - 90%. At higher humidities a decrease of the expansion can be observed because of the hydrolytic degradation of the layer silicates. Added Ca(OH)<sub>2</sub> reduces the expansion. Salt admixtures influence the size of expansion depending on the kind of cations and anions and their concentration by influencing the electrical double layer equilibrium between the single silicate layers. The expansion retarding effect of Li salt addition in the model system is investigated by <sup>29</sup>Si MAS NMR methods and a mechanism of their action is discussed.

Keywords: chemical model for ASR mechanism, alkali layer silicate formation, influence of salts and humidity, <sup>29</sup>Si MAS NMR.

## **INTRODUCTION**

To get an insight into the chemical reactions of the alkali-silica reaction Cong et al. (1993) treated opal with potassium hydroxide and investigated the resulting product by <sup>29</sup>Si MAS NMR measurements. They found that the three-dimensionally connected SiO<sub>4</sub>-tetrahedra (Q<sup>4</sup>-groups) of silica (SiO<sub>2</sub>) are slowly converted to a layer silicate structure in which the SiO<sub>4</sub> tetrahedra are only connected with three SiO<sub>4</sub> tetrahedra (Q<sup>3</sup>-groups). Some years later Brough et al. (1996) published similar results of layer silicate formation during the hydration reaction of C<sub>3</sub>S in the presence of KOH and silica. Nearly at that time a patent (Tapper et al. 1994) described the formation of the mineral Kanemite NaH[Si<sub>2</sub>O<sub>5</sub>] · 3H<sub>2</sub>O with a layer silicate structure by a reaction of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with silica in the presence of small amounts of water at normal conditions according the following equation:

$$\delta \operatorname{Na_2Si_2O_5} + 2\operatorname{SiO_2} + 7\operatorname{H_2O} \rightarrow 2(\operatorname{NaH}[\operatorname{Si_2O_5}] \cdot 3\operatorname{H_2O}). \tag{1}$$

A detailed investigation of this reaction and the properties of Kanemite (Wieker et al. 1995) gave rise to the idea that this reaction is very similar to the alkali-silica reaction (ASR). Our further studies of this reaction have shown that the formation of Kanemite is connected with an expansion of the reaction product (Wieker et al. 1996). Therefore, we concluded that the reaction mentioned above can be used as a model reaction for the study of the ASR. In order to get more information on the chemical reactions running off in the ASR we investigated the Kanemite formation in more detail, especially the different factors influencing this reaction.

#### STUDIES OF ASR MODEL REACTIONS

In our studies we used pressed tablets from 1:2 molar mixtures of water-free alkali layer silicates and  $SiO_2$  sources, treated them at room temperature under different relative humidities (r.h.) in a desiccator at nearly 85 % r.h. or in a special device, as described elsewhere (Wieker et al. 1996, Hübert et al. 1998), and measured their expansion in dependence of the reaction time. The reaction products were characterised by X-ray diffraction and by <sup>29</sup>Si MAS NMR measurements.

#### The Reaction of 8-Na2Si2O5 with SiO2

Influence of the Silica Source -- We started our studies according to equation 1 with reaction mixtures of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and reactive (precipitated) SiO<sub>2</sub>. Later on, the silica in this reaction was substituted by minerals which have a known sensitivity to ASR in concrete. Our results (see fig. 1) show that these reactions result also in expansions similar but smaller as those found in experiments on  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> - SiO<sub>2</sub> samples. The analytical characterisation of the corresponding reaction products shows in every case a formation of Kanemite. Like in real concretes quartz gives only very small expansions in our model reaction and a formation of Kanemite could not be detected during this reaction.

<u>Influence of Liquid Water and Humidity</u> — Because it is known from the ASR in concrete that the magnitude of expansion depends on the water content we investigated the influence of liquid water and humidity on the reaction described by equation 1. In these experiments the tablets were stored in a desiccator over sulphuric acid of different

concentrations to fix definite humidities during the experiments. The one-dimensional free expansions of the tablets were estimated by measuring the changes of their heights with a precision of  $\pm 0.02$ mm.



The results of these experiments (see fig. 2) show that at 16% r.h. practically no expansion can be observed. At 56% r.h. a considerable expansion can be noticed. The highest expansion was obtained by curing the samples at 87% r.h. This value corresponds very well to those given in the literature for concretes (between 80% and 95% r.h.). Unexpected was the fact that at 100% r.h. the expansion was lower than that of the samples treated by 87% r.h.. The difference between these two samples was that the sample stored under 100% r.h. adsorbed during the first 10 days much more water (~ 60 weight %) than the sample treated at 87% r.h. (~ 30 weight %). From special investigations on the stability of Kanemite in the presence of liquid water we know that the layer structure is partially decomposed under these conditions to silicates of lower molecular size (Wieker et al. 1993). Therefore, we assume that the detected decrease in expansion at 100% r.h. is connected with the degradation of the silicate layer structure which is responsible as mentioned above for the expansion.

Influence of Ca(OH)<sub>2</sub> — One of the main differences between our model reaction and the cementious materials is that we do not have Ca<sup>2+</sup>-ions in our reaction system. Therefore, we added different molar amounts of Ca(OH)<sub>2</sub> to the mixture of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> and measured the expansion during the hydration at 87% r.h. and 20°C (Wieker et al. 1998). The addition of Ca(OH)<sub>2</sub> causes a retardation of the expansion which was the higher the more moles of Ca(OH)<sub>2</sub> were added to the mixtures of 1 mol  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and 2 mol SiO<sub>2</sub>. This result corresponds partially with the results of a study on the influence of Ca(OH)<sub>2</sub> on the expansion of concrete due to ASR (Thomas 1998). X-ray diffraction pattern of our reaction products show that there is partially a formation of Kanemite but after 40 days there is still a remarkable amount of unreacted  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> detectable. This result could mean that a reaction rim of Ca-silicates is formed which reduces the reaction velocity. Another possibility for the retardation of the expansion could be that by ion exchange processes  $Ca^{2+}$ -ions with a much higher field strength than alkali Me<sup>+</sup>-ions enter the Kanemite lattice. The consequence of this would be that by the higher electrostatic forces between the  $Ca^{2+}$ -ions and the negatively charged silicate layers (in fig. 3) the ability to swell is reduced. Such a process is well known from investigations on clay systems. But the other effect that Ca(OH)<sub>2</sub> also increases the expansion of concrete caused by ASR (Chatterji 1979, Thomas et al. 1998) can not be explained by our experiments. It is imaginable that in concrete isolated areas can be formed by C-S-H phases with high Ca/Si ratios. Inside such areas the condensation reaction of alkali silicates can occur without beeing influenced by  $Ca^{2+}$ -ions up to layersilicates by an uptake of SiO<sub>2</sub> from the aggregates so that an expansion could appear. But for a clear understanding of this increasing expansion of concrete by an addition of Ca(OH)<sub>2</sub> much more investigations are needed.

δ-Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> 6,88 Å	$\begin{array}{c} - \overset{i}{Si} - 0 \\ - \overset{i}{Si} - 1 & - \overset{i}{I} & 1 \\ 0 & 0 & 0 & 0 \\ \end{array}$ $\begin{array}{c} Na \\ Na $	
	$\downarrow$ + water + silica	
Kanemite		+ Na(OH)
10.3Å	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	→salt hydrolysis and reaction with SiO <sub>2</sub>
condensation of Si-O-Si bonds	$-H_2O \uparrow \downarrow +H_2O$	hydrolysis of Si-O-Si bonds
decomposition products	Na H Na H O O O O HO-Si-O-Si-OH/HO-Si-OH/HO-Si-	
free mobility in solution	OOOOOO HNAHNA AOOOOOO	
	HO-SI-OH/HO-SI-O-SI-OH/HO-SI-OH               O O O O Na H Na H	

Proposed Reaction Scheme of the Alkali-Silica Reaction

Fig. 3: Proposed reaction scheme of the alkali-silica reaction

From the results mentioned so far one can draw the following scheme (fig. 3) for the reaction between  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub>. This sketch shall demonstrate two layers of  $\delta$ -Na2Si2O5 or Kanemite, respectively, each of which are positioned vertically to the paper surface. The sodium ions between these two layers are bound to oxygen atoms in the  $\delta$ -Na2Si2O5. The distance of the silicate layers estimated by X-ray diffraction in this compound is ~ 6.8 Å. In the presence of water by the chemical process of salt hydrolysis. sodium hydroxide is formed which reacts with the added SiO2 and leads to the formation of Si-OH-groups in the silicate layers. Because of the increasing negative charges at the layer silicate sheets and the lower number of positively charged sodium ions in this electrical double layer, the distance between the silicate layers increases as a result of the increasing electrostatic repulsion up to 10.3 Å in the Kanemite. A further uptake of water leads to a separation of the single layers from which, by hydrolysis of Si-O-Si bonds, lower molecular silicate species and at least a water glass solution is formed, which does not give expansion reactions in our experiments. The same effect can be observed on concretes. But this observation raised the question: what happens when sodium water glass solutions evaporate and amorphous gels containing layer silicates are reformed. Therefore, we dried water glass solutions with the same SiO2/Na2O ratio as in Na2Si2O5 to an amorphous powder and mixed it with reactive SiO2. Pressed tablets were cured at 87 % r.h. The results in fig. 4

show clearly that amorphous dried water glass samples with a molar ratio Na/Si = 1 also react with reactive SiO2 but the measured expansions are much smaller than those with crystalline  $\delta$ -Na2Si2O5. The reason for these quantitatively different behaviours probably comes from the fact that δ-Na2Si2O5 used in our experiments is crystalline and anhydrous while the dried water glass samples were amorphous and contained about 16 % of its weight as H2O. Therefore, a relative high amount of water is present in the reaction mixture from dried water glass and SiO2. This leads already in the first reaction periods to a degradation reaction of the partially protonated alkali layer silicates. An indication Fig. 4: Comparison of the expansions for such an assumption is the fact that there is, starting from about 7 days, a decrease in the expansion which points in that direction. But further investigations are needed to get a clear interpretation of that result.



produced by cristalline δ-Na2Si2O5 and dried water glass samples of the same composition in mixtures with reactive SiO2

# Reaction of K2Si2O5 with reactive SiO2

If one tries to transfer the results mentioned above to Portland-cement- mortars and -pastes the important question arises: to which extent and by which way is there an influence of the potassium  $(K^+)$  ions and especially of potassium hydroxide (KOH) which are present in the hydration products of Portland cements.

K2Si2O5 was prepared by heating a mixture of potassium carbonate and SiO2 up to a melt (~ 1200°C) and treating it for crystallisation at 780°C for 6 days. As in the experiments with δ-Na2Si2O5 we prepared mixtures of K2Si2O5 and reactive SiO2 pressed tablets and stored them under different r.h. in desiccators. The reaction products were characterised by <sup>29</sup>Si MAS NMR measurements. The corresponding NMR spectra are shown in fig. 5. The spectra of those samples which were treated at 18% r.h. (fig. 5a and b) show that they mainly consist of the signals of the starting material of -110 ppm (SiO<sub>2</sub>) and of -91.7 and -92.4 ppm (K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>). In analogy to the reaction of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with reactive SiO<sub>2</sub> which leads to the formation of Kanemite we expected in the present reaction the formation of a KH[Si<sub>2</sub>O<sub>5</sub>] • xH<sub>2</sub>O corresponding to NaH[Si<sub>2</sub>O<sub>5</sub>] • 3H<sub>2</sub>O. But an increase of the signal at -91.4 ppm from KHSi<sub>2</sub>O<sub>5</sub> can not be prooved. Instead of this expected signal a small signal is detectable at -96.6 ppm, the intensity of which slowly increases with increasing reaction time. This signal can not be attributed to a definite chemical compound, but from its chemical shift value of -96.6 ppm it derives from Q<sup>3</sup> groups in layer silicate structures.



Fig. 5: <sup>29</sup>Si MAS NMR spectra of the reaction products of K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with reactive SiO<sub>2</sub> : a -after 2 days at 18% r.h., b - after 26 days at 18% r.h. and c - after 4 days at 87% r.h.

A quite different spectrum was received from the same mixture when it is stored at 87% r.h. for four days (fig 5 c). It consists of four signals at -79.9, -87.9, -96.4 and -106 ppm. These chemical shift values are very similar to those from water glass solutions containing a mixture of low and high molecular silicates. This result shows that a mixture of K2Si2O5 and SiO<sub>2</sub> is much more hygroscopic than that of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> and that the layer silicates in the K2Si2O5 system are hydrolysed very quickly to silicates of lower condensation degree (Wieker et al. 1998). This is supported by expansion measurements we performed with pressed mixtures of δ-Na2Si2O5 + SiO2 and K2Si2O5 + SiO2 at nearly 80% r.h. The results show clearly that in the  $K_2Si_2O_5 + SiO_2$  system there is a relatively high expansion in the first 50 hours but after this period a strong decrease of the expansion can be observed. In contrast to this there is in the  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> + SiO<sub>2</sub> system a slower increase in the expansion to a value of 25% which seems to be stable over a longer time period. In mixtures of both systems we got results in which the overlapping of these properties clearly can be demonstrated (Wieker et al. 1998). To see if these results can be transferred to cement bound materials we prepared mortar prisms from a Portland cement with a very low Na<sub>2</sub>O<sub>eq.</sub> = 0.36% using a mixture of unreactive quartz sand and a crushed Duran glass which is well known to be reactive in alkali-silica reaction as aggregate. The alkali content in these test prisms was increased to a Na2Oeq. of 1.2% by adding Na2SO4 or NaOH, respectively by K2SO4 or KOH. The prisms were stored at 40°C under 100% r.h., The oneaxial expansions of test prisms are plotted in fig. 6.

As expected the expansion of the  $K_2SO_4$  and KOH containing prisms are always smaller than those to which  $Na_2SO_4$  or NaOH was added respectively. This result shows again that the behaviour of the chemical model  $Me_2Si_2O_5$  (Me=Na,K) corresponds qualitatively well with the observations on alkali-silica reactions in real building materials (Stark et al. 1993).

The fact that potassium layer silicates give lower expansions than the sodium layer silicates is only valid when these systems are exposed to relative high r.h. because of the very high hygroscopicity of the potassium layer silicates. But in a surrounding of low r.h. the potassium layer silicates become more stable, so that higher expansions by these layer silicates can be expected. Such a situation is present in high and superhigh strength concrete.



Fig. 6: Expansion of mortar bars from a cement with  $Na_2O_{eq.} = 0.36\%$  and standard sand and alkali reactive Duran glass as aggregates to which  $Na_2SO_4$  and  $K_2SO_4$  and the corresponding hydroxides are added in the same molar amount to a  $Na_2O_{eq.}$  content of 1.2%

# Influence of Salt Additions to the Model System &-Na2Si2O5 + SiO2

As mentioned above in Kanemite an electrical double layer is formed (Verwey and Overbeek 1948) between the silicate layers with negative charges at the  $\equiv$ Si-O<sup>-</sup> groups and the positive charges at the hydrated sodium ions which are situated between these layers. According to this, the distance of the silicate layers depends on an equilibrium between the repulsive electrostatic forces of the negative charges at the silicate layers and the attractive forces from the sodium cations with these negative charges. The protons do not give a big contribution to these attractive forces because the acidic  $\equiv$ Si-OH groups show only a very low dissociation according to equation

$$\equiv \text{Si-OH} \rightarrow \equiv \text{Si-O}^- + \text{H}^+$$
 (2)

From several investigations it is known that the equilibrium between repulsive and attractive forces can be influenced by the addition of salts to these systems with electrical double layer characteristics, which results in changes of the distance between the single layers and produces increasing or decreasing expansions by this way. Recently such an influence of salt admixtures on the expansion of cement mortars by ASR was reported which the authors (Prezzi et al. 1997, 1998) attributed to salt effects on the electrical double layers formed in the studied system. Therefore, we tried to find such effects by adding salt to our model system too. We added to mixtures of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> different solid potassium and lithium salts and pressed these reaction mixtures to tablets. The corresponding tablets were treated at ~ 87% r.h. and their expansion was measured in dependence on the reaction time. The results are given in fig. 7 for addition of potassium chloride, - sulfate and - carbonate each in two amounts (0.1 and 0.5 mol salt per mol  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> in the mixtures).



There is a clear reduction of the expansion in dependence on the amount and the anion type of added salts. The reduction in expansion increased with increasing amount of salt added and in the sequence  $Cl^- < SO_4^{2-} < CO_3^{2-}$  compared with the salt free sample.

The influence of lithium salts on the expansion of our model system is summarised in fig. 8. There is also a clear decrease in expansion with increasing amounts of added salts. The effect to reduce the expansion is higher for the Li-salts than for the corresponding potassium salts (see fig 7). The influence of the anion types  $OH^-$ ,  $Cl^-$ ,  $NO_3^-$  on the reduction of the expansion seems not to be so marked as in the case of the potassium salts. Why  $Li_2CO_3$  has only a small effect on the expansion is not understandable in the moment. It could be that the low solubility of this salt is the reason for this behaviour. Especially the results of our experiment with the Li-salts are totally comparable with the practical experience to avoid alkali-silica reactions in concretes by addition of Li-salts (Stark et al. 1993).

The characterisation of the hydration products of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with SiO<sub>2</sub> and lithium salts by means of <sup>29</sup>Si MAS NMR became more complicated because a  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> sample was used which was contaminated with the  $\alpha$  and the  $\beta$  modification of Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. This leads to the appearance of some additional signals in the NMR spectra of the

investigated samples. The NMR spectrum of the used  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> sample is presented in fig. 9a. The spectrum of the reaction product of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with SiO<sub>2</sub> after 3 days at 87% r.h. shows that the Kanemite is the only reaction product which is formed (fig. 9b). The addition of 0.25mol Li<sub>2</sub>CO<sub>3</sub> per mol Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> to the reaction mixture with SiO<sub>2</sub> shows again that after a reaction time of 3 days at 87% r.h. the Kanemite is formed (fig. 9c). The amount of this Kanemite is smaller than in the case without a Li<sub>2</sub>CO<sub>3</sub> addition. In contrast to the addition of Li<sub>2</sub>CO<sub>3</sub>, the addition of 0.5 mol LiOH/ $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> shows that even after 4 days a formation of Kanemite is not detectable in the reaction product (fig. 9d). But in samples of longer reaction time there is the evidence that small amounts of Kanemite are formed.



Fig. 9: <sup>29</sup>Si MAS NMR spectra of δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (a), the reaction product of δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> with reactive SiO<sub>2</sub> after 3 days at 87% r.h. (b), the reaction product of δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub> and 0.25 mol Li<sub>2</sub>CO<sub>3</sub> after 3 days at 87% r.h. (c) and the reaction product of δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub> and 0.5 mol LiOH after 4 days at 87% r.h. (d)

From these experiments it is to conclude that under the used reaction conditions the Li salts addition up to amounts of 0.5 mol to the reaction mixture of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> gives only a delay in the Kanemite formation and that no other products are formed during the hydration of these mixtures. This result leads to the conclusion that there are at least two possibilities to explain the avoiding or reducing effect on the expansion of the reaction products by means of Li-salt addition:

- formation of a cover by adsorption of Li ions at the near surface areas of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> or the reactive SiO<sub>2</sub> (or both of them) that hinders the ion transport out of the  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> or into the SiO<sub>2</sub>
- formation of precipitates of Li silicates possibly on both starting materials which also hinders the progress of the reaction.

In order to get further insight into these reactions, new experiments with an addition of higher amounts of Li salt are in preparation at this moment.

## CONCLUSIONS

The results presented in this paper together with those published before show clearly that our chemical model gives comparable results to those which are reported from experiments on concretes with respect to the alkali-silica reaction. But further investigations are needed to understand all facts known till now about this concrete damaging process.

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