

## Influence of alkali supply from outside on the dissolution behavior of aggregates

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### Abstract

Reactive aggregates, humidity and alkalis are necessary for ASR in concrete structures. If alkalis come additionally from outside, the damaging reaction can be strongly accelerated. However, the reasons therefore are not completely understood. Some researchers discuss a direct attack of alkali ions on the Si-O-Si bonds of quartz structures. This paper provides another point of view to understand this phenomenon.

Different aggregates (grain size 2-8mm) were stored in a highly alkaline KOH solution. Additionally to this solution, sodium chloride with different concentrations was added. The aggregates were selected on the one hand according to their reaction behavior in concrete structures, on the other hand to their dissolution behavior. Long-term dissolution experiments were performed over several months. The silica, the aluminum and of course the sodium concentrations were determined. It can be expected, that under the influence of sodium the silica concentrations in the alkaline solution raise up. The question here is: What happens with the aluminum concentration at the same time? Very surprisingly was, that Al reaches a maximum after some days and then it decreases. Exactly from this time when the Al concentration decreases the silica concentration raises up extremely. The reason therefore can only be a precipitation process. Obviously, there is a correlation between the aluminum content in the solution and the extreme silica release of aggregates, both affected by alkali ions from outside.

Aggregates, which do not release aluminum because of their composition (e.g. quartzite), do not show this behavior. The conclusion is that such aggregates are not so sensitive against alkali attack from outside.

**Keywords:** aggregate grains; aluminium concentration; deicing salt; dissolution experiments; silica release

## 1. INTRODUCTION

ASR is still often the reason for countless damages of concrete structures worldwide. The reaction requires three partners: reactive aggregates, moisture and alkalis. Alkalis can come from the cement binder (as a typical origin), from the aggregates (has been discussed over several years) and from outside (from de-icing salts) too. Sodium chloride (NaCl) is in this case, commonly used in concrete pavements. Especially in the eastern part of Germany in the 1990s, many pavements were produced with concrete using regional aggregates. Frequently after less than ten years such concrete pavements showed cracks, which led to a complete destruction of the pavement. To prevent this accelerated damaging reaction a system of concrete and aggregate testing procedures have been developed during the last decade, which involve a performance test of concrete recipes too. However, the reasons for this behaviour cannot be explained by ASR performance tests.

Already Bérube et.al [1, 2] discussed the influence of NaCl solutions on the alkali silica reactivity, especially on the expansion of concrete and mortar bar prisms. Such investigations based on earlier works from Chatterji et.al [3, 4], who studied the effect of NaCl and Ca(OH)<sub>2</sub> on the alkali silica reaction. Additionally affected was the ASR discussion by deicing salts, which are used for concrete airfield pavements. The very high concentrated solutions of K-acetate and -formate led here to a very fast

destruction of concrete structures. airfield pavements. The very high concentrated solutions of K-acetate and –formate led here to a very fast destruction of concrete structures.

Dressler [5] investigated the influence of NaCl on the ASR gel composition and found that sodium can substitute the normal potassium content of an ASR gel. Gels with an increased sodium amount lead to a higher expansion of concrete prisms. However the presence of NaCl in the pore solution leads to a higher gel amount. The alkali silica gel is rich on sodium ions and has therefore a lower viscosity. Such gel can penetrate in to deeper concrete areas, which can lead in dependence on the calcium content to a higher swelling of concrete structures.

Giebson [6] divided the complicated system in two different parts called “cement stone” and “aggregate”. By presence of chloride ions Friedel’s salt was detectable in the cement stone. Not detectable was an increase of the pH value of the pore solution. Therefore the higher solubility of aggregate parts is not caused by a higher pH value.

Investigations in the aggregate system showed a normal dissolution process (under consideration of a pH value decrease) of amorphous silica without any presence of NaCl and Ca(OH)<sub>2</sub>. With presence of NaCl the formation of N/K-S-H phases have been proven. Similar effects could be measured in the aggregate system using quartz.

In summary a direct influence of NaCl on the SiO<sub>2</sub> dissolution process could be discussed caused by the formation of a special surface complex nSiO-Na<sup>+</sup>. Also Dove [7, 8, 9] has already reported on this fact.

However in real aggregate systems always aluminium is present and can influence the dissolution process in its own way. This aspect should be taken into account in this paper.

## 2. MATERIALS AND METHODS

Solubility experiments have been done with different aggregates stored in different alkaline solutions. The storage conditions were 80°C and 0.1mol KOH solution. Therefore, the starting OH<sup>-</sup> ion concentration was 100 mmol/L. Different NaCl amounts were added to this basic solution, 0.5%, 1%, 2%, 3%, 5% and 10% regarding to the solution volume.

Different aggregates were chosen, in a first step two natural rocks (greywacke, rhyolite) and two gravels with grain sizes of 2-8 mm and 8-16 mm. For the mineralogical compositions, see Table 2.1.

Table 2.1: Mineralogical composition of aggregates used

Agg 1 (gravel)_2-8 mm	wt.-%	error	Agg 2 (greywacke)_2-5mm	wt.-%	error
Biotite	3.6	1.5	Biotite	10.9	2.5
Hematite	1.3	0.5	Calcite	2.4	0.5
Kaolinite	2.1	1.5	Chlorite	6.9	3.5
Microcline	12.4	2.0	Microcline	-	
Muscovite	2.0	1.5	Muscovite	16.4	1.5
Plagioclase Albite	7.6	1.0	Plagioclase Albite	19.8	1.5
Quartz	71.0	2.5	Quartz	43.6	2.5

Agg 3 (rhyolite)_2-5mm	wt.-%	error	Agg 4 (gravel)_2-8mm	wt.-%	error
gamma-Al <sub>2</sub> O <sub>3</sub>	3.5	2.0	Biotite	7.8	2.0
Maghemite	2.7	0.5	Chlorite	10.6	2.0
Microcline	40.1	2.0	Hematite	1.8	0.5
Plagioclase Albite	19.2	2.0	Kaolinite	6.2	1.0
Quartz	37.9	2.5	Microcline	6.5	1.0
			Muskovite	9.9	1.5
			Plagioclase Albite	18.0	1.5
			Quartz	38.5	2.5

In a second step, two further aggregate materials were specifically selected based on their different Al content. Once a quartzite material with a SiO<sub>2</sub> content of more than 98wt.-% (rest is muscovite), on the other hand an andesite rock material containing a very high feldspare content. The andesite provides a relatively high amount of soluble aluminum, into alkaline solutions. Both aggregates were investigated using a grain size of 2-8 mm.

90g of each material was stored in 900ml alkaline solution containing different NaCl contents. The ratio between aggregate and solution was always 1:10. The first four aggregates were stored 56 days the last described two aggregates over duration of nearly 300 days in the alkaline solutions.

Approx. 2 ml volume was taken away from the 900ml alkaline solution at different times. In addition, here, there are differences between the first four aggregates and the second two one. During the first series, the removal took place only at 4, 14, 28 and 56 days. The second series were done in a deeper way that is why the investigation were performed until 168 and 280days respectively.

At each time, the solution, taken away from the whole system, was analysed with ICP-OES spectroscopy. The concentrations of Si, Al and of course Na were measured. In the following figures, all concentration values are specified as oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>), the recalculation bases on the dilution (varied between 1:50 until 1:200) and the relation between the molar mass of Si and SiO<sub>2</sub> (2.14) and Al and Al<sub>2</sub>O<sub>3</sub> (1.89) respectively.

### 3. RESULTS

#### 3.1 Solubility investigations up to 56 days

The following figures present the dissolution results of the four aggregates (2-8 mm grain size only) until 56days. The figures on the left demonstrate the SiO<sub>2</sub> concentrations the figures on the right contain the Al<sub>2</sub>O<sub>3</sub> concentrations for different NaCl contents. The assignment of the aggregates to rock types can be taken from Table 2.1.

Already during the storage period of only 56 days, typical solubility behaviours can be observed. The silica solubility of each aggregate increases in general in dependence on the NaCl content. The higher

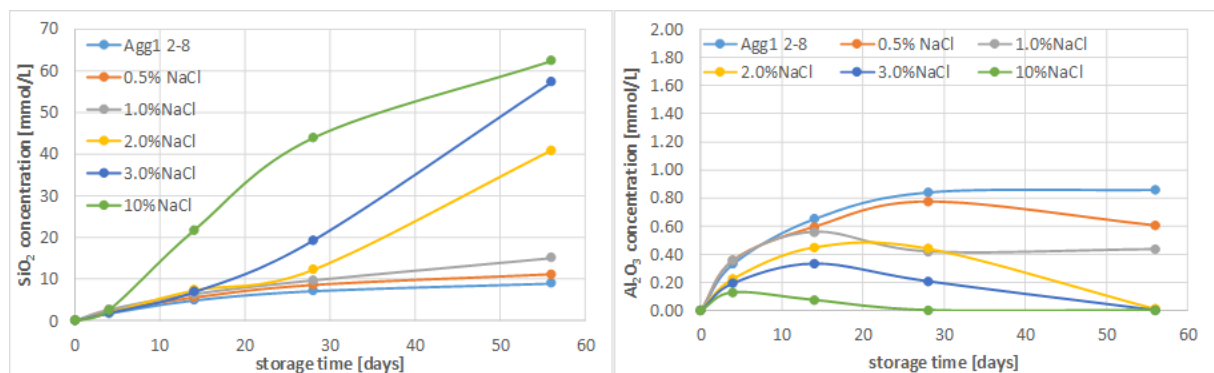


Figure 3.1: SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations of aggregate 1 (gravel)

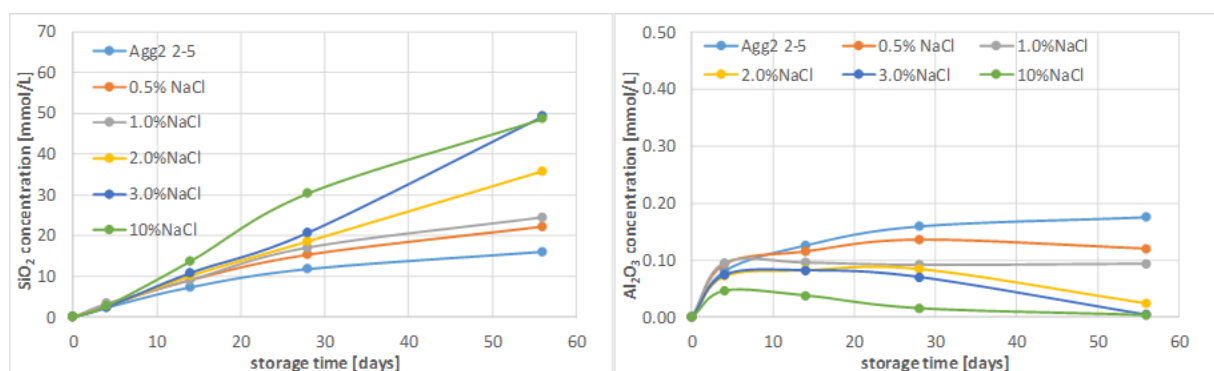


Figure 3.2: SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations of aggregate 2 (greywacke)

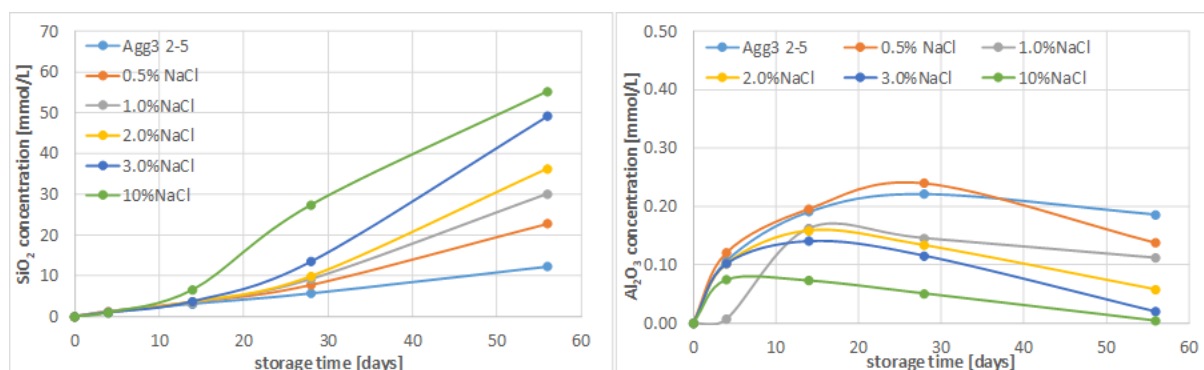


Figure 3.3: SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations of aggregate 3 (rhyolite)

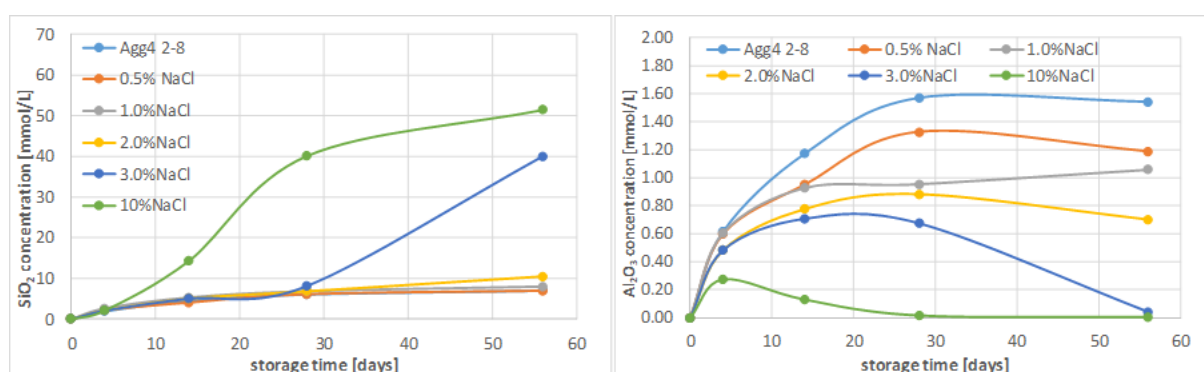


Figure 3.4: SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations of aggregate 4 (another gravel)

the NaCl concentration the higher the silica concentration in the solution after 56 days storage. In opposite to this the solubility curves of aluminum show a changed behaviour. Aluminum goes through a maximum and the time of reaching this maximum depends obviously on the NaCl content in the solution. The higher the NaCl concentration the earlier the maximum of Al release.

### 3.2 Investigations up to 280 days

Because of the fact that these measured results described in section 3.1 are obviously typical for complex aggregates, in a second series the investigations were repeated with specially selected aggregates. Q1 is a natural quartzite material, consisting of approx. 99wt.-% SiO<sub>2</sub>. The mineralogical composition is: 98-99wt.-% quartz and approx. 1-2wt.-% muscovite. Under an assumption of a typical muscovite composition K<sub>2</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>20</sub>(OH)<sub>4</sub>, the exact SiO<sub>2</sub> content can be calculated.

The other rock material is an andesite called M1. The composition can be specified with: 11wt.-% hematite (Fe<sub>2</sub>O<sub>3</sub>), 12.2wt.-% microcline (K-feldspare), 38.8wt.-% andesite, 14.5wt.-% albite (Na-feldspare) and 18.9wt.-% quartz. Based on the mineralogical composition the chemical composition can be specified especially regarding SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with: 63wt.-% SiO<sub>2</sub> and 13wt.-% Al<sub>2</sub>O<sub>3</sub>. The difference to 100% consists of other oxides.

Using these materials for solubility experiments (0.1 M KOH, 80°C) the following results can be measured.

Figure 3.5 shows the solubility of Q1 with different NaCl concentrations. It can be seen under consideration of a measurement error, that the investigated quartzite grains have the same solubility behaviour, independent of the NaCl concentration in the alkaline solution. The slope at the beginning is the same and the end values reached after approx. 100 days are in the same range too. Obviously here, the sodium ions do not have any influence on the dissolution rate and the maximum amount of SiO<sub>2</sub> in the alkaline solutions.

On the other hand, rock material M1 shows a dramatically changed behaviour as it can be seen in both parts of Figure 3.6.

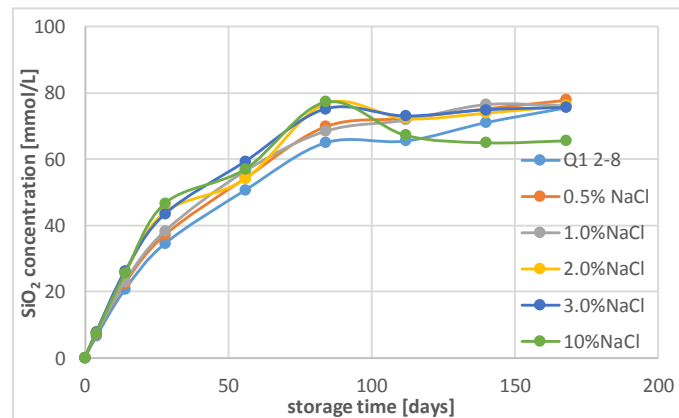


Figure 3.5: Solubility curves of quartzite stored in different NaCl solutions

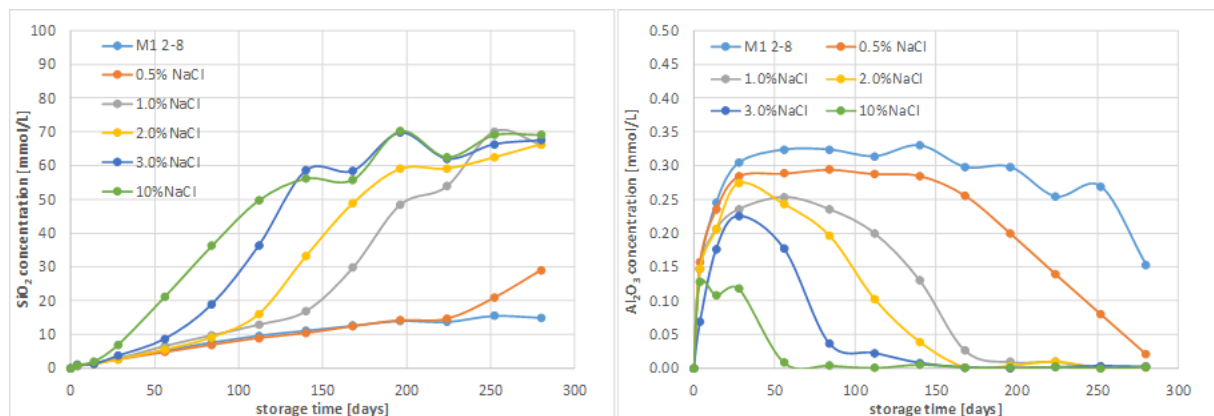


Figure 3.6: SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations of aggregate M1

The M1 material, stored in a pure KOH solution, has a very slow dissolution rate of SiO<sub>2</sub>. After 280 days, only 15 mmol/L SiO<sub>2</sub> can be determined. The same sample (pure KOH solution) delivers the highest amount of soluble aluminum in the alkaline solution. In a very short period of time the Al<sub>2</sub>O<sub>3</sub> concentration reaches the maximum, keep constant until 150 days, but decreases until the end of the investigation period (see the light blue curve in Figure 3.6 right side).

In dependence on the NaCl content in the alkaline solution, the silica solubility rate increases and reaches its maximum with 10 wt.-% NaCl content. At the same time, the maximum values of the soluble aluminum decrease and reach their minimum with 10 wt.-% NaCl content. The solubility curves of the other systems (0.5, 1, 2, 3 wt.-% NaCl) are in between. Very interesting is another fact. Independent on the NaCl content in the alkaline solution the maximum silica concentration is always the same and reaches here a value of approx. 65-70 mmol/L SiO<sub>2</sub>. It can be assumed, that the silica concentration in the system with 0.5 wt.-% NaCl will also reach this value however later. In opposite to this the maximum values of soluble aluminum depend on the NaCl content in the alkaline solution but not the dissolution rate at the beginning. As it can be seen in the figure, the slope of the Al curve is always the same. In all dissolution attempts, NaCl was added in excess, which means that the measured concentration of Na by ICP-OES did not change measurably.

These solubility results hide basic dissolution relations of natural rocks, which release not only silica but also aluminum into the alkaline solution. Additionally, sodium ions change these processes in an important way.

#### 4. DISCUSSION

What can be the first conclusions from the two pictures in Figure 3.6? The pure aggregate material M1 releases a certain amount of silica and aluminum into alkaline solutions. The silica concentration is very low but increases dependent on the added NaCl amount. It seems that the increasing silica release is

controlled by the sodium chloride concentration added. However, there is also another conclusion. The silica release is controlled by soluble aluminum, which comes from the aggregate M1 too. And the soluble amount of aluminium depends on the sodium concentration, which means when Al is reduced (e.g. here by precipitation), then the amount of SiO<sub>2</sub> in the solution increases.

Is there any chance to proof this assumption?

Figure 4.1 demonstrates the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> dissolution of the andesite material M1 summarized in one diagram without any presence of NaCl. Measured values are pointed; the coloured lines are calculated curves. The calculation bases on a thermodynamic and kinetic model developed in the last decade [12-17]. The model involves a kinetic module, which considers a surface controlled Si and Al dissolution process into the alkaline solution (for deeper information see paper for ICAAR2020 "Thermodynamic modeling of silica dissolution kinetics of quartzitic aggregates stored in highly alkaline solution" by Huenger/Kositz [18]).

The model bases on the following Equation system:

$$\left. \begin{aligned}
 \frac{dc_{Si}}{dt} &= \frac{k_{1,si} * A_{Si,eff}(t)}{V} * \left(1 - \frac{c_{Si}(t)}{c_{Si,eq}(t)}\right) \\
 \frac{dA_{Si,eff}}{dt} &= A_{Si}(t) - \frac{c_{Si}(t) * A_{Si,t=0}}{n_{Si}(t)} \\
 \frac{dc_{Si,eq}}{dt} &= \frac{dOH^-}{dt} \\
 [OH^-] &= [K^+] + [H^+] - 2[H_2SiO_4^{-2}] - [H_3SiO_4^-]
 \end{aligned} \right\} \quad (1)$$

with:

$dc_{Si}/dt$  = change of the SiO<sub>2</sub> concentration as a function of time [mol/(l\*d)],

$A_{Si,eff}$  = for dissolution processes effective surface [m<sup>2</sup>/g], changes with time t,

$V$  = volume of the alkaline solution (here 900ml), changes with each withdrawal,

$k_{1,si}$  = velocity constant of the silica release [1/d],

$c_{Si}$  = SiO<sub>2</sub> concentration of the solution at a certain time t [mol/l],

$c_{Si,eq}$  = thermodynamic equilibrium concentration of SiO<sub>2</sub> (depends on the SiO<sub>2</sub> structure and changes with the OH<sup>-</sup> concentration),

$n_{si}$  = represents the number of SiO<sub>2</sub> monomers on the mineral surface, expressed in concentrations, contains conversion factors to recalculate surfaces in concentrations

$dOH^-/dt$  = change of the OH<sup>-</sup> ion concentration during silica release.

For Al release the principle same Equation system (1) is valid (instead of si there is then al), the last line has to be extended by Al(OH)<sub>4</sub><sup>-</sup> species.

The differential Equation system (1) can be solved by numerical integration systematically with the starting condition: at time t = 0d the SiO<sub>2</sub> concentration  $c_{Si}$  and the Al<sub>2</sub>O<sub>3</sub> concentration  $c_{Al}$  respectively are zero. Each calculation step delivers a dissolved SiO<sub>2</sub> (and Al<sub>2</sub>O<sub>3</sub>) concentration, which can be recalculated from a change of the surface and a change of OH<sup>-</sup>. The new surface and the new OH<sup>-</sup> concentration enter into the next calculation step. That's why differential equations for  $A_{Si}$  and  $A_{Al}$  are required too. Additionally the equilibrium concentration  $c_{Si,eq}$  determined by thermodynamic calculations also changes because it depends on the OH<sup>-</sup> concentration too (which means on the pH value). Activity coefficients using WATEQ-Debye-Hueckel equation, valid up to I = 1Mol/kg (equations can be found in [12] and [13]) are also taken into account in the calculations.

The ionic strength I for M1 under conditions 0.1M KOH and 80°C is approx. 0.1 Mol/kg, however I increases rapidly by addition of NaCl. For 0.5 wt.-% NaCl I = 0.3 Mol/kg, for 1 wt.-% 0.5 Mol/kg (Davies limit is exceeded) and for 2 wt.-% 0.9 Mol/kg. With the addition of 3% NaCl, the limit, which the WATEQ-Debye-Hueckel theory specifies, is exceeded too.

The aluminum concentration for M1 reaches its maximum very fast (see Figure 4.1). Without any precipitation, the Al release can be described with the dark blue curve, which means that the concentration should actually remain constant. The silica release can be calculated in the same way and gives the yellow curve. Of course, the velocity constants  $k_{Si}$  and  $k_{Al}$  are different. However, after approx. 150 days the Al concentration decreases, the solution is supersaturated and the supersaturation is reduced by a precipitation of Al and surely Si species (alumino silicate species) together, probably affected by sodium in the solution. However, there is no information what happens exactly in the system because the kind and the composition of the precipitation products are unknown. In any case, cloudiness is not observed, so that no further structural analysis studies could be carried out. However, NMR investigations of the alkaline solutions gave advices that certain alumino silicate structures are formed during dissolution of natural rocks [19].

The base for every precipitation is an interaction of nucleation and crystal growth. Now, it is tried to describe these processes by the following differential Equation system (2):

$$\left. \begin{aligned} \frac{dx_{Sial}}{dt} &= (1 - x * n)^p - \left( \frac{K^3}{IAP(t)} \right) \\ \frac{dn_{Sial}}{dt} &= n^{2/3} * (1 - x * n)^q - \left( \frac{K^3}{IAP(t)} \right) \end{aligned} \right\} \quad (2).$$

with:

$dx_{Sial}/dt$  = change of the nucleation rate as a function of time, normalized to 1,

$dn_{Sial}/dt$  = change of the crystal growth rate as a function of time, normalized to 1,

$1-x*n$  = concentrations or activities respectively as the product of nucleation and crystal growth, normalized to 1,

$p, q$  = orders of the nucleation ( $p$ ) and crystal growth reaction ( $q$ ),

$IAP$  = ionic activity product as a function of time  $t$  [ $Mol^3/L^3$ ],

$K$  = equilibrium concentration of an expected sodium containing alumino silicate product [ $Mol/L$ ].

The first part of Equation system (2) describes the nucleation process as a function of the change of the ion concentration (activities). The need to set up the second equation arises from the appearance of the variable  $n$  in the first equation. The growth rate is proportional to the surface of the crystallites and the concentration (activities) of the ions, the term  $n^{2/3}$  results from the simple assumption of a linear growth in one dimension ( $dn \sim 3\sqrt{O} = 3\sqrt{6} * n^2 \sim n^{2/3}$ ).

Such a simple system was developed in the 50<sup>th</sup> and 60<sup>th</sup> of the last century [20] and used for precipitation of gypsum or other salts from supersaturated solutions in the 80<sup>th</sup> and 90<sup>th</sup> [21, 22]. Unknown in this system here are  $p$  and  $q$  as the orders of the certain reactions and of course  $K$ , the equilibrium concentration of the precipitation product. However, this system can be solved too by numerical integration and by systematical variation of the unknown parameters.

The best fit is demonstrated as the light blue curve in Figure 4.1. After a dissolution process where  $SiO_2$  and  $Al_2O_3$  go into the alkaline solution, obviously an equilibrium is reached at 150 days, and than, during the further dissolution process, even overstepped. From this time point, which can assigned an exact  $IAP$ , a precipitation process occurs. Parameters for describing this process based on Equation system (2) are:  $p=10, q=10$ , equilibrium constant  $K=0.67$   $Mol/L$ .

With a precipitation of an (assumed) Al and Si containing compound ( $Si/Al$  ratio = 35), the silica release has to decrease too. As it can be seen in the Figure, at the same time where the  $Al_2O_3$  curve decreases,  $SiO_2$  also changes (see the dark yellow curve in the figure).

Obviously, already the storage of the Al containing M1 rock material in a pure KOH solution leads to a formation of alumino silicate structures. Such structures, their compositions, their formation rates and their stabilities are of great importance for understanding the dissolution behaviour of Si and Al containing aggregates in alkaline solutions.

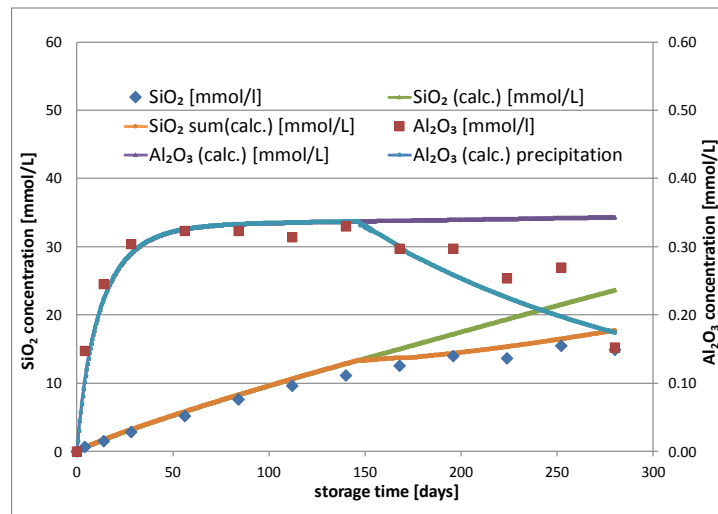


Figure 4.1: proof of the precipitation process for M1

As the investigations demonstrate, the presence of NaCl in alkaline solutions influences exactly this precipitation process (see Figure 4.2). Parameters here regarding Equation system (2) are:  $p=8$ ,  $q=10$ , however  $K=0.43$  Mol/L, in comparison to the NaCl-free system M1 a little bit lower. The Si/Al-ratio of the precipitation products what the calculation is based on is also different to the pure M1 material. Obviously structural other Al containing silicates are formed affected by the highly amount of sodium in the solution. Already during the dissolution of M1 without any added sodium, alumino silicate structures are formed. The presence of Na in the aqueous system influences the precipitation of alumino-silicate structures in an additional way.

However, what happens with the silica concentration? Exactly from this time point, where Al precipitates and alumino silicates are formed, the measured silica concentration raises up. The assumption here is, that the silica rate, better the velocity constant depends on the dissolved aluminum. The less Al in the solution, the higher the Si rate constant. The basic Si-rate constant for M1 in the presence of Al from the aggregate is  $0.06 \text{ d}^{-1}$ , which can be calculated using Equation system (1). If Al precipitates and is approx. zero or near zero, the rate constant raises up and is 200 times higher. Based on this change of the rate constant the silica release can be recalculated. Green and dark yellow curves in Figure 4.2 have approx. the same course, the influence of the precipitation on the silica concentration is low.

Based on this mechanism explained above, de-icing salts can increase the dissolution rate of silica. Aluminum free aggregates cannot show such a behaviour.

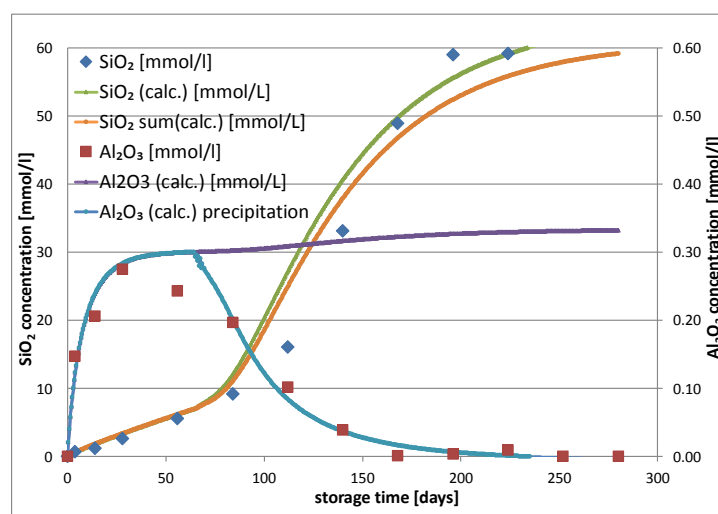


Figure 4.2: influence of the precipitation process by 2wt.-%NaCl



It is a simple nucleation and crystal growth model however, it allows to describe both processes as mathematically separately calculable curves with  $dx/dt$  as the nucleation velocity and  $dn/dt$  as the crystal growth rate. If there is no information about the precipitation products, such an approach is well suited. In addition, with it it is suitable to compare the precipitation processes, which occur under different conditions. The goal is to get deeper information on alumino silicate structures precipitates from highly alkaline solutions of complex composed rock materials.

## 5. SUMMARY AND CONCLUSIONS

Different aggregate grains were stored in highly alkaline solutions at 80°C and 0.1 M KOH variously with and without the presence of NaCl in different concentrations in the solutions. The concentrations of Al and Si were determined by using ICP-OES after certain storage times. Short time investigations gave indications that NaCl affected the silica and the aluminum release in different ways. The sodium concentration did not change measurably. The silica concentrations increased, the aluminum concentrations fell off. However only long-term experiments allow a deeper view in the dissolution process. The following conclusions can be given:

- Largely pure and crystalline silicate materials (as an example here quartzite) are hardly or not influenced in their solubility behaviour by NaCl. This affects both the solubility rate and the maximum of dissolved  $\text{SiO}_2$ .
- The most natural rock materials, which are used as aggregate grains in concrete, consist not only of silica, but also of other minerals (feldspars, micas, other oxides). In addition to  $\text{SiO}_2$ , also  $\text{Al}_2\text{O}_3$  is released to the alkaline solution. In such mostly cases the dissolution behaviour is changed.
- NaCl leads to a preferred precipitation process of probably sodium containing (because of the charge balance) alumino silicate structures.
- The precipitation process depends on the NaCl concentration in the solution and of course on the soluble Al content of the aggregates.
- As long as Al is still present in the solution, the  $\text{SiO}_2$  solubility curve does not increase or only increases marginally. Only when all Al has been consumed to form precipitation products, the Si curve rises sharply.
- However, the maxima of the  $\text{SiO}_2$  solubility are not changed ( $\text{SiO}_2$  reaches a thermodynamic equilibrium state for this conditions) but the time of reaching the maximum is dramatically changed.
- As evidence for these claims, calculations to determine concentrations of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are carried out and a kinetic model is developed, which allows describing the dissolution of rocks.
- Another, relatively simple, precipitation model is adopted from the salt precipitation processes and further developed for alumino silicates.
- Using both models the assumptions and conclusions from measured data could be confirmed.
- With further investigations on other rock materials, the conclusions should be checked and supplemented. In addition, the kinetic model has to be further developed.

Many kinetic and thermodynamic parameters in such aqueous systems are unknown. However the use of relatively simple equation systems which allow to describe the dissolution process on the one hand - equation system (1) - and the precipitation process on the other hand - equation system (2) - is a good tool to get detailed information on the dissolution behavior of natural rocks in alkaline solutions. To transfer it to concrete systems where calcium plays an additional role is the final aim.

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