ALKALI RELEASE FROM SILICATE MINERALS AND ALKALI-SILICA REACTION IN CONCRETE

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Abstract

Release of alkalis from aggregate is suggested to increase the risk of AAR. Thus the mechanism of dissolution of alkali silicates has been reviewed and experiments with expressed pore solutions have been performed.

Alkali bearing minerals, like alkali feldspars and micas, are common in granitic rocks and may release alkalis. It has been suggested that this release of alkalis can increase the risk of AAR. The release of alkalis is, however, fairly complex. It is only at low pH that the alkalis are released due to the exchange with protons. At high pH the alkali bearing minerals will dissolve and the alkalis will be released. Thus the alkali release is linked to bond-breaking and the formation of silica and aluminium complexes, which in turn consumes OH^- ions and thus lowers the pH. Basically the silica complexes together with the alkali ions will form some type of alkali silica gel. To evaluate alkali leaching the whole system including anions and effect on pH must be investigated. In leaching experiments the formed "alkali silica gel" may release the alkalis. This, however, does not automatically lead to ASR swelling.

Experiments with pore fluid expressed from different mortars with cement paste and fine mineral particles and fine ground rocks did not, at room temperature, show and any significant changes of alkali content or pH. The only exception was nepheline that was soluble. In this case alkalis were released but the pH did not increase significantly.

Keywords: Alkali-silica reaction, alkali silicate minerals, mineral dissolution, pore solution

1   INTRODUCTION

Alkali bearing minerals in aggregate can in concrete progressively release alkalis in the pore solution. The release of alkalis ions is a matter of extensive debate and is suggested to increase the risk of alkali-silica reaction [ASR]. Investigations by [1, 2, 3, and 4] have shown that the alkali content of the pore solution in concrete increases with time and suggest that this may result in increased risk of expansive ASR.

In Sweden crushed granitic rocks will, in the near future, replace natural gravel, including the fine aggregate. The fine fraction of crushed granitic rocks contains alkali bearing silicate minerals. Unstrained granites as coarse aggregate do not cause ASR in the Swedish climate, but the surface area of the fine fraction is much larger and may thus cause problems. An investigation and experiments have been performed to find out if alkali bearing minerals in the fine fraction could result in an increased risk of deleterious ASR.

To evaluate the risk of alkali release from silicates on deleterious ASR, one must consider the chemistry of mineral dissolution, alkali exchange and the influence on the mechanism of ASR. The pore solution in concrete is dominated by alkali ions and it is buffered by crystalline calcium hydroxide [portlandite]. The basic mechanism of ASR is that the hydroxide ions in the pore solution break up the Si-O-Si bonds in the silicates and that the alkali ions stabilise the silanol groups [5]. In granitic rocks the solubility is increased when the quartz micro/crypto crystalline or has a strained disordered crystal structure. The product is a gel that can absorb water and give swelling. The solubility or granitic quartz is, however, fairly slow and is linked to the pH. Thus, the ASR does occur with high alkali cement and with silica containing fragments that have a disordered structure like cataclastic fine grained rocks, rhyolites and with amorphous or finegrained silica precipitates like opal, chert etc.

In the presence of Ca^{2+} ions, a lime-alkali-silica complex forms. With enough Ca ions a non-swelling lime-alkali-silica complex may form. This complex may eventually form an alkali-free C-S-H with a CaO/SiO_2 ratio of around 1 [6, 7].

To understand the effect of alkali bearing silicate minerals, common in granites, on the pore water composition and ASR we have to consider how the alkalis are released in the whole system. The alkali release may increase the alkali content of the pore solution but do not necessarily increase the pH. One can not only consider the cations. If alkalis are released something must happen with the anions. Both the solution and the reacting compound have to be electrochemically balanced. Silicate minerals, in general, including quartz, alkali feldspar and micas are soluble at high pH [see below]. The dissolution will, however, consume OH^- ions. Another important aspect is what happens to the portlandite and how it interacts with changing composition of the pore fluid.

To find out what happens, a set of different minerals and fillers from granitic crushed rock were mixed with cement and the resulting pore solutions expressed/extracted at high pressure from the hardened mortars and those were subsequently analysed.

2 AGGREGATE SOLUBILITY

2.1 Alkali release from minerals.

Alkali ions are common in rock minerals. Both alkali feldspar K-Na $(Si_3Al)O_8$, plagioclase (albite part), biotite and muscovite $K_2Al_4(Si_6Al_2O_{20})OH_4$, that are abundant in granitoid rocks, contain alkalis.

The basic framework of the silicates is tetrahedras of Si and Al bound together by oxygen. It is either a three dimensional framework in which silica tetrahedras are linked to one another [by shared oxygen ions] in all directions or a two dimension network forming sheet or a single dimensional string of tetrahedras.

The alkali feldspars are built as three dimensional frameworks of tetrahedras containing large interstices occupied by alkali ions. The alkalis are rather irregularly co-ordinated by nine oxygen ions. The Na-feldspar (albite) is mostly in a solid solution with Ca-feldspar (anorthite) in plagioclase. In the micas [biotite, muscovite] the tetrahedras are ordered in sheets. The basic structural feature of a mica is a composite sheet in which octahedrally coordinated cations are sandwiched between two identical sheets $(SiAl)_2O_4$. One side of the sheet is bound together with octahedrally coordinated ions like Mg, Al or Fe together with hydroxyl ions, while on the other side it is bound by alkali $[K^+]$ ions.

The alkali release is complex. Cation exchange will not increase the amount of alkalis: To increase the amount of alkalis a decomposition/conversion is needed. The first conceptual cornerstone for mineral decomposition is bond-breaking and bond-formation within the overall growth and dissolution of any crystal structure [8]. The plagioclase will on decomposition and bond-breaking release Ca together with the Na ions

The alkali release at low pH is well investigated. This is due to that these reactions occur in nature where the minerals break down [9]. To start with there will be an exchange of alkali ions and protons $[H^+]$. Later the basic structure will break down and more thermodynamically stable clays will form. It is commonly known as weathering. As a result, the pH value will increase and thus the mineral reactions will buffer ground water. The exchange between protons and alkali ions is less likely at a high pH as the content of protons is low.

Feldspar dissolution in both low and high pH is described in [10]. At low pH following reaction, similar to the one with K-feldspar, will occur.

$$2\ NaAlSi_3O_8 + 2H^+ + 9\ H_2O = Al_2Si_2O_5(OH)_4 + 4\ H_4SiO_{4[aq]} + 2\ Na^+$$

This reaction releases alkali ions but it will also create a silica compound and will only take place at low pH, it is thus not relevant for concrete pore solutions. The reaction rate increases with decreasing pH. A dissolution layer will form at the mineral surface and transport trough this layer will control the alkali release.
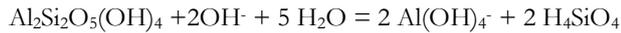
Dissolution of alkali feldspar at high pH has been investigated by [11]. The experiments show that after minima at about pH 6-8, the dissolution rate of K-feldspar increases with increasing pH. This is similar to quartz and silica compounds [12]. In acidic conditions, the result of leaching is a growing residual layer while in alkaline conditions, one observes a rapid and high release of silica and enrichment of Al on the crystal surface [13]. In the later stages the alkali

release decreases to a steady state value where the diffusional flux of alkalis equals the rate of breakdown at the solid/solution interface [14].

In basic solutions, the release of alkalis is related to the breakdown of the aluminate-silicate tetrahedral framework. This will, apart from alkalis, release aluminium and silica ion complexes [10].

$$NaAlSi_3O_8 + OH^- = Na^+ + Al(OH)_4^- + SiO_4^{4+}$$

This is similar to dissolution of clays demonstrated by kaolinite [15]

$$Al_2Si_2O_5(OH)_4 + 2OH^- + 5 H_2O = 2 Al(OH)_4^- + 2 H_4SiO_4$$

The feldspar dissolution is controlled by detachment of Si surface sites that are depronated and carry negative charge. [16]. This is similar to dissolution of quartz and silica [12] that also becomes more soluble at high pH.

The dissolution and precipitation kinetics of sheet minerals including muscovite and biotite is described in [15]. The mechanism is similar to that of feldspars. At low pH, there is an ion exchange between alkalis and protons but at high pH bond-breaking is the main mechanism. Knauss and Wolery [17] investigated muscovite dissolution at different pHs. The muscovite dissolution rates were defined by the silica, aluminium and/or potassium release to solution. Under most pH conditions, the dissolution at steady state was congruent or nearly so. The rate of dissolution will, like with alkali feldspar, go up with increasing pH.

The muscovite dissolution in alkaline solution may be written as follows [17]

$$KAl_2(Si_3AlO_{10})(OH)_2 + 7 H_2O + 5 OH^- = K^+ + 3Al(OH)_4^- + 3 SiO(OH)_3^-$$

The dissolution of biotite is more complicated but, in principle, a similar process. The biotite dissolve at high pH and the rate of dissolution increases with pH.

In conclusion; ion exchange at high pH is unlikely as the concentration or protons is low. A negative hydroxide ion cannot exchange with a positive alkali ion. Thus, an alkali release process requires demands a break down of the silicate framework. Dissolution of silicate minerals will consume hydroxide ions and will thus lower the pH. Moreover ,the dissolution will release aluminium and silicate complexes. The solubility of the silicate minerals in general increases with pH and temperature.

2.2 Mineral reactions and ASR

Bérubé et al. [3] have investigated release of alkalis from different rock types rocks in both saturated calcium hydroxide solutions and 0.7 M alkali hydroxide solutions. The solutions were maintained at 38 °C for more than a year. The solution was sampled and analysed several times during that period. The results showed that the pore solutions enriched in alkalis, but there is no information on the effect on pH. Constantiner and Diamond [4] mixed fine feldspar crystals with cement and water and the pore water was expressed. In this case, the alkali content was increased. The pH of the pore solutions was not mentioned. Yujiang et al [19] made a series of experiments to find out the effect of alkali feldspar (Alaskite rock) on ASR. Moreover, they also investigated the effect of the nepheline and calcite mineral. Nephelin [$(Na_3K)(AlSiO4)_4$] is a framework silicate but with a different structure than the other. The tetrahedras are not as strictly built up as in the alkali feldspars and it is fairly soluble in high pH solutions. Mortar prisms were tested at 20 and 80 °C. The results showed that, as expected, the nepheline quickly gave an expansion in the high temperature accelerated method. The results did also show that the alkali feldspars gave a larger expansion than the calcite. The results also showed that the relative expansion with alkali feldspar was larger if low alkali cement was used but less with a high alkali cement.

3 EXPERIMENTS

The composition of the pore fluid, which in turn is linked to AAR can be analysed by having the pore solution expressed and chemically analysed. To get a faster reaction only fine particles, of both rock powder and minerals were used.

Finely ground normal Portland (CEM I) cement with a Na_2O equivalent around 0.9 % was mixed with aggregate passing the 0.063 mm sieve. The fillers came from both different rock powders and from crushed pure minerals. As a reference, a mix was done with limestone filler [calcite] and nepheline syenite. Both these mixes are supposed to give a different pore water composition.

The mix was 1:1 in weight between filler and cement and 1:1 in weight between water and cement/filler powder. The pastes were cast in small 30 ml plastic cylinders with a diameter of 30 mm. The mix was sealed and stored for 3 month at 20 °C in a humid conditioning room to prevent drying. The pore solution was expressed from the hardened paste under high pressure. The equipment consists of a cylinder, a piston and a bottom plate containing a channel and a hole for collection of the pore fluid. This assembly is placed between the plates of a mechanical press with the sample in the cylinder. The method is the same as [4] used. The pH value was measured directly after extraction. The remaining pore solution was stabilised by a small amount of nitric acid.

The chemical composition of the expressed pore solutions solutions, Table 1, showed similar pH, ion content and ion distribution. Only the sample with nepheline syenite gave, as expected [19] different chemistry. The differences of the other samples lay within the analytical errors.
The sample with most deviation from the average was limestone powder. The limestone powder gave a somewhat higher content of sulphate and potassium. Limestone powder is known to accelerate hydration and interfere with cement hydration [20].

The nepheline releases significant amounts of sodium ions. This is linked to and increased amount of Si and Al presumably as anions. Calcium is being consumed presumably due to reaction with silica complexes. An interesting detail is that the pH has not increased significantly although the alkali content of the pore solution is much higher.

4   DISCUSSION

The alkali silicates are soluble and may release alkalis at high pH. They cannot, however, release alkalis without dissolution and bond-breaking. Both the alkali feldspars and the micas like most silicates dissolve at high pH. This must, however, involve the breakdown of the basic silicate/aluminate structure and it will, apart from alkali ions, also release silica and aluminium compounds. The mechanism of breaking up silica bonds is similar to that of breaking up silica, which is the basic reaction forming an ASR-gel. The reaction will also consume hydroxide ions that are essential to AAR. This is indicated by the nepheline syanite in the experiments where the content of alkalis increased significantly but the pH only somewhat. One can also presume that the speed of reaction is related to the mineral structure and temperature like in ASR. Fine crystalline or disordered structures will promote dissolution.

The dissolution product, consisting of silica and alkalis, will in fact be an ASR-like gel with the alkalis from the alkali minerals. A product similar to an ASR gel formed after leaching at high pH can be observed in the TEM photos shown in Fig. 11 in [18]. The formation and growth of this layer will successively decrease the speed of dissolution. With time this ASR-like gel may react with the Ca ions and form a C-S-H, which in turn may release alkali ions. The speed of reaction and kinetics will be important.

An ASR gel with low contents of Ca is water soluble and would thus give higher contents of alkalis as reported by [3]. It would also explain why the effect will be larger in a low alkali cement mortar as shown by [19]. With pore solutions extracted by high pressure or leaching also the ASR gel will go into the solution.

The investigation shows that in most cases the alkali minerals or granitic fillers do not react or dissolve very slowly. In general the alkali feldspars have an ordered structure. They do not appear as amorphous and disordered as quartz. Undulose extinction is not found. They may, however, be fine-grained like in mylonites and metarhyolites react. It is, however, still unclear if the will enhance the possibility of expansion. An increase in alkalis does not necessarily give more expansion.

5   CONCLUSIONS

Alkali minerals will dissolve at high pH. The dissolution will, however, not increase the pH of the pore solution as is consumes hydroxide ions. The dissolution will give alkali ions and silica and may form a type of ASR gel. This does not necessarily mean that there will be an additional swelling.

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TABLE 1: Chemical composition of pore solutions after 3 month. The granites and the granodiorite
Are sieved rocks powder after crushing. It mainly consists of feldspars, quartz and biotite. The alkali feldspars and calcite are pure minerals sieved to the same size. The wollastonite and nepheline syanite are industrial fine rock powder.

Rock types and minerals	pH	Ca mg/l	SO$_4$ mg/l	K mg/l	Na mg/l	Si mg/l	Al mg/l
Granite	13,4	84,0	53,6	7350	1570	nd	nd
Granite	13,4	89,8	64,2	8650	1700	nd	nd
Granite	13,5	79,2	71,9	9030	1890	nd	nd
Granite	13,4	89,2	57,2	8280	1710	nd	nd
Granodiorite	13,4	82,0	64,1	8800	1670	nd	nd
Granite	13,4	80,2	74,4	8550	1880	nd	nd
K-feldspar	13,4	85,3	73,3	9470	1620	nd	nd
Calcite	13,4	77,4	119.0	10500	1670	nd	nd
Na-feldspar	13,2	79,3	75,0	9010	1730	nd	nd
Wollastonite	13,2	94,3	54,9	9010	1420	nd	nd
Nepheline syenite	13,5	13,0	445	11500	8410	15,3	21,5

ICP-analysis, pH by glass electrode.