

Dissolution of ASR-reactive aggregates and the effect of Al on dissolution rate of amorphous silica at high pH

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Abstract

Cement-based building materials play a key role in modern infrastructures and housing because of their high performance, low cost, the availability of raw materials and relative low environmental footprint per unit mass produced [1]. The occurrence of cracking due to alkali silica reaction (ASR) can affect the service life of concrete structures. ASR is the chemical reaction between amorphous silica (from certain aggregates), water and alkalis (from the pore solution of the cement paste), which is able to produce an expansive gel which creates macroscopic expansion in concrete structures [2].

Dissolution kinetics of concrete aggregates have a direct impact on the extent of the ASR gel formation and thus on the macroscopic expansion. The main goal of the present project is to investigate and quantify the main factors determining the dissolution kinetics of ASR-reactive aggregates.

The first step of the present study was to determine which minerals were particularly reactive in three ASR-reactive aggregates from different places in Switzerland: U, B and P. Reaction tests were carried out at high pH values as also encountered in concrete pore solutions. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) indicated that mainly feldspars and quartz reacted, while little reaction of mica was observed. These observations were confirmed by solution analysis, which showed a clear increase of dissolved Si for all aggregates and of K and Al for the aggregates rich in feldspar.

In second step, the dissolution rate of amorphous silica, as a simple model system, was studied at high pH and in the presence of Al. Results of solution analysis by inductively-coupled plasma - optical emission spectrometry (ICP-OES) showed that Al slows down the dissolution rate of amorphous silica at high pH values.

Keywords: *alkali silica reaction, concrete aggregate, dissolution kinetics, amorphous silica*

1. INTRODUCTION

Building materials play a key role in modern infrastructures and housing for modern societies. In particular, cement based materials are in high demand because of their high performance, availability of raw materials, low cost and relative low environmental footprint per unit mass produced [1]. The durability of concrete structures, however, may be affected by alkali silica reaction (ASR), which can cause expansion and deterioration of the concrete in the long term (Figure 1.1).



Figure 1.1: Typical crack pattern caused by ASR. Horizontal field width = 50 cm.

ASR produces an expansive reaction product as a result of a chemical reaction between amorphous or poorly crystalline silica (from reactive aggregates) and alkalis (from the pore solution of the cement paste). The reaction product is able to create macroscopic expansion in concrete structures [2]. ASR is a worldwide durability problem and many concrete structures are suffering from ASR. In Switzerland, ASR is detected in around 10 to 20% of the concrete dams [3, 4], and more than 90% of Swiss aggregates are classified as ASR-reactive [5]. In the present study, three reactive aggregates from different locations in Switzerland (aggregate U, B and P) have been studied to determine the chemical composition of the reactive minerals. SEM technique is used to locate dissolved areas of the solid phases and to determine their chemical composition by point EDX technique. Amorphous silica has been selected as simple model system to study the effect of Al on its dissolution rate at high pH by solution analysis with ICP-OES.

2. METHODS

2.1 Dissolution of natural aggregates

2.1.1 Reactive aggregates studied

Three different aggregates from different places in Switzerland (U, B and P) have been studied to determine the chemical compositions of the reactive minerals within the aggregates. The X-ray fluorescence (XRF) and X-ray powder diffraction (XRD) analyses of the three samples are summarised in Table 2.1. The XRF analysis indicates that silica is the dominant oxide in all studied aggregates; the B aggregate contains more aluminium than U and P aggregates. Based on the XRD Rietveld analysis, U and P aggregates contain approximately 50 wt. % of quartz (SiO_2) and 26 wt. % and 16 wt. % of feldspar (albite: $\text{NaAlSi}_3\text{O}_8$ and microcline: KAlSi_3O_8), while B aggregates consist almost 25 wt. % of quartz and 50 wt. % of feldspars.

Table 2.1: Chemical and mineralogical composition of the U, B and P aggregates

Technique	Component	U	B	P
XRF (wt. %)	SiO ₂	64.3	69.1	68.0
	Al ₂ O ₃	8.8	14.3	7.2
	CaO	8.7	2.9	8.9
	K ₂ O	2.1	3.4	2.2
	MgO	2.1	1	1.9
	Fe ₂ O ₃	2.0	2.3	1.4
	Na ₂ O	1.7	3.7	1.4
	SO ₃	0.4	0.1	0.1
XRD (wt. %)	Quartz: SiO ₂ [ICSD 174]	51.4	25.1	56.3
	Feldspar: Albite: NaAlSi ₃ O ₈ [ICSD 87657]	18.3	33.5	8.3
	Feldspar: Microcline: KAlSi ₃ O ₈ [ICSD 83531]	7.3	11.7	8
	Feldspar: Orthoclase: KAlSi ₃ O ₈ [ICSD 9543]	—	5.9	—
	Mica: Muscovite 2M1: KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂ [ICSD 75952]	8.8	10.8	7.5
	Calcite: CaCO ₃ [ICSD 73446]	7	10.4	15.4
	Dolomite: CaMg(CO ₃) ₂ [ICSD 66333]	6.7	0.3	4.6
Chlorite: Clinocllore Mg ₅ Al(AlSi ₃ O ₁₀)(OH) ₈ [ICSD 66258]	0.9	2.4	—	

2.1.2 Determination of chemical compositions of the reactive minerals

Samples from each studied aggregates were randomly selected, and impregnated in epoxy under vacuum to remove any air inside the existing aggregate porosity and filling them by epoxy, following the procedure of Leemann et al. [6]. Then the samples were then impregnated under pressure and left at room temperature to be hardened for 1 day. Finally, the prepared samples were polished down to 1/4 µm. Figure 2.1 shows the surface of the samples prepared for dissolution experiments, and it clearly demonstrates that epoxy filled all the existing defects.

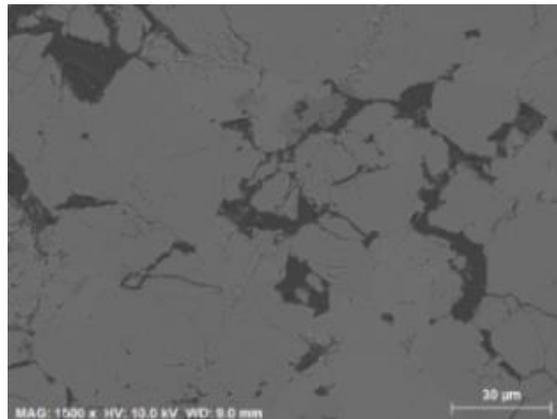


Figure 2.1: SEM backscattered image of P aggregate before dissolution experiment

SEM images were taken from the same area before and after the dissolution experiment. Carbon coating was used for SEM and EDX analyses and soft polishing disc with oil was used to remove carbon coating without creation of any new line or damage.

To accelerate the dissolution reactions of the aggregates, the prepared samples were immersed in 400 mmol/L of KOH solution, and stored at 40 °C. These conditions were selected for dissolution experiments due to similarity to real conditions for ASR. After 3 weeks, the samples were taken out of solution, washed with isopropanol, and dried in oven for 24 hours at 50 °C.

2.1.3 Solution composition

The dissolution of the aggregates was also studied in alkaline conditions using a high water to solid ratio to be able to follow the changes of the solution composition. The studied aggregates (U, B and P) were crushed, sieved to obtain the size fraction of 0.315–0.63 mm, washed with tap water to remove fine particles and dried at 100 °C for 1 day. Dissolution experiments with w/s ratio of 6 were carried out. 20 gr of each type of aggregate were immersed in 120 ml of KOH 400 mmol/L (to track the concentration of released Si, Al and Na) or in 120 ml of NaOH 400 mmol/L (to track the concentration of released K as well) at 40 °C.

At different time, sampling was done and ICP–OES was used to determine solution composition. In all the experiments, ultra–pure water was used to prepare the solutions.

2.2 Dissolution of amorphous silica

Amorphous silica from Lanno Quartz (Xinpu, China) was selected as a simple model system. Characterization of the model system was done to determine crystalline structure, particle size distribution and specific surface area. In all systems, KOH 400mM is present as a reference solution, and AlCl_3 (>99% purity) was added to the reference solution to study the effect of different concentrations of Al on dissolution rate. Water to solid ratio is 1000 (ml/gr) for all dissolution experiments to avoid precipitation during dissolution experiments. Ultra-pure water was used for all solution preparation, and the storage temperature is 40°C. Sampling at different times was done. The sample was filtered by nylon and micro filter 0.2 μm , and diluted by factor 10. ICP-OES was used to measure the concentration of the released Si from the amorphous silica.

2.3 Calculation of dissolution rates

The dissolution rate, r_X^+ , was obtained from the slope of the graph of the normalized concentration of released element X from amorphous silica or feldspar (taking into account solution volume, mass of solid and specific surface area) versus time as summarised in Equation (1) for steady-state dissolution regime and linear trend:

$$r_X^+ = \frac{d(X)}{\Delta t} \frac{v_X V_{sol}}{m S} \quad (1)$$

where v_X is the molar cation fraction of X in amorphous silica or Na-feldspar, m the mass of solid, V_{sol} is solution volume, and S corresponds the initial specific surface area of the powder.

3. RESULTS

3.1 Dissolution of natural aggregates

3.1.1 Determination of chemical compositions of reactive minerals

The surfaces of the aggregates were analysed before and after exposure in 400 mmol/L KOH by SEM to identify dissolved minerals. Figure 3.1 (a) shows SEM secondary electron images of the P aggregate surface of the reference sample before exposure, and Figure 3.1 (b) the P aggregate surface after exposure. The scratches on the reference surfaces of P aggregate, which had hardly been visible before exposure in 400 mmol/L KOH, were well visible afterwards, which shows preferential dissolution along the scratches on the surface and on the edges of the minerals.

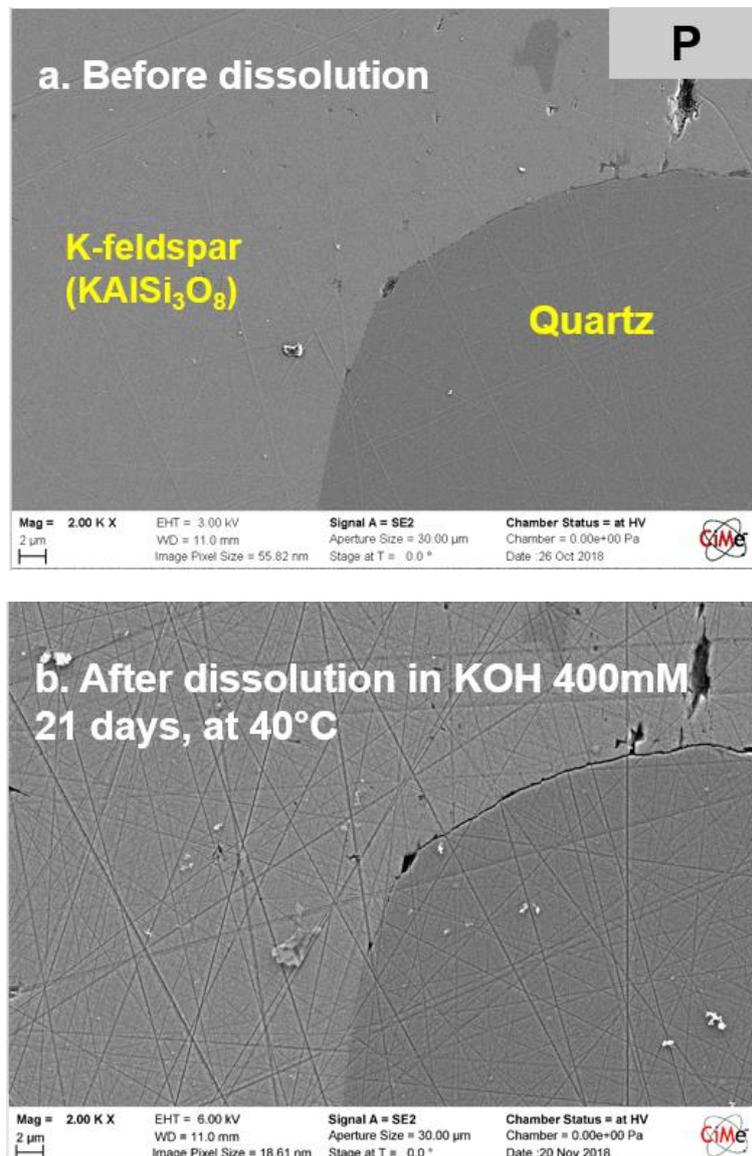


Figure 3.1: SEM secondary electron images of P aggregate a) before dissolution and b) after 21 days immersion in KOH 400mM solution at 40 °C.

Relatively fast dissolution was observed on quartz and K-feldspar (KAISi₃O₈) (see Fig 3.1). In addition, the dissolution Na-feldspar (NaAISi₃O₈) was observed in other areas by SEM and point EDX analyses, while no significant dissolution was observed for muscovite.

3.1.2 Solution composition

Figure 3.2 shows the amount of dissolved silicon from different aggregates at 40 °C as a function of time (a) in 400 mmol/L KOH and (b) in 400 mmol/L NaOH. The continuous rise of the measured concentrations with time indicate that no significant precipitation occurred during these dissolution experiments.

Based on the obtained data, no significant difference was observed in Si concentration between the NaOH and KOH, indicating that the type of alkali has no or only little influence on the dissolution of the aggregates. In both, KOH and NaOH, aggregate U was the most reactive aggregate, while aggregate B dissolved slower while aggregate P was the least reactive one. A possible reason for the higher reactivity of aggregate U could be the presence of amorphous silica as reported in [7] for aggregate U.

Based on the ICP-OES results in KOH 400 mmol/L or NaOH 400 mmol/L, around 0.3% of the SiO₂ originally present in the P and B aggregates dissolved after 63 days. Approximately, 0.5% of U aggregate dissolved in NaOH 400 mmol/L and 0.7% in KOH 400 mmol/L after 63 days.

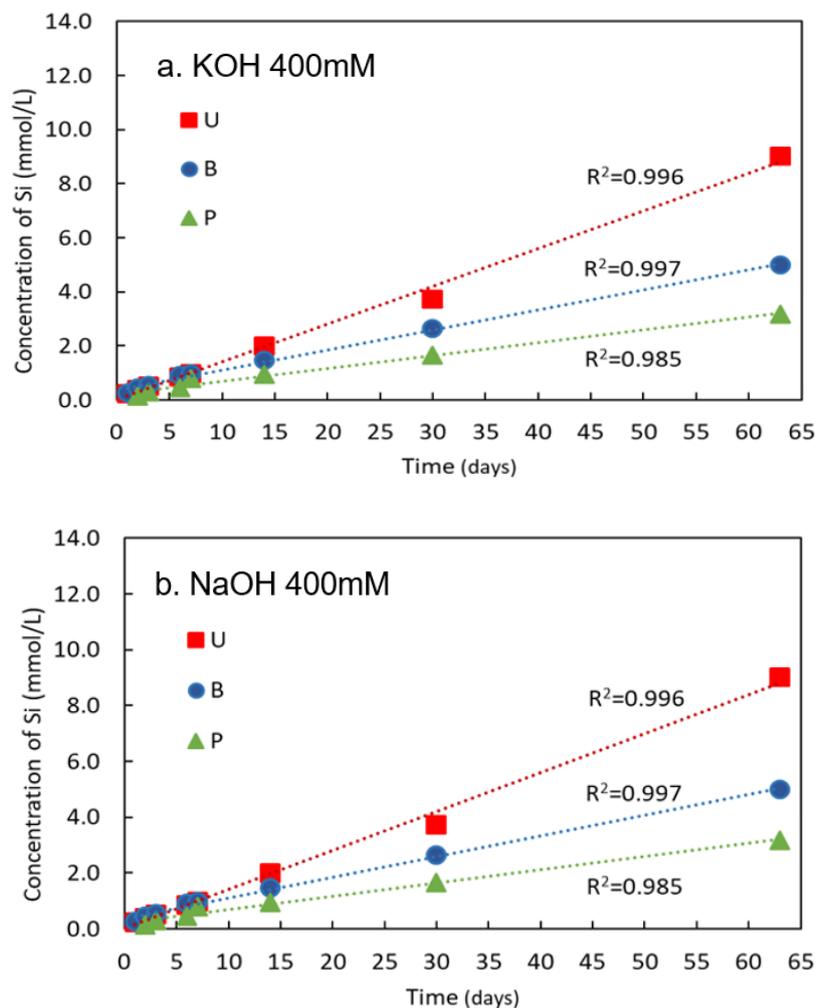


Figure 3.2: The concentration of dissolved Si from different aggregates (U, B and P) per mmol/L at 40 °C as a function of time (a) in KOH 400 mmol/L and (b) in NaOH 400 mmol/L.

In addition to Si, also increasing aluminium and alkali concentrations were measured during the dissolution test in both 400 mmol/L KOH and 400 mmol/L NaOH, confirming the dissolution of feldspar observed by SEM analysis.

3.2 Dissolution of amorphous silica

Amorphous silica is used as simple model system to study the effect of Al on its dissolution rate at high pH, as it has been observed that Al can suppress ASR [8]. Figure 3.3 shows the dissolution rate of

amorphous silica derived from the measured increase of Si concentrations as a function of time in solutions containing 400 mmol/L KOH and 0 to 3 mmol/L Al.

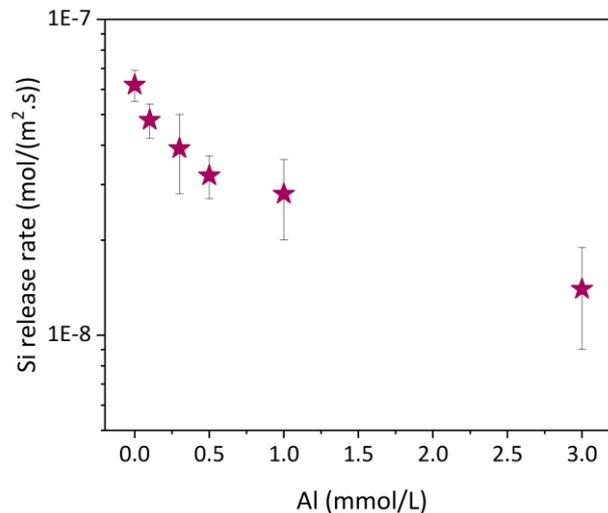


Figure 3.3: Dissolution rate of amorphous silica per mol/(m².s) as a function of Al concentration in KOH 400 mmol/L solution at 40 °C

It is obvious that increased Al concentrations slow down the dissolution rate of amorphous silica; the biggest effect was observed for 3 mmol/L Al. No significant change in pH was detected during dissolution experiments. This confirms the previous observations of a slowed down dissolution rate of silica [8], and silica rich glasses [9]. It has been suggested that such a slow down is due to the formation of bi- or multinuclear complexes of cations with the silica surface causing blockage of the surface groups [10]. Therefore, it seems possibly that Al can form surface complexes also at high pH values, which slow down the dissolution rate of silica.

4. CONCLUSION

- Quartz (possibly amorphous SiO₂), K-feldspar and Na-feldspar are reactive minerals in the studied aggregates. These minerals dissolved preferentially on mechanically damaged surface sites.
- Based on the obtained data, the increasing concentration of silica in diluted alkaline solutions is a good indicator for the determination of the reactivity of aggregates.
- At 40 °C, the type of alkali (NaOH or KOH) does not significantly affect the dissolution rate of the aggregates.
- U aggregate was identified to be the most reactive aggregate compared to B and P.
- The presence of 3mM Al in 400 mmol/L KOH slowed down the dissolution of silica by a factor of 3.

5. REFERENCES

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