Aggregate dissolution kinetics

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The alkali-silica reaction (ASR) starts with the dissolution of silica in alkali-reactive aggregates. Although the dissolution kinetics of silica has been investigated frequently, data for concrete-like environments (pH > 12) and under special influences important for concrete as the impact of NaCl (de-icer) or the release of Al from feldspars are rare or missing.

In the present study, long-term (2.5 years) dissolution tests were performed to obtain kinetic data for two types of aggregate (granodiorite, rhyolite) under concrete-like conditions (pH 13.8, with/without $Ca(OH)_2$ and NaCl) at temperatures of 25, 45 and 60 °C. The objective was to provide silica dissolution rates (r_1) appropriate for the simulation of ASR induced expansion and damage with a novel multiscale approach, reported elsewhere [1]. For the study, granodiorite and rhyolite samples were crushed, rinsed with water, sieved (0-0.5 and 0.5-1 mm) and dried at 105 °C. The samples were placed in 6 different model concrete pore solutions, sealed airtight and stored over a period of 2.5 years at 3 different temperatures. The resulting solutions were analysed (pH, ICP-OES) periodically while solids were analysed (XRD) if needed. The data were used to calculate species distributions and dissolution rates. For the latter, it was particularly considered that fractions of Si bound into Al-Si complexes are assumed to be unavailable for the ASR. Hence, the amount of Si bound into $SiAlO_3(OH)_4^{3-}$ was subtracted from the totally released Si to obtain dissolution rates effective for ASR.

The findings show that the silica dissolution rates effective for ASR differ up to 4 orders of magnitude, ranging from (log r_1) -13.13 to -9.96 mol/m²s as a function of aggregate type, temperature, presence of $Ca(OH)_2$ and NaCl concentration (Figure 1). In general, the dissolution rates increased with rising temperature and NaCl concentration and are lower in presence of $Ca(OH)_2$.

By adding NaCl, the Si concentrations increased by factors up to 15, especially at 60 °C. For the higher dissolution of silica with increasing NaCl concentration, the formation of Na-Si complexes as $Si_2(OH)_4O_3Na^-$ would be one explanation. The activation energy E_a of 84 ± 4 kJ/mol for the silica (granodiorite) dissolution is close to values reported earlier (Figure 2, left) and has not changed significantly by adding NaCl, particularly there was no decrease. This means that NaCl is not a catalyst in the chemical sense, but directly involved in the dissolution reaction, as by forming Na-Si complexes.

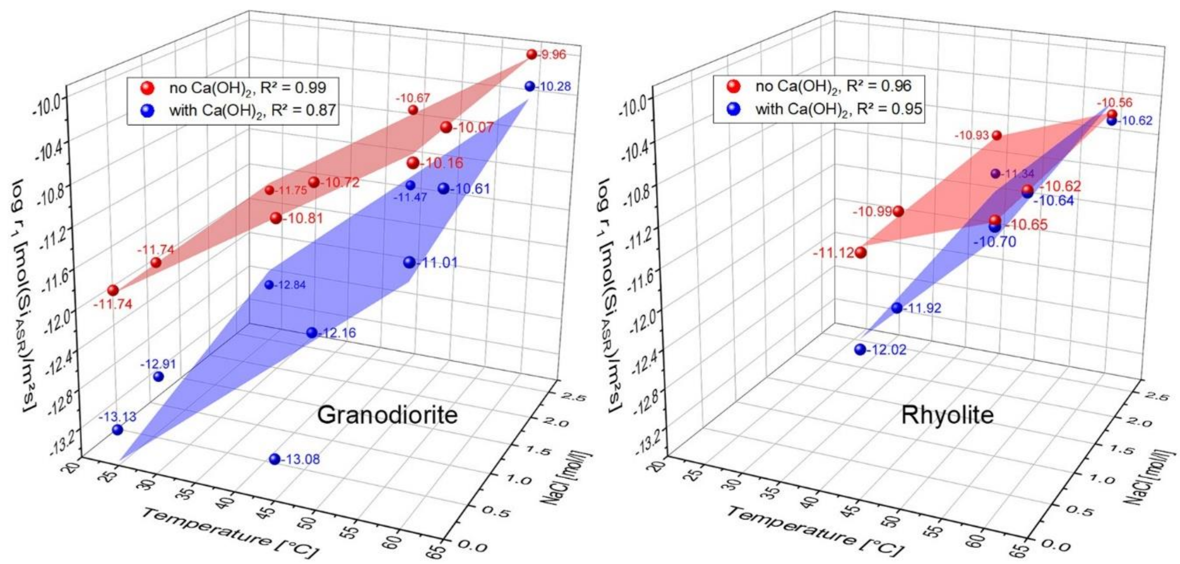

Figure 1: ASR-effective silica dissolution rates (log r_1) at quasi steady state for the different temperatures and NaCl concentrations, granodiorite (left) and rhyolite (right)

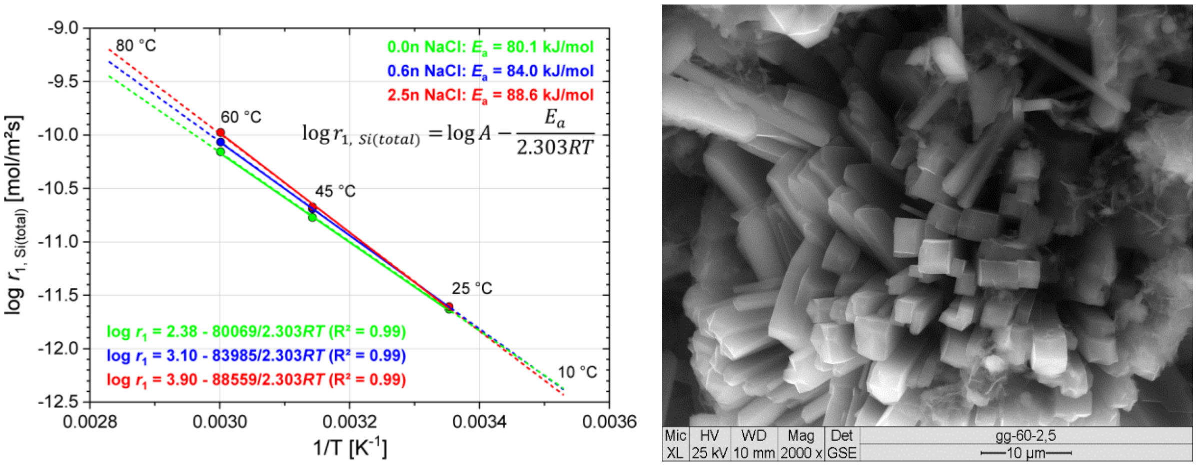

Figure 2: ARRHENIUS plots of the total silica dissolution rates (log r_1) for the granodiorite in the model pore solutions without $Ca(OH)_2$ and different NaCl concentrations (left) and SEM image (right) of a phillipsite type aluminosilicate (identified as $(K_{2.5}Na)Al_{4.7}Si_{11.3}O_{32}\cdot 13H_2O$ by XRD) as precipitate in the granodiorite (0.5-1 mm) solution at 60 °C without $Ca(OH)_2$ and 2.5 mol/l of NaCl

With increasing temperature and NaCl concentration, dissolved Al was removed faster from the solutions. Hence, Al-driven effects in decreasing the solubility of silica will be reduced under such conditions. In absence of $Ca(OH)_2$, Al was precipitated in an phillipsite type aluminosilicate (Figure 2, right) while in presence of $Ca(OH)_2$ a tobermorite type phase and an amorphous phase were evident.

In presence of $Ca(OH)_2$, the dissolution rates are lower than without $Ca(OH)_2$ but with rising temperature and NaCl concentration, the rates increased faster (Figure 1). Currently, this behaviour is not yet fully understood and requires further investigations.

For modelling, the dissolution rates can be used for different scenarios. The rates without $Ca(OH)_2$ are representative for conditions inside the aggregate grain while the rates with $Ca(OH)_2$ are representative for conditions near the cement paste. It is important to note that (1) the dissolution rates are valid for the specific aggregates and pH only, (2) in concrete the fine aggregate will release additional Si and most important (3) that it is unknown so far when and at which rate ASR gel will start to form and (if so) swell.

Overall, especially high temperatures (> 45 °C) influenced the dissolution and reaction mechanisms significantly, what confirms known issues with ASR test methods running at 60 °C or more.

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[1] Iskhakov T, Giebson C, Timothy JJ, Ludwig HM, Meschke G (2021) Deterioration of concrete due to ASR: Experiments and multiscale modeling. Cem Concr Res 149. https://doi.org/10.1016/j.cemconres.2021.106575

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