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Discussion

Reply to the discussion by C. Shi of the paper "Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity"☆

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The authors are grateful to Mr. Caijun Shi for his interest in their work, and will address hereafter the points raised in his discussion.

1. Ion exchange or chemical reactions

All comments made by Mr. Shi are based on his assumption that the only mechanism involved in the extraction tests described in the paper is ion exchange. We are in total disagreement with such an assumption.

Many studies [1–6] have clearly demonstrated that chemical reactions take place when certain mineral or aggregate particles are immersed in NaOH, KOH, or $Ca(OH)_2$ solutions, with or without solid lime in excess in the latter case. These reactions include dissolution of certain mineral phases and precipitation of new phases as well, for instance amorphous or microcrystalline CSH, CASH, and ASR products, which contain calcium, silicon, and alkalis. For instance, in the studies by Van Aardt and Visser [1] and Bérubé et al. [3], common rock-forming and soil-forming minerals, including silica minerals, feldspars, and clay minerals, were tested in a saturated lime solution with solid lime in excess; many of the minerals tested reacted in such conditions and new phases (CSH, CASH, ASR products) were formed. In the study by Choquette et al. [4], several common rock-forming and soil-forming minerals (calcite, dolomite, chert, quartz, mica, clay minerals, alkali feldspars) were unstable in a pure 1 N NaOH solution and suffered dissolution; however, new phases were not observed except for dolomite (residual brucite as a result of dedolomitization). However, Ouali [5] observed reaction products that formed during immersion of aggregate particles even in pure KOH and NaOH solutions. In the study by Fournier et al. [6], ASR gel and rosettelike microcrystalline products containing calcium, silicon, and alkalis were produced when small rock cylinders made of siliceous limestone were immersed in a 1 N NaOH solution, which indicates that calcium for the formation of calcium silicate hydrates can be supplied by the aggregates themselves, calcium carbonate (calcite) in this particular case. The presence of $Ca(OH)_2$ in excess, as in real concrete, thus allows the precipitation of CSH and CASH by combination of the calcium released by the portlandite, with the alumina and/or the silica released by the aggregates. However, as mentioned, the formation of such hydrates can also be observed even in pure KOH and KOH solutions [4, 5], since calcium can be also released by aggregates.

2. Reliability of immersion tests in NAOH and KOH solutions

Mr. Shi questions the reliability of extraction tests in 0.7 N NaOH and KOH solutions to evaluate the alkalis released by aggregates. As detailed in our reply to a discussion by Professor Tang of our paper, also published in this issue, after a few days, the concrete pore solution is largely dominated by alkali hydroxides (NaOH, KOH), the concentration of which depends on the alkali content in the portland cement used and the water to cement ratio. Calcium is only present as traces in solution. Thus, pure alkaline solutions of 0.7 N (Na,K)OH must be considered as realistic, except that portlandite, a source of Ca and OH ions in concrete, is not present.

It is clear from the literature that different ionic species (Na^+, K^+, Ca^{2+}, $H_2SiO_4^{-2}$, $Al(OH)_4^-$, etc.) can be re-

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leased with time in the concrete pore solution by various common silicate minerals present in the aggregates (e.g., silica minerals, alkali feldspars, micas, clay minerals, etc.). In the presence of calcium ions, CSH, CASH, and ASR products will readily precipitate even if just a minor amount of calcium is present in solution, like in the concrete pore solution, because of their very low product of solubility [3,4,7]. The solid portlandite or $Ca(OH)_2$ readily supplies OH ions to reach equilibrium with the cation charge in solution, mostly composed of sodium and potassium ions, and releases also calcium, which allows the precipitation of CSH and CASH. These hydrates may contain certain amounts of alkalis, as the cement hydrates do [8]. Therefore, when using immersion tests in a saturated lime solution with solid lime in excess, some of the alkalis released by the aggregates can be readily incorporated into the new reaction products formed, then underestimating the actual alkali contribution by these aggregates. In other words, the amount of alkalis released by the aggregates into a saturated lime solution may be masked by the uptake of alkali ions by CSH, CASH, and ASR products as well.

On the other hand, as for ASR, the reactions with the aggregates are mostly driven by the OH ion concentration (or the pH). These reactions consume OH ions. When NaOH and KOH solutions (with no solid lime in excess to supply OH ions) are used for the extraction of alkalis, the OH concentration thus progressively decreases due to chemical reactions with the aggregate particles, then decreasing the rate of reaction and tending to reach equilibrium. The flattening curves of alkali releases in alkaline solutions observed in our study and by Ouali [5] are likely explained by this effect. Such a decrease in the [OH] should not take place when using a lime-saturated solution with solid lime in excess, and in real concrete as well, because the lime (portlandite in concrete) will supply OH ions to reach equilibrium with the alkali ions. Even more, in such conditions, the OH ion concentration, then the pH, should increase with time as the alkali concentration increases. Such a pH increase is observed by Newton and Sykes [9] after these authors added Na_2SO_4 to a saturated lime solution (with solid lime in excess). In the recent study by Constantiner and Diamond [10], the pore solution of mortar specimens was expressed under high pressure and chemically analyzed for potassium and sodium; the results obtained clearly demonstrate, despite a very low initial alkali concentration and pH, that alkali-feldspars release significant amounts of alkalis into the pore solution and that the alkali concentration progressively increases with time, while suggesting that the OH ion concentration and the pH (not measured) also increased accordingly, based on a higher ASR activity. On the other hand, a saturated lime solution is (initially) much less aggressive than the pore solution in normal concrete, as mentioned earlier. In our study, the alkaline solutions used extracted on average about three times more alkalis from the aggregates than the lime-saturated solution (with solid lime in excess), but this may be also the result of the uptake of some of the released alkalis by the new calcium hydrates formed in the latter solution.

Thus, when using 0.7 N NaOH (for measurement of K) and KOH (for measurement of Na) solutions for alkali extraction, less reaction products are normally formed than with a saturated lime solution with solid lime in excess, but the aggressivity of the solutions, initially higher and more representative of the chemistry of the concrete pore solution, will inevitably decrease with time as the reaction progresses. It is thus important to use a high solution to aggregate ratio to minimize this depletion effect.

3. Solution to aggregate ratio

In this respect, Mr. Shi also questions the solution to aggregate ratio of 1 used in our study compared with a ratio of less than 0.1 in real concrete. However, considering that the pore solution in real concrete may contain very high (Na,K)OH concentrations up to 5 M before reaching saturation (which corresponds to more than 20 kg soluble Na_2O_e per cubic meter of concrete), it appears then preferable to use a high solution to aggregate ratio for preventing ion saturation (which would stop the reactions with the aggregates), and for minimizing depletion of OH ions (which should not take place in concrete due to the presence of portlandite) and precipitation of alkali-bearing reaction products (which would result in underestimated amounts of alkalis released by aggregates).

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