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Discussion

A reply to the discussion by Mingshu Tang 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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Professor Tang questions whether or not the alkalies released by the aggregates are as aggressive with respect to ASR as alkalies released by the cement. This question constitutes the main concern of his discussion and is very critical for the design of new concrete structures. In actual fact, the aggressive ion species towards the aggregates are the OH ions rather than the alkali ions. Professor Tang certainly does not contest that aggregates can release alkalies in the concrete pore solution, such as his question could be rewritten as it follows: "Are the alkali ions released by the aggregates increase by about the same amount the OH ions, then the pH, in the concrete pore solution?" Unfortunately, in our study, this concentration or the pH was not measured in the test solutions. However, it is our belief that the answer is yes to the above question. The mechanisms invoked hereafter are already known by Professor Tang; however, we consider important to recall them for the benefit of the readers of his discussion.

In normal concrete, after a few days, the pore solution is largely dominated by Na, K, and OH ions in the form of soluble alkali hydroxides (NaOH, KOH), while all other ions (Ca^{+2}, SO_4^{-2}, etc.) are normally present as traces in solution. For instance, in the pore solution of a concrete made with a water to cement ratio of 0.5 and a cement containing 1% Na_2O_e, according to Diamond [1], the [OH] concentration is almost equal to the alkali ($Na^+ + K^+$) concentration and around 0.74 N (pH ≈ 13.85) after 28 days and even more in the long term as a result of more complete cement hydration, which decreases the amount of pore water. So, the 0.7 N NaOH and KOH solutions used in the extraction tests described in our paper must be considered as realistic in terms of chemical composition and pH, with the exception that solid portlandite or $Ca(OH)_2$ is not present, which constitutes an important source of Ca^{+2} and OH^- ions in real concrete.

Based on a number of studies such as those by Choquette et al. [2] and Ouali [3], it is a matter of fact that some common silicate minerals present in aggregates (e.g., silica minerals, feldspars, micas, clay minerals, etc.) react in highly alkaline and basic solutions and release different ionic species (Na^+, K^+, $H_2SiO_4^{-2}$, $Al(OH)_4^-$, Ca^{+2}, etc.) with time. In the total absence of calcium in solution, these reactions consume OH ions, then the pH decreases, but the anion species released by the aggregates (e.g., $H_2SiO_4^{-2}$, $Al(OH)_4^-$) may remain in solution while satisfying to ionic equilibrium with the cations released (e.g., Na^+, K^+), and this as long as ion saturation is not achieved. For instance, in the study of Choquette et al. [2], several rock- and soil-forming silicate minerals suffered dissolution in a pure 1 N NaOH solution, while new silicate hydrates were not observed. However, in the presence of calcium in solution, even as traces, CSH, CASH, and ASR products as well, which contain calcium, silicium, and alkalies, will readily precipitate because their product of solubility is very low [2,4,5]. As discussed in more details in our reply to a discussion by Mr. Cajun Shi of our paper, also published in this issue, the formation of the above hydrates was clearly demonstrated by a number of previous studies [4,6,7] involving immersion of mineral or aggregate particles in saturated $Ca(OH)_2$ solution (with solid lime in excess). However, the formation of such hydrates was even observed in pure KOH and KOH solutions [3,8], which suggests that calcium can be also released by aggregates.

For sure, the new hydrates formed may entrap certain but limited amounts of alkalies, like the cement hydrates can do [9]. Assuming that not all alkalies released by the aggregates are entrapped in these new hydrates, the alkali concentration

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will grow up in the concrete pore solution. The solid portlandite or $Ca(OH)_2$ will then supply OH ions to reach equilibrium with the cation charge in solution, still mostly composed of alkali hydroxides, then also calcium ions that causes more precipitation of new hydrates. Consequently, the pH will grow up, which accelerates all reactions with the aggregates, including ASR.

The recent study by Constantiner and Diamond [10] supports the hypothesis that the OH ion concentration and the pH increase as alkalies are released by aggregates in the pore solution of hydraulic systems. In this study, the pore solution was expressed under high pressure from mortars made with a very low-alkali cement (0.11% Na_2O_e), an inert limestone, and incorporating or not a very reactive calcined chert and ground alkali feldspars of various types. Despite very low initial alkali and OH ion concentrations [0.088 M (Na,K)OH after 28 days for the control mortar], significant amounts of alkalies were progressively released with time with no falling off in the rate of alkali release at the end of the test, i.e., after 4 months, suggesting that the process is continuing. The authors then arise ‘‘the implication that alkali release in field concrete is likely to be a slower, but prolonged affair’’. Moreover, the comparison of the results obtained with and without the addition of K-feldspar, however, in the presence of the highly reactive calcined chert indicates that a significant proportion of the alkalies released by alkali feldspars can participate in the formation of ASR products, which ‘‘confirms that the release of alkali from aggregates in field concretes may be of importance in many practical ASR problems, especially where low alkali cements have been used in the expectation that such use would prevent ASR’’. The authors [10] conclude their paper at it follows: ‘‘Direct measurement of alkali concentrations in pore solutions expressed from mortars with and without feldspars of several kinds show that (1) feldspars (and presumably other alkali rich aggregates) embedded in a cement matrix do release alkali ions into the pore solution and (2) that if ASR-reactive aggregates are present, these released alkali ions can participate actively in ASR’’. It must be mentioned that the OH ion concentration and/or the pH were apparently not measured in this study [10]; however, the observed increase in the rate of formation of ASR products indirectly confirms that the pH increased as a result of alkali release by the alkali feldspars.

Nevertheless, as suggested by Professor Tang, a further study should be initiated, in which the OH ion concentration and/or the pH should be measured along with the sodium and potassium concentrations, in order to demonstrate more positively if whether or not the alkalies released by the aggregates are as aggressive with respect to ASR as those released by the cement, in other words that the OH ion concentration increases accordingly.

Professor Tang also comments about the alkali content in Portland cement hydrates, indicating that ‘‘alkali can’t be detained in them’’. We assume that he was meaning ‘‘in significant amounts’’. For the benefit of the readers, let us recall that the cement hydrates normally contain certain but limited amounts of alkalies, and that the alkali content is affected at some extent by the amount of total alkalies in the original system. Duchesne and Bérubé [9] have shown that the more important the total alkali in systems incorporating Portland cement and various amounts of silica fume, fly ash, or blast furnace slag, the higher is the alkali content in the cement hydrates formed. For instance, the alkali content in hydrates was on average 1.25%, 1.55%, and 2.41% Na_2O_e in systems containing 60% Portland cement, which contained 1.05% Na_2O_e and 40% fly ashes A, B, and C, which contained 2.34%, 3.07%, and 8.55% Na_2O_e, respectively, despite quite similar CaO/SiO_2 ratio in these hydrates (1.35, 1.41, and 1.40, respectively). In the meantime, the alkali content of the hydrates produced in the presence of the Portland cement only was 0.43%. It is our belief that this content would vary with the alkali content of the cement used.

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