

**MICROSTRUCTURE AND COMPOSITION OF AAR PRODUCTS
IN CONVENTIONAL STANDARD AND NEW ACCELERATED TESTING**

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ABSTRACT

Some Australian and overseas reactive and non-reactive aggregates were used in mortar bars and concrete prisms for expansion measurement under conventional standard and new accelerated testing, based on storage of specimens in 1M NaOH solution at 80°C, and storage at 38 ± 2°C, 100% RH, respectively. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) showed that specimens that did not expand in the tests contained no alkali-aggregate reaction product, whereas those that did expand in the new accelerated test contained large amounts of amorphous and crystalline reaction products. Specimens that expanded in the conventional standard mortar bar test also showed the same morphological and compositional types of reaction products but to a lesser degree. Although expansion of a given specimen occurred much more rapidly under the new accelerated than under conventional or field conditions, the reaction products appear to be the same, indicating that reaction mechanisms are the same but differ only in rates. Therefore, the use of the accelerated test to predict the alkali reactivity of aggregates in field concrete is justified.

1. INTRODUCTION

Alkali-aggregate reaction (AAR) is normally a very slow phenomenon which takes many years to manifest itself in a structure that contains the necessary ingredients for the reaction. Therefore, some form of acceleration of this reaction is required for predicting the reactivity of aggregates, to be used in projected structures, in a reasonably short time. Conventional mortar bar tests such as the Australian Standard method AS 1141-38 [1], in which mortar bars containing a high alkali cement and fine aggregate are stored at 38°C and 100% RH, are procedures for accelerating the reaction between the alkali-hydroxide and the aggregate. Although highly reactive aggregates containing opaline material result in large mortar bar expansions in a relatively short time (less than six months), less reactive materials take much longer to produce significant expansions in this test. Therefore researchers have attempted to develop more rapid accelerated tests for quick evaluation of the alkali-reactivity of aggregates.

A new accelerated method (hereafter referred to as the accelerated test or method) which is based on storage of mortar bars in 1M NaOH at 80°C has been found to give useful results in 10-22 days [2,3] in comparison with one year taken by the conventional mortar bar method. However, it could be argued that the elevated levels of alkali and temperature could result in different reaction products, and that the mechanism(s) of expansion could be different in the two methods.

This paper reports the results of scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) of specimens treated under the conditions of both methods, and provides data showing that the methods differ in reaction rate not reaction mechanism.

2. EXPERIMENTAL

For conventional testing at 38°C, 100% RH all the mortar bars (25 x 25 x 285 mm) were made according to the Australian Standard AS 1141-38 [1], and the concrete prisms (75 x 75 x 285 mm) according to AS 1012-13 [4]. The aggregates tested are listed in Table 1. The Type A cement used contained 0.84% available alkali (Na₂O equivalent), and higher alkali levels were achieved by adding KOH or NaOH to the mixing water. The specimens containing the GSN, TKA, HC, NBB and JDM aggregates were the mortar bars made for an earlier study [5] and contained added KOH to raise the alkali level of the cement to 1.38%. For mortar bars containing the other aggregates (MDH, DP, SA and JA), the level of cement alkali was raised by the addition of NaOH to 1.74% Na₂O equivalent.

Table 1. List of aggregates used for AAR testing

| Rock type | Designation | Locality | Remarks |
|---------------|-------------|---------------|-------------------------|
| Metadolerite | GSN | Western Aust. | Reactive in service |
| River gravel | TKA | Western Aust. | Reactive in testing |
| River gravel | HC | Western Aust. | Reactive in testing |
| Sandstone | NBB | Western Aust. | Shows pessimum effect |
| Metadolerite | JDM | Western Aust. | Non-reactive in testing |
| Dacite | MDH | Victoria | Reactive in service |
| Basalt | DP | Victoria | Non-reactive in service |
| Metagreywacke | SA | South Africa | Reactive in service |
| Andesite | JA | Japan | Reactive in service |

For accelerated testing, mortar bars were made as before but without the addition of alkali, and stored in 1M NaOH at 80°C as described by Shayan *et al.* [3]. After 60 days of treatment under these conditions, the specimens were removed from the NaOH bath and stored in a fog room (23°C) until they were due for SEM and EDX examination. All the specimens to be examined were broken open and selected pieces were dried at 50°C for 3 days, then prepared for SEM examination. Mortar portions separated from some specimens were also subjected to X-ray powder diffraction (XRD) analysis.

3. RESULTS AND DISCUSSION

3.1 Testing for reactivity

Results of expansion measurements made on specimens subjected to the accelerated and conventional tests are given in Table 2. Although mortar bars made with the reactive aggregates expanded more than 0.1% in 10 days in the accelerated test, the 20 day results are given to show that those made with the non-reactive aggregates (DP and JDM) did not expand. The reactive aggregates also resulted in significant expansions in either mortar bars or concrete prisms or both, except for the NBB specimens which did not expand significantly in conventional tests, but showed a pessimum effect in the accelerated test.

3.2 Scanning electron microscopy

3.2.1 Field concrete. The microstructure and composition of reaction products found in structures where GSN and MDH aggregates had been used have been reported previously [6,7]. These are similar to reaction products found in other structures in Australia [8], South Africa [9,10],

and Canada [11]. In the following sections it will be shown that these reaction products also form in mortar or concrete specimens subjected to the conventional or accelerated tests.

Table 2. Expansion of mortar and concrete specimens made with difference aggregates at the given ages

| Aggregate | Accelerated test – expansion of mortar bars at 20 days (%) | AS 1141-38 (38°C, 100% RH) | | | |
|-----------|--|----------------------------|-------------------------------|------------------------|-------------------------------|
| | | Mortar bar | | Concrete prism | |
| | | Alkali level (%) | Expansion at 1 year (%) | Alkali level (%) | Expansion at 1 year (%) |
| GSN | 0.207 | 1.38 | 0.097 | 1.8 | 0.057 |
| TKA | 0.270 | 1.38 | 0.048* | 1.8 | 0.048 |
| HC | 0.243 | 1.38 | 0.102 | 1.8 | 0.018 |
| NBB | 0.027† | 1.38 | 0.014 | 1.8 | 0.011 |
| JDM | 0.040 | 1.74 | 0.027‡ | 2.0 | 0.024‡ |
| MDH | 0.373 | 1.74 | 0.036 | 1.38 | 0.096 |
| DP | 0.018 | 2.0 | 0.025 | 1.8 | 0.010 |
| SA | 0.426 | 1.74 | 0.042 | 2.0 | 0.142 |
| JA | 0.418 | 1.74 | 0.036 | 2.0 | 0.190 |

* Abundant gel formation.

† Shows pessimum effect; 15% NBB + 85% DP expands to 0.101% at 21 days.

‡ Specimens 38 weeks old.

3.2.2 **Mortar bars in 1M NaOH at 80°C.** Most specimens, particularly those containing the SA and JA aggregates, developed a white crust on their exterior during the accelerated testing in NaOH at 80°C. This soft material was scraped off with a blade and subjected to X-ray diffraction. In the case of the JA aggregate, the material was a mixture of calcite, aragonite and vaterite (all varieties of CaCO_3) in a decreasing order, and amorphous material (gel) which gave a very diffuse reflection at about 12-14 Å and a hump around 3.2 Å spacing. In the case of the SA aggregate the white crust was a mixture of calcite, monohydrocalcite, aragonite and a tobermonite phase (11.3 Å) which produced distinct reflections in addition to the amorphous material that produced a hump at about 3.2 Å spacing. Crusts on the mortar bars made with the other aggregates, particularly the less reactive ones were less pronounced and were assumed to be the same as those mentioned above and were not studied further. Bulk samples of some of the mortar bars were also studied by XRD but the only newly formed phases detected were calcium carbonate and tobermonite, despite the fact that other crystalline AAR products were visible under the SEM. No AAR products were found in the specimens that contained the non-reactive aggregates.

Figures 1 and 2 show scanning electron micrographs of a variety of reaction products observed within the mortar specimens subjected to the accelerated tests. They vary from massive gel (Fig. 1a) and spongy material (Fig. 1b) to partially crystalline (Figs 1c-e) and well-formed platy crystals (Fig. 1f and Figs 2a-e) sometimes in a rosette shape. All or most of these morphological forms were found in each of the mortar bars that contained the reactive aggregates. The composition of these phases were rather similar. As indicated in Fig. 3, all were Na-rich calcium silicates except that where the aggregate contained a potassium-rich silicate the reaction product also contained this element (e.g., Fig. 3b). It is clear that the gel material is the precursor to the crystalline platy or rosette-shaped materials as seen in Figs 1d and 1e, where the crystalline materials are being formed from the gel.

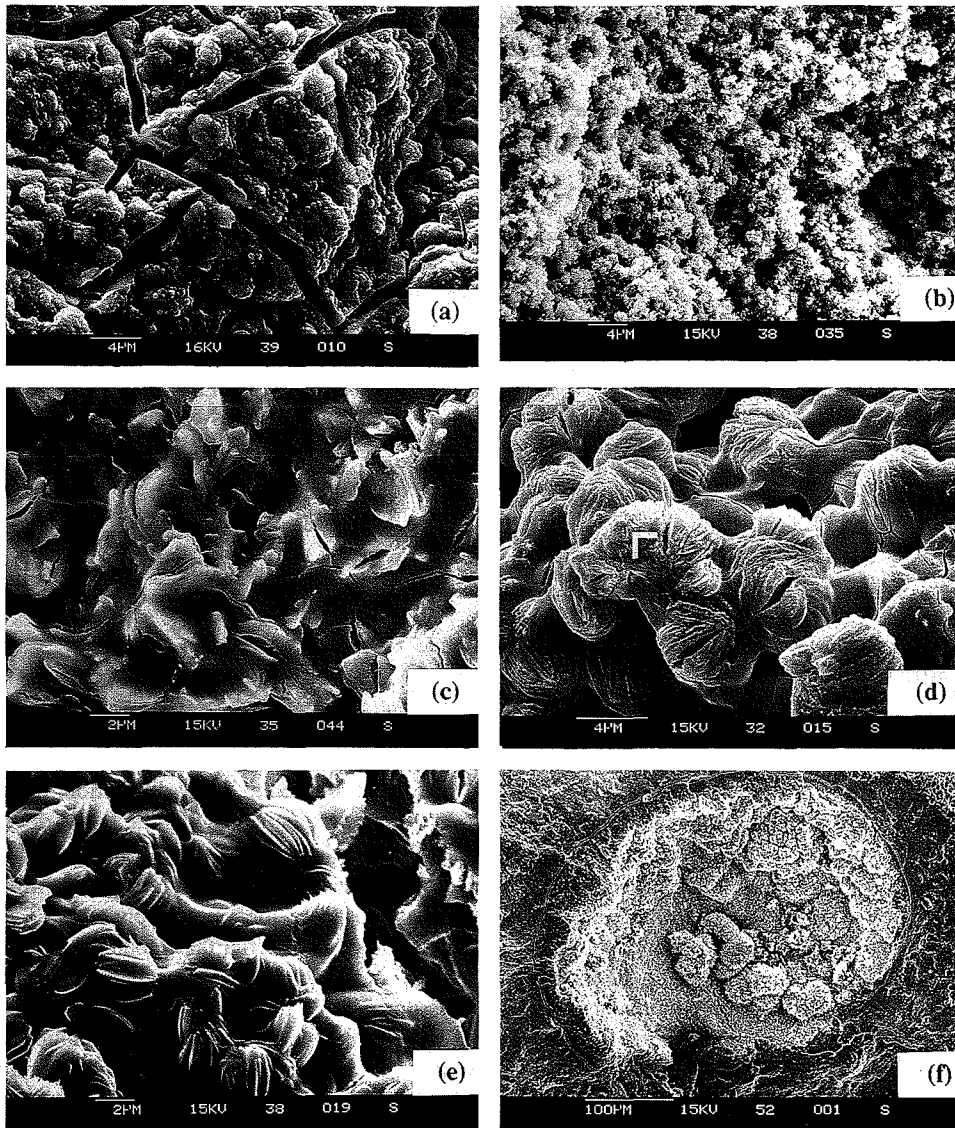


Figure 1. Scanning electron micrographs of some gel and partially crystalline products formed within mortar bars subjected to 1M NaOH at 80°C. Aggregates used were (a) GSN, (b) MDH, (c) TKA, (d) JA, (e) MDH, and (f) HC. Formation of rosette-type crystals from gel is evident in (d) and (e). (f) shows residue of a reactive particle, now a crystalline mass (see Fig. 2d) formed due to reaction with alkali.

Considering the large amount of Na available in the accelerated test, the morphological and compositional features of the reaction products formed in the specimens containing the reactive aggregates are very similar to those found in concretes affected by AAR [6-11] indicating that the reaction products and probably mechanisms are the same but differ in rates of reaction. This

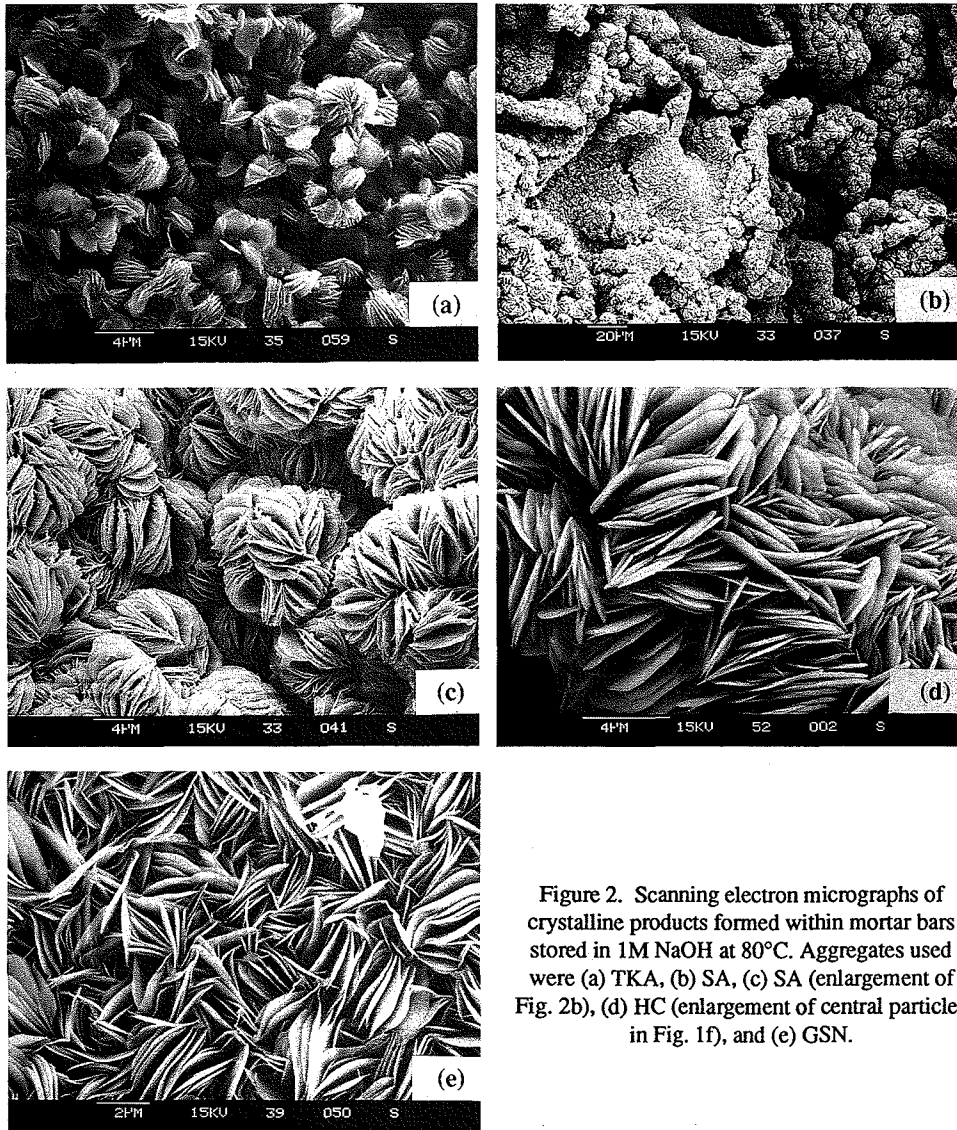


Figure 2. Scanning electron micrographs of crystalline products formed within mortar bars stored in 1M NaOH at 80°C. Aggregates used were (a) TKA, (b) SA, (c) SA (enlargement of Fig. 2b), (d) HC (enlargement of central particles in Fig. 1f), and (e) GSN.

justifies the use of the accelerated test to predict the reactivity of aggregates in concrete. Concurrent with our work, Davies and Oberholster [12] reported similar findings in relation to the similarity of reaction products in field concrete and specimens subjected to 1M NaOH at 80°C.

3.2.3 Mortar specimens at 38°C, 100% RH. Mortar bars that contained the non-reactive aggregates and showed no significant expansion at one year did not contain any AAR product. Those made with the very reactive SA and JA aggregates, although containing some massive gel, like that shown in Fig. 1a, did not contain any crystalline reaction products. This is in agreement with the low expansion values at one year (Table 2) which probably arose from a lower Na/Si ratio in mortar bars containing fine aggregate than in concrete specimens made with coarse aggregates, which expanded considerably at one year and did contain large amounts of AAR products. Mortar

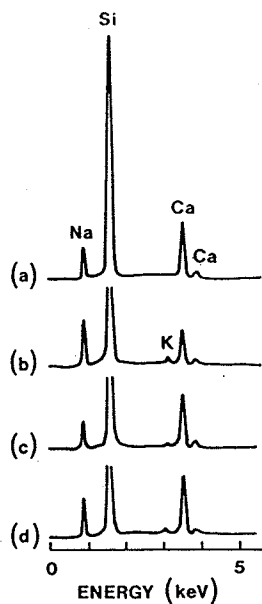


Figure 3. Representative energy-dispersive X-ray spectra showing composition of (a) platy crystals shown in Fig. 2d; (b) spongy gel material shown in Fig. 1b. Materials shown in Fig. 1e also had the same composition. The K content originates from the aggregate constituents. (c) platy crystals shown in Fig. 2e. Rosette crystals in Figs 2c and 1d had a similar composition. (d) massive gel shown in Fig. 1c (also crystalline material shown in Fig. 2a).

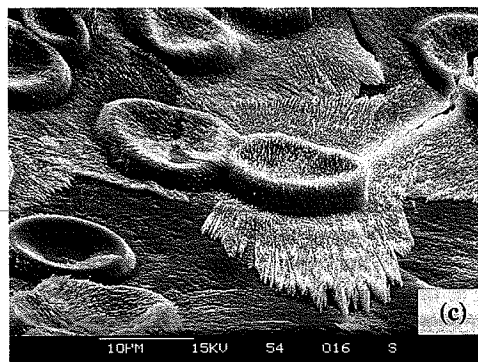
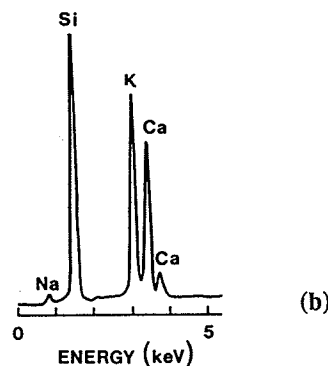
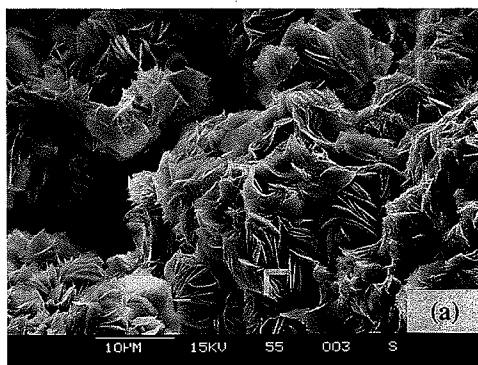


Figure 4. Scanning electron micrograph (a), and energy-dispersive spectrum of platy crystals (b), of some reaction product formed within mortar bars made with the HC aggregate and subjected to standard (AS 1141-38) testing. KOH was added to the mix to increase the alkali level of the cement. (c) shows secondary calcium carbonate grown on gel products in a three-year-old mortar bar made with the GSN aggregate.

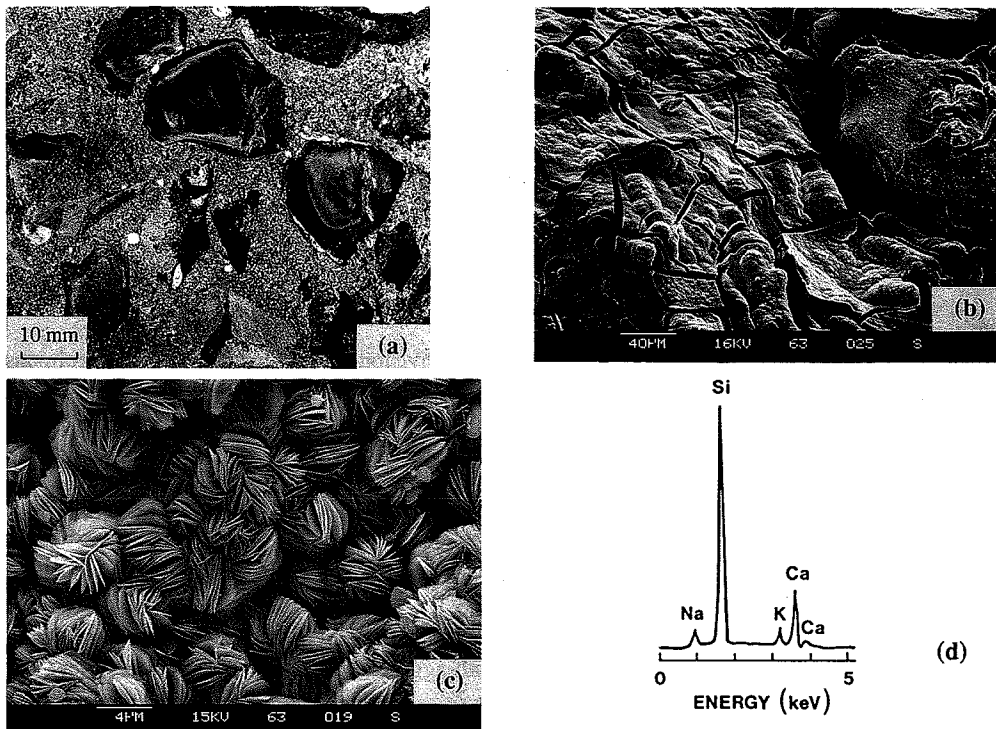


Figure 5. (a) photograph of fracture surface of a concrete prism made with the SA aggregate at cement alkali level of 1.74% Na_2O equivalent. Reaction rims around aggregate particles and pores filled with reaction product are evident; (b) scanning electron micrograph of massive gel surrounding the reacted particle right of centre in (a); (c) scanning electron micrograph of the white rim surrounding the reacted particle in (a); (d) energy dispersive spectrum of the platy crystals in (c).

bars that showed relatively large expansions at one year, e.g., those made with the GSN, TKA, and HC aggregates (Table 2) contained the various forms of the reaction products, as seen in Fig. 4 for the HC specimen. The platy crystals shown in Fig. 4a had the composition shown by the EDX analysis (Fig. 4b) and was rich in K because the mortar bars contained added KOH (Shayan *et al.* [5]). Because these mortar bars were about three years old at the time of examination they had become carbonated to some extent as shown by the secondary calcium carbonate developed on the massive gel (Fig. 4c). Except for the understandable K-rich nature of the reaction products in these specimens they are very similar to those formed under the accelerated conditions and in reacted field concretes.

3.2.4 Concrete prisms at 38°C, 100% R.H. Concrete prisms that showed small expansions, as expected, did not contain reaction products but those that showed large expansions, particularly those made with the SA and JA aggregates (for which mortar bars showed small expansions and little reaction products) cracked considerably and contained a large amount of reaction products. Figure 5 shows some features observed for the SA concrete prism. The fracture surface of the concrete (Fig. 5a) shows reaction rims and pores filled with reaction products. Massive gel (Fig. 5b) is present around the reacted aggregates, and the microstructure of the reaction rim (Fig. 5c) and its composition (Fig. 5d) are very similar to those found in specimens treated under the accelerated conditions (Fig. 2c), and in structures made with this aggregate and suffering from AAR [12].

4. CONCLUSION

This work has provided evidence that the reaction products formed under the conditions of the accelerated test are similar to those formed in concrete and in specimens subjected to the conditions of the standard test, although they form at a faster rate under the accelerated conditions. It is therefore justified to use this accelerated test (storage of mortar bars in 1M NaOH solution at 80°C) to predict the potential reactivity of aggregates in concrete.

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