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The effect of metakaolin on alkali–silica reaction in concrete

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Abstract

This article reports on a study to evaluate the efficacy of high-reactivity metakaolin (HRM) in controlling expansion due to alkali–silica reaction (ASR). The expansion of concretes and mortars containing 0–20% HRM as a partial replacement for OPC was studied. Concrete prisms were prepared according to the CAN/CSA A23.2-14A concrete prism method with two alkali–silica reactive aggregates: a siliceous limestone (Spratt) and a greywacke-argillite gravel (Sudbury). The amount of HRM required to control the expansion to <0.04% at 2 years was found to be between 10% and 15% depending on the aggregate. A modified version of the accelerated mortar bar method (CAN/CSA A23.2-25A) was also conducted with HRM and both reactive aggregates. In addition to expansion testing, the chemistry of expressed pore solutions from cement pastes containing 0%, 10%, and 20% metakaolin was determined over a 2-year period. Incorporation of 20% metakaolin was found to significantly reduce the long-term OH^-, Na^+, and K^+ ion concentrations in pore solutions. The reduction in the pH and the alkalinity of pore solutions correlate well with the observed reduction in expansion of the concrete prisms and mortar bars. © 2000 Elsevier Science Inc. All rights reserved.

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1. Introduction

High-reactivity metakaolin[1] (HRM) is a mineral admixture, which is relatively new to the concrete industry that has the potential for improving the durability of concrete. HRM differs from the more commonly used mineral admixtures, such as fly ash and silica fume, in that it is not a by-product; it is manufactured under a carefully controlled process by thermally activating purified kaolinite clay within a specific temperature range (650–800°C). The resulting anhydrous alumino-silicate ($Al_2Si_2O_7$) is mainly amorphous material, which behaves as a highly reactive artificial pozzolan.

The pozzolanic nature of metakaolin has been reported [1,2]. When used as a partial replacement for OPC, metakaolin is capable of reacting with portlandite to form supplementary calcium-silicate-hydrate similar in composition and structure to those obtained from Portland cement [2]. Research has shown that for metakaolin produced from china clay, the supplementary calcium-silicate-hydrate that are formed have a low Ca:Si ratio (in the range of 0.8 to 1.5), which allows them to entrap alkali ions from the pore solution [3]. Reduction in alkalinity (and associated pH) in the pore solution and depletion of portlandite are considered as the most beneficial effects of pozzolans in reducing expansion due to alkali–silica reaction (ASR). In light of this, the potential for using metakaolin to control alkali–silica expansion in concrete has been reported [3–5].

This article reports on a study to evaluate the efficacy of a commercial grade of HRM in controlling the expansion due to ASR. Two laboratory test methods were performed to determine the minimum effective level of HRM required as a partial cement replacement to control deleterious expansion in the presence of reactive aggregates. The results of the expansion tests are compared to the chemistry of expressed pore solutions to help elucidate the mechanisms by which HRM may suppress expansion.

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[1] The term “high-reactivity” is used to distinguish a white, purified, manufactured, thermally activated kaolinite from lesser reactive calcined clay pozzolans, which contain impurities that cannot be activated to a pozzolanic form at the temperatures used to produce metakaolin.

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Table 1
Chemical composition of HRM and cements

		Type 10 Portland cement		
Oxide (%)	HRM	A	B	C
SiO_2	52.06	20.83	22.28	19.97
Al_2O_3	45.29	5.11	4.02	5.08
Fe_2O_3	0.60	2.01	2.55	2.26
TiO_2	1.64	0.24	0.20	–
Mn_2O_3	0.02	0.05	0.05	–
MgO	0.00	2.43	2.57	2.66
CaO	0.05	62.98	63.27	62.69
Na_2O	0.21	0.28	0.22	0.30
K_2O	0.16	1.12	0.47	1.04
P_2O_5	0.10	0.13	0.05	–
SrO	0.10	0.08	0.06	–
SO_3	0.00	3.25	2.66	3.30
LOI	0.51	0.92	1.52	2.20
% Na_2O_e	0.32	1.02	0.61	0.98

2. Materials

The chemical composition of the HRM and the Portland cements used in this study are presented in Table 1. The three cements used in this study met the CSA A5 Specification for Type 10 cements (and the ASTM C 150 Specification for Type I cements). Table 2 shows the physical properties of the HRM used in this study. This material was produced from Georgia (USA) kaolin that has been water-processed to remove impurities. Additionally, two known reactive aggregates were used for expansion tests: a highly reactive siliceous limestone aggregate from the Spratt Quarry in Ottawa, Ontario and a lesser reactive greywacke-argillite gravel from Sudbury, Ontario.

3. Experimental methods

According to the Canadian Standards Association CSA A23.1-94 Appendix B, the most suitable method for assessing the efficacy of pozzolans and slag in reducing expansion due to ASR is the CAN/CSA A23.2-14A (similar to ASTM C 1293) concrete prism method (Potential Expansivity of Aggregates, Procedure for Length Change due to Alkali–Aggregate Reaction in Concrete Prisms). Current experience suggests that a 2-year testing period is sufficient for the evaluation of mineral admixtures, with an expansion limit criterion of 0.04%.

In accordance with the standard, concrete prisms (75 × 75 × 300 mm) were cast with each coarse reactive aggregate, a non-deleteriously reactive sand, and a normal Type 10 high-alkali Portland cement with a 1.02% equivalent soda content (or Na_2O_e). Prisms containing the Spratt aggregate were cast with 0%, 5%, 10%, 15%, and 20% HRM as a partial cement replacement, and prisms containing the Sudbury aggregate were cast with 0%, 10%, and 15% HRM replacement levels. Concrete mixes were proportioned to have a total cementitious material (C+HRM) content of 420 kg/m^3 and a water–cementitious material ratio (W/(C+HRM)) controlled between 0.42 and 0.45. In concrete mixes containing 10% or more HRM, a calcium-based high-range water-reducer was used to maintain workability. The total alkali content of the concrete was increased to 1.25% Na_2O_e by mass of the Portland cement by adding technical grade NaOH to the mixing water. Concrete prisms were demolded 24 h after casting and subsequently stored at 38°C above water in sealed plastic pails, which were lined with a saturated absorbent paper to maintain 100% RH. Length change measurements were taken periodically over 2 years.

The accelerated mortar bar method (CAN/CSA A23.2-25A or ASTM C 1260), modified for testing mineral admixtures, was also conducted. Although there has been a reluctance to adopt the accelerated mortar bar method for evaluating the efficiency of pozzolans and slag, the newly revised Canadian Standard for Supplementary Cementing Materials (CAN/CSA A23.5-98) allows the use of the accelerated mortar bar method as an optional requirement for assessing the ability of fly ash, slag, silica fume, and natural pozzolans to control expansion due to ASR. It is thought that this standard is the first to include the accelerated mortar bar method for evaluating preventive measures. The standard requires that mineral admixtures be tested for a range of replacement levels to determine the minimum ‘safe level’ required to limit expansion in the presence of an alkali–silica reactive aggregate to $\leq 0.10\%$ at the end of the test period. The standard further requires that the reactive aggregate used in the test produce expansions of at least 0.30% when tested without mineral admixtures.

Mortar bars (25 × 25 × 285 mm) were cast with each reactive aggregate (crushed and graded in accordance with CAN/CSA A23.2-25A), a normal Type 10 high-alkali cement (0.98% Na_2O_e), and the same levels of HRM used in the concrete prism test. Mortar mixes were proportioned to have an aggregate–cementitious material ratio of 2.25 and a water–cementitious material ratio of 0.5. It should be noted that a high-range water-reducer was not used in any of the mortar mixes. Consequently, mortars with 15% and 20% HRM had considerably reduced flow and required a greater effort to compact. Mortar bars were subsequently stored in a 1 M NaOH immersion solution at 80°C for 14 days and the length change was measured.

Table 2
Physical properties of HRM

Property	
BET surface area, m^2/g	15
Particle size distribution	
% < 5 μm	86
% < 2 μm	62
% < 1 μm	41
% < 0.5 μm	12
+325 mesh residue (wet), %	< 0.1
G.E. brightness	86

In conjunction with expansion testing, pore solutions were expressed from cement pastes for chemical analyses over a 2-year period. Paste cylinders (Ø50 × 100 mm) were cast at a W/(C+HRM) ratio of 0.5 with 0%, 10%, and 20% HRM and two normal Type 10 cements: a high-alkali cement (1.02% Na_2O_e) and a moderate-alkali cement (0.61% Na_2O_e). Pastes were mixed in a high-speed blender to provide a shearing force sufficient to disperse the HRM. A high-range water-reducer was used in mixes containing 20% HRM to ensure proper mixing. The paste cylinders were sealed to prevent evaporation and stored at room temperature above water. Pore solutions were expressed using a high-pressure extraction method with a maximum applied pressure of 540 MPa. The OH^- ion concentration of pore solutions was determined by direct titration against 0.05-M H_2SO_4 solution; Na^+ and K^+ ion concentrations were determined by flame-photometry.

4. Results and discussion

4.1. Chemistry of pore solution in pastes

Figs. 1 and 2 show the hydroxyl ion concentration of expressed pore solutions from pastes containing 0%, 10%, and 20% HRM as a function of curing time, for both high- and moderate-alkali cements, respectively. For high hydroxyl ion concentrations, the relationship $[OH^-] \approx [Na^+] + [K^+]$ was generally observed.

The alkalinity of pore solutions from the control specimens (0% HRM) increased slightly over time; this is most likely a result of hydration, which consumes pore water, resulting in an increase of all ion concentrations in solution. At 7 days, pastes containing 10% or 20% HRM had significantly lower pore solution alkalinity than control pastes. However, in pastes with only 10% HRM, an increase in the hydroxyl ion concentration was observed beyond 7 days. This might suggest that at a 10% level of replacement, alkalis that may initially be entrapped in the supplementary calcium-silicate-hydrate formed by pozzolanic reaction, are later released. It has been reported that in cement pastes containing 10% or less metakaolin, there is a marked increase in the portlandite content between 14 and 28 days [6]. With this in mind, it is possible that for lower metakaolin contents (~10%), when all of the HRM is consumed by pozzolanic reaction, excess calcium hydroxide becomes available from subsequent hydration and cation exchange of Ca^{2+} with the Na^+ and K^+ ions entrapped in the supplementary calcium-silicate-hydrate occurs, releasing these alkalis to the pore solution over time. There is no indication that this behavior is a result of the HRM contributing alkalis to the pore solution. Furthermore, an increase in pore solution alkalinity was not observed in pastes containing 20% HRM; presumably, because there is sufficient metakaolin available for pozzolanic reaction to restrict the availability of calcium hydroxide.

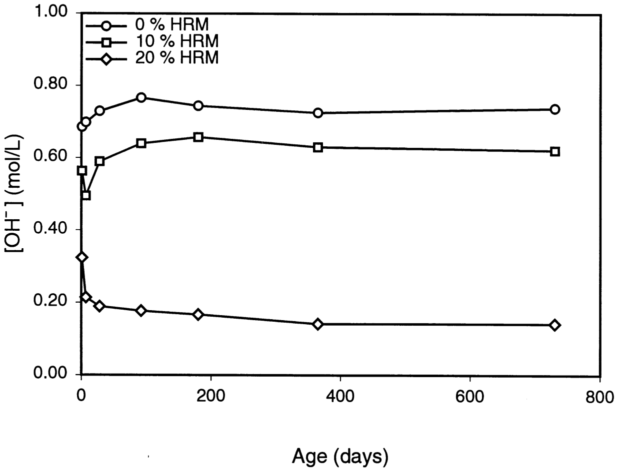

Fig. 1. Hydroxyl ion concentration of pore solutions expressed from pastes containing HRM and a high-alkali cement (cement A).

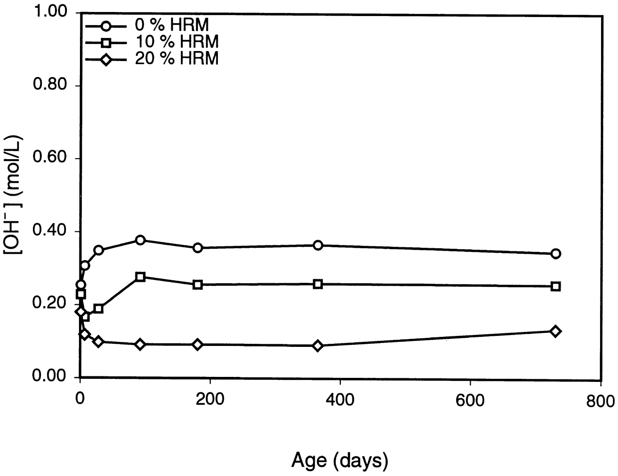

Fig. 2. Hydroxyl ion concentration of pore solutions expressed from pastes containing HRM and a moderate-alkali cement (cement B).

The long-term reduction in the alkalinity of pore solutions in pastes containing 10% HRM was not significantly more than would occur by replacing 10% of the cement with an inert material. In the pastes containing 20% HRM, however, the reduction in alkalinity was greater than 75%, and the long-term OH^- concentration was reduced to less than 0.20 to 0.25 mol/l, which is suggested as the alkalinity required to sustain ASR [7,8]. It was also observed that the reduction in OH^- concentration was greater in the pastes made with the high-alkali cement, which may indicate that there is a threshold concentration below which alkalis are no longer entrapped in the supplementary hydrates or that alkalis are more readily entrapped at higher alkali concentrations. Nevertheless, the pH of the pore solution in both the high- and moderate-alkali pastes containing HRM was still sufficiently higher than the pH required to depassivate reinforcing steel, even at a 20% level of replacement.

4.2. Expansion of concrete prisms at 38°C and 100% RH

Figs. 3 and 4 show the expansion evolution of concrete prisms stored at 38°C and 100% RH containing different levels of HRM for the two reactive aggregates used in this study. These data show that expansion decreased as the level of HRM increased. Both control specimens (0% HRM) exceeded the expansion limit criterion of 0.04%. The siliceous limestone aggregate (Spratt) reacts very rapidly and control specimens exceeded 0.04% expansion at 56 days. The greywacke aggregate (Sudbury) is slower reacting, but exceeded 0.04% expansion at about 150 days. Both control specimens also exhibited visual signs of distress early on; surface cracking with exuded gel and an associated white streaking was observed in Spratt control prisms at 90 days and in Sudbury control prisms at 180 days.

Initially, all prisms containing HRM had a negative expansion, presumably due to autogenous shrinkage. At a 5% level of replacement, prisms with the Spratt aggregate showed no expansion at 56 days; however, beyond this period, rapid expansion occurred. At 125 days, the expansion had exceeded 0.04%, and at 6 months, visible signs of distress were observed. These prisms continued to expand to more than 0.2% at 2 years.

At a 10% (or more) level of replacement, a significant reduction in expansion was observed with both reactive aggregates tested. At 125 days, there was no measured expansion in these prisms; thereafter, these specimens had a slow, but steady expansion. At 2 years, the expansion of the prisms containing 10% and 15% HRM with the Sudbury aggregate, and the prisms containing 15% and 20% HRM with the Spratt aggregate was less than the 0.04% expansion limit criterion. Moreover, these prisms did not have any visible cracking or exudation of gel at 2 years. The prisms made with 10% HRM and the Spratt aggregate, however, exceeded 0.04% expansion at 18 months. These prisms performed similarly to those with 15% and 20% HRM up to 9 months, but then began to expand at a faster rate. This behavior may be due to an increase in the alkalinity of the pore solution over time, which was suggested by the pore solution analysis of pastes containing 10% HRM. The results of the expansion tests also show that at equivalent levels of HRM, the prisms made with the Spratt aggregate expanded more than those made with the Sudbury aggregate. This would indicate that the level of HRM required to control deleterious expansion is dependent on the nature of the reactive aggregate.

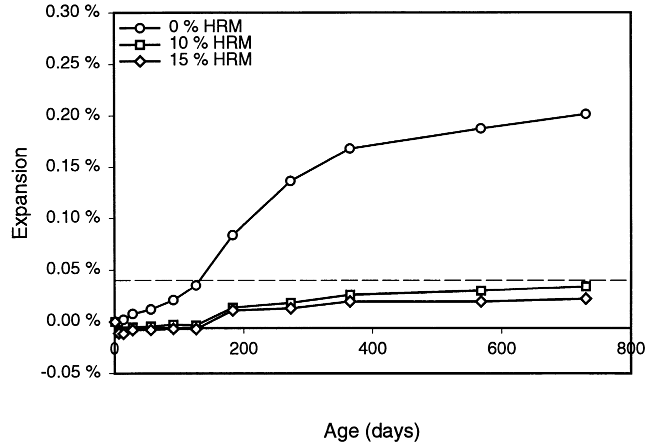

Fig. 4. Expansion evolution of CAN/CSA A23.2-14A concrete prisms containing HRM and cement A with Sudbury aggregate.

While HRM was effective in suppressing expansions to <0.04% at 2 years when used in sufficient quantity, it should be appreciated that those samples, which passed the expansion criterion, did show trends of expansion late in the testing period. The implication of this long-term persistent expansion in the CAN/CSA A23.2-14A concrete prism test on field concrete under normal service conditions is unclear. However, similar trends have been observed with some blended cements containing slag, which give good field performance [9]. A longer testing period may be required to

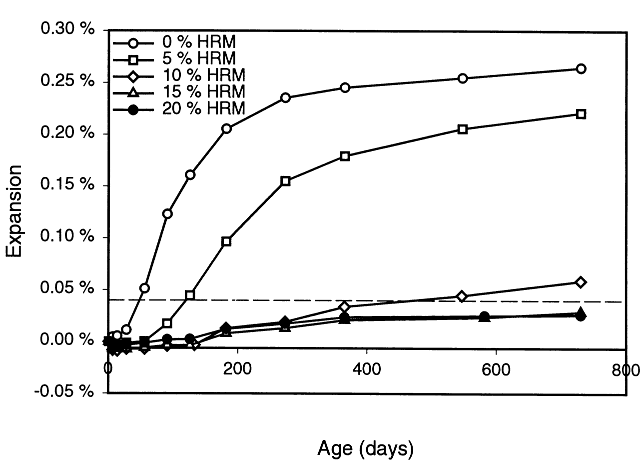

Fig. 3. Expansion evolution of CAN/CSA A23.2-14A concrete prisms containing HRM and cement A with Spratt aggregate.

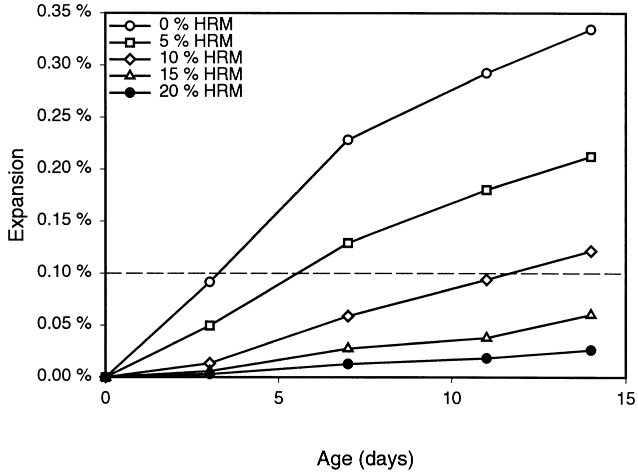

Fig. 5. Expansion evolution of CAN/CSA A23.2-25A mortar bars containing HRM and cement C with Spratt aggregate.

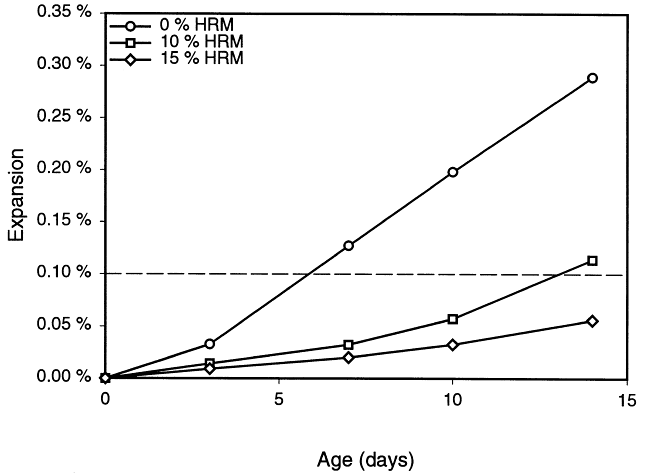

Fig. 6. Expansion evolution of CAN/CSA A23.2-25A mortar bars containing HRM and cement C with Sudbury aggregate.

assess the performance of concrete containing HRM, and for this reason, the concrete prisms in this study will continue to be monitored beyond 2 years.

4.3. Expansion of mortar bars at 80°C in 1 M NaOH

Figs. 5 and 6 show the expansion evolution of mortar bars stored at 80°C in 1 M NaOH solution containing HRM at the same levels of cement replacement used in the concrete prism test. There was generally good correlation between the concrete prism test and the accelerated mortar bar method when the performance criteria used were expansion of concrete prisms $\leq 0.04\%$ at 2 years and expansion of mortar bars $\leq 0.10\%$ at 14 days.

The control specimens exceed 0.10% expansion relatively quickly in the accelerated mortar bar test. As in the concrete prism test, control specimens made with the Spratt aggregate expanded more rapidly and to a greater extent than those made with the Sudbury aggregate. At the end of the 14-day immersion period, the Spratt control specimens had expanded to more than 0.33% and the Sudbury control specimens to 0.29%. It should be mentioned that the accelerated mortar bar method conducted with the Sudbury aggregate did not meet the requirement of CAN/CSA A23.5-98 that control specimens produce expansions of at least 0.30%. However, the difference in this case seems insignificant.

The results of the expansion tests show that the rate of expansion decreased systematically as the level of HRM increased. A 15% level of cement replacement with HRM was needed to reduce the 14-day expansion to less than 0.10% for both reactive aggregates tested. This is somewhat incongruous to the results of the concrete prism test in which 10% HRM was sufficient to suppress deleterious expansion with the Sudbury aggregate. Conclusions based solely on the results of the accelerated mortar bar test would suggest that a higher level of HRM was required to suppress deleterious expansion. However, this test method is more severe than the concrete prism test, and certainly if data are available from the concrete prism test, they should supersede the results from the accelerated mortar bar test. It was further observed that mortar bars with 20% HRM had lower expansions than mortar bars with 15% HRM. In the case of the concrete prisms, there was almost no difference in expansion between prisms containing 15% and 20% HRM. This may be explained by a lower permeability of the mortar bars with 20% HRM, which would affect the rate of diffusion of alkalis from the immersion solution into the sample, and because equilibrium of the alkali content between the mortar bar pore solution and the 1 M NaOH immersion solution is unlikely to be achieved with a testing period of 14 days.

5. Conclusions

(1) The alkali concentration of pore solutions expressed from pastes is significantly reduced when HRM is used to replace up to 20% of the OPC. The long-term hydroxyl ion concentration was reduced to below 0.2 mol/l for both a moderate-alkali cement and a high-alkali cement.

(2) Incorporation of HRM as a partial cement replacement between 10% and 15% may be sufficient to control deleterious expansion due to alkali–silica reaction in concrete, depending on the nature of the aggregate. At 2 years, the expansion of concrete prisms by the CAN/CSA A23.2-14A concrete prism test was reduced to <0.04% when 10% HRM was used in prisms with a greywacke-argillite reactive aggregate or when 15% was used in prisms with a siliceous limestone reactive aggregate. Fifteen percent HRM was required to suppress expansion to $\leq 0.10\%$ when tested with a modified version of the CAN/CSA A23.2-25A accelerated mortar bar test.

(3) The mechanism by which HRM may suppress expansion due to alkali–silica reaction appears to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions.

Acknowledgments

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