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Increasing concrete durability with high-reactivity metakaolin

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Abstract

High-reactivity metakaolin (HRM) is a manufactured pozzolan produced by thermal processing of purified kaolinitic clay. Field performance and laboratory research of concrete containing HRM have demonstrated its value for bridge decks, bridge deck overlays, industrial flooring, high-strength concrete and masonry products. This paper discusses laboratory evaluations to assess the long-term performance of concrete containing HRM produced in North America for resistance to chloride penetration and reduction in expansion due to alkali-silica reactivity. Bulk diffusion testing indicated that HRM substantially reduced chloride ion penetration in concrete with w/cm of 0.30 or 0.40. Reductions in diffusion coefficients compared to control specimens were of the order of 50% and 60% for concrete with 8% and 12% HRM, respectively. Also, the performance of the concrete containing 8% or 12% cement replacement with HRM showed improved performance versus merely reducing the w/c from 0.4 to 0.3. Such reductions can be expected to have a substantial impact on the service life of reinforced concrete in chloride environments. Expansion tests on concrete prisms containing reactive aggregates showed that 15% HRM can prevent deleterious expansion due to alkali-silica reactivity (ASR). The mechanism of control is likely linked to the substantial reduction in pore solution alkalinity seen in pastes containing 20% HRM in comparison to the control specimen which contained no supplementary cementing materials. However, the reduction was not large enough to depassivate steel reinforcement.

Keywords: Concrete durability; High-reactivity metakaolin; HRM

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1. Introduction

With the focus on increasing the service life of concrete structures, supplementary cementing materials have gained popularity. High-quality, low-permeability concrete offers increased durability by inhibiting the ingress of solutions containing soluble chloride ions towards reinforcing steel and reducing deleterious expansions from alkali-silica reactions. This concrete often has a low water-to-cementitious materials ratio (w/cm) and incorporates one or more supplementary cementing materials.

High-reactivity metakaolin (HRM), one of the newest supplementary cementing materials to prove its merit in field application, has been used in concrete to offer an increase in compressive strength and a reduction in permeability while offering good workability [1]. During production, high-purity kaolin clay is heated using controlled thermal activation to dehydroxylate the hydrous kaolin particle without causing recrystallization of the structure. The end result is an almost 100% reactive pozzolan, which will chemically combine with calcium hydroxide to form additional cementitious products. The reactivity of the metakaolin depends on the purity of the kaolin and the thermal processing conditions [2–4]. The term ‘high-reactivity metakaolin’ is used to distinguish this material from less active calcined mixed clays and volcanic ashes that have sometimes been referred to as ‘metakaolin’ due to the inclusion of some kaolin component.

Other research has shown that, with appropriate replacement levels, mixtures containing HRM exhibit performance similar to those containing silica fume in terms of strength and permeability [5,6]. HRM has also been shown to reduce the damage caused from external sulfate attack [7]. Also, HRM, because of its white color, does not darken concrete, making it suitable for color matching and other architectural applications. Research and field performance have shown HRM to be effective in improving durability and appearance of alkali-resistant (AR) glass fiber reinforced cement (GFRC) composites [8].

In the studies presented here the effect of HRM on chloride penetration is evaluated using various testing

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methods, including rapid chloride penetration and bulk diffusion. Furthermore, the effect of HRM on alkali-silica reactivity (ASR) is evaluated through long-term concrete prism expansion tests and by analyzing the pore solution in hydrated cement pastes.

2. Properties of high-reactivity metakaolin (HRM)

HRM is produced by thermal activation of high-purity kaolin clay within a specific temperature range. The heating process drives off water from the kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and collapses the material structure, resulting in an amorphous aluminosilicate ($Al_2O_3 \cdot 2SiO_2$), metakaolin.

The HRM evaluated in this study is a white powder with a Hunter L whiteness value greater than 90 (on a scale from '0 – black' to '100 – maximum whiteness'), making HRM particularly suitable for color matching and other architectural applications. It has an average particle size of less than 2 μm and specific gravity of approximately 2.5. The chemical composition of the material used for the chloride penetration and ASR studies reported here is given in Table 1.

When combined with portland cement, metakaolin reacts rapidly with calcium hydroxide that is released from the hydration of cement to form various hydrates, including CSH, strätlingite – C_2ASH_8 and hydrogarnet – C_3AH_6 [4,9–11].

3. Effect of HRM on chloride penetration in concrete

Previous studies [12,13] have shown that the charge passed in ASTM C1202 tests, the so-called rapid chloride permeability test (RCPT) is significantly reduced by including HRM in concrete and that the reduction is of the same order of magnitude as for similar concrete containing silica fume. The RCPT provides an indirect measure or index of the resistance of concrete to chloride ion penetration. These results cannot be used directly to predict the rate of chloride penetration under field conditions since true service life models require the measurement of the mass transport coefficients that govern chloride movements in concrete. Depending on field conditions, the mechanisms may include ionic diffusivity, hydraulic conductivity, and capillary suction (sorptivity). This paper reports the results of bulk diffusion tests to determine the apparent diffusion coefficient [14] and RPCT results of concrete containing HRM.

Six air-entrained concrete mixtures were cast at w/cm of 0.30 or 0.40 and 0%, 8%, or 12% by mass replacement of cement with HRM manufactured by Engelhard Corporation. The portland cement was ASTM Type I/II low-alkali produced by Lafarge Canada. The fine aggregate had a density of 2700 kg/m^3, absorption of 1.4%, and fineness modulus of 2.56. Because of differences in specific gravity between the cement and the HRM, adjustments were made in the fine aggregate to maintain the yield. The coarse aggregate was crushed 10 mm limestone with a density of 2670 kg/m^3 and absorption of 1.67%. All mixtures included ASTM Type A water-reducer, sodium naphthalene sulfonate-based superplasticizer and polymer-based air-entraining agent, adjustments were made in the chemical admixtures to achieve the targeted slump and air content. The volumetric mix designs and fresh concrete properties are summarized in Table 2. Compressive strength results were reported elsewhere [15].

Specimens (100 mm diameter × 50 mm thick) were sealed with epoxy on all sides except the test face, vacuum saturated, and then immersed in 1 M NaCl solution at 23°C. After various immersion times (28, 90 and 365 days), the specimens were removed from solution, allowed to dry, and then ground in a precision milling machine to produce samples at incremental depths (of 0.5 mm or more) from the test face. These samples were oven dried and analyzed for total chloride using nitric acid digestion and potentiometric titration with silver nitrate as explained in detail by McGrath [14].

Because the specimens are initially saturated and then submerged in chloride solution, this test measures chloride transport solely as a result of pure diffusion. The test does not, however, correct for chloride binding effects as total (acid-soluble) chloride contents are measured. The beneficial effects of HRM in increasing chloride binding are presented elsewhere [16].

The apparent diffusion coefficient, D_a and surface concentration, C_0 were determined for the various concrete mixtures from the plot of chloride content versus depth according to Fick's Second Law of Diffusion and Crank's Solution (Eqs. (1) and (2)).

$$\frac{dC}{dt} = D_a \frac{d^2C}{dx^2}, \tag{1}$$

Table 1
Chemical analysis of HRM

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	Na_2O	K_2O	P_2O_5	LOI
52.1	45.3	0.60	1.64	0.05	0.21	0.16	0.10	0.51

Table 2
Mixture proportions and fresh properties of concrete evaluated for chloride ion penetration

Mixture	1	2	3	4	5	6
w/cm	0.40	0.40	0.40	0.30	0.30	0.30
OPC	100%	92%	88%	100%	92%	88%
HRM	0	8%	12%	0%	8%	12%
OPC (kg/m^3)	380	350	334	460	423	405
HRM (kg/m^3)	–	30	46	–	37	55
Coarse Agg. (kg/m^3)	1100	1100	1100	1100	1100	1100
Fine Agg. (kg/m^3)	655	647	641	619	608	601
Water (kg/m^3)	152	152	152	138	138	138
25 XL water reducer (ml/100 kg)	325	325	325	325	325	325
SPN Superplasticizer (ml/100 kg)	400	600	800	700	900	1100
Microair entrainer (ml/100 kg)	40	40	40	40	40	40
Slump (mm)	135	125	200	170	90	145
Air content (%)	9.5	7	6	7.5	5	5
Plastic density (kg/m^3)	2275	2353	2424	2346	2459	2473

$$C_{x,t} = C_0\left[1 - \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right)\right], \qquad (2)$$

where $C_{x,t}$ is the chloride concentration at depth x and time t, C_0 is the chloride concentration at the surface ($x = 0$), erfc ( ) is the standard complimentary error function and D_a is the 'apparent' diffusion coefficient. Table 3 shows the bulk diffusion coefficient (D_a) and surface chloride concentration at various exposure times up to one year and RCPT results, following the standard ASTM C1202 procedure, at 28 days.

After 1 year of ponding, the diffusion coefficients continue to decrease for all mixtures. The significance of the reduced diffusivity can be revealed by inspection of Eq. 2. If this equation is used as an oversimplified service life model, then for a given exposure condition (surface chloride concentration, C_s) and depth of cover x, the time t, for chlorides at the rebar to reach the threshold concentration for corrosion $C_{x,t}$, is inversely proportional to the diffusion coefficient D_a. Simply put, all other things being equal, $t \propto 1/D_a$. Thus, if the diffusion coefficient is halved, the service life (time to corrosion initiation) is doubled.

The best performance at all ages was exhibited by the 0.30 w/cm, 12% HRM concrete. It should also be noted that, at all ages, replacing 8% cement with HRM in a 0.40 w/cm concrete improved diffusion characteristics as much or more than only reducing the w/cm to 0.30. After 1 year of exposure, the 0.40 w/cm, 12% HRM mixture showed performance similar to the 0.3 w/cm, 8% HRM mixture. Also, the RCPT ranked the six concrete mixtures in the same order as the chloride diffusion coefficient. Previous testing has demonstrated that this rapid test can provide a reasonable indication of ionic diffusivity across a fairly wide range of concrete quality [17]. Although it is not suggested that this test can provide absolute values for diffusion coefficients, it remains useful as a tool for comparing different mixes or for quality control.

4. Effect of HRM on ASR

In this portion of the evaluation, using two different reactive aggregates, the efficacy of HRM in controlling expansion due to ASR was evaluated using the concrete

Table 3
Results from bulk diffusion tests and RCPT

Mix details		Surface concentration (%) and Bulk diffusion coefficient D_a($\times 10^{-12}$ m^2/s) with Time						RCPT (Coulombs)
W/CM	HRM (%)	28 days		90 days		365 days		28 days
		C_0	D_a	C_0	D_a	C_0	D_a	
0.40	0	0.33	19.1	0.34	11.8	0.63	6.3	2770
	8	0.69	8.2	0.58	5.7	0.68	2.3	560
	12	0.58	5.8	0.53	3.5	0.58	1.7	310
0.30	0	0.42	9.6	0.44	5.9	–	–	2350
	8	0.52	3.7	0.49	2.9	0.83	1.4	400
	12	0.50	2.9	0.48	2.7	0.69	0.9	230

prism test method. The aggregates, from Canada, were Spratt siliceous limestone from near Ottawa, Ontario, and Sudbury greywacke/argillite material from Sudbury, Ontario.

The concrete prism test (ASTM C1293 and CSA A23.2 – 14A) is a recognized test method for evaluating the potential reactivity of aggregate sources. Concrete prisms (typically 75 mm × 75 mm × 300 mm or longer) are cast using a mix with 420 kg/m^3 of high-alkali cement and raising the alkali to 1.25% Na_2O_e ($Na_2O_e = Na_2O + 0.658 \times K_2O$) by dosing the mix water with NaOH. When this test is used to evaluate the effectiveness of mineral admixtures in controlling ASR, it is recommended that concrete prisms are cast with varying amounts of the cement replaced with the admixture under consideration together with a known reactive aggregate. The alkali content of the concrete is raised to 1.25% Na_2O_e on the basis of the portland cement component of the mix (disregarding the alkali present in the mineral admixture). The mineral admixture is considered to be an effective preventive measure at a particular replacement level if the expansion of prisms does not exceed 0.04% after 2 years of storage at 38°C (CSA A23.1 Appendix B, 1994). In this evaluation, the expansion was studied through 2 years.

For the test program with HRM, concrete prisms were cast with 5%, 10%, 15% and 20% of the cement replaced with HRM. The results showed that expansion is reduced with increasing levels of HRM (Fig. 1). The expansion of the 10% HRM concrete prism with the more reactive Spratt aggregate does increase past the 0.04% expansion criteria after 2 years, however, it met the 0.04% expansion after 1 year (Fig. 2). Even after 2 years, both the 15% and 20% HRM remain below the 0.04% expansion.

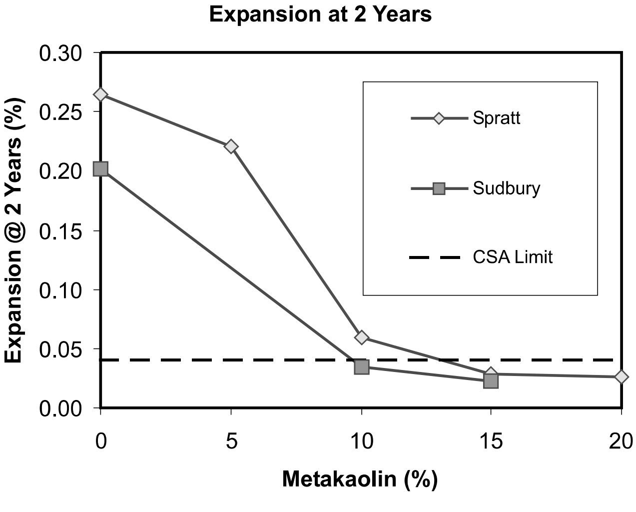

Fig. 1. Control of expansion due to ASR using high-reactivity metakaolin.

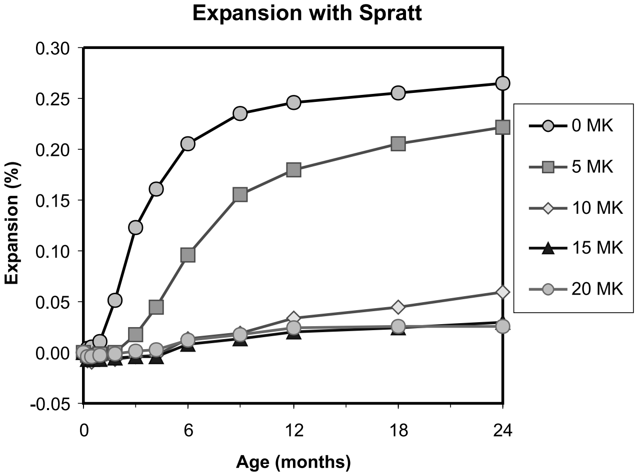

Fig. 2. Long-term control of expansion high-reactivity Metakaolin.

5. Effect of HRM on pore solution

Evaluations were performed on pore solutions from paste specimens cast with a 1.02% Na_2O_e portland cement, 0%, 10% or 20% cement replacement with HRM, and w/cm = 0.50. Specimens (50 mm diameter × 100 mm) were sealed and stored at 23°C over water. At various ages, the pore solution was extracted using similar techniques to those described by Barneyback and Diamond [18] and analyzed for hydroxyl ions (OH^-) by titration, and for sodium (Na^+) and potassium (K^+) by flame photometry.

Results of hydroxyl ion concentration in the pore solution are shown in Fig. 3. Although only the OH^- concentration is reported here, there was good mass balance (i.e., $[Na^+] + [K^+] \cong [OH^-]$). The incorporation of 10% HRM seemed to have little effect on the pore solution alkalinity beyond that of mere dilution since 10% HRM reduced OH^- concentration by

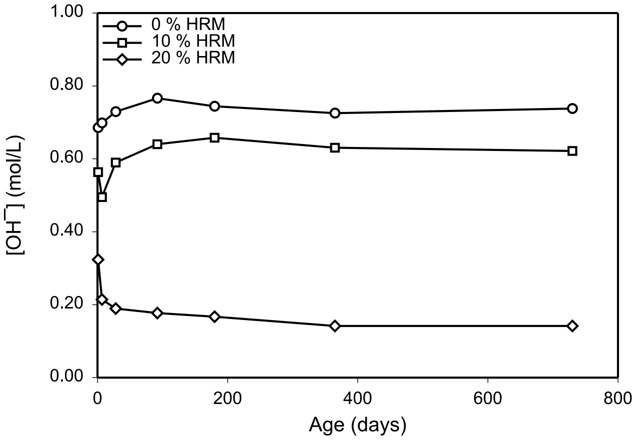

Fig. 3. Hydroxyl ion concentration of pore solution prepared with portland cement of 1.02% Na_2O_e and HRM substitution.

approximately 10% on average compared with the control. There was a much more dramatic effect when 20% of the portland cement was replaced with HRM.

The significance of the pore solution alkalinity is related to the potential of ASR. The solubility of reactive silica increases exponentially as the alkalinity of the pore solution increases in the range 0.1–1.0 M OH^- (i.e., pH 13.0–14.0). Few studies have reported the minimum pore solution alkalinity required to initiate and sustain ASR in concrete, but Diamond [19] and Kolleck et al. [20] report that reaction is unlikely below 0.25 M and 0.20 M OH^-, respectively. The use of 20% HRM would appear to be an effective means of reducing the pore solution alkalinity to a value below that necessary for ASR. However, the pH remains well above the point that would cause degradation of the passivating film layer on steel embedded in HRM concrete [21].

6. Discussion

The appropriate use of pozzolanic materials and slag can significantly improve the long-term durability of concrete. It is demonstrated here that the use of moderate levels (8–12%) of HRM can be used to dramatically increase the resistance to chloride ion penetration and higher concentrations (10–20%) can reduce the risk of deleterious expansion from ASR.

7. Conclusions

1. The use of 8% and 12% HRM significantly lowered the chloride ion diffusion coefficient of concrete. The level of reduction compared to control specimens was on average 50% and 60% for mixes with 8% and 12% HRM, respectively. Such reductions may be expected to have a significant effect on the service life of concrete in a chloride environment.
2. Bulk diffusion values continue to reduce (improve) with increased periods of chloride exposure and support the beneficial effects of HRM.
3. The time-dependent reduction in apparent diffusion coefficients appears to be more pronounced with increased levels of HRM.
4. The use of 10% HRM was sufficient to prevent deleterious expansion in concrete prisms containing highly reactive aggregate after 1 year of storage at 38°C.
5. Pore solution studies showed that the partial replacement of high-alkali cement with 20% HRM significantly reduced the pore solution alkalinity. The hydroxyl ion concentration in pastes with 20% HRM was found to be below the threshold level of 0.20–0.25 M OH^- proposed by other researchers as necessary to sustain ASR, but was well above the pH required to maintain steel passivation.

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