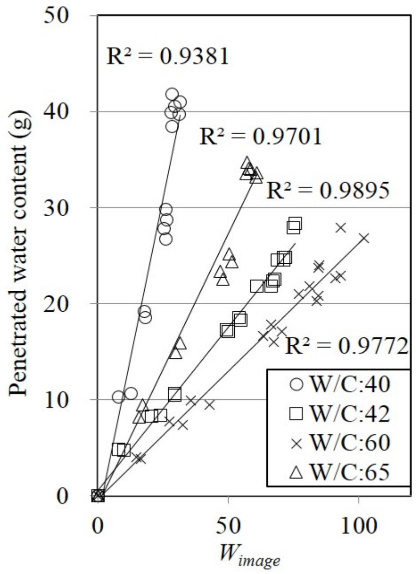

Fig. 3 - Relationship between W_{image} by neutron imaging and water content

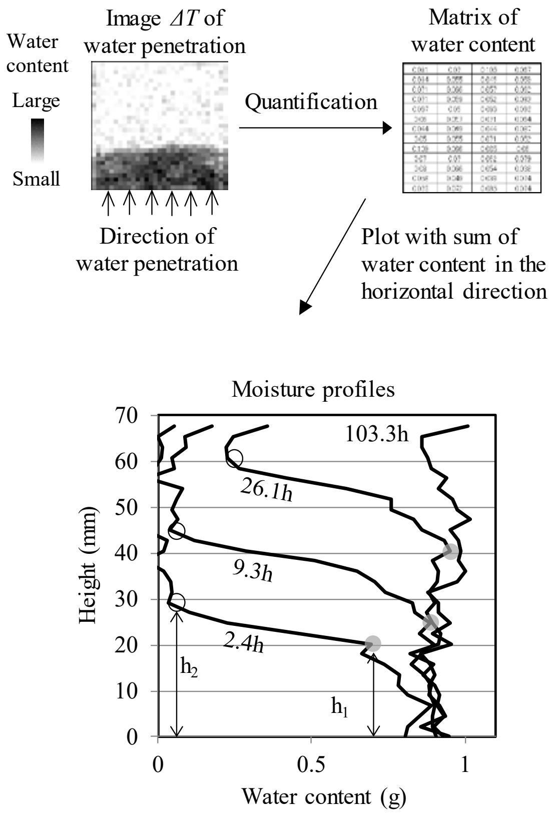

Fig. 4 - Derivation process of penetration height, h_1, h_2

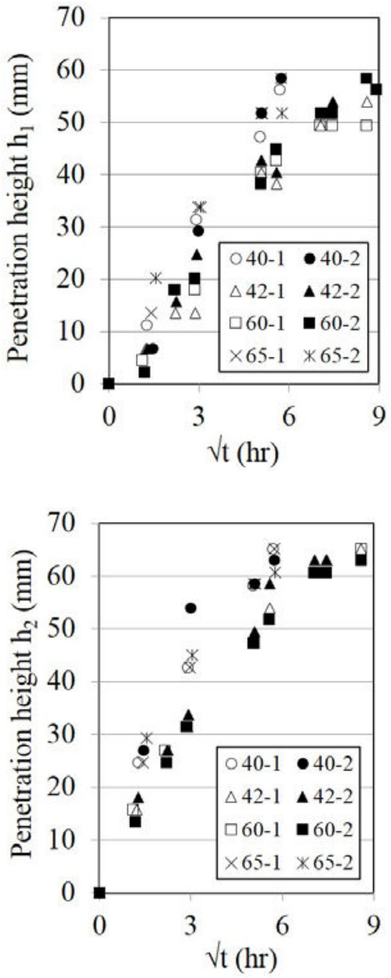

Fig. 5 - Penetration height of water as function of square root of contact time with water (top: penetration height h_1, bottom: h_2)

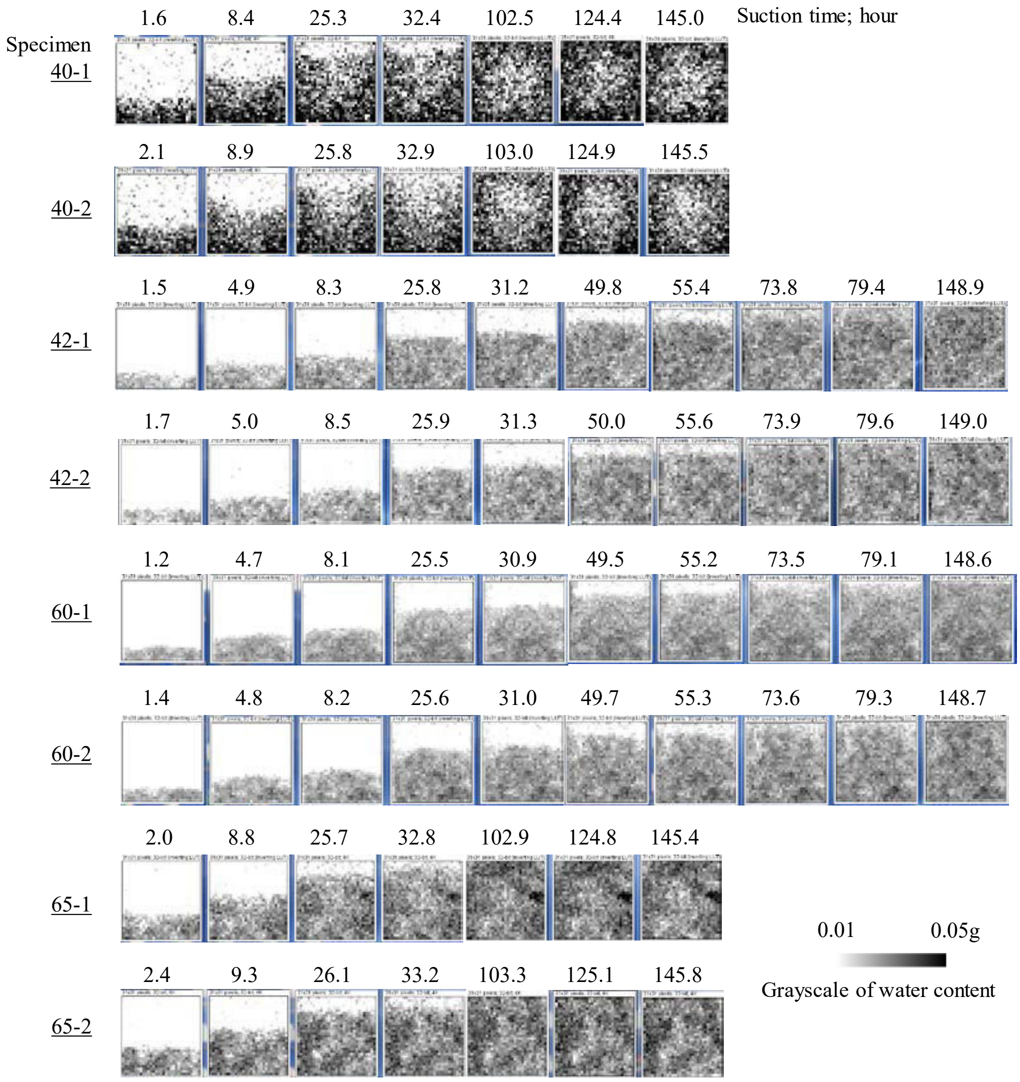

Fig. 6 - Water movement in concrete observed by neutron imaging

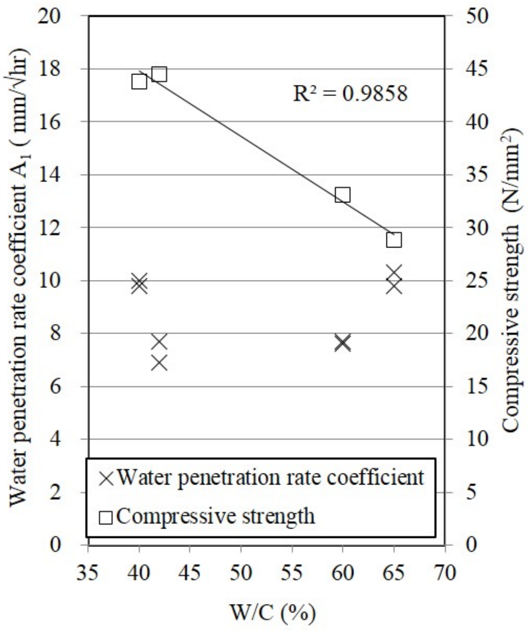

Fig. 7 - Influence of W/C on compressive strength and water penetration rate coefficient

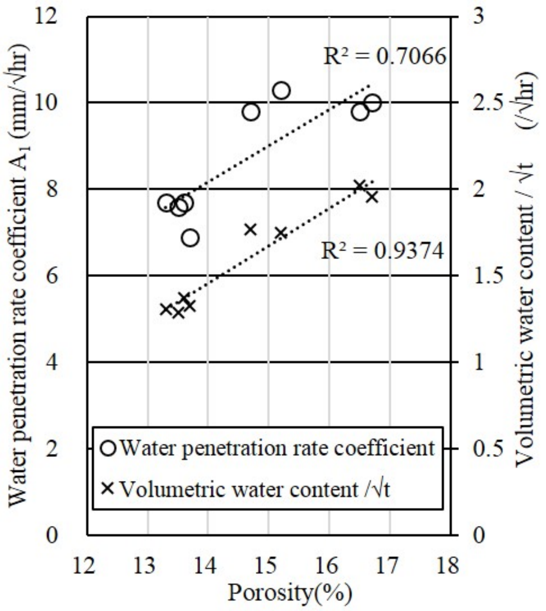

Fig. 8 - Influence of porosity on water penetration rate coefficient and water absorption rate

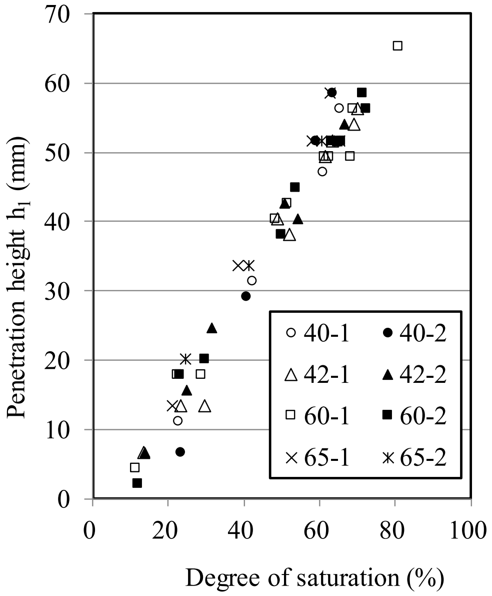

Fig. 9 - Relationship between penetration height h_l and degree of saturation

Durability of alkali-activated slag/fly ash pastes and concretes: an overview of performance regarding freezing and thawing, surface scaling, shrinkage and ASR

Alexandre Rodrigue, Josée Duchesne, Benoit Fournier and Benoit Bissonnette

Synopsis: Alkali-activated slag/fly ash concretes activated with combined sodium silicate and sodium hydroxide show good mechanical and durability properties in general. When tested in terms of resistance to freezing and thawing cycling in water-saturated conditions, the concretes tested in this study show final values of relative dynamic modulus averaging 100% after 300 cycles. However, all tested concretes showed poor performance towards freezing and thawing in presence of de-icing salts with only one tested mixture showing a final average scaling value below 0.5 kg/m². Early-age microcracking is observed on all tested concretes and is correlated to high values of autogenous shrinkage in equivalent paste mixtures. Increasing the fly ash content reduces both the observed autogenous shrinkage and early-age cracking. Low drying shrinkage values ranging from 470 to 530 µm/m after 448 days of measurements at 50% RH and 23°C are noted. The use of fly ash in these alkali-activated concretes reduces the expansion levels of concrete specimens incorporating alkali-silica reactive aggregates. With increasing fly ash contents (20, 30 and 40% replacement), decreasing expansions are observed for any given reactive aggregate. In general, the durability properties measured in this study were improved by partially substituting slag with fly ash as binder material.

Keywords: Alkali-activated concrete, ASR, de-icing salts, durability, freezing and thawing, scaling, shrinkage

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INTRODUCTION

Research regarding alkali-activated systems has demonstrated their environmental advantages as well as their enhanced mechanical properties [1–5]. However, these systems need to show adequate durability properties regarding shrinkage, freezing and thawing cycling resistance, surface scaling in the presence of de-icing salts and ASR in order to be a suitable replacement option for traditional portland cement concrete.

Alkali-activated systems with fly ash, slag or slag/fly ash show higher overall shrinkage values when compared to portland cement systems [6–9]. In this paper, special attention is given to slag/fly ash systems. Higher autogenous shrinkage is observed in these systems [10] with higher slag contents being linked to higher bound water contents [11]. Recent work on similar mixtures presented in this study have shown that autogenous shrinkage could be linked to the presence of early-age cracking in the alkali-activated slag/fly ash paste where increasing fly ash contents and added water dosages result in decreasing autogenous shrinkage and thus, decreasing early-age cracking [9]. Early-age cracking is an important issue to consider whereas it could potentially lead to higher permeability and thus, potential poor performance regarding other durability issues.

When facing freezing and thawing, alkali-activated slag concretes show adequate performances with specimens achieving up to 90% of their initial relative dynamic elasticity modulus after 300 cycles [12,13]. Sun and Wu [14] show that alkali-activated fly ash systems measured on mortar specimens have shown no loss in compressive strength and a higher dynamic modulus retention than portland cement-based mortars. No significant work was done to date on performance of alkali-activated systems towards de-icing salts scaling.

Alkali-silica reaction in concrete infrastructures incorporating reactive aggregates is an important deleterious issue to consider. For ASR to take place, three essential conditions must be met: sufficient humidity (80% and more), high alkalinity and the presence of reactive silica phases in the aggregates [15]. If these conditions are met, the reaction will generate a silico-calco-alkaline gel which will absorb water and thus, expand [16]. Therefore, the expansive ASR gel will generate internal pressures that can lead to overall expansion and cracking of the affected concrete. In the case of alkali-activated systems, highly alkaline solutions are used to dissolve the aluminosilicate-type precursors to allow the formation and hardening of the resulting paste. In alkali-activated fly ash-based systems, high alkali concentrations in the activators results in high alkali concentrations in the pore solutions of the hardened paste [17,18]. However, work done on alkali-activated slag mortars has shown lower expansion values when compared to portland cement mortars which was attributed to the absence of portlandite and thus, lower [OH-] of the pore solution [19]. Finally, the alumina-rich pore solution of alkali-activated systems seems to represent a dominant factor of influence for ASR whereas aluminum incorporates into the surface of reactive silica which reduces the dissolution of amorphous silica [20]. Moreover, the possibility that a non-expansive or lesser expansive ASR gel forms in these systems must also be considered.

RESEARCH SIGNIFICANCE

The objective of this study was to develop an alkali-activated concrete mixture capable of withstanding severe winter conditions, involving repeated freezing and thawing and the exposure to de-icing salts in freezing conditions. This research also addresses the issues of shrinkage and alkali-silica reaction in presence of reactive aggregates. Therefore, improving the overall durability and understanding the mechanisms behind the potential deterioration of these alkali-activated slag/fly ash systems under severe conditions was at aim. The available and widespread test procedures were used to address all matters in order to achieve these goals. Following these tests, more specific analytic methods were used to understand the behaviour of these systems in regards of the general testing.

MATERIALS AND METHODS

Materials

Table 1 presents the chemical composition of the slag and fly ash precursors used in this study. The slag was a grade 80 (activity index) blast furnace slag from Stoney Creek (Ontario), Canada and the class F fly ash was the Sundance fly ash supplied by Lafarge Canada in Calgary (Alberta), Canada.

Table 1- Composition of precursors in major oxides %

Oxides, wt.%	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	TiO_2	LOI
Slag	37.74	10.75	36.20	12.62	0.50	0.41	0.49	0.91	-0.8
Class F fly ash	56.72	24.07	9.29	1.05	3.14	2.5	0.64	0.65	1.2

The activator was a combined 8M sodium hydroxide and a sodium silicate solution with a Na_2SiO_3/NaOH mass ratio of 0.50. The activator was prepared at least 24 hours before mixing to eliminate the heat contribution of the exothermic reaction resulting from the preparation of the solution. Table 2 presents the chemical composition in major oxides of the grade N sodium silicate solution.

Table 2- Chemical composition of sodium silicate (grade N) in major oxides %

Oxides, wt.%	SiO_2	Na_2O	H_2O
Sodium silicate (grade N)	28.70	9.04	62.26

Table 3 presents the aggregates used for the ASR testing in this study with their respective relative density, absorption, type, lithology and ASR reactivity. All the other concretes used a locally available non-reactive crushed granit as fine and coarse aggregate.

Table 3- Physical properties and characteristics of the aggregates

Aggregates	Bulk density, kg/m³ (lb/yd³)	Absorption, %	Type	Lithologies	ASR reactivity
High purity limestone (HP)	2716 (4578)	0.19	Crushed aggregate	Limestone	Non-reactive
Spratt (Sp)	2675 (4509)	0.43	Crushed aggregate	Silicious limestone with traces of chert	High
New Mexico (NM)	2534 (4271)	1.52	Natural gravel	Andesite and rhyolite	Extreme
Sudbury (Su)	2687 (4529)	0.50	Natural gravel	Siltstone, granite, claystone, grauwacke, quartzite sandstone	Moderate

Mixture proportioning

Paste mixtures

Table 4 presents the paste mixtures that were tested in regards of their behaviour towards autogenous shrinkage and subjected to pore solution extraction.

Table 4- Alkali-activated slag/fly ash paste mixtures

Mixture	Binder (slag/Fly ash) (%)	Activator/binder	Na_2SiO_3/NaOH	Added Water/binder
D1	80/20	0.35	0.5	0.16
D2	80/20			0.14
D3	80/20			0.12
D4	70/30			0.14
D5	60/40			0.14

Concrete mixtures

All concrete mixtures were prepared with a binder content of 400 kg/m³ [674 lb/yd³] and an activator-to-binder ratio of 0.35. The sodium hydroxide and sodium silicate contents of the activator were constant at 94 kg/m³ [158 lb/yd³] and 47 kg/m³ [79 lb/yd³] respectively. Table 5 presents the concrete mixtures tested in regards of their behaviour towards drying shrinkage (R1 to R4), freezing and thawing cycling (GD1 to GD6) and de-icing salts scaling (E1 to E8). Table 6 presents the aggregate proportioning adjusted to an equivalent volume for ASR testing. All concrete mixtures had a constant sand content of 670 kg/m³ [1129 lb/yd³].

Table 5- Alkali-activated slag/fly ash concrete mixtures tested for drying shrinkage

ID	Binder Slag%/ Fly ash%	Added Water, kg/m³ (lb/yd³)	AEA, ml/kg binder (oz/lb)	Aggregate proportions, kg/m³ (lb/yd³)			Sand, kg/m³ (lb/yd³)
				14-20 mm	10-14 mm	5-10 mm	
R1	80/20	52 (88)	-	416 (701)	312 (526)	312 (526)	670 (1129)
R2	60/40	52 (88)					
R3	60/40	56 (94)					
R4	80/20	56 (94)					
GD1	60/40	56 (94)	15 (0.225)				
GD2	80/20	52 (88)	10 (0.15)				
GD3	80/20	56 (94)	15 (0.225)				
GD4	60/40	52 (88)	10 (0.15)				
GD5	80/20	64 (108)	15 (0.225)				
GD6	80/20	64 (108)	0				
E1	80/20	56 (94)	10 (0.15)				
E2	60/40	52 (88)	15 (0.225)				
E3	60/40	56 (94)	10 (0.15)				
E4	80/20	56 (94)	15(0.225)				
E5	80/20	52 (88)	15 (0.225)				
E6	60/40	52 (88)	10 (0.15)				
E7	60/40	56 (94)	15 (0.225)				
E8	80/20	52 (88)	10 (0.15)				

Table 6- Coarse aggregate proportions of tested alkali-activated concrete mixtures

Aggregates	Aggregate Proportions, kg/m^3 (lb/yd^3)			
	14-20 mm (0.55-0.79 in.)	10-14 mm (0.39-0.55 in.)	5-10 mm (0.19-0.39 in.)	Total
High purity limestone (HP)	425 (716)	319 (538)	319 (538)	1063 (1792)
Spratt (Sp)	419 (706)	314 (529)	314 (529)	1047 (1765)
New Mexico (NM)	397 (669)	298 (502)	298 (502)	992 (1672)
Sudbury (Su)	421 (710)	316 (533)	316 (533)	1052 (1773)

Testing

Compressive strength

Specimens for compressive strength testing were prepared following CSA A23.2-3C and the testing was performed in accordance with CSA A23.2-9C. A loading rate of 2000 N/s was used and three specimens per mixture were tested.

Chemical shrinkage

The chemical shrinkage of alkali-activated slag/fly ash pastes was evaluated in accordance with the ASTM C1608 standard test method. Four alkali-activated paste mixtures and one portland cement (W/C=0.5) paste mixture were tested (two specimens per mixture). Two liquid (water + activator)-to-binder ratios (0.48 and 0.49) and two fly ash replacement levels (20 and 40%) were tested. The paste mixtures were prepared and pored into glass vials. Once in place, water is delicately pored over the paste to avoid additional mixing and the vial is then sealed with a graduated capillary tube sticking out for water level measurement throughout the test procedure. Measurements are made every hour for the first 8 hours of testing and at every 8-hour interval afterwards until completion of the procedure at 24 hours. During the procedure, the test specimens are maintained in an isothermal bath to maintain a constant temperature of the specimens throughout testing and avoid temperature-related volumetric variations.

Autogenous shrinkage

The autogenous shrinkage of alkali-activated slag/fly ash pastes was evaluated in accordance with the ASTM C1698 standard test method. For each mixture presented in table 4, two specimens were tested and compared to a portland cement paste (W/C=0.5). The specimens are prepared by pouring the fresh paste into a corrugated tube. Then, the tubes are placed in a controlled chamber kept at 50 % R.H. and 23 ± 1°C [73.4°F]. Once the final setting of the paste is reached, the length of each tube is determined at 0, 1, 3, 7, 14 and 28 days. Using the length measurements carried out in accordance with ASTM C1698, the autogenous strain at a given time ($\varepsilon_{autogenous}$(t)) is calculated as follows:

$$\varepsilon_{autogenous}(t) = \frac{L(t) - L(t_{fs})}{L(t_{fs})} * 10^6\ \mu m/m$$

where $L(t)$ and $L(t_{fs})$ are the length at time t and the length at the time of final setting (t_{fs}), respectively.

Drying shrinkage

The drying shrinkage of alkali-activated slag/fly ash pastes was evaluated in accordance with the ASTM C157 standard test method. For each mixture presented in table 5, six specimens were tested. The test specimens were concrete prisms of 100 mm [3.94 in] square cross-section and 285 mm [11.2 in] long. After curing, three specimens per mixture were kept in lime-saturated water and three were kept at a 50 % R.H. and 23 ± 2 °C [73.4°F]. The specimens stored in lime-saturated water had their length measured at 8, 16, 32 and 64 weeks including the curing period and the air-stored specimens had their length measured at 4, 7, 14 and 28 days and after 8, 16, 32 and 64 weeks.

Freezing and thawing resistance

The freezing and thawing cycles testing was done in accordance with the ASTM C666 standard test method. For each mixture presented in table 5, three specimens were tested in water saturated conditions. Measurements were done at each interval of 36 cycles until the 300 cycle limit of the standard procedure was reached. The temperature range of the test was from -18°C [-0.4°F] to 4°C [39.2°F]. After each 36 cycle interval, the fundamental transverse frequency and the mass of each specimen was measured. Using this parameter, the relative dynamic modulus of elasticity (P_c) can be determined using the following relation:

$$P_c = ({}^{n_1}/_{n})^2 \cdot 100$$