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Properties of concrete produced from multicomponent blended cements

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Abstract

This paper presents a study on the behavior of concrete produced from multicomponent blended cements. These blends were prepared by blending 20–60% ASTM Type I cement with the combination of Class C fly ash and clean coal ash. Two percent to four percent sodium sulfate anhydrite was added to the blends as a chemical activator. Tests were conducted on the prepared concrete for strength development, freezing and thawing resistance, resistance to chloride ion penetration, sulfate resistance, and alkali silica reaction. Test results show that concrete produced from blended cements had equivalent or higher strength than the control mixture at all test ages. Blended cements were effective in controlling expansions due to sulfate attack or alkali silica reaction. They also reduced the deterioration of concrete due to freezing and thawing action and greatly increased the resistance to chloride ion penetration into the concrete.

Keywords: Activator; Blended cement; Concrete; Sulfate attack; Fly ash

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1. Introduction

In the last few decades, industrial by-products such as fly ash, blast-furnace slag and silica fume have been increasingly used as mineral additives in cement and concrete. The use of these artificial pozzolans can achieve not only economical and ecological benefits but technical benefits as well. It is generally agreed that, with proper selection of admixture, mixture proportioning and curing technique, mineral additives can greatly improve the durability of concrete.

Nevertheless, it is also well established that mineral additives may reduce early strength of concrete, especially with high cement replacement rates [1,2]. The loss of early strength may be compensated by: (1) curing under elevated temperature [3], (2) chemical activation [4,5], (3) high fineness cement and additives [6,7] and (4) more than one to one replacement of cement by mineral additives and lower water to cementitious materials ratio (W/C) [8,9]. In recent years, it has been reported that ternary blended cements could substantially improve the performance of concrete compared with the conventional binary blended cements or regular Portland cement. Ternary blended cement consisting of Portland cement, granulated blast-furnace slag and fly ash (PC–SL–FA system) was developed in Japan for mass concrete construction due to its very low heat of hydration [10]. This system can be treated as slag cement incorporating fly ash. The addition of fly ash can increase workability and reduce bleeding of slag cement concrete. However, the strength development of this system is relatively slower at early age [11]. By incorporating silica fume in slag cement or fly ash cement, the ternary PC–SL–SF (Portland cement, blast-furnace slag and silica fume) and PC–FA–SF (Portland cement, fly ash and silica fume) blended cements were developed and commercially manufactured in Canada [12]. Similar to the effect of silica fume addition in Portland cement, the fluidity of PC–SL–SF system cement is impaired by silica fume. The addition of a water-reducing agent or a superplasticizer is inevitable for PC–SL–SF system cement. Fly ash in PC–FA–SF system may have water-reducing effect depending on its quality that may totally or partially compensate the increased water requirement caused by silica fume. By incorporating 25% fly ash and up to 5% silica fume, the flow of mortar had no significant change

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compared to ASTM Type I cement mortar [13]. It was also reported that addition of silica fume could only slightly increase the early strength of PC–FA–SF system cement. The strength did not increase so much at and after 28 days because $Ca(OH)_2$ produced was preferentially consumed by the pozzolanic reaction of silica fume, thereby decreasing extensively the quantity of $Ca(OH)_2$ available for the fly ash [14]. Based on the same reason, it is expected that for PC–SL–SF system, the early strength may be even lower than slag cement.

In the mid-1990s, UWM Center for By-Products Utilization (UWM-CBU) started various projects for the development of high-performance blended cements containing high-volume coal combustion by-products, including low-quality Class F fly ash and out-of-specification clean coal ash. The clean coal ash initially studied at UWM-CBU had strong retarding effect [15]. To compensate the loss of early strength, several chemicals were used to activate the hydration of blended cements. Sodium sulfate was found to be one of the most effective and economical chemicals. The details about the optimization of the blending proportions are reported in a separate paper [16]. In this paper, the properties of concrete produced from three selected blended cements containing up to 80% coal combustion by-products are presented. Results are compared with the control mixture prepared from ASTM Type I cement only.

2. Experimental details

2.1. Materials

ASTM Type I cement, Class C fly ash and clean coal ash were used for preparation of blended cements. Clean coal ash is derived from dry flue gas desulfuration (FGD) collection system. Lime slurry is sprayed as a fine mist into the flue gas in a reaction vessel where the atomized slurry reacts with SO_2 from the flue gases and forms calcium sulfite. A portion of the calcium sulfite is further oxidized to calcium sulfate. The utilization rate of clean coal ash is much lower than conventional Class C or Class F fly ash due to its high content of sulfate/sulfite. Technical-grade sodium sulfate anhydrite was blended with cementitious materials as a chemical activator. The chemical composition and physical properties of the cementitious materials are shown in Tables 1–3.

Table 1
Chemical composition of cementitious materials

Composition	Type I cement	Class C fly ash	Clean coal ash
SiO_2 (%)	18.5	35.0	27.5
Al_2O_3 (%)	4.3	18.5	15.1
Fe_2O_3 (%)	2.8	5.4	3.0
$SiO_2+Al_2O_3+Fe_2O_3$ (%)	–	58.9	45.6
CaO (%)	67.9	27.7	26.4
MgO (%)	1.6	5.5	3.6
TiO_2 (%)	–	1.4	0.5
SO_3 (%)	2.3	2.4	19.7
$Na_2O+0.658K_2O$ (%)	0.6	3.7	1.1
Moisture content (%)	0.4	0	0.2
Loss on ignition (%)	1.7	0.2	2.2

Table 2
Physical properties of fly ashes

Properties	Test results		ASTM C618		
	Class C fly ash	Clean coal ash	N	F	C
Density (g/cm^3)	2.69	2.52	–	–	–
Fineness, by air permeability test method (m^2/kg)	4350	9,500	–	–	–
Fineness, amount retained on no. 325 sieve (%)	5.2	2.4	≤ 34	≤ 34	≤ 34
Strength activity index					
With Portland cement at 7 days (% of control)	99	101	≥ 75	≥ 75	≥ 75
With Portland cement at 28 days (% of control)	102	107	≥ 75	≥ 75	≥ 75
Water requirement (% of control)	93	95	≤ 115	≤ 105	≤ 105
Soundness: autoclave expansion or contraction (%)	0.1	0.01	≤ 0.8	≤ 0.8	≤ 0.8

Table 3
Physical properties of cements

Properties	Type I cement	Blended cements			ASTM C1157, GU
		BC40	BC60	BC80	
Fineness, by air permeability test method (m^2/kg)	390	415	488	546	–
Autoclave expansion (%)	-0.01	0	-0.01	-0.02	≤ 0.80
Compressive strength (MPa)					
1 day	12.4	12.6	6.6	2.4	–
3 days	23.9	32.8	27.4	20.8	≥ 10.0
7 days	31.7	42.7	41.2	33.7	≥ 17.0
28 days	41.7	49.2	52.5	41.0	$\geq 28.0^a$
Time of setting, Vicat method, initial setting (min)	165	390	210	190	≥ 45 ≤ 420

[a] Optional requirement.

Table 4
Blending proportions of blended cements

Blended cement	Composition (%)			
	Type I cement	Class C fly ash	Clean coal ash	Na_2SO_4[a]
BC40	60	20	20	2
BC60	40	30	30	2
BC80	20	40	40	4

[a] Percent of total cementitious materials.

2.2. Preparation of blended cements

Table 4 shows the details of the three selected blending proportions. ASTM Type I cement, together with Class C fly ash, clean coal ash and sodium sulfate anhydrite was charged into a ball mill and blended for 5 min. The properties of the prepared blended cements are shown in Table 3.

2.3. Preparation and test of concrete specimens

For comparison, the blended cement concrete mixtures were proportioned to have the same slump and same cement content (by weight per unit volume of concrete) as Type I cement concrete (control mixture). The control mixture was proportioned to achieve compressive strength of 41 MPa (6000 psi) at age of 28 days and a slump of 40–60 mm (2 ± 1/2 in.). The detailed mixture proportions are given in Table 5. 100 (diameter) × 200 mm (4 × 8 in.) cylinders and 75 × 100 × 300 mm (3 × 4 × 12 in.) prisms were prepared and cured according to ASTM C 192. Compressive strength was determined at the ages of 3, 7, 28 and 91 days. After 28-day curing, prism specimens were subjected to freezing and thawing cycles according to ASTM C 666, Procedure A, Rapid Method. Specimens were immersed in water and subjected to − 18 to 4 °C (0–40 °F) freezing and thawing cycles. The dynamic Young's modulus and loss of weight were determined every 50 cycles. Chloride ion penetration resistance test was carried out according to ASTM C 1202. It was measured as the total charge passed through a slice of concrete cylinder in 6 h. Sulfate resistance of blended cements was evaluated based on length change of mortar bars stored in 0.35 M sodium sulfate solution (ASTM C 1012). The potential alkali reaction of blended cements with aggregate was tested according ASTM C 227. Mortar bars containing crushed glass as reactive aggregate was stored in 1.0 N alkali solution at 80 °C. Length of mortar bars was measured at specified ages.

Table 5
Mixture proportions of concretes

Mixture no.	Control	C4	C6	C8
Type of cement	Type I	BC40	BC60	BC80
Cement (kg/m^3)	369	370	369	367
Sand (kg/m^3)	744	745	743	739
20-mm aggregate (kg/m^3)	1112	1114	1110	1104
Water (lb/yd^3)	170	154	154	153
W/C	0.46	0.42	0.42	0.42
Slump (mm)	60	50	60	45
Air content (%)	1.5	1.6	1.5	1.8
Unit weight (kg/m^3)	2395	2384	2376	2363

3. Test results and discussion

3.1. Properties of fresh concrete

The properties of fresh concrete are given in Table 5. Compared to the control mixture, the amount of water required to produce the same slump was reduced by approximately 10% for blended cements. The water reducing effect did not change between the different blended cements used. This is consistent with the result obtained in a previous study, which stated that the water reducing effect of fly ash increased with cement replacement rate up to about 40% [17]. The air content did not change much between the mixtures. The unit weight of fresh concrete decreased slightly with the increase of mineral additives (Class C fly ash and clean coal ash).

3.2. Compressive strength development of concrete

Table 6 shows the compressive strength of the four mixtures up to age of 91 days. The strength of Mixture C4 was higher than the control mixture at all ages, even at the age of 3 days. Mixture C6 had an equivalent strength to the control mixture at the age of 3 days and higher strength thereafter. Except at the early age (3 days), Mixture C8 showed equivalent strength compared to the control mixture. It should be noted that the four mixtures contained essentially the same amount of cementitious materials. The higher strength of blended cement concrete may stem from the water reducing effect of fly ash and the accelerated hydration due the activation of sodium sulfate.

3.3. Freezing and thawing resistance

The freezing and thawing resistance of concrete was measured by the loss of its dynamic modulus of elasticity. Fig. 1 shows the relationship between the relative dynamic modulus of elasticity and the number of freezing and thawing cycles. The concrete was non-air-entrained. The

Table 6
Compressive strength of concrete

Mixture designation	Compressive strength (MPa)			
	3 days	7 days	28 days	91 days
Control	32.6	38.2	46.9	56.8
C4	36.8	45.4	55.9	63.4
C6	32.4	40.7	54.8	59.0
C8	26.3	36.1	45.3	53.5

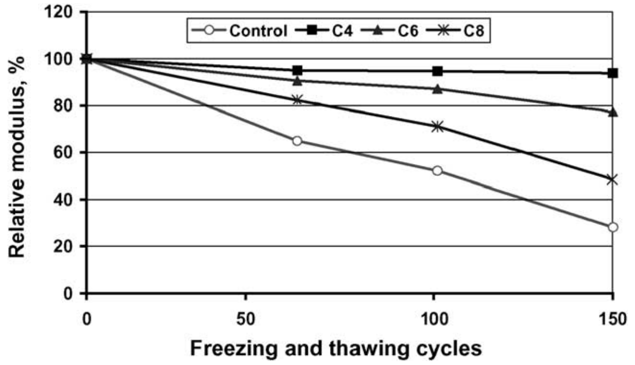

Fig. 1. Loss of dynamic modulus of elasticity with freezing and thawing cycles.

freezing and thawing resistance, therefore, is relatively lower than the air-entrained concrete. The control mixture showed the least resistance to freezing and thawing. It showed scaling on the surface even after the first 60 cycles and its dynamic modulus of elasticity decreased by 35%. Mixture C8 showed less scaling on its surface than the control mixture and lost 18% of its dynamic modulus of elasticity after the first 60 cycles. Mixtures C4 and C6 did not show any scaling after the first 60 cycles. Even after 150 cycles, Mixture C4 showed little scaling and only lost 6% of its dynamic modulus of elasticity. At the 150 cycles, the control mixture lost 72% of its dynamic modulus of elasticity and lost integrity at the edges of the specimens. After 150 cycles, the control mixture lost 2.5% of its total weight, while Mixtures C4 and C6 had much less loss of weight (Fig. 2). Mixture C8 had the highest loss of weight, which indicated that at very high replacement level, the surface scaling resistance of concrete was noticeably reduced.

3.4. Resistance to chloride ion penetration

The chloride ion penetration was measured by the total charge (expressed as coulomb) passed through a slice of concrete cylinder in 6 h. The results are shown in Fig. 3. The resistance to chloride penetration was greatly increased wit the use blended cements. The total charge passed through the specimens decreased with the increase of mineral additive content in the blended cements. The total charge passed through Mixture C4 was about one-third of the control mixture, and it decreased to about one-fifth and one-sixth for Mixtures C6 and C8, respectively. This improvement in resistance to chloride penetration is mainly due the low-permeability of blended cement concrete.

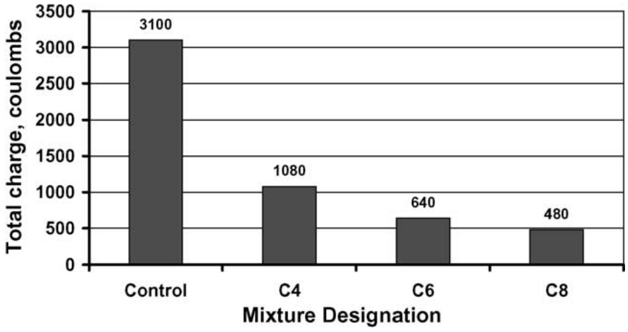

Fig. 3. Resistance to chloride ion penetration in concrete.

3.5. Sulfate resistance

The relationship between length of mortar bars and the immersion time in sulfate solution is shown in Fig. 4. In the first 4 weeks, blended cement mixture BC40 had similar expansion as the control mixture made with Type I cement. After that, the expansion of the control specimens accelerated and was approaching 0.1% in 4 months. The expansion of blended cement mixture BC40 specimens slowed down after 4 weeks of immersion. The overall expansion of blended cement mixture BC60 is very small (about 0.01%) and stabilized after only 4 weeks of immersion. At all test ages, specimens of blended cement mixture BC80 did not show any expansion in sulfate solution. The addition of sodium sulfate and the soluble sulfate/sulfite in clean coal ash and Class C fly ash reacted rapidly with aluminate and calcium hydroxide. As a result, large amount of ettringite was formed at early age. No further ettringite formation occurred when the samples were subsequently exposed to

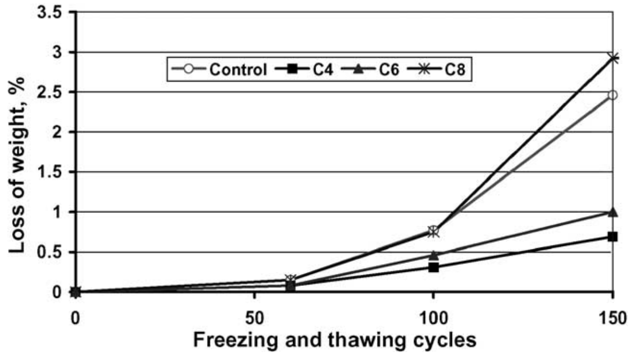

Fig. 2. Loss of weight with freezing and thawing cycles.

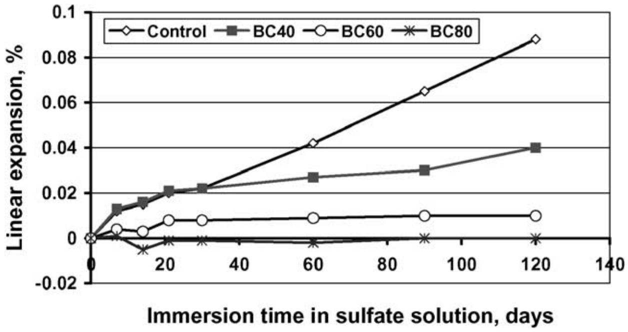

Fig. 4. Linear expansion of mortar bars in sulfate solution.

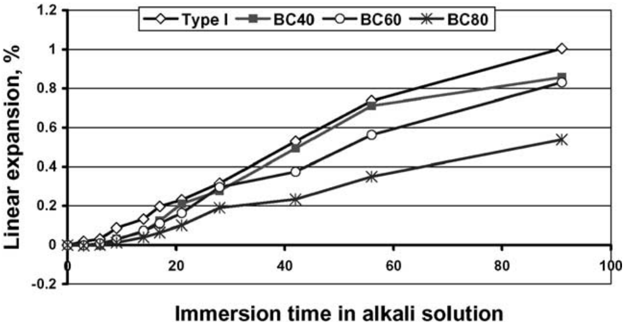

Fig. 5. Linear expansion of mortar bars in alkali solution.

attack by sulfate solution. Based on the same assumption, Prusiski and Carrasquillo [18] developed a parameter termed "sulfation point," which was defined as the point where a stoichiometric balance of sulfate is provided to react with all the C_3A and other reactive aluminates in fly ash completely. They also found that if four times sulfation point amount of gypsum was added to Type I or Type II cement blended with 25–35% Class C fly ash, sulfate expansion could be controlled. It was also reported that the addition of sodium sulfate was even more effective than gypsum on controlling sulfate expansion [19]. The depletion of calcium hydroxide due to pozzolanic reaction in blended cement concrete prevented the formation of gypsum and poorly alkaline magnesium hydroxide when the specimens were exposed to the attack of sodium sulfate or magnesium sulfate solution [20]. The decrease of permeability of blended cement mortar may have also contributed to the reduction in expansion.

3.6. Alkali silica reaction

Additional alkali (Na^+) was incorporated in the blended cements as a chemical activator. This may cause expansion due to alkali-silica reaction. On the other hand, mineral additives in blended cements tend to reduce ASR expansion. Test results show (Fig. 5) that all tested blended cements had lower expansion than the control mixture made with Type I cement at test ages up to 91 days. The ASR expansion decreased with the increasing amount of mineral additives. However, none of the blended cements can be classified as "low reactivity with alkali-reactive aggregates" according to ASTM C 1157 (14 days $<0.02\%$ and 56 days $<0.06\%$).

4. Conclusions

At the same cement content and same slump, concrete produced from the multicomponent blended cements performed better than the Type I cement concrete. Concretes produced from blended cements with 40% and 60% mineral additives had higher strength and durability than the control mixture. With 80% mineral additives, the concrete had equivalent strength development and freezing and thawing resistance as the Type I cement concrete, but it had much higher resistance to alkali silica reaction and sulfate attack.

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References

[1] T.R. Naik, S.S. Singh, Fly ash generation and utilization—an overview, in: A.K. Suri, A.B. Harapanahalli (Eds.), Recent Trends in Fly Ash Utilization, SOFEM Publisher, New Delhi, India, 1998, pp. 1–25.

[2] P.K. Mehta, Mineral admixtures for concrete—an overview of recent developments, in: M.W. Grutzeck, S.L. Sarkar (Eds.), Advances in Cement and Concrete, ASCE, New York, 1994, pp. 243–256.

[3] Y.M. Maltais, J. Marchand, Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars, Cem. Concr. Res. 27 (7) (1997) 1365–1377.

[4] J. Davidovits, High-alkali cements for 21st century concretes, in: P.K. Mehta (Ed.), Concrete Technology—Past, Present, and Future, vol. SP-144, ACI, Farmington Hills, MI, 1994, pp. 385–397.

[5] C.S. Poon, S.C. Kou, L. Lam, Z.S. Lin, Activation of fly ash/cement systems using calcium sulfate anhydrite ($CaSO_4$), Cem. Concr. Res. 31 (6) (2001) 873–881.

[6] P.K. Mittal, K. Kumar, Experience in Separate Grinding Systems for Blended Cement, World Cement, Palladian Publishing, Farnham, UK, 1996, pp. 42–44 (Feb.).

[7] B. Osback, F.L. Smith, Effect of grinding on properties of fly ash cements, Proceedings of Materials Research Society Annual Meeting, MRS, Boston, MA, 1981, pp. 281–288 (Fall).

[8] T.R. Naik, B.W. Ramme, Low cement content high strength concrete, Cem. Concr. Res. 17 (3) (1987) 283–294.

[9] V.M. Malhotra, CANMET investigations dealing with high-volume fly ash concrete, in: V.M. Malhotra (Ed.), Advances in Concrete Technology, CANMET, Ottawa, Canada, 1992, pp. 433–471.

[10] H. Uchikawa, T. Okamura, Binary and ternary components blended cement, in: S.L. Sarkar (Ed.), Mineral Additives in Cement and Concrete, ABI Books Private, New Delhi, India, 1993, pp. 1–79.

[11] E.E. Berry, Strength development of some blended cement mortars, Cem. Concr. Res. 10 (1) (1980) 1–11.

[12] M. Nehdi, Ternary and quaternary cements for sustainable development, Concr. Int. 23 (4) (2001) 35–42.

[13] S. Popovics, Portland cement–fly-ash–silica–fume system in concrete, Adv. Cem. Based Mater. 1 (2) (1993) 83–91.

[14] M. Regourd, B. Mortureux, H. Hornain, Use of condensed silica fume as filler in blended cement, in: V.M. Malhotra (Ed.), Proceedings of First CANMET/ACI International Conference on Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete, Montebello, Canada, vol. SP-79, ACI, Farmington Hills, MI, 1983, pp. 847–865.

[15] Z. Wu, T.R. Naik, Spray–dryer ash as a setting regulator for blended

cements, in: V.M. Malhotra (Ed.), Proceedings of 5th CANMET/ACI International Conference on Recent Advance of Concrete Technology, Singapore, CANMET, Ottawa, Canada, July 29 – August 1, 2001.

[16] Z. Wu, T.R. Naik, Chemical activated blended cements, under review for publication on ACI Mater. J.

[17] T.R. Naik, B.W. Ramme, Effects of high-lime fly ash content on water demand, time of set, and compressive strength of concrete, ACI Mater. J. 87 (6) (1990) 619 – 626.

[18] J.R. Prusinski, R.L. Carrasquillo, Using medium to high volume blended cements to improve the sulfate resistance of high-lime fly ash concrete, in: V.M. Malhotra (Ed.), Proceedings of 5th CANMET/ACI International Conference on Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Milwaukee, WI, vol. SP-153, ACI, Farmington Hills, MI, 1995, pp. 43 – 65.

[19] R.B. Freeman, R.L. Carrasquillo, Production of sulfate-resistant concrete containing high-calcium fly ash and sodium sulfate admixture, in: V.M. Malhotra (Ed.), Proceedings of 5th CANMET/ACI International Conference on Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Milwaukee, WI, SP-153, ACI, Farmington Hills, MI, 1995, pp. 153 – 176.

[20] P.K. Mehta, Concrete Structure, Properties, and Materials, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1993.