# Development Mix Design Alkali-Activated Cement Powder Concrete

Oleksandr HELEVERA<sup>a</sup>, Andrii RAZSAMAKIN<sup>a</sup>, Igor RUDENKO<sup>a,1</sup>, Oleksandr KONSTANTYNOVSKYI<sup>a</sup> and Volodymyr SMESHKO<sup>a</sup>

<sup>a</sup> Scientific Research Institute for Binders and Materials, Kyiv National University of Construction and Architecture, 03037 Povitroflotskyi Avenue, 31, Kyiv, Ukraine

Abstract. The development of reactive powder concretes based on alkali-activated cements for the construction and protection of critical infrastructure is of worldwide importance for improving the safety of their exploitation. The factors influencing the kinetics of strength gain and drying shrinkage of reactive powder concretes using sodium silicate pentahydrate as an alkaline activator were determined. It was shown that increasing the ratio of alkali-activated cement to sand from 1/3 to 1/1 and using the activator in the liquid state increased the concrete strength gain: the compressive strength was 52.3 MPa, 85.0 MPa, 100.6 MPa, and 116.7 MPa at 1, 3, 28, and 90 d. The ratio of compressive strength to flexural strength was in the range of 5.3...5.9 after 28 d, indicating high fracture toughness of the concrete. Higher content of alkali-activated cement caused a decrease in the influence of sand granulometry on concrete strength. This was due to "floating" placement of aggregate in the cement matrix. The introduction of fine calcite as an additive ensured to reduce the shrinkage of concrete by 1.3...1.5 times at 90 d due to the densification of the microstructure and the intensification of crystallization processes. The implementation of these measures resulted in high strength alkali-activated cement reactive powder concrete of strength class C80/95, high fracture toughness, and reduced drying shrinkage.

Keywords. Reactive powder concrete, alkali-activated cement, high strength, drying shrinkage

#### 1. Introduction

The development of ultra-high performance concretes (further, UHPC) for implementation in structures with high requirements for protection, impermeability, and durability (fortifications, nuclear power plants, hydraulic structures, bridge decks, bomb shelters, etc.) is a current global trend in security and defense industry [1, 2, 3].

UHPC provide high strength (45...55 MPa and 70...150 MPa at the ages of 1 and 28 d) [4], crack resistance [5], corrosion resistance [6], etc. However, UHPC require the use of expensive additives-modifiers, as well as high production standards and concrete curing [7].

**Reactive powder concretes.** Reactive powder concretes (further, RPC), effective UHPC in the mentioned constructions, are characterized by high strength and crack

<sup>&</sup>lt;sup>1</sup> Igor RUDENKO, Corresponding author, Scientific Research Institute for Binders and Materials, Kyiv National University of Construction and Architecture, 03037 Povitroflotskyi Avenue, 31, Kyiv, Ukraine; E-mail: igor.i.rudenko@gmail.com.

resistance, fracture energy, ultimate tensile strain, fire resistance, etc. [8]. RPC is achieved by an approach that includes the elimination of coarse aggregate, reducing the water-to-cement ratio, lowering the CaO/SiO<sub>2</sub> ratio by using the silica-fume, and applying the microfiber [9-11]. High content of cement (up to 1000 kg/m<sup>3</sup>) and silica-fume in RPC reduce material sustainability because of environmental friendliness and high cost and cause high shrinkage [8]. In order to eliminate the above-mentioned deficiencies, it is recommended to replace part of the cement (up to 50 % by weight) or silica fume (10...15 % by mass) with such additional materials as limestone, various slags, fly ash, glass powder, etc. [12].

Alkali-activated cements. The most effective cements in RPC are those obtained by alkaline activation of blast furnace cements CEM III/C (at a ground granulated blast furnace slag content of 81-95 % per EN 197-1:2011). Such alkali-activated cements (further, AAC) (or alkali-activated slag cement per the Ukrainian National Standard DSTU B V.2.7-181:2009) are effective because of a comprehensive approach to the consumption of natural resources and energy, as well as a responsible attitude to the environment [13, 14]. It is known that the most effective activators are sodium silicates, the anions of which are similar to hydrated primary products of destruction of the aluminum-silicon-oxygen framework, and serve as their additional reserve [15]. The use of sodium silicates in the form of an aqueous solution promotes greater intensification of the structure formation processes in cements compared with dry powder [16]. The use of AAC based on sodium metasilicate in RPC ensures, in addition to high strength, high heat resistance [17], sulphate resistance [18], frost resistance [19, 20], and resistance to marine environments [21]. Increased fracture toughness is another well-known benefit of AAC materials [22].

**Drying shrinkage.** It is known that AAC are characterized by higher shrinkage compared to Portland cements due to the increased content of gel-like and submicrocrystalline phases in the hydration products in the absence of crystalline phases of portlandite  $Ca(OH)_2$  and ettringite  $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$  [15]. This feature complicates the issue of regulation shrinkage in RPC based on AAC. A well-known way to reduce the shrinkage of AAC is the use of mineral additives (limestone, fly ash, silica fume), chemical additives (shrinkage reducing agents, expanding agents, surfactants, superabsorbent polymers, and nanoadditive), and different fibres (steel fibres, polypropylene fibres, carbon fibres, glass fibres) [23-27].

The aim of this study was mix design of high-strength alkali-activated cement reactive powder concrete with reduced drying shrinkage.

#### 2. Raw Materials and Testing Techniques

Used as components of AAC were:

- Ground granulated blast furnace slag (further, GBFS) (oxides, % by mass: CaO - 50.98; SiO<sub>2</sub> - 32.13; Al<sub>2</sub>O<sub>3</sub> - 11.48; Fe<sub>2</sub>O<sub>3</sub> - 0.40; MgO - 1.14; K<sub>2</sub>O+Na<sub>2</sub>O - 0.77; SO<sub>3</sub> - 1.80; LOI - 1.30), specific surface area (S) = 400 m<sup>2</sup>/kg (by Blaine), modulus of basicity  $M_b = 1.18$ , glassy phase content - 84.0 %;
- CEM I 42.5 N (oxides, % by mass: CaO 65.00; SiO<sub>2</sub> 21.00; Al<sub>2</sub>O<sub>3</sub> 5.60; Fe<sub>2</sub>O<sub>3</sub> 4.80; MgO 2.50; SO<sub>3</sub> 0.70; K<sub>2</sub>O+Na<sub>2</sub>O 0.15; LOI 0.25) per EN 197-1:2011, specific surface area (S) = 390 m<sup>2</sup>/kg (by Blaine).

Sodium metasilicate pentahydrate (Na<sub>2</sub>O·SiO<sub>2</sub>·5H<sub>2</sub>O) per CAS 497-19-8 was used in a solid aggregate state (a non-hygroscopic powder) and in a liquid aggregate state (a solution with a density of 1.24 g/ml). Sodium metasilicate was added in two aggregate states, both in equal quantities - 10.0 % (calculated on dry matter) or 2.9 % (calculated by Na<sub>2</sub>O).

Used as fine aggregates in RPC were:

- Siliceous sand with non-optimized granulometry (fraction, %: 0...0.16 mm 13.1, 0.16...0.315 mm 65.00, 0.315...0.63 mm 16.00, 0.63...1.25 mm 5.10, 1.25...2.5 mm 0.6; 2.5...5.0 mm 0.2) per the National Standard of Ukraine DSTU B V.2.7-232:2010;
- Monofractional siliceous sand (fraction, %: 0.16...0.315 mm 0.20, 0.315...0.63 mm 16.50, 0.63...1.25 mm 83.30) per National Standard of Ukraine DSTU B V.2.7-189:2009;
- Siliceous sand with optimized granulometry (sieve residue, %: 0.16...0.315 mm 22.47, 0.315...0.63 mm 32.36, 0.63...1.25 mm 45.17.

The optimum ratio of silica sand fractions was determined by approximating the overall granulometric curve to the ideal fuller curve, which ensures minimal intergranular voids. The fraction passed through the 0.16 mm sieve was not used.

Finely dispersed calcium carbonate (CaCO<sub>3</sub>) per CAS 471-34-1 was used for regulation of RPC drying shrinkage.

RPC were prepared in a standard Hobart mixer.

The fracture toughness of concrete was estimated from the values of compressive strength to tensile strength in flexural ratio.

The proper deformations of fine-grained concrete were determined on specimens  $40 \times 40 \times 160$  mm. After manufacturing and hardening in forms with an insulated surface for 1 d, the samples were removed from forms and stored for 7 d under the normal conditions (t =  $20\pm2$  °C, R.H. =  $95\pm5$  %). Then the samples were stored over saturated solution of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) at t =  $20\pm2$  °C and R.H. = 65 % till the control age. The length of samples after 1 d was taken as the initial one (zero).

# 3. Results and Discussions

## 3.1. Effect of Cement: Sand Ratio on Strength RPC

#	Compositions of AAC, % by mass			AAC- to-	water-	Consis tency	Compressive strength / flexural strength, MPa, age, d						
	GBFS	CEM I 42.5 N	sodium metasilicate	sand ratio	ratio	(flow), mm	1	2	3	7	28	90	
1	- 85 -		10	1:1	0.227	180	<u>35.7</u> 5.9	<u>55.1</u> 6.7	<u>63.8</u> 7.4	<u>73.6</u> 10.5	<u>87.5</u> 14.8	<u>101.5</u> 15.9	
2		5		1:2	0.220	165	<u>27.1</u> 6.0	<u>42.8</u> 7.1	<u>50.7</u> 8.8	<u>57.7</u> 9.2	<u>67.7</u> 11.0	<u>78.5</u> 13.0	
3				1:3	0.210	145	<u>20.7</u> 5.6	<u>31.4</u> 5.8	<u>35.7</u> 6.1	<u>42.4</u> 8.3	<u>49.8</u> 10.5	<u>57.0</u> 12.5	

Table 1. Strength of alkali-activated cement RPC vs. AAC-to-sand ratio.

The influence of the AAC-to-sand ratio on strength was investigated using siliceous sand with non-optimized granulometry (table 1). Sodium metasilicate was used in a solid aggregate state.

The rise of AAC content in the RPC increased strength. The compressive strength of RPC for the AAC-to-sand ratios of 1:1, 1:2, and 1:3 was 87.5 MPa, 67.7 MPa and 49.8 MPa at the age of 28 d, and 101.5, 78.5 and 57.0 MPa respectively at 90 d. The ratio of compressive strength to flexural strength was 4.7...5.9 at 28 d and 4.6...6.4 at 90 d, indicating high fracture toughness [28].

#### 3.2. Influence of Sand Granulometry on Strength RPC

Sodium metasilicate was used in a solid aggregate state. The compressive strength of the RPC with different sands was 35.7...40.0 MPa, 87.5...91.8 MPa, and 101.5...106.4 MPa at the ages of 1, 28, and 90 d (table 2). The ratio of compressive strength to flexural strength was 5.3...5.9 at 28 d and 5.8...6.5 at 90 d, indicating a high fracture toughness of the material.

The effect of sand granulometry on strength at AAC-to-sand ratio of 1:1 is insignificant, which is due to the "floating" placement of the sand in the cement matrix.

#	Composition of RPC, % by mass									Compressive strength / flexural strength, MPa, age, d					
	AAC		type of sand and AAC-to-sand ratio			cm <sup>2</sup> /g									
	GBFS	CEM I 42.5 N	sodium metasilicate	with optimized granu- lometry	with non-optimized granulo- metry	monofraction	pecific surface area of sand	water- to- AAC ratio	Consistency (flow), mm	1	2	3	7	28	90
4				1:1	-	-	111	0.218	200	<u>40.0</u> 7.5	<u><b>61.1</b></u> 7.9	<u>68.8</u> 9.6	<u>77.8</u> 14.3	<u>91.8</u> 17.3	<u>106.4</u> 18.0
5	85%	5%	10%	- 1:1	_	345	0.227	180	<u>35.7</u> 6.3	<u>55.1</u> 6.8	<u>63.8</u> 7.5	<u>73.6</u> 10.8	<u>87.5</u> 14.8	<u>101.5</u> 15.9	
6	-			_	_	1:1	85	0.200	160	<u>38.0</u> 7.2	<u>58.0</u> 7.8	<u>65.8</u> 8.1	<u>76.3</u> 13.2	<u>90.0</u> 15.8	<u>104.4</u> 16.1

Table 2. Strength of alkali-activated cement RPC vs. sand granulometry.

3.3. Influence of the Aggregate State of the Alkaline Component on the Strength of RPC

The solution was used instead of mixing water (table 3).

Sodium metasilicate was used in a liquid aggregate state (a solution with a density of 1.24 g/ml). The use of metasilicate in solution increased strength by 28.2...33.9 %, 9.6...10 % and 9.1...9.6 % at 2, 28, and 90 d.

#	Composition of RPC, % by mass					l, cm²/g			Compressive strength / flexural strength, MPa, age, d					
	AAC		type of AAC-to	sand and sand ra	1 itio	Specific surface area of sand	Solution -to- AAC ratio	Consistency (flow), mm		2	3	7	28	90
	GBFS	CEM I 42.5 N	with optimized granulometry	with non-optimized granulometry	monofraction				1					
7	95%		1:1	_	_	111	0.24	205	<u>52.3</u> 7.5	<u>76.3</u> 8.0	<u>85.0</u> 8.9	<u>94.3</u> 9.0	<u>100.6</u> 14.7	<u>116.7</u> 16.0
8		5%	_	1:1	_	345	0.26	190	<u>49.1</u> 7.4	<u>73.8</u> 8.5	<u>81.1</u> 9.6	<u>87.8</u> 10.2	<u>96.3</u> 13.8	<u>110.8</u> 14.5
9			_	_	1:1	85	0.22	170	<u>51.0</u> 7.0	<u>74.4</u> 7.2	<u>83.0</u> 7.7	<u>91.3</u> 9.1	<u>98.8</u> 14.2	<u>114.6</u> 15.2

Table 3. Strength of alkali-activated cement RPC vs. aggregate state of the alkaline component

### 3.4. Drying Shrinkage of RPC

Drying shrinkage mitigated with increasing cement paste content and decreasing sand content (figure 1). The optimum amount of  $CaCO_3$  additive to provide minimum shrinkage is 20 %. The addition of this additive reduced shrinkage at AAC-to-sand ratio of 1:1 from 0.88 down to 0.6 mm/m and of 1:3 – from 0.66 down to 0.51 mm/m.



Figure 1. Shrinkage deformations of alkali-activated cement RPC at AAC-to-sand ratio of 1:1 composition (*a*) and 1:3 (*b*).

## 4. Conclusions

(a) The possibility of obtaining high-strength alkali-activated cement reactive powder concretes with reduced drying shrinkage was demonstrated due to maximised structure densification and increased the degree of crystallisation of cement matrix hydration products.

(b) An increase in the proportion of alkali-activated cement in the system "binder: sand" from 1:3 to 1:1 was accompanied by an increase in the compressive strength of the concretes in the range 72.5...78.7 %, with values of 35.7 MPa, 55.1 MPa, 63.8 MPa, 73.6 MPa, 87.5 MPa, and 101.5 MPa after 1, 2, 3, 7, 28, and 90 d.

(c) The use of sodium metasilicate in liquid form, instead of in dry form, ensured the maximum reduction of the liquid phase, resulting in a further increase in the kinetics of concrete strength development by 37.5 %, 34.0 %, 27.1 %, 19.3 %, 10.1 %, and 9.2 %, providing 49.1 MPa, 73.8 MPa, 81.1 MPa, 87.8 MPa, 96.3 and 110.8 MPa at the ages of 1, 2, 3, 7, 28 and 90 d respectively. The ratio of compressive strength to flexural strength in the range of 5.3...5.9 confirmed the high fracture toughness of the concrete.

(d) The modification of the concrete by the calcite  $(CaCO_3)$  caused a decrease in the drying shrinkage by 1.3...1.5 times at 90 d due to the densification of the microstructure and the intensification of crystallization processes.

(e) The effect of sand granulometry on concrete strength decreases with higher cement content. This was caused by "floating" placement of sand in the cement matrix. In this case the strength was provided mainly by the density of the concrete microstructure.

(f) A high strength alkali-activated cement reactive powder concrete with a strength class of C80/95 with high early strength gain (52.3 MPa, 76.3 MPa, 85 MPa after 1, 2, and 3 d), high fracture toughness (ratio between compressive strength and flexural strength 5.3...5.9), and reduced drying shrinkage was obtained.

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