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Response Surface Methodology to optimize the cement paste mix design: Time-dependent contribution of fly ash and nano-iron oxide as admixtures

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ABSTRACT

Response Surface Methodology with a three factor, two level (2^3) face centered, central composite design showed that the optimum paste mix design with the water-to-binder at 36.0%, fly ash (FA)-to-binder at 29.5% and nano-iron oxide (NI)-to-binder at 0.78% produced a spread percentage of the fresh paste at 107.0% and, at the same time, compressive strengths of the hardened paste at 22.1, 60.4 and 79.8 MPa after 3, 28 and 90 days of curing, respectively. FA began to play a significant role for the compressive strength after 28 days of curing, whereas NI did after 90 days of curing, indicative of time-dependent contribution of FA and NI to the development of compressive strength. These were further supported by the SEM microstructure analysis. Such a delayed involvement of FA and NI in the cement chemistry should be taken into consideration with care when translating laboratory research results typically based on a 28-day strength to field practice where a shorter curing is typically provided for cost reasons.

1. Introduction

The manufacturing of cement accounts for ~5% of the total anthropogenic release of CO_2 to the atmosphere [1,2]. In an effort to reduce anthropogenic CO_2 emission and economic reasons, coal fly ash (FA) has been commonly used to partly replace the Portland cement in concrete [1,3]. Equally important to mention is that partial replacement of Portland cement with FA has generally shown improvement of the workability of the fresh concrete and the mechanical strength and durability of the hardened concrete [4,5]. However, as commonly reported, FA substitution for the Portland cement reduces the rate of strength development [6].

Structural design of ordinary Portland cement concrete is typically based on the strength of the concrete specimens cured for 28 days in the controlled laboratory settings. However, in practice, such a long curing period is not provided mainly to reduce the cost of construction [7]. Not to mention that proper curing ensures concrete structures to meet the requirements for their design life, improper curing generally causes concrete failures at most of the field sites [8,9].

Cement hydration is a chemical reaction of cement with water to form the hydration products, calcium silicate hydrate (C–S–H), portlandite ($Ca(OH)_2$) and calcium sulfoaluminate hydrates (ettringite/monosulfate). The C–S–H gel is the principal hydration product of cement contributing to the early strength development of concrete. The rate and extent of cement hydration are governed mainly by the type of cementing materials, the presence of admixtures and mixture proportions. Pozzolanic reaction by FA with the formed $Ca(OH)_2$ produces additional C–S–H gel. Therefore, the curing period should be prolonged for FA-cement concretes due to a slower pozzolanic reaction, especially when a high volume of FA is used. For example, evidence of FA reaction, determined by $Ca(OH)_2$ consumption, was noticed after 7 days of curing and a significant increase of compressive strength in FA-cement pastes was observed after 28 days [6]. Similarly, pore filling effect and pozzolanic reaction in FA cement concrete occurred after 28 days of curing and a significant contribution of FA addition to the strength was noticed after 91 days of curing [10].

Nano-sized SiO_2, Al_2O_3 and Fe_2O_3 have also been added to cement and concrete as nuclei and/or filler to its microstructure [11–13]. It is known that these metal oxide nanoparticles react with $Ca(OH)_2$ increasing the C-S-H gel production, leading to a denser microstructure, thereby not only decreasing permeability but also improving durability and mechanical strength [11,14]. As they are involved in the chemistry of cement hydration and pozzolanic reactions for FA cement concretes, the rate and extent of nano-sized metal oxide contribution to the strength development would also depend on the curing period.

As such, this study aimed to assess significance of curing period for the development of compressive strength of the cement pastes containing FA and nano-iron oxide (NI) as admixtures. To this end, a global optimization of the mixture was made to find the mix design possessing the desired

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Table 1
Physiochemical properties of Portland cement and fly ash.

Properties	Portland cement	Fly ash
Mineralogical composition (wt.%)		
SiO_2	27.14	30.84
Al_2O_3	6.68	9.93
Fe_2O_3	3.71	5.01
CaO	55.47	39.61
MgO	1.62	0.35
K_2O	0.48	1.01
Na_2O	0.59	0.90
SO_3	3.48	11.43
TiO_2	0.32	0.45
P_2O_5	0.11	0.11
Lime Saturation Factor (LSF)[a]	0.64	n.a.[e]
Silica Ratio (SR)[b]	2.61	n.a.
Alumina to Iron Ratio (AF)[c]	1.80	n.a.
Loss-on-Ignition (% wt.)	5.52	7.62
Blaine (m^2/kg)	554	441
Fineness (% wt.)[d]	92.6	73.7
Specific gravity	2.86	2.55

[a] $LSF = {CaO}/{(2.8\cdot SiO_2 + 1.2\cdot Al_2O_3 + 0.65\cdot Fe_2O_3)}$.
[b] $SR = {SiO_2}/{(Al_2O_3 + Fe_2O_3)}$.
[c] $AF = {Al_2O_3}/{Fe_2O_3}$.
[d] Wet sieve percentage passing the No. 325 (45 μm) sieve (ASTM C430).
[e] n.a.: not applicable.

spread percentage of the fresh pastes and the maximum achievable compressive strength of the hardened pastes cured for 3, 28 and 90 days.

2. Materials and method

2.1. Cement, FA and NI

Portland cement Type IP in compliance with ASTM C595 was used and FA was obtained from a local coal-fueled power plant (AES Puerto Rico) (Table 1). It should be noted that the FA complies with the Class C FA for the most of its mineralogical compositions, except for the SO_3 content (11.4%) that is much higher than the maximum percentage of 5% specified in ASTM C618.

The NI solution was purchased from the Ferrotec (Bedford, NH). It consisted of (in % vol.) nominal 10-nm magnetite (2.8–3.5), proprietary surfactant(s) (2.0–4.0), and water (92.5–95.2) and it had a density of 1.245 g/mL.

2.2. Specimen design and preparation

This study was designed in a three factor, two level (2^3) face centered, central composite design aiming to assess the main, quadratic and interaction effects of the independent variables, the percentages of water-to-binder (W/B, 35–37, X_1), FA-to-binder (FA/B, 20–40, X_2) and NI-to-binder (NI/B, 0.5–3.0, X_3), on the dependent response variables, spread percentage (Y_1) of the fresh pastes and compressive strength (Y_2) of the hardened pastes (Table 2). In this study, the binder is defined as the total amount of Portland cement and FA. Response Surface Methodology (RSM) was utilized to optimize the mix design in order to obtain a time-dependent maximum compressive strength of cement pastes cured for 3, 28 and 90 days and achieve the desired spread percentage of the fresh pastes simultaneously.

A mechanical mixer was used to prepare the cement paste specimens in accordance to the ASTM C192. Mixed paste was cast in plastic molds of 2-in in diameter and 4-in in height. The standard rodding consolidation method was used for compaction of each specimen in accordance to the ASTM C192. After 24 h, specimens were demolded and cured in lime-saturated tap water at ambient temperature (24 ± 2 °C).

2.3. Response Surface Methodology

Central composite design (CCD) has been the most commonly used design method with RSM in statistically assessing the mathematical relationship between the independent variables and the responses. For example, CCDs with RSM were employed to optimize the amount of the Portland cement and silica fume to yield an acceptable mechanical strength of ultra-high-performance-fiber reinforced concrete [15]. CCD involves the use of a two-level of full or fractional factorial points (8 points for a 3 factor design (i.e., k = 3)), 2*k* axial points, and center points. The number of center points depends on the replication. CCD can have different design properties by controlling the value of α that is the distance from each axial point to the center of the design space.

Table 2
Matrix of 2^3 face centered central composite design and the measured dependent variables.

Run	Point[a]	Mix design of independent variables[b]						Measured dependent variables[c]			
		Coded			Uncoded (% wt.)			Y_1 (%)	$Y_{2,3d}$ (MPa)	$Y_{2,28d}$ (MPa)	$Y_{2,90d}$ (MPa)
		X_1	X_2	X_3	X_1	X_2	X_3				
1	F	−1	−1	−1	35	20	0.5	89.5	20.6 ± 0.5	59.6 ± 1.4	78.8 ± 1.6
2	F	1	−1	−1	37	20	0.5	110.0	21.1 ± 1.0	47.5 ± 6.3	69.2 ± 2.4
3	F	−1	1	−1	35	40	0.5	84.8	17.8 ± 0.3	49.3 ± 14.8	64.6 ± 3.5
4	F	1	1	−1	37	40	0.5	97.3	14.2 ± 0.9	46.6 ± 6.6	69.0 ± 3.7
5	F	−1	−1	1	35	20	3.0	137.3	18.9 ± 0.8	54.6 ± 0.8	72.1 ± 2.9
6	F	1	−1	1	37	20	3.0	135.5	22.8 ± 0.3	27.9 ± 2.2	56.5 ± 3.2
7	F	−1	1	1	35	40	3.0	106.8	19.5 ± 2.1	55.0 ± 1.7	64.8 ± 21.4
8	F	1	1	1	37	40	3.0	115.8	16.3 ± 2.3	47.8 ± 7.9	60.1 ± 4.7
9	A	−1	0	0	35	30	1.75	97.0	26.4 ± 2.4	59.5 ± 9.0	72.6 ± 5.2
10	A	1	0	0	37	30	1.75	120.3	27.1 ± 1.1	51.1 ± 11.8	63.7 ± 7.7
11	A	0	−1	0	36	20	1.75	126.8	37.4 ± 1.9	46.1 ± 7.9	57.8 ± 6.5
12	A	0	1	0	36	40	1.75	101.8	21.3 ± 1.1	49.3 ± 8.1	64.1 ± 2.0
13	A	0	0	−1	36	30	0.5	97.3	26.8 ± 1.3	60.3 ± 14.9	79.1 ± 5.8
14	A	0	0	1	36	30	3.0	121.5	31.2 ± 0.7	52.3 ± 23.9	79.3 ± 2.6
15	C	0	0	0	36	30	1.75	113.5	17.0 ± 1.0	60.8 ± 2.5	60.6 ± 16.2
16	C	0	0	0	36	30	1.75	115.8	16.5 ± 0.3	62.4 ± 5.8	75.5 ± 2.7
17	C	0	0	0	36	30	1.75	150.0	16.7 ± 1.1	60.5 ± 7.0	76.1 ± 3.7
18	C	0	0	0	36	30	1.75	119.0	26.7 ± 0.9	64.3 ± 2.8	76.8 ± 3.2
19	C	0	0	0	36	30	1.75	114.0	27.9 ± 0.6	42.8 ± 29.7	72.2 ± 3.9
20	C	0	0	0	36	30	1.75	115.3	27.8 ± 0.5	53.4 ± 14.6	74.7 ± 5.9

[a] F: factorial point, A: axial point, C: center point.
[b] X_1: W/B, X_2: FA/B, X_3: NI/B.
[c] Y_1: spread % (single measurement), Y_2: 3-, 28-, and 90-day compressive strengths (mean ± standard deviations, n = 3).