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Effect of fly ash and grading agent on the properties of mortar using response surface methodology

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ABSTRACT

In this study, the concept of Response Surface Methodology (RSM) was presented to optimize and compare the effect of fly ash and grinding agent on the cement compressive strength at 7, 28 and 90 days.

This method showed that the optimum paste mix design with the fly ash (FA) to binder at 0%, clinker (KK) to binder at 66.4% and debit grinding agent (GA) to binder at 306 kg/t produced a spread compressive strengths of the hardened paste at 29.0, 38.0 and 50.4 MPa after 7, 28 and 90 days of curing, respectively. The fly ash began to play a significant role for the compressive strength after 28 days of curing, whereas grinding agent was reactive after 7 days of curing, indicative of time dependent contribution of fly ash and grinding agent to the development of compressive strength. These were further supported by the SEM microstructure analysis. Such a delayed involvement of fly ash and grinding agent in the cement chemistry should be taken into consideration with care when translating laboratory research results typically based on 28 days 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 [31,9]. In an effort to reduce anthropogenic CO_2 emission and for the economic reasons as reducing the clinker grinding energy, the grinding agent has been commonly used to partly replace the Portland cement in concrete and to improve its properties [5]. Equally important to mention is that addition of the grinding agent in Portland cement has generally shown improvement of the workability of the fresh concrete [2], the mechanical strength and durability of the hardened concrete [15,37]. However, as commonly reported, the grinding agent increases the rate of strength development and it also reduces the appearance of cracks and minor deterioration [26,8].

Cement is a widely used construction material worldwide. The raw materials are easily available and it does not require complex or expensive equipment to create. But due to its popularity and demand as a construction material, some of its component should have an alternative source. In this context, fly ash (FA) and grinding agent have been commonly used to partly replace the Portland cement in concrete.

Fly ash is a by product waste material of thermal power plants. The manufacturers of these days use this waste as substitute to various construction materials and it is sold at a low cost. Pozzolanic reaction by fly ash (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 [10]. Similarly, porefilling effect and pozzolanic reaction in FA cement concrete occurred after 28 days of curing and a significant contribution of fly ash addition to the strength was noticed after 90 days of curing [7].

Due to its increasing demand, it is not easy to find the fly ash available in market, which presents a serious problem. In addition, another solution is applied, the use of grinding agent (GA) which presents a revolution in the cement industry. It is known that this grinding agent is used to facilitate the grinding of the Portland clinker and to improve the cement physicochemical properties. This GA adsorbed on the surface of the material to be comminuted, i.e. either on the exterior surfaces or on the microcrack walls where it manages to enter. An immediate effect is a decrease in hardness accompanied by phenomena of adhesion and clogging [39]. Also, this cement addition gets adsorbed on the surface of the material undergoing grinding and reduces the surface energy, which only leads to further breakage and it facilitates the grinding of the clinker (The Rebinder effect) [30–36]. In

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addition, the effect of this agent on the improvement of cement quality is presented by the formation of a dense film between the cement grains, during the cement hydration, which develops the physicochemical properties of the cement.

Due to the high importance and efficiency of these products, the aim of this research wasto assess significance of curing period for the development of compressive strength of the cement pastes containing fly ash and grinding agent as admixtures. To this end, a global optimization of the mixture was made to find the mix design possessing the minimum of cement grinding time and the maximum achievable compressive strength of the hardened pastes cured for 7, 28 and 90 days.

2. Materials and methods

2.1. Cement, fly ash and grinding agent

- Two types of cement were used: Portland limestone cement type CEM II/A-L 32.5N and Portland siliceous fly ash cement type CEM II/A-V 32.5N in compliance with ASTM C595 were used.The different types of cement were prepared according to the following experiment matrix:

1. Fly ash was obtained from a local coal-fueled power plant (Mahammedia-Marrocco). This fly ash complies with the Class C for all of its mineralogical compositions (Table 1).

The chemical composition of the two cement types and fly ash, showing major components as oxides determined by X-ray fluorescence (XRF) are shown in Table 2.

1. The grinding agent solution was purchased from the MAPEI Company. The chemical composition and the property of the MAPEI adjuvant are presented in the Table 3.

2.2. Preparation of mortars

All mortars were prepared by using distilled water and a binder/sand weight ratio of 1:3, following the procedures described in EN 196-1 [12]. Due to the different fines content of the aggregates, and in order to get suitable workability, the water/binder ratio was 0.5 for mortars made with standard silica sand. The fly ashand grinding agent were dosed as an addition to the total cement mass (w/w%). These two additives were added to the clinker before cement grinding.

Table 1
Experience matrix of the prepared cements.

N° Experience	Clinker	Fly Ash	Gypsum	Limestone	Grinding agent debit
	%	%	%	%	Kg/t
1	60	0	3	37	0
2	70	0	3	27	0
3	60	12	3	25	0
4	70	12	3	15	0
5	60	0	3	37	500
6	70	0	3	27	500
7	60	12	3	25	500
8	70	12	3	15	500
9	60	6	3	31	250
10	70	6	3	21	250
11	65	0	3	32	250
12	65	12	3	20	250
13	65	6	3	26	0
14	65	6	3	26	500
15	65	6	3	26	250

2.3. Compressive strength

Three cubical specimens (4×4×16 cm) for each mix given in the experimental work plan were produced to test compressive strength. The samples were cured under water for 7, 28and 90 days at 20 ± 2 °C temperature and then tested using a hydraulic press following the standard [12]. Each compressive strength value was obtained from the average value of three tests.

2.4. Specimen design and preparation

This study was designed in a three factors, 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 clinker (KK, 60–70, X_1), Fly Ash (FA, 0–12, X_2) and debit grinding agent (GA, 0–700, X_3), on the dependent response variables, compressive strength (Y) of the hardened pastes (Table 4). Related literature and preliminary studies were used to choose these variables and the respective regions of interest [4–41].

In this study, the binder is defined as the total amount of Portland cement and fly ash. 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 7, 28 and 90 days. A mechanical mixer was used to prepare the cement paste specimens in accordance to the ASTM C192.

2.5. Response surface methodology

Onefactoratatime (OFAT) methodology is a conventional approach for optimizing multifactor experiments. OFAT is a changeable single factor method for a specific experiment design while other factors are kept constant and this method is unable to generate appropriate output because the effects of interaction among all factors in the design are not examined truly, and so it is not capable of reaching the true optimum value [13,20]. Hence, response surface methodology (RSM) has been introduced for parameter optimization in a way that number of experiments and interaction among the parameters are reduced to minimal value [3–17].

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 Aldahdooh et al., [1]. Understanding these effects allows manipulation of the levels of the studied factors to manufacture sustainable light weight mortars with durable properties. While there is limited research using statistical designs to produce mortars or concrete, such as: Response Surface Methodology [33] full factorial designs [34], standard orthogonal arrays [16] or mixture experimental designs [42], as far as the authors are aware no studies have used Response Surface Methodology to assess and to optimize the impact of the fly ash, grinding agent and the synergic effect of the interactions on the final properties of lightweight cement mortars.

In this study, cement paste specimens were made in triplicate in a 2^3 face centered CCD (Table 4). Face centered central composite design (CCF) is a special case of CCD where α is equal to one. This forces the axial points of CCF to locate on the surface of the cubic, instead on the sphere space as in CCD, and therefore makes CCF a three-level CCD. The second order polynomial equation (Eq. (1)) was used to fit the data of the CCF:

$$Y=\beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{N} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

Where Y represents the predicted response (i.e., compressive strength), β_0 the intercept, β_i the first-order (linear) coefficient, β_{ii} the second-

Table 2
Variation of chemical composition for the cement types and Fly Ash used to manufacture the mortars.

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI[a]	CaO_l[b]	Blaine (m^2/kg)	Fineness (% wt.)[c]
CEM II/A-L 32.5N	17.7 ± 0.6	3.8 ± 0.1	3.0 ± 0.1	57.1 ± 1.1	2.5 ± 0.2	2.3 ± 0.2	12.3 ± 1.9	0.7 ± 0.1	3565 ± 2.0	3.5 ± 0.4
CEM II/A-V 32.5N	17,5 ± 0.2	3,8 ± 0.1	2,9 ± 0.0	56,4 ± 1.0	2,5 ± 0.1	2,3 ± 0.3	13,2 ± 1.5	0,6 ± 0.1	3565 ± 2.0	3,5 ± 0.3
Fly Ash	52.06	22.23	5.45	5.69	2.36	0.41	7.8	n.a[d]	n.a	14.2

[a] LOI: loss on ignition
[b] Free lime
[c] Dry sieve percentage passing the No. 325 (80 µm)
[d] n.a: not applicable

Table 3
The chemical composition and property of the MAPEI adjuvant.

Chemical composition of the MAPEIadjuvant	
Components	**vol.%**
1,1',1''-Nitrilotripropane-2-Ol	10–12,5
1-(N,N-bis(2-hydroxylethyl)amino))propan-2-olo	7–9,99
Water	40–45
Property of the MAPEI adjuvant	
Density	1.04 g/mL
pH	8.2

order (quadratic) coefficient, β_{ij} the coefficient of interaction effect, x_i and x_j the coded levels of the independent variables X_i and X_j, respectively, and ε the associated random error [19].

Mathematical and statistical interpretations of data were done with NemrodW(Mathieu, 2007). For the spread percentage and the compressive strength after 7, 28 and 90 days of curing, a total of 15 combinations of independent variable settings were run with one replicate at the center points.

The significance of each of the independent variables to the dependent variable and their interactions were determined by an analysis of variance (ANOVA) [21]. Factors with a p-value of 0.05 or lower were determined to be statistically significant, and therefore considered for the predictive regression model. The relationship between the independent variables and the response variables was evaluated by contour plots.

2.6. Scanning electron microscopy

To evaluate the microstructural differences that could be attributed to time-dependent contribution of fly ash (FA) and grinding agent (GA) to the chemistry of the cement pastes. To avoid the effect of the cement composition, four different specimens of Portland cement were prepared with combinations of fly ash/grinding agentratio (FA/GA) at the levels of 0%/0 kg/t or 0%/306 kg/t, 6%/306 kg/t and 6%/0 kg/t, respectively. This ratio is formed from the optimum values of fly ash (6%) and grinding agent (306 kg/t). The reference sample is prepared without fly ash and grinding agent (0%/0 kg/t).

In this case, theclinker percentage was fixed at 97% and 91%. The specimens were cured for 28 and 90 days, and tested for the compressive strength. Then, the microstructure of the fractured surface from the compressive strength test was analyzed by Scanning Electron Microscope operated at 30 keV.

3. Results and discussion

The Y's were measured in the range of 22.44–35.5, 30.12–45.7 and 43.6–59.7 MPa for the hardened pastes cured for 7, 28 and 90 days, respectively. These results clearly showed that the Y was further developed even after 28 days of curing to gain additional Y during late age of curing (i.e., 90 days) (Fig. 1 and Table 4).

3.1. Statistical models of the response surface methodology

The ANOVA for each dependent variable is shown in Table 5. The

Table 4
Matrix of 2^3 face centered central composite design and the measured dependent variables.

Run	Point[a]	Mix design of independent variables[b]						Measureddependentvariables[c]		
		Coded			Uncoded			$Y_{1,7d}$ (MPa)	$Y_{1,28d}$ (MPa)	$Y_{1,90d}$ (MPa)
		X_1	X_2	X_3	X1%	X2%	X_3 Kg/t			
1	F	−1	−1	−1	60	0	0	24.27	32.3	41.8
2	F	1	−1	−1	70	0	0	32.02	41.5	53.13
3	F	−1	1	−1	60	12	0	22.44	30.12	43.8
4	F	1	1	−1	70	12	0	30.25	39.4	39.4
5	F	−1	−1	1	60	0	700	27	35.5	45.5
6	F	1	−1	1	70	0	700	35.5	45.7	57.5
7	F	−1	1	1	60	12	700	24.86	33	42.6
8	F	1	1	1	70	12	700	30.76	40	32.9
9	A	−1	0	0	60	6	350	26.21	34.6	50.8
10	A	1	0	0	70	6	350	31.4	40.74	51.7
11	A	0	−1	0	65	0	350	28	36.7	49
12	A	0	1	0	65	12	350	25.7	34	41
13	A	0	0	−1	65	6	0	27.4	36	46.1
14	A	0	0	1	65	6	700	29.6	38.6	47.8
15	C	0	0	0	65	6	350	27.7	36.35	49

[a] F: factorial point, A: axial point, C: center point.
[b] X_1: %kk, X_2: %FA, X_3: debit of milling agent.
[c] Y_1: 7-, 28-, and 90-days compressive strengths (mean ± standard deviations, n=3).

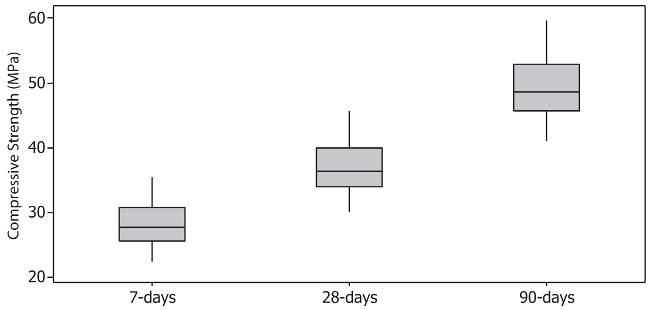

Fig. 1. Box plots of the compressive strength.

Table 5
ANOVA and full regression models statistics.

Term	Y: Compressive strength					
	7 days		28 days		90 days	
	p-value	coefficient	p-value	coefficient	p-value	coefficient
Constant	< 0.01	27.83	< 0.01	36.50	< 0.01	49.70
X_1[a]	< 0.01	3.52	< 0.01	4.18	< 0.01	5.02
X_2	0.004	−1.28	0.005	−1.52	0.005	−1.81
X_3	0.007	1.13	0.007	1.35	0.008	1.62
$X_1{\times}_2$	0.11	NS[b]	0.11	NS	0.13	NS
$X_2{\times}_2$	0.09	NS	0.10	NS	0.10	NS
$X_3{\times}_2$	0.25	NS	0.26	NS	0.26	NS
$X_1{\times}_2$	0.30	NS	0.30	NS	0.31	NS
$X_1{\times}_3$	0.62	NS	0.66	NS	0.63	NS
$X_2{\times}_3$	0.19	NS	0.20	NS	0.21	NS

XiXj: interactions between the independent variables i et j
[a] X_1: %clinker, X_2: %fly ash, X_3: debit of ginging agent
[b] NS: The contribution of the terms was not statistically significant.

suitability of the model was validated by checking residual plots and the lack of-fit at a significance level of 0.05. Residual plots confirmed that the residuals were independent, were normally distributed, and had equal variances.

Lack of fit for each response resulted in p-values much greater than 0.05, indicating that the models accurately fit the data. The high regression coefficients (R^2) of 98.1, 98.0 and 98.0% for the 7, 28 and 90 days compressive strengths, respectively, also described the adequacy of the model. Themain, quadratic and interactive effects of independent variables (X's) on the dependent variable (Y) were also assessed at a significance level of 0.05 (Table 5). The estimated regression models after removing insignificant terms for the Y's are given in Eqs. (2) to (4):

$$Y_{7d} = 27.83 + 3.52X_1 - 1.28X_2 + 1.13X_3 \tag{2}$$

$$Y_{28d} = 36.50 + 4.18X_1 - 1.52X_2 + 1.35X_3 \tag{3}$$

$$Y_{90d} = 48.70 + 5.00X_1 - 1.80X_2 + 1.60X_3 \tag{4}$$

It should be noted that the coefficient values were for the terms of uncoded independent variables. As shown in Eqs. (2, 3 and 4), the three linear terms of X_1, X_2 and X_3 factors significantly affected the Y at different ages (7, 28 and 90 days) with the X_1 influencing the most. Thereby, the X_2 and X_3 had the same effects on Y, but the variable X_2 has a negative effect, which means that the value of Y decreases as the percentage of fly ash increases. A significant increase of the Y could be attributed to an enhanced fluidity caused by the surfactants coated on the chemical composition and the percentage of clinker and the fly ash used, also the surfactants coated on the grinding agent. An enhanced-cementcompressive strengthdue to the addition of fly ash was also reported previously [24].

In other words, the 7, 28, 90 days compressive strengths of the paste were predicted to decrease by the replacement of Portland cement with fly ash, but only slightly. This could be due to the slow development of compressive strength in fly ash cement pastes [10].

The Y_{7d}, the Y_{28d} and Y_{90d} were predicted with first order polynomial models. Thereby, the 7, 28, 90 days compressive strengths of the paste were predicted as a function of the linear terms of clinker percentage and fly ash and also of the flow rate of the grinding agent. Although, no interactions between the independent variables were found to be statistically relevant to any of the dependent variables (Table 5). Thereby, they were not factored into the prediction models.

Table 6
Optimization criteria for each dependent variable.

Dependent variable	Measured Y's		Optimization	
	Lower	Upper	Goal	Target
Y: compressive strength (MPa)				
7 days	22.4	35.5	Maximum	35.5
28 days	30.1	45.7	Maximum	45.7
90 days	41.0	59.7	Maximum	59.7

3.2. Response optimization of the cement pastes

Table 6 summarizes the optimization goals of the response surface methodology (RSM) to find the best combination of independent variable settings that could produce the greatest Y's at the different curing periods. The greatest compressive strengths measured (Fig. 1) were selected as the optimality criteria of Y's.

The desirability functions were utilized to simultaneously optimize the responses. As shown in Table 7, the optimum independent variable setting at 66.4% X_1, 0% X_2 and 306kg/t X_3 resulted in the Y_{7d}, Y_{28d} and Y_{90d} at 29.0, 37.9 and 50.4 MPa, respectively. This was attained with the global desirability value at 96.23% and with the specific desirability values of responseat96.75, 95.00and 96.95% for the Y_{7d}, Y_{28d} and Y_{90d}, respectively. It should be noted that the optimization goals could be assigned at different weights and importance. In the current study, however, the target responses had an equal weight and importance.

The maximum compressive strength of the cement for the three ages can be reach at the same time, with just using a grinding agent as the additive cement and without using fly ash. The grinding agent has the ability to improve the quality of the cement by forming a dense film around the cement grains which solidifies the crystal lattice of cement and fills the voids between the grains. Thus, the fly ash effect is negligible in front of the grinding agent effect which will improve the cement quality a remarkable way.

3.3. Contour plots for response surface methodology at the optimum settings

Contour plots of the dependent responses were drawn in a function of two independent variables while the third independent variable was held at its optimal value. As shown in Fig. 2, the Y increased with the decrease of fly ash percentage (X_2) and increase of grinding agentdebit(X_3) at the same time, while the clinker percentage (X_1) was held at the optimum level of 65%. So, the values of Y decrease as

Table 7
The desirability functions of Y's.

Dependent variable	Name of dependent variable	Value	desirability values %
Y_{7d}	CS* 28 days	37.89	96.75
Y_{28d}	CS 7 days	28.98	95.00
Y_{90d}	CS 90 days	50.35	96.95
	Global Desirability		96.23

* CS: Compressive strength

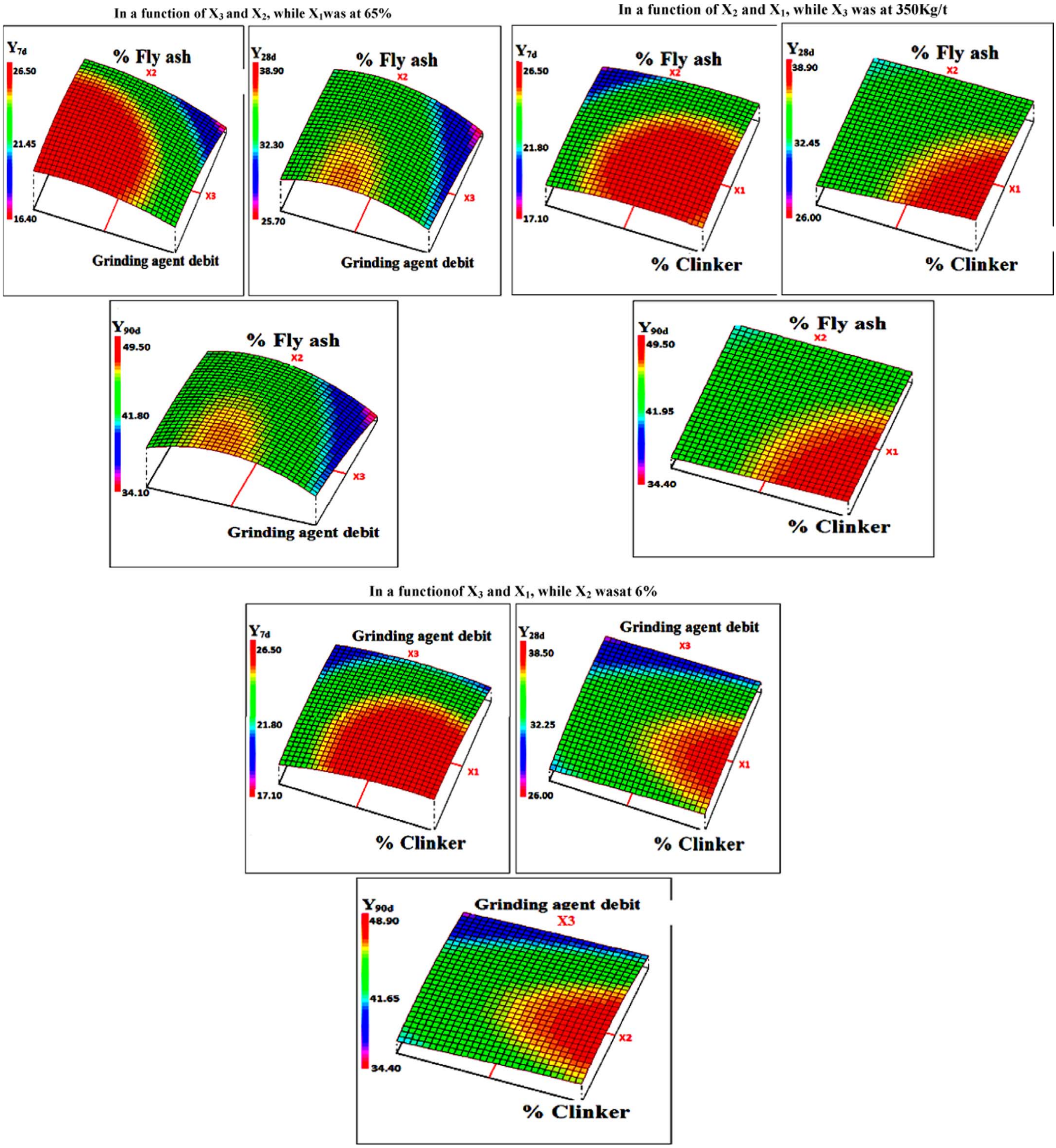

Fig. 2. Contour plots of the Y_{7d}, Y_{28d}, and Y_{90d} in an interactive effect of two independent variables while the third one was held at its optimum level.

the fly ash percentage exceed the 6% despite the increased throughput of the grinding agent. This shows that the fly ash has an effect on the pozzolanic cement, which leads to improving the compressive strength of the cement, but when the percentage of fly ash exceeds 6%, this product has a negative effect on the cement curing.

When the X_2 was held at the optimum level of 6%, the simultaneous increase of X_1 and X_3 enhanced the Y. With the X_3 held at the optimum level of 250kg/t, an enhanced Y was found with the increase of X_2 and the increase of X_1 at the same time.

Overall, a greater Y was found with a greater $X_1$and X_3 but with a lesser X_2. The increase of X_3 would facilitate fluidity of the cement pastes attributed to the polymer (amino alcohol) coated on the grinding agent. This was in agreement with Ouyang et al. Ouyang et al., [24] who documented an increased fluidity of cement with the addition of grinding agents. As shown in Table 1, the fly ash had higher Fineness than the Portland cement used in the study. Therefore, more volume of coarse fly ash was required for making the same weight to the Portland cement, resulting in a reduced Y. This effect was counteracted with an

Table 8
Validation results of the optimum independent variable settings for the dependent variables.

Optimum mix (wt.%)			Y: compressive strength (MPa)[a]								
X_1:KK[d]	X_2:FA[d]	X_3:GA[d]	7-days			28-days			90-days		
			Pred.	Meas.	PE[b]	Pred.	Meas.	PE	Pred.	Meas.	PE
66.4%	0%	306kg/t	31.2	28.8 (±0.7)[c]	8.6	40.3	38.4 (±1.1)	5.1	51.9	50.9 (±1.3)	1.9

[a] Data are the average of triplicate samples.
[b] **luterelativepercenterror** = $\left|1 - \frac{\mathbf{Value_{predicted}}}{\mathbf{Value_{measured}}}\right| \times 100\%$
[c] Standard deviations (n=3).
[d] kk: clinker, FA: fly ash, GA: grinding agent

increase of the X_1 and X_3 in the mixture. The extent of contribution that independent variables had on the development of compressive strength was time dependent.

Increasing Y with the increase of X_3 implies that the addition of grinding agent was effective in supporting the chemistry in cement paste at later curing stages and probably the hydration reactions and hydrate formation were favored and improved. This resulted in higher strength development due to densification of the cement pastes [11,21].

3.4. Model validation

The accuracy of the prediction model was validated by performing another set of experiment where the specimens were made in triplicate at the global optimum mix ratio obtained in Section 3.2 and by comparing the predicted and measured responses. As shown in Table 8, the lowest absolute relative percent error (PE) of the Y's, was found for the Y_{90d} (1.9%), followed by 5.1% for the Y_{28d}. and 8.6% for the Y_{7d}. Therefore, the models generally predicted the dependent variables of Y_{7d}, Y_{28d} and Y_{90d} with good accuracy.

3.5. Fly ash and grinding agent effect on cement grinding time

The grinding of cement is an operation that consumes a large amount of energy and which influences the selling price of cement. So this part of the study consists to check that the use of fly ash and the grinding agent can reduce the grinding time of the cement without affecting its quality.

The Fig. 3 shows that the grinding time increases with the increase of the clinker percentage (case of GA= 0 kg/t and FA=0%), which indicate that the grinding time depends strongly to the clinker percentage. Since clinker is the major component of cement (more than 50%). This compound is presented in the form of nodules so the grinding time is strongly dependent on the diameter and the hardness of these nodules.

The fly ash and grinding agent can reduce the grinding time, but the effect of the grinding agent was better than fly ash. The fly ash presents an abrasive middle for the clinker grains which facilitates their crushing. While, the efficiency of grinding agent was due to the improvement of grinding through the milling agents which is a result of mechanical-chemical effects that affect the fragmentation of grains (Rehbinder effect) and to change in the rheological properties and agglomeration of the powder cement. Wilshaw, Hartley [39].

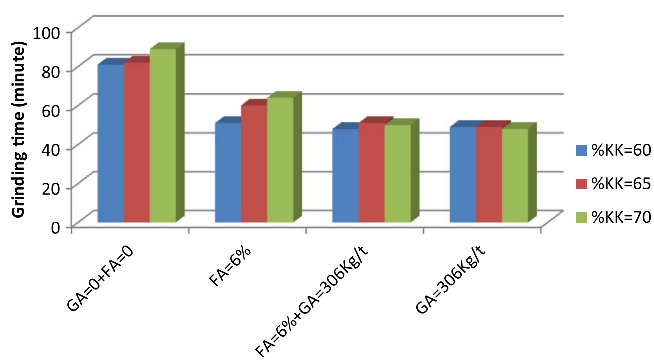

Fig. 3. Grinding time of the cement pastes prepared.

3.6. Microstructural analysis

As shown in Fig. 4, at young ages (7 days) the pastes containing FA (FA6GA0 and FA60GA306)had approximately 5% lower Y_{7d}'s than those without FA (i.e., pastes containing grinding agent FA0GA306) but kept developing the Y_{28d}'s, although still lower than the FA0GA306. The deference between different specimens begins to appear at the 28 days. The compressive strength of the paste containing the grinding agent (FA6GA306 and FA0GA306) had 12% and 21% higher Y_{28d}'s and Y_{90d}'s, respectively than those with fly ash (i.e, FA6GA0). These were in good agreement with the results discussed in Sections 3.1 and 3.3 that X_1 and X_3 have played an important and significant role in the development of Y at the late age of curing. The above findings were qualitatively supported by the SEM microstructural analysis (Fig. 5).

After a 28 days curing, FA6GA0 (Fig. 5E) has a microstructure similar to the control paste (Fig. 5A) having the hydration products of C–S–H gel, $Ca(OH)_2$ and Ettringite phases. For FA6GA0, unreacted fly ash (FA) particles were visible after 7 days of curing (Fig. 5G), but they were under reaction after 28 days of curing (Fig. 5H). In this case, the FA grains fill the pores of the cement paste. These phenomena are not observed for FA0GA306 and FA0GA0 (Fig. 5A and E).This is proved by the fact that the replacement of the cement with fly ash increases the water/cement ratio. For this reason, the initial porous structure of fly ash cement is initially more open than that of reference cement, which decreases the cement mechanical performance at younger ages [38–40].

Between 7 and 28 days, the fly ash initiates their pozzolanic activity, which means that the porosity of the cement matrix begins to decrease. Consequently, the fly ash cement will become more impermeable than reference cement [25–28].

In these age (28 days), the paste containing the grinding agent (GA)

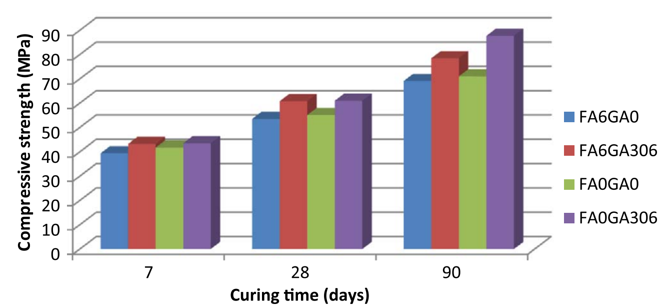

Fig. 4. Compressive strength of the cement pastes prepared for the SEManalysis. Data are means with the standard deviations (n=3).

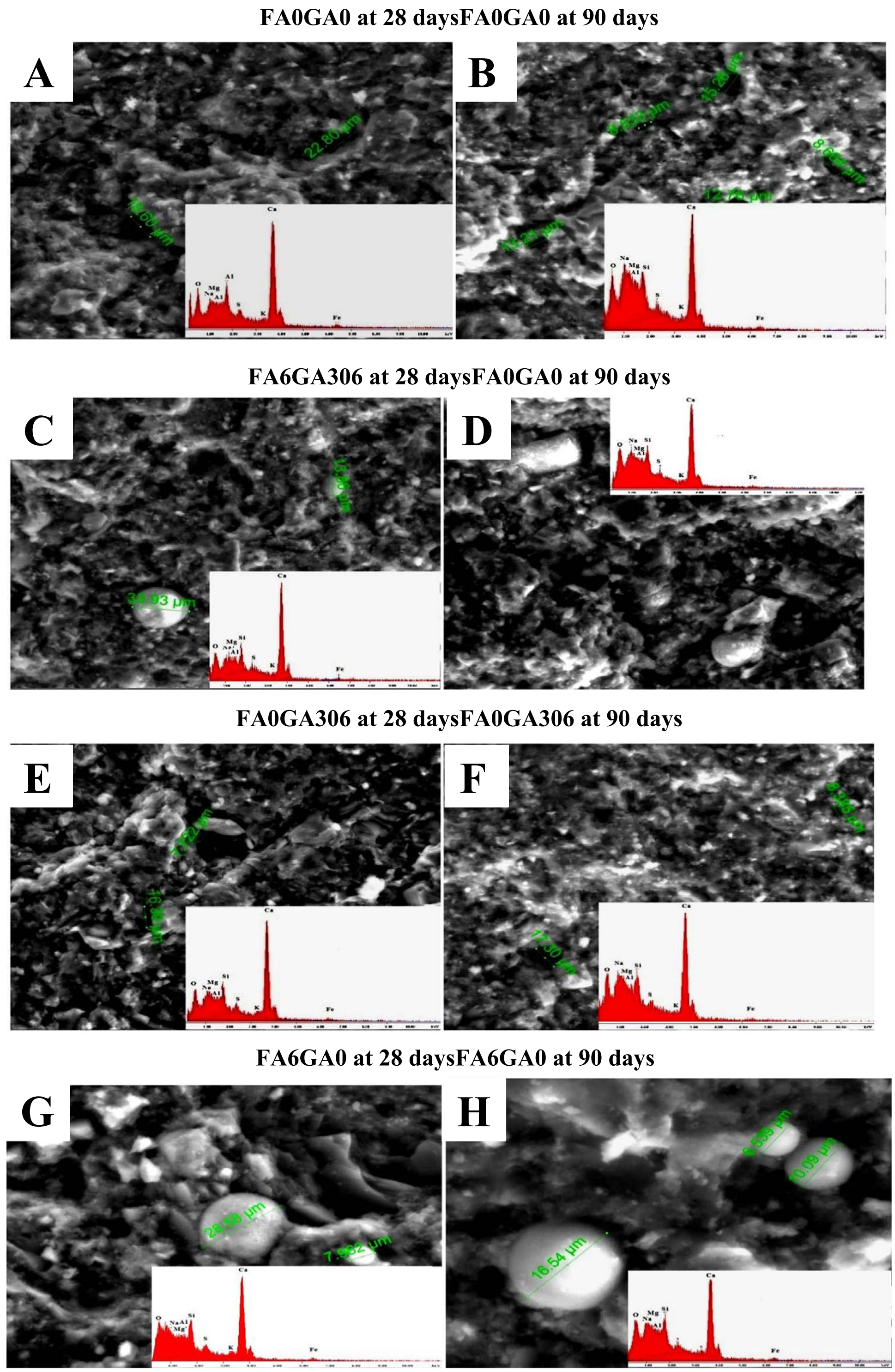

Fig. 5. Scanning electron microscopic images of the hardened cement pastes cured for 7-, 28- and 90- days. FAxGAy stands for x% of FA and y% of GA in themixture.

(Fig. 5F and D) became denser, but they had more flexible microstructures that the control dough (Fig. 5B). This was in agreement with the corresponding results of the compressive strength (Fig. 4) and the time-dependent involvement of fly ash and grinding agent in cement chemistry (Fig. 3). The cement paste had denser microstructures after 90 days of curing (Fig. 5D and F), which is in line with similar 90 days compressive strengths of the pastes (Fig. 4). This implies that grinding agent (GA) creates links result of potential reactions occurring between the GA and the various chemical components of the cement paste at early stage of curing, which leads to the formation of links between the grains by filling the pores, as a consequence, it increases the cement compressive strength. The addition of an adequate amount of the grinding agent accelerates the initial reaction of C_3A with calcium sulphate and it delays the hydration of the C_3S. These reactions improve the cement compressive strength at a young age (7 days) and the cement compressive strength becomes greater after 28 days [14–27].

4. Conclusion

In this investigation, the experimental results of the optimization of mix ratio of the cement paste for the desired spread percentage of the fresh paste and the maximum possible compressive strengths of the hardened pastes for 7, 28 and 90 days, allowed making the following conclusions:

- The link between the cement compressive strength at 7, 28, 90 days and the percentage of clinker, fly ash and the grinding agent debit is presented by linear model.
- the best values of compressive strength at 7, 28 and 90 days can be achieved at the same time by fixing the percentage of clinker at 66.4%, fly ash at 0% and the grinding agent debit at 306 kg/t.
- The compressive strength of pastes significantly increased with the increase of grinding agent debit but with the decrease of fly ash. Such a grinding agent and clinker play a significant role in the development of compressive strength at different age of curing, whereas the addition of grinding agent was found effective in supporting the chemistry in cement paste at early age (i,e., 7 days) and later curing stages, especially after 90 days of curing.
- During hydration, the grinding agent develops the cement hydrates and a crystal system of cement which increases the cement compressive strength.
- SEM microstructural analysis supported delayed contribution of fly ash and grinding agent to the development of compressive strength at late age of the hydration.

Consequently, even the grinding agent is used with a low dose (306 kg/t) it has a double effect and it presents better results than fly ash. On the one hand, it facilitates the grinding of the clinker by improving the cement fineness and on the other hand it develops the cement quality by increasing its compressive strength at young age and in the long term. Therefore, the grinding agent presents a good cement additive.

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