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A STATISTICAL INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF MAGNESIUM PHOSPHATE CEMENT

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ABSTRACT: Magnesium phosphate cement (MPC) is a promising material applied for rapid patch repairing in civil engineering and waste immobilisation in nuclear industry. However, the rheological properties of this new binder material which highly affects its engineering application, is to be explored. The current work aims at investigating the rheological properties of MPC along

with determining the optimum conditions to obtain MPC materials with desirable rheological performances. The Response Surface Methodology (RSM) accompanied by Central Composite Design (CCD) were adopted to establish mathematical model describing the rheological characteristics of MPC in terms of yield stress (Pa) and plastic viscosity (Pa.s), as a function of three independent variables namely W/S ratio, M/P ratio and Borax dosage. The analysis of variance (ANOVA) was also conducted to assess the significance and adequacy of the regression models attained. The results showed that the M/P ratio and Borax dosage could affect significantly the yield stress of MPC, while W/S ratio was the significant coefficient influencing the plastic viscosity. The numerical optimised values of the W/S ratio, M/P ratio and Borax dosage were 0.25, 8.97 and 0.17 respectively, and a MPC paste with desirable rheological characteristics (yield stress of 0.40 Pa and plastic viscosity of 0.93 Pa.s) can be obtained. Further experiments will be carried out to verify the predicted optimum conditions and study the interactions between the factors in relation to the responses.
Keywords: Central composite design, Magnesium phosphate cement, Plastic viscosity, Response surface methodology, Yield stress.

INTRODUCTION

Magnesium phosphate cement (MPC) is an alternative clinker-free binder, which consists mainly of struvite families produced by the acid-based through-solution reactions between the dead-burnt magnesium oxide (MgO) and an acid phosphate source (e.g., KH_2PO_4) [1]. Compared to the conventional PC-based materials, MPC possesses many improved characteristics such as super-fast setting, rapid strength-gain, high bonding strength and better durability. These properties make MPC remarkably popular in fast-repairing and strengthening concrete structures such as pavements, highways and airport runways. In recent decades, MPC has also demonstrated huge potential for immobilising radioactive wastes [1, 2], which attracted increasing attentions worldwide. In order to utilise efficiently MPC based materials in industry, their rheological properties need to be investigated which could benefit significantly the transporting, placing and finishing processes in real engineering. The flow properties of conventional Portland cement (PC) based concrete has been well established and most described using a Bingham model defined by yield stress and plastic viscosity [3]. However, in case of MPC based materials, too few study exists which adequately covers its rheological characteristics.

Response Surface Methodology (RSM) is a mathematical and statistical technology using empirical modelling to explore the relationships between independent (explanatory) variables (factors) and dependent (response) variables as well as the interactions between the independent variables, and to optimise process settings. The Central Composite Design (CCD) is the most used surface response design method, which runs much fewer experiments than a full factorial design but provides almost the same information. In the current work, RSM methodology was adopted in an attempt to investigate the rheological behaviour of MPC materials and optimise the mix proportion in terms of water/solid ratio (W/S), MgO/MKP ratio (M/P) and Borax dosage, with yield stress (τ) and plastic viscosity (μ) considered as responses. The CCD design was conducted to develop a three variables (factors) (n=3) experiment matrix with 20 runs in total.

EXPERIMENTALS

Materials

MgO, provided by Richard Baker Harrison Ltd, UK, was a Dead Burned Magnesite (DBM) calcining at about 1750 °C with purity of 90% and mesh size of 200. Monopotassium phosphate (MKP, KH_2PO_4) was a food-grade MKP with specified purity > 99%, from Prayon UK. Sodium tetraborate decahydrate (Borax, $Na_2B_4O_7 \cdot 10H_2O$), supplied by Sigma-Aldrich US, was employed as the retarder. It was ACS reagent grade with assay ≥ 99.5% and pH of 9.15-9.20.

Experimental design

In this work, a 2^3 CCD deign with 3 variables (n=3) and 2 extreme levels (coded as +α & -α) was applied for developing mathematical equation and quantifying the rheological properties of MPC in terms of yield stress and plastic viscosity. The three variables investigated were water/solid ratio (W/S) (X_1), MgO/MKP ratio (M/P) (X_2) and Borax dosage (X_3), which affect the rheological properties significantly. A total of 20 runs, including 8 ($2^n=2^3$) factor points, 6 (2n=2*3) axial points and 6 (replications) centre points, were carried out. The CCD design and data analysis associated with analysis of variance (ANOVA) and RSM optimisation were conducted using Design Expert 10 (Stat-Ease, USA) software. Table 1 below reports the coded and actual values of the factors. Please note the ranges/levels of the variables were determined based on the results from previous work.

Mixing &Testing

A total of 20 MPC pastes were fabricated in a High-shear mixer as per the mix proportions designed by CCD method. The borax was first mixed with water and followed by adding MKP and MgO for a blending of total 3mins. Immediately after mixing, the pastes were transferred into the container (92 mm diameter) of a modified and calibrated rheometer (Viscotester 550), which uses a helical impeller to establish the relationship between different shear stress and shear rate. The results were recorded by the software and the yield stress and plastic viscosity were fitted by the Bingham model.

Table 1. *Actual values for the variables used in the experiment design*

Independent variables	Symbols	Actual values for the coded values				
		- α (-1.682)	**- 1**	**0**	**+ 1**	**+ α (+1.682)**
W/S Ratio	X_1	0.18	0.20	0.24	0.28	0.30
M/P Ratio	X_2	2	4.03	7	9.97	12
Borax dosage	X_3	0.13	0.14	0.16	0.17	0.18

RESULTS AND DISCUSSION

Fitted regression model and analysis of variance (ANOVA)

The experiment data in terms of yield stress and plastic viscosity obtained from 20 trials were analysed by Design Expert 10, and the best fitting surface response models for describing the yield stress and plastic viscosity are generated and suggested to be two-factor interaction (2FI). The regression equations in coded value attained correlating the responses and the three independent variables are shown in Eq. 1 (yield stress) and Eq. 2 (plastic viscosity) respectively. The analysis of variance (ANOVA) with Fisher's F-test was conducted to assess the significance and adequacy of the models, which are reported in Table 2 below.

$$Y_1 = 9.61 - 9.67X_1 + 11.60X_2 - 10.41X_3 - 14.25X_1X_2 + 14.33X_1X_3 - 15.23X_2X_3 \quad (1)$$

$$Y_2 = 0.73 - 0.43X_1 - 0.04X_2 + 0.20X_3 + 0.24X_1X_2 - 0.37X_1X_3 + 0.52X_2X_3 \quad (2)$$

Table 2. *Analysis of variance (ANOVA) of fitted models of two responses respectively*

Source	**Responses**									
	Y_1 (Yield stress)					**Y_2 (Plastic viscosity)**				
	Sum of Squares	**DF**	**MS**	**F -value**	***p*-value (Prob>F**	**Sum of Square**	**DF**	**MS**	**F -value**	***p*-value (Prob>F**
Model	9716.05	6	1619.34	5.13	0.0066	6.84	6	1.14	2.30	0.0979
X_1	1277.66	1	1277.66	4.05	0.0655	2.57	1	2.57	5.18	0.0404
X_2	1836.17	1	1836.17	5.82	0.0314	0.02	1	0.02	0.04	0.8384
X_3	1480.18	1	1480.18	4.69	0.0496	0.57	1	0.57	1.15	0.3030
X_1X_2	1624.22	1	1624.22	5.14	0.0410	0.44	1	0.44	0.89	0.3623
X_1X_3	1642.51	1	1642.51	5.20	0.0401	1.08	1	1.08	2.18	0.1636
X_2X_3	1855.32	1	1855.32	5.88	0.0307	2.16	1	2.16	4.37	0.0569
Residual	4104.84	13	315.76			6.44	13	0.50		
Lack of fit	4104.33	8	513.04	5086.84	2.41E-09	6.43	8	0.80	533.79	6.74E-07
Pure Error	0.50	5	0.10			0.01	5	0.002		
Cor Total	13820.88	19				13.28	19			
R-squared	0.70					0.52				
Adeq Precision	9.67					6.15				

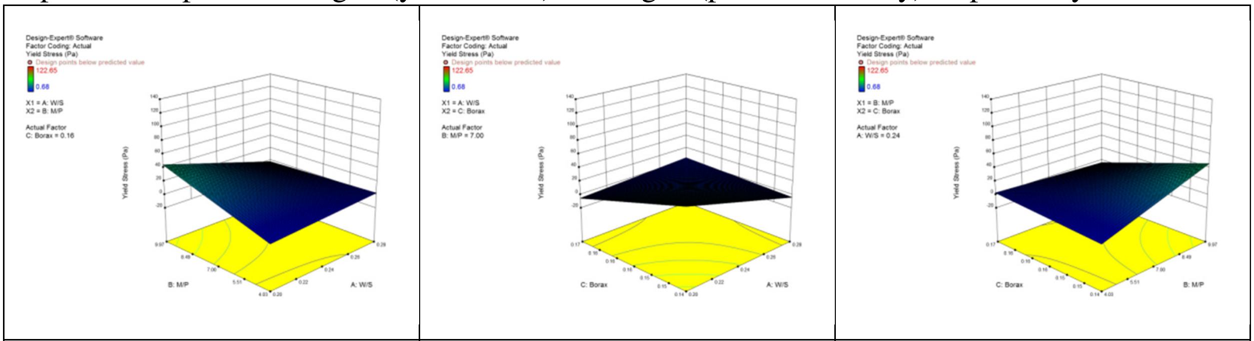
N.B.: DF - Degree of freedom, MS – Mean square

Model describing yield stress: The *p*-value obtained was 0.0066 (<0.05) which implied the regression model was highly significant at a 5% significance level, and there was only 0.66% chance that an F-value this large could occur due to noise. The *goodness of fit* of the model was assessed by the coefficient of determination $R^2 = 0.70$, which indicated that about 70% variation in this system was attributed to the independent variables and only 30% of the variation could not be explained by the model. In addition, the adequate precision value measures the *signal-to-noise* ratio and a value greater than 4 is desirable. The value obtained from the current model was 9.67, suggesting the adequate signal was obtained and this model can be used to navigate the design space. Moreover, the significance of each of the coefficient can be checked by the *p*-value as listed in Table 2 as well, and $p<0.05$ could suggest the term was significant. From our results, the X_2, X_3, X_1X_2, X_1X_3 and X_2X_3 were significant model terms. This suggests the M/P ratio (X_2) and Borax dosage (X_3) affecting significantly the yield stress of MPC, and there are significant interactions between W/S ratio & M/P (X_1X_2), W/S & Borax dosage (X_1X_3), M/P and Borax dosage (X_2X_3).

Model describing Plastic viscosity: The current model ($p<0.1$) could be still considered as significant at a 10% significance level. The determination coefficient obtained was 0.52, which suggested this model could interpret 52% of the total variation. Besides, the adequate signal was retrieved as evidenced by the adequate precision value of 6.15 here. More importantly, the X_1 was observed to be the only significant coefficient in the current model, which implied that W/S ratio played important role adjusting the viscosity of the MPC materials.

Three-dimensional (3D) response surface plotting

The three-dimensional (3D) response surface plots offer graphical interpretations to the regression models. Since the current model has three factors, one factor was held at the central level (0) while plotting the other two variables. Hence, there were three response surface diagrams for each response as reported in Fig. 1 (yield stress) and Fig. 2 (plastic viscosity) respectively.

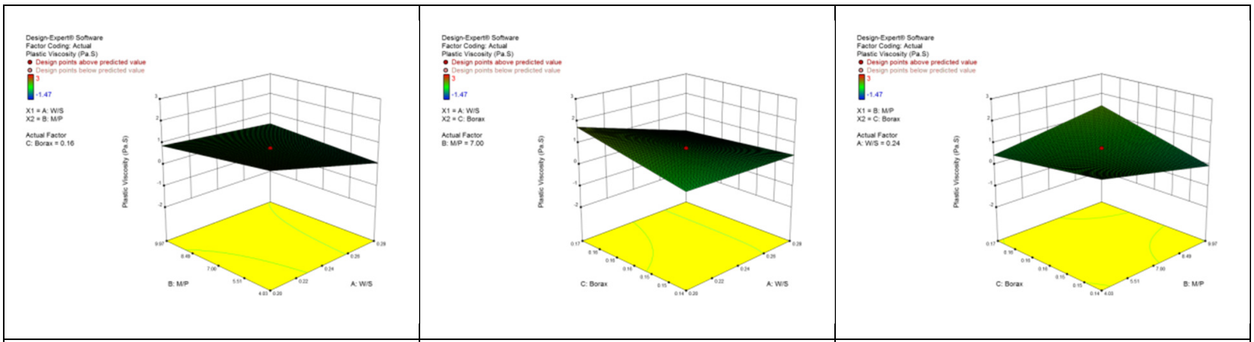


(a) as a function of W/S (X_1) & M/P (X_2)	(b) as a function of W/S (X_1) & Borax (X_3)	(c) as a function of M/P (X_2) & Borax (X_3)

Fig. 1: *The response surface plots of yield stress (Y_1)*

Fig. 1(a) illustrates the effect of W/S and M/P ratios on the yield stress of MPC, while keeping the Borax dosage at the middle level (0.16). Apparently, yield stress increased with increasing the M/P whereas the change of the W/S imposed little effect on the performance of yield stress. A possible reason may be the increment of MgO proportion would enhance the yield stress. This finding accords well to the aforementioned ANOVA analysis that M/P was a significant factor to the yield stress. Fig. 1(b) shows the response surface plots of the yield stress as a function of W/S and Borax dosage. As expected, the decrease of yield stress with increasing W/S as well as Borax dosage has been observed. In Fig. 1(c), the yield stress increased with the increment of M/P while Borax here demonstrated negligible effect. Obviously, there could be interactions between three factors in relation to the yield stress, and further study needs to be carried out to clarify their roles.

Fig. 2(a) shows the dependence of plastic viscosity on W/S and M/P ratios for the Borax dosage set at its central level (0.16). There were slight decreases of plastic viscosity with increasing the W/S and M/P ratios. This phenomenon may be attributed to the fact that the change of W/S and MgO proportion could affect the cohesion of the fluids. On the other hand, the effects of W/S and dosage of the retarder on the viscosity is presented in Fig. 2(b). It was obvious that the plastic viscosity increased as the Borax dosage increased towards its high level. In contrast, the plastic viscosity decreased slightly along with increasing W/S, which was in agreement with the finding in Fig. 2(a). In Fig. 2(c), the viscosity reduced as per the increment of both the M/P and Borax dosage.



(a) as a function of W/S (X_1) & M/P (X_2)	(b) as a function of W/S (X_1) & Borax (X_3)	(c) as a function of M/P (X_2) & Borax (X_3)

Fig. 2: *The response surface plots of plastic viscosity (Y_2)*

Determination of the optimal

The primary objective of current work is to determine the optimum values of three independent variables. The goals in terms of yield stress and plastic viscosity were set as 'minimised' and 'in range' so as to obtain a MPC system with desirable rheological properties. The optimum conditions of the three factors generated were 0.25, 8.97 and 0.17 for the W/S ratio, M/P ratio and Borax dosage respectively. At these optimum settings, the predicted values for the two responses were 0.40 Pa (yield stress) and 0.93 Pa.s (plastic viscosity) with desirability equals 1. A further experiment with these optimum conditions will be carried out to verify the predicted results.

CONCLUSIONS

The rheological properties of MPC materials, along with its optimum settings in terms of W/S ratio, M/P ratio and Borax dosage, were investigated using RSM methodology by considering two response variables, i.e. yield stress and plastic viscosity, in the regression model. The dependence of each response on the two variables, while the third variable kept at middle level, was evaluated by the 3D response surface plots. ANOVA analysis showed the M/P ratio and Borax dosage could affect significantly the yield stress of MPC, while W/S ratio played important role adjusting the viscosity. The numerical optimised values of the W/S ratio, M/P ratio and Borax dosage were 0.25, 8.97 and 0.17 respectively, with which a MPC system with desirable rheological characteristics can be achieved at yield stress of 0.40 Pa and plastic viscosity of 0.93 Pa.s. Further experiments will be carried out to study the interactions between the factors in relation to the response variables, as well as to verify the predicted optimum conditions.

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