

## Synergistic Interactions of Chemical Additives on the Strength Development of Silicate Cement by a Box-Behnken Model Optimization

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**ABSTRACT:** The effect of water-soluble polymers (polyvinyl alcohol (PVA), polyacrylamide (PAM)) and chemical additives (silicone defoamer (SD), polycarboxylate superplasticizer (PC)), on the development of the strength of mortar was investigated using the Box-Behnken design (BBD). Quadratic equations were obtained for the correlation between dosages of chemicals and the strength of the mortar, and the order of the effectiveness of the chemicals was validated in Pareto charts with contour plots to illustrate the chemicals and their interactions on the strength enhancement of mortar. The results showed that the interaction effects of SD and PAM enhanced the strength of cement mortar for all curing times, and the rates of contribution were 16.5%, 20.1%, and 19.4%, respectively. On the basis of the performance analysis of the four additives, optimized formulations were highlighted via overlapped contour plots. Heat of hydration and scanning electron microscope (SEM) images were introduced to confirm the interaction between SD and PAM. The improvement of compressive strength attributes to the synergistic interactions between SD and PAM, including the physical interaction resulted from the doping of SD, which promoting the damage of air bubble, decreasing the porosity and increasing the compressive strength, and the chemical interaction resulted from the doping of PAM, which producing ionic compounds and forming dense structure. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41071.

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### INTRODUCTION

As the largest artificial materials, concrete and cement have made huge contributions to social civilization and to the progress of technology. They are the main materials of foundation engineering because they are abundant resources, have good durability and have convenient molding processing. However, their disadvantages, such as low strength, high fragility, and large self-weight, impose restrictions on the field of construction. It is difficult to develop a final product by adjusting the mineral composition of cement or changing the process of cement production. The principal role of chemical additives is to improve working performance and mechanical properties and extend the useful life of concrete.<sup>1–3</sup> Regarding modern civil engineering, the ever-growing demand for polymer modified cement-based materials has been widely studied.

According to previous studies that introduced polymer to cement and concrete to modify the mechanical properties and the durability, some researchers selected 12 types of typical polymers for a comparative study; the results showed that no

obvious signs of chemical reaction between the organic materials and cement, except for two water-soluble polymers: polyacrylamide and polyvinyl alcohol.<sup>4</sup>

Polyacrylamide (PAM) is a water-soluble acrylate polymer formed from acrylamide subunits. It is highly hydrophilic because of the amide ionogenic in its molecular chain. PAM has been widely used in chemical engineering, paper production, water treatment, coal mining, food production, and textile production. Additionally, PAM is propitious for modifying the properties of products made with cement. On the one hand, during the cement hydration phase, PAM reacts with  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  cations to form ionic compounds, acting as a flexible filler and reinforcement in the hole of the cement mortar, and thereby decreasing the porosity and improving the compressive strength.<sup>5–7</sup> On the other hand, PAM introduces closed air bubbles into the cement paste, which affects the compressive strength of the cement mortar.<sup>8</sup> In general, the ultimate impact of PAM on cement strength can be attributed to the competition results of two contrary effects. Most researchers commit themselves to adjusting the concentration of PAM to seek the

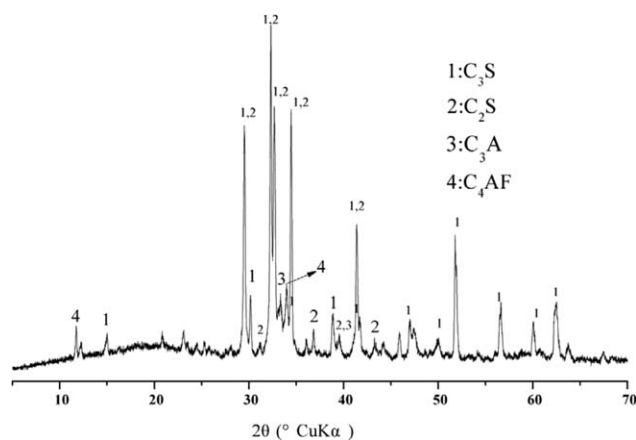


Figure 1. XRD pattern of P.II 52.5 cement.

best result. Some scholars have come up with the idea of reducing the number of bubbles in cement mortar mixed with a small amount of defoamer to improve the strength of the cement mortar, but this idea was not researched specifically. Meanwhile, as a thickener and flocculant, the viscosity of the PAM aqueous solution increased, and thus, postponed the setting time, increased the amount of the needed water to the cement, and reduced the fluidity of the cement paste.<sup>6,8,9</sup>

Polyvinyl alcohol (PVA) is another water-soluble polymer that is used as a cement modifier to improve the workability.<sup>10–13</sup> Some researchers have found that PVA decreased the mechanical properties of the mortar and concrete and affected the air content of the paste and mortar<sup>11</sup>; others have noted that PVA can significantly increase the bond strength between the cement paste and the aggregates in concrete.<sup>10</sup> An important modification that has been observed by the addition of small amounts of PVA is significantly improving the compressive strength and reducing the porosity due to the formation of some new compounds or a film.<sup>13,14</sup>

Previous studies have investigated the effects of single chemicals on the property modifications of cement. However, the purpose of this study was to investigate the interaction effects of several chemical additives, such as polyacrylamide, polyvinyl alcohol, and polycarboxylate superplasticizer (PC) with the ability of water reducing and silicone defoamer (SD) with the ability of defoaming on the strength of cement. Additionally, the dosages of the chemicals were low, which was closer to the conditions in actual applications. The preparation, compressive strength, heat of hydration, microstructure, and mechanism were investigated.

## EXPERIMENTAL

### Materials

The P.II 52.5 cement used was from Jiangnan Onoda, it has a typical composition of  $C_3S$  (alite,  $C_3S$  containing impurities is called alite),  $C_2S$  (belite),  $C_3A$  (tricalcium aluminate also called “aluminate”), and  $C_4AF$  (tetracalcium aluminoferrite also called as “ferrite”), the four primary chemical phases are combined of CaO (commonly expressed as “C” in cement chemistry shorthand),  $SiO_2$  (S),  $Al_2O_3$  (A),  $Fe_2O_3$  (F). The mineral and

Table I. Chemical Composition of P.II52.5 Cement

Chemical analysis	Wt %
CaO	63.9
$SiO_2$	19.8
$Al_2O_3$	4.4
$SO_3$	3.8
$Fe_2O_3$	3.1
MgO	1.6
$K_2O$	0.4
$Na_2O$	0.1
Loss on ignition	2.2

chemical compositions of cement are analyzed by XRD and XRF shown in Figure 1 and Table I. The compressive strength of blank cement after 1, 3, and 28 days are shown in Table II. Industrial raw materials such as SD (from Huipu Industrial Chemical, the solid content is 35%) and PC (from Jiangsu Sobute, the solid content is 42%) were used in the present experiment. Polyvinyl alcohol, which was 97% hydrolyzed and with a molecular weight of  $1.05 \times 10^5$  was used. The PVA was supplied by Xi Long Chemical. Polyacrylamide produced by Sinopharm Chemical Reagent, a type of white dry powder with a molecular weight of  $3 \times 10^6$ . Both of them were analytical reagent grade.

### Determination of Compressive Strength

Four common types of chemical components of the chemical admixtures were selected for the experiment: silicone defoamer, polyvinyl alcohol, polyacrylic amide, polycarboxylate superplasticizer. The performance of these four chemicals was evaluated by measuring the compressive strength of the corresponding treated cement. The maximum dosages of these four chemicals were determined by experiment and they are 8.1 g, 6.75 g, 6.75 g, and 4.5 g. All chemicals were diluted to 1 wt % aqueous solution and were added to the mixing water that was used to prepare the cement mortar. Cement mortar was prepared according to GB/T17671. Each batch for the three test specimens consisted of  $450 \pm 2$  g of cement,  $1350 \pm 5$  g of ISO standard sand, and  $225 \pm 1$  g of mixing water.

Prismatic samples ( $40 \times 40 \times 160$  mm<sup>3</sup>) were cured at  $20 \pm 1^\circ C$  and 95% relative humidity (RH). Then, the samples were removed from the mould after 1 day and immersed in water at  $20^\circ C$  until they were utilized for compressive strength testing. After the specimens were cured for 1, 3, and 28 days, the compressive strengths were tested using the unconfined compression machine with a maximum load of 200 KN. The loading rate of the machine is 5 mm/min. Each compressive

Table II. Compressive Strength of P.II 52.5 Cement

Cement	Compressive strength/MPa		
	1d	3d	28d
P.II 52.5	19.4	38.7	63.0

**Table III.** Symbol, Coded, and the Actual Values of the Chemicals Treated in Cement

Chemical	Symbol	Low level		Intermediate level		High level	
		Coded	Actual/ $10^{-4}$	Coded	Actual/ $10^{-4}$	Coded	Actual/ $10^{-4}$
SD	$X_1$	-1	0	0	4.05	1	8.1
PVA	$X_2$		0		3.375		6.75
PAM	$X_3$		0		3.375		6.75
PC	$X_4$		0		2.25		4.5

strength value represents the average of the results from six specimens tested.

### Determination of Heat of Hydration

The hydration heat release of the cements with and without additives was determined by a conduction calorimeter. The calorimetry tests were conducted in an eight-channel Thermometric TAM Air instrument using plastic ampoules, and the heat flow was collected for time periods up to 72 h at a temperature of 20°C and an atmosphere of air. The cement pastes (water/cement ratio of 0.5) were mixed before testing ( $4 \pm 0.01$  g sample mass).

### Materials Characterization

The microstructures of the pastes with and without additives were obtained using a scanning electron microscope (SEM) (Model JSM-5900, JEOL, Japan). The specimens were fractured; then, small samples were affixed to the SEM specimen holder using an epoxy resin and then coated with a very thin layer of gold to promote electrical conductivity.

### Box-Behnken Design

The response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes.<sup>15</sup> The RSM is comprised of the central composite design (CCD), Doehlert matrix (DM), and Box-Behnken design (BBD).<sup>16</sup> BBD is one class of experimental designs for the response surface methodology. They are rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. Comparing the BBD to the other response surface designs reveals that the BBD is more efficient than the CCD, DM, and the other three-level factorial for the number of experiments. Additionally, BBD does not contain combinations for which all factors are simultaneously at their highest or lowest levels. Thus, these designs are useful in avoiding experiments performed under extreme conditions for which unsatisfactory results might occur.<sup>15</sup>

The BBD was used to investigate the influence of four chemical additives on the compressive strength of cement mortar at 1, 3, and 28 days. It can not only make an accurate statistical analysis of experimental data but also provides image analysis with continuity characteristics, as well as intuitively understands the correspondence relationship between the factors and the response; it has been widely used in several fields such as biochemistry, agriculture, chemical engineering, material, etc.<sup>15–19</sup>

Before designing the experiment, the levels of the factors must be coded; they were investigated at a low level (-1), intermedi-

ate level (0), and high level (1). The ranges and levels of the chemicals used in the experiment are presented in Table III.

The BBD uses a quadratic regression equation to characterize the relationship between the factor and the response.

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \varepsilon \quad (1)$$

where  $Y$  is the predicted response (the compressive strength of cement mortar at each curing age);  $\beta_0$  is the model constant;  $x_1$ ,  $x_2$ ,  $x_3$ , and  $x_4$  are the independent variables (SD, PVA, PAM, and PC);  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  are the linear coefficients;  $\beta_{12}$ ,  $\beta_{13}$ ,  $\beta_{14}$ ,  $\beta_{23}$ ,  $\beta_{24}$ , and  $\beta_{34}$  are the cross product coefficients; and  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{33}$ , and  $\beta_{44}$  are the quadratic coefficients.  $\varepsilon$  is the error, which includes the experimental error and the lack-of-fit error.

## RESULTS AND DISCUSSION

The influence of polyvinyl alcohol, polyacrylamide, silicone defoamer, and superplasticizer were well studied by BBD. The design matrix of the Box-Behnken model and the statistical data of the compressive strength of treated cement at each curing age are shown in Table IV. The preliminary analysis of the variance of the Box-Behnken model for the strength of treated cement is presented in Table V.

The values of “lack-of-fit” for modeling the strength at 1 and 3 days are both greater than 0.05, which means that the models are reasonable, the “lack-of-fit” value for the strength at 28 days is less than 0.05, which indicates that the model needs to be revised. Furthermore, to increase the reliability of the model, items with a high  $P$ -value must be removed from the model. Analysis of the variance of the revised Box-Behnken model for the strength of treated cement is shown in Table VI, which includes the coefficient and  $t$ -value for the significant terms. The absolute values of  $t$  for each chemical were used to generate a Pareto chart, which describes the cumulative effectiveness of each chemical in the cement additive. The regression coefficient was used to build a quadratic regression equation. Mathematic models for the compressive strength of the treated cement can be expressed by the following equations:

$$Y_{1d} = 19.5 + 0.2x_1 - 1.1x_2 - 0.13x_3 + 0.675x_1x_3 - 0.925x_1x_4 \quad (2)$$

$$Y_{3d} = 39.79 + 0.3167x_1 - 0.7167x_2 + 0.375x_1x_2 + 1.025x_1x_3 - 1.9x_1x_4 \quad (3)$$

**Table IV.** Design Matrix of the Box-Behnken Model and the Compressive Strength of Treated Cement

Point Type	Run No.	Coded value				Compressive strength/MPa		
		$X_1$	$X_2$	$X_3$	$X_4$	1 d	3 d	28 d
Central Point	1	0	0	0	0	20.5	40.9	63.5
	2	0	0	0	0	20.2	38.5	63.3
	3	0	0	0	0	19.9	39.7	63.6
	4	-1	-1	0	0	21.0	42.0	68.5
	5	-1	0	-1	0	21.0	41.9	70.6
	6	-1	0	0	-1	17.6	35.7	63.5
	7	-1	0	0	1	20.4	40.4	65.2
	8	-1	0	1	0	18.6	40.3	64.3
	9	-1	1	0	0	17.6	39.3	64.0
	10	0	-1	-1	0	20.6	39.8	68.2
	11	0	-1	0	1	19.4	38.5	63.7
	12	0	-1	0	-1	18.2	38.3	64.5
Edge Point	13	0	-1	1	0	21.3	43.6	69.2
	14	0	0	-1	-1	20.7	40.9	69.2
	15	0	0	-1	1	19.5	40.4	66.8
	16	0	0	1	1	17.8	36.6	63.5
	17	0	0	1	-1	19.8	38.7	63.5
	18	0	1	-1	0	17.9	40.0	67.5
	19	0	1	0	-1	17.6	38.0	68.6
	20	0	1	0	1	16.7	36.6	63.4
	21	0	1	1	0	20.3	40.9	67.4
	22	1	-1	0	0	20.7	42.0	70.9
	23	1	0	-1	0	19.4	39.3	68.1
	24	1	0	0	1	20.0	38.3	64.3
	25	1	0	0	-1	20.9	41.2	70.2
	26	1	0	1	0	19.7	41.8	68.1
	27	1	1	0	0	17.9	40.8	67.6

$$Y_{28d} = 64.76 + 1.092x_1 - 1.342x_3 - 1.050x_4 + 1.810x_3^2 + 2x_1x_3 \quad (4)$$

### Effectiveness and Function of the Chemicals

The quadratic equations only show the quantitative relationship between the compressive strength and the chemicals used at each curing age. To further investigate the function of the chemicals, a Pareto chart must be used to illustrate the effectiveness of the enhancement in compressive strength.

Interpretations of the Pareto charts, which are shown in Figure 2(a–c) for the compressive strength of treated cement on each curing day, can be summarized as follows:

For the compressive strength at 1 day, the order of the effectiveness of chemicals is PVA (46.7%) > SD (8.6%) > PAM (5.7%); the effectiveness of PC is not obvious. Additionally, interactions exist between SD and PC (22.9%), and between SD and PAM (16.7%); the effectiveness of PC was lower than that of PVA, but slightly higher than that of SD and PAM. In general, PVA played a dominant role in the enhancement of the mortar strength at 1 day.

For the 3 days compressive strength, the order of effectiveness of the chemicals is PVA (24.4%) > SD (10.8%) and interactions between SD and PC (37.4%), between SD and PAM (20.1%) and between SD and PC (7.4%) existed. However, the effect of PVA decreased. The interaction effects among SD and three other chemicals on the strength at 3 days all increased.

For the compressive strength at 28 days, the order of effectiveness of chemicals is PAM (22.5%) > SD (18.3%) > PC (17.6%); an interaction between SD and PAM (19.4%) existed. Moreover, a quadratic term ( $x_3^2$ ) appeared in the equations of strength at 28 days; the contribution of PAM to the 28 days strength enhancement accounts for 44.7% ( $x_3 + x_3^2$ ) as can be observed in Figure 2(c), which indicates that PAM was crucial for strength enhancement after 3 days.

To better understand the function of each chemical, contour plots of the compressive strength at 1, 3, and 28 days are provided. Contour plots not only show the individual behavior of each chemical's contribution to the development of the cement

**Table V.** Analysis of the Variance of the Box–Behnken Model for the Strength of Treated Cement

Term	1d strength			3d strength			28d strength		
	Coef.	t	P	Coef.	t	P	Coef.	t	P
Const.	20.2000	30.398	0.000	39.7000	46.955	0.000	63.4667	67.070	0.000
x <sub>1</sub>	0.2000	0.602	0.558	0.3167	0.749	0.468	1.0197	2.307	0.040
x <sub>2</sub>	-1.1000	-3.311	0.006	-0.7167	-1.695	0.116	-0.4000	-0.845	0.414
x <sub>3</sub>	-0.1333	-0.401	0.695	-0.0333	-0.079	0.938	-1.3417	-2.836	0.015
x <sub>4</sub>	-0.0833	-0.251	0.806	-0.1667	-0.394	0.700	-1.0500	-2.219	0.047
x <sub>1</sub> <sup>2</sup>	-0.1083	-0.217	0.832	0.7208	1.137	0.278	1.9458	2.742	0.018
x <sub>2</sub> <sup>2</sup>	-0.8083	-1.622	0.131	0.3208	0.506	0.622	1.9333	2.724	0.018
x <sub>3</sub> <sup>2</sup>	0.1167	0.234	0.819	0.8708	1.373	0.195	2.2958	3.235	0.007
x <sub>4</sub> <sup>2</sup>	-0.8833	-1.772	0.102	-1.7042	-2.687	0.020	0.0083	0.012	0.991
x <sub>1</sub> x <sub>2</sub>	0.1500	0.261	0.799	0.3750	0.512	0.618	0.7250	0.885	0.394
x <sub>1</sub> x <sub>3</sub>	0.6750	1.173	0.264	1.0250	1.400	0.187	2.0000	2.441	0.031
x <sub>1</sub> x <sub>4</sub>	-0.9250	-1.607	0.134	-1.9000	-2.595	0.023	-1.9000	-2.318	0.039
x <sub>2</sub> x <sub>3</sub>	0.4250	0.739	0.474	-0.7250	-0.990	0.342	-0.2750	-0.336	0.743
x <sub>2</sub> x <sub>4</sub>	-0.5250	-0.912	0.380	-0.4000	-0.546	0.595	-1.1000	-1.342	0.204
x <sub>3</sub> x <sub>4</sub>	-0.2000	-0.348	0.734	-0.4000	-0.546	0.595	0.6000	0.732	0.478
Lack-of-Fit	–	–	0.055	–	–	0.448			0.007

**Table VI.** Analysis of the Variance of the Revised Box-Behnken Model for the Strength of Treated Cement

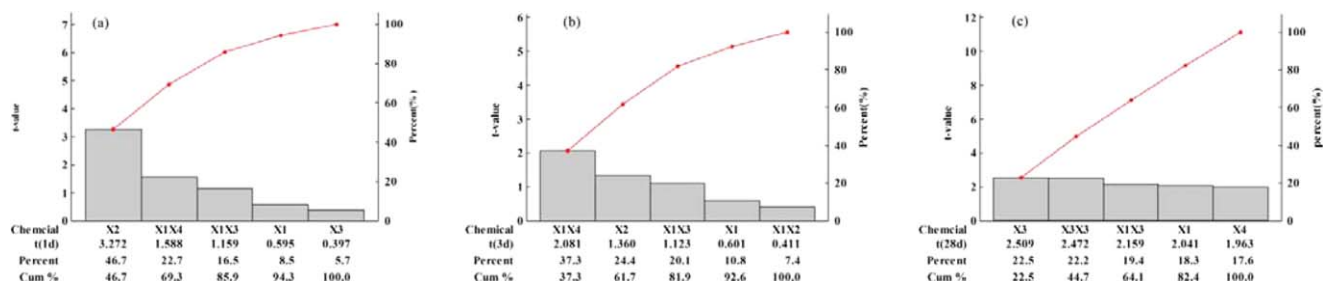
1 d			3 d			28 d		
Term	Coef	t	Term	Coef.	t	Term	Coef.	t
Const.	19.4519	86.779	Const.	39.7926	113.246	Const.	64.761	104.876
x <sub>1</sub>	0.200	0.595	x <sub>1</sub>	0.317	0.601	x <sub>1</sub>	1.092	2.041
x <sub>2</sub>	-1.100	-3.272	x <sub>2</sub>	-0.717	-1.36	x <sub>3</sub>	-1.342	-2.509
x <sub>3</sub>	-0.133	-0.397	x <sub>1</sub> x <sub>2</sub>	0.375	0.411	x <sub>4</sub>	-1.050	-1.963
x <sub>1</sub> x <sub>3</sub>	0.675	1.159	x <sub>1</sub> x <sub>3</sub>	1.025	1.123	x <sub>3</sub> <sup>2</sup>	1.810	2.472
x <sub>1</sub> x <sub>4</sub>	-0.925	-1.588	x <sub>1</sub> x <sub>4</sub>	-1.900	-2.081	x <sub>1</sub> x <sub>3</sub>	2.000	2.159

strength on each curing time but also illustrate how the chemicals interact.

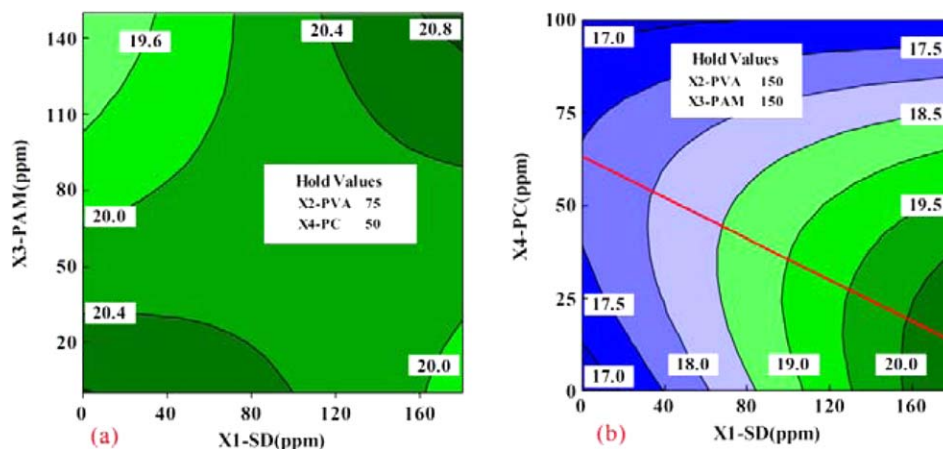
The regularity of the influence of chemicals on the 1 day compressive strength of the treated cement is shown in Figure 3.

Figure 3(a) shows the correlation between SD and PAM; their interaction tends to occur on the saddle surface. The strengths

of both the lower and higher concentration levels are higher than the strength of the area of saddle surface. Along the main diagonal, the 1 day compressive strength first decreases then increases; in contrast, along the counter diagonal, the strength first increases then decreases. The concentrations of SD and PAM are 180 ppm and 150 ppm, respectively, whereas the dosages of PVA and PC are holding statistical mean values (75

**Figure 2.** Pareto charts for the significant factors contributing to the 1 d, 3 d, and 28 d strength development of cement. (a) 1 d strength, (b) 3 d strength, (c) 28 d strength. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 3.** Influence of chemicals on the 1 d compressive strength of treated cement. (a) X1-SD vs. X3-PAM, (b) X1-SD vs. X4-PC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ppm and 50 ppm, respectively); the 1 day compressive strength can reach up to 20.8 MPa, and comparing the 1 day compressive strength of the blank, it improved 7.2%. The correlation between SD and PC is presented in Figure 3(b). Once the dosage of PC exceeds the red line on the right (increases vertically) at a certain dosage of SD, the compressive strength tends to decrease. To the left of the red line, at a certain dosage of PC, with increasing dosage of SD, the strength tends to increase.

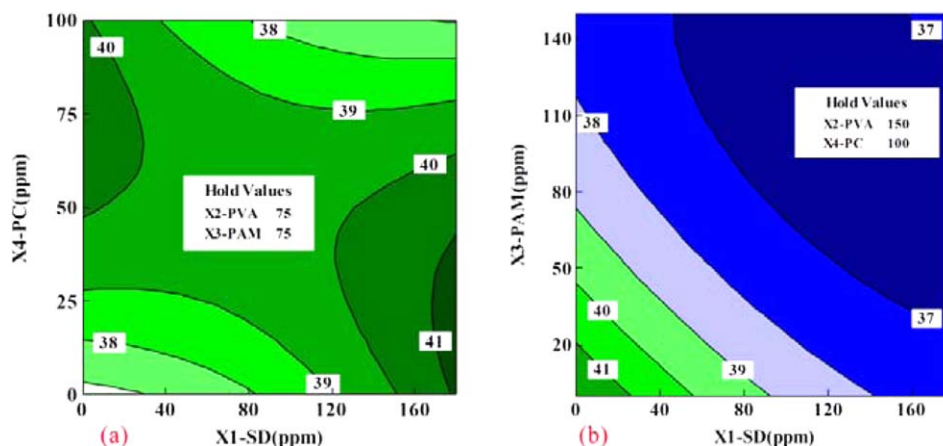
Figure 4(a) shows the interaction of SD and PC on the strength at 3 days. When the dosage of PC is below 50 ppm, the higher the dosage of SD, the higher the compressive strength is. However, the strength decreases even though the dosage of SD is increased when the dosage of PC exceeds 50 ppm, which indicates that there is an optimal dosage at which to enhance the compressive strength. The correlation between SD and PAM is shown in Figure 4(b); their interaction tends to occur at lower concentration levels. For example, when the dosage of SD and PAM are 90 ppm and 80 ppm, respectively, the interaction effects can decrease the strength of the cement to ~38 MPa. However, if the SD dosage exceeds 140 ppm and the PAM

dosage exceeds 110 ppm, the effect of the interaction is not obvious.

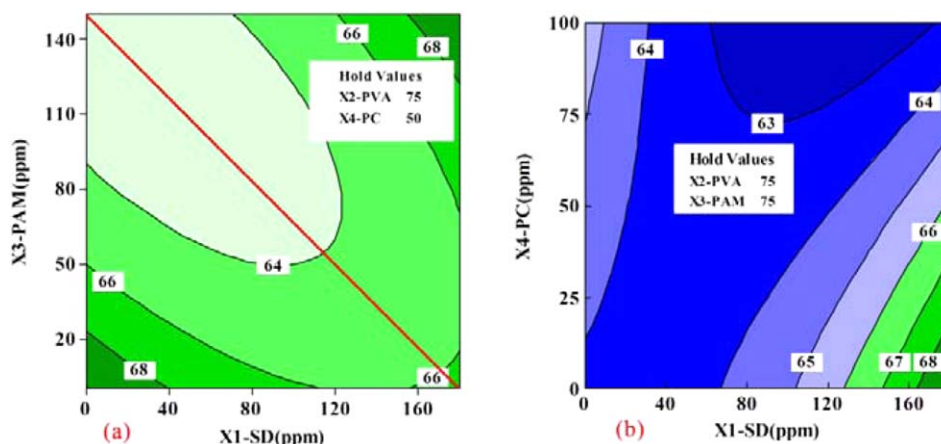
Figure 5 shows the behaviors of SD, PAM and PC related to strength enhancement at 28 days. The interactions among the chemicals are different. Figure 5(a) shows the correlation between SD and PAM. The interaction occurs at both lower and higher concentration levels. For example, when the dosage of SD and PAM are reduced to 120 ppm and 80 ppm, respectively, the interaction effect is apparent. The interaction effect of SD and PC in some ranges is obvious and can be observed in Figure 5(b). When the dosage of SD exceeds 80 ppm and that of PC is below 75 ppm, their interaction effect on the strength is apparent.

#### Optimization of the Performance of Formulation

The effectiveness and the function of each independent variable on a single response were elucidated in the preceding analysis. The improvement in the development of the cement strength is not just aimed at either early stages or later stages; the work now aims to seek the optimal matching zones that can satisfy



**Figure 4.** Influence of chemicals on the 3 d compressive strength of treated cement. (a) X1-SD vs. X4-PC, (b) X1-SD vs. X3-PAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Influence of chemicals on the 28 d compressive strength of treated cement. (a) X1-SD vs. X3-PAM, (b) X1-SD, vs. X4-PC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

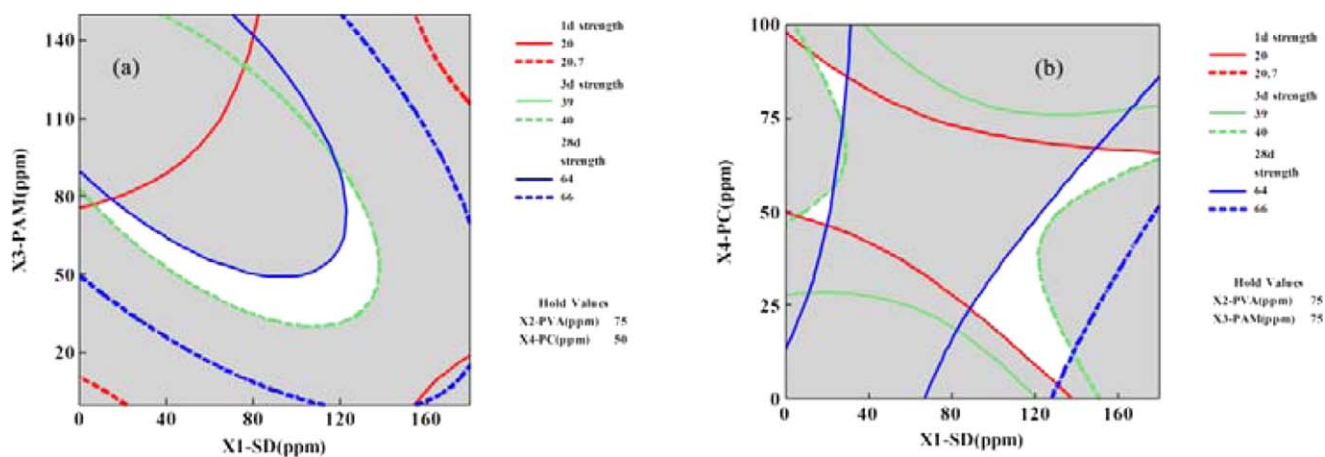
the three responses (1, 3, and 28 days) simultaneously. Because different components make various contributions to the development of the strength, the interactions between the components may also affect the performance of the recipe; therefore, it is necessary to control the matching of each chemical additive accurately. According to the principle of simultaneous optimization of multiple responses, overlapped contour plots were adopted. Based on the compressive strength of blank cement, the target strength on each curing day should be 20–20.7 MPa, 39–40 MPa, and 64–66 MPa, respectively. The contour plots of SD and PAM, and of SD and PAM are overlapped to search for the optimum zones of the chemicals. The overlapped contour plots are shown in Figure 6.

The shadow regions in Figure 6 are the areas that failed to meet the target strength. In contrast, the white regions are the feasible regions. In Figure 6(a), when the dosages of PVA and PC maintain statistical mean values (75 ppm and 50 ppm, respectively), the dosages of SD and PAM are in the feasible regions. In Figure 6(b), when the dosages of PVA and PAM maintain statistical

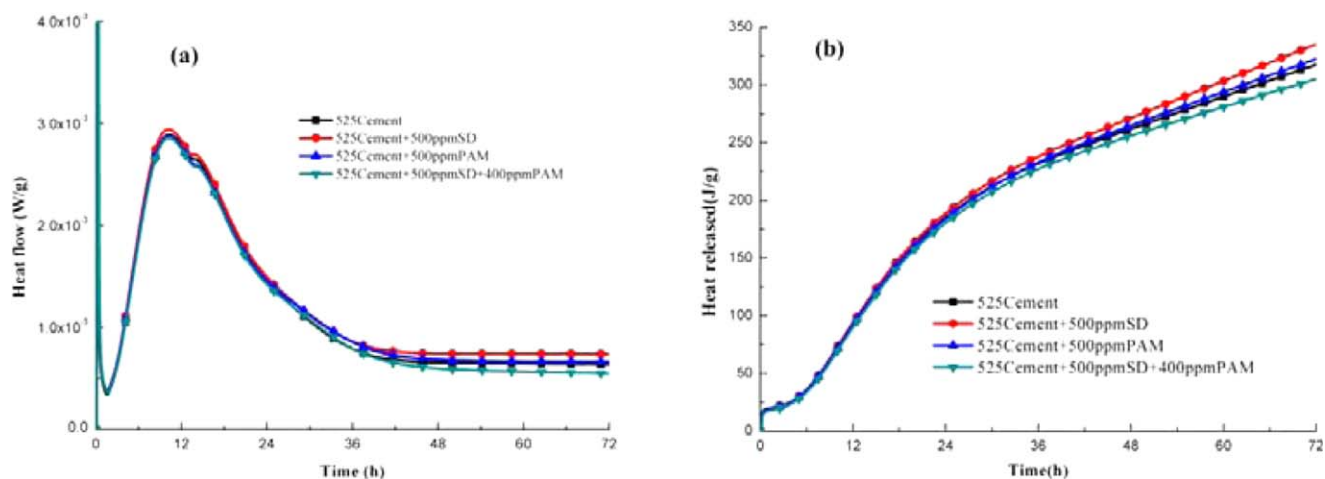
mean values (75 and 75 ppm, respectively), the dosages of SD and PC are in the feasible regions. Therefore, it can be concluded that the effective dosage range is narrow in both figures.

#### Heat of Hydration

To further study the effects of the interaction between SD and PAM, heat of hydration was also investigated. Plots of the heat flow and the cumulated heat evolution versus the hydration time are shown in Figure 7 for the pastes with and without additives. The initial period is characterized by rapid reactions between the  $C_3A$  and water. The first peak and the second peak are associated with ettringite (Aft) crystallized and the monosulfate (AFm) phase formation according to eqs. (5) and (6). The heat flow associated with Aft and AFm phase formation decreases when the cement with SD and PAM [Figure 7(a)]. The heat released without and with SD, PAM, SD, and PAM are 318 J/g, 323J/g, 337 J/g, and 300 J/g, respectively [Figure 7(b)], which indicates the interaction effectiveness is remarkable. Because the polar functional groups of SD and PAM can interact with inorganic ions to form the cationic polymer, the ionic

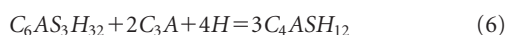


**Figure 6.** Matching zones for the chemicals designed for different target strengths. (a) Overlapped contour plot of SD vs. PAM, (b) Overlapped contour plot of SD vs. PC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Isothermal conduction calorimetry of the different pastes (a) heat flow curves and (b) the cumulated heat curves. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

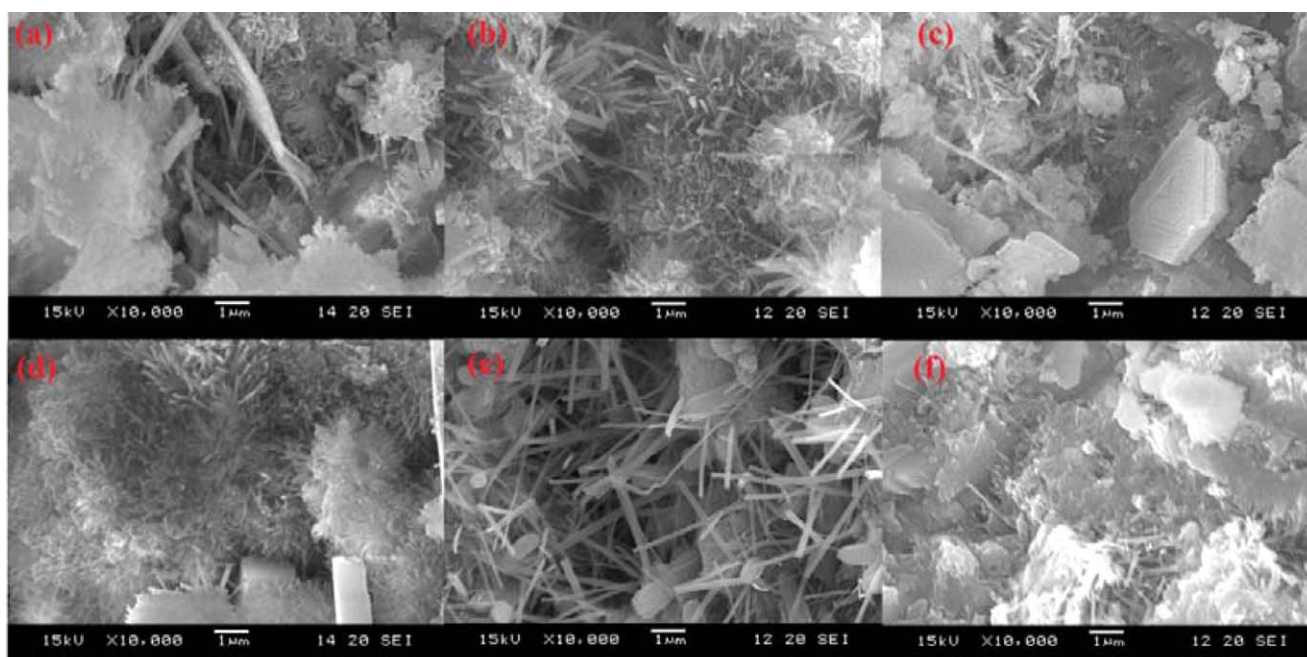
compounds together with the C-S-H gel attached to the particle surface of unhydrated cement, inhibiting the hydration reaction of cement and decreasing the heat flow and the heat released.



#### Microstructure of Cement Paste with SD and PAM

SEM images of the cement pastes with and without additives at different hydration stages were also investigated. Figure 8(a,d) showed the SEM photographs of the pastes hydrated at 1 day. In the blank sample, cement paste surface is covered with same C-S-H gel, but there is a gap between the hydration products,

which is due to inadequate hydration of the initial period. In the presence of SD and PAM, cement paste surface is covered with a large number C-S-H gel (a shaped fiber and clusters) and the density of gel increases. Figure 8(b,e) highlights the AFT phase (a shaped long column) in 3 days hydration. Comparing with the blank sample, the AFT phase of the paste with SD and PAM shows a more complete needle shape, the edge is neat and angular. Figure 8(c,f) showed the microstructure of the pastes hydrated at 28 days, in the absence of SD and PAM, the gap between the cement layer decreases, more dense C-S-H gel and  $Ca(OH)_2$  crystals (a shaped hexagonal flake) are clearly seen here. While the paste with SD and PAM, the C-S-H grows thicker and a lot of  $Ca(OH)_2$  stacks. All the phenomena described above indicate the double-doping of SD and PAM can



**Figure 8.** SEM micrographs of pastes for (a) 1 day, (b) 3 days, (c) 28 days of blank sample, (d) 1 day, (e) 3 days, (f) 28 days with SD and PAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



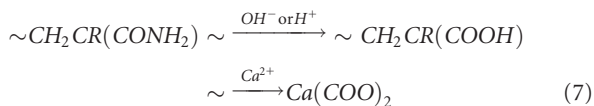
effectively enhance the strength of cement pastes in all the stages of hydration.

### Mechanism of SD and PAM Modified the Cement

In terms of the behavior of polymer during cement hydration process, some researchers<sup>20–22</sup> believe that the improvement of polymer to cement and concrete performance is based on its physical behavior in the cement hydration process, the polymer film covered the cement gel surface or polymer particles filled in the gap between the hydration products, blocking the pore channels and increasing the density of the cement gel, eventually enhancing its impermeability and improving the compressive strength. But this interpretation of the physical behavior of SD and PAM interaction mechanism is not appropriate here, because the dosage of polymer mentioned in the viewpoint above reaches to 10%. While the dosage of polymer here is thousand grading, by contrast, the dosage is very low, the polymer is not enough to form the film and fill the gap between the hydration products.

In this article, first, the air is introduced during the preparation of cement paste, because of the high viscosity of cement paste, it can't be discharged in the molding process, and thus the air bubble will be permanently left in the cement paste. Second, the cement grain size distribution of the particles is not continuous and cement particles are not the densely packed, thus forming a number of small voids in the cement, which can accommodate a small amount of air. Both the presence of bubbles results in the decrease of the compressive strength. SD with low surface tension and good spread ability on the bubble film can quickly diffuse and expand in the bubble surface, spreading the surfactant molecules in the surface of the bubble film, reducing the surface tension of bubble wall, promoting the disruption of air bubble,<sup>23</sup> decreasing the porosity and increasing the compressive strength.

The increase in mechanical properties is not only because of physical interaction between the cement and SD producing a dense microstructure of very low porosity but also because of chemical interaction between the cement phases and the functional groups present in PAM. PAM has  $-\text{CH}_2$  and  $-\text{NH}_2$  functional groups out of which  $-\text{NH}_2$  on hydrolysis is likely to interact with  $\text{Ca}^{2+}$  ions of cement hydrates to form calcium acetate and cross-linked product according to eq. (7).<sup>2,3</sup> The ionic compounds together with the C-S-H gel attached to the surface of hydrated cement phases forming more dense structure and improving compressive strength. Consequently, the improvement of compressive strength attributes to the synergistic interactions between SD and PAM, including the physical interaction mainly resulted from the doping of SD and the chemical interaction mainly resulted from the doping of PAM.



### CONCLUSIONS

1. The relationship between the compressive strength of the treated cement on each curing age and the dosage of each chemical can be predicted by the quadratic eqs. (2), (3), and (4).

2. The effectiveness and function of silicone defoamer, polyvinyl alcohol, polyacrylic amide, polycarboxylate superplasticizer, and their possible interactions that contributed to the strength of the treated cement on each curing age can be quantitatively summarized as follows:

- 1d X2(46.7%)>X1X4(22.7%)>X1X3(16.5%)>X1(8.5%)>X3(5.7%)  
 3d X1X4(37.3%)>X2(24.4%)>X1X3(20.1%)>X1(10.8%)>X1X2(7.4%)  
 28d X3(22.5%)>X32(22.2%)>X1X3(19.4%)>X1(18.3%)>X4(17.6%)

x1, x2, x3 and x4 are independent variables (SD, PVA, PAM, and PC, respectively)

3. According to the performance analysis of the four additives, optimized formulations were brought forward via overlapped contour plots. When the desired strength needed to be achieved, SD and PAM coexisted in a narrow window, whereas the dosages of PVA and PC maintained their values (75 and 50 ppm, respectively); however, SD and PC coexisted in a narrow window, whereas the dosages of PVA and PAM maintained their values (75 and 75 ppm, respectively).
4. The improvement of compressive strength attributes to the synergistic interactions between SD and PAM, including the physical interaction mainly resulted from the doping of SD, which promoting the disruption of air bubble, decreasing the porosity and increasing the compressive strength, and the chemical interaction mainly resulted from the doping of PAM, which producing ionic compounds and forming dense structure.

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### REFERENCES

1. Aiad, I.; Hafiz, A. A. *J. Appl. Polym. Sci.* **2003**, *90*, 482.
2. Lv, S. H.; Ju, H. B.; Qiu, C. C.; Ma, Y. J.; Zhou, Q. F. *J. Appl. Polym. Sci.* **2013**, *128*, 3925.
3. Kilinckale, F. M.; Dogan, G. G. *J. Appl. Polym. Sci.* **2007**, *103*, 3214.
4. Hu, S. G. *Advanced Cement Based Composite Materials*, Science Press: Beijing, **2009**; Chapter 6, p 172.
5. Negro, C.; Sanchez, L. M.; Fuente, E.; Blanco, A.; Tijero, J. *Chem. Eng. Sci.* **2006**, *61*, 2522.
6. Rai, U. S.; Singh, R. K. *Mater. Sci. Eng. A* **2005**, *392*, 42.
7. Sun, Z. Z.; Xu, Q. W. *Mater. Sci. Eng. A* **2008**, *490*, 181.
8. Yan, L.; Yu, X. *Concrete* **2012**, *3*, 113.

9. Zhang, C. Q.; Chao, Z. Y. *J. Chongqing Jiao Tong Univ.* **2011**, *30*, 1339.
10. Kim, J. H.; Robertson, R. E. *Adv. Cem.-Based Mater* **1998**, *8*, 66.
11. Kim, J. H.; Robertson, R. E.; Naaman, A. E. *Cem. Concr. Res.* **1999**, *29*, 407.
12. Mansur, A. A. P.; Santos, D. B.; Mansur, H. S. *Cem. Concr. Res.* **2007**, *37*, 270.
13. Xi, X. L.; Fang, M. M.; Ziyun, W. J. *Mater. Sci. Eng.* **2008**, *28*, 264.
14. Singh, N. B.; Rai, S. *Cem. Concr. Res.* **2001**, *31*, 239.
15. Wang, Z. Y.; Li, J.; Cheong, S.; Bhaskar, U.; Akihiro, O.; Zhang, F. M.; Dordick, J. S.; Linhardt, R. J. *J. Biotechnol.* **2011**, *156*, 188.
16. Bingol, D.; Veli, S.; Zor, S.; Ozdemir, U. *Synth. Met.* **2012**, *162*, 1566.
17. Dicholkar, D. D.; Gaikar, V. G.; Kumar, S.; Natarajan, R. *J. Anal. Appl. Pyrolysis* **2012**, *96*, 6.
18. Muthukumar, M.; Mohan, D.; Rajendran, M. *Cem. Concr. Compos.* **2003**, *25*, 751.
19. Vanderghem, C.; Brostaux, Y.; Jacquet, N.; Blecker, C.; Paquot, M. *Ind. Crop. Prod.* **2012**, *35*, 280.
20. Schulze, J. *Cem. Concr. Res.* **1999**, *29*, 909.
21. Liu, J.; Vipulanandan, C. *Tunn. Undergr. Sp. Tech.* **2001**, *16*, 311.
22. Gorninski, J. P.; Dal Molin, D. C.; Kazmierczak, C. S. *Cem. Concr. Res.* **2004**, *34*, 2091.
23. Pelton, R. J. *Ind. Microbiol. Biot.* **2002**, *29*, 149.