Mixture Design and Its Application in Cement Solidification for Spent Resin

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SUMMARRY

The study is aimed to assess the usefulness of the mixture design for spent resin immobilization in cement. Although a considerable amount of research has been carried out to determine the limits for the composition of an acceptable resin-cement mixture, no efficient experimental strategy exists that explores the full properties of waste form against composition relationship. In order to gain an overall view, this report introduces the method of mixture design and mixture analysis, and describes the design of experiment of the 5-component mixture with the constraint conditions. The mathematic models of 28-day compressive strength varying with the ingredients are fitted, and the main effect and interaction effect of two ingredients are identified quantitatively along with the graphical interpretation using the response trace plot and contour plots.

KEY WORD mixture design spent resins cement solidification
compressive strength ingredients

INTRODUCTION

Many spent ion-exchange resins were generated and accumulated from the nuclear facilities in China Institute of Atomic Energy (CIAE), which are still in tanks for intermediate storage. The final treatment of these spent resins has been

put on the agenda as the nuclear facilities in CIAE will enter into decommissioning stage in several years. Presently, a treatment workshop of the radioactive waste is being constructed in CIAE, which is assembled with a set of cementation process. For this reason, CIAE adopts the option of cement solidification to treat these spent resins.

Cement solidification of spent resin is a difficult and time-consuming task due to the resin-cement mixture usually contain many constituents and are often subject to several performance constraints. A considerable amount of research [1-3] has been carried out to determine the limits for the composition of an acceptable resin-cement mixture. However, no efficient experimental strategy exists that explores the full properties of waste form against composition relationship. In order to gain an overall view, mixture design method[4] is used to statistically evaluate the effect of various ingredient involved in resin solidification.

Mixture design

Mixture experiments are a special of response surface experiments in which the product under investigation is made up of several components or ingredients. In these situations, the response is a function of the proportions of the different ingredients in the mixture.

As a simple (hypothetical) example of a mixture experiment, consider waste form as a mixture of three components: water (x_1), cement (x_2), and resin (x_3) where each x_i represents the weight fraction of a component. The weight fraction of these components sum to one,

$$x_1+x_2+x_3=1 \quad \cdots\cdots \quad (1)$$

and the region defined by this constraint is the regular triangle(or simplex)shown in Figure 1. The axis for each component x_i extends from the vertex labeled $(x_i=1)$ to the midpoint of opposite side of the triangle $(x_i=0)$.

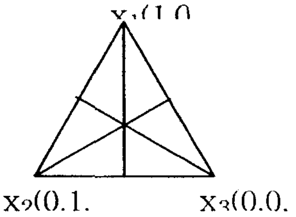

Figure1.Experimental region for three components mixture

The vertex represents the pure component. For example, the vertex labeled x_1 is the pure water "mixture" with $x_1=1$, $x_2=0$, and $x_3=0$, or (1,0,0) . The coordinate where the three axes intersect is $(\frac{1}{3},\frac{1}{3},\frac{1}{3})$ and called the centroid.

A good experiment design for studying properties over the entire region of a three-component mixture would be the simplex-centroid design shown in Figure 2.

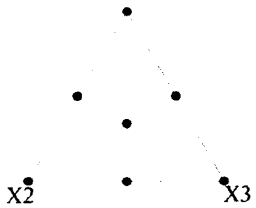

Figure2 Layout of experiment design for three component simplex-centroid mixture

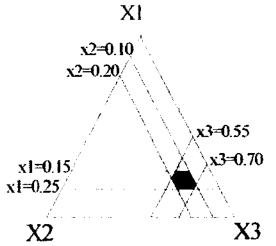

Figure 3 Example of constrained experimental region

This example is included for illustrative purposes only, since much of this region doesn't represent feasible resin-cement mixtures. The points shown in Figure 2 represent mixtures included in the experiment. This design includes all vertices, midpoints of edges, and the overall centroid. All properties of interest would be measured for each mix in the design and modeled as a function of the components. Typically, Scheffé-type[5] polynomials are used for modeling, but other functional forms can be used as well. For q components, the Scheffé linear polynomial for a response y is

$$y=\sum_{i=1}^{q}\beta_i x_i \quad \cdots\cdots \quad (2)$$

Similarly the Scheffé quadratic polynomial is expressed as

$$y=\sum_{i=1}^{q}\beta_i x_i+\sum_{i}\sum_{j}^{q}\beta_{ij}x_i x_j \quad \cdots\cdots \quad (3) \quad (i<j)$$

Where both β_i and β_{ij} represent the unknown coefficients in the model. Since feasible resin-cement mixes do not exist over the entire region shown in Figure 1, a meaningful subregion of the full simplex must be defined by constraining the component proportion. An example of a possible subregion for the three components example is shown in Figure 3. It is defined by the following weight fraction constraints ($x_1 =$ water, $x_2 =$ resin, $x_3 =$ cement).

$$0.15 \le x_1 \le 0.25, \quad 0.10 \le x_2 \le 0.20, \quad 0.60 \le x_3 \le 0.70$$

In this case the simplex design are generally no longer appropriate and the other designs [6] are used. These designs typically include the extreme vertices of the constrained region and a subset of the remaining centroids(e.g., centers of edges, faces, etc). The details can be seen in reference [4].

EXPERIMENTAL

Experiment design for the five-component study

The proportions for the five-component mixture experiment were initially selected in terms of weight fraction for batching. The minimum and maximum levels of each component were chosen based on weight fraction with the constraint that the weight fraction sum to unity. In addition to the individual constraints on each component, the admixture fraction of the mixture (coal fly ash and blast furnace slag) was required to range from 20 to 40 percent by weight. The five components and final ranges of their weight fractions in this experiment are shown in Table 1.

The selection of an appropriate experiment design depends on several criteria, such as ability to estimate the underlying model, ability to provide an estimate of repeatability, and ability to check the adequacy of the fitted model. These issues are addressed below.

The "best" experiment design depends on the choice of an underlying model which will adequately explains the data. For this experiment, in order to screen the design and analyse the two-component interaction effect, the Scheffé linear polynomial and quadratic polynomial were chosen as the reasonable models for each property as a function of the five components, respectively. Since there are 15 coefficients in the quadratic polynomial, the design must have at least 15 runs (15 distinct mixes) to estimate these coefficients. In addition to the 15 required runs, three additional runs (distinct mixes) were included to check the adequacy of the fitted model, and no mixes were replicated to provide an estimate of repeatability in this experiment. In all, a total of 18 mixes were planned.

Table 1 Mixture Components and Weight Fraction

Component	ID	Minimum Weight fraction	Maximum Weight fraction
Water	x_1	0.16	0.19
Slag	x_2	0.10	0.28
Ash	x_3	0.10	0.28
Cement	x_4	0.17	0.37
Resin (wet)	x_5	0.15	0.30
Slag+Ash	$x_2 + x_3$	0.20	0.40

Commercially available computer software for experiment design was used for design and analysis of the experiment. The program selected 18 points from a list of candidate points that is known to include the best points for fitting a quadratic polynomial. A distance-based optimality was chosen to ensure that the design selected could estimate the quadratic mixture model while spreading the design points uniformly over the design space. Table 3 summarizes the mixes used in the experiment. The run order was randomized to reduce the effects of extraneous variables not explicitly included in the experiment.

Specimen Fabrication and Test

The materials used in this study are listed in Table 2 including their some characters.18 batches of mixture, each approximately 1 liter in volume, were prepared in one day. A cement mortar mixer with a 2-liter capacity was used to mix the resin-cement mixture.

Each batch included sufficient mortar for two slump tests [8], and seven 50mm(diameter) by 50mm(high) cylinders. In order to obtain adequate consolidation, cylinders for mortar with slumps less than 100mm were vibrated on a table. The cylinders were left in molds for 28 days in this summer (humility:70% ~ 90%; temperature:25 ~ 35℃).

Table 2 Materials Used in this Study

Ingredient	Resource /Producer	Special feature/role
Fly ash	By-product of coal combustion Nei menggu ChiFeng. Electric power plant	First-class ash [7] Reduce water in solidification Reduce heat of hydration
Blast furnace slag	By-product of steel making China shougang group	Specific surface 0.42-0.45m^2/g Reduce heat of hydration Reduce crack during solidification Increase denseness
Ordinary Portland Cement 42.5	AnHui conch cement company limited	Low hydration heat Resistance to sulfate attack
Resin (wet) 001x7(33%) 201x7(67%)	Shanghai resin plant	Crosslinking degree 7%, Size 0.3-1.2um Strongly acidic cation exchange resin Strongly basic anion exchange resin
Water	Tap water	

Compressive strength tests [9] were conducted on the cylinders at the ages of 28 days. In most cases, three cylinders were tested. A fourth test was performed in some cases if one result was significantly lower or higher than the others. Before testing, the cylinder ends were ground parallel to meet the requirements of GB14569.1-93 [10] using an end-grinding machine.

Table 3 Mix Proportions and Test Results

No.	Run Order	Water (g)	Slag (g)	Ash (g)	Cement (g)	Resin (g)	28-day Strength (KN)
1	50	240	150	150	555	405	21.92±2.82
2	13	285	180	420	255	360	13.81±1.14
3	30	240	420	150	255	435	13.35±1.42
4	28	240	420	150	465	225	47.13±7.16
5	29	240	150	420	465	225	46.68±14.98
6	8	263	259	259	385	334	21.98±2.26
7	14	285	150	285	555	225	38.02±5.35
8	24	285	285	150	555	225	38.73±6.41
9	1	251	340	205	320	384	17.74±1.11
10	43	251	205	332	320	392	16.33±4.79
11	16	251	205	205	470	369	21.54±1.94
12	42	251	295	205	470	279	36.12±5.35
13	49	251	205	295	470	279	30.23±7.25
14	53	285	150	360	255	450	7.34±1.55
15	46	285	150	150	465	450	15.29±3.53
16	38	274	340	220	387	279	32.43±2.05
17	44	274	220	340	387	279	30.40±4.27
18	2	285	420	180	255	360	14.81±1.34

RESULT AND INTERPRETATION

The values of 28-day compressive strength for each batch are shown in Table 3. The statistical analysis is described in details for 28-day compressive strength.

Screening Components

To screen out the unimportant components or to single out the important components, we often set up the Scheffé linear model like Equation (2) .

$$y=-91.60\,x_1+90.23x_2+83.44x_3+124\,x_4-93.86x_5 \quad \cdots\cdots \quad (4)$$

Table 4 ANOVA of Equation (4)

Source	DOF	Sum of square	Mean square	F value	P value
Regression	4	2350.11	587.527	62.83	0.00
Linear	4	2350.11	587.527	62.83	0.00
Residual error	13	121.57	9.352		
total	17	247.68			

R2A= 93.57%

A mixture regression procedure was employed to achieve a regression Equation (4) representing the relationship between the 28-day compressive strength and each component in mortar. The analysis of variance (ANOVA), along with the adjusted coefficient of determination denoted as R2A, is given in Table 4.

Some information can be seen from Table 4. The regression row tests whether the terms in the model (4) have any effect on the response. The regression model is significant for P value of 0.00 less than 0.05, that is, at least one of the terms in the regression equation makes a significant impact on the mean response. The row with source of the linear tests whether any linear coefficients differ from zero. Since the P value (0.00) is also less than 0.05, we conclude that the linear terms should be included in the model. In addition, the adjusted coefficient of determination, R2A= 93.57%, which represents the proportion of variation in the response data that is explained by the predictor, suggests the acceptance of the fitted model for the purpose of predicting 28-day strength values.

However, although a fitting model is significant, it doesn't mean that each variable represented by each term in model has same important effect on response. In order to describe the magnitude of individual effect on 28-day compressive strength, the t-test[11] for a single effect in mixture design is performed. Table5 lists the t_i value of each component.

It can be seen from Table 5 that all components have significant effect on 28-day strength concluded by $|t_i| > t_{(13,0.975)}$, which is agreeable with the result from ANOVA. Moreover, among these components the magnitude of positive effect is Ecement >Eslag >Eash while that of negative effect is Eresin>Ewater by comparison of t_i value.

Table 5 Comparison of t_i Value

Component	t_i	$t_{(13,0.975)}$	Significant
Water	-2.31	2.16	S
Slag	4.80		S
Ash	3.69		S
Cement	7.43		S
Resin	-6.86		S

S: significant

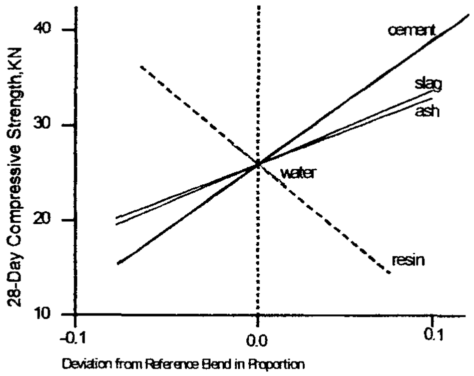

Figure 4 Trace plot for 28-day compressive strength

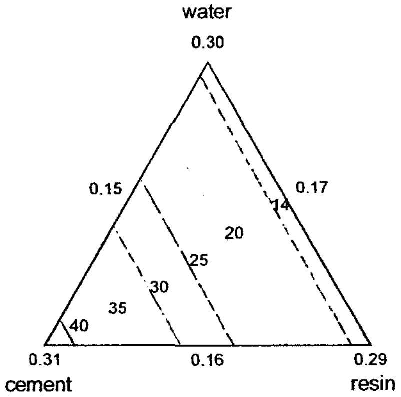

Figure 5 Contour plot for 28-day strength(KN) in water,cement and resin(slag=0.19,ash=0.19)

Once a valid model is obtained, it can be interpreted graphically using a response trace plots. A response trace plot is shown in Figure 4. This figure consists of five overlaid plots, one for each component. For a given component the fitted value of the response is plotted as the component is varied from its low to high sitting in the constrained region, while the other components are held in the same relative ratio as a specified reference mixture, here the centroid. The plot shows the "effect" of changing each component on 28-day strength. As expected, increasing the amount of resin or water decreased strength, while increasing the amount of cement, or slag, or ash increased strength.

Two-Component Interaction

In order to analysis two-component interaction effect, a stepwise regression procedure was employed to achieve a quadratic polynomial expressed as Equation （5） . It can be seen that only x_1x_5 term enters in the regression Equation from the candidate terms including x_1x_2, x_1x_3, x_1x_4, x_1x_5, x_2x_3, x_2x_4, x_2x_5, x_3x_4, x_3x_5, and x_4x_5. From the ANOVA (P=0.019<0.05) of and R2A value, we conclude that the water and resin (x1x5) act synergistically or are complementary, maybe the reason of which is the resin having the effect of preservation water.

$$y = -507.4x_1 + 180.4x_2 + 165.7x_3 + 215.7x_4 - 410.9x_5 + 2308.3x_1x_5 \quad \cdots\cdots \quad (5)$$

Table 6 ANOVA of Equation (5)

Source	DOF	Sum of Square	Mean Square	F value	P
Regression	5	2396.17	479.2347	75.94	0.000
Linear	4	2350.29	44.9801	7.13	0.004
Quadratic	1	45.88	45.8811	7.27	0.019
Residual error	12	75.72	6.3103		
Total	17	2471.90			

R^2_A=95.66%

Contour plots are used to identify conditions which give maximum (or minimum) response. Because contour plots can only show three components at a time (the others components are set at fixed conditions), several must be examined. Figure 5 shows a contour plot of 28-day strength in water, cement, and resin and Figure 6 shows a contour plot of 28-day strength in slag, ash and resin. In each case, the other components are fixed at the centroid setting. These plots show that strength increases for low water, low resin, high cement, high slag, and high ash. The best overall setting can be found using the contour plot shown in Figure7 for slag, cement and resin.

The best setting marked by a circle in Figure7 are water=0.16, slag=0.10, ash=0.10, cement=0.32, and resin=0.32(expressed as weight fractions) with a predicted value of strength of slightly over 14kN (7Mpa), which not only meets the requirement as the Chinese operational standard [10] but also loads maximal content of resin.

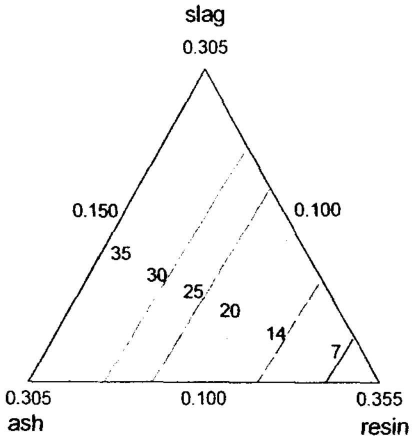

Figure 6 Contour plot for 28-day strength inslag,ash and resin(water=0.18,cement=0.27)

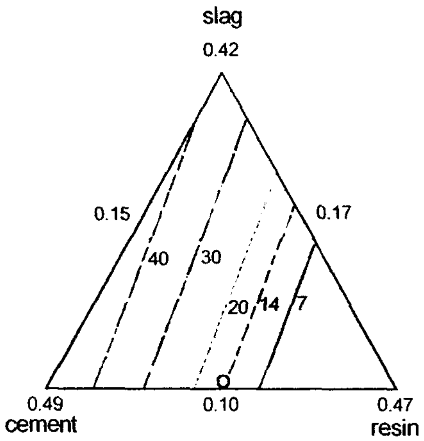

Figure7 Contour Plot of 28-day strength in slag,cementandresin(kN)(water=0.16,ash=0.10)

CONCLUSIONS

1. Mixture design and analysis methods is a strong and efficacious strategy for study on the immobilization of spent resin in cement, especially when the resulting waste forms contain many constituents and are subject to several constraints.

2. In this study, the magnitude of the positive effect of individual component on 28-day compressive strength is Ecement >Eslag >Eash while that of negative effect is Eresin>Ewater by the statistical analysis of mixture data.

3. In this study, the water and resin (x_1x_5) has an interaction effect on 28-day compressive strength of waste form.

4. The recommended composition is, water=0.16, slag=0.10, ash=0.10, cement=0.32, and resin=0.32(expressed as weight fractions) with a predicted value of strength of slightly over 14kN (7Mpa), which resulting form not only meets the relevant criteria of China but also loads the maximal content of resin.

5. The slump and immersion properties will be statistically examined in next study.

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