Application of mixture design to optimize cementation of simulated spent radioactive ion exchange resins

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Abstract The aim of this study was to assess the usefulness of a mixture design for spent resin immobilization in cement as well as to examine the cement-slag-ash system for spent resin solidification. Eighteen distinct combinations, consisting of Portland cement, blast furnace slag, fly ash, organic ion exchange resins and water, were selected by a mixture design computer procedure to compose representative experiment points. The measured properties of solidified forms resulting from the combinations included 28-day compressive strength, 42-day immersion strength, 42-day immersion weight and slump. These data were fit to a mathematic model with the aid of Scheffé quadratic polynomial, and the effects of each ingredient on the measured properties were identified through an analysis of the response trace plots and contour plots. Utilization of an optimality function singled out an optimal combination comprising water=0.16(wt/wt), slag=0.21, ash=0.10, cement=0.27 and resin=0.26 from which the resulting response was 11MPa for the 28-day strength, 110mm for the slump and 5.4% for the 42-day increase in strength.

Key words Optimization, Solidification, Spent resin, Cement, Mixture design
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1 Introduction

Cement solidification is a major immobilization technology for the treatment of radioactive waste like mining tails, evaporator concentrates, spent ion-exchange resins and so on. The current trend in cementation of wastes is toward maximizing waste loadings in resulting waste form on the premise of its performances meeting the acceptance criteria of interim storage or final disposal. For cement encapsulation of spent organic ion exchange resins, a considerable amount of research has been carried out to determine the limits for the composition of an acceptable resin-cement mixture, however, the approach used in these researches, “one factor at a time” or “trial and error”, is difficult to provide the best combination to meet a number of performance criteria simultaneously, especially for the multi-component mixture. Currently, there are several reports in the scientific literature on the application of experiment design, an efficient experiment strategy, in the study of waste solidification. The mixture design[1] and Taguchi design[2] have been used in contaminated soil vitrification[3] and resin cementation,[4] respectively. Response surface methodology[5] has been used in cementation of an evaporator concentrate[6] and a phosphogypsum.[7] A study of employing the mixture design to optimize the resin-cement mixture is still unavailable, hence an attempt of using it to solve this kind of problems will be tried in this work.

Mixture experiments are special 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 different ingredients and some process variables such as time, temperature, etc. The function can be expressed by

$$y = f(x_1, x_2, x_3.....x_i, v_1, v_2, v_3......v_j) \qquad (1)$$

where y stands for the properties of the product, x_i and v_i represent the proportions of components and process variables, respectively.

The details about the mixture design can be seen

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in Ref. [1].

2 Experimental

2.1 Software, apparatus and materials

2.1.1 Software

Minitab Release 13.1 (Minitab Inc. USA) was used for the design and analysis of the experiment; Microsoft Excel 2000 (Microsoft Corporation. USA) was used to deal with part of data.

2.1.2 Apparatus

JJ-5 Cement mortar mixer; NLD-2 Motorized cement mortar flow table; HBY-40A Concerete standard curing cabinet; NYL-300A Compression testing machine (all made in Wuxi Jianyi Instrument & Machinery Co. Ltd).

2.1.3 Materials

Ordinary Portland cement 42.5 (Conch Cement Company Limited, Anhui);

Blast furnace slag, specific surface 0.42-0.45m^2/g (China Shougang Group, Beijing);

Fly ash, first-class ash [8] (Chifeng Electric Power Plant, Inner Mongolia);

Resin, wet mixture with a ratio of anion resin to cation resin=2:1, crosslinking degree 7%, size 0.3-1.2μm (Shanghai Resin Plant);

Water, tap water.

2.2 Experimental design

The proportion of each component was selected in terms of the weight fraction and restricted within a limit as well as the sum of the proportions in unity. A suitable mixture design, extreme vertices design,[9] was employed to design this experiment and fifty-seven blends as candidate points were initially determined by it. Scheffé[10] quadratic polynomial was chosen as a reasonable model to describe the dependence of each property on the five components. Since there are 15 coefficients in the model, the design must cover at least 15 runs (15 distinct mixtures) to estimate these coefficients. In addition to the 15 required runs, three additional runs (distinct mixtures) were included to check the adequacy of the fitted model. So a total of 18 mixtures was planned and chosen from the candidate points utilizing a distance-based optimality function. The constraint conditions of the components and experimental arrangement are listed in Table 1 and Table 2, respectively.

Table 1 Mixture components and condition restrictions

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

2.3 Specimen fabrication

A specified volume of resin-cement mixture was put into the cement mortar mixer and mixed. After that the mortar was cast to be 50 mm (diameter) by 50 mm (high) cylinders. Eighteen batches of the cylinder were prepared in one day and left in molds for 28 days in the summer of 2003 (humility: 70%~90%; temperature: 25~35℃).

2.4 Performance test

2.4.1 Slump test

The slump tests[11] were taken on the cement mortar flow table immediately after mix.

2.4.2 Compression test

Compression tests[12] were conducted on the cylinders at the twenty-eighth day. 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 [13] using an end-grinding machine.

2.4.3 Immersion test

The cylinders were immersed in tap water, and taken out for the compression test and weight measurement at the forty-second day. The percentage increase in weight, I_w, and the percentage increase in strength, I_p, were determined by using Eqs. (2) and (3), respectively.

$$I_w = 100(w - w_0)/w \quad (2)$$

$$I_p = 100(p - p_0)/p \quad (3)$$

where w_0 and w denote the weight of the dried form and that of the wet form after the 42 day immersion, respectively, and p_0 and p represent the 28-day strength and the 42-day immersion strength, respectively.

3 Results and analysis

The average values for slump, compressive strength and water immersion tests for each batch are shown together with the design matrix in Table 2, in which no values in Blend Nos. 1, 11 and 15 are accessible due to the crack of the solidified forms during the water immersion test. Since it was difficult to insure the samples parallel for some inexplicable reasons, even if they came from the same batch, the relative deviations of the strength, especially for those blends with high strength, presented remarkable ranges, and even so, the data were still accepted in the analysis of properties for the usefulness of the average values.

Table 2 Mixture proportions and test results

Blend No.	Water (g)	Slag (g)	Ash (g)	Cement (g)	Resin (g)	Slump (mm)	28-day strength (MPa)	42-day immersion test		
								Strength(MPa)	Incr.wei (%)	Incr.stre(%)
1	240	150	150	555	405	90	11.18±1.44		crack	
2	285	180	420	255	360	160	7.05±0.59	10.94±3.24	11.98±1.69	35.59
3	240	420	150	255	435	135	6.81±0.72	10.06±0.43	11.93±0.60	32.27
4	240	420	150	465	225	55	24.05±3.65	35.07±5.34	6.37±0.8	31.43
5	240	150	420	465	225	75	23.82±7.66	30.44±4.07	6.77±0.52	21.77
6	263	259	259	385	334	155	11.22±1.15	14.12±0.54	11.10±0.43	20.59
7	285	150	285	555	225	95	19.40±2.73	25.84±6.17	8.67±0.80	24.94
8	285	285	150	555	225	85	19.76±3.27	28.40±3.44	8.30±0.25	30.43
9	251	340	205	320	384	140	9.05±0.57	12.95±1.28	10.95±0.81	30.13
10	251	205	332	320	392	153	8.33±2.45	9.23±0.46	12.18±0.86	9.73
11	251	205	205	470	369	105	10.99±0.99		crack	
12	251	295	205	470	279	80	18.43±2.73	26.44±1.01	7.83±0.14	30.31
13	251	205	295	470	279	85	15.42±3.70	22.87±4.92	8.63±0.71	32.55
14	285	150	360	255	450	200	3.75±0.79	3.66±0.82	16.90±1.32	-2.23
15	285	150	150	465	450	170	7.80±1.80		crack	
16	274	340	220	387	279	90	16.55±1.04	21.52±3.81	9.30±1.08	23.1
17	274	220	340	387	279	95	15.51±2.18	20.36±1.27	8.87±0.63	23.81
18	285	420	180	255	360	140	7.56±0.68	13.35±0.83	11.70±0.25	43.41

Incr.stre(%): the increase in strength that is relative to the 28-day waste form.
Incr.wei(%): the increase in weight that is relative to the 28-day waste form.

3.1 Analysis of compressive strength

In order to analyze the dependence of the 28-day compressive strength on the compositions of the solidified forms, a plausible model (Eq.(4)) was fitted and assessed using the analysis of variance and correlation coefficient (R^2) in Table 3.

$$y = -507.4x_1+180.4x_2+165.7x_3+215.7x_4-410.9x_5+2308x_1x_5 \quad (4)$$

where x_1, x_2, x_3, x_4 and x_5, respectively, represent the weight proportions of water, slag, ash, cement and resin in the cement-resin mixture.

Table 3 Analysis of variance and correlation coefficient (R^2) for Eq.(4)

Source	DOF	Sum of square	Mean square	F value	p value	R^2 value
Regression	5	2396	479.2	75.99	0.000	96.94%
Linear	4	2350	44.98	7.13	0.004	
Quadratic	1	45.90	45.90	7.28	0.019	
Residual error	12	75.67	6.31			
Total	17	2471				

Table 3 indicates that the linear terms and quadratic terms should be included in the model (Eq.(4)) for their p-values are less than 0.05 and the model is significant, which is further supported by the R^2 values (correlation coefficients), with a value close to 1 meaning a perfect fit to the experimental data.

As expected, the trace plot (Fig.1), constructed by using Eq.(4), shows that the 28-day strength decreases with the resin or water increase while it increases with the cement, or slag, or ash increase. The relative magnitude of the favorable effects on 28-day strength is higher in order of cement > slag> ash, and that of the adverse effects resin > water by the steepness comparison of the lines in the trace plot. Nevertheless, a different conclusion was obtained with Taguchi method[4] in studying the relationship between the 28-day strength and the compositions in solidified form, in which the slag has been revealed to be possessing the most contribution to the strength, even more than that of cement. A possible explanation is in that the natural curing, 70%~90% of humility and 25~35℃ of temperature, was used to fabricate the solidified forms in this study while the standard curing of 99% humility and 25℃ temperature in Taguchi's study used, the latter more benefited the slag behavior that enhanced the compressive strength.

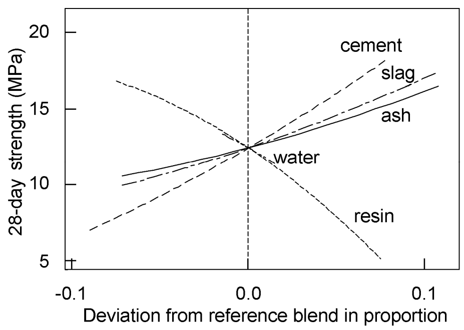

Fig.1 Trace plot for 28-day strength (reference blend: water 0.18, slag 0.17, ash 0.17, cement 0.26, resin 0.22).

Fig.2 also constructed by using the model shows the contour plot of the 28-day strength for the cement-water-resin ternary system, where the other components are fixed at the lower bound settings. An observation of the water-resin binary system in Fig.2 finds that the 28-day strength increases initiatively to an extreme point at about 0.33 of the resin content, and then decreases with increasing the resin content. This result reflects the fact that there existed a two-component interaction between the water and the resin during the solidification process.

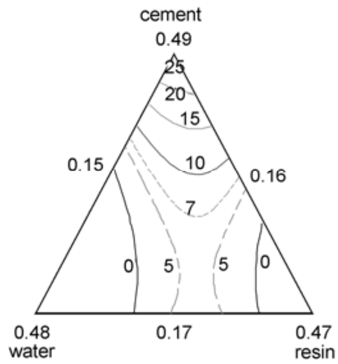

Fig.2 Contour plot for 28-day strength (MPa) in cement, water and resin (slag=0.10, ash=0.10).

Similarly, Eqs.(5), (6) and (7), depicting the dependence of the increase in the compressive strength, the increase in weight and the slump on the compositions respectively, were obtained applying the same regression procedure and evaluation method.

$$y = 1956x_1 - 1264x_2 - 1237x_3 + 1607x_4 - 2408x_5 - 7769x_1x_4 + 936x_2x_3 + 7439x_2x_5 + 6995x_3x_5 \tag{5}$$

$$y = -45.35x_1 - 0.10x_2 + 2.82x_3 + 15.14x_4 - 38.56x_5 + 588.7x_1x_5 \tag{6}$$

$$y = 936.1x_1 - 190.9x_2 - 64.7x_3 - 294.4x_4 + 341.0x_5 \tag{7}$$

3.2 Analysis of the increase in strength

It can be concluded that an interaction effect on the increase in the strength, respectively, existed in water-cement, slag-resin and ash-resin during the water immersion process since these terms are involved in Eq.(5).

The trace plot (Fig.3) provides some information about the component effects on the increase in strength. As the proportion of slag in the mixture increases (and the other mixture components decrease), the increase in strength rises, but in about 0.24 of the slag content it begins to decline. A similar change exists in the ash as well. For the cement, the increase in strength rises whether its proportion increases or decreases. For the water, as its proportion increases, the increase in strength declines rapidly. For the resin, as its proportion increases, the increase in strength rises initiatively, and then declines rapidly. Furthermore, the magnitude order of slag> ash >cement for the favorable effects and that of water>resin for the adverse effect on the increase in strength are presented by the steepness comparison of the trace curves near the reference blend.

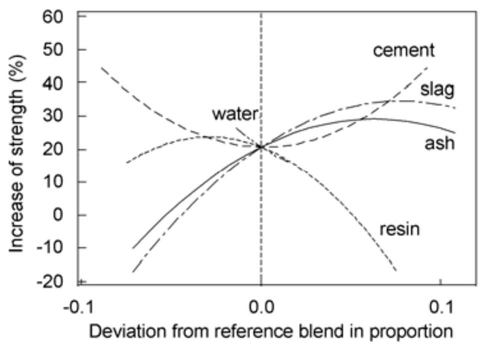

Fig.3 Trace plot for the increase of strength (reference blend: water 0.18, slag 0.17, ash 0.17, cement 0.26, resin 0.22).

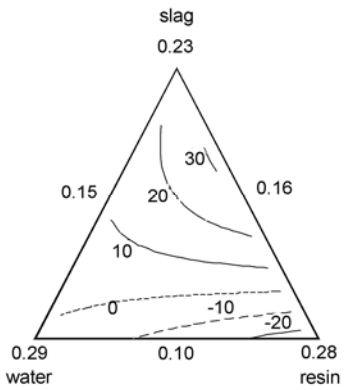

Fig.4 Contour plot for the increase of strength (%) in slag, water and resin (ash=0.10, cement=0.27).

In addition, an examination of water-resin edge in slag-water-resin ternary system (Fig.4) indicates that the increase in strength decreases with increasing resin proportion even though the steepness of trace line of water is more than that of resin, which implies that the total effect of water should be less than that of resin due to the minor range of the water content.

3.3 Analysis of the increase in weight

Resin with water has a two-component interaction for the term of x_1x_5 enters Eq.(6). The trace plot of the increase in weight (Fig.5) shows that, as the proportion of cement, or slag, or ash increases, the increase in weight decreases; as the proportion of resin or water increases, the increase in weight increases. Moreover, the relative magnitude order of slag> ash >cement for the favorable effects and that of water>resin for the adverse effect on resistance to water penetration can be obtained by the steepness comparison of trace curves, only slag slightly more than ash.

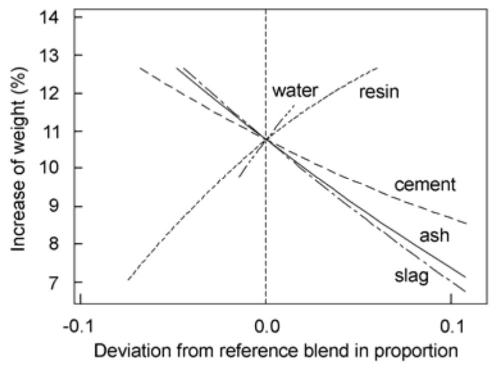

Fig.5 ... end: water 0.18, slag 0.17, ash 0.17, cement 0.26, resin 0.22).

Based on the analysis above, it is found that the increase in strength was consistent with the increase in weight, and the slag played a role of promoting the strength and resisting the water penetration in the process of water immersion.

3.4 Analysis of the slump

It can be seen from the trace plot (Fig.6) that, as the proportion of cement, or slag, or ash increases, the slump decreases; as the proportion of resin or water increases, the slump increases. Furthermore, the relative magnitude order of water>resin for the favorable effects and that of cement > slag > ash for the adverse effect on slump can be concluded by the steepness comparison of the trace lines.

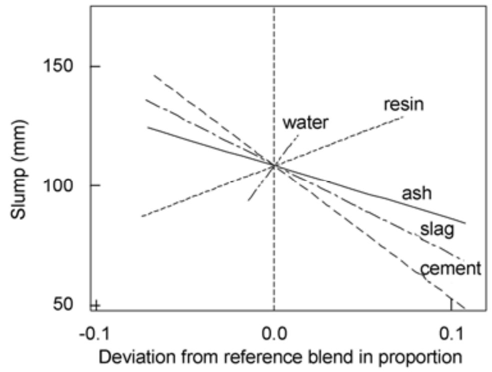

Fig.6 Trace plot of slump (reference blend: water 0.18, slag 0.17, ash 0.17, cement 0.26).

3.5 Selection of optimum mix

Formula optimization is intended to search for a combination of input variables that jointly optimize a set of responses by satisfying the requirements for each response in the set. In this study, the requirements for the 28-day strength, slump and increase in strength are listed in Table 4.

A numerical optimization using a desirability function[14] was used to find the optimum mix. Maximum functions with 1 of weight were used for the 28-day strength and the increase in strength, and target functions with 1 of weight for the slump, as indicated in Fig.7. The final results, including the optimal combination and its evaluation, are given in Table 5, and the evaluation, the one of the desirability, suggested that the mix was satisfied and acceptable.

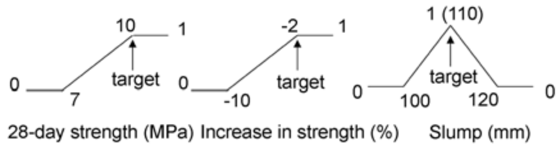

Fig.7 Desirability function for optimization.

Table 4 Response optimization

Parameters	Goal	Lower	Target	Upper	Weight	Import
28-day stre. (MPa)	Maximum	7	10	10	1	1
Slump(mm)	Target	100	110	120	1	1
Incr.stre. (%)	Maximum	-10	-2	-2	1	1

28-day stre.: 28-day compressive strength; Incr.stre.: increase of strength in immersion test.

Table 5 Predicted responses and desirability

Ingredients	Optimum proportion	Response	Predicted value	Desirability	Composite desirability
Water	0.16	Strength	11MPa	1	
Slag	0.21	Slump	110 mm	1	1
Ash	0.10	Incr. stre	5.4%	1	
Cement	0.27				
Resin	0.26				

4 Conclusions

After investigation of effects of ingredients on performances of the waste form by the mixture design and analysis method, an amount of information, such as the main effect, the interaction effect and the order of effect magnitude, was obtained. Thus we can conclude that the method is a strong and efficacious strategy for the study of immobilization of spent radioactive resins in cement, especially when the resulting waste forms contain many constituents and are subject to several constraints. Additionally, taking into account the requirements for the performances of the waste form resulting from the Portland cement-slag-ash mixture, the recommended composition was water=0.16(wt/wt), slag=0.21, ash=0.10, cement=0.27 and resin=0.26, and the resulting response was 11MPa for the 28-day strength, 110mm for the slump and 5.4% for the 42-day increase in strength.

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