ESTABLISHMENT OF PCP COMPOSITION DIAGRAMS FOR CEMENTATIONS OF BORATE WASTES USING RESPONSE SURFACE METHODOLOGY

Ching-Tsven Huang
Institute of Nuclear Energy Research, Taiwan, China

ABSTRACT

For the purpose of quality assurance, it is requested by the regulatory authority in the solidification of low-level radioactive waste (LLRW) to implement the "process control program (PCP)", in which the condition of solidification should be decided in advance of solidification according to the so-called "PCP composition diagrams", to assure that the condition of solidification is within established process parameters and that the quality of solidified LLRW meets quality criteria.

In this paper, PCP composition diagrams for the cementation of radioactive liquid borate wastes were established with response surface methodology, including using the simplex centroid design to allocate experimental conditions and statistical curve-fitting techniques to construct quality models. The constructed models were verified to have a confidence level higher than 95% by doing the lack-of-fit test on them. Quality contours of solidified borate wastes were thus established based on mathematical and statistical principles and have been used as composition diagrams in the process control program of radioactive borate wastes solidification at Ma-An-Shan nuclear power station of Taiwan Power Company.

The solidification agent used in this study was a mixture of Portland type-II cement and lime powder with a weight ratio of 1/0.22. Quality contours for solidified borate wastes including free-standing water content, compressive strength, water resistance, thawing and freezing resistance, irradiation resistance, and leaching resistance were established. Characteristics of these quality contours were also discussed.

With these contours, the performance of the final waste form can be assured and consequently a volume reduction will also be achieved, when the PCP is implemented.

INTRODUCTION

The solidification of low level radioactive wastes (LLRW) is a very important treatment procedure before final disposal, as it provides LLRWs long-term chemical and physical stability. Due to the fact that wastes are unretrieveable once they are solidified and the characterization of solidified wastes is tedious work, any improper conditioning during the solidification of LLRWs could cause the generation of a huge amount of unqualified waste to be formed. Thus, it is requested by FCMA, the regulatory authority in Taiwan, as well as by the NRC in the USA, that a process control program be established and implemented in the solidification of LLRW, and the mixing ratio of wastes and materials used in solidifications should follow the so-called "composition diagrams" to assure that the quality of solidified wastes meets criteria established by the authority. The composition diagrams showing the region of qualified composition for solidification are not only useful in determining the mixing ratio of waste and materials, but also in predicting the quality of solidified wastes that could be obtained, and thus the frequency of quality verifications of solidified wastes could be considerably reduced.

The establishment of PCP composition diagrams has so far been in an arbitrary manner; there was no formal method reported in the literature. In this study, we established quality contours of solidified borate wastes in a composition map using response surface methodology,[1] including using the simplex centroid design[2] to decide experimental conditions, and statistical curve-fitting techniques to construct quality models. The confidence level of the quality models was verified to be >95% by doing the lack-of-fit test on it. The establishment of PCP composition diagrams was thus completed in agreement with mathematical and statistical principles.

PCP composition diagrams established in this study using Portland type-II cement and lime powder as the solidification agent have been used in the LLRW solidification process control program implemented in the Ma-An-Shan nuclear power station (MAS nps) of Taiwan Power Corporation.

RESPONSE SURFACE METHODOLOGY

Response surface methodology was developed first by Box and Wilson,[1]. Procedures involved in the methodology were: (a) conduct pre-planned experiments to obtain data, (b) construct the mathematical model fitted to the data by statistical curve-fitting techniques, (c) additional blends are made in some selected regions to verify experimentally the model predictions.

Simplex Centroid Design

The simplex-centroid design was proposed for mixtures by Scheffe in 1963[4]. The design generates a satisfactory spread of experiments through the region of interest with very few points. Applying this design to a q-components mixture, the number of experiments (n) is determined by the equation:

$$n = 2^q - 1 \quad \text{...} \ (1)$$

Thus, the number of distinct points is 7 for a three-components and 15 for a four-components mixture. These points are taken by dividing the fraction (X_i) of each component into m+1 equal portions, i.e.

$$X_i = 0, 1/m, 2/m, \ldots, 1$$

and spread to include the q permutations of (1, 0, 0,…, 0), the (q/2) permutations of (1/2, 1/2, 0, …, 0), the (q/3) permutations of (1/3, 1/3, 1/3, 0,…,0) and so on, and finally with the overall centroid point (1/q, 1/q, 1/q, …, 1/q). The simplex-centroid design for a three-components mixture is illustrated in Figure 1; the experiments conducted on the points from 1 to 7 in the figure are for model construction, and the extra points from 8 to 10 are that for the lack-of-fit test of the model.

Experience has shown that the m-order canonical polynomial of equation (2) is useful for obtaining an acceptable representation of data. In equation (2) the parameter b_i represents the expected response to the pure component i and is called for the linear blending value of component i; b_{ij} is the coefficient of the non-additive blending of components i and j.

$$Y = \sum_{i=1}^{q} b_i x_i + \sum_{i<j}^{q}\sum b_{ij} x_i x_j + \sum_{i<j<k}^{q}\sum\sum b_{ijk} x_i x_j x_k + \ldots\ldots + b_{12\ldots q} x_1 x_2 \ldots x_q \quad \text{...............}(2)$$

The other b_{ijk} ’s are defined similarly. Data on the response (Y) of the quality are fitted to equation (2) to find the values of the parameters. According to equation (2), the quality contours for the three-components mixture are plane drawings, and for the four-components mixture are cubic drawings. In this study, for the reason of simplicity, the solidification blending was supposed to be a three-components mixture including water, waste and solidification agent, so that the number of experiments is 10, and the quality contours are plane drawings.

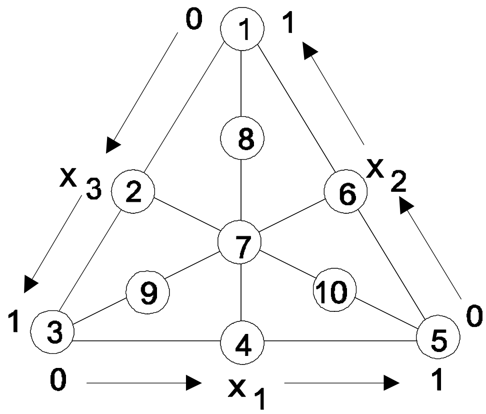

Figure 1 The simplex-centroid design including 3 interior points

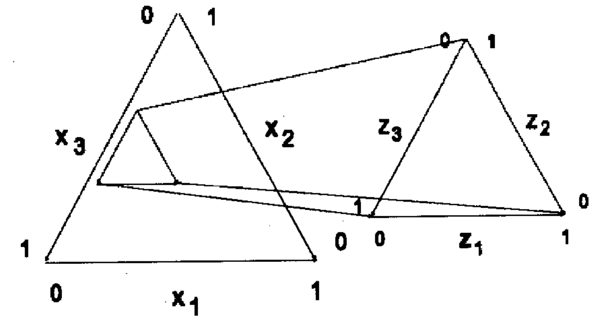

Figure 2 Transformation of a sub-region of the original simplex to a full L-pseudocomponent simplex

The suitable mixing ratio of the components for solidification is constrained by the mixing workability of the blending, the quality of the product, and the volume efficiency of solidification. Therefore, we are interested only in constructing the quality model in a sub-region of the full composition diagram and arranging the points of experimental conditions over the sub-region by doing the simplex-centroid design with L-pseudocomponents.

The concept of using L-pseudocomponents to scale up a sub-region to a full scale simplex is illustrated in Figure 2 for a three-components mixture. The sub-region of the original simplex with borders constituted by the low bounds of the components is scaled up to a full L-pseudocomponent simplex using the linear transformation of:

$$Z_i = (X_i - L_i)/(1 - L) \quad (3)$$

where Z_i denotes the fraction of the L-pseudocomponent i, L_i the low bounds for component i and $L = L_i < 1$. The polynomial model for the L-pseudocomponent is the same as equation (2) except that X_i is replaced by Z_i.

EXPERIMENTAL

Materials

The solidification agent used in this study was prepared by mixing one part of Portland type-II cement with 0.22 parts of lime powder; this powder mixture has been used as the solidification agent for years in the solidification of concentrate wastes in MAS npp. Surrogate liquid borate wastes were used for this study. They were prepared by dissolving boric acid and sodium hydroxide in de-ionized water and were adjusted to have pH 7.2. Chemicals listed in Table 1 were added to the surrogate waste to make concentrations as indicated in the same table. These chemicals make up the highest possible concentrations of impurities including ionic and nonionic species that have ever been presented in the concentrate borate waste of MAS npp.

Chloride solutions of ^{137}Cs and ^{60}Co supplied by ORIS/DAMRI Co. France were used in this study to determine the leachability of these nuclides.

Table 1 Concentrations of chemical impurities in surrogate waste

chemicals	content, ppm	chemicals	content, ppm
$MgSO_4$	3,500	Fe_2O_3	3,600
$Mg(NO_3)_2$	600	SiO_2	20,000
$MgCl_2$	6,800	Na_2CrO_4	6,300
$CaCl_2$	43,000	$Ca(H_2PO_4)_2$	4,500
total content of chemical impurities		88,300 ppm	

Procedures

Surrogate waste forms were prepared following the procedures: (1) boric acid, ^{137}Cs and ^{60}Co nuclides and chemical impurities listed in Table 1 were added in predetermined ratios into de-ionized water in a vessel under agitation, the liquid was heated to 50 C to enhance the dissolution of boric acid and chemicals; then a 50% sodium hydroxide solution was added gradually to adjust the solution to have pH 7.2 and then cooled the solution to a temperature of 25 C; (2) loaded the surrogate waste solution into a bowl type mixer having a volume of 20-liters, and equipped with a planetary stirrer, then the solidification agent was added gradually under agitation; after 5 minutes the agitation was ended and a homogeneous paste was thus obtained; (3) cast the paste into cylindrical polyethylene molds having 5cm in diameter and 11cm in height; air bubbles in the paste were removed by applying a high frequency vibration for 3 minutes; (4) sealed the mold and put in room for curing; (5) after 90 days, the polyethylene mold was removed, and the solid forms were cut into 10 cm in length and characterized.

Characterizations of Waste Forms

Characterizations of the waste forms were conducted following the USNRC methods: ASTM C39 for compressive strength, ANS 16.1 for leaching index, ASTM B533 for thermal cycling resistance, ANS 55.1 for free standing water and.. etc. For each measurement, five pieces of the solid-form sample were tested and their averaged value was reported.

RESULTS AND DISCUSSIONS

Determination of Compositions Low Bounds

According to the method described above, the composition low bounds of the components should be decided so that the borders of the small triangle of Figure 2 can be located. Some preliminary experiments were done for this, the solidification composition ranges for water (0.32 - 0.44), solidification agent (0.56 - 0.68) and waste (0 - 0.12) were thus decided. These ranges constituted the small triangle in Figure 2. With the composition range decided, the upper bound of the waste loading was 0.12, which was higher than the normal waste loading currently in use at MAS nps, thus providing a volume for promoting the waste loading from this study.

Curing Time

It is known that boric acid is a retarder for cement pastes setting, therefore the curing time of cementatious borate wastes is longer than the normal curing time, 28 days, for concrete. The curing time we used in this study was 90 days. , This was determined according to the experiments conducted previously in which the time for sufficient curing of the cementatious borate waste with upper-bound borate loading were investigated, and a curing time of 90 days was found to be good enough for all the conditions used in this study.

pH of Borate Wastes

In this study, the surrogate borate wastes were adjusted with sodium hydroxide to have a pH around 7.2. In our pre-experiments, it was found that a higher pH value of the borate waste could result in a higher strength of solidified borate wastes. However, a higher pH may also result in a lower solubility of borate and thus may cause the crystallization of sodium borates. Also, a higher pH means that more sodium hydroxide has to be added to the waste, and consequently results in the increase of the volume of waste.

Quality Contours

Under the conditions described above, the quality contours of solidified borate wastes including free standing water content, compressive strength, water-immersion resistance, thermal-cycling resistance, irradiation resistance, and leaching resistance were constructed using the response-surface methodology. The contours were prepared for both surrogate wastes with and without impurities, the effect of the impurities on qualities can be understood by comparison.

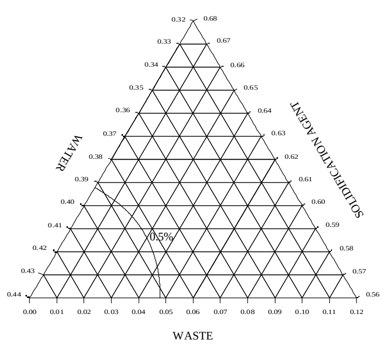

Figure 3 Contour of 0.5% free-standing water (no added impurities)

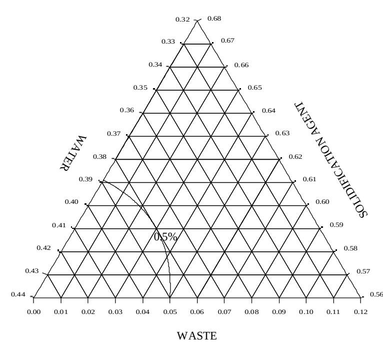

Figure 4 Contour of 0.5% free-standing water (added impurities)

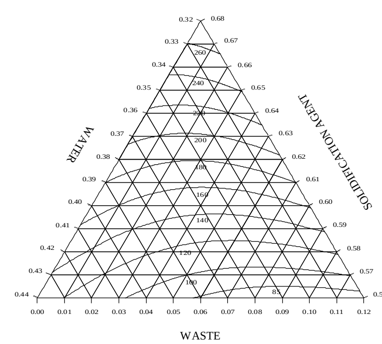

Figure 5 Contours of compressive strength (no added impurities)

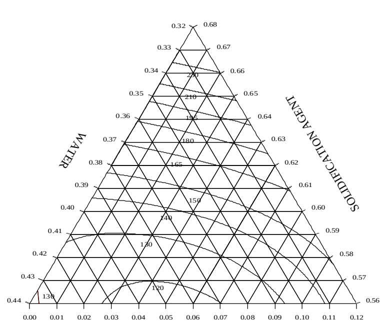

Figure 6 Contours of compressive

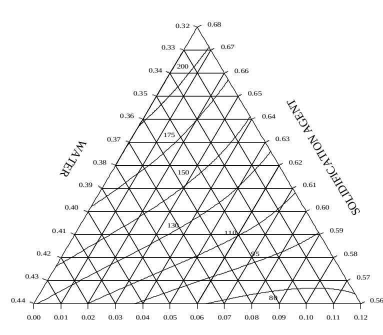

Figure 7 Contours of water-

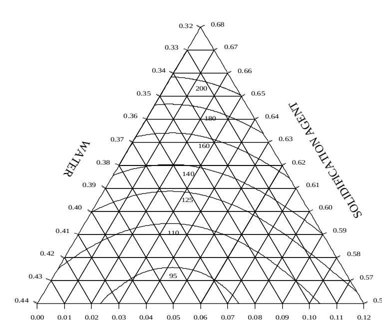

Figure 8 Contours of water-

strength (added impurities)

immersion resistance (no added impurities)

immersion resistance (impurities added)

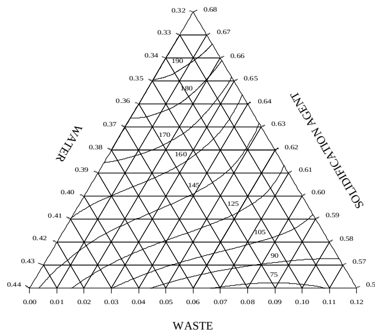

Figure 9 Contours of thermal cycling resistance (no added impurities)

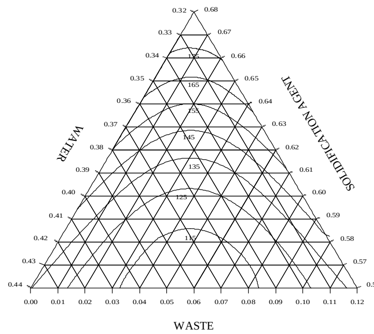

Figure 10 Contours of thermal cycling resistance (added impurities)

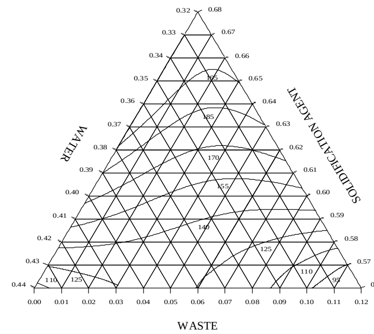

Figure 11 Contours of irradiation resistance (no added impurities)

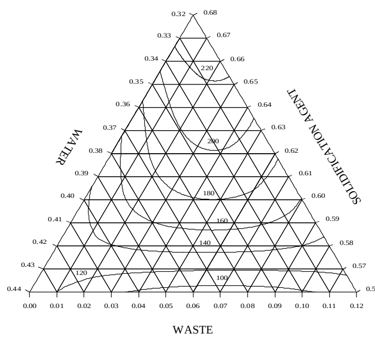

Figure 12 Contours of irradiation resistance (added impurities)

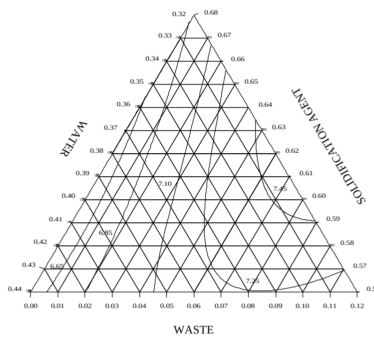

Figure 13 Contours of leaching index (no added impurities)

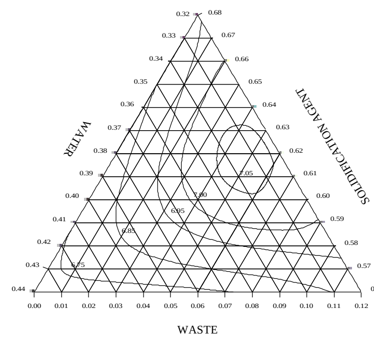

Figure 14 Contours of leaching index (added impurities)

Free standing water

The contour of the 0.5% free standing water content of the solidified wastes was shown in Figure 3 for the surrogate waste without the addition of impurities as indicated in Table 1, and in Figure 4 with the addition of impurities. The reason only the 0.5% contour is shown is because 0.5% is the highest allowable free standing water content. The composition in the region below the contour at the left corner generated the free standing water higher than 0.5% and thus failed to meet the USNRC requirement. From Figures 3 and 4, we can see that the presence of the impurities resulted in a little higher content of free standing water in the solidified waste.

Compressive strength

The contours in Figure 5 and Figure 6 showed that the compressive strength of solidified wastes increases with the weight fraction of solidification agent ignoring whether the wastes contained the Table 1 impurities or not. When the wastes contained the impurities, the compressive strength increased from 85 kg/cm^2 for a weight fraction of solidification agent 0.56 to 260 kg/cm^2 for a weight fraction 0.68, and when the wastes did not contain the impurities it increased from 120 kg/cm^2 to 230 kg/cm^2. The contours also showed that the compressive strength of the solidified waste was not lowered by a higher waste loading less than 0.12.

Water-immersion resistance

The water-immersion resistance contours were shown in Figure 7 and Figure 8 indicating that the water-immersion resistance of the solidified wastes was still significantly affected by and increased with the weight fraction of solidification agent. Under constant dosages of the solidification agent, the water-immersion resistance decreased with the increasing waste loading for the solidified wastes not containing Table 1 impurities; and the contour lines were in convex shapes for that contained the impurities. Comparing Figure 5 and Figure 6 with Figure 7 and Figure 8 respectively, we can see that the solidified wastes containing Table 2 impurities were more resistant to water immersion than those not contained the impurities.

Thermal-cycling resistance

The thermal-cycling resistance contours were shown in Figure 9 and Figure 10. Their profiles are very similar to those of the water-immersion resistance; obviously, the presence of the Table 1 impurities had a significant effect on the contours, it changed the contour's shape from that of monotonous increasing with the waste loading to that of convexity and resulted in a better thermal-cycling resistance for the blending containing a lower dosage of solidification agent.

Irradiation resistance

Figure 11 and Figure 12 show the irradiation resistance contours, convex and concave profiles that were obtained for the presence and absence of the Table 1 impurities, respectively. Similar to the water immersion resistance and thermal cycling resistance contours, the presence of the impurities also resulted in a better irradiation resistance.

Leaching resistance

The leaching resistance of solidified wastes was expressed in term of a "leaching index" which was defined in ANSI16.1. Contours of the leaching index of ^{137}Cs were shown in Figure 13 and Figure 14, which indicated that ignoring the presence of Table 1 impurities, the leaching index increased with the waste loading for the same dosage of solidification agent. However, the difference was small, the index varied from 6.65 to 7.45 in the absence of the impurities and from 6.75 to 7.05 in the presence of the impurities. Cesium leaching index of the irradiated solidified wastes was also measured and no significant effect caused by a 10^6 Gy irradiation was found.

Confidence Of Quality Models

According to the experimental results and the model established, the lack-of-fit tests on the quality models of compressive strength, water-immersion resistance, thermal cycling resistance and irradiation resistance were conducted using the statistic analysis method. The F values obtained for different quality models were less than the $F_{0.95,3,40}$ value, i.e. 2.84. This meant that the confidence of the models was higher than 95% by the lack-of-fit tests

CONCLUSIONS

Using the response surface methodology and simplex-centroid design, quality models of solidified borate wastes was successfully established with only 10 sets of experimental data. The establishment of the quality models was in agreement with the mathematical and statistical principles, and the models have a 95% statistic confidence. The PCP composition diagrams for the solidification of LLWs were thus constructed with a very low cost.

The quality contours enable us to know the appropriate condition of solidification and the quality of solidified wastes in advance of conditioning, thus provide a large flexibility of operation, and also simplify the quality assurance procedures.

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KEY WORDS

Solidification, Radioactive Borate wastes, Process Control Program, Composition Diagram, Simplex Design

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