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STATISTICAL EXPERIMENTAL DESIGN FOR SALTSTONE MIXTURES

INTRODUCTION

We used a mixture experimental design for determining a window of operability for a process at the U.S. Department of Energy, Savannah River Site, Defense Waste Processing Facility (DWPf).

The high-level radioactive waste at the Savannah River Site is stored in large underground carbon steel tanks. The waste consists of a supernate layer and a sludge layer. ^{137}Cs will be removed from the supernate by precipitation and filtration. After further processing, the supernate layer will be fixed as a grout for disposal in concrete vaults. The remaining precipitate will be processed at the DWPf with treated waste tank sludge and glass-making chemicals into borosilicate glass.

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PROBLEM BACKGROUND

The leach rate properties of the supernate grout, formed from various mixes of solidified salt waste, needed to be determined. The effective diffusion coefficients for NO_3 and Cr were used as a measure of leach rate. Various mixes of cement, $\text{Ca}(\text{OH})_2$, salt, slag and flyash were used. These constituents comprise the whole mix. Thus, a mixture experimental design was used.

The distinguishing feature of mixture experiments is that the proportions (X_1, X_2, \dots, X_n) of constituents sum to unity for any mix. As such, the related experimental design is a selection of points from an $(n-1)$ - dimensional tetrahedron since we have n variables.

Standard designs consist of the vertices, mid-edges, face centroids, and interior centroid of the tetrahedron. However, in addition to the basic mixture constraint, we have constraints of the form $a_i < X_i < b_i$, $i=1$ to n , for each of the $n = 5$ variables where a_i and b_i are constants.

DEFINITIONS & CONSTRAINTS

The response variable is $Y = \text{Average Diffusion Coefficient for } \text{NO}_3 \text{ or Cr (cm}^2/\text{s)}$.

Let X_1 , X_2 , X_3 , X_4 , and X_5 be the proportion of cement, $\text{Ca}(\text{OH})_2$, salt, slag and flyash, respectively. We have the double edge constraints: $.00 \leq X_1 \leq .10$, $.00 \leq X_2 \leq .10$, $.40 \leq X_3 \leq .55$, $.10 \leq X_4 \leq .40$ and $.10 \leq X_5 \leq .40$.

Since we are dealing with proportions, we have the mixture constraint

$$X_1 + X_2 + X_3 + X_4 + X_5 = 1. \quad (1)$$

Also, we have the two formulation constraints,

$$\text{If } X_1 > 0 \text{ then } X_2 = 0 \text{ or} \quad (2.1)$$

$$\text{If } X_2 > 0 \text{ then } X_1 = 0, \quad (2.2)$$

since both cement and $\text{Ca}(\text{OH})_2$ cannot be present at the same time.

THE MODEL

The basic design was for a mixture model with five components. However, separate analyses were done based on the absence of cement or $\text{Ca}(\text{OH})_2$.

Suppose cement is absent (i.e., $X_1 = 0$). The quadratic model written in Scheffe's canonical form is

$$Y = \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \dots + \beta_{45} X_4 X_5. \quad (3)$$

The absence of the constant term is due to the constraint $\sum X_i = 1$. The second order quadratic terms do not appear explicitly because the mixture constraint implies $X_k^2 = X_k(1 - \sum X_j)$ for j not equal to k .

THE DESIGN

Equations (1), (2.1), (2.2) and the double edge constraints define the experimental design space. The intersection points of these boundaries, their "extreme vertices"¹, are the points which delimit this space. These computed vertices² were augmented by their pair-wise, triple-wise, ... averages to form 62 candidate design points consisting of the vertices themselves, the mid-points of their pairwise edges, the mid-points of all higher order edges, and the overall centroid.

Since 62 points were many more than needed to generate estimates of the slopes in Equation (3), a further sub-

selection was made by a geometric coverage algorithm³ to identify those having essential leverage on the model. This resulted in 25 such points which formed the initial experimental mixes.

However, unexpectedly, when formulated half of these 25 mixes were either too viscous or too fluid to be acceptable. Clearly, additional constraints applied. To derive them, each of the 25 mixes was labelled as "Good", "Too Thick", or "Too Thin" and the label plotted at its corresponding point in the design space. Using matrix algebra⁴, these processibility labels were projected onto various rotations of the coordinate axes until one was found which perfectly separated the "Good's" from the "Bad's". The resulting discriminants were:

$$(X_1=0, X_2>0) \quad -0.326 X_2 + 0.794 X_3 \geq 0.30 \quad (4.1)$$

and

$$(X_1>0, X_2=0) \quad 1.31X_1 + 0.26 X_4 \geq 0.08. \quad (4.2)$$

Since the remaining half of the 25 original design points were insufficient to support the model, additional design points which obeyed these further constraints had to be selected. Any design point giving a non-negative dot-product with the normals to these constraints obeys these

constraints, and is thus an eligible candidate. There were 32 such of the original 62 points, and they comprised the final design.

IMPLEMENTATION

The regression procedure (PROC REG) in SAS⁵ was used to produce analysis of variance (ANOVA) statistics. In addition, detailed model diagnostics are readily available for identifying suspicious observations. For convenience, tri-linear contour (TLC) plots, a standard graphical tool for examining mixture response surfaces, of the fitted model were produced using ECHIP⁶.

The ANOVA statistics were produced by SAS- PROC REG by allowing a constant term to be fit in the model but restricting its value to be zero. Since our data were averaged over replicate points, we specified the weights, W_i , equal to the number of points averaged for each test condition.

RESULTS

Once the additional data were collected, they were fit to the second order model(3). The model was then used to

interpolate, using TLC plots, among the relatively few formulations examined to identify regions of suitable and perhaps optimal mixes.

We split the NO_3 data into two parts for analysis : 1) without cement and 2) without $\text{Ca}(\text{OH})_2$. For illustration, the analysis without cement is presented.

1) NO_3 Without Cement

The mixture components explain a significant portion of the variation in the data. The ANOVA statistics are $F=15.939$ ($p= 0.0007$), $R^2=95\%$, and the adjusted $R_a^2=89\%$. The R^2 ranges between 0 and 1 with $R^2=1$ being a perfect fit of the model to the data. Also the G-Efficiency= 0.63. Wheeler⁷ suggests a design with G-efficiency ≥ 0.50 is a good design.

The TLC plots were used for interpretation of the estimated response (Plot 1). The convex hull of the design is also shown. The TLC contains three on axes variables (X_5, X_4 , and X_3) with $X_1=0$ and $X_2= 0.058$. The sum of all component proportions must equal unity. Specific points were easily tested in ECHIP for significance. Various other TLC plots were generated for determining regions of optimal processing conditions.

- 1 McLean, R.A., & Anderson, V.L., "Extreme vertices design of mixture experiments," Technometrics, 8, 447-456 (1966).
- 2 Snee, R.D., & Marquardt, D.W., "Extreme vertices designs for linear mixture models," Technometrics, 17, 149- 159 (1974).
- 3 Kennard, R.W., and Stone, L.A., "Computer aided design of experiments," Technometrics, 11,137-148 (1969).
- 4 Flury, B.K., & Riedwyl, H., "Standard distance in univariate and multivariate analysis," American Statistician, Vol. 40, No. 3, 249 -251 (1986).
- 5 SAS VERSION 5.18, SAS Institute, Cary, N.C.
- 6 A commercial experimental design package for PC- DOS. ECHIP, INC., HOKESSIN, DE.
- 7 Wheeler,R.E., "Efficient Experimental Design," E.I. Du Pont De Nemours & Co. ESD # 14316 (1972).

DISCLAIMER

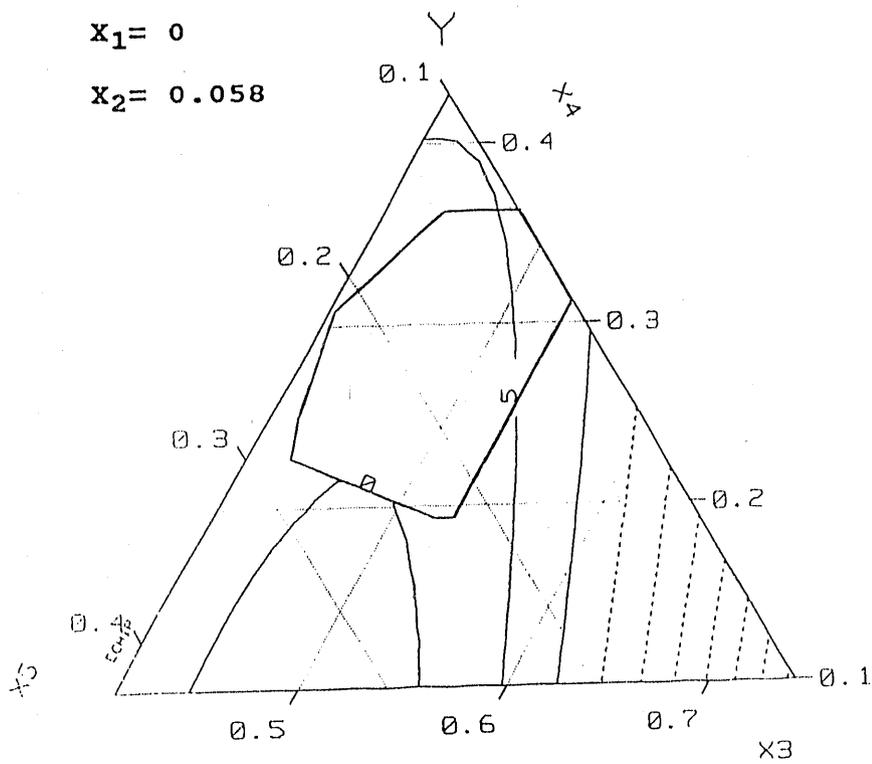
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PLOT 1

TRI-LINEAR CONTOUR PLOT OF NO₃ LEACH RATES

$X_1 = 0$

$X_2 = 0.058$



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