Statistical Techniques to Assist Decision Makers in Selecting Complex Mixtures[a]

Roger Spence
Oak Ridge National Laboratory[b]
Oak Ridge, TN 37831-6202
(865) 574-6782
spencerd@ornl.gov

Richard Counts
Oak Ridge National Laboratory
Oak Ridge, TN 37831
(865) 574-8264
countsrw@ornl.gov

Christine Langton
Savannah River Technology Center[c]
Aiken, SC 29808
(803) 725-5806
christine.langton@srs.gov

ABSTRACT

The relative proportions of the components of complex mixtures often control the properties of interest. Statistically designed experiments reveal not only which ingredients control a given property but also generate response surface models to predict performance as a function of compositions. A mixture experiment is in progress to predict properties of common interest for four generic grout ingredients plus one admixture used to fill and close tanks. Two examples of response surface models are presented for a previously generated statistical design. The generic 30-mix design in progress is also presented with preliminary results for the tank closure properties. A baseline formulation can be selected from the results and models from such designs targeting the site-specific criteria for a given tank closure can be generated.

I. INTRODUCTION

Statistical experimental design and analysis methods have been developed specifically for the purpose of optimizing mixtures, such as grout, in which the final product properties depend on the relative proportions of the components rather than on the absolute amounts. Mixture experiments combined with response surface optimization provide the methodologies for finding the proportions that provide the best settings to meet a number of performance criteria simultaneously.[1]

This paper presents two response surface models, previously generated from a statistical design, to illustrate the contour plots that can be generated from such statistical designs. The mixture experiment currently in progress, with its preliminary results for enhanced grouts for tank closure, is presented. By the time of the Spectrum Conference, the final results and corresponding response surface models are expected to be completed and work initiated on the site-specific goals of Hanford tank closure.

II. PREVIOUS RESPONSE SURFACE MODELS

A statistical design was previously used to explore high salt contents of slag-cement waste forms.[2] This design was used to generate the response surface models given in Equations 1 and 2 (from Ref. 2). Equation 1 estimates the percentage of chromium extracted during Toxicity Characteristic Leaching Procedure (TCLP) testing, and Equation 2 estimates the unconfined compressive strength (UCS):

$$\% \text{ Cr} = -4.59 + 90.5 \text{ cement/waste solids} - 16.0 \text{ slag/waste solids} - 32.3 (\text{cement/waste solids})^2 + 2.37 (\text{slag/waste solids})^2 \quad \text{(Eq. 1)}$$

[a] Supported by the U.S. Department of Energy, Office of Environmental Management and Office of Science and Technology, Tanks Focus Area, Tank Closure, under Technical Task Plan OR16WT51, 3RBS.

[b] Managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.
[c] Managed by Westinghouse Savannah River Co., for the U.S. Department of Energy under contract DE-AC09-96SR18500

UCS = – 526 + 1153 cement/waste solids + 806 slag/waste solids – 3523 clay/waste solids + 3693 chloride/waste solids +1747 sulfate/waste solids + 2151 nitrate/waste solids –309 water (Eq. 2)

where

% Cr	=	percentage chromium extracted during TCLP testing (wt %),
waste solids	=	mass of waste solids,
cement	=	mass of cement,
slag	=	mass of slag,
clay	=	mass of clay,
chloride	=	mass of sodium chloride,
sulfate	=	mass of calcium sulfate,
nitrate	=	mass of sodium nitrate, and
water	=	qualitative water factor,

(-1 is low water and +1 is high water).

Figures 1 and 2 show contour plots for these two models.

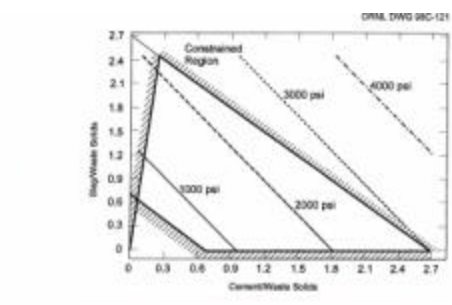

Figure 1. Contour plots of unconfined compressive strength as function of slag and cement content.

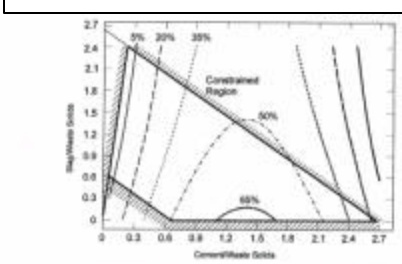

Figure 2. Contour plots of percentage of chromium extracted during TCLP as function of slag and cement content.

III. MIXTURE EXPERIMENT DESIGN IN PROGRESS

The number of batches (samples) that must be prepared for the mixture experiments depends on the number of grout components (independent variables) to be investigated and the specific model that will be fit to the experimental data. Linear models require fewer experiments but provide little information concerning nonlinear effects. The purpose of fitting a linear model to data collected using a minimal-sample-size design would be to determine which of the grout components considered in the experiments are most influential in determining grout properties. If the purpose of the experimentation is to optimize the grout formulations, then linear (first order) models are inadequate. Experience has shown that quadratic (secondorder) models usually provide an adequate representation of each property over the range of interest while requiring only a moderate increase in sample size. Quadratic models will help to provide understanding of the linear and nonlinear blending effects of the components.

U.S. Department of Energy (DOE) sites have a common set of desired physical properties for a grout used to fill an “empty” tank during formal closure in order to physically stabilize the tank void space and prevent future subsidence. These common properties include being pumpable, flowable, self-leveling, bleedless, and low heat evolving. Other properties of interest, whose criteria values vary from site to site, include set time, strength, pH, and standard oxidation potential (E_h).

The experimental design points formed a “region of interest.” Preliminary testing and prior knowledge determined the constraints for this “region of interest,” which were used to generate sets of compositions to test in the laboratory. The statistical experiment provided the following benefits:

- Verification: Verify that the baseline grout formulations used at the various sites result in desirable properties.
- Optimization: Determine if there are other grout formulations in the vicinity of the baseline formulation that improve the grout properties.
- Sensitivity: Determine if moderate deviations from the baseline formulations would significantly affect the grout properties.

Physical properties of grout formulations are flexible. For example, the physical properties of any of the design formulations can likely be adjusted to a target range by manipulating the water content and use of admixtures. In other words, practitioners usually select a favorite composition with proven properties and adjust to the desired properties by such compositional manipulation. In addition, it is important that such manipulation be allowed in the field to compensate for field conditions that cannot be controlled, such as local temperature and humidity. Modeling all of these effects would have required a design beyond the resources and scope of this project.

Nevertheless, a design was generated that illustrated the importance of the dry blend materials on the resulting properties and provided a basis for selection of a generic grout formulation for filling tanks. In order to do this, the number of variables was restricted, so that a reasonable number of design formulations resulted. First, formulations were restricted to a wet grout fill, eliminating pneumatic filling with dry materials for this design. Second, gravel was eliminated as an aggregate for this design. Finally, the design was limited to grouts composed of the following ingredients:

- sand,
- fly ash,
- cement,
- ground granulated blast furnace slag (slag),
- water, and
- one admixture (Kelco-crete®) out of many possibilities.

Specifying the water content in the design was difficult because each dry ingredient has a different level of water demand and requires a different amount of water to allow the particles to slide past each other. For this reason, the water content was considered one of the dependent variables to be measured rather than specified in the design. Thus, the minimum water content needed to make a wet mixable paste in the laboratory equipment was determined subjectively as a part of each test. This gives a measure of the water demand of the dry blend and a starting point for the minimum water content, with the understanding that increasing the water content and/or addition of admixtures can be used to achieve the desired properties for a given dry blend.

The mixture experiment was designed for a dry blend of four basic components — sand, fly ash, cement, and slag — leaving the admixture as a parameter since it constitutes such a minor part of the dry blend mass. Although fly ash or mortar (cement-slag) fills perform satisfactorily, the formulations already selected by some sites for filling tanks tend toward sand fills. These sand fills are designated as flowable fills or controlled low strength materials (CLSMs). The main reason for this focus on CLSM formulations is the low cost of sand and the fact that fill strength is generally not a requiremement. (If a site requires an intruder barrier, higher cement contents may be needed, for example, at the top of the tank.) However, the entire compositional range (0-100% for each of the four ingredients) was open for the design, if constructible grouts could be made. “Constructible” in this case was defined as the ability to measure the properties in question. Formulations that bleed were allowed in the design region. Bleed can usually be controlled by manipulating the composition to increase high-water-demand ingredients (for example, cement), by decreasing the water content, and/or by using admixtures (for example, fluidizers, water reducers, and air entrainers).

Preliminary testing was conducted to explore the properties of selected formulations and boundary limits on the region of interest. Sand was found to be the only one of the four bulk dry ingredients that required Kelco-crete® in order to flow, and the Kelco-crete® must be added with one of the finer materials (fly ash, cement, or slag). Hence, the entire compositional regime was included in the region of interest, with the exception of a tiny region consisting of almost 100% sand. A further constraint was included, requiring addition of some cement if slag was used, to guarantee activation of the slag. The constraints follow:

1) Sand + Fly Ash + Cement + Slag = 1, with the Admixture as a process variable
2) If Sand > 0 then
   i) Admixture > 0
   ii) Fly Ash + Cement + Slag > 0
3) If Slag > 0 then Cement > 0

where,
Sand = mass fraction of sand in dry blend
Fly Ash = mass fraction of fly ash in dry blend

Cement = mass fraction of cement in dry blend
Slag = mass fraction of slag in dry blend
Admixture = ratio of mass of the admixture to total mass of dry blend (sand + fly ash + cement + slag).

For a four-component dry blend, a linear model requires testing a minimum of 7–9 samples and a quadratic model requires testing a minimum of 13–15 samples. Twenty mixes were selected as the design target. Some 20-mix designs were generated using the above constraints with a G efficiency greater than 50%, the hallmark of a good design. One design was selected for the 20-mix design and combined with five replicates and five optional mixes to give the test set of 30 mixes listed in Table I. Four of the optional mixes represent grout tank fills previously selected by Oak Ridge National Laboratory (2), Idaho National Engineering and Environmental Laboratory (1), and Savannah River Site (1). Preliminary testing made constructible grouts with sand contents as high as 95 wt % in the dry blend. The final optional blend in the design pushed the sand content to 99 wt %.

Table II lists some preliminary results measured for this set of 30 mixes. These results include the following:

- minimum water content to make a wet mixable paste,
- flow consistency test [ASTM D6103-97 (Ref. 3)],
- unit weight [ASTM C138/138M-01a (Ref. 4)],
- entrained air [ASTM C231-97e1 (Ref. 5)],
- workability index (qualitative estimate, 1 = worst, 10 = best),
- bleed [ASTM C232-99 (Ref. 6)],
- set time [ASTM C403/C403M-99 (Ref. 7)],
- pH as measured by pH paper (maximum of 11),
- maximum temperature evolved,
- unconfined compressive strength (values at 28 days shown in Table II) [ASTM C232-99 (Ref. 8)],
- E_h [ASTM D1498-00 (Ref. 9)].

SUMMARY

A mixture experiment was designed to define the generic region of enhanced grout formulations for tank closure for physical properties of common interest to all U.S. DOE sites. This mixture experiment is currently in progress but is expected to be completed before the Spectrum 2002 Conference. Response surface models will be generated for some properties, such as compressive strength. Two examples of such models from previous work were presented. Other properties, such as bleed, have an insofficient number of measurable values for modeling, but should help to identify a broad region of acceptability, as well as areas that tend to generate bleed. This generic design illustrates the power of using statistical techniques to assist end users in selecting what complex mixture to use for a given application and in predicting the acceptable range of variation in composition during implementation.

ACKNOWLEDGMENTS

The U.S. DOE Office of Science and Technology supported this work through Tanks Focus Area Tank Closure managed by Larry Bustard (Sandia National Laboratory) and Bill Holtzscheiter (Savannah River Techno;ocy Center). Bill Mhyre, Neal Shranek, John Cook, Wyman Pope, and John Mueller mixed and tested the formulations in the concrete laboratory at the Westinghouse Savannah River Company.

Table I. Mixture experiment design

Run No.	Dry Blend Components (mass fraction)				Admixture (g/g dry blend)
	Sand	Fly Ash	Cement	Slag	
1	0.000	1.000	0.000	0.000	0.0010
2	0.000	0.000	0.050	0.950	0.0000
3	0.475	0.000	0.525	0.000	0.0010
4	0.784	0.202	0.014	0.000	0.0000
5	0.475	0.525	0.000	0.000	0.0010
6	0.475	0.525	0.000	0.000	0.0001
7	0.475	0.000	0.025	0.500	0.0010
8	0.000	0.500	0.025	0.475	0.0010
9	0.000	0.500	0.500	0.000	0.0000
10	0.696	0.203	0.101	0.000	0.0000
11	0.950	0.000	0.002	0.048	0.0002
12	0.000	1.000	0.000	0.000	0.0000
13	0.000	1.000	0.000	0.000	0.0010
14	0.475	0.000	0.025	0.500	0.0005
15	0.000	0.000	0.525	0.475	0.0000
16	0.950	0.000	0.002	0.048	0.0010
17	0.950	0.000	0.002	0.048	0.0010
18	0.475	0.000	0.525	0.000	0.0005
19	0.000	0.000	1.000	0.000	0.0010
20	0.777	0.127	0.025	0.071	0.0007
21	0.000	0.000	1.000	0.000	0.0010
22	0.000	0.500	0.025	0.475	0.0005
23	0.000	0.000	0.050	0.950	0.0010
24	0.000	0.000	1.000	0.000	0.0000
25	0.000	0.500	0.500	0.000	0.0005
26	0.990	0.000	0.001	0.009	0.0010
27	0.000	0.000	0.525	0.475	0.0005
28	0.000	0.000	0.050	0.950	0.0000
29	0.000	1.000	0.000	0.000	0.0000
30	0.974	0.000	0.026	0.000	0.0000

Table II. Preliminary mixture experiment results

Run No.	Water (g/g blend)	Flow (in.)	Unit Wt (lb/ft^3)	% Air	Work Index	pH	Bleed (vol %)	Max. Temp. (ºF)	Strength (psi)
1	0.48	13.25	99	0.8	6	7	1.0	74	4
2	0.44	7.5	113	0.5	2	10	0.0	77.5	2,165
3	0.29	11.25	126	0.6	2	11	0.9	91.2	4,780
4	0.18	11.5	130	0.4	7.5	11	4.4	73.6	65
5	0.21	9.25	120	0.5	10	8	0.0	73.5	15
6	0.18	11	122	1.3	10	7	0.9	73.7	14
7	0.23	8.25	125	0.5	7	10	0.0	74.9	3,010
8	0.38	7.75	106	0.7	6	10	0.0	73.4	1,640
9	0.34	9	115	1	7	11	0.0	95.6	5,760
10	0.16	8.75	132	0.7	9	11	1.3	74.3	1,635
11	0.16	7.25	115	2.1	5	11	0.0	73.7	90
12	0.32	6.5	105	3.2	3	6	2.2	74	15
13	0.38	8.5	104	1.3	7	7	0.0	74	20
14	0.24	8	127	0.3	10	11	0.0	76	1,755
15	0.32	8	122	0.3	5	11	0.0	97	5,655
16	0.16	8	120	0.3	2	11	0.0	74	60
16A	0.26	7.5	121	2.4	2	11	0.0	74	80
17	0.24	7.5	119	2.1	5	11	0.0	74	95
18	0.23	9.5	130	0.3	9	11	0.0	92	5,340
19	0.38	6.5	122	0.9	4	11	0.0	130	8,310
20	0.16	8	128	1	10	11	0.0	74	790
21	0.16	7.75	124	0.2	8	11	0.0	131	7,285
22	0.42	7.75	109	0.5	8	10	0.6	77	1,100
23	0.45	7.75	113	0.2	2	10	0.0	82	3,230
24	0.29	6	131	0.9	2	11	0.0	151	5,935
25	0.38	7	113	0.6	2	11	0.0	102	3,445
26	0.29	7.75	117	2.1	4	7	0.0	74	0
27	0.39	6.5	119	0.6	3	11	0.0	108	7,780
28	0.39	6.25	119	0.5	1	10	0.0	80	2,730
29	0.38	13.25	103	0		9	5.0	73.1	10
30	0.27	7.75	119	1.9	8	10	0.0	75	0

REFERENCES

1. J. A. CORNELL, *Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data*, 2nd ed., John Wiley & Sons, Inc., New York, 1990.

2. R. D. SPENCE, *Cementitious Stabilization of Mixed Wastes with High Salt Loadings*, ORNL/TM-13725, Oak Ridge National Laboratory, Oak Ridge, TN, 1999.

3. ASTM D6103-97, "Standard Test Method for Flow Consistency of Controlled Low Strength Material (CLSM)," American Society for Testing and Materials, Philadelphia, PA.

4. ASTM C138/138M-01a, "Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete," American Society for Testing and Materials, Philadelphia, PA.

5. ASTM C231-97e1, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method," American Society for Testing and Materials, Philadelphia, PA.

6. ASTM C232-99, "Standard Test Method for Bleeding of Concrete," American Society for Testing and Materials, Philadelphia, PA.

7. ASTM C403/C403M-99, "Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance," American Society for Testing and Materials, Philadelphia, PA.

8. ASTM C39/C39M-01, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens," American Society for Testing and Materials, Philadelphia, PA.

9. ASTM D1498-00, "Standard Practice for Oxidation-Reduction Potential of Water," American Society for Testing and Materials, Philadelphia, PA.