DP-1404

663139

TIS FILE
RECORD COPY

MEASUREMENT AND CONTROL OF CEMENT SET TIMES IN WASTE SOLIDIFICATION

J. A. STONE
P. D. d'ENTREMONT

SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

Record Cy

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy $3.50; Microfiche $2.25

kb 3154

DP-1404
UC-70

MEASUREMENT AND CONTROL OF CEMENT SET TIMES IN WASTE SOLIDIFICATION

by

J. A. STONE
P. D. d'ENTREMONT

Approved by

M. L. Hyder, Research Manager
Separations Chemistry Division

Publication Date: September 1976

E. I. DU PONT DE NEMOURS AND COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

ABSTRACT

Fixation of radioactive waste in concrete was investigated on laboratory scale. Some cement formulations containing simulated or actual sludges from the Savannah River Plant had set times that would be too short for reliable handling in plant equipment. Set times could be controlled by use of excess water, but the concrete forms produced had inferior strength. A commercial organic retarder was found to be effective for increasing set times of cement-sludge formulations. However, the dosage of retarder required to control set times of high-alumina cement formulations was 1.0 to 1.5 wt % of dry solids, which is 5 to 10 times the normal dosage for Portland cements. Data were obtained to predict the optimum content of retarder and water.

CONTENTS

LIST OF TABLES

Table

LIST OF FIGURES

Figure

MEASUREMENT AND CONTROL OF CEMENT SET TIMES IN WASTE SOLIDIFICATION

INTRODUCTION

Concrete has been proposed as a candidate form for fixation of high-level radioactive waste at the Savannah River Plant[1] (SRP). Concrete has been used at various sites, both in the United States and in Europe, for solidification of low-level and intermediate-level radioactive wastes. SRP wastes are expected to be compatible with concrete; aged SRP wastes generate relatively low heat from decay of radionuclides, are alkaline, and have large volumes. The conceptual SRP waste solidification flowsheet,[1,2] and work on incorporation of SRP wastes into concrete and glass have been described.[3-5]

Prior work, with both simulated and actual SRP waste sludges, has shown that cement set times are accelerated by addition of sludge.[5,6] For concrete to be a viable option for waste solidification, the set time of freshly mixed cement, waste, and water must be sufficiently long to allow transfer of the paste to storage containers. This report describes work done to determine factors affecting set times of waste-cement pastes and to demonstrate methods of controlling set times.

Relationship to Prior Work

The earlier studies[5] demonstrated the feasibility of solidifying SRP waste sludges in relatively strong concrete forms with relatively low leachabilities. A factorial experiment was designed to test six types of cement, three simulated sludges, three levels of sludge loading, and three levels of water content. The cements used were four standard types of Portland cement[7] as defined by ASTM (Type I, II, III, and V), a Portland-Pozzolanic cement (Type I-P),[8] and a high-alumina cement (HAC).[9] The simulated sludges were various combinations of hydrous oxides of iron, aluminum, manganese, and mercury that were believed to be representative of the wide range of sludge compositions in SRP waste tanks. The sludge loadings were 10, 25, and 40 wt % of the solids. Water contents were adjusted to give pastes with good, too-dry, or too-wet workability.

Several interesting properties of concrete-sludge specimens were determined and evaluated in the earlier studies. In all formulations the water/cement ratio increased with increasing sludge content, indicating that the sludges were hydrophilic. Compressive strengths and leachabilities of specimens from each formulation were measured. The predominant factor affecting compressive strength of the concrete waste forms was the level of sludge loading. The compressive strengths decreased from about 10,000 psi with no sludge, to the range of 2000 to 3000 psi with 40% sludge. The range of 2000 to 5000 psi is considered satisfactory for most commercial applications of concrete. Of the six cements tested, HAC and Type I-P had the best all-around properties, based on compressive strength and leachability. Therefore, these two cements were selected for further testing with actual SRP waste sludges.

In shielded cell facilities, concrete specimens were prepared with HAC and Type I-P cement; three different SRP waste sludges were incorporated at three levels of sludge loading. The formulations were prepared with the equipment shown in Figure 1. Dry sludge, cement, and water were blended in the bowl; then a vibrator was used to transfer the paste through a spout in the bowl into plastic molds. During those operations, the possibility of a set-time problem with actual sludges first became apparent.

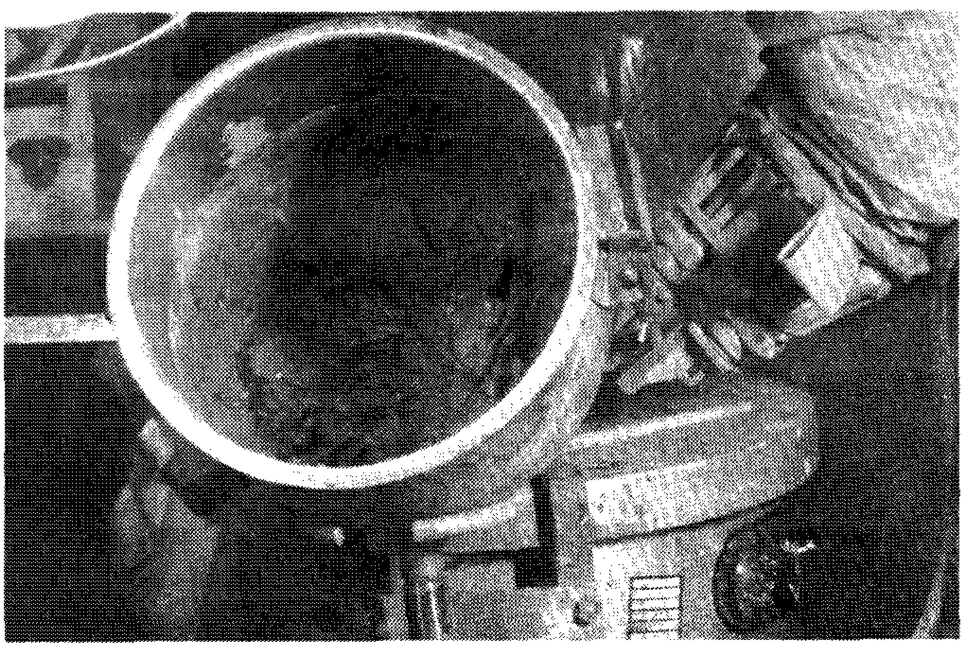

FIGURE 1. Preparation of Concrete Forms Containing SRP Waste Sludges

In one test, while preparing a formulation of HAC with 40% sludge (Tank 13),[10] the mixture flash set in the bowl. Additional water was added to the set material, primarily to remove it from the bowl before hardening, and castings were made of this mixture. In two subsequent formulations with HAC and 40% sludge, excess water (about 20% more than required for good workability) was added to prevent flash setting. In all other formulations with either cement, the correct amount of water was used, and no flash setting was observed.

Compressive strengths of some of the radioactive specimens are shown in Figure 2. The compressive strengths of the forms containing excess water were exceptionally low. Previous results with simulated sludges and the correct amount of water indicated that the logarithm of compressive strength decreased almost linearly with increased sludge loading.[5] Because the use of excess water appeared to give longer set times at the expense of strength of the concrete-waste form, alternative methods of controlling set times were desirable.

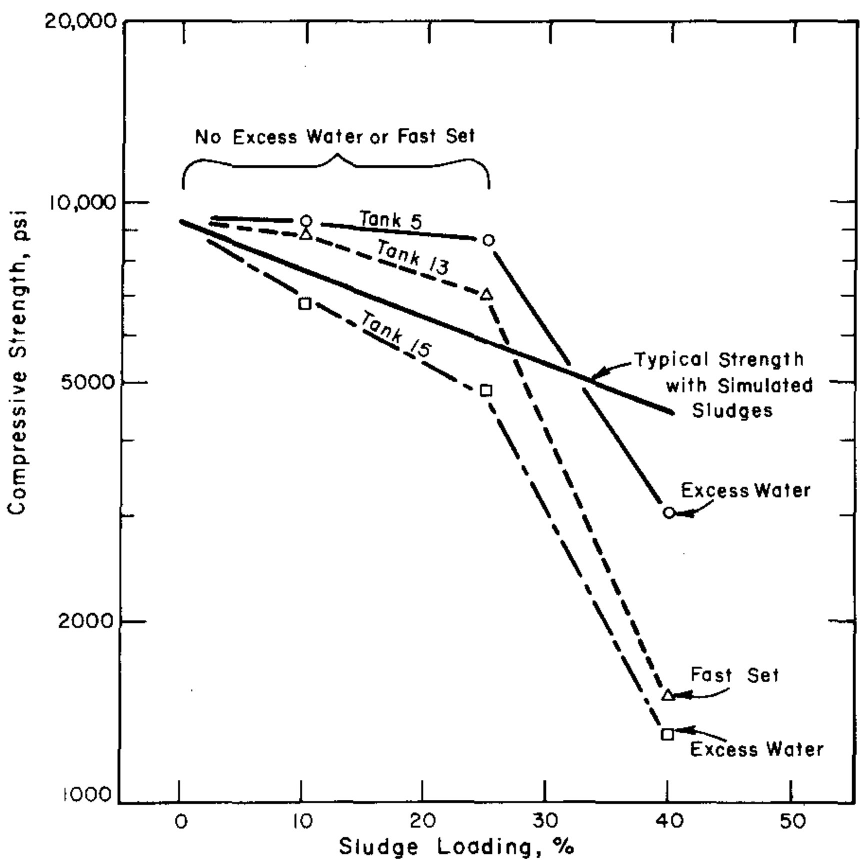

FIGURE 2. Compressive Strengths of Concrete Forms Containing High-Alumina Cement and Actual SRP Waste Sludges

MEASUREMENT AND CONTROL OF SET TIMES

Set Retarders

Set retarders are commonly used by the concrete industry to lengthen set times, especially when placing concrete in hot weather. A large variety of organic and inorganic compounds are effective set retarders; these admixtures alter the rate of hydration but not the nature of the hydration products of cements.[11] Common organic retarders include derivatives of hydroxylated carboxylic acids and their salts and derivatives of lignin, such as lignosulfonic acids and their salts. Inorganic compounds such as zinc salts, phosphates, silicofluorides, boric acid, and borax act as set retarders. Several set retarders, both organic and inorganic, are available commercially. An organic retarder, Pozzolith 122-R (Master Builders, Cleveland, Ohio), was used in this study. This set retarder is a multi-component liquid admixture of the hydroxylated polymer type; its composition is proprietary.

Plackett-Burman Screening Test

A Plackett-Burman screening experiment[12] was performed to determine the major factors affecting set times in cement-waste-water systems. Details of the experiment are given in the Appendix. The factors studied were:

- Cement type (Type I-P and HAC)
- Sludge type (Tank 5 sludge and Tank 13 sludge, both simulated, at 40% loading)
- Amount of retarder (none and the recommended dose of 0.19 wt % of dry solids)
- Water content (too-dry and good workability)
- Mixing procedure (mixing cement with wet or dry sludge)

The Plackett-Burman screening experiment indicated that the major factors affecting set times were (a) cement type and (b) water content. The data show that in pastes containing 40% sludge, HAC sets much faster than Type I-P cement. Also, pastes with insufficient water set faster than pastes with the proper amount of water for good workability. Any effect of retarder (using the recommended amount, ~0.2 wt % of the dry solids), sludge type, or mixing procedure was not statistically significant in the screening test. The failure of the retarder to produce a significant effect is attributed to the low dosage used.

In these tests and others described in the following sections, times of initial set were measured with a Vicat apparatus, using a modification of the standard test method.[13] Because only limited amounts of sludges were available, each set time measurement was performed with about half of the amount of paste required by the standard test. The pastes were contained in cups made from the lower portion of 8-oz polyethylene bottles, rather than using the hard rubber ring supplied with the Vicat apparatus. Preliminary experiments showed that results with the modified test are about 6% higher than with the standard test.

The simulated sludges used in this work had the nominal compositions[10] shown in Table 1. The hydrous oxides were precipitated by neutralizing a solution of the nitrate salts. The sludges then were washed and dried to yield free-flowing powders that were subsequently mixed with cement, water, and retarder for set time measurements. The cements were Type I-P (Santee Portland Cement Co., Holly Hill, South Carolina) and "Lumnite" HAC (Universal Atlas Division of U.S. Steel Corp., Pittsburgh, Pennsylvania).

TABLE 1

Composition of Simulated Sludges, mol %

	Tank 5	*Tank 13*	*Tank 15*
Fe	53	50	4
Mn	22	16	3
Al	6	25	92
U	7	2	-
Ca	2	6	0.5
Ni	10	1	0.5

Additional Tests with Simulated Sludges

Additional tests were made with the faster-setting formulations (HAC with 40% sludge) to study further the effects of water and retarder content. Figure 3 shows the effect on set times of retarder contents up to 2.3 wt % of the dry solids. The expected trend was observed: increasing retarder content gives longer set times. Even with retarder, the set times measured for HAC with 40% sludge are faster than for HAC neat paste, which sets in ∿500 minutes without retarder. Formulations containing aluminum-rich simulated sludges (Tank 15) set faster than those containing the other simulated sludges (Tanks 5 and 13). Based on these results, from 1.0 to 1.5 wt % retarder (approximately 5 to 10 times the recommended dose) probably would be required in large-scale operations with HAC, to ensure that the waste-cement paste would not set in the mixing equipment. One to two hours would be available for mixing and transferring operations in a large-scale process.

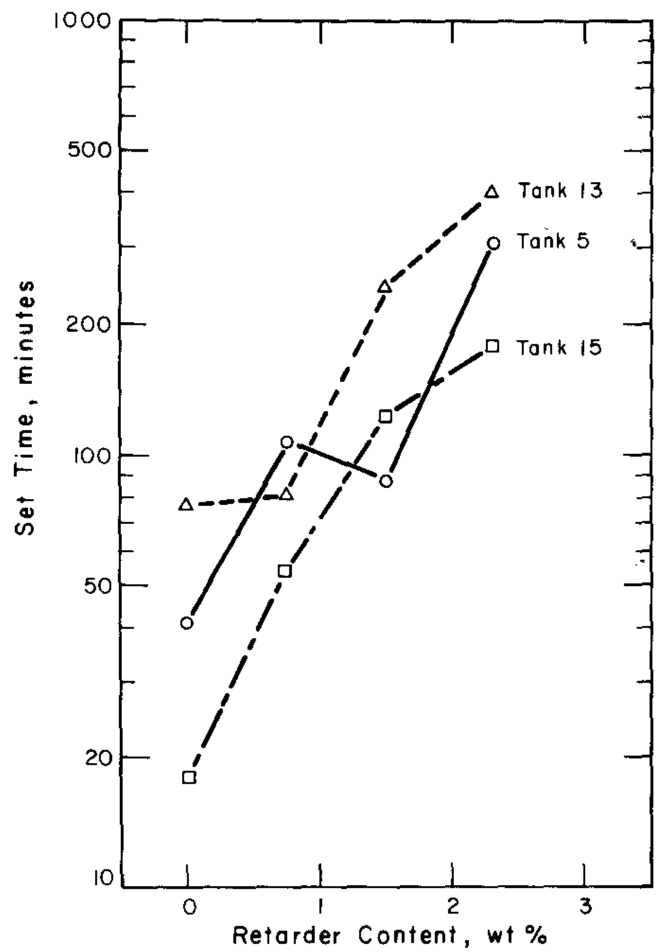

FIGURE 3. Effect of Retarder on the Set Times of High-Alumina Cement Formulations Containing 40% Simulated Sludges

The effect of water content on set times of HAC with 40% sludge and no retarder is shown in Figure 4. These data indicate that, regardless of sludge type, additional water will retard the set time, but with water/cement ratios above about 0.7 no further retardation occurs. Set times of 80 to 100 minutes appear to be the maximum achievable with excess water. The data also indicate that fast sets are more probable for sludges that require the least water for proper workability in HAC pastes. Thus, control of set times with excess water appears to be undesirable because water is less effective than retarder and the final waste forms have decreased compressive strength.

The combined effects of water content and retarder content are summarized in Figure 5. In this graph, no distinction is made between sludge types, and the straight lines through the data points indicate trends only, not true linearity of the data. For HAC with 40% sludge, the set time can be controlled by adjusting both the retarder content and the water content. In a plant process, a balance between these two factors would be necessary to obtain a workable paste and to ensure a product with adequate compressive strength.

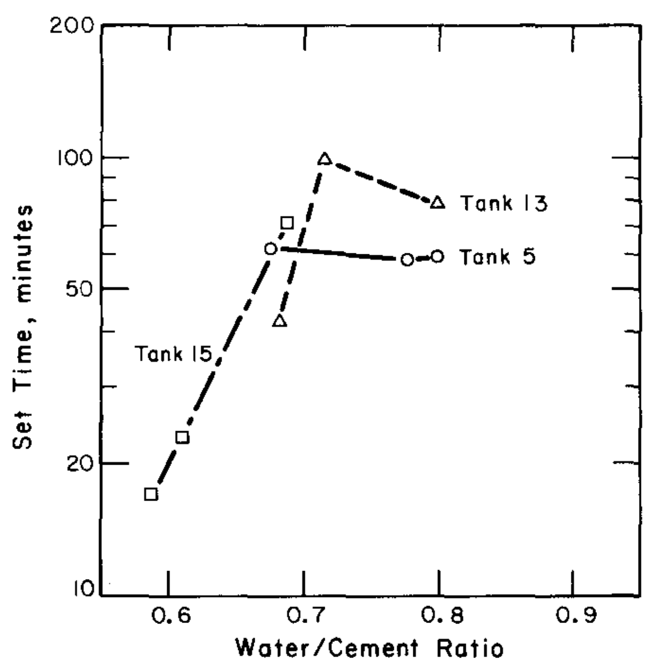

FIGURE 4. Effect of Water/Cement Ratio on the Set Times of High-Alumina Cement Formulations Containing 40% Simulated Sludges and No Retarder

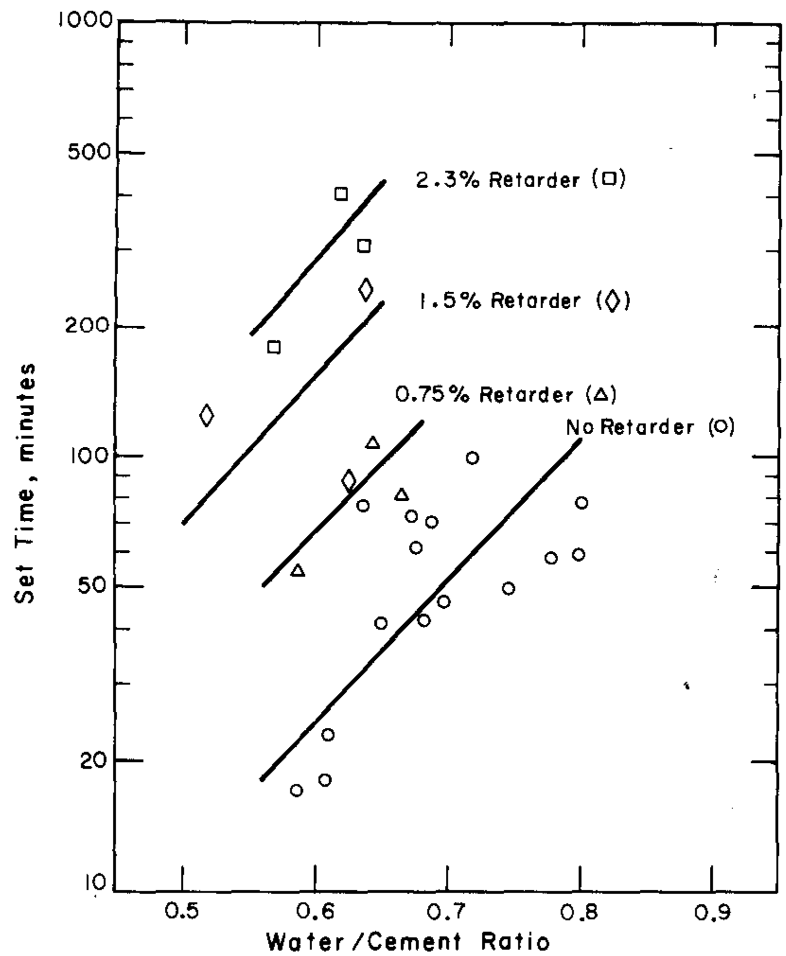

FIGURE 5. Effect of Retarder and Water/Cement Ratio on the Set Times of High-Alumina Cement Formulations Containing 40% Simulated Sludges

Tests with Actual SRP Sludges

To demonstrate control of set times with actual SRP sludges, small batches of formulations were prepared with and without retarder, for set time measurements. In shielded cell facilities, 40% loadings of washed, dried sludges[10] from Tanks 5, 13, and 15 were blended with HAC and sufficient water for good workability; similar formulations with 1.5% retarder added also were prepared. Results of the set time measurements are shown in Table 2. In each case, the retarder changed the set time from about 30 minutes to 4 or more hours. Thus, the retarder is effective for increasing set times with actual SRP sludges and could be used in a large-scale process to maintain a waste-cement paste in the plastic state while transferring to storage containers.

TABLE 2

Set Times with Actual SRP Sludges

Waste Tank	*Water/Cement Ratio*		*Set Time, minutes*	
	No Retarder	*1.5% Retarder*[a]	*No Retarder*	*1.5% Retarder*[a]
5[b]	0.606	0.552	32	280
13[b]	0.675	0.596	30	240
15[c]	0.831	0.775	30	290

a. Pozzolith 122-R (Master Builders, Cleveland, Ohio)

b. 40% sludge, 60% high-alumina cement

c. 37.5% sludge, 2.5% Cs-loaded zeolite (see Reference 2), 60% high-alumina cement

CONCLUSIONS AND FUTURE WORK

The results of this investigation showed that excess water and a commercial retarder can control cement-waste set times effectively. Retarder was more effective than excess water, but 5 to 10 times the quantity of retarder recommended by the manufacturer was necessary to control the set time of formulations containing HAC with 40% sludge. With 1.0 to 1.5% retarder, set times of 70 to 290 minutes were measured.

Future tests will measure compressive strengths of concrete specimens containing 40% actual SRP sludges and prepared with set retarder. Radiolytic destruction of retarder in concrete will be investigated. Gas composition and production rate will be measured. Also, control of set times with inorganic retarders may be studied.

ACKNOWLEDGMENT

Compressive strength measurements on radioactive concrete-waste specimens were made by D. H. Taylor of the Savannah River Laboratory. One of the authors (P. D. d'Entremont) was a Cooperative Education student in chemical engineering from Georgia Institute of Technology.

APPENDIX

This Appendix contains computational details of the Plackett-Burman screening experiment[12] performed to determine variables most strongly affecting cement-waste set times. The factors studied are given in Table A-1, together with notation used in the experimental design. The combinations of factor levels tested, the measured set times, and the computations are shown in Table A-2. The analysis shows that for any variable to be significant at the 90% confidence level, the absolute value of its factor effect must be greater than 60.6. Only the cement type (X1) and water content (X4) variables met this criterion. The other variables, sludge type, mixing procedure, and retarder (at the content tested) were not significant at the 90% confidence level. The analysis also may be performed with logarithms of the set times, with the same conclusions.

TABLE A-1

Plackett-Burman Screening Experiment:
Factors and Levels Tested

Variable	*Factor*	*+ Level*	*- Level*
X1	Cement Type	High-Alumina Cement	Type I-P
X2	Sludge Type	Simulated (Tank 5)	Simulated (Tank 13)
X3	Retarder Content	0.19 wt %	None
X4	Water Content	Proper Workability	Too-Dry
X5	Mixing Procedure	Mix Cement with Wet Sludge	Mix Cement with Dry Sludge

TABLE A-2

Plackett Burman Screening Experiment: Computation Table for 12-Run Design

		Factors Studied					*Unassigned Factors*						
Trial	*Mean*	*X1*	*X2*	*X3*	*X4*	*X5*	*X6*	*X7*	*X8*	*X9*	*X10*	*X11*	*Set Times, minutes*
1	+	+	+	-	+	+	+	-	-	-	+	-	49
2	+	+	-	+	+	+	-	-	-	+	-	+	97
3	+	-	+	+	+	-	-	-	+	-	+	+	221
4	+	+	+	+	-	-	-	+	-	+	+	-	50
5	+	+	-	-	-	-	+	-	+	+	-	+	46
6	+	+	-	-	-	+	-	+	+	-	+	+	73
7	+	-	-	-	+	-	+	+	-	+	+	+	195
8	+	-	-	+	-	+	+	-	+	+	+	-	47
9	+	-	+	-	+	+	-	+	+	+	-	-	268
10	+	+	-	+	+	-	+	+	+	-	-	-	161
11	+	-	+	+	-	+	+	+	-	-	-	+	140
12	+	-	-	-	-	-	-	-	-	-	-	-	167
Sum +	1514	476	774	716	991	674	638	887	816	703	635	772	
Sum -	0	1038	740	798	523	840	876	627	698	811	879	742	
Sum	1514	1514	1514	1514	1514	1514	1514	1514	1514	1514	1514	1514	
Difference	1514	-562	34	-82	468	-166	-238	260	118	-108	-244	30	
Effect	126.2	-93.7*	5.7	-13.7	78*	-27.7	-39.7	43.3	19.7	-18	-40.7	5	

Estimate of error: $S_{FE} = [\Sigma(\text{Unassigned Factor Effects})^2/6]^{1/2} = 31.2$

t (90% confidence level) for 6 degrees of freedom = 1.943

Minimum significant effect = $t \cdot S_{FE} = 60.6$

* Significant effect

REFERENCES

1. R. M. Wallace, H. L. Hull, and R. F. Bradley. *Solid Forms for Savannah River Plant High-Level Waste.* USAEC Report DP-1335, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, SC (1973).

2. J. R. Wiley and R. M. Wallace. *Removal of Cesium from Savannah River Plant Waste Supernate.* ERDA Report DP-1388, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, SC (1975).

3. J. A. Kelley. *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste. Nonradioactive and Tracer Studies.* ERDA Report DP-1382, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, SC (1975).

4. J. A. Kelley. *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste. Radioactive Studies.* ERDA Report DP-1397, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, SC (1975).

5. J. A. Stone. "Incorporation of Savannah River Plant Radioactive Waste Into Concrete." *Am. Ceram. Soc. Bull. 54,* 463 (1975).

6. *Savannah River Laboratory Long-Term Waste Storage Program. Progress Report #5. March-April 1974.* USAEC Report BNL-18978, Brookhaven National Laboratory, Upton, NY (1974).

7. "Standard Specification for Portland Cement." ASTM C-150-74. American Society for Testing Materials, Philadelphia, PA (1974).

8. "Standard Specification for Blended Hydraulic Cements." ASTM C-595-74. American Society for Testing Materials, Philadelphia, PA (1974).

9. T. D. Robson. *High-Alumina Cements and Concretes.* Wiley, New York, NY (1962).

10. J. A. Stone, J. A. Kelley, and T. S. McMillan. *Sampling and Analyses of SRP High-Level Waste Sludges.* ERDA Report DP-1399, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, SC (1976).

11. J. F. Young, ed. *Cements Research Progress 1974.* American Ceramic Society, Columbus, OH (1974).

12. R. L. Plackett and J. P. Burman. "The Design of Optimum Multifactorial Experiments." *Biometrika 33,* 305 (1946).

13. "Standard Method of Test for Time of Setting of Hydraulic Cement by Vicat Needle." ASTM C-191-74. American Society for Testing Materials, Philadelphia, PA (1974).