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**SOLIDIFICATION OF HIGH
LEVEL WASTES, PART V.
A FACTORIAL STUDY OF THE EFFECT
OF VARYING THE CONCENTRATION
OF THE COMPONENTS
OF PUREX TYPE WASTE
ON THE PROPERTIES
OF PHOSPHATE SOLIDS**

G. B. BARTON, J. A. WEED

JANUARY 1968

**AEC RESEARCH &
DEVELOPMENT REPORT**

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OF PUREX TYPE WASTE ON THE PROPERTIES
OF PHOSPHATE SOLIDS

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APPENDIX
RESPONSE SURFACE STATISTICAL ANALYSIS

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January 1968

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SOLIDIFICATION OF HIGH LEVEL WASTES
PART V. A FACTORIAL STUDY OF THE EFFECT
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G. B. Barton and J. A. Weed

INTRODUCTION

This is the fifth report of work that has been performed to determine the range of properties of the solids that can be produced from various waste compositions by using various additives. The earliest scouting work indicated solids, meltable below 1200 °C, could be formed by adding phosphate, borates, silicates, or mixtures of these to Purex and high alumina type wastes. The phosphate system has the advantages of (a) minimum additives to produce a meltable solid, (b) reduced segregation into two or more phases when making such minimum additive melts. It has the disadvantage of greater corrosivity than the silicate or borosilicate melts. Because of the number of variables involved (fission products, process components, corrosion products, impurities, additives, etc.), the investigations ⁽¹⁾ have proceeded stepwise through (a) scouting of a few waste types with a few levels of additives, (b) systematic variation of phosphate addition with several levels of fission products in a fixed process waste matrix, (c) variation of individual fission products and chemical families of fission products; to this present study of (d) the factorial variation of individual process components, fission product, and phosphate.

These laboratory scale studies paved the way for and supplement the large scale hot demonstration work of Allemann ⁽²⁾, Upson ⁽³⁾, and WSEP ⁽⁴⁾ (Waste Solidification Engineering Prototypes). The demonstration work was largely planned around fixed

waste compositions with additives to produce the desired solid. This laboratory work provides some additional information from which one could know what would be required for an operating plant handling wastes of varying composition.

The Purex process, as presently operated, introduces certain cations into the high level radioactive waste stream. These are primarily sodium, iron, aluminum, chromium, and nickel. They are used as process reagents, or are introduced as impurities, or by corrosion of the processing equipment. From data accumulated by analysis of various samples from the Hanford Purex process and various projected flowsheet modifications, a range of concentration of each of the above elements was selected as being probable. These were combined with the data published in BNWL-80^(1d) on the effect of changing phosphate ratio and fission product level to define the parameters it was desired to investigate. A statistical pattern of experimentation was then designed by J. A. Weed to yield the maximum amount of information from the set of experiments.

The previous work had indicated there were minima in the curves of drip temperature and solubility versus phosphate ratio for a fixed waste composition. The new experiments were planned with the hope that those curves could be represented by quadratic equations and the minima would be in the range of variations selected. If this proved to be the case, the equations could be used for predictive purposes also.

SUMMARY

As part of the overall investigation of the effects of changing composition on the solids one might propose as waste storage forms, this report presents the results of a statistically designed and interpreted plan for examining the effects of changing the concentration of some of the individual components of Purex type wastes converted to phosphate solids. The

components and range over which they were varied were: sodium 0.45 to 0.90M, aluminum 0.03 to 0.13M, iron 0.06 to 0.26M, chromium 0.012 to 0.052M, nickel 0.006 to 0.026M, fission products 836 to 11,290 MWd/MT of uranium, and phosphate to give M/P ratios of 2.5 to 1.7. Three levels of each component were tested and the whole was subjected to statistical analysis of the results of measuring the drip temperature and solubility of the various materials prepared. The materials were examined both in a chill cast condition and after slow cooling at a rate of 1 °C/min.

From these results it was concluded that the statistically designed plan gave results that could be represented by equations that fairly well described the system. From these equations, one could suggest areas for further examination if one were seeking a particular range of the drip temperature or solubility. Changes in composition of one component interact with the remaining components, thus simple rules of thumb are not forthcoming.

Most phosphate solids in this M/P range [M/P is the ratio of cation equivalents to phosphate as meta phosphate; e.g., tri-sodium phosphate (Na_3PO_4) has an M/P of 3] are of low solubility (less than 0.5% in 24 hr) when chill cast, but generally devitrify when slow cooled and become more soluble. This behavior indicates a need to rely on container and environment rather than intrinsic insolubility, if this type phosphate solid were used as the final storage form of high level wastes. There is considerable range in drip temperatures (660 to 1060 °C measured) that result as composition varies in the range examined. Of the two criteria used, it appears that drip temperature would be the one first applied when considering whether or not a given waste could be converted to a suitable phosphate solid.

These results indicate the possibility of designing a plan for collecting the information that would permit prediction of the properties of a wide range of waste compositions when

converted to phosphate solids. However, the present series of experiments are too thinly scattered to give equations of great reliability. It is suggested that the study be extended and intensified to give a rational basis for adjusting compositions to produce solids having the properties one desires (within the range that is intrinsically available).

CONCLUSIONS

Even in the relatively limited range of variation in composition of the waste that might be turned out by a Purex process, one finds that the components interact on each other to such an extent that generalizations such "sodium increase always results in a solubility increase," are not valid. It is demonstrated, however, that a properly designed experimental plan will allow determination of the overall effect of these interactions to the extent that predictions of the direction to look for the desired properties is valid, as well as approximation of the magnitude of these properties.

In the range of phosphate additions studied, the materials resulting after slow cooling (which is considered the best approximation to industrially useful conditions) are too soluble to be exposed to water. Therefore, the primary criterion for selection of a composition is whether or not its temperature-flow characteristics are such that it can be processed under the limiting conditions of the process equipment. (There may be other ranges of phosphate addition; e.g., M/P 1.0 where this may not hold.)

The quadratic equations used to describe the system seems to follow the general behavior, but are probably too low an order to follow some of the perturbations. Intuitively, it seems that one would have difficulty finding equations that would describe a general system in which there were eutectics and compound formation such as appear to be the case in the range of composition examined.

DISCUSSION OF EXPERIMENTAL DESIGN

After some consideration of the desirability of changing to one of the later compositions chosen for WSEP,⁽⁴⁾ it was decided to stay with the base composition chosen earlier and used for work reported in BNWL-80. The range of variation in composition would cover the WSEP PW-2 case, but not reach the high iron level proposed for PW-1.

The selected range of compositions is given in Table I. Solutions were prepared containing these components combined in accordance with the experimental pattern indicated in Table II-A. (Appendix) The fission product mixture was prepared to represent Yankee reactor fuel at a burnup of 20,000 MWd/MT. (For these experiments, it was decided to neglect the change in fission product distribution with exposure. This variable was investigated earlier.)⁽⁵⁾

The experimental design plan selects a very small fraction (49 out of 729) of the total number of experiments that would be prepared by changing the variables, one at a time, to cover all the possible combinations. These were clustered in a symmetrical pattern about the center point. (Figure 1 indicates the distribution of experimental points.)

It was conceived that this plan would yield response surfaces on which it would be possible to select the minimum drip temperature and minimum solubility points. The change in these properties from the minima as the various components changed in concentration, would indicate the change that could be made by adjusting composition.

The experimental design and analysis of data by Mr. Weed is presented as an Appendix to this report.

TABLE I. Range of Concentration of Components of Purex Type Waste Selected for Investigation

<u>Variable</u>	<u>Level</u>		
	<u>Lower (-1)</u>	<u>Center (0)</u>	<u>Upper (+1)</u>
Na	0.45M ⁽¹⁾	0.70M	0.95M
Al	0.03	0.08	0.13
Fe	0.06	0.16	0.26
Cr ⁽²⁾	0.012	0.032	0.052
Ni	0.006	0.016	0.026
FP ⁽³⁾	10%	35%	60%
MWd/T	836	4050	11,290
M/P	2.5	2.1	1.7

(1) Concentration at a volume of 50 gal/MT of uranium.

(2) Chromium and nickel were treated as a single variable.

(3) Fission products (FP) are expressed as weight percent of the oxide in the waste oxides of center level process composition. The Weight Percent actually varied with each variation of the other variables, and so is more properly expressed in terms of the fission products from a given exposure fuel.

EXPERIMENTAL PROCEDURE

The individual sample compositions indicated in Table II-A were calculated for a basic quantity of oxides of 50 g, assuming center points composition. To simplify calculations, the quantity of fission products used in each sample was used as the reference constant; i.e., the three levels of fission products corresponded to 5, 17.5 and 30 g, or alternatively, it could be considered that it was equivalent to 1067, 771, and 474 ml of solution of center level containing fission products from fuels of 836; 4050; 11,290 MWd/MT, respectively. A stock fission product solution was prepared (composition is given in Table II). This was combined with the quantity of nitrate salt of the individual components (Na, Al, Fe, Cr, Ni), water, and phosphoric acid required to give the desired composition. The resulting solution or slurry was then dried in a small laboratory spray drier. The resulting solid was ground in a mortar to give a uniform powder.

Melts were prepared from the powder by adding small portions to a preheated platinum crucible at 4 min intervals until a total of 30 g of powder was melted. This scheme of melting approximates that of a spray drier-melter in which the powder from the dryer falls directly into the melter. It also decreases the time required, compared with the process of starting with all the powder in a crucible in a cold furnace and then heating until a melt is produced. Usually, this latter procedure produces a pasty or bubbly stage that results in material being expelled from the crucible unless the heating is very slow. For this preset series of experiments, all melts were made at 1200 °C since previous work⁽⁶⁾ had shown a decrease in drip temperature as the melting temperature was raised from 900 to 1200 °C. Also, it was expected that some compositions would have rather high melting points, but would still be less than the 1200 °C operating limit set for the platinum melter in the WSEP.

TABLE II. Simulated Fission Product Stock Solution

Calculated to represent the elements whose abundance exceeds 1% of the zirconium except for the rare gases and technetium as produced in the Yankee Reactor fuel on irradiation to 20,000 MWd/MT and allowed to cool 2 yr after discharge.

<u>Element</u>	<u>Concentration</u>	<u>Chemical Form Added</u>
	<u>M x 10³</u>	
Se	1.56	SeO ₂
Br	0.59	KBrO ₂
Rb	10.98	RbNO ₃
Sr	24.93	Sr(NO ₃) ₂
Zr	100.00	ZrO(NO ₃) ₂ ·2H ₂ O
Mo	89.85	Acidified Ammonium Molybdate Solution
Ru	50.95	Ru(NO ₃) _x Solution
Rh	11.36	Rh(NO ₃) ₃ Solution
Pd	25.71	Pd(NO ₃) ₂ Solution
Ag	1.25	Ag NO ₃
Cd	1.23	Cd (NO ₃) ₂ Solution
Sn	0.96	Sn(NO ₃) ₂ Solution
Te	9.56	TeO ₂
I	1.48	HIO ₃
Cs	55.98	CsNO ₃
Ba	27.93	Ba (NO ₃) ₂
Rare Earths	186.10	Mixed Rare Earth Nitrates
Cation equivalents/liter		1.428
Anion equivalents/liter		0.187
Net cation equivalents/liter		1.241

The effects of cooling rate were partially examined by comparing materials that were cast on a steel plate with those that were furnace cooled at 1 °C/min. It is likely that an actual waste product would be intermediate between these. It is unlikely the cooling rate could be as high as from the chill casting on the steel plate. The interior of containers with a substantial heat generation rate would cool at a much slower rate than the one used in these experiments, but the surface would probably cool faster than 1 °C/min since it is planned to use air blast cooling of the container (at least in WSEP). Therefore, the material in the containers would grade in properties (and possibly in composition) between the moderately rapidly cooled next to the container wall, to the slower cooled in the center.

The properties that were used in evaluation of the various product specimens were: closure temperature, drip temperature, and solubility or leachability. The methods of measuring these properties are described in detail in BNWL-80. Briefly, closure temperature is the temperature at which the material flows enough to close the opening in the neck of the tube of the drip temperature crucible. The drip temperature is that at which the first drop falls from a 1/4 in. diameter tube on the bottom of a platinum crucible. Solubility was measured by sieving out the -40 +60 mesh fraction of a crushed sample for enclosure in stainless steel wire cloth bags which were suspended in hot (97 °C) distilled water. Loss in weight after 24 hr was measured and was used as the solubility criteria.

These properties may relate to the operating or storage forms in the following way:

- A. Drip temperature of the "as-cast" material represents the temperature at which the melted material will flow

from the melter. This does not necessarily represent the temperature at which the material would melt, but rather, the minimum temperature at which it would continue to flow freely after being melted at a higher temperature.

- B. Drip temperature of the recrystallized material gives an indication of the temperature at which the slow cooled material would still move under gravity. It does not represent a eutectic temperature (to which it may be related), but rather, is the temperature at which sufficient liquid is formed to lubricate flow of the remaining crystals.
- C. Solubility (first 24 hr) of the "as-cast" material does not represent a material that is likely to be produced on a production scale. As discussed above, the containers are likely to cool more slowly and with a temperature gradient that will yield a product more nearly resembling the recrystallized product. The solubility of the cast material appears to represent the least soluble form of a given composition. There are a few exceptions to this generalization.
- D. Solubility (first 24 hr) of the recrystallized material gives a better measure of the behavior one would predict for the material in a storage container, should that material be exposed to the action of water.

RESULTS AND DISCUSSION

The results of the measurements made on the various samples are summarized in Table III and on Figure 1. These results obtained on the forty-nine compositions prepared according to the experimental plan will be discussed first. Then, the results of the statistical analysis will be considered. The closure temperature data were not subjected to statistical analysis, but are presented in Table III to give some information on the relation of closure and drip temperatures. The results are missing for a

TABLE III. Summary of Results of the Measurements Made on Various Samples

Specimen No.	Cast						Recrystallized					
	Temperature		Solubility in 24 hr				Temperature		Solubility in 24 hr			
	Closure	Drip	1st	2nd	3rd	Total	Closure	Drip	1st	2nd	3rd	Total
1	841	855	0.28	0.21	0.19	0.68	707	724	6.96	5.47	3.91	16.34
2	794	802	0.47	0.31	0.34	1.12	698	716	4.77	2.87	2.07	9.71
3	824	831	0.58	0.40	0.57	1.55	764	768	17.29	4.28	3.30	24.87
4	---	753	1.23	1.27	1.62	4.12	---	732	13.61	1.93	1.50	16.84
5	1007	1041	0.07	0.05	0.03	0.15	905	931	3.47	4.23	4.35	12.05
6	951	979	0.06	0.05	0.07	0.18	904	920	5.99	6.16	4.04	16.19
7	986	1026	0.09	0.08	0.02	0.19	831	870	5.53	6.21	5.85	17.59
8	913	944	0.24	0.12	0.15	0.51	768	806	23.57	3.13	0.65	27.35
9	947	978	0.10	0.07	0.05	0.22	911	933	21.28	1.80	0.67	23.75
10	923	990	0.16	0.10	0.10	0.36	864	881	5.47	1.08	0.90	7.45
11	864	906	0.36	0.45	0.86	1.67	753	873	13.34	11.74	6.83	31.91
12	816	863	0.30	0.30	0.39	0.99	---	728	34.01	2.68	1.16	37.85
13	951	982	0.21	0.12	0.13	0.46	870	913	26.97	1.58	0.67	29.22
14	856	928	0.22	0.11	0.09	0.41	763	782	14.61	1.19	0.62	16.42
15	802	928	3.98	5.79	5.80	15.57	832	863	18.06	8.16	6.57	32.79
16	---	802	1.10	0.96	0.78	2.84	807	836	1.35	0.72	0.80	2.87
17	972	1008	0.25	0.11	0.13	0.49	844	888	19.08	2.79	1.85	23.72
18	878	923	0.16	0.09	0.07	0.32	772	817	2.88	2.58	4.78	10.24
19	935	951	0.25	0.26	0.25	0.76	878	899	27.04	2.02	1.25	30.31
20	821	864	0.52	0.25	0.21	0.98	789	812	4.30	1.69	1.53	7.52
21	876	905	1.75	1.41	1.14	4.30	---	711	48.46	2.48	1.20	52.14
22	729	790	7.54	4.87	4.65	17.06	---	706	5.72	5.11	3.13	13.96
23	---	855	1.14	1.36	1.61	4.11	795	809	13.22	2.77	2.11	18.10
24	711	734	15.28	3.90	1.88	21.06	---	660	9.56	1.62	1.81	12.49
25	876	913	1.40	0.40	0.55	2.35	660	783	31.54	5.58	1.56	38.68
26	802	809	0.44	0.20	0.22	0.86	777	806	1.40	0.46	0.37	2.23
27	817	855	1.32	1.00	2.16	4.48	776	829	6.94	1.99	1.78	10.71
28	---	782	1.41	0.81	0.76	2.98	755	767	1.20	0.68	0.56	2.44
29	993	1061	2.87	0.53	0.43	3.83	898	936	21.87	2.70	0.99	25.56
30	915	973	2.02	1.22	1.08	4.32	856	825	2.92	1.46	1.12	5.50
31	944	992*	0.13	0.10	0.16	0.39	931	964	25.95	1.77	0.69	28.41
32	886	924	0.22	0.08	0.09	0.38	838	851	5.55	1.42	1.56	8.53
33	926	963	0.25	0.44	0.74	1.43	934	954	39.31	1.27	0.77	41.35
34	816	937*	0.24	0.16	0.14	0.54	859	947	8.07	5.97	4.28	18.32
35	923	958	1.53	0.30	0.35	2.18	815	848	24.33	0.43	0.22	24.98
36	844	904	0.36	0.19	0.15	0.70	824	846	13.74	1.63	1.16	16.53
37	916	938	1.03	2.08	3.59	6.70	797	937	44.32	1.48	2.59	48.39
38	795	861	7.64	9.64	9.52	26.80	801	897	11.50	2.99	17.33	31.82
39	900	928	0.90	0.43	0.56	1.85	---	819	13.00	0.20	0.11	43.31
40	841	915	0.89	0.62	0.52	2.03	715	741	26.48	7.32	2.40	36.20
41	924	948	1.12	0.38	0.40	1.90	849	868	28.59	2.66	1.83	33.08
42	865	923	0.55	0.31	0.28	1.14	770	788	4.29	1.07	0.88	6.24
43	---	846	0.93	0.81	1.00	2.74	---	759	17.93	3.87	2.89	24.69
44	740	748	2.18	1.27	1.28	4.73	703	723	32.26	5.86	4.23	42.35
45	954	983	0.14	0.06	0.08	0.28	923	954	2.17	3.80	3.75	9.72
46	946	991	0.10	0.03	0.02	0.15	873	900	9.36	0.86	0.40	10.62
47	936	961	0.20	0.28	0.33	0.81	825	858	43.89	1.43	1.11	46.43
48	806	850	1.83	1.09	0.86	3.78	752	789	1.96	0.79	0.66	3.41
49a	876	907	0.19	0.09	0.11	0.39	702	741	10.78	6.68	5.09	22.55
49b	873	901	0.21	0.10	0.12	0.53	703	740	10.52	6.93	4.93	22.38
49c	876	903	0.27	0.11	0.12	0.50	---	745	7.19	6.08	5.25	18.52
49d	876	904	0.25	0.13	0.08	0.46	712	748	7.57	6.28	4.65	18.50
49e	873	903	0.23	0.11	0.11	0.44	704	735	13.10	8.23	4.43	25.76
49f	871	896	0.26	0.12	0.12	0.50	711	737	11.61	7.35	5.02	23.98
50									11.72	7.92	4.57	24.21
51									11.82	6.15	5.46	23.43
52									12.55	7.82	4.61	24.98
53									13.05	7.44	4.57	25.06
54									7.72	6.52	5.16	19.40
55									7.48	6.20	5.89	19.57
									34.30	4.11	2.66	41.07
									917	38.39	1.69	41.97
									766	791	49.17	59.70
									---	741	5.32	11.61
									881	900	23.00	26.06
									864	880	11.08	13.97

* Fraction during dripping was observed.

number of the samples that had a low drip temperature because the closure flow occurred earlier than expected and was not observed. The different closure flows for cast materials occurred at temperatures ranging from 711 to 1007 °C. Table IV summarizes the distribution of the results into 100 °C temperature intervals. The recrystallized material showed closure flows at generally lower temperatures.

TABLE IV. *Distribution of Results of Closure and Drip Temperatures for Materials Prepared in This Factorial Investigation*

<u>Material Condition</u>	<u>Property</u>	<u>No. of Specimens in Interval</u>	
Cast	Closure Temperature	8	< 800 °C
		19	801 - 900
		20	901 - 1000
		1	> 1000
Recrystallized	Closure Temperature	3	< 700
		17	701 - 800
		17	801 - 900
		6	> 901
Cast	Drip Temperature	5	700 - 800
		12	801 - 900
		28	901 - 1000
		4	> 1001
Recrystallized	Drip Temperature	1	< 700
		16	701 - 800
		21	801 - 900
		11	> 900
Cast Minus Recrystallized (Temperature Differences)	Drip Temperature	18	> 100
		16	50 - 100
		12	1 - 50
		3	< 0
Cast (Temperature Differences)	Drip Minus Closure	4	< 10
		21	10 - 39
		17	40 - 100
		2	> 100
Recrystallized (Temperature Differences)	Drip Minus Closure	1	< 10
		32	10 - 39
		6	40 - 100
		3	> 100

When we look at the drip temperature data, we see that there is the same spread between the cast and recrystallized materials. The difference in closure temperature of the cast and recrystallized materials ranged from a decrease of 216 °C to an increase of 43 °C. There were twelve materials out of thirty-nine for which data were obtained that showed decreases exceeding 100 °C, in addition to the one showing the 216 °C difference; eleven differences lie between 50 and 100 °C; eleven lie between 0 and 50 °C and four showed increases on recrystallization. Such an increase could result from the formation of crystals in a matrix, with no change in flow temperature of the matrix itself, because the crystals block free flow; thereby, requiring lower viscosity (produced by increasing temperature) of the matrix before the mixture will flow. The difference in drip temperatures between the cast and recrystallized materials did not cover quite as wide a range as the closure temperature differences, but there were proportionately more drip temperature differences at higher temperatures. Of the forty-nine materials, the range was 174 °C decrease to 36 °C increase with the distribution being: greater than 100 °C, eighteen; 50 to 100 °C, sixteen; 1 to 50 °C, twelve; and increases, three.

The difference between closure and drip temperatures for a given material is a measure of the plastic range. For a pure salt such as sodium chloride, there is no observable difference, while a silicate glass of high viscosity shows a range of several hundred degrees. The data in Table V for the cast materials, showed temperature increases between closure and dripping ranging from 7 to 186 °C. The distribution for forty-four materials is also summarized in Table V. None of them showed the tendency to spin threads as has been observed for silicate glasses and a few phosphate mixtures. When recrystallized, the materials show a more salt-like behavior; i.e., have a smaller range from closure to drip. The maximum difference was somewhat greater,

*TABLE V. Temperature and Temperature Differences
For Closure and Drip Measurements*

	Cast			Recrystallized			Cast Minus Recrystallized	
	Close	Δ	Drip	Close	Δ	Drip	Close	Drip
1	841	14	855	707	17	724	134	131
2	794	8	802	698	18	716	96	86
3	824	7	831	764	4	768	60	63
4			753			732		21
5	1007	34	1041	905	26	931	102	110
6	951	28	979	904	16	920	47	59
7	986	40	1026	831	39	870	155	156
8	913	31	944	768	38	806	145	138
9	947	31	978	911	22	933	36	45
10	923	67	990	864	17	881	59	109
11	864	42	906	753	120	873	111	33
12	816	47	863			728		135
13	951	31	982	870	43	913	81	69
14	856	72	928	763	19	782	93	146
15	802	126	928	832	31	863	30	65
16			802	807	29	836		34
17	972	36	1008	844	44	888	128	120
18	878	45	923	772	45	817	106	106
19	935	16	951	878	21	899	57	52
20	821	43	864	789	23	812	32	52
21	876	29	905			711		194
22	729	61	790			706		84
23			855	795	14	809		46
24	711	23	734			660		74
25	876	37	913	660	123	783	216	130
26	802	7	809	777	29	806	25	3
27	817	38	855	776	53	829	41	36
28			782	755	12	767		15
29	993	68	1061	898	38	936	95	125
30	915	58	973	856	19	875	59	98
31	944	48	992	931	33	964	13	28
32	886	38	924	838	13	851	48	73
33	926	37	963	934	20	954	-8	+9
34	816	121	937	859	88	947	-43	-10
35	923	35	958	815	22	848	108	110
36	844	60	904	824	33	846	24	58
37	916	22	938	797	140	937	119	1
38	795	66	861	801	96	897	-6	-36
39	900	28	928			819		109
40	841	74	915	715	26	741	126	174
41	924	24	948	849	19	868	75	80
42	865	58	923	770	18	788	95	135
43			846			759		87
44	740	8	748	703	20	723	37	25
45	954	29	983	923	31	954	31	29

TABLE V. (contd)

	Cast			Recrystallized			Cast Minus Recrystallized	
	Close	Δ	Drip	Close	Δ	Drip	Close	Drip
46	946	45	991	873	27	900	73	91
47	936	25	961	825	33	858	111	103
48	806	44	850	752	37	789	54	61
49	876	31	907	702	39	741	174	166
	873	28	901	703	37	740	170	161
	876	27	903			745		158
	876	27	904	712	36	748	164	151
	873	30	903	704	31	735	169	168
	871	25	896	711	26	737	160	159

Analysis of Above Data Into Number in Interval

Cast				Recrystallized				Cast Minus Recrystallized		
Interval	Close	Δ	Drip	Interval	Close	Δ	Drip		Close	Drip
Max.	1007	126	1061		934	140	964		216	174
Min.	711	7	734		600	4	660		-43	-36
700-800	9		5	600-700	2		1			
800-900	19		12	700-800	17		16			
900-1000	19		28	800-900	17		21			
10+	1		4	900+	6		11			
<10		4		<10	1			>100	13	18
10-39		21		10-39	32			50-100	11	16
40-100		17		40-100	6			0-50	11	12
>100		2		>100	3			<0	4	3

being 140 °C, and the minimum was smaller, being only 4°C; the distribution was more toward the smaller range. The recrystallized materials having large differences were not the same ones as the cast ones of large difference.

Another way the raw data was examined was to compare the drip temperatures of pairs of materials that differed only in the level of one component. There were twelve such pairs. The data for these are in Table VI. For the cast materials, iron and chromium-nickel, additions at the high level all result in temperature increases. All sodium additions resulted in temperature decreases. In one of the twelve pairs of phosphate variation, the low (M/P 2.5) level melted at higher temperature than the high level, and in the fission product comparison, two such cases were found. Aluminum at high level increased the drip temperature in eight of the twelve pairs. (Such a method of looking at the data is far short of the information gained from the full statistical analysis that factors in the interactions of the components and the interpolation of the effects between the two outside levels and the center level. This will be discussed in more detail later on.)

Solubility of the materials varied widely both within a given condition and with heat treatment to produce a given condition. In general, the solubility of the cast materials was considerably lower than when recrystallized. In the first 24 hr, the cast materials ranged from 0.06 to 15.3% and the recrystallized from 1.2 to 48.5%. Half of the cast materials had solubilities of less than 0.5%, while the half figure for the recrystallized material was about 13%. Low solubility in one form did not coincide with low solubility in the other. This is not unexpected since the cast forms were mostly glasses that, generally, dissolve uniformly with little preferential leaching, while the recrystallized materials are heterogenous collections of various compounds that exhibit differential solubility.

TABLE VI. Drip Temperature and Solubility Differences For Pairs of Materials That Differed Only in the Level of Addition of One Component

Note: Data are for the component indicated at +1 level minus -1 level.

Variable	Pair	Cast ΔT	Recryst. ΔT	Cast Δ 1st Leach	Recryst. Δ 1st Leach	Variable	Pair	ΔT	Recryst. ΔT	Cast Δ 1st Leach	Recryst. Δ 1st Leach
Cr-Ni	1-2	53	8	-0.19	2.19	Fe	9-11	72	60	-0.26	7.94
	3-4	74	36	-0.55	3.68		10-12	127	153	-0.14	28.54
	5-6	62	11	.01	-2.52		13-15	54	50	-3.77	8.91
	7-8	82	64	-0.16	-18.04		14-16	126	-54	-0.88	13.26
	17-19	57	-11	0	-7.96		17-21	103	177	-1.50	-29.38
	18-20	59	5	-0.36	-1.42		18-22	133	111	-7.38	-2.84
	21-23	50	-98	0.61	35.24		19-23	96	90	-0.89	13.82
	22-24	56	46	-7.74	-3.84		20-24	130	152	-14.76	-5.26
	25-27	58	-46	0.08	24.60		41-43	102	109	0.19	10.66
	26-28	27	39	-0.97	0.20		42-44	175	65	-1.63	-27.97
	29-31	69	-28	2.74	-4.08		45-47	22	96	-0.06	-41.72
	30-32	49	24	1.80	-2.63		46-48	141	111	-1.73	7.40
Al							54-52		109		-26.17
	1-3	24	-34	-0.30	-10.33	FP	9-10	-12	52	-0.06	15.81
	2-4	49	-16	-0.76	-8.84		11-12	43	145	0.06	-20.67
	5-7	15	61	-0.02	-2.06		13-14	54	131	-0.01	12.36
	6-8	35	114	-0.18	-20.10		15-16	126	27	2.88	16.71
	9-13	-4	20	-0.11	-5.69		25-26	104	-23	0.96	30.14
	10-14	-62	99	-0.06	-9.14		27-28	73	62	-0.09	5.74
	11-15	-22	10	-3.62	-4.72		29-30	92	61	0.85	18.95
	12-16	61	-108	-0.80	32.66		31-32	68	113	-0.09	20.40
	33-37	25	17	-0.78	-5.01		33-35	5	106	-1.28	14.98
	34-38	76	50	-7.40	-3.43		34-36	33	101	-0.12	-5.67
	35-39	30	29	0.63	-18.67		37-39	10	118	0.13	1.32
	36-40	-11	105	-0.53	-12.74		38-40	-54	156	6.75	-14.98
	55-54		-20		-10.92						

TABLE VI. (contd)

Variable	Pair	Cast ΔT	Recryst. ΔT	Cast Δ 1st Leach	Recryst. Δ 1st Leach	Variable	Pair	ΔT	Recryst. ΔT	Cast Δ 1st Leach	Recryst. Δ 1st Leach
Na	1-5	-186	-207	0.21	3.49	P	17-18	85	71	0.09	16.20
	2-6	-177	-204	0.41	-1.22		19-20	87	87	-0.27	22.74
	3-7	-195	-102	0.49	11.76		21-22	115	5	-5.79	42.74
	4-8	-191	-74	0.99	-9.96		23-24	121	149	-14.14	3.66
	25-29	-148	-153	-1.47	9.67		33-34	26	7	0.01	23.32
	26-30	-164	-69	-1.58	-1.52		35-36	54	2	1.17	10.59
	27-31	-137	-135	1.18	-19.01		37-38	77	40	-6.61	32.82
	28-32	-142	-84	1.19	-4.35		39-40	13	78	0.01	16.52
	41-45	-35	-86	0.98	26.42		41-42	25	80	0.57	24.30
	42-46	-68	-112	0.45	-5.07		43-44	98	36	-2.25	-14.33
	43-47	-115	-99	0.73	-25.96		45-46	-8	54	0.04	-7.19
	44-48	-102	-66	0.35	30.30		47-48	111	69	-1.63	41.93
	52-50		26		14.9		53-51		-176		-33.07

When the paired variation comparison (Table VI) is made of the cast materials, high iron and high aluminum are found to decrease solubility; sodium to generally increase it; and the other three major components are more random in their effect. Phosphorus, however, tends to decrease solubility more than increase it for the equal number of cases in which one or the other effect is noted. With the recrystallized material, the effect of iron is randomized, but aluminum shows the same effect as it does in cast material; i.e., increased aluminum--decreased solubility. Fission products and phosphorus have the opposite effect to aluminum, and sodium and chromium-nickel are random.

The appearance of the various melts is summarized in Table VII. From this, one can determine that the cast materials were almost two-thirds glasses and one-third evidenced varying degrees of crystallinity. The materials designated "recrystallized" had been cooled at 1 °C/min; of these, four were almost entirely glass and two more were a substantial fraction still in the glassy form. Many of the slow-cooled materials had a dark grey to black layer on the bottom and around the sides. It appeared that this might be RuO_2 . This could present complications in a material that is slow-cooled, permitting the radioactive fission-product, ruthenium, to concentrate and thus make a localized hot spot. The slow-cooled materials also gave visual evidence of the separation of a number of different compounds. There were different colors and crystal forms visible to show the separation of various compounds in different parts of the mass, and from different composition melts.

M/P RATIO AS A UNIFYING CONCEPT

This set of experiments offered an opportunity to test the utility of the M/P ratio as a unifying concept. The variation in cation composition through the various mixtures tested was such that for a given M/P ratio there was a range of mixtures of different valence types. The distribution by element and

TABLE VII. *Appearance of Solids*

	Cast	Recrystallized
1.	Glassy. Two phase appearance, black in dark grey milky glass. Fracture surface: many crystal points.	Thin black layer on outer surface and bottom. Major fraction: platy green crystals interspersed with patches of yellow to brown glass.
2.	Glassy. Fracture surface: fewer crystal points than (1).	Black layer thicker on bottom than sides. Top: greenish yellow crystals. Green glassy layer underneath this interspersed with crystalline patches.
3.	Glassy. Fracture surface: fewer crystal points than (2). Dendrites on bottom.	Similar to (3) but with less glass in crystalline layer.
4.	Glassy. Fracture surface: conchoidal fracture with some crystal points.	Bottom: approximately 1/8 in. of dark grey. Interior: green glass with crystal patches on top and at interface with bottom layer.
5.	Glassy. Fracture surfaces were dulled by microcrystals quite uniformly spread through sample. Bottom: black and grey mottled.	Compact crystalline mass of dark grey color with a patchy, thin surface layer of green crystals.
6.	Glassy. Fracture surface: more roughened by crystals than (5). Top surface slightly orange peel.	Dark grey with a patchy, thin surface layer of yellowish green crystals in rosettes. Readily crushed.
7.	Glassy. Fracture surface: somewhat mottled and streaked with microcrystalline particles.	Dark grey body of much finer crystals than (6) with a thin layer of green crystals on top.
8.	Glassy. Fracture surface: mottled but more glassy than (7).	Dark grey body with larger crystals than (7) and with some shrinkage voids. Top: about 1/8 in. of yellowish green needle shaped crystals in rosettes.
9.	Glassy. Top surface: mottled orange peel and glassy patches. Fracture surface: mottled glassy and microcrystalline patches.	Dark grey with larger crystals and shrinkage voids. Thin layer of green needles and rosettes on top.
10.	Fracture surface: glassy with trace of crystals.	Long green needles in a roughly circular pattern. Bottom: contained some patches of green and tan glasses. Quite friable.
11.	Top surface: mottled and patterned with raised patches. Fracture surface: dull with a few glassy patches.	Dark grey with some shrinkage voids. Top: thin green layer.
12.	Glassy. Thin layer from crucible wall translucent enough to see dark particles suspended in it. Fracture surface: glassy with milkiness near the bottom.	Elongated green crystals with a few patches of yellow crystals and black skin. Some tendency for surface crystals to parallel walls of crucible to give a roughly circular pattern.
13.	Glassy mottled top. Fracture surface: dull with glassy streaks near the top. Opaque in a thin layer.	Dull grey with thin greenish yellow layer on top.
14.	Glassy with four small crystal patches on top. Fracture surface: glassy with a few crystals showing.	Green top greying toward the bottom. Body mixed green and tan crystals with black skin next to crucible. Friable.

TABLE VII. (contd)

Cast	Recrystallized
15. Glassy; somewhat mottled surface. Fracture surface: dull.	Bottom: dark grey with more than usual glassy appearance. Top: highly fragmented green and yellow glass.
16. Glassy. Fracture surface: a few crystals visible.	Remained glassy. A few more crystal nuclei visible than in cast specimen but there is essentially no crystal growth.
17. Top surface showed a few crystals and the bottom was mottled. Fracture surface: mostly glassy with streaks of microcrystals.	Bottom: approximately 1/8 in. of dark grey with yellow patches. Balance: yellowish green crystals with some yellow crystals. Surface: large needles in roughly circular pattern.
18. Top surface: dulled orange peel. Fracture surface: dull microcrystalline with a few glassy streaks.	Nearly equal layers of dark dull grey with a few interspersed green crystals on bottom; green with tan and amber patches of crystals on top.
19. Glassy with a crystal patch on top. Fracture surface: glassy with streaks of microcrystalline area.	Bottom and skin next to crucible black, with the body of tan crystals.
20. Top and fracture surface: dull	Top: light green crystals. Intermediate layer of brown glass and tan crystals. Bottom: dark dull grey small crystals.
21. Top dulled. Fracture surface: dulled but with glassy patches.	Bottom: approximately 1/8 in. of dark grey with a few green crystals. Intermediate mixed green and yellow crystals. Top: green needles in suggestion of circular pattern.
22. Top: patchy, dull and glassy areas. Fracture surface: dull with glassy streaks.	Bottom: approximately 1/8 in. of dull grey. Intermediate: light green fragment layer below a dark green glass. Top: thin, crystallized layer.
23. Top: eggshell. Fracture surface: semigloss with glassy streaks.	Bottom: more glossy than (22), of dark grey with remainder very similar to (22).
24. Mixed glass and crystals.	Bottom: fine grained dark grey with patches of green crystals. Above this, a shattered light green layer, then dark green glass with interspersed shattered areas. Top: thin layer of platy crystals.
25. Mottled top with semiglossy fracture.	Dark grey with a thin layer of green crystals on top.
26. Fracture surface: glassy with a few crystal points showing.	Remained almost all glass. Thin layer of crystals on top and shattered light green patches on bottom.
27. Top surface: orange peel. Fracture surface: dull.	Fine grained grey body with a thin layer of yellow crystals on top.
28. Glassy. Fracture surface: very few crystal points showing.	Thin layer of crystals on top, but bulk glassy with a few crystal points showing.
29. Top: dull streaked with glassy runs.	Dark grey with a few green patches in it; a thin layer of green needles on top.
30. Bottom of quenched glass and top of green crystals.	Bottom and skin: black. Bulk: green needles with patches of amber material in them.
31. Surface semiglossy with dull fracture.	Fine grained dark grey with thin layer of yellow crystals on top and some patches of the same scattered through the body.
32. Glassy fracture.	Black skin with body of greyish green needles containing tan and amber patches.

TABLE VII. (contd)

	Cast	Recrystallized
33.	Surfaces mottled. Fracture semiglossy with patchy crystalline areas.	Bottom: grey layer with greenish tan upper layer with some of it scattered through the grey.
34.	Dull with a few glossy patches scattered through it.	Fine grained dull grey with some yellowish green spots mixed in and a thin layer of the same on top.
35.	Top: crystallized but fracture surface mostly glassy.	Greyish green crystals with some glassy areas mixed in. Top: rosettes and long needles.
36.	Some surface mottling. Fracture surface: mostly glassy with a few crystals.	Black skin. Top had square crystals but bulk of specimen was green plates with patches of tan and amber glass.
37.	Surface mottled. Fracture surface: semiglossy and patchy.	Bottom: dark grey with interspersed yellow patches. Top: yellow crystals. Yellow crushed more easily than grey.
38.	Top: crystallized with bottom quenched glass.	Dark grey fine grained with patches of amber crystals and a thin layer of yellowish green crystals on top. Hard and tough.
39.	Some crystals on outer edge of surface. Fracture surface: glassy with a few crystal points.	Green plates in a yellow matrix with a top skin of green plates. No black or grey.
40.	Crystals on top appeared as if they might have come from a second liquid layer. Fracture surface: glassy.	Black skin, bulk green plates in a yellow matrix. Top: light green square crystals.
41.	Fracture surface: glassy with some crystal points. Thin layer translucent with black particles showing.	Top: green plates or needles with bulk being greyish green crystalline mass with black skin on sides and bottom.
42.	Top: crystalline. Fracture surface: glassy with crystalline patches.	Bottom: approximately 1/16 in. of black Body: greyish tan with some glassy patches. Top: square crystals.
43.	Sparkling green glass. Fracture surface: glassy with some crystal points. Thin layer translucent.	Bulk was dark green glass that had shattered badly. Black layer on bottom.
44.	Some mottling. Fracture surface: glassy with some crystal points.	Body: light green with darker green particles. Black layer on bottom.
45.	Fracture surface: semiglossy.	Grey tan body with yellowish green rosettes on top. Black skin on bottom.
46.	A skin of crystals on part of the top. Fracture surface: semiglossy.	Dark grey body with green rosettes of fine needles on top.
47.	Fracture surface: glassy with bands of crystals interspersed.	Bottom: approximately 5/16 in. of dark grey. Layer of green needles on top in roughly circular pattern. When crushed, green phase appeared to concentrate in solubility sample.
48.	Top: crystal patches isolated by shrinkage. Fracture surface: dull semiporcelain.	Dull grey fine grained with a thin top layer of light green crystals. Hard.
49.	Fracture surface: semiglossy with patches of glass in crystals.	Bottom: approximately 1/4 in. of mixture of dark and light grey. Top: approximately 1/2 in. mixed green and amber crystals with green plates on top.

valence type is shown in Tables VIII and VII-A. When these are combined and the fraction of atoms in each valence calculated, another parameter is available for comparing the data. This is shown by Figures 2 and 3 on which are plotted drip temperature versus atom percent phosphorous (omitting oxygen from the atoms counted). It is apparent that the results fall into three groups according to the three M/P ratios, but there is also some overlap or intermingling; particularly for the recrystallized material. The lines drawn are the least square lines calculated for the points of each group. The deviation from the line is not entirely random or experimental error, but is the result of the variation in composition as well. When the individual valence groups of cations are plotted, we obtain the results shown on Figures 4 through 13. These do not all show the same separation into groups according to the M/P ratio. The single valence elements, of which sodium is over 90%, do not show any tendency to group (Figure 4) according to the M/P ratio.

As a generalization, we can say that the drip temperature tends to decrease as the fraction of univalent cations increases, but this holds only for the envelope of the group of data. This envelope is about 125° wide. The plus two elements make up only a small fraction of the total; therefore, the almost random pattern produced when they are plotted (Figure 5) against the drip temperature is not unexpected. There does appear to be a slight tendency to group according to M/P ratio. When the plus two and plus one elements are added together and plotted (Figure 6), there is very little change from the plus one alone. When the total of the plus three elements is plotted (Figure 7), a pattern is observed that is almost the inverse of the phosphate plot; i.e., the M/P 2.5 group lies below the 2.1 group rather than above. The plus three group is large enough that some of the individual elements can be plotted. When this is

*TABLE VIII. Atom Percent Distribution in Make Up
Solution for Various Specimens*

(Based on assumptions that all atoms of waste solution except water, nitric and sulfuric acids would remain with the solid and that the oxygen atoms combined with these atoms could be neglected.)

Specimen No.	Na	Al	Fe	Cr	Ni	FP	P
1	36.54	5.00	6.15	2.00	1.00	6.13	43.18
2	38.56	5.28	6.49	0.49	0.24	6.47	42.47
3	40.30	1.27	6.79	2.21	1.10	6.76	41.57
4	42.78	1.35	7.21	0.54	0.27	7.17	40.68
5	24.17	6.98	8.59	2.79	1.40	8.56	47.51
6	26.08	7.53	9.27	0.69	0.35	9.23	46.84
7	27.80	1.85	9.88	3.21	1.61	9.84	45.81
8	30.35	2.02	10.79	0.81	0.40	10.75	44.88
9	23.57	4.38	8.75	1.08	0.54	14.94	46.75
10	32.49	6.03	12.07	1.49	0.74	1.53	45.66
11	28.18	5.23	2.42	1.29	0.64	17.86	44.38
12	37.68	7.00	7.42	1.72	0.86	1.77	43.56
13	25.67	1.10	9.53	1.17	0.59	16.27	45.67
14	36.62	1.57	13.60	1.67	0.84	1.72	43.99
15	24.57	1.05	10.89	1.12	0.56	15.58	46.23
16	44.84	1.92	7.40	2.05	1.03	2.11	40.65
17	26.87	3.07	9.98	2.00	1.00	6.12	50.97
18	32.10	3.67	11.93	2.38	1.19	7.31	41.42
19	28.56	3.27	10.61	0.49	0.24	6.50	50.34
20	34.04	3.89	12.65	0.58	0.29	7.75	40.80
21	34.11	3.90	2.92	2.53	1.27	7.76	47.51
22	40.22	4.60	3.45	2.99	1.50	9.16	38.10
23	36.88	4.22	3.16	0.63	0.32	8.39	46.41
24	43.31	4.95	3.71	0.74	0.37	9.86	37.06
25	31.22	2.63	5.26	1.71	0.86	14.58	43.75
26	42.65	3.59	7.18	2.33	1.17	1.48	41.60
27	32.68	2.75	5.51	0.41	0.21	15.26	43.18
28	45.43	3.83	7.65	0.57	0.29	1.57	40.67
29	19.52	3.47	6.94	2.26	1.13	19.25	47.43
30	30.21	5.37	10.74	3.49	1.75	2.21	46.23
31	20.75	3.69	7.38	0.55	0.28	20.46	46.89
32	33.26	5.91	11.82	0.89	0.44	2.43	45.25
33	23.18	4.31	5.30	1.06	0.53	14.69	50.94
34	27.69	5.14	6.33	1.27	0.63	17.55	41.39
35	25.51	1.09	5.83	1.17	0.58	16.17	49.64
36	30.33	1.30	6.93	1.39	0.69	19.22	40.13
37	33.18	6.16	7.58	1.52	0.76	1.56	49.24
38	39.39	7.32	9.00	1.80	0.90	1.85	39.75
39	38.19	1.64	8.73	1.75	0.87	1.79	47.04
40	44.95	1.93	10.27	2.06	1.03	2.11	37.65
41	32.48	2.74	8.89	1.09	0.55	5.45	48.81
42	38.49	3.24	10.53	1.30	0.65	6.45	39.34
43	40.05	3.37	2.53	1.35	0.68	6.72	45.31
44	46.84	3.95	2.96	1.58	0.79	7.85	36.04
45	21.12	3.75	12.20	1.50	0.75	7.48	53.20
46	25.45	4.53	14.70	1.81	0.91	9.01	43.60
47	28.52	5.07	3.80	2.03	1.01	10.09	49.48
48	33.88	6.02	4.52	2.41	1.21	11.99	39.97
49	34.29	3.92	7.84	1.57	0.78	7.81	43.80

FIGURE 2. Drip Temperature Versus Atom Percent Phosphorus for Cast Materials

FIGURE 3. Drip Temperature versus Atom Percent Phosphorus for Recrystallized Materials

FIGURE 4. Drip Temperature Versus Atom Percent +1 Valence Elements for Cast Materials

FIGURE 5. Drip Temperature Versus Atom Percent +2 Valence Elements for Cast Materials

FIGURE 6. Drip Temperature Versus Sum of the Atom Percent +1 and +2 Valence Elements for Cast Materials

FIGURE 7. Drip Temperature Versus Atom Percent +3 Valence Elements for Cast Materials

FIGURE 8. Drip Temperature Versus Atom Percent Aluminum for Cast Materials

FIGURE 10. Drip Temperature Versus Atom Percent Fission Products for Cast Materials

FIGURE 11. Drip Temperature Versus Atom Percent +4 Elements for Cast Materials

FIGURE 12. Drip Temperature Versus Sum of the Atom Percent +3 and +4 Valence Elements for Cast Materials

done for aluminum, a random plot (Figure 8) is produced. The plot for iron (Figure 9) shows a slight tendency to segregate into groups according to the M/P ratio, and for the drip temperature to increase as the iron content increases. However, the samples with maximum and minimum temperatures differ in iron content by less than 1%. Since nearly one-third of the fission product atoms fall in this plus three group, the plot of them is considered with the iron and aluminum. As can be seen in Figure 10, this plot is nearly random also. When we turn to the plus four elements, which originate entirely in the fission products, we get a somewhat more oriented plot (Figure 11). The sum of the plus three and four elements is about the same as the sum of plus three alone (Compare Figures 7 and 12). When the two, three, and four valent groups are added together and plotted (See Figure 13), rather distinct separation into the three groups according to M/P ratio occurs. There is an increase in drip temperature with increase of these elements.

These various methods of plotting the data point out that there is a definite separation of the data according to M/P, but that changes in the ratios of other components will produce large changes in drip temperature. The only parameter that does not show a tendency to segregation of the different M/P ratios is atom percent of plus one elements (Figure 4). These data show the complexity of the problem and help one to appreciate the power of the statistical analysis to bring more order and unity to the picture, as is presented in the Appendix.

DISCUSSION OF STATISTICAL ANALYSIS

Any graphical representation of the results of a multi-variable system is a compromise that is made in an effort to synthesize a picture of the interrelationships involved. In the present case of six variables, it was elected to try to represent the results of the statistical analysis of the data by

a system of eighty-one plots of the contour lines of equal properties. The distribution and magnitude of the measurements made is shown in Figure 1 and gives some idea of the economy of testing that was utilized. In addition to the forty-nine points of the experimental design, six mixtures were prepared and measured to determine how well the calculations fit when extrapolated outside the experimental region. These extra compositions are specified in Table IX and the results are in Table III with the others.

TABLE IX. *Additional Points to Check on Agreement Between Equations from Statistical Analysis and Experimental Data in Regions of Pattern Not Covered by Points of Original Design*

<u>Specimen Number</u>	<u>Na</u>	<u>Al</u>	<u>Fe</u>	<u>Cr</u>	<u>FP</u>	<u>M/P</u>
50	-1	-1	-1	-1	0	0
51	+1	-1	-1	-1	0	-1
52	+1	-1	-1	-1	0	0
53	+1	-1	-1	-1	0	+1
54	+1	-1	+1	-1	0	0
55	+1	+1	+1	-1	0	0

As discussed above, one can consider various ways of examining the data, but none of them are as effective as the statistical analysis and graphical presentation of the contour lines that represent the response surface, as the variables are changed. The graphs presented in the Appendix indicate the relationships of the changing composition to the measured property. In this section, the chemical aspects of the data and relationships will be discussed.

When this program was planned, it was assumed there would be more or less marked variation in properties as the concentration of a given ingredient changed. Part of the information sought was whether or not the direction and magnitude of change would remain constant as one or more of the other ingredients was simultaneously changed.

Examination of Figure 1-A to 4-A in the Appendix shows they are composed of eighty-one individual graphs on which are plotted the contour lines of uniform property level (drip temperature or solubility) as a function of changing fission product level, and M/P ratio when the other four variables are held constant. The choice of which variables to use as the primary ones was arbitrarily made on the basis that these were the two variables investigated earlier. The graphs were originally drawn by the computer after it had calculated the values of M/P for a given contour level and various fission product levels, while the other variables were held constant. The individual graphs were reduced by photographic and mechanical means until they could be presented on a single sheet to allow the eye to readily shift from one plot to another, so relationships would be more readily grasped. As pointed out in the Appendix, the equations used to model the data should not be used to extrapolate. The graphs are drawn from the equation chosen as the best model. Plots were also made of the full quadratic model of the drip temperature of the "as cast" samples. There was considerable difference in the contour surfaces calculated from the two models; the full quadratic one being of gentler slope, but greater concavity. However, as pointed out in the Appendix, there was better agreement within the region of experimentation with the adjusted equation, rather than with the full quadratic. These equations and plots can be used for several purposes:

- 1) For predicting the properties of the solid produced from waste of a certain analysis
 - 2) For predicting the effects of adjusting the composition of a given waste
 - 3) For selecting compositions for more detailed examination.
- The last is the most reliable use. Examination of Figure 1 indicates sparsity of coverage and Table I indicates the limitation of composition range. Therefore, this study is but

the first stage of what is needed if one wants a detailed knowledge of phosphate solids that might be produced from wastes of the Purex process. The statistical analyses of the data have been valuable in interpreting the data collected and pointing the way to expand the study. Examination of Figure 1 shows the four "corner" blocks of plots are "sampled" with only two points in each.

To determine how well the model represented the actual behavior outside the experimental region, six samples were prepared and measured. The results are presented as Specimens 50 through 55 in Table III and Figure 1. The differences between observed and predicted values point up the danger of using the predicted values without verification by experiments.

Only the drip temperature and first 24 hr solubility data were subjected to full statistical analysis because of the time and expense involved and, furthermore, because these are the most significant screening properties. The results of these analyses will be related to the six variables in terms of the chemical effects involved.

The drip temperature of the "as-cast" material varies greatly over the composition range studied. The graphs of Figure 2-A appear as if the specimens belonged to two families, the first being the one with lowest iron content and the other being the other two iron levels.

The first family has a generally steeper slope to the response surface, with a tendency to have a lower drip temperature than the other family. Within this family, the drip temperature decreases as the fraction contributed by fission products decreases, and also as the M/P ratio is increased. Increasing sodium decreases the drip temperature, but changing the aluminum or chromium-nickel levels has a relatively minor effect; both tending to raise the drip temperature as they are

increased. At the lowest sodium level, the drip temperatures tend to be quite a bit higher than at the other two sodium levels, especially at the higher fission product concentrations. The lowest drip temperatures are predicted in this family (the calculations were not taken below 700 °C), but generally at low fission product levels. It is not surprising that increasing the fission product level increases the drip temperature since the fission products are so rich in the rare earths. The rare earths form high melting phosphates.

At the two higher iron levels there is the same trend as at the lower level, of decreasing drip temperature with increasing sodium level. The most marked difference is the much smaller change with changing fission product or phosphate levels. It appears as if a matrix is produced that dissolves much more material with little change in its properties. There is no appearance of minimum in the drip temperature as the M/P ratio is varies through this range. Aluminum and chromium-nickel both tend to increase the drip temperature as they increase, with chromium-nickel having somewhat greater effect than aluminum. At the highest iron level, the drip temperatures are rather high over the entire range of other constituents.

The four corner blocks of graphs of Figure 2-A seem to have slightly different patterns than the cross formed by the other five.

The first thing that catches the eye when Figure 1-A (Drip Temperature of Recrystallized Materials) is examined is the appearance of a minimum as a function of both M/P ratio and fission product levels throughout the whole system. It was expected that some of this would be seen but not so extensively. This minimum in drip temperature versus M/P ratio was observed in the data published in BNWL-80 and was the basis of choosing a quadratic model for experimental design and for choosing the range of phosphate ratios.

When one compares the other variables to see if they also produce minima, it is seen that at the lowest iron level and two lowest sodium levels, aluminum does exert such an effect. When the iron and sodium levels are high, the midlevel of aluminum produces a maximum in the drip temperature. In other parts of the system, increasing the aluminum level may increase, decrease, or not affect the drip temperature. At the low iron level and low or midlevel of aluminum, sodium produces a minimum. Over the balance of the system, sodium increase results in a drip temperature decrease. Increasing the iron and the chromium-nickel levels generally raises the drip temperature. So, if one has a waste of certain composition with drip temperature higher than desired, one can consult these curves as a guide to determine the direction for adjusting the composition to achieve the drip temperature desired. That this prediction needs to be verified is shown by the data for the six trial materials shown on Figure 1. If one is in the more central region of the composition range, the predictions should be more reliable than at the fringes.

Solubility of the recrystallized solid during the first 24 hr of exposure to hot (97 °C) water varied considerably (from 1.2 to 44%). The contour plots presented as Figure 3-A reflect a wide variation in calculated pattern of change of solubility with changing composition. As the iron and sodium levels are changed, the patterns change, with sodium exerting a somewhat greater effect. The generalization is often made that increasing the sodium content of a glass increases its solubility. Such a statement cannot be made about the calculated solubility of these solids. There is a strong interaction of the various components of the system. This would probably be reflected in a study of the compounds that crystallize from the different melts. With a system containing as many components as the present one, there should be a wide variety of compounds crystallizing out, leading to a variety of residues or intergranular materials of

varying solubility. The problem of what crystallizes out at what temperature and composition in this system, is almost as complex as that of magmatic differentiation that the geologists deal with. If the statistical model is a good representation of this system over its entirety, there is a great deal of control of solubility possible by varying the phosphate addition. The results on the six proof samples indicate a need to prove the results if any particular level of solubility is being sought. The areas indicated to have solubilities of zero or less, probably are of the order of 1%. This is sufficiently low to slow activity spread if the container should leak in a wet environment, but not enough to eliminate the need for a container.

It is to be noted that in Table VII specimens 16, 26, 28, and 43 are described as being largely, if not entirely glassy after the slow cooling that normally results in crystallization of the solid. Specimen 24 is described as largely glass with layers on top and bottom containing crystals. These five compositions, then, indicate that there are certain limited compositions that will be slow to crystallize and of these, some are of the lowest solubility measured on the slow-cooled materials, but they were still greater than 1%. Only two of the forty-nine compositions tested, fall in the regions where the statistical model predicts zero solubility, and both of these showed greater than 3% solubility.

In trying to interpret the graphs in terms of the individual variables, it appears that changing the M/P ratio produces the greatest change in solubility, but this is subject to qualification as to the level of the other variables. One might be tempted to say that increasing the sodium content increased the solubility, but this is not a valid generalization. In fact, there does not appear to be any single generalization that holds over the range of the variables covered by the model chosen.

What this study does point out is that a mixture of the complexity of these wastes cannot be successfully treated by simple "rules of thumb."

When we turn from the solubility of the recrystallized material to that of the cast material, we find Figure 4-A presents an entirely different picture. Here we are dealing with glasses almost entirely. Table VII, describing their appearance, lists only a few materials that were distinctly crystalline in appearance. Those of highest solubility were among these. The contour graphs are much more uniform in appearance and vary much more regularly with changing concentration of a given variable. The absolute solubility of these glassy materials is much lower than when they have crystallized.

The lowest solubility is found in those areas of low sodium and high aluminum. (This could be considered as similar to the silicate glasses where reduced sodium content increases their resistance to water attack. Aluminum orthophosphate is a structural equivalent of silicon dioxide and will form similar glasses.) The highest solubility is found in the medium to high sodium levels with low or medium aluminum, high M/P ratio, and generally high fission products. If the cast material were the stable form, one might fairly well predict the effect of adjusting a given waste composition on its solubility. However, the slow cooling that a container undergoes will almost surely produce a material similar to that tested here as the slow-cooled or recrystallized material. This is more soluble and less predictable. Thus, for the phosphate solids, it does not appear as if minimum solubility is a "good" criterion to apply in selecting or modifying a composition of waste to be solidified.

There are also other statistical ways of considering the data from these experiments. One of these is to lump all elements of a given valence and see if statistical inclusion of

the interaction terms is more informative than consideration of the individual elements as variables, as was done above in discussing M/P ratio as a unifying concept.

The graphical simplification made in this case was to lump variables two and four as if they were a single one and treat the system as if it were a four-component system that could be plotted at different levels of this combined variable and, thereby, show the effects of changing the other three variables. Contour levels of the drip temperature were calculated over the range of the experiments and are graphically represented on Figure 5-A. The experimental points grouped around the various levels as is pointed out in the Appendix. Superimposing a graph on the related diagram indicates a "poor" fit. Certainly, the change from one level to another contributes substantially to this. When the three diagrams at $X_4 = 0.020$ are compared, one sees that changing X_2 in 1% steps produces rather marked shifts in the system of contour lines, crowding them together and raising the drip temperature at the high anion end. If one examines the system of contour lines at a constant level of everything except anions or phosphate, a minimum is observed as a function of phosphate or in other terms of M/P ratio. It does not appear that this approach is as fruitful as the original system.

RECOMMENDATIONS

It appears desirable to extend factorial type investigation to cover the range of phosphate addition near M/P ratio of one.

If the wastes to be processed are in or near the fringes of the range of composition covered and it is desirable to know more about the system, this study could be expanded. The present factorial design has worked quite well, but for a system of this complexity, it appears to sample too thinly; particularly around the fringes (the four corner blocks of the eighty-one graph representation).

Any repetition or expansion of this work should probably be done on a more restricted range of fission product concentrations, 3000 to 10,000 MWd/MT of uranium is suggested. In this range of phosphate addition, it appears that approximately 40% fission products in the waste oxides is as much as can be handled without excessive separation of the rare earth phosphates from the melt.

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APPENDIX A
RESPONSE SURFACE STATISTICAL ANALYSIS
OF PHOSPHATE ADDITIVE SYSTEM EXPERIMENT

by
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APPENDIX A

RESPONSE SURFACE STATISTICAL ANALYSIS
OF PHOSPHATE ADDITIVE SYSTEM EXPERIMENT

THE EXPERIMENTAL DESIGN:

Several considerations influenced the choice of an experimental design to study the area of waste solidification involving phosphate as the sole additive. It was desired to employ a design which, with a minimum amount of experimentation, would permit efficient modeling of multidimensional response surfaces by second degree polynomials. Such a model is useful because it facilitates the interpretation of an experiment and can make possible the prediction of a response variable by interpolation. It was determined that the composition of a single experimental specimen could be easily specified by selecting a level for each of six independently controlled variables: sodium, aluminum, and iron each in terms of equivalents per liter, chromium and nickel (combined) in equivalents per liter, fission product (FP) in weight percent (or more accurately MWd/MT), phosphate in terms of metal oxide equivalents to phosphate ratio (M/P). The range of interest of each of these controlled variables was conveniently represented by three levels, as shown in Table I-A.

TABLE I-A. *Variables Used in Experimental Design*

<u>Variable</u>		<u>Levels</u>			
		Lower (-1)	Center (0)	Upper (+1)	
1.	Na	0.45	0.70	0.95	equiv./liter
2.	Al	0.09	0.24	0.39	equiv./liter
3.	Fe	0.18	0.48	0.78	equiv./liter
4.	Cr + Ni	0.048	0.128	0.208	equiv./liter
5.	F. P.	10	35	60	weight percent
6.	M/P	2.5	2.1	1.7	

The design finally chosen to investigate this phase of waste solidification was a three level, second order, incomplete factorial design, devised by Box and Behnken.⁽⁷⁾ It is a specially selected portion of the 3^6 factorial which allows efficient estimation (by least squares) of a second degree graduating polynomial of the form

$$\begin{aligned}
 y = & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 + b_6x_6 \\
 & + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^2 + b_{55}x_5^2 + b_{66}x_6^2 \\
 & + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{15}x_1x_5 + b_{16}x_1x_6 \\
 & + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{25}x_2x_5 + b_{26}x_2x_6 + b_{34}x_3x_4 \\
 & + b_{35}x_3x_5 + b_{36}x_3x_6 + b_{45}x_4x_5 + b_{46}x_4x_6 + b_{56}x_5x_6 .
 \end{aligned}$$

Here $x_1, x_2, \dots, x_6$ represent the controlled variables and y represents the response variable, or measured property, such as drip temperature or solubility. A desirable property of this design is its high degree of orthogonality: only the constant term b_0 and the estimates of the coefficients b_{ii} of the second degree terms are correlated one with another. The specimens included in the design are presented in Table II-A, where $x_1, x_2, \dots, x_6$ respectively denote the six controlled variables and the numbers -1, 0, +1 denote the lower, center, and upper levels of these variables, as indicated in Table I-A. This design requires 48 off-center points plus six independent observations on the center point for a total of 54 observations (specimens). The six center point observations provide five degrees of freedom for estimating experimental error and testing for goodness of fit.

The experiments were performed in accordance with the stated design and in the manner described in the main text above. A response surface statistical analysis was carried out on the observed data for each of the following four response variables.

TABLE II-A. *Experimental Design*

<u>Specimen #</u>	<u>x₁ (Na)</u>	<u>x₂ (Al)</u>	<u>x₃ (Fe)</u>	<u>x₄ (Cr+Ni)</u>	<u>x₅ (FP)</u>	<u>x₆ (M/P)</u>
1	+1	+1	0	+1	0	0
2	+1	+1	0	-1	0	0
3	+1	-1	0	+1	0	0
4	+1	-1	0	-1	0	0
5	-1	+1	0	+1	0	0
6	-1	+1	0	-1	0	0
7	-1	-1	0	+1	0	0
8	-1	-1	0	-1	0	0
9	0	+1	+1	0	+1	0
10	0	+1	+1	0	-1	0
11	0	+1	-1	0	+1	0
12	0	+1	-1	0	-1	0
13	0	-1	+1	0	+1	0
14	0	-1	+1	0	-1	0
15	0	-1	-1	0	+1	0
16	0	-1	-1	0	-1	0
17	0	0	+1	+1	0	+1
18	0	0	+1	+1	0	-1
19	0	0	+1	-1	0	+1
20	0	0	+1	-1	0	-1
21	0	0	-1	+1	0	+1
22	0	0	-1	+1	0	-1
23	0	0	-1	-1	0	+1
24	0	0	-1	-1	0	-1
25	+1	0	0	+1	+1	0
26	+1	0	0	+1	-1	0
27	+1	0	0	-1	+1	0
28	+1	0	0	-1	-1	0
29	-1	0	0	+1	+1	0
30	-1	0	0	+1	-1	0
31	-1	0	0	-1	+1	0
32	-1	0	0	-1	-1	0
33	0	+1	0	0	+1	+1
34	0	+1	0	0	+1	-1
35	0	+1	0	0	-1	+1
36	0	+1	0	0	-1	-1
37	0	-1	0	0	+1	+1
38	0	-1	0	0	+1	-1
39	0	-1	0	0	-1	+1
40	0	-1	0	0	-1	-1
41	+1	0	+1	0	0	+1
42	+1	0	+1	0	0	-1
43	+1	0	-1	0	0	+1
44	+1	0	-1	0	0	-1
45	-1	0	+1	0	0	+1
46	-1	0	+1	0	0	-1
47	-1	0	-1	0	0	+1
48	-1	0	-1	0	0	-1
49	0	0	0	0	0	0(6)

1. Recrystallized specimen drip temperature, listed in Table III-A;
2. Cast specimen drip temperature, listed in Table IV-A;
3. Recrystallized specimen solubility in first 24 hrs, listed in Table V-A;
4. Cast specimen solubility in first 24 hrs, listed in Table VI-A.

GENERAL FORM OF RESPONSE SURFACE STATISTICAL ANALYSIS

The objective of the response surface statistical analysis was to account for, or "explain," as much of the total variability in the data as possible. There were essentially two sources for this variability:

1. The true or natural effects and interactions of the six controlled variables;
2. Experimental error, denoted by σ_e^2 .

The main effort of the analysis was directed toward obtaining an optimal model which would account for a maximum amount of variability in the data with a minimum number of terms and which would come nearest to yielding a set of random, normally distributed residuals. For a given model (fit to a set of observed data) and a given combination of the levels of $x_1, x_2, \dots, x_6$, the residual is defined to be the difference $(y - \hat{y})$ between the observed value (y) of the response variable and the corresponding value ($\hat{y}$) predicted by the fitted model.

The response surface statistical analysis for each of the four response variables proceeded in essentially five steps. First, the full quadratic model stated above was fit (by least squares) to the observed data, which consisted of 49 points. The 49th point was the average of the six observed center specimens, indicated by an asterisk in the tables.

Second, a normal plot of the t-statistics for the 28 coefficients was used to select those terms in the full quadratic model which were statistically significant, i.e., which accounted for a significant portion of the variability in the

data, and to eliminate those terms which made little contribution; this procedure established a "basic" model.

Third, groups of three-way interactions, $b_{ijk}x_i x_j x_k$, and groups of second degree two-way interactions, $b_{ijj}x_i x_j^2$, were added to the "basic" model (insofar as they were estimable), until an optimal combination of terms, as defined above, was achieved within the limitations of the design. (The design limited the choice of groups of three-way and second-degree two-way interactions which could be used because these terms have statistical "aliases" among the terms in the full quadratic model.) Generally, an optimal combination was obtained when each term in the model accounted for a statistically significant portion of the total variability and no addition of any other term or group of terms would account for a further significant portion. The orthogonality in the design greatly facilitated the selection of terms for the final model. All of these first three steps were carried out with $x_1, x_2, \dots, x_6$ in terms of -1, 0, +1, so that, in order to convert the x_i 's to their original levels in equivalents per liter, etc., certain terms had to be added to the final model.

Fourth, a test for "goodness of fit" of the final model was performed by comparing the residual variance, S^2 , with the sample variance, $\hat{\sigma}_e^2$, of the six center replicates. The sample variance of the six center replicates is an estimate of σ_e^2 , basic experimental error (source 2), and is defined by

$$\hat{\sigma}_e^2 = (1/5) \sum_{i=1}^6 (y_i - \bar{y})^2 ,$$

where y_i = ith center replicate observed value and $\bar{y}$ =

$(1/6) \sum_{i=1}^6 y_i$. The residual variance, S^2 , estimates a combination

of σ_e^2 and of all remaining variability over and above experimental error for which the model does not account; S^2 is defined by

$$S^2 = (1/f) \sum_{i=1}^{49} (y_i - \hat{y}_i)^2,$$

where y_i = ith specimen observed value,

$\hat{y}_i$ = value predicted by model for ith specimen,

y_{49} = mean of the six center replicates,

f = 49 - # of parameters in final model.

If the value of the ratio $S^2/\hat{\sigma}_e^2$ is "too large" from a statistical standpoint, then this indicates a "poor" fit in the sense that the chosen model does not explain all variability in excess of experimental error.

Fifth, contour maps of the final model were calculated and plotted by the computer. A discussion of the results of this five-step analysis will be given below for each individual response variable.

A useful single measure of how well a given model fits the experimental data is given by the square of the multiple correlation coefficient, and is called the coefficient of determination, or the correlation index. This measure can lie between 0% and 100% and is defined by

$$R^2 = \frac{\sum_{i=1}^{49} (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^{49} (y_i - \bar{y})^2}$$

$$= \frac{\text{"Sum of squares explained by regression model"}}{\text{"Total sum of squares (corrected for the mean)"}}$$

where, as above,

y_i = observed value of i th specimen,

$\hat{y}_i$ = predicted value of i th specimen,

$$\bar{y} = (1/49) \sum_{i=1}^{49} y_i .$$

Alternatively, it can be shown that

$$\begin{aligned} R^2 &= 1 - \frac{\sum_{i=1}^{49} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{49} (y_i - \bar{y})^2} \\ &= 1 - \frac{\text{"residual sum of squares"}}{\text{"total (corrected) sum of squares"}} \end{aligned}$$

A percentage of zero implies that the model (fit by least squares) and the response variable are totally unrelated, i.e., that the model explains none of the variability in the observed data. But if $R^2 = 100\%$, then the model explains all the variability in the data. R^2 , $\hat{\sigma}_e^2$, and S^2 will be stated for each of the models discussed below. It should be recognized that, even though R^2 may be very near to 100%, the test for goodness of fit using $S^2/\hat{\sigma}_e^2$ may indicate a "poor" fit because the experimental error σ_e^2 may be very small compared to the remaining variability not explained by the model.

The last two columns in each of the Tables III-A, IV-A, V-A, VI-A, and VIII-A present 95% confidence limits for the true value of the corresponding response variable for each of the specified specimen compositions. These limits are calculated, under certain statistical assumptions, to give 95% confidence that they contain the true value of the response variable being measured, even though the observed value may not lie within the limits. They are useful in indicating the extent to which the true response surface has been successfully modeled.

TABLE III-A. Recrystallized Drip Temperature

Specimen	Observed Drip Temperature (y)	Full Quadratic Predicted ($\hat{y}$)	Full Quadratic Residual (y- $\hat{y}$)	Final Model Predicted ($\hat{y}$)	Final Model Residual (y- $\hat{y}$)	95% Confidence Lower Limit	Upper Limit
1	724	725	-1	727	-3	696	759
2	716	745	-29	724	-8	692	755
3	768	776	-8	747	21	715	779
4	732	756	-24	743	-11	711	755
5	931	904	27	932	-1	901	964
6	920	916	4	929	-9	897	960
7	870	837	33	834	36	802	867
8	806	809	-3	830	-24	798	862
9	933	982	-49	934	-1	891	977
10	881	896	-15	880	1	836	923
11	873	832	41	874	-1	831	917
12	728	751	-23	726	2	683	770
13	913	903	10	927	-14	884	970
14	782	810	-28	767	15	724	810
15	863	862	1	877	-14	834	920
16	836	773	63	821	15	778	864
17	888	853	35	888	0	848	928
18	817	832	-15	835	-18	796	875
19	899	877	22	881	18	841	920
20	812	776	36	812	0	772	852
21	711	744	-33	708	3	668	748
22	706	731	-25	728	-22	688	768
23	809	791	18	787	22	748	827
24	660	699	-39	664	-4	624	703
25	783	803	-20	796	-13	760	831
26	806	784	22	810	-4	775	846
27	829	837	-8	826	3	790	862
28	767	750	17	772	-5	737	808
29	936	957	-21	930	6	894	965
30	875	870	5	877	-2	841	913
31	964	983	-19	960	4	924	996
32	851	827	24	839	12	803	875
33	954	940	14	954	0	918	990
34	947	919	28	933	14	897	969
35	848	864	-16	861	-13	825	897
36	846	827	19	824	22	788	860
37	937	943	-6	945	-8	909	981
38	897	867	30	870	27	834	906
39	819	860	-41	845	-26	809	881
40	741	768	-27	754	-13	718	789
41	868	844	24	853	15	820	886
42	788	785	3	792	-4	759	826
43	759	755	4	761	-2	728	795
44	723	704	19	709	14	676	743
45	954	970	-16	962	-8	928	995
46	900	907	-7	901	-1	868	934
47	858	864	-6	854	4	820	887
48	789	810	-21	801	-12	768	835
49*	741	741	0	739	2	709	769
49	741						
50	740						
51	745						
52	748						
53	735						
54	737						

* Average of specimens 49 to 54.

TABLE IV-A. Cast Drip Temperature

Specimen	Observed Drip Temperature (y)	Full Quadratic Predicted ($\hat{y}$)	Full Quadratic Residual (y- $\hat{y}$)	Final Model Predicted ($\hat{y}$)	Final Model Residual (y- $\hat{y}$)	95% Confidence Lower Limit	Upper Limit
1	855	872	-17	855	0	830	881
2	802	831	-29	797	5	772	822
3	831	850	-19	821	10	796	846
4	753	786	-33	763	-10	738	788
5	1041	1011	30	1037	4	1012	1062
6	979	958	21	979	0	954	1004
7	1026	999	27	1014	12	989	1039
8	944	924	20	956	-12	931	981
9	978	994	-16	995	-17	968	1022
10	990	990	0	983	7	956	1009
11	906	915	-9	920	-14	893	947
12	863	846	17	844	19	818	871
13	982	970	12	975	7	945	1001
14	928	948	-20	946	-18	919	972
15	928	899	29	900	28	873	926
16	802	814	-12	807	-5	781	834
17	1008	979	29	994	14	968	1021
18	923	946	-23	926	-3	900	953
19	951	920	31	938	13	911	964
20	864	883	-19	866	-2	839	892
21	905	902	3	920	-15	893	946
22	790	805	-15	788	2	761	814
23	855	848	7	863	-8	837	890
24	734	747	-13	727	7	700	754
25	913	902	11	912	1	885	939
26	809	839	-30	824	-15	797	851
27	855	837	18	853	2	826	881
28	782	800	-18	765	17	738	793
29	1061	1041	20	1055	6	1027	1082
30	973	989	-16	977	-4	950	1004
31	992	964	28	996	-4	969	1023
32	924	937	-13	918	6	891	946
33	963	995	-32	950	13	917	983
34	937	921	16	917	20	884	950
35	958	949	9	974	-16	942	1007
36	904	894	10	913	-9	880	946
37	938	977	-39	955	-17	922	988
38	861	899	-38	871	-10	838	904
39	928	915	13	917	11	884	950
40	915	854	61	897	18	864	930
41	948	925	23	941	7	914	969
42	923	885	38	924	-1	897	951
43	846	821	25	838	8	811	866
44	748	717	31	758	-10	730	784
45	983	1030	-47	993	-10	966	1020
46	991	1000	-9	976	15	948	1003
47	961	983	-22	947	14	920	974
48	850	889	-39	865	-15	838	893
49*	902	902	0	901	1	864	938
49	907						
50	901						
51	903						
52	904						
53	903						
54	896						

* Average of specimens 49 to 54.

TABLE V-A. Recrystallized Solubility

Specimen	Observed Solubility (y)	Full Quadratic Predicted ($\hat{y}$)	Full Quadratic Residual ($y-\hat{y}$)	Final Model Predicted ($\hat{y}$)	Final Model Residual ($y-\hat{y}$)	95% Confidence Lower Limit	Upper Limit
1	6.96	14.52	-7.56	9.26	-2.30	1.34	17.18
2	4.77	1.62	3.12	-0.10	4.87	-8.02	7.82
3	17.29	16.35	0.94	19.09	-1.80	11.17	27.01
4	13.61	10.50	3.11	9.73	3.88	1.81	17.65
5	3.47	5.94	-2.47	0.81	2.66	-7.11	8.73
6	5.99	7.56	-1.57	5.93	0.06	-1.99	13.85
7	5.53	8.02	-2.49	10.64	-5.11	2.72	18.56
8	23.57	16.65	6.92	15.76	7.81	7.84	23.68
9	21.28	13.03	8.25	18.61	2.67	5.98	31.24
10	5.47	-1.56	7.03	-0.75	6.22	-13.38	11.88
11	13.34	21.83	-8.49	17.20	-3.86	4.57	29.83
12	34.01	23.31	10.70	34.32	-0.31	21.69	46.95
13	26.97	30.56	-3.59	17.19	9.78	4.55	29.82
14	14.61	13.23	1.38	15.50	-0.89	2.87	28.14
15	18.06	17.97	0.09	14.81	3.25	2.18	27.44
16	1.35	16.71	-15.4	8.77	-7.42	-3.87	21.40
17	19.08	21.34	-2.26	19.71	-0.63	8.08	31.34
18	2.88	-2.99	5.87	3.18	-0.30	-8.44	14.81
19	27.04	21.28	5.76	31.06	-4.02	19.44	42.69
20	4.30	13.22	-8.92	7.99	-3.69	-3.64	19.61
21	48.46	39.92	8.54	49.71	-1.25	38.08	61.33
22	5.72	11.10	-5.38	5.86	-0.14	-5.77	17.48
23	13.22	19.47	-6.25	17.82	-4.60	6.19	29.44
24	9.56	6.93	2.63	13.11	-3.55	1.48	24.74
25	31.54	23.86	7.69	28.77	2.77	18.89	38.65
26	1.40	11.06	-9.66	10.84	-9.44	0.96	20.72
27	6.94	8.76	-1.82	19.41	-12.50	9.53	29.29
28	1.20	7.44	-6.24	1.48	-0.28	-8.40	11.36
29	21.87	16.27	5.60	21.19	0.68	11.31	31.07
30	2.92	1.74	1.18	1.52	1.40	-8.36	11.40
31	25.95	15.65	10.30	26.31	-0.36	16.43	36.19
32	5.55	12.60	-7.05	6.65	-1.10	-3.24	16.53
33	39.31	39.79	-0.48	36.42	2.89	26.42	46.42
34	8.07	13.99	-5.92	5.13	2.94	-4.87	15.13
35	24.33	24.00	0.33	26.05	-1.72	16.05	36.04
36	13.74	16.68	-2.94	13.26	0.48	3.26	23.26
37	44.32	48.50	-4.18	47.62	-3.30	37.62	57.62
38	11.50	18.95	-7.45	16.33	-4.83	6.33	26.34
39	43.00	29.97	13.03	34.51	8.49	24.52	44.51
40	26.48	18.89	7.59	21.72	4.76	11.72	31.72
41	28.59	22.22	6.37	28.43	0.16	16.03	40.83
42	4.29	12.22	-7.93	3.74	0.55	-8.66	16.14
43	17.93	26.35	-8.42	10.62	7.31	-1.78	23.03
44	32.26	11.87	20.40	25.31	6.95	12.92	37.71
45	2.17	22.94	-20.80	7.22	-5.05	-5.19	19.63
46	9.36	0.56	8.80	14.02	-4.66	1.62	26.42
47	43.89	35.58	8.31	41.78	2.11	29.37	54.19
48	1.96	8.71	-6.75	0.24	1.72	-12.17	12.65
49*	10.42	10.42	0.0	11.03	-0.61	3.88	18.17
49	10.78, 10.52						
50	7.19, 7.57						
51	13.10, 11.61						
52	11.72, 11.82						
53	12.55, 13.05						
54	7.72, 7.48						

* Average of specimens 49 to 54.

TABLE VI-A. Cast Solubility

Specimen	Observed Solubility (y)	Full Quadratic Predicted ($\hat{y}$)	Full Quadratic Residual ($y-\hat{y}$)	Final Model Predicted ($\hat{y}$)	Final Model Residual ($y-\hat{y}$)	95% Confidence Lower Limit	Upper Limit
1	0.28	0.19	0.09	0.19	0.09	0.07	0.51
2	0.47	0.30	0.17	0.53	-0.06	0.19	1.45
3	0.58	0.42	0.16	0.41	0.17	0.15	1.13
4	1.23	1.32	-0.09	2.30	-1.07	0.84	6.30
5	0.07	0.14	-0.07	0.08	-0.01	0.03	0.22
6	0.06	0.04	0.02	0.04	0.02	0.02	0.11
7	0.09	0.29	-0.20	0.17	-0.08	0.06	0.46
8	0.24	0.17	0.07	0.17	0.07	0.06	0.47
9	0.10	0.07	0.03	0.10	0.0	0.04	0.23
10	0.16	0.21	-0.05	0.18	-0.02	0.08	0.42
11	0.36	0.36	0.0	0.25	0.11	0.11	0.59
12	0.30	0.39	-0.09	0.46	-0.16	0.20	1.08
13	0.21	0.23	-0.02	0.33	-0.12	0.14	0.76
14	0.22	0.15	0.07	0.13	0.09	0.06	0.31
15	3.98	4.47	-0.49	3.18	0.80	1.36	7.46
16	1.10	1.09	0.01	1.28	-0.18	0.54	3.00
17	0.25	0.63	-0.38	0.28	-0.03	0.12	0.63
18	0.16	0.23	-0.07	0.18	-0.02	0.08	0.42
19	0.25	0.42	-0.17	0.40	-0.15	0.18	0.90
20	0.52	0.49	0.03	0.26	0.26	0.12	0.59
21	1.75	1.77	-0.02	1.49	0.26	0.66	3.39
22	7.54	4.72	2.82	7.07	0.47	3.13	15.96
23	1.14	0.75	0.39	2.13	-0.99	0.94	4.81
24	15.28	6.37	8.91	10.12	5.16	4.48	23.00
25	1.40	1.63	-0.23	1.24	0.16	0.55	2.80
26	0.44	0.60	-0.16	1.05	-0.61	0.46	2.39
27	1.32	2.16	-0.84	1.02	0.30	0.45	2.32
28	1.41	2.26	-0.85	0.87	0.54	0.38	1.97
29	2.87	0.85	2.02	1.79	1.08	0.79	4.06
30	2.02	0.59	1.43	1.52	0.50	0.67	3.46
31	0.13	0.20	-0.07	0.27	-0.14	0.12	0.60
32	0.22	0.40	-0.18	0.23	-0.01	0.10	0.51
33	0.25	0.27	-0.02	0.27	-0.02	0.11	0.64
34	0.24	0.46	-0.22	0.46	-0.22	0.19	1.13
35	1.53	1.13	0.40	1.13	0.40	0.47	2.75
36	0.36	0.36	0.0	0.36	0.0	0.15	0.86
37	1.03	0.72	0.31	0.72	0.31	0.30	1.73
38	7.64	7.14	0.50	7.14	0.50	2.94	17.29
39	0.90	0.68	0.22	0.68	0.22	0.28	1.65
40	0.89	1.22	-0.33	1.22	-0.33	0.50	2.94
41	1.12	0.78	0.34	0.96	0.16	0.38	2.41
42	0.55	0.33	0.22	0.64	-0.09	0.25	1.60
43	0.93	1.05	-0.12	0.65	0.28	0.26	1.63
44	2.18	3.22	-1.04	3.11	-0.93	1.25	7.77
45	0.14	0.09	0.05	0.15	-0.01	0.06	0.36
46	0.10	0.09	0.01	0.10	0.0	0.04	0.24
47	0.20	0.34	-0.14	0.28	-0.08	0.11	0.70
48	1.83	2.52	0.69	1.32	0.51	0.53	3.32
49*	0.24	0.24	0.0	0.24	0.0	0.07	0.78
49	0.19						
50	0.21						
51	0.27						
52	0.25						
53	0.23						
54	0.26						

* Average of Specimens 49 to 54.

RESPONSE SURFACE FOR RECRYSTALLIZED SPECIMEN DRIP TEMPERATURE

Table III-A presents in columns 2, 3, and 4, respectively, the observed drip temperature for 54 recrystallized specimens, the drip temperature predicted by the full quadratic model, and the residuals for the full quadratic. The total variability among the 49 observations used in the least squares fits was

$$\begin{aligned} S_T^2 &= \frac{1}{48} \sum_{i=1}^{49} (y_i - \bar{y})^2 \\ &= \frac{1}{48} (\text{total adjusted sum of squares}) \\ &= \frac{1}{48} (303674.5) = 6326.55 \end{aligned}$$

The experimental error σ_e^2 was estimated from the last six specimens (49 to 54) to be

$$\hat{\sigma}_e^2 = 23.60$$

For the full quadratic model, the residual variance and coefficient of determination (defined above) were

$$S^2 = 1383.19 \text{ (with 21 degrees of freedom)}$$

and

$$R^2 = 90.4\%$$

According to the procedure outlined above, the final model and the least squares estimates of its coefficients were to be

$$\begin{aligned} y &= b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 + b_6x_6 \\ &\quad + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{55}x_5^2 + b_{66}x_6^2 + b_{12}x_1x_2 \end{aligned}$$

$$\begin{aligned}
& + b_{13}x_1x_3 + b_{15}x_1x_5 + b_{23}x_2x_3 + b_{25}x_2x_5 + b_{26}x_2x_6 \\
& + b_{34}x_3x_4 + b_{35}x_3x_5 + b_{36}x_3x_6 + b_{45}x_4x_5 + b_{46}x_4x_6 \\
& + b_{56}x_5x_6 + b_{235}x_2x_3x_5 + b_{346}x_3x_4x_6 + b_{122}x_1x_2^2 \\
& + b_{233}x_2x_3^2 + b_{113}x_1^2x_3 + b_{223}x_2^2x_3 + b_{115}x_1^2x_5 ;
\end{aligned}$$

b_0	= 3695.27	b_{25}	= 1002.24
b_1	= -2513.12	b_{26}	= 226.249
b_2	= -4049.01	b_{34}	= 3710.74
b_3	= -1764.34	b_{35}	= 542.643
b_4	= -2766.66	b_{36}	= 194.231
b_5	= -1423.47	b_{45}	= -856.851
b_6	= -1246.49	b_{46}	= 1417.20
b_{11}	= 1704.80	b_{56}	= 41.1810
b_{22}	= 6924.90	b_{235}	= -2185.54
b_{33}	= 449.042	b_{346}	= -1653.40
b_{55}	= 1132.11	b_{122}	= -4079.47
b_{66}	= 222.454	b_{233}	= -1263.07
b_{12}	= 1173.84	b_{113}	= -977.281
b_{13}	= 1313.29	b_{223}	= -5909.22
b_{15}	= 2024.31	b_{115}	= -1638.87
b_{23}	= 5415.96		

(The original chemical levels of the variables $x_1, x_2, \dots, x_6$ must be used in this final model and with these coefficients.)

Table III-A presents in columns 5, 6, 7 and 8, respectively, the final model predicted values, residuals, and 95% lower and upper confidence limits. The residual variance and coefficient of determination for the final model were

$$S^2 = 482.733 \text{ (with 18 degrees of freedom)}$$

and

$$R^2 = 97.1\%$$

The "goodness of fit" test for the final model was carried out by calculating the ratio

$$\frac{S^2}{\hat{\sigma}_e^2} = \frac{482.733}{23.60} = 20.455 \quad [\sim F(18,5)]$$

which is "significant" at the 0.005 level but not at the 0.001 level. This indicates that the final model does not explain all variability in excess of σ_e^2 , although it does explain a statistically significant portion of the variation in the observations (about 97%). Thus, the final model does fit sufficiently well to indicate real surface trends within the region of experimentation, but it cannot be expected to provide predictions accurate within experimental error as estimated from the six center observations. It is possible that the value $\hat{\sigma}_e^2 = 23.60$ underestimates the true $\hat{\sigma}_e^2$ because the six specimens all had the same composition and were all done at very nearly the same time.

Figure 1-A shows 81 contour graphs of the final model, representing 81 possible combinations of the three levels of each of the four variables Na, Al, Fe, Cr + Ni. The abscissa of each graph is fission product (FP) and the ordinate is M/P ratio.

RESPONSE SURFACE FOR CAST SPECIMEN DRIP TEMPERATURE

Table IV-A presents in columns 2, 3, and 4, respectively, the observed drip temperature for 54 cast specimens, the drip temperature predicted by the full quadratic model, and the residuals for the full quadratic. The total variability among the 49 observations used in the analysis was

$$S_T^2 = \frac{1}{48} (297525.5) = 6198.45 \quad .$$

The experimental error σ_e^2 was estimated from specimens 49 to 54 to be

$$\hat{\sigma}_e^2 = 13.467$$

For the full quadratic model, the residual variance and coefficient of determination were

$$S^2 = 1411.14 \text{ (with 21 degrees of freedom)}$$

and

$$R^2 = 90.0\% \quad .$$

The final model and the estimates of its coefficients were determined to be

$$\begin{aligned} y = & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 + b_6x_6 \\ & + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^2 + b_{55}x_5^2 + b_{66}x_6^2 \\ & + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{15}x_1x_5 + b_{25}x_2x_5 + b_{26}x_2x_6 \\ & + b_{35}x_3x_5 + b_{36}x_3x_6 + b_{46}x_4x_6 + b_{56}x_5x_6 + b_{256}x_2x_5x_6 \\ & + b_{122}x_1x_2^2 + b_{133}x_1x_3^2 + b_{115}x_1^2x_5 + b_{335}x_3^2x_5 \\ & + b_{446}x_4^2x_6 \quad ; \end{aligned}$$

$$b_0 = 832.750$$

$$b_1 = 813.656$$

$$b_2 = -739.125$$

$$b_3 = 1308.91$$

$$b_4 = -4535.94$$

$$b_5 = 1991.19$$

$$b_6 = -176.00$$

$$b_{11} = -778.00$$

$$b_{22} = 2796.00$$

$$b_{33} = 1531.37$$

$$b_{44} = 18888.7$$

$$b_{55} = 276.781$$

$$b_{66} = -11.047$$

$$b_{12} = 1763.33$$

$$b_{13} = -1254.16$$

$$b_{15} = -3756.28$$

$$b_{25} = -1725.48$$

$$b_{26} = -248.427$$

$$b_{35} = -1369.74$$

$$b_{36} = 133.315$$

$$b_{46} = 2653.77$$

$$b_{56} = -229.61$$

$$b_{256} = 768.635$$

$$b_{122} = -3514.84$$

$$b_{133} = 1504.37$$

$$b_{115} = 2712.41$$

$$b_{335} = 1206.12$$

$$b_{446} = -10243.5$$

(The original chemical levels of $x_1, x_2, \dots, x_6$ must be used with these coefficients.)

Table IV-A presents in columns 5, 6, 7 and 8, respectively, the final model predicted values, residuals, and 95% lower and upper confidence limits. The residual variance and coefficient of determination for the final model were

$$S^2 = 316.096 \text{ (with 21 degrees of freedom)}$$

and

$$R^2 = 97.8\%$$

The ratio for the "goodness of fit" test was calculated to be

$$\frac{S^2}{\hat{\sigma}_e^2} = \frac{316.096}{13.467} = 23.472 \text{ [} \sim F(21,5) \text{]}$$

which is significant at the 0.005 level but not at the 0.001 level. Thus, the final model does explain a significant portion of the variation in the observations (about 98%), but it does not explain all variability in excess of σ_e^2 .

Figure 2-A shows the 81 contour graphs of the final model for cast drip temperature, as explained above. In keeping with the above analysis, these graphs may be used to interpret the effects of the various controlled variables (chemicals) on drip temperature, but they cannot provide interpolation accuracy within the experimental error as estimated at the center point.

RESPONSE SURFACE FOR RECRYSTALLIZED SPECIMEN SOLUBILITY (FIRST 24 HR)

Table V-A presents in columns 2, 3 and 4, respectively, the observed (%) solubility for 54 recrystallized specimens, the solubility predicted by the full quadratic model, and the residual for the full quadratic. The total variability among the 49 observations used in the analysis was

$$S_T^2 = \frac{1}{48} (8406.71) = 175.14$$

As indicated in Table V-A, a solubility observation was obtained for each of two samples taken from each of the six center specimens. A one-way analysis of variance was carried out on these 12 observations to obtain estimates of the variability between specimens, denoted by ω^2 , and of the variability between samples, denoted by θ^2 , as follows:

$$\hat{\omega}^2 = 5.581 \text{ (with about 5 degrees of freedom)}$$

$$\hat{\theta}^2 = 0.229 \text{ (with 6 degrees of freedom).}$$

The experimental error σ_e^2 referred to above is actually composed of two parts, ω^2 and θ^2 , such that we can write $\sigma_e^2 = \omega^2 + \theta^2$ as the error in any single measurement. In the case of recrystallized solubility, it is clear that the larger portion of the experimental error σ_e^2 comes from ω^2 , the variability between specimens. An estimate of experimental error σ_e^2 , which can be used in a "goodness of fit" test, was obtained as follows:

$$\hat{\sigma}_e^2 = \hat{\omega}^2 + \hat{\theta}^2 = 5.581 + 0.229 = 5.810$$

with 5 degrees of freedom (5.19 by Satterthwaite's approximation.)

For the full quadratic model, the residual variance and coefficient of determination were

$$S^2 = 139.838 \text{ (with 21 degrees of freedom)}$$

and

$$R^2 = 65.1\%$$

The final model and the estimates of its coefficients were determined to be

$$\begin{aligned} y = & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 + b_6x_6 \\ & + b_{11}x_1^2 + b_{33}x_3^2 + b_{55}x_5^2 + b_{66}x_6^2 + b_{13}x_1x_3 + b_{14}x_1x_4 \\ & + b_{15}x_1x_5 + b_{16}x_1x_6 + b_{23}x_2x_3 + b_{25}x_2x_5 + b_{34}x_3x_4 \\ & + b_{35}x_3x_5 + b_{36}x_3x_6 + b_{46}x_4x_6 + b_{56}x_5x_6 + \\ & + b_{136}x_1x_3x_6 + b_{235}x_2x_3x_5 + b_{346}x_3x_4x_6 \end{aligned}$$

$$+ b_{233}x_2x_3^2 + b_{115}x_1^2x_5 + b_{116}x_1^2x_6 ;$$

$b_0 = 116.563$	$b_{16} = -97.582$
$b_1 = 476.438$	$b_{23} = -743.852$
$b_2 = 218.772$	$b_{25} = -236.072$
$b_3 = -229.965$	$b_{34} = -1461.84$
$b_4 = 855.571$	$b_{35} = -55.364$
$b_5 = 330.552$	$b_{36} = 189.037$
$b_6 = -223.580$	$b_{46} = -412.897$
$b_{11} = -672.668$	$b_{56} = -46.248$
$b_{33} = -127.086$	$b_{136} = -365.508$
$b_{55} = 90.067$	$b_{235} = 453.748$
$b_{66} = 52.979$	$b_{346} = 594.950$
$b_{13} = 795.915$	$b_{233} = 485.657$
$b_{14} = 181.045$	$b_{115} = 521.795$
$b_{15} = -737.449$	$b_{116} = 217.105$

(The original chemicals levels of $x_1, x_2, \dots, x_6$ must be used with these coefficients.) Table V-A presents in columns 5, 6, 7 and 8, respectively, the final model predicted values, residuals, and 95% lower and upper confidence limits. The residual variance and coefficient of determination for the final model were

$$S^2 = 47.250 \text{ (with 21 degrees of freedom)}$$

and

$$R^2 = 88.2\%$$

The ratio for the "goodness of fit" test was found to be

$$\frac{S^2}{\hat{\sigma}_e^2} = \frac{47.250}{5.810} = 8.133 \quad [\sim F(21,5)]$$

which is significant at the 0.025 level but not at the 0.01 level. The implication of this test is that the final model does not explain all variability in excess of σ_e^2 , although it very nearly does so. Indeed, the final model for recrystallized solubility comes much closer to explaining all variability in excess of σ_e^2 than any of the other three models. Thus, in the present case, the final model only explains about 88% of the total variability; however, experimental error will account for a considerable portion of the remaining 12%.

Figure 3-A shows the 81 contour graphs of the final model for recrystallized solubility. For practical purposes, any negative predictions in Table V-A or any negative contours in Figure 3-A should be read as zero, or near zero. This emphasizes that the primary use of these graphs is to facilitate the interpretation of the effects of the controlled variables.

RESPONSE SURFACE FOR CAST SPECIMENS SOLUBILITY (FIRST 24 HR)

The quadratic polynomial proved to be a very poor model for cast specimen solubility observations in their original form. It was decided, on the basis of two main considerations, to apply a natural logarithmic transformation to the data prior to regression analysis. First, a majority of the values are near zero and only seven are larger than 2%, with one as high as 15.28%, so that a log transformation could be expected to remove exponential trends in the data and, thus, allow a quadratic polynomial to model the resulting data better. Moreover, no negative solubilities could be predicted by taking anti-logarithms. Second, it is quite probable that the experimental error increases with the size of the observation;

i.e., there would be more error in measuring a solubility around 10% than one around 0.5%. The log transformation tends to stabilize the experimental error and to put greater emphasis on the smaller values in the least squares fit. Thus, the effect of the log transformation should be a better fit of the quadratic to a majority of the observations. The following regression analysis was done entirely in terms of log transformed data.

The total variability among the 49 transformed observations used in the analysis was

$$S_T^2 = \frac{1}{48} (76.79994) = 1.6417 \quad .$$

The experimental error σ_e^2 was estimated from specimens 49 to 54 to be

$$\hat{\sigma}_e^2 = 0.01832 \quad .$$

For the full quadratic model, the residual variance and coefficient of determination were

$$S^2 = 0.55181 \text{ (with 21 degrees of freedom)}$$

and

$$R^2 = 85.3\% \quad .$$

Table VI-A presents in columns 2, 3 and 4, respectively, the observed (untransformed) solubility for 54 cast specimens, the (anti-log of the) solubility predicted by the full quadratic model, and the corresponding residual for the full quadratic.

The final model and the estimates of its coefficients were determined to be:

$$\begin{aligned}
y = & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 + b_6x_6 \\
& + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^2 + b_{55}x_5^2 + b_{66}x_6^2 \\
& + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 \\
& + b_{25}x_2x_5 + b_{26}x_2x_6 + b_{36}x_3x_6 + b_{56}x_5x_6 + b_{122}x_1x_2^2 \\
& + b_{133}x_1x_3^2 + b_{113}x_1^2x_3 + b_{223}x_2^2x_3 + b_{114}x_1^2x_4 + b_{224}x_2^2x_4 ;
\end{aligned}$$

$b_0 =$	-5.7698	$b_{22} =$	-78.3846
$b_1 =$	68.6792	$b_{33} =$	-13.0432
$b_2 =$	47.4223	$b_{44} =$	83.0830
$b_3 =$	37.2565	$b_{55} =$	13.0124
$b_4 =$	31.8110	$b_{66} =$	5.3734
$b_5 =$	-15.3603	$b_{12} =$	-53.2298
$b_6 =$	-19.6409	$b_{13} =$	-73.2441
$b_{11} =$	-39.7814	$b_{14} =$	-218.288
$b_{23} =$	-30.0645	$b_{122} =$	110.552
$b_{24} =$	223.859	$b_{133} =$	19.6091
$b_{25} =$	-10.0464	$b_{113} =$	41.3421
$b_{26} =$	-7.2495	$b_{223} =$	77.9313
$b_{36} =$	-4.1048	$b_{114} =$	140.615
$b_{56} =$	4.2787	$b_{224} =$	-436.646

(The original chemical levels of $x_1, x_2, \dots, x_6$ must be used with these coefficients. Also, this model is for the logarithm of the cast solubility. Predicted solubility may be obtained by taking the natural anti-logarithm of the model value.)

Table VI-A presents in columns 5, 6, 7 and 8, respectively, the anti-log of the final model predicted value, the anti-log residual, and 95% lower and upper confidence limits (in anti-log) for the true value of the response variable. The residual variance and coefficient of determination for the final model were

$$S^2 = 0.32251 \quad (\text{with 21 degrees of freedom})$$

and

$$R^2 = 91.4\%$$

The ratio for the "goodness of fit" test was calculated to be

$$\frac{S^2}{\hat{\sigma}_e^2} = \frac{0.32251}{0.01832} = 17.604 \quad [F(21,5)]$$

which is significant at the 0.005 level but not at the 0.001 level. Thus, the final model does explain a significant portion of the variation in the transformed observations (about 91%), but it does not explain all variability in excess of $\hat{\sigma}_e^2$. Although it was intended that the log transformation should stabilize the experimental error, it is possible that the value $\hat{\sigma}_e^2 = 0.01832$ is an underestimate of this stabilized variance, hence, that the fit is actually better than the above test indicates. An important consideration in future experiments of this kind would be to obtain replicate observations on more than one specimen composition, so that experimental error estimates would be less influenced by specimens with an unusually low replicate variability.

Figure 4-A shows the 81 contour graphs of the final model for cast solubility. These graphs were calculated by determining the position of the contours for the logarithmic levels -3, -2, -1, 0, 1, 2, 3, which correspond to the anti-logarithmic levels 0.05, 0.14, 0.37, 1.00, 2.72, 7.39, 20.09.

TABLE VII-A. Total Atom Percent In Each Valence

Specimen #	$x_1 = +1$	$x_2 = +2$	$x_3 = +3$	$x_4 = +4$	$x_5 = +6 \text{ \& P}$
1	37.230	1.814	15.169	1.550	44.229
2	39.289	1.102	14.384	1.636	43.582
3	41.063	2.001	12.488	1.710	42.730
4	43.586	1.223	11.454	1.815	41.914
5	25.132	2.534	21.180	2.165	48.980
6	27.119	1.574	20.536	2.336	48.425
7	28.905	2.915	18.184	2.490	47.498
8	31.561	1.832	17.156	2.719	46.722
9	25.250	2.524	19.123	3.779	49.308
10	32.660	0.946	20.087	0.386	45.921
11	30.185	3.018	14.812	4.518	47.448
12	37.876	1.096	16.718	0.448	43.860
13	27.498	2.749	17.158	4.116	48.461
14	36.808	1.066	17.408	0.435	44.281
15	26.325	2.632	18.184	3.941	48.903
16	45.081	1.305	12.067	0.533	41.013
17	27.555	1.811	17.058	1.547	52.021
18	32.926	2.164	20.383	1.849	42.670
19	29.288	1.108	16.501	1.645	51.452
20	34.912	1.321	19.668	1.960	42.131
21	34.980	2.299	11.908	1.964	47.507
22	41.252	2.712	14.044	2.316	39.667
23	37.821	1.432	10.769	2.124	47.845
24	44.418	1.681	12.646	2.494	38.751
25	32.860	2.793	14.392	3.689	46.250
26	42.815	1.363	13.594	0.373	41.853
27	34.401	2.235	13.691	3.862	45.295
28	45.604	0.495	12.540	0.398	40.936
29	21.689	3.687	19.002	4.870	50.731
30	30.462	2.039	20.330	0.558	46.617
31	23.052	2.995	18.351	5.176	50.403
32	30.528	0.766	19.421	0.615	45.668
33	24.829	2.482	15.495	3.717	53.462
34	29.665	2.966	18.512	4.440	44.399
35	27.332	2.732	13.410	4.091	52.417
36	32.494	3.248	15.943	4.864	43.431
37	33.357	0.965	15.775	0.347	49.506
38	39.596	1.146	18.725	0.468	40.062
39	38.389	1.111	12.698	0.454	47.347
40	45.191	1.308	14.949	0.534	38.016
41	31.089	1.271	14.508	1.378	49.748
42	39.214	1.507	17.193	1.633	40.446
43	40.801	1.567	9.460	1.699	46.465
44	47.722	1.833	11.064	1.987	37.387
45	21.957	1.744	19.915	1.891	54.485
46	26.463	2.102	24.001	2.279	45.146
47	29.651	2.356	14.219	2.554	51.210
48	35.228	2.799	16.893	3.034	42.032
49	35.166	1.821	15.893	1.975	45.136

TABLE VIII-A. *Cast Drip Temperature Valence Sum Model*

Specimen #	Observed Cast Drip Temperature	Quadratic Predicted	Quadratic Residual	95% Confidence	
				Lower Limit	Upper Limit
1	855	885	-30	867	903
2	802	837	-35	809	865
3	831	833	-2	806	859
4	753	775	-22	743	807
5	1041	1021	20	985	1055
6	979	955	24	919	990
7	1026	990	36	956	1024
8	944	910	34	887	934
9	978	980	-2	954	1005
10	990	947	43	908	986
11	906	921	-15	891	951
12	863	902	-39	879	925
13	982	956	26	937	974
14	928	912	16	888	937
15	928	967	-39	948	990
16	802	817	-15	785	849
17	1008	997	11	964	1030
18	923	943	-20	909	976
19	951	936	15	896	976
20	864	901	-37	862	941
21	905	911	-6	859	963
22	790	821	-31	775	866
23	855	843	12	804	882
24	734	756	-22	716	796
25	913	899	14	873	926
26	809	854	-45	824	885
27	855	848	7	805	891
28	782	804	-22	760	848
29	1061	1058	3	1007	1109
30	973	996	-23	947	1045
31	992	996	-4	952	1040
32	924	936	-12	886	986
33	963	990	-27	954	1025
34	937	941	-4	905	978
35	958	965	-7	922	1007
36	904	896	8	852	939
37	938	950	-12	915	985
38	861	896	-35	861	931
39	928	904	24	868	941
40	915	824	91	786	861
41	948	933	15	887	978
42	923	863	60	835	891
43	846	832	14	790	873
44	748	723	25	680	766
45	983	1023	-40	978	1067
46	991	998	-7	951	1045
47	961	971	-10	936	1006
48	850	892	-42	860	925
49*	902	894	8	876	913

* Average of specimens 49 to 54.

RESPONSE SURFACE FOR CAST SPECIMEN DRIP TEMPERATURE
IN FRAMEWORK OF TOTAL ATOM PERCENT BY VALENCE

In order to carry out a response surface analysis on cast drip temperature observations in terms of total atom percent by valence, it was convenient to regard the experiment as a mixture problem involving five components. A mixture-type experiment is characterized by the fact that the percents of all components (controlled variables) must add up to 100% for each specimen. Table VII-A presents a breakdown of the composition of each of the 49 different specimens into total atom percent (minus oxygen) in each valence. Variable x_5 contains total anions.

The following quadratic model is the most general form of the corresponding full second degree graduating polynomial in five independent variables subject to the restriction that

$$\begin{aligned}
 x_1 + x_2 + x_3 + x_4 + x_5 &= 1 \\
 y &= b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 \\
 &\quad + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{15}x_1x_5 \\
 &\quad + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{25}x_2x_5 + b_{34}x_3x_4 \\
 &\quad + b_{35}x_3x_5 + b_{45}x_4x_5
 \end{aligned}$$

The above quadratic model was fit to the cast drip temperature observations to obtain the following coefficient estimates:

$$\begin{array}{ll}
 b_1 = 38.125 & b_{14} = -19168.0 \\
 b_2 = -28832.0 & b_{15} = -1166.0 \\
 b_3 = 4226.25 & b_{23} = 11128.0 \\
 b_4 = 18384.0 & b_{24} = 34512.0 \\
 b_5 = 2155.0 & b_{25} = 53824.0
 \end{array}$$

$$\begin{aligned}
 b_{12} &= 17200.0 & b_{34} &= 1456.0 \\
 b_{13} &= 724.172 & b_{35} &= -8684.0 \\
 b_{45} &= -33936.0
 \end{aligned}$$

(The fraction levels, not the percent levels, of the variable $x_1, x_2, \dots, x_5$ must be used in the above model and with these coefficient estimates.)

Table VIII-A presents in columns 2, 3, 4, 5 and 6, respectively, the observed cast drip temperature and the quadratic model predicted value, residual, and 95% lower and upper confidence limits for the true value of the response variable for each specimen.

An attempt to improve the quadratic model by adding three-way interactions proved unsuccessful because the coefficient matrix for the normal equations was ill conditioned. This adversely affected the matrix inversion procedure in the least squares fit. The situation was not unexpected due to the fact that the original experiment was not specifically designed for the purpose of making a mixture-type response surface analysis.

As reported above, the total variability among the 49 observations used in the analysis was

$$S_T^2 = \frac{1}{48} (297525.5) = 6198.45,$$

and the experimental error $\hat{\sigma}_e^2$ was estimated to be

$$\hat{\sigma}_e^2 = 13.467.$$

For the quadratic (mixture) model, the residual variance and coefficient of determination were

$$S^2 = 1146.59 \text{ (with 34 degrees of freedom)}$$

and

$$R^2 = 83.2\%.$$

The ratio for "goodness of fit" test was

$$\frac{S^2}{\sigma_e^2} = \frac{1146.59}{13.467} = 85.14 [\sim F(34,5)]$$

which is highly significant. Thus, the quadratic model explains a significant portion (83%) of the variation in the data, but does not explain all variation in excess of σ_e^2 .

Figure 5-A presents five contour graphs of the quadratic model for cast drip temperature. These were chosen for presentation because the specimen observations formed three rather distinct groups relative to x_4 atom % from the three levels of fission product additions. The first group had x_4 atom % values centering at about 0.5%, while the corresponding x_2 atom percents ranged from 0.5% to 1.5%. This suggested the first map in Figure 5-A with $x_4 = 0.5\%$ and $x_2 = 1.0\%$. The second group had x_4 atom % values centering at 2%, while the corresponding x_2 atom percents ranged from 1% to 3%, suggesting maps at $x_4 = 2\%$, $x_2 = 1\%$, at $x_4 = 2\%$, $x_2 = 2\%$, and at $x_4 = 2\%$, $x_2 = 3\%$. The third group had x_4 values centering at about 4%, while corresponding x_2 atom percents ranged from 2.5% to 3.5%, suggesting the last map at $x_4 = 4\%$, $x_2 = 3\%$. The contour maps generally cover the regions containing the levels of x_1, x_3 and x_5 for all specimens. As before, these graphs are most useful for interpreting the effects of the various components, but they cannot provide predictions by interpolation accurate within experimental error. Extrapolation in any sense cannot be advocated for any of the five groups of contour maps.

FIGURE 1-A. Contour Lines at Equal Drip Temperatures as Calculated from the Statistical Model of Best Fit-Recrystallized Material

FIGURE 2-A. Contour Lines at Equal Drip Temperatures as Calculated from the Statistical Model of Best Fit-Cast Material

FIGURE 3-A. Contour Lines at Equal Solubility in First 24 hr as Calculated from the Statistical Model of Best Fit-Recrystallized Material

FIGURE 4-A. Contour Lines at Equal Solubility in First 24 hr as Calculated from the Statistical Model of Best Fit-Cast Material

FIGURE 5-A. Graphs of Drip Temperature Contours as a Function of x_1 , x_3 , and x_5 Elements at Various, Constant, Levels of x_2 and x_4

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