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REPORT

SOLIDIFICATION OF HIGH LEVEL WASTES
PART VI
MIXED PHOSPHATE, BORATE, SILICATE MELTS
FOR FIXATION OF PUREX TYPE WASTES

G. B. Barton

TABLE TO			

January 1967

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SOLIDIFICATION OF HIGH LEVEL WASTES - PART VI
MIXED PHOSPHATE, BORATE, SILICATE MELTS FOR FIXATION
OF PUREX TYPE WASTES

(Appendix A. Response Surface Calculated from
Statistical Analysis - J. A. Weed)

by

G. B. Barton

Chemical Research Section
Chemistry Department

January 1967

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Pacific Northwest Laboratory
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SOLIDIFICATION OF HIGH LEVEL WASTES
PART VI.

Mixed Phosphate, Borate, Silicate Melts for Fixation of Purex Type Wastes

Introduction

Both borates and silicates are compatible with phosphates in glasses over a certain range. Borates are known to reduce the melting temperature and viscosity of both silicate and phosphate glasses or melts. There is some indication that small additions of silica improve the "glassy" properties of phosphate melts. Therefore, it was deemed desirable to scout the effects of these additives to the phosphate system that has been previously examined. A single Purex composition was chosen and the additions were based on a statistically designed pattern to allow economical experimentation and interpretation of results.

Summary

A study was made of the effects of substituting various fractions of borate, silicate, and mixtures of them, for phosphate, with a fixed waste composition of the Purex type. The ratio of waste to additives varied from 70 to 40 reduced atom per cent; i.e., of all known atoms except oxygen, the specified per cent came from the waste and the balance was added as the phosphorous, boron or silicon of phosphate, borate or silicate. This corresponds to a range of M/P of 3.95 to 1.13. Only at the 40 atom per cent waste level was there definite indication of improvement of properties of the phosphate solid by adding borates and silicates. At the other levels there was a general deterioration. This was either in the form of increased solubility or separation into two liquid phases during melting.

Separation of a second liquid phase is deemed a major drawback of the mixed system. It is undesirable since it will lead to fission product fractionation. One phase is of increased solubility and most generally one phase was much more viscous than the other.

The use of a statistically designed pattern of mixtures permitted calculation of contour surface maps of the properties tested. These maps are found to represent trends in the properties but not accurate representations, since the variation in properties is greater or of finer structure than can be expressed by equations of the orders tested. The general agreement is good and the equations can be used to predict fruitful areas to look to for further work.

Experimental Method

Stock solutions of Purex Process components and synthetic fission products were prepared as outlined in BNWL-80 and 139. For ease of reference, the compositions are reproduced in Table I. The proportion of fission products (calculated as oxides) to process components (calculated as oxides) is 1:1.5, or 40% (weight) fission product oxides. Choice of this level was based on two facts: 1) experiments with various ratios had shown this to be near or above the maximum that could be retained in a homogeneous phosphate melt, and 2) it is about the concentration calculated for WSEP tests based on a 20,000 MWD/MT "Yankee" fuel processed by a Purex-type cycle.

The experimental pattern was developed by J. A. Weed. Together with the statistical analysis of the data, it is presented in the Appendix to this report. It had previously been determined (BNWL-80) that an area of particular interest occurred near an M/P ratio of 2.5. This is approximately 60% of the total atoms (minus oxygen) coming from the waste, and the remaining 40% from the phosphate or mixed additives. The mixtures are expressed in terms of "per cent of the atoms (minus oxygen)" because oxygen is variable with the oxidation state of the elements, and these states were not known to be fixed but rather are expected to vary with processing conditions. Changes in composition due to volatilization were ignored, since in any process the starting point analyses would be similar information to the solution composition information used for calculating the mixtures.

TABLE I

Composition of Solutions Used in Preparing MixturesSimulated Purex Process Waste Stock

	<u>Molarity</u>	<u>Equivalents</u>
Na	1.4	1.4
Al	0.16	.48
Fe	0.32	.96
Cr	0.07	.21
Ni	0.035	.07
SO ₄ ⁼	0.52	-(1.04)
SiO ₂	0.016	-.064
F	0.0016	-.0016

Net cation equivalents* 3.06/L, assuming the sulfate will volatilize out. (All cations were added as nitrates, the sulfate as sulfuric acid, the silica as a colloidal sol (Ludox), and the fluoride as NaF.)

Simulated Fission Product Waste Stock

<u>Element</u>	<u>Concentration x 10³</u>		<u>Form Added</u>
	<u>Molarity</u>	<u>Equivalents</u>	
Se	1.56	-3.12	SeO ₂
Br	0.59	-0.59	KBrO ₃
Rb	11.0	11.0	RbNO ₃
Sr	24.9	49.8	Sr(NO ₃) ₂
Zr	100	400.	ZrO(NO ₃) ₂
Mo	89.9	-179.7	Acidified Ammonium Molybdate
Ru	51.0	204.	Ru(NO ₃) _x
Rh	11.4	34.2	Rh(NO ₃) ₃
Pd	25.7	51.4	Pd(NO ₃) ₂
Ag	1.25	1.25	AgNO ₃
Cd	1.23	2.46	Cd(NO ₃) ₂
Sn	0.96	3.84	Sn O
Te	9.56	-19.12	TeO ₂
I	1.48	-1.48	HIO ₃
Cs	56.0	56.0	CsNO ₃
Ba	27.9	55.8	Ba(NO ₃) ₂
Rare Earths	186	558	Mixed Rare Earth Nitrate Salt

Net Cation Equivalents* 1.242/L

These are the fission product elements (other than the noble gases, precious metals and technetium) present in excess of 1% of the amount of zirconium.

*Net cation equivalents are those available to combine with the added phosphate, i.e., they are those in excess of the quantity combined with the permanent anions of the solution. Such anions are silicate, tellurate, molybdate, etc.

The M/P ratios calculated for the various levels of "metal" atoms are presented in Table II. For purposes of designing these experiments, it was assumed that boron and silicon would substitute for phosphorous, atom for atom.

TABLE II

Calculated M/P Ratios for the Various Levels of Metal Atoms

<u>Metal Atoms</u> <u>Per Cent</u>	<u>M/P</u>
70	3.95
65	3.14
60	2.54
55	2.07
50	1.69
40	1.13

Supplementary Samples - Phosphate Only
(Samples 65 - 68 Table III)

48.2	1.57
42.9	1.27
37.9	1.03
33.3	0.85

Metal atoms expressed as per cent of the total number of atoms (minus oxygen) that come from the waste solution.

The total numbers of atoms of phosphorous, boron, and silicon to be added to each batch were calculated and translated to the corresponding weights of phosphoric acid, boric acid, or silica (as Ludox, a colloidal silica). These were added to the proper weights of Process Solution and Fission Product Solution to contain 50 g of mixed waste oxides. The combined mixtures were dried in stainless steel beakers. The resulting solids were ground to a powder and thoroughly mixed before taking portions to melt.

Melting was performed by placing a platinum crucible containing a small quantity of the powder in a furnace heated to 1200°C. Additional portions were added at four minute intervals until a total of 30 grams of the powder was melted. The melts were then allowed to remain in the furnace at temperature for one hour, removed, and allowed to air cool in the crucible. When cold, they were removed

from the crucible by tapping; generally they adhered to the crucible and so had to be broken out. The fragments were then crushed and screened to obtain samples for measuring leachability and drip temperature. Details of these methods of measurement are given in BNWL-80.

Preparation of the samples for leachability testing resulted in some fractionation of the materials, particularly when the samples were two-phase, due to different grinding and crushing rates of different parts of the sample. This decreases the precision of measurement, especially when one phase is much more soluble than the other. This condition existed with many of the samples in this set of experiments.

The measured drip temperatures also reflect the influence of separation into two liquid phases. The figure reported as the drip temperature is the temperature at which the first drop falls. Many of the samples formed a fluid low-melting phase (frequently yellow) and a viscous high-melting phase (dark brown to black with drip temperature above 1085°C). This separation is deemed one of the major drawbacks of this mixed system, and will be discussed further below.

A few experiments were performed to determine the influence of a reducing atmosphere on this separation into two phases, by melting several samples in platinum boats while passing a stream of nitrogen and ammonia around the sample. The samples were heated to 1200°C for approximately one hour. Only visual observation was used to determine whether or not the second phase was eliminated.

Samples 36, 37, 57 and 64 were melted in a reducing atmosphere.

Results and Discussion

The results of the measurements are summarized in Table III and in Figures 1 to 6. They are partially repeated in the Appendix, where the statistical analysis

TABLE III

Results of Measurements on Phosphate - Borate - Silicate - Waste System

Specimen Number	Temperature		Leachability in 24 Hrs				Appearance of Second Phase?
	Closure	Drip	1st	2nd	3rd	Total	
1	785	806	22.2 %	2.13%	0.97%	25.3 %	No
2	789	819	30.5	3.17	1.36	35.0	No
3	772	806	31.9	4.34	1.31	37.6	No
4	864	970	30.1	2.82	1.82	34.7	Yes
5	865	992	29.3	2.94	1.08	33.3	Yes
6	842	849	14.1	1.45	1.26	16.8	Yes
7	839	953	28.7	5.39	1.79	35.8	Yes
8	810	823	37.7	3.35	0.75	41.8	Yes
9	ca 1250		29.8	1.43	0.92	32.1	Yes
10	845	873	22.6	2.25	0.89	25.7	No
11	768	798	22.6	3.35	1.63	27.6	No
12	789	818	29.0	3.61	1.47	34.1	Yes
13	791	877	26.6	4.02	2.01	32.7	Yes
14	838	883	19.8	2.70	1.93	24.5	Yes
15	814	837	26.7	5.29	2.25	34.2	Yes
16	802	874	32.2	7.17	2.31	41.7	Yes
17	810	842	22.1	3.81	2.15	28.0	Yes
18	809	824	4.16	2.71	2.18	8.65	No
19	839	869	5.45	3.36	6.09	14.9	No
20	829	863	9.86	6.44	2.85	19.2	No
21	936	1008	16.8	2.65	0.86	20.3	No
22	795	812	25.2	3.15	2.21	30.5	No
23	913	925	8.47	1.35	0.90	10.7	Yes
24	945	955	11.9	1.56	1.14	14.6	Yes
25	801	856	17.0	2.22	1.89	21.1	No
26	807	856	15.9	3.68	1.80	21.4	No
27	822	838	13.2	3.99	3.45	20.6	Yes
28	825	842	12.1	3.57	3.17	18.8	Yes
29	854	878	9.93	0.45	0.42	10.8	Yes
30	771	792	20.2	5.15	2.46	27.8	No
31	790	819	19.7	3.40	1.84	24.9	No
32	773	781	26.5	4.96	2.81	34.2	No
33	804	856	21.2	3.38	1.72	26.3	No
34	810	893	28.1	5.69	3.45	37.3	Yes
35	815	911	20.7	6.39	3.04	30.1	Yes
36	945	963	44.5	2.46	0.62	47.6	Yes
37	1037	1056	24.2	0.57	0.32	25.1	Yes
38	884	905	0.31	0.15	0.15	0.61	No
39	887	933	20.1	3.50	1.63	25.2	No
40	888	915	11.4	4.79	3.55	19.8	No
41	953	993	7.99	1.74	1.40	11.1	No
42	820	844	25.01	10.82	3.46	39.3	No
43	831	868	16.0	3.82	1.95	21.8	No
44	760	783	20.8	6.00	4.39	31.2	No
45	773	804	21.7	3.89	2.20	27.8	Yes
46	842	868	18.4	6.26	4.71	29.4	No
47	797	850	25.0	7.09	3.34	35.5	Yes

TABLE III (Continued)

Specimen Number	Temperature		Leachability in 24 Hrs				Appearance of Second Phase?
	Closure	Drip	1st	2nd	3rd	Total	
48	926	935	0.30	0.23	0.39	0.96	No
49	1073	1091	0.30	0.17	0.12	0.59	No
50	849	869	0.44	0.44	0.90	1.78	No
51	817	863	27.7	6.02	2.30	36.1	No
52	974	1048	20.5	2.06	0.70	23.3	No
53	844	885	25.5	3.12	1.08	29.7	No
54	842	886	23.8	2.80	1.00	27.6	No
55	783	812	24.4	8.42	2.43	36.2	No
56	850	856	30.4	0.36	0.68	31.4	No
57	827	964	21.2	9.10	4.18	34.5	Yes
58	901	931	0.64	1.73	3.00	5.37	No
59	947	963	7.76	3.84	3.72	15.3	No
60	884	904	36.9	3.92	1.95	42.7	No
61	885	921	12.2	11.1	4.85	28.1	No
62	910	985	40.7	3.50	2.29	46.5	Yes
63	> 1200		---	---	---		---
64	1012	1090	6.07	0.31	0.16	6.54	Yes
65	917	928	0.27	0.31	0.38	0.96	No
66	877	906	0.61	0.59	0.64	1.94	No
67	730	828	1.01	1.08	1.13	3.22	No
68	880	907	2.45	2.56	2.64	7.65	No

also is presented. The "closure temperature" is that at which the material was observed to flow around the thermocouple wall in the "drip temperature" measurement. (See BNWL-80 for description of method.) The leachability per 24 hour period gives two bits of information: 1) the existence of a markedly soluble phase, as shown by a large initial leachability and a marked decrease in succeeding periods, 2) a general measure of the resistance to leaching of the particular formulation that does not show marked separation of a soluble phase.

The column labeled "Appearance of a Second Phase?" indicates whether or not there was visual evidence of the separation of two liquid phases. Many of the samples appeared to have had a solid phase precipitate from them. One of these (Specimen No. 60) was examined by x-ray fluorescence analysis to determine whether or not this was ruthenium concentrating, since it looked like ruthenium oxides.

Figure 1
Closure and Drip Temperatures
(Upper number closure, lower number drip temperature °C)

Figure 2
Closure and Drip Temperatures
(Upper number closure, lower number drip temperature °C)

Figure 3
Closure and Drip Temperatures
(Upper number closure, lower number drip temperature °C)

Figure 4
Per Cent Leached 1st 24-Hour Period

Figure 5
Per Cent Leached 1st 24-Hour Period

13

Figure 6
Per Cent Leached 1st 24-Hour Period

This measurement indicated about three-fold increase in ruthenium concentration in the bottom of the piece where the black crystals were concentrated. Judging from this analysis and the appearance of many of the specimens, there is a distinct possibility that ruthenium may concentrate in the lower part of any mass that is held molten for a period of time.

One of the important findings of this investigation was that there is a wide composition range in which separation into two liquid phases occurs in the molten state. If one looks at the tetrahedron of composition, it appears that a plane slicing through the figure (as indicated by the dotted lines in Figure 1A in the Appendix) represents a boundary between one-liquid-phase and two-liquid-phase compositions. Two observations are pertinent to this: 1) many of the light phase specimens were yellow and readily leachable, 2) melting in a reducing atmosphere eliminated or reduced the second phase in specimens 36, 37, 57, and 64 (the only ones so tested). The high borate content of 36 resulted in two phases. In this sample the color of the lighter phase changed from yellow to white, and the volume reduced, after melting in the reducing atmosphere. (The yellow color is at least partially due to sodium chromate but no quantitative analyses were made.) Segregation is undesirable from two aspects: 1) the greater leachability of this phase, and 2) segregation of fission products.

These data indicate there is a substantial range of compositions in which borate and silicate can be incorporated in phosphate melts with little or no separation. The primary reasons for considering borate addition are to lower the melting temperature and to increase fluidity.

Examination of the data indicates that small additions are not particularly helpful in reducing the closure and drip temperatures. Trying to interpret multi-dimensional behavior from the various plane sections is a difficult thing. Two of

the six planes, namely 65 and 50 atom per cent, show that the smallest measured borate additions were effective in reducing the closure and drip temperatures, while the other planes showed increases in these temperatures.

It is also observed that for none of the samples containing borate or silicate additions is there an improvement in the leach rate or solubility in the first 24-hour period, so it appears that if we are going to use phosphate as a major part of any fixation form, it should be the only anion added.

Of course, the work of other investigators has shown that the silicate and borosilicate systems can be melted with the incorporation of substantial quantities of waste. Some earlier work published in BNWL-80, along with this work, indicates the phosphate system is more efficient (i.e., requires fewer atoms of phosphorous per equivalent of waste cations -- larger M/P) in producing homogenous or pseudo-homogenous melts, with Purex-type wastes, than are borate or silicate or any combination of these two. This may be an important consideration if it is necessary to minimize the volume of the final solid.

Any final selection of a fixation form must be a trade-off of the advantages and disadvantages of the various compositions. The phosphates have the above indicated volume reduction advantage together with greater fluidity of melts and generally lower melting temperatures. There are rather restricted compositional ranges of low leachability, and it appears the silicates and borosilicates may have a wider composition range, in this respect. However, this property is obtained at the expense of increased volume and higher viscosity melts. Minimum addition melts of silicates generally are higher melting than the comparable phosphates, but it is possible to compound silicate or borosilicate melts that melt in the same range as the phosphates. Generally, the phosphate system is more corrosive than the silicate system and produces a more obnoxious off-gas. However, phosphate is simpler to add. This was one of the prime reasons for its initial investigation.

The value of the statistical analysis of this data lies primarily in the contour maps that were developed for each plane and the equations that permit interpolation. These show the directions of trends if we wish to examine in detail a given composition range. They cannot be relied on to predict exactly how a given mixture will behave, but will indicate directions a particular property may change. Extrapolation outside the experimental region is unsatisfactory.

When this investigation was being planned, it was hoped there would be sufficient smoothing and elimination of eutectics by the complex composition that the low-order equations used would adequately model the melting behavior. However, examination of the individual results, as shown in Figures 1 to 3, in comparison with the computed contour maps, indicates a finer structure variation than can be modeled by a cubic or lower degree equation. In terms of future investigations, this is interpreted as meaning that an individual waste system needs to be studied intensively over a narrow composition range if one is interested in optimizing its properties.

In terms of the mixed phosphate-borate-silicate system, this study is taken to indicate that there are very limited regions of interest. These would be defined as:

- 1) The phosphate system with less than 5 atom per cent borate or silicate near the 60% waste level.
- 2) The phosphate system with larger additions possibly up to 25% near the 40% waste level.
- 3) The silicate, borosilicate, or ternary system at less than 40 atom per cent waste near the pure silicate corner.
- 4) The limits of second phase formation when category (3) systems with more waste are melted under reducing conditions.

Since this report terminates the author's work in waste fixation, the

following general observations are offered.

The phosphate system is not amenable to "broad brush" treatment when one is trying to optimize the properties of the final solid to be produced from a given waste. Detailed investigation will be necessary to optimize phosphate content, processing temperature, and waste composition. However, when other than minimum leachability or minimum drip temperature is acceptable, the phosphate system offers the prospects of greatest volume reduction, with minimum additive that will produce an adequately mixed (not grossly segregated) melt at a temperature and viscosity that can be confidently and readily handled in remote operation. Any system that is likely to give a practical final volume of solid is unlikely to produce a solid that is insoluble enough to warrant transferring reliance for safety from the container and its storage environment to the insolubility of the solid incorporating the waste.

APPENDIX A

Statistical Analysis of Response Surface Based on
Closure Temperature, Drip Temperature, and Leachability Data
from a P-B-Si Additive System Experiment
in Purex Type Waste Solidification

J. A. Weed

Introduction

In developing the experimental design for the study of this area of waste solidification, several considerations were taken into account. First, very little information, if any, was available concerning drip temperature and solubility for specimens involving the desired ranges of the composition (controlled) variables. Second, it was desired to minimize the number of required specimens (experimental units), because the desired measurements are time consuming and hence relatively expensive. Third, it was desired to model the multi-dimensional response surfaces with second or third degree polynomials so that interpolation would be possible. Fourth, it was recognized that the ranges of the composition variables would have to be limited consistent with the requirements (a) that a second or third degree polynomial could be hoped to give a satisfactory fit to the data in the chosen ranges, and (b) that the ranges would be large enough to make the experiment scientifically and economically feasible.

The Experimental Design

Due to the nature of the desired ranges of the composition variables in the phosphate-borate-silicate system, it was reasonable to regard the study of this system as a mixture problem involving four components. The fourth component (in addition to phosphate, borate, and silicate), which will be referred to as "Metal", is a Purex waste prototype with 40 weight per cent fission product described on page 2. The basic framework for a four component mixture problem is a tetrahedron lattice, as illustrated in Figure 1A. Each point within the tetrahedron represents

* Atom per cent from waste

Figure 1A
Tetrahedron with Portion of Lattice

by its position the composition of the corresponding specimen: the position dictates, in the present case, the reduced atom per cent (defined on Page 1) of each component in the specimen. Clearly, the atom per cents for all four components must add up to 100% at each point.

In view of the four design considerations stated above, plus the fact that certain portions of the tetrahedron were not of interest, it was decided not to use the full lattice design. The region of interest was from 70 atom per cent to 40 atom per cent of the "Metal" component, which in the phosphate additive system corresponds roughly to the range of 3.5 M/P to 1.0 M/P. Here, M/P is the ratio of metal oxide equivalents to phosphate. The region of interest was further narrowed by requiring an emphasis on the phosphate component.

The set of composition points finally incorporated in the experimental design was formed by combining essentially two subsets of points. The first subset, a fairly symmetrical design in the region of interest, contained points which lay on three concentric "spheres" about the center point designated by 60% M, 20% P, 10% B, 10% Si. Points on the central "sphere" were obtained by adding 10% and subtracting 10% from two components to get all combinations which add to 100%. The inner "sphere" was obtained by adding and subtracting 5%, and the outer "sphere" by adding and subtracting 20%. Seven of these points were replicated twice to provide seven degrees of freedom for estimating experimental error and testing for goodness of fit. The second subset consisted of additional points of compositional interest. All points included in the design are listed in Table IA. The complete design is sufficient to estimate the parameters in a third degree graduating polynomial.

The experiment was carried out in accordance with the stated design and yielded closure temperature data listed in Table IIA, drip temperature data listed in Table IIIA, and solubility data listed in Table IVA. The statistical analysis of each

TABLE IA

Experiment Design

<u>Specimen #</u>	<u>Atom Per Cent "Metal"</u>	<u>Atom Per Cent Phosphorus</u>	<u>Atom Per Cent Boron</u>	<u>Atom Per Cent Silicon</u>
1	70	30	0	0
2	70	20	10	0
3	70	20	10	0
4	70	20	0	10
5	70	20	0	10
6	70	13.3	8.3	8.3
7	70	10	10	10
8	70	10	20	0
9	70	10	0	20
10	65	35	0	0
11	65	25	5	5
12	65	20	10	5
13	65	20	5	10
14	65	18.3	8.3	8.3
15	65	15	10	10
16	65	15	15	5
17	65	15	5	15
18	60	40	0	0
19	60	30	10	0
20	60	30	10	0
21	60	30	0	10
22	60	20	20	0
23	60	20	0	20
24	60	20	0	20
25	60	20	10	10
26	60	20	10	10
27	60	10	20	10
28	60	10	20	10
29	60	10	10	20
30	60	25	10	5
31	60	25	5	10
32	60	20	15	5
33	60	20	5	15
34	60	15	15	10
35	60	15	10	15
36	60	0	30	10
37	60	0	10	30
38	55	45	0	0
39	55	35	5	5
40	55	30	10	5

TABLE IA (Continued)

<u>Specimen #</u>	<u>Atom Per Cent "Metal"</u>	<u>Atom Per Cent Phosphorus</u>	<u>Atom Per Cent Boron</u>	<u>Atom Per Cent Silicon</u>
41	55	30	5	10
42	55	25	15	5
43	55	25	5	15
44	55	20	15	10
45	55	20	10	15
46	55	25	10	10
47	55	15	15	15
48	50	50	0	0
49	50	40	0	10
50	50	40	10	0
51	50	30	20	0
52	50	30	0	20
53	50	30	10	10
54	50	30	10	10
55	50	20	20	10
56	50	20	10	20
57	50	10	20	20
58	40	40	10	10
59	40	26.6	16.6	16.6
60	40	20	30	10
61	40	20	10	30
62	40	0	30	30
63	40	10	0	50
64	40	0	10	50
65	48.2	51.8	0	0
66	42.9	57.1	0	0
67	37.9	62.1	0	0
68	33.3	66.7	0	0

TABLE IIA

Closure Temperature

<u>Specimen #</u>	<u>Observed Value</u>	<u>Value Predicted by Special Cubic</u>	<u>Differences</u>
1	785	794	- 9
2	789	768	21
3	772	768	4
4	864	878	-14
5	865	878	-13
6	842	815	27
7	839	849	-10
8	810	831	-21
9	1200	1105	95
10	845	837	8
11	768	802	-34
12	789	782	7
13	791	827	-36
14	838	798	40
15	814	808	6
16	802	787	15
17	810	882	-72
18	809	868	-59
19	839	823	16
20	829	823	6
21	936	898	38
22	795	820	-25
23	913	958	-45
24	945	958	-13
25	801	795	6
26	807	795	16
27	822	809	13
28	825	809	16
29	854	873	-19
30	771	796	-25
31	790	832	-42
32	773	784	-11
33	804	853	-49
34	810	788	22
35	815	821	- 6
36	945	940	5
37	1037	1055	-18
38	884	886	- 2
39	887	862	25
40	888	824	64
41	953	860	93
42	820	801	19
43	831	861	-30
44	760	784	-24
45	773	809	-36
46	842	811	31
47	797	790	7

TABLE IIA (Continued)

<u>Specimen #</u>	<u>Observed Value</u>	<u>Value Predicted by Special Cubic</u>	<u>Differences</u>
48	926	892	34
49	1073	983	90
50	849	877	-28
51	817	855	-38
52	974	989	-15
53	844	854	-10
54	842	854	-12
55	783	794	-11
56	850	822	28
57	827	799	28
58	901	1024	-123
59	947	940	7
60	884	872	12
61	885	847	38
62	910	923	-13
63	> 1200	1163	---
64	1012	930	82
65	917	891	26
66	877	879	- 2
67	730	855	-125
68	880	822	58

TABLE IIIA

Drip Temperature

<u>Specimen #</u>	<u>Observed Value</u>	<u>Value Predicted by Special Cubic</u>	<u>Differences</u>	<u>Two Phase?</u>
1	806	846	-40	No
2	819	807	12	No
3	806	807	- 1	No
4	970	952	18	Yes
5	992	952	40	Yes
6	849	881	-32	Yes
7	953	915	38	Yes
8	823	838	-15	Yes
9	1250	1139	111	Yes
10	873	868	5	No
11	798	852	-54	No
12	818	826	- 8	Yes
13	877	885	- 8	Yes
14	883	852	31	Yes
15	837	863	-26	Yes
16	874	824	50	Yes
17	842	939	-97	Yes
18	824	885	-61	No
19	869	843	26	No
20	863	843	20	No
21	1008	949	59	No
22	812	821	- 9	No
23	925	1002	-77	Yes
24	955	1002	-47	Yes
25	856	842	14	No
26	856	842	14	No
27	838	847	- 9	Yes
28	842	847	- 5	Yes
29	878	922	-44	Yes
30	792	832	-40	No
31	819	881	-62	No
32	781	814	-33	No
33	856	904	-48	No
34	893	830	63	Yes
35	911	872	39	Yes
36	963	966	- 3	Yes
37	1056	1084	-28	Yes
38	905	897	8	No
39	933	895	38	No
40	915	857	58	No
41	993	902	91	No
42	844	830	14	No
43	868	906	-38	No
44	783	822	-39	No
45	804	854	-50	Yes

TABLE IIIA (Continued)

<u>Specimen #</u>	<u>Observed Value</u>	<u>Value Predicted by Special Cubic</u>	<u>Differences</u>	<u>Two Phase?</u>
46	868	851	17	No
47	850	835	15	Yes
48	935	904	31	No
49	1091	1018	73	No
50	869	909	-40	No
51	863	884	-21	No
52	1048	1030	18	No
53	885	891	- 6	No
54	886	891	- 5	No
55	812	826	-14	No
56	856	862	- 6	No
57	964	848	116	Yes
58	931	1062	-131	No
59	963	964	- 1	No
60	904	904	0	No
61	921	867	54	No
62	985	1011	-26	Yes
63	---	---	---	---
64	1090	1004	86	Yes
65	928	905	23	No
66	906	905	1	No
67	828	900	-72	No
68	907	891	16	No

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TABLE IVASolubility

<u>Specimen #</u>	<u>Observed Value</u>	<u>Value Predicted By Cubic</u>	<u>Differences</u>
1	22.2	27.4	-5.2
2	30.5	31.1	-0.6
3	31.9	31.1	0.8
4	30.1	31.4	-1.3
5	29.3	31.4	-2.1
6	14.1	27.9	-13.8
7	28.7	23.4	5.3
8	37.7	38.0	-0.3
9	29.8	23.5	6.3
10	22.6	11.9	10.7
11	22.6	22.1	0.5
12	29.0	22.5	6.5
13	26.6	22.7	3.9
14	19.8	22.3	-2.4
15	26.7	20.5	6.2
16	32.2	22.7	9.5
17	22.1	20.8	1.3
18	4.16	3.33	0.8
19	5.45	13.6	-8.2
20	9.86	13.6	-3.8
21	16.8	14.7	2.1
22	25.2	27.9	-2.7
23	8.47	16.7	-8.2
24	11.9	16.7	-4.8
25	17.0	19.9	-2.9
26	15.9	19.9	-4.0
27	13.2	21.3	-8.1
28	12.1	21.3	-9.2
29	9.93	17.7	-7.7
30	20.2	18.9	1.3
31	19.7	19.3	0.4
32	26.5	21.3	5.2
33	21.2	19.8	1.4
34	28.1	19.6	8.5
35	20.7	18.8	1.9
36	44.5	42.2	2.3
37	24.2	23.3	0.9
38	0.31	-0.15	0.5
39	20.10	13.7	6.4
40	11.48	17.1	-5.7
41	7.99	17.3	-9.3
42	25.0	20.7	4.3
43	16.0	19.0	-3.0
44	20.8	21.5	-0.7
45	21.7	20.7	1.0
46	18.4	19.8	-1.4

TABLE IVA (Continued)

<u>Specimen #</u>	<u>Observed Value</u>	<u>Value Predicted By Cubic</u>	<u>Differences</u>
47	25.0	20.7	4.3
48	1.26	-0.27	1.5
49	0.30	8.02	-7.7
50	0.44	8.74	-8.3
51	27.7	22.6	5.1
52	20.5	9.16	11.3
53	25.5	18.5	7.0
54	23.8	18.5	5.3
55	24.4	26.1	-1.7
56	30.4	22.1	8.3
57	21.2	24.2	-3.0
58	0.64	5.10	-4.5
59	7.76	7.51	0.3
60	36.9	38.3	-1.4
61	12.2	15.2	-3.0
62	40.7	39.5	1.2
63	----	----	----
64	6.07	2.44	3.6
65	0.27	0.17	0.1
66	0.61	1.88	-1.27
67	1.01	2.60	-1.59
68	2.45	0.94	1.51

kind of data included essentially three steps; first, selection of the "best" of three polynomial models within the capacity of the design; second, tests for "goodness of fit" of the chosen model to the data; third, contour mapping of the chosen response surface model. A discussion of this analysis will be given below for each individual response variable.

Three models were fit to the observed data for each response variable. If we denote

y = value of response variable

x_1 = atom per cent of "Metal" component

x_2 = atom per cent of phosphorus

x_3 = atom per cent of boron

x_4 = atom per cent of silicon,

then the three models take the following forms:

Quadratic:

$$y = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4$$

Special cubic:

$$y = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4 + b_{134}x_1x_3x_4 + b_{234}x_2x_3x_4$$

Cubic:

$$y = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + c_{12}x_1x_2(x_1-x_2) + c_{13}x_1x_3(x_1-x_3) + c_{14}x_1x_4(x_1-x_4) + c_{23}x_2x_3(x_2-x_3) + c_{24}x_2x_4(x_2-x_4) + c_{34}x_3x_4(x_3-x_4) + b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4 + b_{134}x_1x_3x_4 + b_{234}x_2x_3x_4.$$

The quadratic and cubic models above are the most general forms of the corresponding full second and third degree graduating polynomials in four independent variables subject to the restriction that $x_1 + x_2 + x_3 + x_4 = 1$.

Closure Temperature Response Surface Analysis

Each of the three models displayed above was fit to the observed closure temperature data. The appropriate statistical test indicated that the quadratic model does explain a statistically significant portion of the variation in the data (about the mean observation). Further statistical tests showed that the special cubic model provides a statistically significant improvement in fit over the quadratic model, but the cubic model does not significantly improve the fit over the special cubic.

A useful 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. This measure can lie between 0% and 100%. A percentage of zero implies that the model and the response variable are totally unrelated; i.e., that the model explains none of the variability in the observed data. If the coefficient of determination is 100%, then the model determines the true value of the response variable, i.e., the model explains all the variability in the data over and above experimental or random error. In the case of closure temperature, the coefficients of determination for the three models are:

quadratic - 36.0%

special cubic - 67.0%

cubic - 64.5%

It will be noted that the coefficient of determination for the cubic model is less than that for the special cubic. The coefficient of determination is a function of the number of parameters in the model, so an intuitive explanation of this situation would be that the additional variability in the data accounted for by the cubic model (over the special cubic model) is very small relative to the number of parameters added (6). Thus these coefficients of determination express quantitatively the conclusions drawn from the statistical tests described above. In view of this analysis, the special cubic was selected as the "best" of

the three models considered.

Seven of the experimental points were replicated twice, and these observations provided an estimate of "experimental error", i.e., random or chance error inherent within the experimental procedure itself. A statistical test for "goodness of fit" uses an estimate of experimental error to determine whether a given model does or does not explain all the variation among the observations over and above experimental error. In the case of closure temperature, the appropriate test indicated that the special cubic gives a "poor" fit to the data, in the sense that it does not explain all variation among the observations over and above experimental error.

In summary, then, for the case of closure temperature, it was found that the special cubic does the "best" job among the three basic models in explaining a statistically significant portion of the variation in the observations (about 67%), but that it does not explain all variation over and above experimental error, i.e., there is a significant portion of the systematic variation which is left unexplained. Thus, the special cubic cannot be expected to provide accurate predictions because the model does not adequately represent the true surface, but the model does fit sufficiently well to indicate real gross trends within the region of experimentation.

The estimates of the coefficients for the closure temperature special cubic were calculated by least squares as follows:

$b_1 = 276.735$	$b_{23} = 12424.6$
$b_2 = 270.491$	$b_{24} = 32530.9$
$b_3 = -2317.48$	$b_{34} = 35878.2$
$b_4 = -8101.56$	$b_{123} = -24140.8$
$b_{12} = 2474.38$	$b_{124} = -56674.6$
$b_{13} = 7069.44$	$b_{134} = -62766.8$
$b_{14} = 17669.4$	$b_{234} = -37757.4$

It is to be observed that when these coefficient estimates are used in the special cubic model to predict values of closure temperature, the decimal values of the composition variables should be used, not the percentages; for example, substitute $x_1 = .60$, $x_2 = .20$, $x_3 = .10$, $x_4 = .10$, not $x_1 = 60$, $x_2 = 20$, $x_3 = 10$, $x_4 = 10$.

In addition to the observed value, Table IIA lists the predicted value for each experimental point in the design. Figures 2A, 3A, 4A, and 5A show contour graphs of the special cubic for closure temperature at cross sections of 70, 60, 50 and 40 atom per cent "Metal" component, respectively. The dashed portions of the curves represent extrapolations of the surface outside the region of experimentation.

Drip Temperature Response Surface Analysis

The response surface analysis for closure temperature and drip temperature were similar in several respects, probably due to the nature of the physical relationship between the two response variables. Each of the three models was fit to the observed drip temperature data and the appropriate statistical tests indicated 1) that the quadratic model explains a statistically significant portion of the variability in the data, 2) that the special cubic gives a significant improvement in fit over the quadratic, and 3) that the cubic does not significantly improve the fit over the special cubic. The coefficients of determination (defined above) for the three models are:

quadratic	- 36.2%
special cubic	- 60.8%
cubic	- 60.1%

Again the cubic coefficient of determination is lower than that for the special cubic, as explained above. Therefore, just as in the case of closure temperature, the special cubic was selected as the "best" of the three models considered.

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Figure 2A

Closure Temperature Special Cubic Contour Graph at 70% M.

Figure 3A

Closure Temperature Special Cubic Contour Graph at 60% M.

Figure 4A

Closure Temperature Special Cubic Contour Graph at 50% M

Figure 5A

Closure Temperature Special Cubic Contour Graph at 40% M

The appropriate "goodness of fit" test indicated that the special cubic gives a "poor" fit to the observed drip temperature data, in the sense that it does not explain all variation among the observations over and above experimental error.

Thus, the special cubic is the "best" of the three models in accounting for a statistically significant portion of the variation in drip temperature observations, and hence it may be used to indicate real trends within the region of experimentation. However, the special cubic will not provide accurate predictions because the model does not adequately represent the true response surface. Since the cubic does not significantly improve the fit over the special cubic, it is reasonable to suggest that higher degrees than the cubic, as well as higher order interactions, would be required to account for an additional significant portion of the variation.

The estimates of the coefficients for the drip temperature special cubic were calculated by least squares as follows:

$b_1 = 607.822$	$b_{23} = 13960.7$
$b_2 = 695.587$	$b_{24} = 28270.7$
$b_3 = -1967.74$	$b_{34} = 31993.9$
$b_4 = -7199.97$	$b_{123} = -25028.2$
$b_{12} = 1009.54$	$b_{124} = -46255.5$
$b_{13} = 5267.73$	$b_{134} = -49719.3$
$b_{14} = 14970.2$	$b_{234} = -45786.7$

As previously noted, when these coefficient estimates are used in the special cubic model, the decimal values of the composition variables should be used, not the percentages.

Table IIIA lists both predicted and observed values for each experimental point in the design. Figures 6A, 7A, 8A and 9A show contour graphs of the special cubic for drip temperature at cross sections of 70, 60, 50, and 40 atom per cent "Metal" component, respectively. Dashed portions indicate extrapolations of the

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Figure 6A

Drip Temperature Special Cubic Contour Graph at 70% M.

Figure 7A

Drip Temperature Special Cubic Contour Graph at 60% M.

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Figure 8A

Drip Temperature Special Cubic Contour Graph at 50% M.

Figure 9A

Drip Temperature Special Cubic Contour Graph at 40% M.

surface.

Solubility Response Surface Analysis

Each of the three models was fit to the observed solubility data and the corresponding coefficients of determination were calculated as follows:

quadratic	- 59.1%
special cubic	- 59.8%
cubic	- 66.2%

The appropriate statistical tests indicated that

- 1) The quadratic model explains a statistically significant portion of the variability in the data; i.e., the quadratic coefficient of determination of 59.1% is significantly different from zero and is not likely to have occurred this large simply by chance;
- 2) The special cubic does not significantly improve the fit over the quadratic; i.e., the difference between the quadratic and special cubic coefficients of determination is not statistically significant;
- 3) The cubic gives a statistically significant improvement in fit over the special cubic; i.e., the special cubic and cubic coefficients of determination are significantly different: the difference between 59.8% and 66.2% is so large that it is not likely to have occurred purely by chance.

The appropriate "goodness of fit" test indicated that the cubic model gives a "poor" fit to the observed solubility data, in the sense that it does not account for all variation among the observations over and above experimental error.

Thus, the cubic model, which is the "best" of the three models considered, may be used to indicate real trends in the true response surface within the region of experimentation; but it will not provide accurate predictions because the model does not adequately represent the true surface.

The estimates of the coefficients for the solubility cubic were calculated by least squares as follows:

$$\begin{array}{ll}
 b_1 = 363.411 & c_{12} = -1174.55 \\
 b_2 = -204.421 & c_{13} = -965.410 \\
 b_3 = 1864.35 & c_{14} = -1857.88 \\
 b_4 = 320.593 & c_{23} = 1943.08 \\
 b_{12} = -319.047 & c_{24} = 1374.66 \\
 b_{13} = -3149.59 & c_{34} = -2743.77 \\
 b_{14} = -829.599 & b_{123} = 8411.00 \\
 b_{23} = -5126.95 & b_{124} = 8328.07 \\
 b_{24} = -3527.32 & b_{134} = 9519.26 \\
 b_{34} = -6585.60 & b_{234} = 8353.79
 \end{array}$$

When these estimates are used in the cubic model, the decimal values of composition variables should be used, not percentages.

Table IVA lists both predicted and observed values for each experimental point in the design. Figures 10A, 11A, 12A and 13A show contour graphs of the cubic model for solubility at cross sections of 70, 60, 50 and 40 atom per cent "Metal" component, respectively. Due to the method of calculating these contour maps for a cubic model, it was more convenient to plot them as shown than to retain the true relative scale between levels as was done for special cubic contours. As before, all dashed portions indicate extrapolations of the surface beyond the region of experimentation.

Figure 10A

Solubility Cubic Contour Graph at 70% M.

Figure 11A

Solubility Cubic Contour Graph at 60% M.

Figure 12A

Solubility Cubic Contour Graph at 50% M.

Figure 13A

Solubility Cubic Contour Graph at 40% M.

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