Selection of a Glass-Ceramic Formulation to Immobilize Fluorinel-Sodium Calcine

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ABSTRACT

Glass-ceramic forms have been developed for immobilizing Fluorinel/Na calcine. The glass-ceramic products are created by hot isostatically pressing (HIPing) each combination of additives and calcine at high temperatures and high pressures. Products of three formulations appeared to have good potential in developmental testing for immobilizing this waste type. However, none had been subjected to a processability test in which the sensitivity of a characteristic to change in processing conditions is identified. The ability of these forms to retain durability properties with systematic changes in process parameters is defined in this investigation.

In this investigation the candidate formulations were subjected to a rigorous processability test based on response surface methodology using the XSTAT statistical design software package. Dominant processing parameters identified in a precursor screening study were used as independent variables. The combinations of independent variables under which the formulations were formed were determined by commanding XSTAT to derive a face centered cube design. Products of each formulation were formed under these conditions, then subjected to the MCC-1 static leach test to determine resistance to aqueous corrosion. Responses to the test were used not only to identify the formulation with the most durable products but also that whose products were least sensitive to changes in processing conditions.

Based on the results of this application, glass-ceramic products of the titanium-based formulation are clearly the most durable and least sensitive to changes in processing conditions. Titanium-based glass-ceramic products are therefore recommended as most suitable for preparing glass-ceramics from radioactive Fluorinel/Na calcines and for use in scale-up tests. It is further recommended that response to a processability test, such as applied here, be routinely used to aid in determining the best glass or glass-ceramic formulation to immobilize each calcine type.

EXECUTIVE SUMMARY

One option for immobilizing calcined high level wastes produced by nuclear fuel reprocessing activities at the Idaho Chemical Processing Plant (ICPP) is conversion to a glass-ceramic form through hot isostatic pressing. Calcines exist in several different chemical compositions, and thus candidate formulations have been developed for converting each to glass-ceramic forms which are potentially resistant to aqueous corrosion and stable enough to qualify for repository storage. Fluorinel/Na, a chemically complex calcine type, is one of the types being stored at ICPP, and development efforts have identified three formulations with potential for immobilizing it. These are a glass forming additive that uses aluminum metal to enhance reactivity, a second glass forming additive that uses titanium metal to enhance reactivity and a third that uses not only a combination of silicon and titanium metals but enough phosphorous pentoxide to form a calcium phosphate host phase in the glass-ceramic product. Glass-ceramics of each formulation performed well in restricted characterization tests. However, none of the three was subjected to rigorous testing that would provide information on whether each was processable, that is able to retain favorable characteristics over a practical range of processing conditions.

The first step in observing processability is to identify those processing (independent) variables that have dominant effects on important product characteristics. This is accomplished through screening experiments, and such was a precursor to this study. Through application of traditional screening methods, amount of metal used to enhance reactivity, calcine particle size, HIPing time, HIPing temperature and calcine loading were determined as dominating the durability of the glass-ceramic product. After this determination, processability as a function of dominant process parameters can be investigated by forming the product in systematic testing using the limits of dominant process parameters in order to represent the ranges possible in processing conditions. The most efficient means of doing this is through the use of response surface methodology. This empirical procedure uses mathematically derived test matrices to produce quadratic models that define the relationship between dominant processing parameters and product characteristics. The test matrices enlarge with the number of process parameters (independent variables) being tested. Because five process parameters were used in this test the matrix consisted of 32 tests. Response surface models have the form:

$$y = b_0 + \sum_{j=1}^p b_j x_j + \sum_{\substack{j=1 \\ j'=1 \\ j'>j}}^p b_{jj'} x_j x_{j'} + \sum_{j=1}^p b_{jj} x_j^2 + \epsilon,$$

In this model for p independent variables x_j and $x_{j'}$ are discrete independent variables (process parameters), b_0 , b_j , $b_{jj'}$ and b_{jj} are coefficients, ϵ is experimental error and y is an dependent variable (response). Thus because the effects of five process parameters were observed, the models derived in this study contained 21 terms. The test arrays, model derivation, statistical diagnoses, response surfaces and transmitted error operations used in this study were performed using the XSTAT experimental design software package. The result was the derivation of

models that define the resistance to aqueous leachability of Al, B, Ca, Cd, Cr, K, Na, Si and total mass as a function of process variables for products of each formulation studied. Resistance to aqueous leachability was defined using the response to the 14- and 28-day MCC-1 static leach test.

The derivation and application of response surface models in this study identify the glass-ceramic with superior durability and processability properties for immobilizing Fluorinel/Na calcine. Equally important, the processability, or the range of parameter conditions which permits processing in order to obtain a product with the best durability properties is identified. This vital information cannot be obtained from studies in which only components or a single parameter are varied to obtain a desired response. Specifically, the process parameters that dominate elemental and total mass leachabilities and the sensitivities of these leachabilities to changes in process parameters are determined in this study for each candidate formulation. The principal results of this application are that within the processing conditions of the test:

1. The titanium-based glass-ceramic waste forms were superior to aluminum and phosphate based waste forms tested with respect to elemental leaching properties as measured by the MCC-1 static leach test.
2. These properties of the titanium-based glass-ceramic waste forms were also the least sensitive of the formulations studied to changes in the subject process parameters.
3. HIPing time, HIPing temperature and calcine particle size affected elemental leaching properties of the titanium-based glass-ceramics more than calcine loading and amount of titanium metal.
4. The leachability of all elements investigated, except Cd and Cr, from the titanium-based waste forms did not differ between the 14- and 28-day MCC-1 leach test.
5. Empirical models, that in most cases fit data well, have been derived to express the relationships between elemental leachabilities and dominant process parameters held within ranges that could be equivalent to those of the full-scale process.

It is recommended that the titanium metal based formulation be used in future scale-up studies for the preparation of glass-ceramic forms from nonradioactive Fluorinel/Na calcines produced in the engineering scale calciners. The other formulations investigated in this study cannot be recommended for either radioactive or scale-up studies until their glass and crystalline phases are improved to a durability similar to that of the titanium-based waste form.

Because of the amount and type of new information acquired in this study, it is strongly recommended that a test be applied routinely to determine the relative processability of the best formulations for immobilizing each calcine type. Response surface methodology or some other systematic exposure to operating conditions should make up the processability test. This action would be applied to glass and glass-ceramic candidate waste forms developed through theoretical

and empirical approaches in which only compositions are altered. Its application would identify the best performer in a processing scenario. Adopting such a development strategy provides a sounder basis for selecting the best candidates for further development and provides basic information for technical personnel tasked with developing a full-scale process for producing the waste form.

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SELECTION OF A GLASS-CERAMIC FORMULATION TO IMMOBILIZE FLUORINEL-SODIUM CALCINE

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December, 1994

I. INTRODUCTION

Since 1963 highly radioactive liquid wastes generated from the reprocessing of nuclear fuels at the Idaho Chemical Processing Plant (ICPP) have been routinely calcined to solid granular waste. Presently nearly 4000 cubic meters of calcined high-level waste (HLW) are stored at the ICPP eliminating the problems of storing liquid wastes on a long term basis. However, the calcined waste is not suitable for permanent storage because it is dispersable and leachable.^{1,2,3} Thus a major goal of the Idaho High-Level Waste Management Program is to develop materials that immobilize the radioactive and hazardous components of calcined wastes in a manner that is required by repository storage criteria. One of the options being investigated on a laboratory scale basis for suitable immobilization of calcine is densification, through hot isostatic pressing (HIPing), to a glass-ceramic form. Glass-ceramic materials are attractive because they are as durable as borosilicate glass waste forms developed for calcined ICPP HLW and HLW at other USDOE sites. Glass-ceramic forms can also be loaded up to 75 wt% with calcined ICPP HLW and densified through HIPing to reduce final volumes by 60% over that achievable by glass forms developed for the same purpose.^{4,5}

Glass-ceramic precursors are prepared by thoroughly mixing glass forming additives, certain crystalline phase forming additives and conditioners with ground, stabilized calcine. Nonradioactive calcines prepared in pilot and engineering scale calciners are being used in the studies performed to date. These calcines are prepared to simulate the product obtained in the New Waste Calcining Facility from calcining aluminum, Fluorinel or zirconium fuel wastes blended with sodium-rich wastes from decontamination activities and laboratory effluents. These wastes are known as alumina/Na, Fluorinel/Na and zirconia/Na calcines, respectively. Additives to densify the calcine to a durable and stable glass-ceramic product are derived through use of the CERCOMP spreadsheet and through applying phase equilibria principles in systematic experimentation.^{6,7} After mixing, the calcine-additive mixture is compacted into a can which is evacuated, sealed then HIPed at high temperature and pressure for at least four hours to result in a glass-ceramic product. Within the product is a glass phase to host alkali oxides and boric oxide from the HLW. Primary crystalline phases retained from calcine (calcium fluoride and zirconia) are present. These have potential to host certain radionuclides and hazardous species. Secondary crystalline phases, those formed during HIPing (zircon, zirconolite, sphene and apatite), are also present. These also have the potential to host radionuclides.

The glass-ceramic forms produced are subjected to testing in order to evaluate their potential for further development. This testing primarily investigates the chemical durability and stability of the forms through:

1. X-ray diffraction analysis (XRD) to identify the crystalline phases present,
2. Scanning electron microscopy (SEM) to observe the physical structure of the product and to analyze the chemical composition of the phases present,
3. Pycnometry to determine the density of the product and
4. Leach testing through application of the MCC-1 static leach test and others to evaluate the ability of the product to withstand aqueous corrosion.

Further testing of mechanical and thermal properties of the glass-ceramic forms will be performed to obtain information on their suitability for future development.

II. PURPOSE

The purpose of this study is to define the practical range of dominant processing parameters over which the subject formulations for immobilizing Fluorinel/Na calcine will result in glass-ceramic waste forms that retain desirable properties and thus have potential for further development. This study thus provides vital information to evaluate the practicality of converting Fluorinel/Na calcines to glass-ceramic forms on a full-scale basis and for developing a process to prepare them. The processing parameters which govern the conversion of calcined ICPP HLW to durable glass-ceramic forms were identified through the use of scoping tests, the application of the Plackett-Burman screening design and full factorial design experiments.^{8,9,10,11,12,13} The dominant process parameters identified by these include reactant mixing, HIPing soak time, HIPing temperature, calcine particle size, amount of glass forming additive and amount of calcine. This practice provides the best conditions for identifying the potential of a formulation to produce a glass-ceramic that will immobilize HLW. It does not, however, provide information on the "processability" of the product or on its ability to retain desirable properties when processing conditions deviate from optimal. Such information can be obtained only from a rigorous investigation in which the effects of systematically changed process parameters on properties of the product are observed.

III. METHODOLOGY

After the formulation of a product is defined, the next logical action is the identification of those processing variables which determine its characteristics. Such actions have been performed, as discussed above, in the development of ICPP glass-ceramic waste forms through scoping and screening studies.^{8,9,10,11,12,13} When dominant processing variables are identified, the next major action which must be performed is to define the relationship between the product characteristics, $y_{1...m}$ and the dominant process parameters, $X_{1...m}$ within the practical range of processing conditions, or:

$$y = f(X_1, X_2, \dots, X_m)$$

The most useful way of defining this relationship is through mathematical modeling. A complete modeling expression must contain terms which define the effects on characteristics of continuous independent variables and of the interaction of independent variables on product characteristics of interest. Complete theoretical expressions may exist for the relationship of dependent to independent variables in a complex process, but they can rarely be defined in a practical manner. However, empirically derived polynomial models can be defined over limited ranges of independent variables to adequately approximate the theoretical relationships.^{14,15} First order polynomial models are rarely useful because they estimate only constant and linear terms. The most useful models are second order quadratic expressions because they estimate constant, linear, interaction and second order terms.^{15,16,17} Cubic and higher order terms are seldom useful in these models. Typically these polynomial expansions have the form:

$$y = b_0 + \sum_{j=1}^p b_j x_j + \sum_{\substack{j=1 \\ j'=1 \\ j'>j}}^p b_{jj'} x_j x_{j'} + \sum_{j=1}^p b_{jj} x_j^2 + \epsilon,$$

for p independent variables. These models are known as response surface designs because the response of the product characteristic, y , can be represented as a surface in process parameter subspaces.⁸ In this empirical model, x_j and $x_{j'}$ are discrete independent variables (process parameters), b_0 , b_j , $b_{jj'}$ and b_{jj} are coefficients, ϵ is experimental error and y is an dependent variable (response). Where two independent variables, x_1 and x_2 , are being considered such a model would have the form:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + \epsilon.$$

The practical value of these models is their ability to predict responses over an experimental region and to produce response surfaces that define the total effects of independent variables on system responses within that region. In response surface methodology, the dependent variables (y 's) are obtained by conducting systematic tests in which the independent variables (x 's) are controlled over arbitrary ranges defined by minimum, maximum and midpoint values. The coefficients (b 's) in the response surface model are obtained by multiple regression techniques based on least squares methods.¹⁴ The coefficients estimate the relative importance of the independent variables, their interactions and second order effects.

Where coefficients derived from multiple regression techniques allow the model to fit the values of dependent variables adequately, response surface models interpolate excellently within the chosen ranges of the independent variables. Beyond these ranges the response surface designs deviate rapidly from theoretical expressions. Thus a good response surface design interpolates well but extrapolates poorly.

Before response surface designs are applied, the number of independent variables (process parameters) that will be used are determined through scoping or screening tests. The number of these variables used will determine the number of tests that must be run to derive a response surface model and therefore the complexity of that model. Many response surface designs have been defined, and certain of these are useful in special experimental situations.¹⁶ For example, the face-centered cube design, a composite fractional factorial design, minimizes the number of

tests required to be run at the minimum, maximum and midpoint of the range of the independent variables.¹⁶ Where five independent variables (factors) are being investigated, the face-centered cube design has the form given in Table 1. A single test can be performed to determine the response, Y_i , of a run, however it is better practice to perform replicate tests and use the arithmetic mean of these to determine the response, Y_i . The information generated by this design (responses) is symmetrical allowing constant prediction variance because the minimum and maximum values of the controlled parameters (independent variables) are chosen to be equidistant from the midpoint. In Table 1 the minimum, maximum and midpoint values of the independent variables (X_{1-5}) tested in this study are represented by -, + and o respectively, and Y_{1-i} represents any number of dependent variables (responses).

Performing response surface methodology then requires running each test in the design matrix and determining the values of the responses for the characteristic of interest. The numerical values of these responses are used by multiple regression techniques to determine the coefficients in the second order model for the response. In this manner a model can be derived for any continuous response of interest.

In order to derive useful models, however, the following criteria must be met;

1. Experimental error must be approximately the same at each point in the design or must be a constant fraction of the response at any point in the design.
2. The minimum and maximum levels of the independent variables must be far enough apart such that their effects are greater than experimental error.
3. The tests of the design should be run in a random order to reduce the influence of systematic error.
4. The limit and midpoint values of the independent variables being studied must be repeated as closely as possible in each test.
5. Independent variables not being studied must be controlled as much as possible at constant levels.

Personal computer software packages have been created to perform the multiple regression operations that derive the response surface models. These packages also perform various operations with the models including optimization of independent variables, application of transmitted error and perturbation analysis. They also contain statistical diagnostic routines including analysis of variance, residuals analysis and lack of fit exercises that evaluate the fit of the model to the responses. The response surface methodology applied in this study is from the software package XSTAT, version 1.1 (John Wiley & Sons, Inc. New York, New York). XSTAT can derive response surface models for quadratic equations with up to five independent variables and for an essentially unlimited number of continuous responses. Macros developed at the DuPont Quality Management & Technology Center were also applied to enhance the capabilities of XSTAT in defining and analyzing the response surface models derived in this study.

Table 1
Face-Centered Cube Design for Five Independent Variables

	Controlled Parameters					Responses
Run No.	X_1	X_2	X_3	X_4	X_5	$Y_1 \dots Y_i$

Run No.	X_1	X_2	X_3	X_4	X_5	$Y_1 \dots Y_i$
1	-	+	-	-	+	
2	+	+	-	-	-	
3	-	-	-	-	-	
4	+	-	-	-	+	
5	-	+	+	-	-	
6	+	+	-	-	+	
7	-	-	+	-	+	
8	+	-	+	-	-	
9	-	+	-	+	-	
10	+	+	-	+	+	
11	-	-	-	+	+	
12	+	-	-	+	-	
13	-	+	+	+	+	
14	+	+	+	+	-	
15	-	-	+	+	-	
16	+	-	+	+	+	
17	-	0	0	0	0	
18	+	0	0	0	0	
19	0	+	0	0	0	
20	0	-	0	0	0	
21	0	0	-	0	0	
22	0	0	+	0	0	
23	0	0	0	-	0	
24	0	0	0	+	0	
25	0	0	0	0	-	
26	0	0	0	0	+	
27	0	0	0	0	0	
28	0	0	0	0	0	
29	0	0	0	0	0	
30	0	0	0	0	0	
31	0	0	0	0	0	
32	0	0	0	0	0	

IV. MATERIALS

4.1 Additives

Three basic additive formulations have been identified as having superior potential for converting Fluorinel/Na calcine to glass-ceramic forms.^{6,7,13} All of these formulations contain additives that create an aluminoborosilicate glass phase in the product. They are prepared with substances that either enhance the durability of the glass phase or promote the growth of desirable crystalline phases. Other components of the additives form auxiliary crystalline phases that have the potential to host specific radionuclides. The compositions of the formulations used in this study were prepared with simulated Fluorinel/Na calcine to make a product containing 70 wt% calcine. They are given in Table 2.

Table 2

Formulations Evaluated in this Study, Wt%

Component	Aluminum Additive	Titanium Additive	P ₂ O ₅ Additive
Calcine	70.0	70.0	70.0
Aluminum	2.0	0.0	1.0
Titanium	0.0	5.0	0.0
Silicon	0.0	0.0	2.0
SiO ₂	28.0	22.6	14.0
B ₂ O ₃	0.0	2.4	0.0
P ₂ O ₅	0.0	0.0	5.0
MgO	0.0	0.0	8.0
Total	100.0	100.0	100.0

4.1.1 Aluminum Formulation

This reactant was generated through use of the CERCOMP spreadsheet and consists of aluminum metal and silica.^{6,7,9} Silica forms an aluminoborosilicate glass phase with the alkali oxides, alumina, and boric oxide in the calcine. When properly reacted, this glass phase should also host certain radionuclides and hazardous species from the calcines. Aluminum appears to condition the glass phase viscosity by controlling the ratio of bridging to nonbridging oxygen bonds in the glass structure. At an optimal viscosity level a metastable microcrystalline structure of fluorite and zirconia results which minimizes aqueous leachability of the glass phase. When a glass-ceramic product loaded at 70 wt% Fluorinel/Na calcine is prepared, about 2 wt% aluminum appears to optimize this phenomenon resulting in a reduction of total mass and normalized elemental leach rates to less than 1 g/m²-day. In this case there is a silica content of 28 wt% in the product.

4.1.2 Titanium Formulation

This reactant was also generated through use of the CERCOMP spreadsheet and consists of titanium metal, boria and silica.¹² Silica forms an aluminoborosilicate glass phase with the alkali oxides, alumina and boric oxide in the calcine. Titanium added in the range of 3-6 wt% appears to condition the glass phase viscosity in a manner similar to aluminum resulting in a metastable crystallinity that minimizes aqueous leachabilities. Additional boric oxide over that present in the calcine appears to be required to obtain proper glass phase reactivity in the presence of titanium. When a glass-ceramic product loaded at 70 wt% Fluorinel/Na calcine is prepared, about 5 wt% titanium appears to result in a reduction of total mass and normalized elemental leach rates to less than 1 g/m²-day. In this case there is a silica content of 22.5 wt% and a boric oxide content of 2.5 wt% in the product.

4.1.3 Phosphate Formulation

This reactant was conceived through phase equilibrium studies in order to evaluate the ability of a crystalline phosphate phase to form in a glass-ceramic without adversely affecting the glass phase.¹³ Silica is included in this additive to react with waste alkali oxides, alumina and boric oxide to form the aluminoborosilicate glass phase. Phosphorous pentoxide in the additive combines with waste calcium to form calcium phosphate in the form of apatite, a thermodynamically favorable phase, which has the potential to host transuranic species. The optimal amount of phosphorous pentoxide appears to be around 5 wt% in the product when it is loaded with 70 wt% calcine. Under these conditions about 8 wt% magnesium oxide is required in the additive to act as a fluxing agent in the glass phase. The presence of magnesium oxide in the glass also controls the amount of calcium that enters the glass phase. Small amounts of aluminum and silicon metals are added to control the glass phase viscosity and therefore its reactivity.

4.2 Calcine

Run 17 simulated Fluorinel/Na calcine prepared in the enclosed 30-cm calciner was the waste used in this study. Each of the three reactant formulations identified above were combined with this calcine in proportions dictated by the limits (see Table 4) of the five factor face-centered cube design given in Table 1. Calcine was prepared for use by combining four parts by weight of particles with one part by weight of fines. As-formed particles were used as the upper size limit for the calcine particle size variable in the face-centered cube design (see Tables 5-7). These are designated "16" in the design. Calcine particles ground to pass a 140 mesh screen (US std sieve) were used for the lower size limit of this variable. These are designated "140" in the design. Calcine particles ground to pass a 78 mesh screen (US std sieve) were used for the midpoint of this variable. These are designated "78" in the face-centered cube design (see Tables 5-7), but an 80 mesh screen was used to collect this fraction. All calcine was stabilized at 600°C for thirty hours to remove the bulk of volatile species adsorbed during the calcination process. The nominal oxide composition of the calcine before stabilization is given in Table 3.

Table 3

Composition of Calcine Used in This Study

	Element Wt% Fluorinel/Na Run 17		Oxide Wt% Fluorinel/Na Run 17 ^a
Al	5.6	Al ₂ O ₃	11.8
B	1.0	B ₂ O ₃	3.4
Ca	24.9	CaO	10.2
Cd	4.6	CdO	5.9
Ce	<0.1	Ce ₂ O ₃	<0.1
Cr	1.0	Cr ₂ O ₃	1.6
Cs	<0.1	Cs ₂ O	<0.1
F	17.3	CaF ₂	40.0
Fe	0.3	Fe ₂ O ₃	0.5
Hg	<0.1	HgO	<0.1
K	0.8	K ₂ O	1.1
Mn	0.1	MnO ₂	0.2
Na	3.5	Na ₂ O	5.3
Ni	0.1	NiO	0.2
Sr	<0.1	SrO	0.1
Zr	13.1	ZrO ₂	19.7

^a Calculated normalized values after removal of volatile species

V. APPLICATION

The primary characteristic of interest of the glass-ceramic forms being developed to immobilize ICPP calcined HLW is the ability to withstand aqueous corrosion in a manner that meets expected repository acceptance criteria. The results of studies referred to above indicate that the following processing variables appear to dominate this characteristic of the glass-ceramic forms:

1. Calcine Particle Size
2. HIPing Temperature
3. HIPing Time
4. Calcine Loading
5. Amount of Redox Control Additive
6. Mixing

Based on experience in conducting past glass-ceramic waste form development studies and projections of full-scale processing requirements, upper and lower limits for these processing variables were selected. These are given with midpoints in Table 4.

Table 4

Values of Limits and Centerpoints of Independent Variables Used in Response Surface Study

Level	Wt% Reactant	Particle Size ^a	HIP Time, hrs	HIP Temp °C	Wt% Calcine Loading
-	^b	<140	4	975	65
0	^c	<78	16	1025	70
+	^d	>16	28	1075	75

^a As formed calcine particles for + level are >16 mesh, US Std sieve (1190 microns). At the midpoint all calcine particles are <78 mesh, US Std sieve (184 microns), and are <140 mesh, US Std sieve (105 microns) for the - level.

^b 1 wt% for aluminum formulation, 4 wt% for titanium formulation and 3 wt% for phosphate formulation.

^c 2 wt% for aluminum formulation, 5 wt% for titanium formulation and 5 wt% for phosphate formulation.

^d 3 wt% for aluminum formulation, 6 wt% for titanium formulation and 7 wt% for phosphate formulation.

Thus, when these values are placed in the face-centered cube array for five independent variables (see Table I above) the following three test matrices given in Tables 5-7 result. All conditions of preparation, formation test conditions and sampling, other than those in the design, were held constant as much as possible throughout this test.

The calcine and additive loading variables are applied not only to determine the effects of amount of each, but also to identify the effects of incomplete calcine-additive mixing. In such an application the lower limits would give the effects of "lean" amounts of each and upper limits would give the effects of "rich" amounts of each. The particle size variable is included to determine the effects of differing maximum calcine particle size. The HIPing temperature variable spans the region from minimum practical glass phase reactivity to an upper limit determined by the onset of weld failure in the 304 stainless steel HIP cans. The HIPing time variable is included to identify the effects of various soak times on glass-ceramic product properties. The range chosen spans from the shorter soak periods used in laboratory development studies to the longer soak periods that can be expected in a full scale process.

Responses determined (Ys) for products of each formulation investigated in this study include:

1. Density.
2. Total mass loss when subjected to the MCC-1 Static Leach Test¹⁸.
3. Leachability of Al, B, Ca, Cd, Cr, Cs, K, Na, Si, Sr when subject to the MCC-1 Static Leach Test¹⁸.
4. Glass phase Al, Ca and Na content.

Other responses of the products of each formulation may be determined in future studies. The HIPing cans used to contain the products formed in this study have also been retained in order to observe changes in metallurgical properties resulting from varying the HIPing conditions used in this study.

Table 5

Face-Centered Cube Design of Five Independent Variables for Aluminum Formulation
Controlled Parameters

Run No.	Wt% Al	Calcine Particle Size ^a	HIP Time Hrs	HIP Temp. °C	Calcine Loading Wt%	Responses
1	1	16	4	975	75	Y ₁Y _n
2	3	16	4	975	65	
3	1	140	4	975	65	
4	3	140	4	975	75	
5	1	16	28	975	65	
6	3	16	28	975	75	
7	1	140	28	975	75	
8	3	140	28	975	65	
9	1	16	4	1075	65	
10	3	16	4	1075	75	
11	1	140	4	1075	75	
12	3	140	4	1075	65	
13	1	16	28	1075	75	
14	3	16	28	1075	65	
15	1	140	28	1075	65	
16	3	140	28	1075	75	
17	1	78	16	1025	70	
18	3	78	16	1025	70	
19	2	16	16	1025	70	
20	2	140	16	1025	70	
21	2	78	4	1025	70	
22	2	78	28	1025	70	
23	2	78	16	975	70	
24	2	78	16	1075	70	
25	2	78	16	1025	65	
26	2	78	16	1025	75	
27	2	78	16	1025	70	
28	2	78	16	1025	70	
29	2	78	16	1025	70	
30	2	78	16	1025	70	
31	2	78	16	1025	70	
32	2	78	16	1025	70	

^a16: <1190 microns, 78: <184 microns, 140:>105 microns

Table 6

Face-Centered Cube Design of Five Independent Variables for Titanium Formulation

Run No.	Controlled Parameters				Calcine Loading Wt%	Responses
	Wt% Ti	Calcine Particle Size ^a	HIP Time Hrs	HIP Temp. °C		
1	4	16	4	975	75	Y ₁ Y _n
2	6	16	4	975	65	
3	4	140	4	975	65	
4	6	140	4	975	75	
5	4	16	28	975	65	
6	6	16	28	975	75	
7	4	140	28	975	75	
8	6	140	28	975	65	
9	4	16	4	1075	65	
10	6	16	4	1075	75	
11	4	140	4	1075	75	
12	6	140	4	1075	65	
13	4	16	28	1075	75	
14	6	16	28	1075	65	
15	4	140	28	1075	65	
16	6	140	28	1075	75	
17	4	78	16	1025	70	
18	6	78	16	1025	70	
19	5	16	16	1025	70	
20	5	140	16	1025	70	
21	5	78	4	1025	70	
22	5	78	28	1025	70	
23	5	78	16	975	70	
24	5	78	16	1075	70	
25	5	78	16	1025	65	
26	5	78	16	1025	75	
27	5	78	16	1025	70	
28	5	78	16	1025	70	
29	5	78	16	1025	70	
30	5	78	16	1025	70	
31	5	78	16	1025	70	
32	5	78	16	1025	70	

^a16: <1190 microns, 78: <184 microns, 140: >105 microns

Table 7

Face-Centered Cube Design of Five Independent Variables for P_2O_5 Formulation

Run No.	Wt% P_2O_5	Controlled Parameters			Calcine Loading Wt%	Responses
		Calcine Particle Size ^a	HIP Time Hrs	HIP Temp. °C		
1	3	16	4	975	75	$Y_1, \dots, Y_n$
2	7	16	4	975	65	
3	3	140	4	975	65	
4	7	140	4	975	75	
5	3	16	28	975	65	
6	7	16	28	975	75	
7	3	140	28	975	75	
8	7	140	28	975	65	
9	3	16	4	1075	65	
10	7	16	4	1075	75	
11	3	140	4	1075	75	
12	7	140	4	1075	65	
13	3	16	28	1075	75	
14	7	16	28	1075	65	
15	3	140	28	1075	65	
16	7	140	28	1075	75	
17	3	78	16	1025	70	
18	7	78	16	1025	70	
19	5	16	16	1025	70	
20	5	140	16	1025	70	
21	5	78	4	1025	70	
22	5	78	28	1025	70	
23	5	78	16	975	70	
24	5	78	16	1075	70	
25	5	78	16	1025	65	
26	5	78	16	1025	75	
27	5	78	16	1025	70	
28	5	78	16	1025	70	
29	5	78	16	1025	70	
30	5	78	16	1025	70	
31	5	78	16	1025	70	
32	5	78	16	1025	70	

^a16: <1190 microns, 78: <184 microns, 140: >105 microns

VI. PREPARATION

In the preparation of all formulations the calcine-additive mixture was mechanically precompacted at 5000 psi into 304 stainless steel HIPing cans. These cans measure one inch in diameter by three inches in length with a wall thickness of 0.028 inch. After filling, the cans were evacuated to 100 millitorr and sealed by welding. Sealed cans were transferred to the HIP and processed according to the conditions dictated by the test choice taken from the designs given in Tables 5-7. A 10.5°C per minute heat up and cool down time was used to enter and exit the HIP soak time period. After HIPing, the ends and bodies of the cans were removed and samples taken by diamond saw cutting from the glass-ceramic product for leach testing by the MCC-1 static leach test, scanning electron microscopy (SEM) and x-ray diffraction analysis (XRD). Product samples were taken at random locations for leach testing and prepared in accordance with directions given for the MCC-1 static leach test.¹⁸ Product samples taken to evaluate the information on glass phase composition by SEM techniques were polished and coated with graphite conductor. Product samples taken for XRD analysis were ground using an impact mortar to pass a 200 mesh (US std) sieve.

VII. CHARACTERIZATION

7.1 Density

Although this test was designed to investigate the effects of dominant process parameters on glass-ceramic leaching properties as determined by the MCC-1 static leach test, the effects on product density were also observed and subjected to the modelling actions by XSTAT. The density of each product was determined by subjecting duplicate monoliths to helium displacement pycnometry, a nondestructive technique, before leach testing. Three replicates of each measurement were taken, and an arithmetic mean of each was used by XSTAT response surface methodology to derive density models. The arithmetic means of the densities determined for formulation products subjected to the test design are given in Table 8.

Table 8

Densities Obtained by Performing the Face Centered Cube Test
Array on Products of Subject Formulations

No.	Wt% ^a	Controlled Parameters			Calcine Loading Wt%	Density g/cm ³		
		Calcine Particle Size ^b	HIP Time Hrs	HIP Temp. °C		Al ^c	Ti ^d	P ₂ O ₅ ^e
1	-	16	4	975	75	3.18	3.08	3.19
2	+	16	4	975	65	3.00	3.10	3.07
3	-	140	4	975	65	2.96	2.98	3.12
4	+	140	4	975	75	3.10	3.15	3.02
5	-	16	28	975	65	2.97	3.05	3.09
6	+	16	28	975	75	3.08	3.21	3.06
7	-	140	28	975	75	3.00	3.13	3.06
8	+	140	28	975	65	2.99	3.14	3.17
9	-	16	4	1075	65	2.95	3.05	3.09
10	+	16	4	1075	75	3.09	3.17	3.08
11	-	140	4	1075	75	3.03	3.23	3.20
12	+	140	4	1075	65	2.99	3.15	3.22
13	-	16	28	1075	75	3.05	3.14	3.19
14	+	16	28	1075	65	3.00	3.16	3.34
15	-	140	28	1075	65	3.08	3.01	3.06
16	+	140	28	1075	75	3.08	3.20	3.13
17	-	78	16	1025	70	3.03	3.15	3.12
18	+	78	16	1025	70	3.03	3.13	3.19
19	0	16	16	1025	70	3.08	3.16	3.17
20	0	140	16	1025	70	3.05	3.20	3.21
21	0	78	4	1025	70	3.02	3.11	3.21
22	0	78	28	1025	70	3.05	3.18	3.26
23	0	78	16	975	70	3.04	3.17	3.11
24	0	78	16	1075	70	3.05	3.15	3.03
25	0	78	16	1025	65	3.02	3.13	3.12
26	0	78	16	1025	75	3.07	3.11	3.03
27	0	78	16	1025	70	3.05	3.04	3.23
28	0	78	16	1025	70	3.03	3.15	3.18
29	0	78	16	1025	70	3.01	3.14	3.19
30	0	78	16	1025	70	3.03	3.11	3.20
31	0	78	16	1025	70	3.04	3.09	3.24
32	0	78	16	1025	70	3.04	3.12	3.16

^a See Table 4 for limit and centerpoint amounts of additives in each formulation.

^b U. S. Std sieve size; 16; > 1190 microns, 78; < 184 microns, 140: < 105 microns

^c Aluminum formulation products

^d Titanium formulation products

^e P₂O₅ formulation products

7.2 Leaching Properties

Sample monoliths of products formed in this study were subjected to the 14-day MCC-1 static leach test in order to observe the effects of process parameters on durability. The test was conducted at 90 °C with deionized distilled water in the sample surface area to leachate volume (SA/V) ratio of 10 cm⁻¹. Elemental concentrations in the leachates were determined by inductively coupled plasma atomic emission spectroscopy (ICP) for Al, B, Ca, Cd, Cr, Si and Sr and atomic emission spectroscopy (AES) for Cs, Na and K. Leachate elemental concentrations were corrected by subtracting the corresponding blank concentrations. The elemental leachabilities and total mass losses from test matrix samples for each formulation are given in Tables 9-11. Total mass loss of the sample monoliths was determined by direct weighing before and after the test. Normalized elemental leaching rates were calculated by the equation:

$$NL_i = \frac{C_i}{f_i (SA/V) d}$$

where:

NL_i = the normalized mass of element "i" lost per unit surface of the sample per day (g/m²-day)

C_i = concentration of element "i" in the leachate, corrected for blank

f_i = mass fraction of element "i" in the specimen before leaching

SA/V = ratio of sample surface area (m²) to volume of leachate (m³)

d = days leached.

Total mass loss rates were calculated by the equation:

$$TMLR = \frac{W_i - W_f}{(SA/V)d}$$

where:

TMLR = total mass loss rate (g/m²-day)

W_i = initial mass of the sample (g)

W_f = sample mass after leach test (g)

SA/V = ratio of sample surface area (m²) to volume of leachate (m³)

d = days leached.

Tables 9-11 collect the leaching responses of products of each formulation in the face-centered cube test design.

Table 9
Elemental Leachabilities and Total Mass Losses (TMLR) of Products Formed from
Aluminum Additive and Fluorinel/Na Calcine

Run	Process Parameters ^a				Leaching Response to the MCC-1 Static Leach Test (g/m ² -day)											TMLR
	Aluminum	Meshsize	HIPTime	HIPTemp	Loading	Al	B	Ca	Cd	Cr	Cs	Na	K	Si	Sr	
1	1.0	16.0	4.0	975.0	75.0	1.87	10.20	0.96	0.03	0.0	0.00	6.41	1.16	0.25	0.71	1.05
2	3.0	16.0	4.0	975.0	65.0	1.15	8.38	0.79	0.05	0.2	0.00	2.81	0.91	0.30	0.29	0.63
3	1.0	140.0	4.0	975.0	65.0	0.32	4.20	3.78	0.78	81.9	0.00	13.68	3.55	0.36	5.89	3.88
4	3.0	140.0	4.0	975.0	75.0	0.37	1.65	0.25	0.42	0.0	0.00	1.12	0.64	0.25	0.01	0.35
5	1.0	16.0	28.0	975.0	65.0	0.37	3.14	3.79	0.65	100.0	0.00	30.73	13.24	0.28	7.19	4.35
6	3.0	16.0	28.0	975.0	75.0	0.74	2.56	0.33	0.03	0.0	0.00	1.91	1.10	0.46	0.03	0.42
7	1.0	140.0	28.0	975.0	75.0	0.36	1.89	3.66	1.04	87.6	0.00	20.82	11.47	0.29	7.55	5.00
8	3.0	140.0	28.0	975.0	65.0	0.28	2.04	0.35	0.21	0.0	0.00	1.83	0.86	0.23	0.10	0.20
9	1.0	16.0	4.0	1075.0	65.0	0.34	0.67	2.96	0.72	66.1	0.00	0.98	1.92	0.29	3.75	2.91
10	3.0	16.0	4.0	1075.0	75.0	0.37	0.31	0.25	0.75	0.0	0.00	0.80	0.49	0.31	0.01	0.41
11	1.0	140.0	4.0	1075.0	75.0	0.48	0.69	2.20	0.38	80.7	0.00	19.00	0.99	0.43	3.71	1.27
12	3.0	140.0	4.0	1075.0	65.0	0.20	0.61	0.31	1.40	0.0	0.00	0.44	0.26	0.17	0.01	0.36
13	1.0	16.0	28.0	1075.0	75.0	0.57	0.56	1.07	0.26	0.0	0.00	22.03	5.27	0.43	1.43	3.42
14	3.0	16.0	28.0	1075.0	65.0	0.32	1.04	0.52	0.19	0.0	0.00	1.16	0.87	0.29	0.10	0.32
15	1.0	140.0	28.0	1075.0	65.0	0.36	0.49	3.13	0.71	41.5	0.00	7.95	1.93	0.37	4.13	2.54
16	3.0	140.0	28.0	1075.0	75.0	0.38	0.35	0.31	0.19	0.0	0.00	1.41	0.79	0.42	0.01	1.01
17	1.0	78.0	16.0	1025.0	70.0	0.45	0.76	3.08	0.59	107.2	0.00	25.29	4.58	0.35	4.86	4.06
18	3.0	78.0	16.0	1025.0	70.0	0.33	1.75	0.26	0.20	0.0	0.00	1.24	0.96	0.29	0.19	0.37
19	2.0	16.0	16.0	1025.0	70.0	0.35	0.94	0.87	0.49	0.0	0.00	8.81	2.40	0.35	0.66	1.33
20	2.0	140.0	16.0	1025.0	70.0	0.42	1.56	1.05	0.01	0.1	0.00	9.72	2.68	0.38	1.51	1.67
21	2.0	78.0	4.0	1025.0	70.0	0.59	2.52	0.48	0.02	0.0	0.00	2.12	1.40	0.54	0.30	0.64
22	2.0	78.0	28.0	1025.0	70.0	0.37	1.50	1.66	0.40	0.0	0.00	13.48	3.42	0.34	2.46	2.28
23	2.0	78.0	16.0	975.0	70.0	1.27	1.46	0.64	0.01	0.0	0.00	3.75	2.30	0.26	0.01	2.69
24	2.0	78.0	16.0	1075.0	70.0	0.38	0.32	0.84	0.07	0.1	0.00	6.35	1.10	0.31	1.29	1.23
25	2.0	78.0	16.0	1025.0	65.0	0.29	1.63	1.70	0.59	0.0	0.00	5.58	2.05	0.31	1.92	1.50
26	2.0	78.0	16.0	1025.0	75.0	0.32	0.85	0.67	0.36	0.0	0.00	5.92	1.83	0.36	0.14	1.02
27	2.0	78.0	16.0	1025.0	70.0	0.34	1.25	1.01	0.46	0.1	0.00	6.87	3.47	0.35	1.29	2.00
28	2.0	78.0	16.0	1025.0	70.0	0.37	1.50	1.08	0.24	0.0	0.00	10.37	2.79	0.37	1.14	1.60
29	2.0	78.0	16.0	1025.0	70.0	0.33	0.77	0.69	0.82	0.0	0.00	8.55	3.63	0.35	0.99	1.20
30	2.0	78.0	16.0	1025.0	70.0	0.42	1.85	1.51	0.11	0.0	0.00	11.78	3.02	0.57	1.52	1.80
31	2.0	78.0	16.0	1025.0	70.0	0.38	1.65	1.34	0.42	0.0	0.00	8.27	2.45	0.43	1.10	1.45
32	2.0	78.0	16.0	1025.0	70.0	0.36	1.03	0.87	0.94	0.0	0.00	7.23	1.72	0.33	0.72	1.16

- a Aluminum = weight per cent Al metal in product
 Meshsize = Maximum sieve size (U.S. Std) of calcine particles
 HIPTime = HIPing soak time in hours
 HIPTemp = HIPing soak temperature in Deg. C
 Loading = Weight percent calcine in product

Table 10
Elemental Leachabilities and Total Mass Losses (TMLR) of Products Formed from Titanium
Additive and Fluorinel/Na Calcine

Run	Process Parameters ^a					Leaching Response to the MCC-1 Static Leach Test (g/m ² -day)										TMLR
	Titanium	Meshsize	HIPTime	HIPTemp	Loading	Al	B	Ca	Cd	Cr	Cs	Na	K	Si	Sr	
1	4.0	16.0	4.0	975.0	75.0	2.83	2.75	0.92	0.01	0.01	0.00	3.02	0.49	0.34	0.08	0.44
2	6.0	16.0	4.0	975.0	65.0	1.23	1.47	0.33	0.03	0.62	0.00	1.66	1.09	0.54	0.04	0.41
3	4.0	140.0	4.0	975.0	65.0	0.41	0.41	0.25	1.05	0.99	0.00	0.53	0.48	0.29	0.07	0.31
4	6.0	140.0	4.0	975.0	75.0	0.66	0.57	0.21	0.99	0.01	0.00	0.89	0.80	0.55	0.01	0.30
5	4.0	16.0	28.0	975.0	65.0	0.83	1.05	0.29	0.13	0.43	0.00	1.88	1.10	0.49	0.04	0.51
6	6.0	16.0	28.0	975.0	75.0	0.98	0.99	0.23	0.03	0.55	0.00	1.76	1.34	0.74	0.01	0.34
7	4.0	140.0	28.0	975.0	75.0	0.75	0.99	0.34	0.20	0.51	0.00	5.80	1.40	0.53	0.91	1.08
8	6.0	140.0	28.0	975.0	65.0	0.22	0.38	0.41	0.52	0.54	0.00	0.86	0.49	0.14	0.14	0.10
9	4.0	16.0	4.0	1075.0	65.0	0.53	0.46	0.36	1.23	0.32	0.00	1.59	0.82	0.39	0.13	0.49
10	6.0	16.0	4.0	1075.0	75.0	0.78	0.76	0.24	0.06	0.16	0.00	1.21	1.13	0.71	0.01	0.35
11	4.0	140.0	4.0	1075.0	75.0	0.94	0.84	0.21	0.32	1.13	0.00	1.15	1.34	0.89	0.48	0.32
12	6.0	140.0	4.0	1075.0	65.0	0.76	2.44	0.34	0.39	0.37	0.00	2.41	1.78	0.51	0.01	0.39
13	4.0	16.0	28.0	1075.0	75.0	0.80	0.78	0.22	0.06	0.01	0.00	1.47	1.13	0.68	0.01	0.32
14	6.0	16.0	28.0	1075.0	65.0	0.89	1.04	0.35	0.03	0.01	0.00	2.54	1.67	0.61	0.10	0.38
15	4.0	140.0	28.0	1075.0	65.0	0.48	0.44	0.11	0.28	0.01	0.00	0.92	0.81	0.39	0.10	0.24
16	6.0	140.0	28.0	1075.0	75.0	0.54	0.43	0.30	0.20	0.70	0.00	0.68	0.60	0.52	0.01	0.22
17	4.0	78.0	16.0	1025.0	70.0	1.06	1.21	0.21	0.18	0.61	0.00	1.74	1.22	0.57	0.07	0.39
18	6.0	78.0	16.0	1025.0	70.0	1.01	2.40	0.11	0.39	0.52	0.00	2.51	0.94	0.24	0.24	0.40
19	5.0	16.0	16.0	1025.0	70.0	0.87	0.89	0.21	0.32	0.01	0.00	1.81	1.33	0.52	0.01	0.34
20	5.0	140.0	16.0	1025.0	70.0	0.74	0.93	0.17	0.20	1.20	0.00	1.60	1.04	0.44	0.52	0.29
21	5.0	78.0	4.0	1025.0	70.0	0.31	0.29	0.24	0.32	0.52	0.00	0.46	0.37	0.24	0.11	0.17
22	5.0	78.0	28.0	1025.0	70.0	0.50	0.70	0.21	0.21	0.47	0.00	1.35	0.98	0.37	0.41	0.32
23	5.0	78.0	16.0	975.0	70.0	0.48	0.49	0.24	0.20	0.41	0.00	1.09	0.79	0.32	1.83	0.21
24	5.0	78.0	16.0	1075.0	70.0	0.84	0.87	0.14	0.39	0.98	0.00	1.83	1.27	0.66	0.17	0.35
25	5.0	78.0	16.0	1025.0	65.0	0.49	0.61	0.24	0.32	0.01	0.00	1.14	0.71	0.37	0.01	0.26
26	5.0	78.0	16.0	1025.0	75.0	0.43	0.40	0.20	0.45	0.01	0.00	0.73	0.64	0.36	0.01	0.27
27	5.0	78.0	16.0	1025.0	70.0	0.71	0.92	0.16	0.17	1.25	0.00	1.61	1.16	0.45	0.52	0.40
28	5.0	78.0	16.0	1025.0	70.0	0.90	1.18	0.16	0.38	0.52	0.00	1.89	1.38	0.64	0.33	0.36
29	5.0	78.0	16.0	1025.0	70.0	0.77	1.56	0.23	0.12	0.39	0.00	1.77	1.33	0.50	0.01	0.36
30	5.0	78.0	16.0	1025.0	70.0	0.76	1.22	0.19	0.13	0.01	0.00	1.93	1.27	0.47	0.01	0.40
31	5.0	78.0	16.0	1025.0	70.0	0.70	1.00	0.17	0.15	1.12	0.00	1.71	0.16	0.46	0.42	0.34
32	5.0	78.0	16.0	1025.0	70.0	0.85	1.04	0.17	0.11	1.18	0.00	1.87	1.38	0.50	0.42	0.31

- a Titanium = weight percent Ti metal in product
 Meshsize = Maximum Sieve Size (U.S. Std) of calcine particles
 HIPTime = HIPing soak time in hours
 HIPTemp = HIPing soak temperature in Deg. C
 Loading = Weight percent calcine in product

Table 11
Elemental Leachabilities and Total Mass Losses (TMLR) of Products Formed from Phosphorous
Pentoxide Additive and Fluorinel/Na Calcline

Run	Process Parameters ^a				Leaching Response to the MCC-1 Static Leach Test (g/m ² -day)												TMLR
	P205	Meshsize	HIPTime	HIPTemp	Loading	Al	B	Ca	Cd	Cr	Cs	Na	K	Si	Sr		
1	3.0	16.0	4.0	975.0	75.0	0.72	3.37	0.45	0.01	0.05	0.00	0.75	2.4	0.66	0.08	0.34	
2	7.0	16.0	4.0	975.0	65.0	1.26	6.94	0.15	0.05	0.43	0.00	0.29	4.9	0.57	0.04	0.31	
3	3.0	140.0	4.0	975.0	65.0	0.48	81.21	0.45	0.45	3.88	0.00	16.23	114.6	0.54	0.01	10.03	
4	7.0	140.0	4.0	975.0	75.0	0.26	0.47	0.07	1.31	0.01	0.00	0.76	0.8	0.53	0.01	0.29	
5	3.0	16.0	28.0	975.0	65.0	0.44	88.71	0.40	0.57	2.91	0.00	4.38	120.1	0.49	0.04	8.94	
6	7.0	16.0	28.0	975.0	75.0	0.36	0.60	0.10	0.94	0.46	0.00	0.72	1.1	0.47	0.01	0.37	
7	3.0	140.0	28.0	975.0	75.0	0.45	0.79	0.16	0.23	0.78	0.00	0.27	1.0	0.39	1.23	0.46	
8	7.0	140.0	28.0	975.0	65.0	1.60	5.27	0.38	0.49	0.79	0.00	0.77	3.5	0.80	0.10	0.45	
9	3.0	16.0	4.0	1075.0	65.0	0.40	77.43	0.47	0.32	2.71	0.00	1.91	85.2	0.56	0.01	0.54	
10	7.0	16.0	4.0	1075.0	75.0	0.25	0.44	0.11	1.80	0.01	0.00	0.61	1.0	0.33	0.01	0.24	
11	3.0	140.0	4.0	1075.0	75.0	1.19	1.96	0.21	0.27	1.12	0.00	0.92	3.5	0.98	0.48	0.48	
12	7.0	140.0	4.0	1075.0	65.0	0.75	4.95	0.15	0.27	0.01	0.00	0.31	3.1	0.33	0.01	0.34	
13	3.0	16.0	28.0	1075.0	75.0	0.47	0.61	0.14	0.32	0.01	0.00	0.50	1.0	0.38	0.01	0.22	
14	7.0	16.0	28.0	1075.0	65.0	1.07	7.67	0.54	0.04	0.01	0.00	0.63	6.0	0.70	0.10	0.66	
15	3.0	140.0	28.0	1075.0	65.0	0.03	67.76	0.15	0.07	0.10	0.00	1.85	78.2	0.07	0.10	4.34	
16	7.0	140.0	28.0	1075.0	75.0	0.38	0.43	0.09	0.53	0.42	0.00	0.62	1.0	0.42	0.01	0.16	
17	3.0	78.0	16.0	1025.0	70.0	2.61	16.69	0.02	0.02	0.44	0.00	0.55	16.0	1.25	0.03	1.12	
18	7.0	78.0	16.0	1025.0	70.0	0.59	1.64	0.29	0.12	0.76	0.00	1.00	1.4	0.54	0.38	0.37	
19	5.0	16.0	16.0	1025.0	70.0	0.99	2.12	0.21	0.03	0.01	0.00	0.52	2.7	0.82	0.09	0.45	
20	5.0	140.0	16.0	1025.0	70.0	1.19	3.36	0.16	0.03	1.22	0.00	0.59	3.1	0.89	0.52	0.50	
21	5.0	78.0	4.0	1025.0	70.0	1.16	3.59	0.28	0.02	1.09	0.00	0.72	4.3	0.90	0.09	0.54	
22	5.0	78.0	28.0	1025.0	70.0	1.07	2.18	0.20	0.03	0.50	0.00	0.49	2.6	0.85	0.30	0.50	
23	5.0	78.0	16.0	975.0	70.0	0.95	3.27	0.01	0.03	0.42	0.00	0.60	2.8	0.62	1.83	0.38	
24	5.0	78.0	16.0	1075.0	70.0	0.85	2.04	0.20	0.02	1.35	0.00	0.48	2.7	0.76	5.91	0.44	
25	5.0	78.0	16.0	1025.0	65.0	1.83	40.34	0.12	0.02	0.01	0.00	0.80	2.6	0.43	0.01	1.26	
26	5.0	78.0	16.0	1025.0	75.0	0.49	0.47	0.14	0.78	0.01	0.00	0.41	0.7	0.30	0.01	0.42	
27	5.0	78.0	16.0	1025.0	70.0	1.10	2.38	0.19	0.04	1.22	0.00	0.47	2.7	0.89	0.51	0.41	
28	5.0	78.0	16.0	1025.0	70.0	0.67	1.70	0.17	0.15	0.67	0.00	0.45	2.2	0.48	0.03	0.28	
29	5.0	78.0	16.0	1025.0	70.0	0.53	2.05	0.17	0.12	0.01	0.00	0.47	2.2	0.51	0.01	0.42	
30	5.0	78.0	16.0	1025.0	70.0	1.04	2.22	0.06	0.85	0.01	0.00	0.51	3.0	2.14	0.01	0.57	
31	5.0	78.0	16.0	1025.0	70.0	1.22	2.50	0.18	0.05	1.17	0.00	0.52	3.0	2.91	0.42	0.45	
32	5.0	78.0	16.0	1025.0	70.0	1.31	5.78	0.11	0.07	0.11	0.00	0.73	4.0	2.40	0.01	0.55	

a P205 = weight per cent phosphorous pentoxide in product
Meshsize = Maximum sieve size (U.S. Std) of calcine particles
HIPTime = HIPing soak time in hours
HIPTemp = HIPing soak temperature in Deg. C
Loading = Weight percent calcine in product

VIII. DISCUSSION AND ANALYSIS OF RESULTS

8.1 Density

The data in Table 8 indicate that the densities of the aluminum formulation products are lower than those of products of the other two formulations investigated. Also, the densities of the P_2O_5 formulation products are generally higher than those of the titanium formulation products.

Inspection of the data in Table 8 also indicates that the changes in density for products of each formulation are generally small ($<10\%$). Thus, the models obtained did not fit the density data well in a statistical nature, and they are therefore not presented in this document. The results indicate a dependence on the process parameters investigated, however a more sensitive analysis will be required to obtain statistically accurate models. It is also likely that HIPing pressure has an effect on product density and should therefore be included as a process variable in any response surface methodology application.

8.2 Leaching Characteristics

Certain qualitative observations can be made of the results given in Tables 9-11. Cesium and strontium leachabilities from products of the three formulations investigated are too low to be accurately determined by spectrochemical techniques. Accurate investigations of the leachability of these elements will have to rely on radioassay when radioactive calcines are used to form glass-ceramic products that will be subjected to leach testing. All waste forms tested performed well in immobilizing aluminum, cadmium and silicon. In addition, the titanium-based glass-ceramic was the most durable with respect to calcium and chromium leachability and total mass loss. The generally low chromium leachability from the titanium-based glass-ceramic indicates good conversion of chromium from the very mobile hexavalent state to the less mobile trivalent state. The high leachability of calcium, chromium, potassium and sodium from the aluminum-based glass-ceramic almost always occurs when low amounts of aluminum metal (1 wt%) are present in that formulation. Likewise, a similar correlation may be present for the leachability of boron and sodium from the P_2O_5 -based glass-ceramic to which the low amount (3 wt %) of P_2O_5 is added. Any correlation to main process parameter effects of boron leachability from the aluminum or titanium formulation products is obscure. The leachability data given in the tables above suggests that when subjected to the test matrix of this study the titanium-based glass-ceramic is the most durable of the waste form types tested.

8.3 Derivation of Response Surface Models

Applying the FIT command of XSTAT to the responses given in Tables 9-11 above results in the derivation of regression models for the subject leachabilities. Each is a second order model containing twenty-one terms. These models can be used to interpolate the respective responses everywhere within the experimental region defined by the limits of each process parameter. Response surface models were not derived for cesium and strontium leachabilities because of their extremely low presence (0.1 wt% each) in Run 17 calcine. Likewise, low presence makes the results obtained for modeling chromium (1.0 wt% in Run 17 calcine) and potassium (0.8 wt% in Run 17 calcine) questionable. XSTAT also performs lack of fit analyses on each model. These result in an R^2 lack of fit coefficient for the multiple regression which indicates how well the model fits the response data in Tables 9-11. The R^2 values for each model are given in Table 12.

Based on the R^2 values given in Table 12 most leaching property models derived adequately fit the respective data in Tables 9-11. Models for Cr and K have R^2 generally less than 0.90. These elements are minor constituents in each waste form. Thus, the best reason for their leaching responses not fitting respective models as well as those of other elements is analytical uncertainty. The models obtained for Si leachability have R^2 less than 0.90. This is because Si leachability is insensitive to changes in the process parameters used.

Table 12
Lack of Fit Coefficients (R^2) for Models Derived by XSTAT
for Leaching Characteristics of Subject Products

	<u>Aluminum Formulation</u>	<u>Titanium Formulation</u>	<u>P₂O₅ Formulation</u>
Aluminum	.919	.906	.628
Boron	.942	.872	.989
Calcium	.969	.983	.815
Cadmium	.720	.953	.951
Chromium	.961	.617	.825
Potassium	.976	.854	.957
Sodium	.948	.913	.956
Silicon	.800	.854	.706
Total Mass	.967	.910	.959

The models derived from XSTAT for expressing boron, sodium and silicon leachabilities from the three waste forms subjected to the 14-day MCC-1 test are given in Tables 13-21. Models derived for aluminum, calcium, cadmium, chromium, potassium and total mass leachabilities of the same waste forms to this test are given in Appendix A, Tables A-1 to A-20. Each model includes constant, main effect, interaction and second order terms. The coefficient for each term in the model has been determined by multiple regression, thus the standard error is a measure of its uncertainty. The T-value tests the hypothesis that the coefficient is not zero. Based on this, the confidence level that the coefficient is significant is also given. Each model can be solved to obtain leachability of the subject element within the space defined by the limits of the process parameters used in preparation of the formulation product. Thus, the models can be solved by XSTAT through use of the MINIMUM or MAXIMUM commands to give a singular leachability solution based on any set of process parameter combinations, but it is more useful to derive a response surface which defines leachability over the range of process parameters used.

Table 13
Response Surface Model for Leachability of Boron from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
1.196	1 (constant)	0.2466	4.849	99.9%
-0.2172	ALUMINUM	0.2034	1.068	67.5%
-0.7956	MESHSIZE	0.2034	3.912	99.8%
-0.8700	HIPTIME	0.2034	4.278	99.8%
-1.693	HIPTEMP	0.2034	8.327	99.9%
-0.1744	LOADING	0.2034	0.8578	57.1%
-0.02125	ALUMINUM*MESHSIZE	0.2157	0.0985	19.4%
0.2950	ALUMINUM*HIPTIME	0.2157	1.368	79.5%
0.2937	ALUMINUM*HIPTEMP	0.2157	1.362	79.3%
-0.7525	ALUMINUM*LOADING	0.2157	3.489	99.6%
0.6175	MESHSIZE*HIPTIME	0.2157	2.863	98.7%
0.8787	MESHSIZE*HIPTEMP	0.2157	4.074	99.8%
-0.1975	MESHSIZE*LOADING	0.2157	0.9156	60.1%
0.9350	HIPTIME*HIPTEMP	0.2157	4.335	99.9%
-0.02125	HIPTIME*LOADING	0.2157	0.0985	19.4%
0.03500	HIPTEMP*LOADING	0.2157	0.1623	21.9%
0.1689	ALUMINUM^2	0.5500	0.3071	28.3%
0.1639	MESHSIZE^2	0.5500	0.2980	27.9%
0.9239	HIPTIME^2	0.5500	1.680	88.0%
-0.1961	HIPTEMP^2	0.5500	0.3566	30.7%
0.1539	LOADING^2	0.5500	0.2798	27.0%

Confidence figures are based on 11 degrees of freedom

Table 14
Response Surface Model for Leachability of Sodium from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
2.481	1 (constant)	0.2098	11.83	99.9%
-2.068	ALUMINUM	0.1730	11.95	99.9%
-0.2328	MESHSIZE	0.1730	1.345	78.7%
1.535	HIPTIME	0.1730	8.871	99.9%
-1.201	HIPTEMP	0.1730	6.938	99.9%
-0.1028	LOADING	0.1730	0.5939	43.0%
0.1769	ALUMINUM*MESHSIZE	0.1835	0.9637	62.5%
-1.436	ALUMINUM*HIPTIME	0.1835	7.822	99.9%
1.138	ALUMINUM*HIPTEMP	0.1835	6.201	99.9%
0.1169	ALUMINUM*LOADING	0.1835	0.6368	45.3%
-0.3994	MESHSIZE*HIPTIME	0.1835	2.176	95.3%
-0.2931	MESHSIZE*HIPTEMP	0.1835	1.597	86.1%
1.013	MESHSIZE*LOADING	0.1835	5.520	99.9%
-0.9506	HIPTIME*HIPTEMP	0.1835	5.179	99.9%
0.3181	HIPTIME*LOADING	0.1835	1.733	89.2%
0.4219	HIPTEMP*LOADING	0.1835	2.299	96.3%
0.5630	ALUMINUM^2	0.4680	1.203	73.3%
0.3330	MESHSIZE^2	0.4680	0.7116	49.4%
0.2030	HIPTIME^2	0.4680	0.4339	34.5%
-0.5070	HIPTEMP^2	0.4680	1.083	68.2%
-0.2670	LOADING^2	0.4680	0.5704	41.7%

Confidence figures are based on 11 degrees of freedom

Table 15
Response Surface Model for Leachability of Silicon from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.3600	1 (constant)	0.0160	22.54	99.9%
-0.02111	ALUMINUM	0.0132	1.603	86.3%
-0.006111	MESHSIZE	0.0132	0.4639	36.1%
0.008889	HIPTIME	0.0132	0.6748	47.4%
0.01833	HIPTEMP	0.0132	1.392	80.3%
0.03278	LOADING	0.0132	2.488	97.5%
-0.03375	ALUMINUM*MESHSIZE	0.0140	2.416	97.1%
0.01750	ALUMINUM*HIPTIME	0.0140	1.253	75.3%
-0.02500	ALUMINUM*HIPTEMP	0.0140	1.789	90.2%
0.02125	ALUMINUM*LOADING	0.0140	1.521	84.1%
-0.01625	MESHSIZE*HIPTIME	0.0140	1.163	71.7%
0.01375	MESHSIZE*HIPTEMP	0.0140	0.9842	63.5%
-0.002500	MESHSIZE*LOADING	0.0140	0.1789	22.6%
0.01250	HIPTIME*HIPTEMP	0.0140	0.8947	59.0%
0.01875	HIPTIME*LOADING	0.0140	1.342	78.6%
0.02125	HIPTEMP*LOADING	0.0140	1.521	84.1%
-0.03757	ALUMINUM^2	0.0356	1.055	66.9%
0.007430	MESHSIZE^2	0.0356	0.2086	23.9%
0.08243	HIPTIME^2	0.0356	2.314	96.4%
-0.07257	HIPTEMP^2	0.0356	2.037	93.9%
-0.02257	LOADING^2	0.0356	0.6335	45.1%

Confidence figures are based on 11 degrees of freedom

Table 16
Response Surface Model for Leachability of Boron from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.9366	1 (constant)	0.1230	7.617	99.9%
0.07500	TITANIUM	0.1014	0.7396	50.8%
-0.2139	MESHSIZE	0.1014	2.109	94.7%
-0.2256	HIPTIME	0.1014	2.224	95.8%
-0.09056	HIPTEMP	0.1014	0.8929	58.9%
0.05611	LOADING	0.1014	0.5533	40.8%
0.1700	TITANIUM*MESHSIZE	0.1076	1.580	85.7%
-0.000000	TITANIUM*HIPTIME	0.1076	0.0000	15.9%
0.2913	TITANIUM*HIPTEMP	0.1076	2.708	98.3%
-0.4025	TITANIUM*LOADING	0.1076	3.742	99.7%
0.03250	MESHSIZE*HIPTIME	0.1076	0.3021	28.1%
0.3537	MESHSIZE*HIPTEMP	0.1076	3.289	99.4%
-0.1675	MESHSIZE*LOADING	0.1076	1.557	85.1%
0.04875	HIPTIME*HIPTEMP	0.1076	0.4532	35.5%
-0.04000	HIPTIME*LOADING	0.1076	0.3719	31.4%
-0.2937	HIPTEMP*LOADING	0.1076	2.731	98.4%
1.157	TITANIUM^2	0.2743	4.219	99.8%
-0.01279	MESHSIZE^2	0.2743	0.0466	17.5%
-0.4078	HIPTIME^2	0.2743	1.487	83.2%
-0.2428	HIPTEMP^2	0.2743	0.8852	58.5%
-0.3828	LOADING^2	0.2743	1.396	80.4%

Confidence figures are based on 11 degrees of freedom

Table 17
Response Surface Model for Leachability of Sodium from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
1.543	1 (constant)	0.1365	11.30	99.9%
-0.1989	TITANIUM	0.1126	1.767	89.8%
-0.1167	MESHSIZE	0.1126	1.036	66.0%
0.2411	HIPTIME	0.1126	2.142	95.0%
-0.2050	HIPTEMP	0.1126	1.821	90.8%
0.1806	LOADING	0.1126	1.604	86.3%
-0.1731	TITANIUM*MESHSIZE	0.1194	1.450	82.1%
-0.2569	TITANIUM*HIPTIME	0.1194	2.151	95.1%
0.4856	TITANIUM*HIPTEMP	0.1194	4.067	99.8%
-0.5906	TITANIUM*LOADING	0.1194	4.946	99.9%
0.1944	MESHSIZE*HIPTIME	0.1194	1.628	86.9%
-0.08812	MESHSIZE*HIPTEMP	0.1194	0.7380	50.8%
0.2506	MESHSIZE*LOADING	0.1194	2.099	94.6%
-0.3094	HIPTIME*HIPTEMP	0.1194	2.591	97.9%
0.2144	HIPTIME*LOADING	0.1194	1.795	90.3%
-0.5931	HIPTEMP*LOADING	0.1194	4.967	99.9%
0.7480	TITANIUM^2	0.3045	2.456	97.3%
0.3280	MESHSIZE^2	0.3045	1.077	67.9%
-0.4720	HIPTIME^2	0.3045	1.550	84.9%
0.08297	HIPTEMP^2	0.3045	0.2725	26.7%
-0.4770	LOADING^2	0.3045	1.567	85.4%

Confidence figures are based on 11 degrees of freedom

Table 18
Response Surface Model for Leachability of Silicon from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.4248	1 (constant)	0.0280	15.17	99.9%
0.005000	TITANIUM	0.0231	0.2166	24.2%
-0.05444	MESHSIZE	0.0231	2.358	96.7%
0.007222	HIPTIME	0.0231	0.3128	28.6%
0.07611	HIPTEMP	0.0231	3.296	99.4%
0.08333	LOADING	0.0231	3.609	99.6%
-0.06625	TITANIUM*MESHSIZE	0.0245	2.705	98.3%
-0.03125	TITANIUM*HIPTIME	0.0245	1.276	76.2%
-0.01250	TITANIUM*HIPTEMP	0.0245	0.5104	38.5%
-0.008750	TITANIUM*LOADING	0.0245	0.3573	30.7%
-0.06750	MESHSIZE*HIPTIME	0.0245	2.756	98.5%
0.03125	MESHSIZE*HIPTEMP	0.0245	1.276	76.2%
0.03750	MESHSIZE*LOADING	0.0245	1.531	84.4%
-0.02875	HIPTIME*HIPTEMP	0.0245	1.174	72.1%
0.01250	HIPTIME*LOADING	0.0245	0.5104	38.5%
0.01125	HIPTEMP*LOADING	0.0245	0.4594	35.9%
-0.02337	TITANIUM^2	0.0624	0.3742	31.5%
0.1416	MESHSIZE^2	0.0624	2.268	96.1%
-0.08337	HIPTIME^2	0.0624	1.335	78.3%
0.08663	HIPTEMP^2	0.0624	1.387	80.1%
-0.03837	LOADING^2	0.0624	0.6144	44.1%

Confidence figures are based on 11 degrees of freedom

Table 19
Response Surface Model for Leachability of Boron from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
3.405	1 (constant)	1.331	2.559	97.8%
-17.23	P205	1.098	15.70	99.9%
-1.205	MESHSIZE	1.098	1.098	68.8%
-0.3522	HIPTIME	1.098	0.3209	29.0%
-1.519	HIPTEMP	1.098	1.384	80.0%
-20.62	LOADING	1.098	18.79	99.9%
0.8669	P205*MESHSIZE	1.164	0.7446	51.1%
0.4544	P205*HIPTIME	1.164	0.3903	32.3%
1.658	P205*HIPTEMP	1.164	1.424	81.3%
17.84	P205*LOADING	1.164	15.33	99.9%
-1.484	MESHSIZE*HIPTIME	1.164	1.2757	6.2%
0.05188	MESHSIZE*HIPTEMP	1.164	0.0446	17.4%
1.262	MESHSIZE*LOADING	1.164	1.084	68.2%
-0.7306	HIPTIME*HIPTEMP	1.164	0.6276	44.8%
-0.1681	HIPTIME*LOADING	1.164	0.1444	21.2%
1.408	HIPTEMP*LOADING	1.164	1.210	73.6%
5.284	P205^2	2.969	1.780	90.1%
-1.141	MESHSIZE^2	2.969	0.3845	32.1%
-0.9964	HIPTIME^2	2.969	0.3356	29.7%
-1.226	HIPTEMP^2	2.969	0.4131	33.5%
16.52	LOADING^2	2.969	5.566	99.9%

Confidence figures are based on 11 degrees of freedom

Table 20
Response Surface Model for Leachability of Sodium from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.4571	1 (constant)	3.501	0.1305	20.6%
-22.18	P205	2.888	7.682	99.9%
-0.8722	MESHSIZE	2.888	0.3021	28.1%
-0.2717	HIPTIME	2.888	0.0941	19.2%
-3.863	HIPTEMP	2.888	1.338	78.4%
-22.54	LOADING	2.888	7.805	99.9%
0.4300	P205*MESHSIZE	3.063	0.1404	21.0%
0.4550	P205*HIPTIME	3.063	0.1486	21.4%
4.430	P205*HIPTEMP	3.063	1.446	82.0%
23.54	P205*LOADING	3.063	7.686	99.9%
-4.559	MESHSIZE*HIPTIME	3.063	1.488	83.2%
0.08375	MESHSIZE*HIPTEMP	3.063	0.0273	16.8%
1.099	MESHSIZE*LOADING	3.063	0.3587	30.8%
-0.6063	HIPTIME*HIPTEMP	3.063	0.1979	23.4%
-0.2238	HIPTIME*LOADING	3.063	0.0731	18.5%
4.491	HIPTEMP*LOADING	3.063	1.466	82.6%
10.02	P205^2	7.810	1.283	76.4%
4.241	MESHSIZE^2	7.810	0.5431	40.3%
4.746	HIPTIME^2	7.810	0.6077	43.8%
4.076	HIPTEMP^2	7.810	0.5220	39.1%
2.956	LOADING^2	7.810	0.3785	31.8%

Confidence figures are based on 11 degrees of freedom

Table 21
Response Surface Model for Leachability of Silicon from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.8308	1 (constant)	0.0748	11.11	99.9%
-0.04556	P205	0.0617	0.7388	50.8%
0.008889	MESHSIZE	0.0617	0.1442	21.2%
-0.04000	HIPTIME	0.0617	0.6487	46.0%
-0.02333	HIPTEMP	0.0617	0.3784	31.7%
0.003333	LOADING	0.0617	0.0541	17.8%
0.01938	P205*MESHSIZE	0.0654	0.2962	27.8%
0.1344	P205*HIPTIME	0.0654	2.055	94.1%
-0.02063	P205*HIPTEMP	0.0654	0.3153	28.7%
-0.08188	P205*LOADING	0.0654	1.252	75.3%
-0.04563	MESHSIZE*HIPTIME	0.0654	0.6976	48.6%
-0.02562	MESHSIZE*HIPTEMP	0.0654	0.3918	32.4%
0.06063	MESHSIZE*LOADING	0.0654	0.9269	60.7%
-0.03562	HIPTIME*HIPTEMP	0.0654	0.5447	40.4%
-0.06687	HIPTIME*LOADING	0.0654	1.022	65.4%
0.04313	HIPTEMP*LOADING	0.0654	0.6594	46.5%
0.09739	P205^2	0.1668	0.5840	42.5%
0.05739	MESHSIZE^2	0.1668	0.3441	30.1%
0.07739	HIPTIME^2	0.1668	0.4640	36.1%
-0.1326	HIPTEMP^2	0.1668	0.7952	53.8%
-0.4326	LOADING^2	0.1668	2.594	97.9%

Confidence figures are based on 11 degrees of freedom

8.4 Response Surface Generation and Analysis

The MAP command of XSTAT derives response surfaces from the model for the leachability of each element and total mass loss of the products formed in this study. The response surfaces for boron, sodium and silicon leachabilities from the three waste forms subjected to the 14-day MCC-1 leach test are given in Figures 1-9. Responses surfaces derived for aluminum, calcium, cadmium, chromium, potassium and total mass leachabilities of the same waste forms to the same test are given in Appendix A, Figures A-1 to A-18. MAP generates each of these by varying two parameters at locations declared within the experimental range of the other process parameters investigated. On each response surface the contour lines give a range, according to the key at the right, of leachability in terms of grams/meters²-day (g/m²-day). The points at which the location through lesser parameters is taken are listed below each response surface. In deriving a response surface, it is best practice to vary the two most significant parameters (see Tables 13-21, A-1 to A-18) and declare locations within the ranges of lesser parameters. All surfaces generated in this study are derived in this manner and are located at the midpoint of the ranges of the less significant parameters. When HIPing time is a less significant parameter, however, it is set at 28 hours to best approximate the time that may be used in full scale processing conditions. Contours with negative values are physically impossible and should be regarded as areas where operation will not occur. They can be eliminated by performing a logarithmic transform of the response data, then using the FIT, COEFFICIENT and MAP commands to generate the response surface model and response surface as a function of the base 10 logarithm. The model can also be solved to generate response surfaces at any other location within the limits chosen for less significant parameters simply by declaring these in the MAP command.

The elements whose leaching properties are investigated here are held in different phases within the glass-ceramic structure. Aluminum, boron, cesium, potassium, silicon and sodium are held entirely or principally within the glass phase. Within the glass structure aluminum, silicon and boron form the glass structure, while sodium, potassium and cesium modify the structure. Cadmium, calcium, chromium and strontium are contained primarily in the crystalline phases making up the glass-ceramic waste form. Therefore because of the glass-ceramic makeup and the manner in which they are hosted, the leachability of individual elements may be influenced by different process parameters. The durability of the phases making up the glass-ceramic varies, thus it must be expected that not only will the leachability of individual elements vary, but that the process parameters that influence the leaching behavior of one phase will not necessarily influence that of another. This can be seen in the models given above and the resulting response surfaces given below where the leachability of individual elements may be influenced by different sets of process parameters. Also, the dominant processing parameters affecting the leachability of a given element are not necessarily the same in the three different glass-ceramic compositions formed in this study.

A large area of response insensitivity to change in process parameter setting, as represented by a low concentration of contours, is highly desirable. Such "flat" areas represent favorable sets of conditions on which to run a process. The greater the extent of these areas, particularly at low leachabilities, the more processable the product is in terms of tolerance to variations in process parameters. Based on this criteria, it can be seen by inspection of (Figures 1-9 and A-1 to A-18) that the titanium-based waste form generally retains better elemental leaching properties over wider ranges of dominant process variables than those of the other formulations tested. A comparison of the elemental leachability response surfaces for each formulation follows.

8.4.1 Aluminum Leachability

The aluminum leachability response surfaces for the investigated formulation (Figures A-1, A-7 and A-13) products show that each has considerable areas where dominant process parameter combinations allow leachabilities of less than 1 g/m²-day. The response surface for the titanium-based waste form, however, has the largest area where leachability is relatively insensitive to changes in the dominant process parameters, waste loading and calcine particle size. Only the aluminum leachability response surface for the P₂O₅ based waste form has an area within the limits of the test exceeding 1 g/m²-day.

Figure 1. Response surface for boron leachability dependence on HIPing temperature and HIPing time in aluminum-based glass-ceramic.

Figure 2. Response surface for sodium leachability dependence on HIPing time and aluminum additive in aluminum-based glass-ceramic.


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*.....*
1075. *CC DD EEE EEE DD CC B* A: 0.750
. CC DD EE EEE DD CC . B: 0.900
. CCC DDD EEE EEE DD CCC . C: 1.050
. CC DD EE EE DD CCC. D: 1.200
. B CCC DD EE EE DD CC. E: 1.350
. B CC DDD EE EEE DD . F: 1.500
. B CC DD EE EE DDD . G: 1.650
H .BB CCC DD EE FFFFFFFF EEE DDD. H: 1.800
I .BB CC DD EE FFFF FFFF EEE D. I: 1.950
P .BB CC DD EEE FF FFF EE .
T 1025. *BB CC DD EE FF FFFF EEE *
E . BB CC DD EE FF FFF EE.
M . BB CC DD EE FF FFF .
P . BB CC DD EEE FF GGGGGG FFF .
. BB CC DD EE FF GGGG GGGG FF.
. BB CC DD EE FF GGG GGGG .
. BB CC DDD EEE FF GG GGGG .
. BB CC DD EE FF GGG HHHHHHHH GG.
. BB CC DD EE FF GGG HHHH HHHHHH .
. BB CC DD EE FFF GGG HH HHHHH.
. BBCC DD EE FF GGG HH H.
975. * BBCC DD EE FF GG HHH TTTTTTTTTTTTTT *
*.....*
4.0 16.0 28.0
HIPTIME

```

TITANIUM = 5.000
MESH SIZE = 78.00
LOADING = 70.00

Figure 5. Response surface for sodium leachability dependence on HIPing temperature and HIPing time in titanium-based glass-ceramic.

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*.....*
75.0 * FF FFF GGG HH II * A: 0.2000
. FF FFF GG HH II . B: 0.2400
. FFF FF GG HH III . C: 0.2800
. FF FFF GGG HH II . D: 0.3200
. FF FFF GGG HH II. E: 0.3600
. FFF FFF GGG HH II. F: 0.4000
L . FFF FFF GGG HH I. G: 0.4400
O . FF EEEEEEE FFF GGG HH . H: 0.4800
A . F EEEEE EEEEE FF GG HH . I: 0.5200
D 70.0 * EEEE EEEE FFF GG HH* J: 0.5600
I . EEE EEEE FFF GGG H.
N . EEE EEE FF GGG .
G . EEE DDDDDDDDDDDDD EEE FFF GG .
. E DDDD DDDD EEE FFF GG.
. DDDD DDD EE FF .
. DDD DDD EE FFF .
. DD CCCCCCCC CCCCCCCC DDD EE FF.
. CCCC CCCC DDD EE .
. CCC BBBBBBBBBB BBBBBBBBBB CCCC DDD EE.
65.0 * BBBBB BBBBB BBBBB CCG DDD *
*.....*
975. 1025. 1075.
HIPTEMP

```

TITANIUM = 5.000
MESH SIZE = 78.00
HIPTIME = 28.00

Figure 6. Response surface for silicon leachability dependence on calcine loading and HIPing temperature in titanium-based glass-ceramic.

MESH SIZE - 78.00
 HIPTIME - 28.00
 HIPTEMP - 1025

Figure 7. Response surface for boron leachability dependence on calcine loading and P_2O_5 additive in P_2O_5 -based glass-ceramic.

MESH SIZE - 78.00
 HIPTIME - 28.00
 HIPTEMP - 1025

Figure 8. Response surface for sodium leachability dependence on calcine loading and P_2O_5 additive in P_2O_5 -based glass-ceramic.

8.4.4 Cadmium Leachability

Cadmium can have the characteristic of toxicity when present in high enough concentrations in a solid waste.¹⁹ Thus, an analysis of its leaching behavior from experimental waste forms is not only desirable but may be required in future waste form compliance plans. The cadmium leachability response surfaces of each formulation (Figures A-3, A-9 and A-15) have large areas of insensitivity to change in process parameter setting as well as large regions where dominant process parameter combinations allow leachabilities of less than 1 g/m²-day. Within the process parameter space investigated the aluminum and the titanium-based waste forms have better tolerance to process variability as both have no areas on their response surface exceeding 1 g/m²-day. The simulated Fluorinel/Na calcine used to form the products in this study contains a small amount of sulfur. Thus, cadmium sulfide, CdS, was observed by x-ray diffraction techniques in most products. Remaining cadmium could be distributed between the glass phase and some host crystalline phases such as zirconolite or sphene.

8.4.5 Chromium Leachability

Although hexavalent chromium is a minor component of the waste form, its leaching behavior (see Figure A-4, A-10 and A-16) is of interest because, when present in high enough concentrations, it can have the characteristic of toxicity.¹⁹ Like cadmium its behavior may also be a subject in future waste form compliance plans. Only the model derived for the dependence of chromium leachability from the P₂O₅-based waste form on the studied process parameters fits the data well (see Table 12). That the others do not can be attributed to the analytical uncertainty associated with the low amount of chromium present in the calcine used in this study. Nevertheless, within the process parameter space investigated the titanium-based waste form is less sensitive to chromium leachability because its response surface has no area exceeding 1 g/m²-day (See Figure 5). The chromium leachability from the P₂O₅-based waste form is nearly equivalent to that of the titanium form (See Figure 23). Only a small area of the process parameter space investigated for the P₂O₅-based waste form exceeds 1 g/m²-day in chromium leachability. The leachability of chromium from the aluminum-based waste form (See Figure 5) appears to be dependant mainly on the amount of aluminum metal added.

8.4.6 Potassium Leachability

Potassium is also a minor component of the simulated Fluorinel/Na calcine used in this study. Its leaching behavior from glass ceramic forms (See Figures A-5, A-11 and A-17) should be similar to that of sodium because both elements will be hosted mainly in the glass phase. The products of the titanium-based waste form have the best potassium leaching properties, with respect to process variability, although the model for their leachability does not fit the data as well as is desired. The poor fit of the model to the data could result from error associated with the analysis of potassium which is present in small amounts or insensitivity of potassium leachability to change in process parameters. The high leachability of potassium from the products of the aluminum and the P₂O₅-based formulations indicate a lack of durability in the glass phase of both. This suggests that further development of these formulations is required to improve glass phase durability.

8.4.7 Sodium Leachability

Comparison of the sodium leachability response surfaces (See Figures 2, 5 and 8) of the formulation products prepared in this study indicates that the titanium-based waste form is more tolerant of process variations than the aluminum and P_2O_5 -forms under the conditions tested. However, large portions of the response surface for sodium leachability from the titanium-based waste form exceeds $1 \text{ g/m}^2\text{-day}$. This indicates a high dependence of sodium leachability on the dominant processing variables of HIPing time and HIPing temperature.

The 28-day MCC-1 static leach test was run on the center point products of each formulation in order to observe any changes in leachability from the products as a function of leach test time. Table 22 summarizes these results and gives the ratio of the 28-day test leaching response to that of the 14-day test ($R_{28/14}$). If the leaching rate for the samples subjected to the 14-day is the same as for samples submitted to the 28-day test, then $R_{28/14}$ should be 0.5 suggesting that equilibrium conditions have been established in the leach test system. The data in Table 22 indicates that this is the case for Al, B, Ca, K, Na and Si leachability from the titanium-based waste form as $R_{28/14}$ for these elements is near 0.5. The leachability of Cd and Cr from products of this formulation do not match this trend. In the case of Cd, this may be the result of mobility during HIPing and subsequent inhomogeneous distribution through the product. In the case of Cr, this may be the result of analytical inaccuracies because of its low presence in the calcine used and therefore the product. Sodium leachability has $R_{28/14}$ of about 0.5. Thus a response surface model which describes its leachability from the titanium-based glass-ceramic, when subjected to the 28-day MCC-1 test, is given in Table 23.

Table 22
Results of Applying the 28-day MCC-1 Static Leach Test to Products Formed Under the
Centerpoint Conditions of the Face-Centered Cube Test Matrix.

	14-Day MCC-1	28-day MCC-1	
Ti Formulation <u>Products</u>	Response <u>g/m²-day</u>	Response <u>g/m²-day</u>	<u>R 28/14</u>
Al	0.79	0.38	.48
B	1.20	0.54	.45
Ca	0.18	0.09	.50
Cd	0.22	0.07	.30
Cr	0.72	0.25	.35
K	1.29	0.64	.50
Na	1.76	0.93	.51
Si	0.53	0.24	.45
Al Formulation <u>Products</u>			
Al	0.34	0.18	.53
B	1.17	0.75	.64
Ca	0.93	0.62	.67
Cd	0.49	0.25	.51
Cr	0.04	0.01	.25
K	3.30	1.20	.36
Na	8.60	4.55	.53
Si	0.36	0.22	.62
P ₂ O ₅ Formulation <u>Products</u>			
Al	0.75	0.59	.79
B	2.10	1.75	.83
Ca	0.18	0.06	.33
Cd	0.10	0.16	1.60
Cr	0.63	0.21	.33
K	0.46	0.29	.63
Na	2.46	1.65	.67
Si	0.63	1.24	1.97

Table 23

Response Surface Model for Leachability of Sodium as a Function
of the 28-Day MCC-1 Static Leach Test from Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.7871	1 (constant)	0.0708	11.12	99.9%
-0.07572	TITANIUM	0.0584	1.298	77.0%
-0.05094	MESHSIZE	0.0584	0.8730	57.9%
0.1429	HIPTIME	0.0584	2.450	97.3%
-0.1287	HIPTEMP	0.0584	2.206	95.6%
0.1118	LOADING	0.0584	1.916	92.3%
-0.1142	TITANIUM*MESHSIZE	0.0619	1.845	91.2%
-0.1367	TITANIUM*HIPTIME	0.0619	2.208	95.6%
0.2708	TITANIUM*HIPTEMP	0.0619	4.375	99.9%
-0.3229	TITANIUM*LOADING	0.0619	5.218	99.9%
0.07419	MESHSIZE*HIPTIME	0.0619	1.199	73.2%
-0.02081	MESHSIZE*HIPTEMP	0.0619	0.3363	29.7%
0.1054	MESHSIZE*LOADING	0.0619	1.704	88.6%
-0.1508	HIPTIME*HIPTEMP	0.0619	2.437	97.2%
0.1004	HIPTIME*LOADING	0.0619	1.623	86.8%
-0.2821	HIPTEMP*LOADING	0.0619	4.557	99.9%
0.3789	TITANIUM^2	0.1578	2.401	97.0%
0.1589	MESHSIZE^2	0.1578	1.007	64.6%
-0.2461	HIPTIME^2	0.1578	1.559	85.2%
0.03890	HIPTEMP^2	0.1578	0.2465	25.5%
-0.2461	LOADING^2	0.1578	1.559	85.2%

Confidence figures are based on 11 degrees of freedom

The response surface derived from this model for the dependency of Na leachability as a function of HIPing temperature and HIPing time (at constant soak time, calcine particle size and titanium additive) is given in Figure 10. In this figure the contour lines on the surface give a range, according to the key at the right, of leachability in terms of grams/meters²-day (g/m²-day). In Figure 10, the Na leachability contours are 0.51 the value of those in Figure 5. The points at which the location through lesser parameters (wt% of Ti, calcine particle size, wt% calcine loading) is taken are given below the response surface. The nature of this figure suggests that products of the titanium-based waste form will respond with Na leachabilities of less than 1 g/m²-day over most of the experimental space when subjected to the 28-day MCC-1 static leach test.

8.4.8 Silicon Leachability

The silicon leachability response surfaces for the investigated formulation (See Figures 3, 6 and 9) products show that each has considerable area where dominant process parameter combinations allow leachabilities of less than 1 g/m²-day. The response surfaces for the aluminum and titanium-based forms, however, have the largest areas where leachability is relatively insensitive to changes in waste loading and calcine particle size, or waste loading and

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      *.....*
1075. *B  CC  DD    EE          EE    DD  CC  B*  A:  0.3750
      .B  CC  DD    EE          EEE    DD  CC  .  B:  0.4500
      .BB CCC DDD    EE          EE    DD  CC  .  C:  0.5250
      .BB  CC  DD    EE          EEE    DDD CC.  D:  0.6000
      .BB  CC  DD    EE          EEE    DD  C.  E:  0.6750
      .BB  CC  DD    EE          EE    DD  .  F:  0.7500
      . BB CC  DD  EEE          FFFFF          EEE DDD. G:  0.8250
H      . BB CC  DD  EE          FFFF          FFFF          EEE D. H:  0.9000
I      . BB CCC DD  EE          FF          FFFF          EEE .  I:  0.9750
P      . BB CCC DDD  EEE          FFF          FFF          EE .  J:  1.0500
T 1025. * BB CCC DD  EE          FFF          FFF          EE*
E      . BB CC  DD  EE          FF          FFF          .
M      . BB CC  DD  EE          FF          GGGGGGGGGGGG          FFF .
P      . BB CC  DD  EE          FF          GGG          GGGG          F.
      . BB CC DDD EEE          FF          GG          GGG          .
      . BB CC DD  EE          FFF          GGG          GGGG.
      . BB CC DD  EE          FF          GGG          HHHHHHHHHHHHHHHH          G.
      . BB CC DD  EE          FF          GG          HHH          HHHH          .
      . BBCCDDDD EE          FF          GG          HHH          HHH.
      .BBBCC DD  EE          FF          GGG          HH          IIIIIIIIIIII          .
      .BB CC DD  EE          FFF          GGG          HHH          III          IIIII.
975. *BB CCDDDEEE FF          GG          HHH          III          I*
      *.....*
      4.0                      16.0                      28.0
                        HIPTIME

TITANIUM - 5.000
MESH SIZE - 78.00
LOADING - 70.00

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Figure 10. Response surface for sodium leachability response to 28-day MCC-1 leach test dependent on HIPing temperature and HIPing time in titanium-based glass-ceramic.

amount of aluminum, the respective dominant process parameters. Within the limits of the test, only the silicon leachability response surface for the P_2O_5 -based waste form has an area exceeding 1 g/m²-day. The silicon leachability response surface models for products of each formulation investigated fit respective leaching data poorly (See Table 12). This is most likely because of the relative insensitivity of silicon leachability to the changes in the process parameters used in this study.

8.4.9 Total Mass Loss

This property is determined on leached waste forms only to obtain a rapid estimate of total corrosion resulting from a leach test. The total mass loss response surfaces for products (See Figures A-6, A-12, and A-18) of each formulation have large areas of insensitivity to change in dominant process parameter setting as well as large regions where process parameter combinations allow leachabilities of less than 1 g/m²-day. Sensitivity to change in dominant process parameters is present in the total mass loss response surface for products of each formulation. However, under the testing conditions applied, the products of the titanium-based waste form appear to be the least sensitive to these changes as well as the most durable of the compositions.

8.4.10 Glass Phase Properties of Titanium-based Formulation Products

The glass phase is potentially the least durable component of a glass-ceramic waste form. In a chemically complex system, such as the glass ceramics tested in this study, the glass phase can react with a wide variety of elements which, if incorporated, can alter its characteristics. Thus the content of certain elements in the glass phase of the titanium-based waste form were determined using standardless scanning electron microscopy (SEM) techniques in order to observe their influence on product leachability. The analysis discussed in the sodium leachability section suggests that the glass phases of products of the aluminum and P_2O_5 -based forms have not completely reacted with all components of the Fluorinel/Na calcine. Thus, the following analysis was not performed on products of these formulations.

Aluminum, Ca and Na are three major waste elements in Fluorinel/Na calcine which have the potential to enter the glass phase and alter its durability. Thus, their contents in the glass phase were determined by SEM techniques. Boron was not included in this analysis because it is not well detected by the SEM used in this study. Zirconium was not included because of its low leachability. Other waste elements were not included because of their low concentrations in the waste (Cr, Cs, K, Sr) or their mobility during HIPing (Cd). Table 24 presents the results with standard deviations of the SEM-EDS analyses for Al, Ca and Na in the glass phase of the products of each test in the face-centered cube matrix. Test conditions are omitted for simplicity, but can be observed in Table 6.

Each analysis given is the arithmetic mean of ten analyses performed at random glass phase locations.

Table 24

Aluminum, Calcium and Sodium Contents (Wt%) of Glass Phase in
Glass Ceramic Products of the Titanium Formulation

Run No.	Aluminum	Calcium	Sodium
1	8.68 $\pm$ 1.53	1.03 $\pm$ 0.50	3.84 $\pm$ 0.15
2	8.61 $\pm$ 1.64	5.94 $\pm$ 1.49	3.87 $\pm$ 0.79
3	7.33 $\pm$ 0.51	3.05 $\pm$ 1.84	2.51 $\pm$ 0.22
4	10.08 $\pm$ 1.99	3.18 $\pm$ 0.74	3.94 $\pm$ 0.70
5	7.73 $\pm$ 1.20	2.41 $\pm$ 1.06	2.51 $\pm$ 0.23
6	11.79 $\pm$ 1.23	4.82 $\pm$ 2.20	4.73 $\pm$ 0.66
7	11.49 $\pm$ 0.20	5.99 $\pm$ 0.51	4.88 $\pm$ 0.49
8	10.34 $\pm$ 0.46	4.31 $\pm$ 0.57	3.59 $\pm$ 0.27
9	8.22 $\pm$ 0.51	9.33 $\pm$ 2.00	2.57 $\pm$ 0.45
10	10.57 $\pm$ 0.12	9.39 $\pm$ 1.89	3.97 $\pm$ 0.22
11	9.52 $\pm$ 0.17	9.52 $\pm$ 0.58	2.79 $\pm$ 0.16
12	9.06 $\pm$ 0.20	12.25 $\pm$ 1.19	3.31 $\pm$ 0.13
13	10.08 $\pm$ 0.71	8.35 $\pm$ 1.20	3.73 $\pm$ 0.22
14	8.47 $\pm$ 0.30	11.60 $\pm$ 1.34	3.36 $\pm$ 0.34
15	9.25 $\pm$ 0.33	9.57 $\pm$ 0.47	2.74 $\pm$ 0.23
16	15.81 $\pm$ 0.15	2.74 $\pm$ 0.10	4.20 $\pm$ 0.17
17	10.13 $\pm$ 0.39	6.85 $\pm$ 0.90	3.25 $\pm$ 0.24
18	14.59 $\pm$ 0.21	2.93 $\pm$ 0.63	4.53 $\pm$ 0.29
19	12.19 $\pm$ 0.34	4.91 $\pm$ 1.28	4.33 $\pm$ 0.32
20	12.05 $\pm$ 0.64	5.04 $\pm$ 1.04	4.10 $\pm$ 0.64
21	9.50 $\pm$ 0.41	6.24 $\pm$ 1.14	3.55 $\pm$ 0.15
22	12.19 $\pm$ 0.34	3.57 $\pm$ 0.42	4.62 $\pm$ 0.09
23	10.98 $\pm$ 0.56	4.27 $\pm$ 0.51	3.76 $\pm$ 0.19
24	12.25 $\pm$ 1.70	4.00 $\pm$ 1.18	4.53 $\pm$ 0.50
25	9.83 $\pm$ 0.45	4.34 $\pm$ 0.90	3.20 $\pm$ 0.45
26	11.87 $\pm$ 0.67	6.65 $\pm$ 0.70	4.08 $\pm$ 0.51
27	12.20 $\pm$ 0.54	3.75 $\pm$ 0.61	4.32 $\pm$ 0.36
28	12.55 $\pm$ 0.55	5.88 $\pm$ 0.31	4.59 $\pm$ 0.34
29	11.05 $\pm$ 0.18	6.33 $\pm$ 1.71	4.08 $\pm$ 0.52
30	4.20 $\pm$ 0.41	5.57 $\pm$ 0.42	4.40 $\pm$ 0.40
31	4.33 $\pm$ 0.24	6.90 $\pm$ 0.64	4.33 $\pm$ 0.31
32	4.59 $\pm$ 0.21	4.79 $\pm$ 0.38	4.37 $\pm$ 0.31

Figure 11 is a scatter plot of the mean sodium leachability response to the 14-day MCC-1 test versus glass phase sodium content in the titanium-based products formed in this study. A linear correlation coefficient for the relationship of the leaching response data to the glass phase composition data was not calculated because each product was formed under a different set of conditions dictated by the face centered cube matrix. Thus, a linear function may not be adequate to describe any relationship between these two properties. Nevertheless, inspection of Figure 11 reveals that a slight positive correlation may exist between the Na leaching data and the Na content of the glass phase. This conforms to the well known inverse relationship of durability to the amount of network modifiers contained in most silicate glasses being developed to immobilize nuclear wastes.¹⁹

Figure 11. Scatter plot of sodium content of glass phase versus sodium leachability response to the MCC-1 test.

Boron release is the most accurate indicator of glass corrosion because in a multiphase waste form it is hosted only by the glass phase.²⁰ Most Na in glass-ceramics being developed to immobilize ICPP calcines is also contained in the glass phase. Thus, if the Na content of the glass phase directly determines Na leachability there may be a positive relationship between it and boron leachability. In order to observe such a relationship, a scatter plot was prepared and is given in Figure 12. Again, a linear correlation coefficient for the relationship expressed in the figure is not given because each product was formed under a different set of conditions. A positive correlation between the two mass losses may exist under the test conditions, and this correlation suggests that most leachable sodium could originate from the same source as boron, namely the glass phase.

Figure 12. Scatter plot of sodium content of glass phase versus boron content of the glass phase.

The arithmetic mean of Al, Ca and Na analyses were also used to derive response surface models for the dependence of their content in the glass phase on the process parameters studied. A model was not prepared for potassium, a minor waste component in the glass-ceramic products, because of the uncertainties associated with its analysis. Only the response surface model for Ca content in the glass phase fits the data with any amount of usefulness ($R^2=0.87$). It is therefore given in Table 25. The response surface derived from it for dependence on HIPing temperature and calcine loading, the dominant processing variables, is given in Figure 13. A boundary condition of less than 10 wt% of Ca in the glass is applied to the derivation of the response surface in this figure. In this figure the contour lines on the surface give a range, according to the key at the right, of the weight per cent Ca in the glass phase as determined by standardless SEM techniques. This response surface was derived at 5 wt% titanium additive, maximum calcine particle size of 80 mesh (177 microns) and at a HIPing time of 16 hours.

Table 25

**Response Surface Model for Sodium Content of the Glass Phase
of Titanium-Based Glass-Ceramics**

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
4.985	1 (constant)	0.4599	10.84	99.9%
-0.0072	TITANIUM	0.3793	0.0190	16.5%
-0.0705	MESHSIZE	0.3793	0.1860	22.9%
-0.4683	HIPTIME	0.3793	1.235	74.6%
2.282	HIPTEMP	0.3793	6.015	99.9%
-0.5172	LOADING	0.3793	1.364	79.3%
-0.9037	TITANIUM*MESHSIZE	0.4023	2.246	95.9%
-0.7188	TITANIUM*HIPTIME	0.4023	1.787	90.2%
-0.4613	TITANIUM*HIPTEMP	0.4023	1.147	71.0%
-0.8525	TITANIUM*LOADING	0.4023	2.119	94.8%
-0.3138	MESHSIZE*HIPTIME	0.4023	0.7799	53.0%
-0.3162	MESHSIZE*HIPTEMP	0.4023	0.7861	53.3%
-0.2425	MESHSIZE*LOADING	0.4023	0.6028	43.5%
-0.8388	HIPTIME*HIPTEMP	0.4023	2.085	94.4%
0.1425	HIPTIME*LOADING	0.4023	0.3542	30.6%
-0.7025	HIPTEMP*LOADING	0.4023	1.746	89.4%
0.4408	TITANIUM^2	1.026	0.4297	34.3%
0.1908	MESHSIZE^2	1.026	0.1860	22.9%
0.1208	HIPTIME^2	1.026	0.1178	20.1%
-0.05916	HIPTEMP^2	1.026	0.0577	17.9%
0.7108	LOADING^2	1.026	0.6929	48.4%

Confidence figures are based on 11 degrees of freedom

Figure 13. Response surface for sodium content of glass phase in titanium-based glass-ceramic as a function of calcine loading temperature and HIPing temperature.

IX. CONCLUSIONS AND RECOMMENDATIONS

Response surface methodology is unique in that it provides working models that give the extent and sensitivity of parameter-response interactions. The derivation and application of response surface models in this study, therefore, provides the basis for defining formulations that produce waste forms with acceptable durability under anticipated processing conditions. Equally important, the range of parameter conditions is identified which permits processing in order to obtain a product with the best durability properties. This vital information cannot be obtained from studies in which only components or a single parameter are varied to obtain a desired response. Specifically, the process parameters that dominate elemental leachabilities and the sensitivities of these leachabilities to changes in process parameters are determined in this study for each candidate formulation. The principal results of this application are that under the conditions of the test:

1. The titanium-based waste form is superior for immobilizing Fluorinel/Na calcine to the other formulations tested with respect to elemental leaching properties as measured by the MCC-1 static leach test.
2. Elemental leaching properties of the titanium-based waste form are also the least sensitive of the formulations studied to changes in the process parameters used.
3. HIPing time, HIPing temperature and calcine particle size affect elemental leaching properties of the titanium-based waste form more than calcine loading and amount of titanium metal.
4. The leachability of all elements investigated, except Cd and Cr, from the products of the titanium-based waste form does not appear to differ between the 14- and 28-day MCC-1 leach test.
5. Empirical models, that in most cases fit data well, have been derived to express the relationships between elemental leachabilities and dominant process parameters held within ranges that could be equivalent to those of the full-scale process.

These results indicate that the titanium-based waste form is a superior candidate for further development efforts. However, efforts to improve the other formulations studied should not be abandoned. The leachability of some elements contained mainly outside the glass (Ca, Cd) or that make up the glass phase structure (Al, Si) of the aluminum-based and the P_2O_5 -based waste form are similar to those of the titanium-based glass-ceramic.

The comparison of 14-day and 28-day MCC-1 leach test results suggests that the glass phase in the titanium-based waste form has completely reacted with waste components to form a durable product that is stable under the test conditions. This comparison also suggests that the glass phases in both the aluminum and the P_2O_5 -based forms have not completely reacted under test conditions with waste components to form a durable product. Incomplete reaction of the glass phase in these two forms with the waste elements may also result in the relatively high

leachability of Cr. Thus further formulation development is required to improve the glass phase durability and its sensitivity to process parameter change in products of both formulations. Calcine loading and amount of additive appear to be the most important process parameters in determining the durability of the aluminum and P_2O_5 -based waste forms. Changes in these parameters can be interpreted as mass or mixing effects. Thus, any future process parameter effects studies performed with these formulations should include major attention to component mixing and amount of waste and additive. Other significant results of response surface methodology application in this study include:

6. Process parameters effects on product density could not be modeled because density measurement variance masks these effects.
7. Changes in glass phase composition may be observed through the results of this study. However, a more rigorous investigation is required in order to establish models that define complete glass phase composition and durability as a function of dominant process parameters.

High measurement variances limit the success of applying response surface methodology. This is the case with determining product density and determining the amounts of Al, Ca and Na in the glass phase of products prepared in this study. Limitations in these cases may be overcome by performing further replicate measurements or by using more accurate measuring techniques. Small amounts of the products prepared in this study remain unused. It seems more practical, however, to use this limited material to determine if response surface methodology can be successfully applied to modeling the relationship of the process parameters studied to thermal and physical properties of the products formed.

With respect to leaching properties, the titanium-based waste form is clearly superior to the other formulations tested under the conditions used. Therefore, it is strongly recommended that the titanium-based formulation be used in the upcoming hot cell preparation of glass-ceramic forms from radioactive calcine produced in the Waste Calcining Facility and the NWCF. It is also recommended that this formulation be used in future scale-up studies for the preparation of glass-ceramic forms from nonradioactive Fluorinel/Na calcines produced in the engineering-scale calciners. The other formulations investigated in this study cannot be recommended for either radioactive or scale-up studies until their glass phases are improved to a durability equivalent to that of the titanium-based waste forms.

The processability of a waste form is its ability to retain desired characteristics over a practical range of processing conditions and its sensitivity to changes in these parameters. This is the first investigation performed by the HLW Immobilization section in which relative processability is used as a criterion to identify a superior formulation for immobilizing a specific waste type. In this application, response surface methodology is used not only to identify the range of dominant process variables over which formulation products retain desired characteristics, but also to determine the sensitivity of that characteristic to changes in those variables. Much systematic information not obtainable by other approaches was acquired in this study on the process for producing glass-ceramic waste forms for immobilizing Fluorinel/Na calcine. Candidate formulations exist for producing glass-ceramics for immobilizing other ICPP calcine types. Because of the amount and quality of new information acquired in this study it is strongly

recommended that a "processability test" be applied routinely to determine the relative suitability of the best glass-ceramic formulations for immobilizing each calcine type, and a parallel processability testing program should be developed for glass waste forms. Response surface methodology or some other systematic exposure to operating conditions should make up the processability test. This action would be applied to candidate waste forms of each type developed through theoretical and empirical approaches in which only compositions are altered. Application of a processability test to both waste form types would identify the best performer in respective processing scenarios. Adopting such a development strategy provides a sounder basis for selecting the best candidates for further development and provides basic and timely information for technical personnel tasked with developing a full-scale process for producing the waste form.

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APPENDIX A

RESPONSE SURFACE MODELS AND RESPONSE SURFACES FOR THE LEACHABILITY OF ALUMINUM, CALCIUM, CADMIUM, CHROMIUM, POTASSIUM AND TOTAL MASS FROM FORMULATIONS SUBJECTED TO THE 14-DAY MCC-1 STATIC LEACH TEST

Table A-1
Response Surface Model for Leachability of Aluminum from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.4162	1 (constant)	0.0464	8.968	99.9%
-0.05444	ALUMINUM	0.0383	1.422	81.2%
-0.1617	MESHSIZE	0.0383	4.224	99.8%
-0.1078	HIPTIME	0.0383	2.816	98.6%
-0.1850	HIPTEMP	0.0383	4.833	99.9%
0.1017	LOADING	0.0383	2.656	98.2%
0.01750	ALUMINUM*MESHSIZE	0.0406	0.4311	34.4%
0.06125	ALUMINUM*HIPTIME	0.0406	1.509	83.8%
-0.006250	ALUMINUM*HIPTEMP	0.0406	0.1539	21.6%
-0.1238	ALUMINUM*LOADING	0.0406	3.048	99.1%
0.1087	MESHSIZE*HIPTIME	0.0406	2.679	98.2%
0.1637	MESHSIZE*HIPTEMP	0.0406	4.033	99.8%
-0.05875	MESHSIZE*LOADING	0.0406	1.447	82.0%
0.1375	HIPTIME*HIPTEMP	0.0406	3.387	99.5%
-0.02250	HIPTIME*LOADING	0.0406	0.5542	40.9%
-0.04000	HIPTEMP*LOADING	0.0406	0.9853	63.6%
-0.06331	ALUMINUM^2	0.1035	0.6115	44.0%
-0.06831	MESHSIZE^2	0.1035	0.6598	46.6%
0.02669	HIPTIME^2	0.1035	0.2579	26.0%
0.3717	HIPTEMP^2	0.1035	3.591	99.6%
-0.1483	LOADING^2	0.1035	1.433	81.6%

Confidence figures are based on 11 degrees of freedom

Table A-2
Response Surface Model for Leachability of Calcium from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
1.051	1 (constant)	0.0945	11.12	99.9%
-1.181	ALUMINUM	0.0780	15.15	99.9%
0.1942	MESHSIZE	0.0780	2.490	97.5%
0.1581	HIPTIME	0.0780	2.027	93.8%
-0.1647	HIPTEMP	0.0780	2.113	94.7%
-0.4242	LOADING	0.0780	5.441	99.9%
-0.2909	ALUMINUM*MESHSIZE	0.0827	3.518	99.6%
-0.1153	ALUMINUM*HIPTIME	0.0827	1.394	80.3%
0.1566	ALUMINUM*HIPTEMP	0.0827	1.893	92.0%
0.3091	ALUMINUM*LOADING	0.0827	3.737	99.7%
0.009687	MESHSIZE*HIPTIME	0.0827	0.1171	20.1%
-0.06344	MESHSIZE*HIPTEMP	0.0827	0.7671	52.3%
0.2691	MESHSIZE*LOADING	0.0827	3.254	99.4%
-0.1903	HIPTIME*HIPTEMP	0.0827	2.301	96.4%
0.1097	HIPTIME*LOADING	0.0827	1.326	78.0%
0.02656	HIPTEMP*LOADING	0.0827	0.3212	29.0%
0.6424	ALUMINUM^2	0.2109	3.047	99.1%
-0.06758	MESHSIZE^2	0.2109	0.3205	28.9%
0.04242	HIPTIME^2	0.2109	0.2012	23.5%
-0.2876	HIPTEMP^2	0.2109	1.364	79.3%
0.1574	LOADING^2	0.2109	0.7466	51.2%

Confidence figures are based on 11 degrees of freedom

Table A-3
Response Surface Model for Leachability of Cadmium from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.3291	1 (constant)	0.0873	3.768	99.7%
-0.09889	ALUMINUM	0.0720	1.373	79.6%
0.1072	MESHSIZE	0.0720	1.488	83.2%
-0.05333	HIPTIME	0.0720	0.7403	50.9%
0.08389	HIPTEMP	0.0720	1.164	71.7%
-0.1056	LOADING	0.0720	1.465	82.5%
-0.006875	ALUMINUM*MESHSIZE	0.0764	0.0900	19.1%
-0.1681	ALUMINUM*HIPTIME	0.0764	2.200	95.6%
0.1444	ALUMINUM*HIPTEMP	0.0764	1.889	91.9%
0.03938	ALUMINUM*LOADING	0.0764	0.5153	38.8%
-0.02188	MESHSIZE*HIPTIME	0.0764	0.2863	27.3%
-0.05437	MESHSIZE*HIPTEMP	0.0764	0.7116	49.4%
-0.03688	MESHSIZE*LOADING	0.0764	0.4826	37.1%
-0.1631	HIPTIME*HIPTEMP	0.0764	2.135	95.0%
0.07437	HIPTIME*LOADING	0.0764	0.9734	63.0%
-0.07563	HIPTEMP*LOADING	0.0764	0.9897	63.8%
0.1665	ALUMINUM^2	0.1948	0.8547	56.9%
0.01153	MESHSIZE^2	0.1948	0.0592	17.9%
-0.09347	HIPTIME^2	0.1948	0.4797	36.9%
-0.1885	HIPTEMP^2	0.1948	0.9673	62.7%
0.2465	LOADING^2	0.1948	1.265	75.8%

Confidence figures are based on 11 degrees of freedom

Table A-4
Response Surface Model for Leachability of Chromium from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
3.218	1 (constant)	3.323	0.9683	62.7%
-31.37	ALUMINUM	2.741	11.44	99.9%
6.972	MESHSIZE	2.741	2.544	97.7%
0.02333	HIPTIME	2.741	0.0085	16.2%
-4.525	HIPTEMP	2.741	1.651	87.4%
-6.738	LOADING	2.741	2.458	97.3%
-7.859	ALUMINUM*MESHSIZE	2.907	2.703	98.3%
-0.04125	ALUMINUM*HIPTIME	2.907	0.0142	16.4%
5.067	ALUMINUM*HIPTEMP	2.907	1.743	89.4%
7.560	ALUMINUM*LOADING	2.907	2.601	98.0%
-4.199	MESHSIZE*HIPTIME	2.907	1.444	81.9%
-0.8275	MESHSIZE*HIPTEMP	2.907	0.2847	27.3%
13.19	MESHSIZE*LOADING	2.907	4.537	99.9%
-13.18	HIPTIME*HIPTEMP	2.907	4.532	99.9%
0.8475	HIPTIME*LOADING	2.907	0.2915	27.6%
4.219	HIPTEMP*LOADING	2.907	1.451	82.1%
48.01	ALUMINUM^2	7.412	6.478	99.9%
-5.565	MESHSIZE^2	7.412	0.7508	51.4%
-5.580	HIPTIME^2	7.412	0.7528	51.5%
-5.565	HIPTEMP^2	7.412	0.7508	51.4%
-5.600	LOADING^2	7.412	0.7555	51.7%

Confidence figures are based on 11 degrees of freedom

Table A-5
Response Surface Model for Leachability of Potassium from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
8.518	1 (constant)	0.8553	9.958	99.9%
-7.454	ALUMINUM	0.7054	10.57	99.9%
0.01806	MESHSIZE	0.7054	0.0256	16.8%
2.998	HIPTIME	0.7054	4.250	99.8%
-1.275	HIPTEMP	0.7054	1.807	90.6%
0.7925	LOADING	0.7054	1.123	70.0%
-0.1991	ALUMINUM*MESHSIZE	0.7482	0.2660	26.4%
-2.520	ALUMINUM*HIPTIME	0.7482	3.367	99.5%
1.113	ALUMINUM*HIPTEMP	0.7482	1.488	83.2%
-0.9947	ALUMINUM*LOADING	0.7482	1.329	78.1%
-2.941	MESHSIZE*HIPTIME	0.7482	3.930	99.8%
0.5147	MESHSIZE*HIPTEMP	0.7482	0.6879	48.1%
1.437	MESHSIZE*LOADING	0.7482	1.920	92.4%
-1.246	HIPTIME*HIPTEMP	0.7482	1.665	87.7%
-0.3078	HIPTIME*LOADING	0.7482	0.4114	33.4%
3.219	HIPTEMP*LOADING	0.7482	4.302	99.9%
4.993	ALUMINUM^2	1.908	2.617	98.0%
0.9928	MESHSIZE^2	1.908	0.5203	39.1%
-0.4722	HIPTIME^2	1.908	0.2475	25.6%
-3.222	HIPTEMP^2	1.908	1.689	88.2%
-2.522	LOADING^2	1.908	1.322	77.9%

Confidence figures are based on 11 degrees of freedom

Table A-6
Response Surface Model for Total Mass Loss from
Aluminum-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.9113	1 (constant)	0.1140	7.994	99.9%
-0.3247	ALUMINUM	0.0940	3.454	99.5%
0.06852	MESHSIZE	0.0940	0.7288	50.3%
0.06686	HIPTIME	0.0940	0.7111	49.3%
-0.01981	HIPTEMP	0.0940	0.2107	24.0%
-0.2048	LOADING	0.0940	2.179	95.4%
-0.08990	ALUMINUM*MESHSIZE	0.0997	0.9015	59.4%
-0.1318	ALUMINUM*HIPTIME	0.0997	1.321	77.9%
0.07635	ALUMINUM*HIPTEMP	0.0997	0.7657	52.2%
0.1920	ALUMINUM*LOADING	0.0997	1.926	92.5%
-0.1985	MESHSIZE*HIPTIME	0.0997	1.991	93.3%
0.07085	MESHSIZE*HIPTEMP	0.0997	0.7105	49.3%
-0.03822	MESHSIZE*LOADING	0.0997	0.3833	32.0%
0.06122	HIPTIME*HIPTEMP	0.0997	0.6140	44.1%
-0.08835	HIPTIME*LOADING	0.0997	0.8860	58.6%
-0.01722	HIPTEMP*LOADING	0.0997	0.1727	22.4%
1.035	ALUMINUM^2	0.2543	4.069	99.8%
-0.1900	MESHSIZE^2	0.2543	0.7472	51.2%
-0.09099	HIPTIME^2	0.2543	0.3579	30.7%
-0.2960	HIPTEMP^2	0.2543	1.164	71.7%
-0.4337	LOADING^2	0.2543	1.706	88.6%

Confidence figures are based on 11 degrees of freedom

Table A-7
Response Surface Model for Leachability of Aluminum from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.7034	1 (constant)	0.0643	10.94	99.9%
-0.08667	TITANIUM	0.0530	1.634	87.0%
-0.2356	MESHSIZE	0.0530	4.441	99.9%
-0.1367	HIPTIME	0.0530	2.577	97.9%
-0.1017	HIPTEMP	0.0530	1.917	92.3%
0.1594	LOADING	0.0530	3.006	99.0%
0.04438	TITANIUM*MESHSIZE	0.0563	0.7887	53.5
0.06562	TITANIUM*HIPTIME	0.0563	1.166	71.8%
0.1219	TITANIUM*HIPTEMP	0.0563	2.166	95.3%
-0.2006	TITANIUM*LOADING	0.0563	3.566	99.6%
0.06812	MESHSIZE*HIPTIME	0.0563	1.211	73.7%
0.2219	MESHSIZE*HIPTEMP	0.0563	3.944	99.8%
-0.05562	MESHSIZE*LOADING	0.0563	0.9887	63.7%
0.1281	HIPTIME*HIPTEMP	0.0563	2.277	96.2%
-0.1019	HIPTIME*LOADING	0.0563	1.811	90.6%
-0.1331	HIPTEMP*LOADING	0.0563	2.366	96.8%
0.3902	TITANIUM^2	0.1435	2.720	98.4%
0.1602	MESHSIZE^2	0.1435	1.117	69.7%
-0.2398	HIPTIME^2	0.1435	1.671	87.9%
0.01522	HIPTEMP^2	0.1435	0.1061	19.7%
-0.1848	LOADING^2	0.1435	1.288	76.6%

Confidence figures are based on 11 degrees of freedom

Table A-8
Response Surface Model for Leachability of Calcium from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.1731	1 (constant)	0.0088	19.65	99.9%
-0.02167	TITANIUM	0.0073	2.983	99.0%
-0.04500	MESHSIZE	0.0073	6.195	99.9%
-0.03556	HIPTIME	0.0073	4.895	99.9%
-0.05278	HIPTEMP	0.0073	7.266	99.9%
0.01056	LOADING	0.0073	1.453	82.2%
0.06188	TITANIUM*MESHSIZE	0.0077	8.031	99.9%
0.05938	TITANIUM*HIPTIME	0.0077	7.707	99.9%
0.05937	TITANIUM*HIPTEMP	0.0077	7.707	99.9%
-0.07063	TITANIUM*LOADING	0.0077	9.167	99.9%
0.05687	MESHSIZE*HIPTIME	0.0077	7.382	99.9%
0.02188	MESHSIZE*HIPTEMP	0.0077	2.839	98.7%
-0.02062	MESHSIZE*LOADING	0.0077	2.677	98.2%
0.01688	HIPTIME*HIPTEMP	0.0077	2.190	95.5%
-0.02312	HIPTIME*LOADING	0.0077	3.002	99.0%
-0.03813	HIPTEMP*LOADING	0.0077	4.949	99.9%
-0.007869	TITANIUM^2	0.0196	0.4005	32.9%
0.02213	MESHSIZE^2	0.0196	1.127	70.1%
0.05713	HIPTIME^2	0.0196	2.908	98.8%
0.02213	HIPTEMP^2	0.0196	1.127	70.1%
0.05213	LOADING^2	0.0196	2.654	98.1%

Confidence figures are based on 11 degrees of freedom

Table A-9
Response Surface Model for Leachability of Cadmium from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.1913	1 (constant)	0.0291	6.566	99.9%
-0.04111	TITANIUM	0.0240	1.711	88.7%
0.1289	MESHSIZE	0.0240	5.365	99.9%
-0.1461	HIPTIME	0.0240	6.082	99.9%
-0.008889	HIPTEMP	0.0240	0.3700	31.3%
-0.08667	LOADING	0.0240	3.607	99.6%
0.1075	TITANIUM*MESHSIZE	0.0255	4.219	99.8%
0.06625	TITANIUM*HIPTIME	0.0255	2.600	97.9%
-0.09875	TITANIUM*HIPTEMP	0.0255	3.875	99.7%
0.1388	TITANIUM*LOADING	0.0255	5.445	99.9%
-0.01750	MESHSIZE*HIPTIME	0.0255	0.6868	48.0%
-0.1600	MESHSIZE*HIPTEMP	0.0255	6.279	99.9%
0.05750	MESHSIZE*LOADING	0.0255	2.257	96.0%
-0.02625	HIPTIME*HIPTEMP	0.0255	1.030	65.7%
0.04125	HIPTIME*LOADING	0.0255	1.619	86.7%
-0.06125	HIPTEMP*LOADING	0.0255	2.404	97.0%
0.02777	TITANIUM^2	0.0650	0.4274	34.2%
-0.07223	MESHSIZE^2	0.0650	1.112	69.5%
0.02277	HIPTIME^2	0.0650	0.3504	30.4%
0.02777	HIPTEMP^2	0.0650	0.4274	34.2%
0.1378	LOADING^2	0.0650	2.120	94.8%

Confidence figures are based on 11 degrees of freedom

Table A-10
Response Surface Model for Leachability of Chromium from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.4360	1 (constant)	0.1141	3.820	99.7%
-0.02981	TITANIUM	0.0941	0.3167	28.8%
0.1865	MESHSIZE	0.0941	1.982	93.2%
-0.05119	HIPTIME	0.0941	0.5438	40.3%
-0.02258	HIPTEMP	0.0941	0.2399	25.2%
-0.01364	LOADING	0.0941	0.1450	21.2%
-0.1003	TITANIUM*MESHSIZE	0.0998	1.005	64.5%
0.1327	TITANIUM*HIPTIME	0.0998	1.329	78.1%
0.001162	TITANIUM*HIPTEMP	0.0998	0.0116	16.3%
-0.000913	TITANIUM*LOADING	0.0998	0.0091	16.2%
-0.04009	MESHSIZE*HIPTIME	0.0998	0.4015	32.9%
0.08016	MESHSIZE*HIPTEMP	0.0998	0.8030	54.2%
0.06834	MESHSIZE*LOADING	0.0998	0.6845	47.9%
-0.1043	HIPTIME*HIPTEMP	0.0998	1.045	66.4%
0.1125	HIPTIME*LOADING	0.0998	1.127	70.1%
0.1765	HIPTEMP*LOADING	0.0998	1.768	89.8%
0.08544	TITANIUM^2	0.2546	0.3356	29.7%
0.1244	MESHSIZE^2	0.2546	0.4888	37.4%
0.01244	HIPTIME^2	0.2546	0.0489	17.6%
0.2179	HIPTEMP^2	0.2546	0.8561	57.0%
-0.4761	LOADING^2	0.2546	1.870	91.6%

Confidence figures are based on 11 degrees of freedom

Table A-11
Response Surface Model for Leachability of Potassium from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef < 0
1.037	1 (constant)	0.0634	16.37	99.9%
0.06056	TITANIUM	0.0523	1.159	71.5%
-0.08000	MESHSIZE	0.0523	1.531	84.4%
0.07833	HIPTIME	0.0523	1.499	83.5%
0.1361	HIPTEMP	0.0523	2.605	98.0%
-0.02000	LOADING	0.0523	0.3828	32.0%
-0.1206	TITANIUM*MESHSIZE	0.0554	2.176	95.4%
-0.1206	TITANIUM*HIPTIME	0.0554	2.176	95.4%
0.05687	TITANIUM*HIPTEMP	0.0554	1.026	65.5%
-0.1494	TITANIUM*LOADING	0.0554	2.695	98.3%
-0.1706	MESHSIZE*HIPTIME	0.0554	3.079	99.1%
0.04438	MESHSIZE*HIPTEMP	0.0554	0.8007	54.1%
0.06813	MESHSIZE*LOADING	0.0554	1.229	74.4%
-0.1381	HIPTIME*HIPTEMP	0.0554	2.492	97.5%
0.06812	HIPTIME*LOADING	0.0554	1.229	74.4%
-0.1169	HIPTEMP*LOADING	0.0554	2.109	94.7%
0.1039	TITANIUM^2	0.1413	0.7355	50.6%
0.2689	MESHSIZE^2	0.1413	1.903	92.1%
-0.2861	HIPTIME^2	0.1413	2.024	93.8%
0.1139	HIPTEMP^2	0.1413	0.8063	54.4%
-0.2411	LOADING^2	0.1413	1.706	88.6%

Confidence figures are based on 11 degrees of freedom

Table A-12
Response Surface Model for Total Mass Loss from
Titanium-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef < 0
0.3237	1 (constant)	0.0229	14.13	99.9%
-0.06689	TITANIUM	0.0189	3.540	99.6%
-0.01872	MESHSIZE	0.0189	0.9907	63.8%
0.01817	HIPTIME	0.0189	0.9613	62.4%
-0.03606	HIPTEMP	0.0189	1.908	92.2%
0.03156	LOADING	0.0189	1.670	87.8%
-0.04150	TITANIUM*MESHSIZE	0.0200	2.070	94.3%
-0.06312	TITANIUM*HIPTIME	0.0200	3.149	99.2%
0.07262	TITANIUM*HIPTEMP	0.0200	3.623	99.6%
-0.04300	TITANIUM*LOADING	0.0200	2.145	95.1%
0.02775	MESHSIZE*HIPTIME	0.0200	1.384	80.0%
-0.02925	MESHSIZE*HIPTEMP	0.0200	1.459	82.4%
0.07687	MESHSIZE*LOADING	0.0200	3.835	99.7%
-0.06162	HIPTIME*HIPTEMP	0.0200	3.074	99.1%
0.05725	HIPTIME*LOADING	0.0200	2.856	98.7%
-0.07100	HIPTEMP*LOADING	0.0200	3.542	99.6%
0.1093	TITANIUM^2	0.0511	2.139	95.0%
0.02578	MESHSIZE^2	0.0511	0.5043	38.2%
-0.04322	HIPTIME^2	0.0511	0.8457	56.5%
-0.006224	HIPTEMP^2	0.0511	0.1218	20.3%
-0.02072	LOADING^2	0.0511	0.4055	33.1%

Confidence figures are based on 11 degrees of freedom

Table A-13
Response Surface Model for Leachability of Aluminum from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
1.146	1 (constant)	0.1501	7.631	99.9%
-0.03278	P205	0.1238	0.2647	26.3%
0.03833	MESHSIZE	0.1238	0.3096	28.4%
-0.05111	HIPTIME	0.1238	0.4128	33.5%
-0.07611	HIPTEMP	0.1238	0.6147	44.1%
-0.1889	LOADING	0.1238	1.526	84.3%
-0.01812	P205*MESHSIZE	0.1313	0.1380	20.9%
0.1569	P205*HIPTIME	0.1313	1.194	73.0%
-0.04438	P205*HIPTEMP	0.1313	0.3379	29.8%
-0.2931	P205*LOADING	0.1313	2.232	95.8%
-0.009375	MESHSIZE*HIPTIME	0.1313	0.0714	18.4%
-0.01062	MESHSIZE*HIPTEMP	0.1313	0.0809	18.7%
0.03563	MESHSIZE*LOADING	0.1313	0.2713	26.6%
-0.02812	HIPTIME*HIPTEMP	0.1313	0.2142	24.1%
-0.04937	HIPTIME*LOADING	0.1313	0.3760	31.6%
0.1469	HIPTEMP*LOADING	0.1313	1.118	69.8%
0.3525	P205^2	0.3349	1.053	66.8%
-0.1575	MESHSIZE^2	0.3349	0.4702	36.4%
-0.1325	HIPTIME^2	0.3349	0.3956	32.6%
-0.3575	HIPTEMP^2	0.3349	1.067	67.5%
-0.1925	LOADING^2	0.3349	0.5747	42.0%

Confidence figures are based on 11 degrees of freedom

Table A-14
Response Surface Model for Leachability of Calcium from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.1535	1 (constant)	0.0271	5.667	99.9%
-0.03167	P205	0.0223	1.418	81.1%
-0.04167	MESHSIZE	0.0223	1.865	91.5%
-0.01000	HIPTIME	0.0223	0.4477	35.3%
-0.01389	HIPTEMP	0.0223	0.6218	44.5%
-0.07444	LOADING	0.0223	3.333	99.4%
0.01750	P205*MESHSIZE	0.0237	0.7386	50.8%
0.08500	P205*HIPTIME	0.0237	3.588	99.6%
0.04250	P205*HIPTEMP	0.0237	1.794	90.3%
-0.02125	P205*LOADING	0.0237	0.8969	59.1%
-0.006250	MESHSIZE*HIPTIME	0.0237	0.2638	26.3%
-0.03875	MESHSIZE*HIPTEMP	0.0237	1.636	87.1%
0.01000	MESHSIZE*LOADING	0.0237	0.4221	33.9%
0.003750	HIPTIME*HIPTEMP	0.0237	0.1583	21.8%
-0.03750	HIPTIME*LOADING	0.0237	1.583	85.8%
-0.010000	HIPTEMP*LOADING	0.0237	0.4221	33.9%
-0.002351	P205^2	0.0604	0.0389	17.2%
0.02765	MESHSIZE^2	0.0604	0.4577	35.8%
0.08265	HIPTIME^2	0.0604	1.368	79.5%
0.01765	HIPTEMP^2	0.0604	0.2921	27.6%
-0.02735	LOADING^2	0.0604	0.4527	35.5%

Confidence figures are based on 11 degrees of freedom

Table A-15
Response Surface Model for Leachability of Cadmium from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
-0.09944	1 (constant)	0.4292	0.2317	24.9%
-1.302	P205	0.3540	3.679	99.7%
1.461	MESHSIZE	0.3540	4.127	99.8%
-1.556	HIPTIME	0.3540	4.396	99.9%
1.461	HIPTEMP	0.3540	4.126	99.8%
1.702	LOADING	0.3540	4.808	99.9%
-1.673	P205*MESHSIZE	0.3755	4.454	99.9%
1.573	P205*HIPTIME	0.3755	4.188	99.8%
-1.663	P205*HIPTEMP	0.3755	4.428	99.9%
-1.401	P205*LOADING	0.3755	3.732	99.7%
-1.713	MESHSIZE*HIPTIME	0.3755	4.561	99.9%
1.530	MESHSIZE*HIPTEMP	0.3755	4.075	99.8%
1.606	MESHSIZE*LOADING	0.3755	4.278	99.8%
-1.803	HIPTIME*HIPTEMP	0.3755	4.801	99.9%
-1.761	HIPTIME*LOADING	0.3755	4.691	99.9%
1.751	HIPTEMP*LOADING	0.3755	4.664	99.9%
0.4040	P205^2	0.9574	0.4220	33.9%
0.3640	MESHSIZE^2	0.9574	0.3802	31.8%
0.3590	HIPTIME^2	0.9574	0.3750	31.6%
0.3590	HIPTEMP^2	0.9574	0.3750	31.6%
0.7340	LOADING^2	0.9574	0.7667	52.3%

Confidence figures are based on 11 degrees of freedom

Table A-16
Response Surface Model for Leachability of Chromium from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.5154	1 (constant)	0.1872	2.753	98.5%
-0.5055	P205	0.1544	3.274	99.4%
0.09578	MESHSIZE	0.1544	0.6202	44.4%
-0.1859	HIPTIME	0.1544	1.204	73.4%
-0.2245	HIPTEMP	0.1544	1.454	82.2%
-0.2228	LOADING	0.0772	2.885	98.8%
0.004688	P205*MESHSIZE	0.1638	0.0286	16.9%
0.3238	P205*HIPTIME	0.1638	1.977	93.2%
0.1499	P205*HIPTEMP	0.1638	0.9154	60.1%
0.2276	P205*LOADING	0.0819	2.779	98.5%
-0.1923	MESHSIZE*HIPTIME	0.1638	1.174	72.1%
-0.1649	MESHSIZE*HIPTEMP	0.1638	1.007	64.6%
0.09703	MESHSIZE*LOADING	0.0819	1.185	72.6%
-0.2411	HIPTIME*HIPTEMP	0.1638	1.472	82.7%
0.1166	HIPTIME*LOADING	0.0819	1.424	81.3%
0.1710	HIPTEMP*LOADING	0.0819	2.088	94.5%
0.08511	P205^2	0.4176	0.2038	23.7%
0.1016	MESHSIZE^2	0.4176	0.2433	25.4%
0.2846	HIPTIME^2	0.4176	0.6815	47.7%
0.3771	HIPTEMP^2	0.4176	0.9030	59.4%
-0.1273	LOADING^2	0.1044	1.220	74.0%

Confidence figures are based on 11 degrees of freedom

Table A-17
Response Surface Model for Leachability of Potassium from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.3988	1 (constant)	0.2788	1.430	81.5%
-1.203	P205	0.2300	5.230	99.9%
0.6672	MESHSIZE	0.2300	2.901	98.8%
-0.6817	HIPTIME	0.2300	2.964	98.9%
-0.9411	HIPTEMP	0.2300	4.092	99.8%
-1.201	LOADING	0.2300	5.220	99.9%
-0.7200	P205*MESHSIZE	0.2439	2.952	98.9%
0.8488	P205*HIPTIME	0.2439	3.480	99.6%
1.005	P205*HIPTEMP	0.2439	4.120	99.8%
1.415	P205*LOADING	0.2439	5.801	99.9%
-1.086	MESHSIZE*HIPTIME	0.2439	4.453	99.9%
-0.7400	MESHSIZE*HIPTEMP	0.2439	3.034	99.1%
-0.7475	MESHSIZE*LOADING	0.2439	3.064	99.1%
0.7337	HIPTIME*HIPTEMP	0.2439	3.008	99.0%
0.6362	HIPTIME*LOADING	0.2439	2.608	98.0%
1.070	HIPTEMP*LOADING	0.2439	4.387	99.9%
0.4709	P205^2	0.6220	0.7571	51.8%
0.2509	MESHSIZE^2	0.6220	0.4033	33.0%
0.3009	HIPTIME^2	0.6220	0.4837	37.1%
0.2359	HIPTEMP^2	0.6220	0.3792	31.8%
0.3009	LOADING^2	0.6220	0.4837	37.1%

Confidence figures are based on 11 degrees of freedom

Table A-18
Response Surface Model for Total Mass Loss from
P₂O₅-Based Glass-Ceramic

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
0.3331	1 (constant)	0.2410	1.383	80.0%
-1.627	P205	0.1987	8.188	99.9%
-0.05650	MESHSIZE	0.1987	0.2843	27.2%
-0.1676	HIPTIME	0.1987	0.8434	56.3%
-0.4528	HIPTEMP	0.1987	2.279	96.2%
-1.660	LOADING	0.1987	8.355	99.9%
0.02388	P205*MESHSIZE	0.2108	0.1133	20.0%
0.2431	P205*HIPTIME	0.2108	1.153	71.3%
0.5111	P205*HIPTEMP	0.2108	2.425	97.1%
1.729	P205*LOADING	0.2108	8.205	99.9%
-0.5296	MESHSIZE*HIPTIME	0.2108	2.513	97.6%
-0.2236	MESHSIZE*HIPTEMP	0.2108	1.061	67.2%
0.09387	MESHSIZE*LOADING	0.2108	0.4454	35.1%
-0.09163	HIPTIME*HIPTEMP	0.2108	0.4347	34.6%
0.1676	HIPTIME*LOADING	0.2108	0.7953	53.8%
0.4694	HIPTEMP*LOADING	0.2108	2.227	95.8%
0.5035	P205^2	0.5375	0.9368	61.2%
0.2370	MESHSIZE^2	0.5375	0.4410	34.9%
0.2810	HIPTIME^2	0.5375	0.5228	39.2%
0.1710	HIPTEMP^2	0.5375	0.3182	28.8%
0.5985	LOADING^2	0.5375	1.114	69.5%

Confidence figures are based on 11 degrees of freedom


```

*.....*
75.0 *FFFFFFFFFFFFFFFFFFFF GGGGGGGGGGGGGG HH*
.EEEEEEEEEEEEEEE FFFFFFFFFFFFFFFF GGGGGGG.
.DDDD DDDDDDDDDDDDDDD EEEEEEEEEEEEE FFFFFFFF.
.DDDDDDDDDDDDDDD EEEEEEEEE FFF.
.CCCCCCCC DDDDDDDDD EEEEEEE.
.CCCCCCCC DDDDDDD EEEE.
.BBB CCCCCC DDDD.
L . BBBB CCCC DDD.
O . BBBB CCC DD.
A . BB CC DD.
D 70.0 * BB CC DDD *
I . BBB CCG DDD.
N . BBB CCG DDD.
G . BBBB CCG DDDD EEEE.
.BBBB CCCCC DDDD EEEE FF.
.CCCCCC DDDDD EEEEE FFFFFF.
.CCCCCC DDDDDDD EEEEE FFFFFF GGGG.
.DDDDDDD EEEEEEE FFFFFFFF GGGGGG HH.
.DDDD EEEEEEE FFFFFFFF GGGGGGGG HHHHHH.
.EEEEEEE FFFFFFFF GGGGGGGG HHHHHHHH IIIIIII.
65.0 * FFFFFFFF GGGGGGGGG HHHHHHHH IIIIIIII JJJJJJ*
*.....*
16. 78. 140.
MESH SIZE

ALUMINUM - 2.000
HIPTIME - 28.00
HIPTEMP - 1025

```

```

A: 0.1000
B: 0.1500
C: 0.2000
D: 0.2500
E: 0.3000
F: 0.3500
G: 0.4000
H: 0.4500
I: 0.5000
J: 0.5500

```

Figure A-3. Response surface for cadmium leachability dependence on calcine loading and maximum calcine particle size in aluminum-based glass-ceramic.

```

*.....*
75.0 *IHHGG FFEEDD CC BBB BB CC D*
.IHH GGFF EE DDD CCC BBB BBB CC DD.
.IIHHGG FF EE DD CC BBB BBB CC DD.
.IIHH GGFF EE DD CC BB BBB CC DD.
.IIIHHGG FF EE DD CC BBB BBB CC DD.
.JIIHHGGFF EE DD CC BBB BBB CC DD.
.JIIHHGGFF EE DD CC BBBB CC DDD.
L . JIIHHGG FF EE DD CCC CCC DD.
O . JIIHHGGFF EE DD CC CC DD.
A . JIIHH GG FF EE DDD CC CC DD.
D 70.0 *JJII HHGG FF EE DD CC CC DD *
I . KJIIHHGG FF EE DD CCC CC DD.
N . KJIIHH GGFF EE DDD CC CC DD.
G . KJIIHH GG FF EE DD CC CC DDD.
.KJIIHHGG FF EE DD CC CC DD.
.KJII HHGG FF EE DD CC CC DD.
.KJIIHHGG FF EE DD CC CC DD.
.KKJIIHHGGFF EE DD CC CC DD.
.KKJIIHHGGFF EEE DD CC CC D.
.KKJIIHH GGFF EEE DD CC CC D.
.KKJIIHH GGFF EEE DD CC CC.
65.0 *KKJIIHH GGFF EE DD CC CC *
*.....*
1.00 2.00 3.00
ALUMINUM

MESH SIZE - 78.00
HIPTIME - 28.00
HIPTEMP - 1025

```

```

C: 0.0
D: 10.0
E: 20.0
F: 30.0
G: 40.0
H: 50.0
I: 60.0
J: 70.0
K: 80.0

```

Figure A-4. Response surface for chromium leachability dependence on calcine loading and aluminum additive in aluminum-based glass-ceramic.

Figure A-5. Response surface for potassium leachability dependence on HIPing time and aluminum additive in aluminum-based glass-ceramic.

Figure A-6. Response surface for total mass loss dependence on calcine loading and aluminum additive in aluminum-based glass-ceramic.

```

*.....*
75.0 *H GGG FFF EEE DD CCC BBBBBBBBBBBBBBBBBB* A: 0.0750
.HH GGG FFF EEE DD CCCC B: 0.1500
.HHH GGG FF EEE DD CCCC C: 0.2250
.HH GG FF EE DDD CCCCCC CCCCCCCC D: 0.3000
.HH GG FFF EE DDD E: 0.3750
.I HH GGG FF EE DDD F: 0.4500
.I HH GG FF EE DD G: 0.5250
L .I HH GG FF EEE DD DD H: 0.6000
O .I HH GG FF EE DD I: 0.6750
A .I HHH GG FF EE DD
D 70.0 * HH GG FF EE DD *
I . HH GG FF EE DDD DD
N . HH GG FFF EE DDD DD
G .HH GGG FFF EEE DDD DDD
.H GG FF EE DDD D
.GG FFF EEE DDDD
.GGG FF EEE DDD CCCCCCCCCCCCCC
.G FFF EEE DDD CCCC CCCC
.FFF EEE DDDD CCCC CCC
.FF EEE DDD CCCC BBBBBBBBBBBBBBBBBB
.EEE DDD CCCC BBBBBB BBBBB
65.0 *EE DDDD CCC BBBBB AAAAAAAAAAAAA BB*
*.....*
16. 78. 140.
MESH SIZE

```

TITANIUM = 5.000
HIPTIME = 28.00
HIPTEMP = 1025

Figure A-7. Response surface for aluminum leachability dependence on calcine loading and maximum calcine particle size in titanium-based glass-ceramic.

```

*.....*
140. * BB CC DDDD * A: 0.1000
.BBB CCC DDD B: 0.1250
.BBBB CCC C: 0.1500
.BBB CCC D: 0.1750
.CCCG C: 0.2000
.CCCGCC F: 0.2250
.CCCCCCCC G: 0.2500
H . CCC H: 0.2750
E . CCC I: 0.3000
S . DDDDDDDDDDD CCC
H 78. * DDDDDDDDD CC *
S . DDD CC
I .EEEEEEEE DDD CC
Z . EEEEEEE DDD CC
E .FFF EEEEE DDD CC
.G FFFFFF EEEE DD CC
.G GGGGG FFFF EEE DD CC
.H GGGGG FFF EEE DD CCC
.HHHH GGGG FFF EEE DDD CC
.I HHHH GGG FFF EE DDD CC
16. * IIIII HHHH GGG FFF EEE DD CC*
*.....*
4.00 5.00 6.00
TITANIUM

```

HIPTIME = 16.00
HIPTEMP = 1025
LOADING = 70.00

Figure A-8. Response surface for calcium leachability dependence on maximum calcine particle size and titanium additive in titanium-based glass-ceramic.

```

*.....*
28.0 *   CCC   DD   EEE   FFFF   *
      CCC   DDD   EE   FFF
      .. CCC   DDD   EEE   FFF
      . CC   DD   EE   FFF   GGGGGGGGGG.
      . CC   DD   EEE   FFF   GGGGG
      . CC   DD   EE   FFF   GGG
      . CC   DD   EEE   FFF   GGG
      . CC   DD   EEE   FF   GGG   HHHHHHHHHH.
H      . DDD   EE   FFF   GGG   HHHHHH
I      . DDD   EE   FFF   GGG   HHHH
P      . DDD   EE   FFF   GGG   HHHH
T 16.0 *DDD   EEE   FF   GG   HHHH   *
I      . DD   EE   FFF   GGG   HHH   IIIIIIIIIIII.
M      . EE   FF   GGG   HHH   IIII
E      . EE   FF   GGG   HHH   IIII
      . EEE   FFF   GG   HHH   IIII   JJJJJJJJJJ.
      . EE   FF   GGG   HHH   III   JJJJJJ
      . FFF   GGG   HHH   III   JJJJ
      . FFF   GG   HHH   III   JJJJ   KKKKKKKKKK.
      . FF   GGG   HH   III   JJJ   KKKK
      . F   GGG   HHH   III   JJJ   KKKK
      . GG   HHH   III   JJJ   KKKK   LLLLLLLLLL.
4.0 *GGG   HH   III   JJJ   KKKK   LLLL   *
*.....*
      16.              78.              140.
                      MESHSIZE

```

D: 0.0000
E: 0.0500
F: 0.1000
G: 0.1500
H: 0.2000
I: 0.2500
J: 0.3000
K: 0.3500
L: 0.4000

TITANIUM = 5.000
HIPTEMP = 1025
LOADING = 70.00

Figure A-9. Response surface for cadmium leachability dependence on HIPing time and maximum calcine particle size in titanium-based glass-ceramic.

```

*.....*
28.0 *   BB   CC   DD   EEE   FF   GG*
      BB   CC   DD   EE   FF   GG
      . BBB   CC   DD   EE   FFF   GG
      . BB   CC   DD   EE   FF   GGG
      . BBB   CC   DDD   EE   FF   GG   H.
      . BB   CC   DD   EE   FF   GG   H.
      . BB   CC   DDD   EE   FF   GG   HH.
H      . BB   CC   DD   EEE   FF   GG   HH.
I      . BB   CC   DDD   EE   FF   GG   HH
P      . BBB   CC   DD   EEE   FF   GG   HH
T 16.0 *   BB   CC   DDD   EE   FF   GG   HH*
I      . BB   CCC   DD   EEE   FF   GG   HH   I.
M      . BB   CC   DD   EE   FF   GG   HH   II.
E      . BBB   CC   DD   EE   FF   GG   HH   II.
      . BBB   CCC   DD   EE   FF   GG   HH   III.
      . BBB   CC   DDD   EE   FF   GG   HH   II
      . BBB   CC   DD   EEE   FFF   GG   HH   II   J.
      . BBB   CCG   DD   EE   FF   GG   HH   II   J.
      . BBB   CC   DDD   EE   FFF   GG   HH   II   JJ.
      . BB   CC   DD   EE   FF   GGG   HH   II   JJ.
      . BBB   CC   DD   EE   FF   GG   HH   II   JJ
4.0 *   BBB   CC   DDD   EE   FFF   GG   HH   IIJJJK*
*.....*
      16.              78.              140.
                      MESHSIZE

```

A: 0.3500
B: 0.4000
C: 0.4500
D: 0.5000
E: 0.5500
F: 0.6000
G: 0.6500
H: 0.7000
I: 0.7500
J: 0.8000
K: 0.8500

TITANIUM = 5.000
HIPTEMP = 1025
LOADING = 70.00

Figure A-10. Response surface for chromium leachability dependence on HIPing time and maximum calcine particle size in titanium-based glass-ceramic.

```

*.....*
1075. *JII HH GG FF EEE DDD CCCCCCCCCCCCCC DDD* A: 0.7500
.IIIHH GG FFF EEE DD CCG CCCC D. B: 0.8250
.II HH GG FF EEE DD CCG CCC C. C: 0.9000
.IIHH GG FF EE DD CC CCC D. D: 0.9750
.I HH GG FF EE DDD CC BBBBBBBBBBBB CC. E: 1.0500
.I HHGG FFF EE DD CC BBB BBB C. F: 1.1250
.IHHHGG FF EEE DDD CC BB BB G: 1.2000
H .IHH GG FF EE DD CC BB BB H: 1.2750
I .IHH GG FF EE DD CCG BB BB I: 1.3500
P .IHH GG FF EE DD CC BB BB J: 1.4250
T 1025. *IHH GG FF EE DD CC BB BB * K: 1.5000
E .IHHHGG FF EE DD CC BB BB
M .I HHGG FF EE DD CCG BB BB
P .IIHH GGFFF EE DD CC BB BB
.IIHH GG FF EE DD CC BB BB
.II HHGG FF EEE DD CC BBB BBB
.IIIHH GG FF EE DD CC BBB BB
.JIIHHHGG FF EE DDD CCG BB BBB
.J IIHH GG FF EEE DDD CCG BBB BBB
.JJII HH GG FF EE DDD CC BBBBBBBBBB
.JJJIIHHHGGGGFFF EE DDD CCG C.
975. *KJJ IHHHGG FFF EEE DD CCG CCC*
*.....*
16. 78. 140.
MESH SIZE

```

TITANIUM - 5.000
HIPTIME - 28.00
LOADING - 70.00

Figure A-11. Response surface for potassium leachability dependence on HIPing temperature and maximum calcine particle size in titanium-based glass-ceramic.

```

*.....*
1075. * EE DD CCG BBBB BBB C* A: 0.1500
. EEE DDD CCG BBBBBBBBBBBB C. B: 0.2000
.FF EE DDD CCG CC. C: 0.2500
.FFF EEE DD CCG CC. D: 0.3000
. FF EE DDD CCG CC E: 0.3500
.G FFF EEE DDD CCG CC F: 0.4000
.GGG FF EE DD CCCC CC G: 0.4500
H . GG FF EEE DD CCCC CC H: 0.5000
I .H GG FFF EEE DDD CCCCC CCC I: 0.5500
P .HH GG FF EE DDD CCCCC J: 0.6000
T 1025. * HHH GGG FF EEE DD * K: 0.6500
E .I HHH GGG FF EE DDD L: 0.7000
M .II HHH GG FFF EEE DDD
P . II HH GG FF EEE DD
.J II HH GG FF EE DDD
.JJ II HH GG FF EE DDD
.JJJ II HH GG FF EEE DD
. JJJ II HH GG FFF EE DDD
.K JJJ II HH GG FFF EE DDD
.KK JJJ II HH GG FFF EE DDD
. KK JJ II HH GG FFF EE DD
975. *L KK JJ II HH GG FFF EE DDD *
*.....*
4.00 5.00 6.00
TITANIUM

```

MESH SIZE - 80.00
HIPTIME - 28.00
LOADING - 70.00

Figure A-12. Response surface for total mass loss dependence on HIPing temperature and titanium additive in titanium-based glass-ceramic.

```

*.....*
75.0 *BBBCCC DDD EEEEE EEEEE DDDD CCC *
. CCC DDD EEEE FFFFFFFFFFFFFFFFFF EEE DD CC.
.CCDDD EEE FFFF FFFF EEE DD C.
.DDD EEE FFFF GGGGGGGGGGGGGG FFF EE DD.
.D EER FFFF GGGGG GGGG FFF EEE DD.
.EEE FFF GGGG HHHHHHHHHH GGG FFF EEE D.
.E FFF GGG HHHH HHH GGG FF EEE.
L .FFF GGG HHHH HHH GG FF EEE.
O .F GGG HHH IIIIIIIIIII HH GG FFF EE.
A .GG HHH IIII III HH GG FF EE.
D 70.0 *GG HH IIII III HH GG FF E*
I . HHH IIII II HH GG FF E.
N . HH IIII JJJJJJJJJ II HHH GG FF E.
G .HH IIII JJ JJ II HH GG FF E.
.H IIII JJ JJ II HH GG FF E.
. II JJ JJ II HH GG FF E.
. II JJ JJ II HH GG FF E.
.III JJ JJ II HH GGG FF E.
.II JJ JJ II HH GG FF EE.
.I JJ JJ II HH GG FF EE.
.I JJJ JJ II HH GG FF EE.
65.0 *I JJJ JJJ II HH GGG FF EED*
*.....*
975. 1025. 1075.
HIPTEMP

```

P2O5 = 5.000
MESH SIZE = 78.00
HIPTIME = 28.00

Figure A-13. Response surface for aluminum leachability dependence on calcine loading and HIPing temperature in P₂O₅-based glass-ceramic.

```

*.....*
75.0 *DD CCCCCC BBBBBBBBBBBBBBBBBB*
. DDDDD CCCCCC .
. DDDDD CCCCCC .
.EEEE DDDD CCCCCCCCCCCCCC.
. EEEEE DDDDD .
. EEEEE DDDDDDD .
.FFFF EEEEE DDDDDDDDDDDDDDD.
L . FFFF EEEEE .
O . FFFF EEEEE .
A .GGG FFFF EEEEE .
D 70.0 * GGGG FFFF EEEEEEEEEE*
I . GCGG FFFF .
N .H GGGG FFFF .
G .HHH GGGG FFFFF .
. HHH GCG FFFFFF .
. HHH GCG FFFF .
. II HHH GGGG .
. III HHH GGGG .
. III HHH GGGG .
. III HHH GGGG .
65.0 * II HHH GGGGGGGG*
*.....*
16. 78. 140.
MESH SIZE

```

P2O5 = 5.000
HIPTIME = 28.00
HIPTEMP = 1025

Figure A-14. Response surface for calcium leachability dependence on calcine loading and maximum calcine particle size in P₂O₅-based glass-ceramic.

MESH SIZE - 78.00
HIPTIME - 28.00
HIPTEMP - 1025

Figure A-15. Response surface for cadmium leachability dependence on calcine loading and P_2O_5 additive in P_2O_5 -based glass-ceramic.

MESH SIZE - 78.00
HIPTIME - 28.00
HIPTEMP - 1025

Figure A-16. Response surface for chromium leachability dependence on calcine loading and P_2O_5 additive in P_2O_5 -based glass-ceramic.

MESH SIZE = 78.00
 HIPTIME = 28.00
 HIPTEMP = 1025

Figure A-17. Response surface for potassium leachability dependence on calcine loading and P₂O₅ additive in P₂O₅-based glass-ceramic.

MESH SIZE = 80.00
 HIPTIME = 16.00
 HIPTEMP = 1025

Figure A-18. Response surface for total mass loss dependence on calcine loading and P₂O₅ additive in P₂O₅-based glass-ceramic.

APPENDIX B

TRANSMITTED ERROR ROUTINE APPLICATION TO REDUCE THE NUMBER OF RESPONSE SURFACES

When more than three process parameters have significant effects on product properties the number of response surfaces that address dominant process parameter combinations becomes large. XSTAT 1.01 can be used in conjunction with the DuPont transmitted error macro, to reduce the generated response surfaces to a manageable number. Such is the case where all process parameters investigated except calcine loading have statistically significant effects on calcium leachability from the titanium-based waste forms (see Table 24). In this situation, those process parameters which are most easily controlled (HIPing temperature and HIPing time) or have lesser effects (calcine loading) are designated environmental variables and set at their midpoints (HIP soak time: 16 hours, HIP temperature: 1025°C, calcine loading: 70 wt%). Those which have the most uncertain control (amount of titanium additive and calcine particle size) are designated design variables. Acceptable tolerances, as given in Table B-1, are introduced for each variable. The transmitted error macro converts the effects of the environmental variables into "noise" of the response to the design variables, and the tolerances scale the effects of the noise on the response, in this case on calcium leachability. The result of this operation is that a single response surface model is generated, and it is a function of the design variables, the amounts of titanium additive and calcine particle size. Associated with the new response model is a noise model derived from the transmitted error generated by incorporating the environmental variables. Thus, the design variable response surface has an associated noise response surface which should be treated in the same manner as variance associated with experimental error.

Table B-1

Mean Values and Tolerances Used for Environmental
Variables in Transmitted Error Exercise.

<u>Process Parameter</u>	<u>Centerpoint Value</u>	<u>Tolerance</u>
Titanium Additive	5 wt%	0.1 wt%
Calcine Particle Size	Pass 78 mesh	± 2 mesh
HIPing Time	16 Hr	± 0.2 Hr
HIPing Temperature	1025°C	± 2 °C
Calcine Loading	70 wt%	± 0.5 wt%

The response surface model for the calcine particle size and amount of titanium additive ($R^2=0.91$) without the effects of calcine loading, HIP time and HIP temperature is given for calcium leachability in Table B-2. The associated noise model is given in Table B-3. The response surface for the effect of calcine loading and amount of titanium on calcium leachability, without the effects HIPing time, HIPing temperature and calcine particle size is given in Figure B-1. The associated noise response surface is given in Figure B-2. Observation of the new response surface reveals that it is very similar to the one generated for calcium leachability (Figure 12) before application of the transmitted error routine. This suggests that within parameter ranges used in the study the effects of HIPing time and HIPing temperature cannot be greater than those of calcine particle size or amount of titanium loading, whereas the effect of calcine loading remains relatively minor.

Table B-2

Response Surface Model for Calcium Leachability from
Titanium-Based Glass-Ceramics

Coefficient	Term	Standard Error	T-Value	Confidence Coef $\leq$ 0
0.5655	1 (constant)	0.2572	2.199	97.2 %
-0.02082	TITANIUM	0.1076	0.1936	23.3 %
0.006614	MESHSIZE	0.0006	11.04	99.9 %
-0.000998	TITANIUM*MESHSIZE	0.0001	12.35	99.9 %
0.007869	TITANIUM^2	0.0107	0.7336	51.1 %
0.000006	MESHSIZE^2	0.0000	2.063	96.0 %

Confidence figures are based on 26 degrees of freedom

Table B-3

Noise Model Associated with Response Surface Model for
Design Variables Effects

Coefficient	Term	Standard Error	T-Value	Confidence Coef $\leq$ 0
0.1299	1 (constant)	0.1194	1.088	69.6 %
-0.04456	TITANIUM	0.0499	0.8922	59.7 %
0.000024	MESHSIZE	0.0003	0.0873	19.0 %
-0.000017	TITANIUM*MESHSIZE	0.0000	0.4551	35.9 %
0.004708	TITANIUM^2	0.0050	0.9453	62.5 %
0.000000	MESHSIZE^2	0.0000	0.2293	24.9 %

Confidence figures are based on 26 degrees of freedom

Figure B-1. Response surface for calcium leachability dependence on amount of titanium additive and soak time in titanium-based glass-ceramic.

Figure B-2. Noise surface associated with calcium leachability dependence on amount of titanium additive and soak time in titanium-based glass-ceramic.

Table C-1

Minimum and Maximum Leachabilities (g/m²-day) of
Glass-Ceramic Formed by Titanium-Based Glass-Ceramic

<u>Species</u>	<u>Leachability</u> <u>g/m²-day</u>	<u>Ti Metal</u> <u>Amount</u>	<u>Calcine Ptcl.</u> <u>Size</u>	<u>HIP</u> <u>Time</u>	<u>HIP</u> <u>Temp.</u>	<u>Calcine</u> <u>Loading</u>
Al						
<u>Minimum</u>	0.90	4.8	140	28.0	975	75.0
<u>Maximum</u>	1.71	6.0	16	7.8	975	72.9
B						
<u>Minimum</u>	0.04	4.8	24	23.0	1075	65.0
<u>Maximum</u>	2.67	6.0	140	11.5	1075	65.4
Ca						
<u>Minimum</u>	0.03	4.0	140	17.8	1075	69.1
<u>Maximum</u>	0.91	4.0	16	4.0	975	75.0
Cd						
<u>Minimum</u>	0.01	6.0	45	28.0	1019	67.0
<u>Maximum</u>	1.22	4.0	16	4.0	1075	65.0
Cr						
<u>Minimum</u>	0.15	4.0	16	28.0	1038	73.0
<u>Maximum</u>	1.29	4.0	140	4.0	975	68.8
K						
<u>Minimum</u>	0.28	4.8	58	4.0	985	73.0
<u>Maximum</u>	2.05	6.0	16	14.5	1075	66.7
Na						
<u>Minimum</u>	0.30	4.0	107	4.0	975	65.0
<u>Maximum</u>	5.61	4.0	140	28.0	975	75.0
Si						
<u>Minimum</u>	0.07	6.0	139	28.0	1011	65.0
<u>Maximum</u>	0.81	6.0	16	17.1	1075	72.8
Total						
Mass						
<u>Minimum</u>	0.10	5.9	140	28.0	975	65.0
<u>Maximum</u>	1.07	4.0	140	28.0	975	75.0

^a Amount of Ti metal and calcine loading are in weight percent, calcine particle size is US std sieve size, HIP time is in hours of soak period and HIP temp is soak temperature in degrees Celsius.

APPENDIX D

QUALITATIVE X-RAY DIFFRACTION ANALYSIS OF TITANIUM-BASED FORMULATION GLASS-CERAMIC PRODUCTS

Semiquantitative x-ray diffraction analysis was performed on each titanium-based product formed in this study. The qualitative results of this analysis are given in Table D-1. This table gives the conditions of formation of each glass-ceramic product in the face centered cube test matrix as well as the major and minor phases identified in the product of each test. Calcium fluoride, CaF_2 , is a major component of each glass-ceramic product formed in the test matrix. Zirconia, ZrO_2 , or the most likely phase to which it converts under conditions of this test, ZrSiO_4 , are also major components. Silica is a major phase in one product. Minor phases include albite, $\text{NaAlSi}_3\text{O}_8$; anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$; cadmium; cadmium sulfide, CdS ; rutile, TiO_2 ; silica; sphene, CaTiSiO_5 ; zircon, ZrSiO_4 ; zirconia, ZrO_2 ; and zirconolite, $\text{CaZrTi}_2\text{O}_7$. The dependence of the amount of these phases in a product on processing parameters and their systematic effect on durability would require a more rigorous investigation than performed in this study.

Table D-1
Crystalline Phases Identified in Titanium-Based Glass-Ceramic

Product	Titanium	Formation Conditions ^a			Loading	Major Phases Identified	Minor Phases Identified
		Meshsize	HIPTime	HIPTemp			
1	4.0	16.0	4.0	975.0	75.0	CaF ₂ , ZrO ₂	CaAl ₂ Si ₂ O ₈
2	6.0	16.0	4.0	975.0	65.0	CaF ₂ , ZrO ₂ , SiO ₂	CaTiSiO ₅ , Cd, ZrSiO ₄
3	4.0	140.0	4.0	975.0	65.0	CaF ₂ , ZrSiO ₄	CaTiSiO ₅ , CdS, SiO ₂ , ZrO ₂
4	6.0	140.0	4.0	975.0	75.0	CaF ₂ , ZrO ₂	CdS, ZrSiO ₄
5	4.0	16.0	28.0	975.0	65.0	CaF ₂ , ZrSiO ₄	ZrO ₂
6	6.0	16.0	28.0	975.0	75.0	CaF ₂ , ZrO ₂	CaTiSiO ₅ , Cd
7	4.0	140.0	28.0	975.0	75.0	CaF ₂ , ZrO ₂	CaTiSiO ₅ , CdS, ZrSiO ₄
8	6.0	140.0	28.0	975.0	65.0	CaF ₂ , ZrSiO ₄	CaAl ₂ Si ₂ O ₈
9	4.0	16.0	4.0	1075.0	65.0	CaF ₂ , ZrSiO ₄	CdS, SiO ₂ , ZrO ₂
10	6.0	16.0	4.0	1075.0	75.0	CaF ₂ , ZrO ₂	
11	4.0	140.0	4.0	1075.0	75.0	CaF ₂	CaZrTi ₂ O ₇ , ZrO ₂
12	6.0	140.0	4.0	1075.0	65.0	CaF ₂ , ZrSiO ₄	CdS, ZrO ₂
13	4.0	16.0	28.0	1075.0	75.0	CaF ₂ , ZrO ₂	CdS, TiO ₂ , ZrSiO ₄
14	6.0	16.0	28.0	1075.0	65.0	CaF ₂ , ZrSiO ₄	CaAl ₂ Si ₂ O ₈
15	4.0	140.0	28.0	1075.0	65.0	CaF ₂ , ZrSiO ₄	CaTiSiO ₅ , ZrO ₂
16	6.0	140.0	28.0	1075.0	75.0	CaF ₂	CaZrTi ₂ O ₇ , Cd, ZrO ₂
17	4.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	NaAlSi ₃ O ₈ , ZrO ₂
18	6.0	78.0	16.0	1025.0	70.0	CaF ₂	ZrO ₂ , ZrSiO ₄
19	5.0	16.0	16.0	1025.0	70.0	CaF ₂ , ZrO ₂ , ZrSiO ₄	CdS
20	5.0	140.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaTiSiO ₅ , CdS, ZrO ₂
21	5.0	78.0	4.0	1025.0	70.0	CaF ₂ , ZrO ₂	ZrSiO ₄
22	5.0	78.0	28.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaTiSiO ₅ , ZrO ₂
23	5.0	78.0	16.0	975.0	70.0	CaF ₂ , ZrO ₂ , ZrSiO ₄	CaTiSiO ₅
24	5.0	78.0	16.0	1075.0	70.0	CaF ₂ , ZrO ₂ , SiO ₄	CaTiSiO ₅ , Cd, ZrSiO ₄
25	5.0	78.0	16.0	1025.0	65.0	CaF ₂ , ZrSiO ₄	CaTiSiO ₅ , CdS, ZrO ₂
26	5.0	78.0	16.0	1025.0	75.0	CaF ₂ , ZrO ₂	CaZrTi ₂ O ₇ , CdS, ZrSiO ₄
27	5.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaZrTi ₂ O ₇ , ZrO ₂
28	5.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaZrTi ₂ O ₇ , ZrO ₂
29	5.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaZrTi ₂ O ₇ , ZrO ₂
30	5.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaZrTi ₂ O ₇ , ZrO ₂
31	5.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaZrTi ₂ O ₇ , ZrO ₂
32	5.0	78.0	16.0	1025.0	70.0	CaF ₂ , ZrSiO ₄	CaZrTi ₂ O ₇ , ZrO ₂

^a Titanium = weight percent Ti metal in product

Meshsize = Maximum Sieve Size (U.S. Std) of calcine particles

HIPTime = HIPing soak time in hours

HIPTemp = HIPing soak temperature in Deg. C

Loading = Weight percent calcine in product