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A STUDY OF THE RESPONSE CONTOURS OF THE HOT-PRESSED DENSITY OF THORIUM OXIDE PELLETS

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CONTENTS

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INTRODUCTION

Twenty pellets of thorium oxide were fabricated by the hot pressing method in order to study the effects of time, temperature, and load on the final density. This report is a description of the statistical techniques used to investigate the phenomenon.

THE MATHEMATICAL MODEL

Since hot pressed density is a continuous variable, measureable by real numbers, and since the three factors, time, temperature, and load, which affect hot pressed density are also continuous variables which may be measured on the real line, it is easy to suppose that there exists some continuous mathematical function

$$\eta = f(x_1, x_2, x_3)$$

which expresses the dependence of hot pressed density, η, on the three factors, x_1, x_2, and x_3. This function represents a response surface* in that η is a response to the stimuli, x_1, x_2, and x_3.

An approximation to this function is a Taylor Series expansion

$$\eta = \beta_o + \beta_i \sum_{i=1}^{3} x_i + \sum_{i \leq j=1}^{3} \beta_{ij} x_i x_j$$

wherein all terms beyond the second order are ignored and in which β_o, β_i, and β_{ij} are ten undetermined coefficients. This is frequently called a second order (because the highest order term is of the second order) response surface model and experimental designs have been

*Since the response is in the fourth dimension, hyper-surface would be a better word. However, the custom is to use the word surface.

developed to estimate the coefficients in the second order model in a very efficient manner.

The experimental designs require that observations, Y, on the response, η, be obtained for predetermined combinations of the factors, x_1, x_2, and x_3. It is assumed that

$$Y = \eta + \epsilon$$

where ϵ is a random disturbance with zero mean and constant variance. From the observed responses an estimating equation

$$Y_c = b_o + \sum_{i=1}^{3} b_i x_i + \sum_{i\leq j=1}^{3} b_{ij} x_i x_j$$

is calculated where Y_c, b_o, b_i, and b_{ij} are the best estimates (in a statistical sense) of η, β_o, β_i, and β_{ij} respectively.

THE DESIGN VARIABLES

Time

The experiment was to investigate among other things the effect of the length of time a pellet was pressed on the density of the pellet. The shortest period of time was to be 20 seconds and the longest 15 minutes (900 seconds). Previous study showed that for isothermal pressing, the density of the pellet could be fairly well described by the function

$$\rho = \rho(t^{2/3}) ,$$

where ρ represents final density in g/cc and t is time of pressing in seconds. The function was essentially quadratic.

Because of this functional relationship, the spacing of the levels of time selected for the experimental design was arithmetic in $t^{2/3}$.

Temperature

Another variable chosen for study was the temperature at which the pellet was controlled while being pressed. The range of temperature selected was from $1000^{o}C$ to $1600^{o}C$. The levels of temperature were spaced arithmetically in degrees Centigrade.

Load

The pellets were pressed under different loads which ranged from 0 to 3000 pounds per square inch (psi). As with the temperature variable arithmetic spacing was chosen for the levels of this design variable.

Material

The ThO_2 powder from which the pellets were pressed came from two batches designated TH-3D and TH-3B. The difference in densities of the pellets which were made from these batches was expected to be constant for all combinations of time, temperature, and load. Thus, this essentially qualitative variable could be handled in the same manner in which one may handle possible sources of systematic variation, that is, by "blocking." The design was divided into two blocks so that one block would consist of pellets fabricated from the TH-3D batch and the other would consist of pellets fabricated from the TH-3B batch.

THE EXPERIMENTAL DESIGN

A composite design in three factors (design variables) in two blocks was chosen for the experiment. Twenty pellets were pressed using 15 different combinations of the levels of the three design variables.

Geometrical Description

The design is easily described geometrically and may be represented by the drawing in Figure 1. Consider that the three axes in 3-dimensional space represent the continuous variables, time, temperature, and load. Then a given combination of time, temperature, and load (e.g., 20 seconds, $1300^{o}C.$ and 1500 psi) is represented by a single point in this 3-dimensional space. Several of these points could represent the verteces of a solid geometrical figure.

The central composite design uses the eight vertices of a cube, the six vertices of an octahedron and a point in the center for a total of

15 points. The octahedron is symmetrically and concentrically oriented to the cube with its vertices on perpendiculars to the faces of the cube. The size of the octahedron relative to that of the cube is, in general, open to choice. But if the experimental design is blocked this size is fixed.

Coding

Because the arithmetic is easier and because the design is more easily described when the design points are coded, the following transformations were made:

$$x_1 = \frac{(\text{Time})^{2/3} - 50.29}{26.29}$$

$$x_2 = \frac{\text{Temperature} - 1300}{184}$$

$$x_3 = \frac{\text{Load} - 1500}{919}$$

As may be seen from Figure 1, there are five levels for each of the design variables. When the design is divided into two blocks, orthogonal blocking requires that these levels, in coded form, be -1.633, -1, 0, 1, 1.633. The actual levels of the design variables, using the transforming equations above, become as shown in the table below.

Variable	Levels of Variable				
Coded	-1.633	-1	0	1	1.633
Time (sec.)	20	117.6	356.7	670.1	900
Temp. ($^{\circ}$C)	1,000	1,116	1,300	1,484	1,600
Load (psi)	0	581	1,500	2,419	3,000

Blocking

As was mentioned previously, two batches of ThO_2 were to be used and this factor would be handled by blocking. A second order polynomial model was to be fitted and in order that block effects would not be confused with the effects of the three primary variables, time, temperature, and load, the following conditions were necessary.

First, the coded levels of the variables corresponding to the octahedral points of the design must be at $\pm$ 1.633 if the levels of the variables corresponding to points on the cube are at $\pm$ 1.

Second, one block must consist of all points on the cube and some center points and the other block must consist of all points on the octahedron with some additional center points. One block would be performed using material from one batch and the other block would be performed using material from the other batch.

Third, the number of center points in the block composed of points on the cube must be four, while the number of center points in the other block must be two.

Table I shows the experimental design in units of the design variables and with coded levels in parentheses. For convenience, the response, hot-pressed density of the fabricated pellet in g/cc, is also shown in this table.

ANALYSIS

A first step in the analysis of these 20 results is an investigation of the variation among the numbers, ignoring the fact that the results are a function of the three continuous variables, time, temperature, and load. The numbers are analyzed as 20 determinations on 15 different "treatments." This is done most easily by the analysis of variance technique and the results are shown in Table II. (For convenience, 6.00 was subtracted from each hot-pressed density. This in no way affects the variation among the numbers.)

Results of Preliminary Analysis

In Table II are presented the mean squares attributable to the several sources of variation. The mean square for experimental error in Block I (0.0006) is not significantly different from the mean square for error in Block II (0.0032) at the 5 per cent significance level. (The ratio must be 1:10 to be significant.) We may conclude then that the difference in batches of ThO_2 does not manifest itself by different experimental errors. We will feel free to pool these estimates of experimental error into a single estimate at a later stage in the analysis.

The mean square due to the difference between blocks (0.3234) is significant. This reflects a real difference in the average densities of the pellets made from the two batches.

In both Blocks I and II the mean squares attributable to differences among treatments are significantly larger than those due to error. Since the treatments are different because they represent different combinations of time, temperature, and load we may conclude that time and/or temperature and/or load have a real effect on hot-pressed density. Indeed if this were not so, any further analysis of the data would be only academic.

Response Surface Analysis

The central composite design was selected in order to estimate effectively the coefficients in a second order polynomial model. The model may be written now, as

$$\eta = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i<j=1}^{3} \beta_{ij} x_i x_j + \beta_z z ,$$

in which β_0, β_i, β_{ij}, and β_z are coefficients to be estimated, η is the response, density of hot-pressed pellet, the x_i are as defined earlier, and z is a dummy variable equal to -0.4 for all pellets from Block I and equal to +0.6 for all pellets from Block II. The equation is fitted to the data by the method of least squares.

Analysis in Terms of the Axes of Measurement

In a later section an analysis will be explained in which the response is described as a function of variables defined on different axes from those of time, temperature and load. In this section the analysis will be in terms of the original axes of measurement.

The least squares calculation provided estimates b_0, b_i, b_{ij}, and b_z of the coefficients in the second order model. The contribution of the several coefficients may be assessed by reference to Table III.

Table III is an analysis of variance of the 20 results according to the second order model (This table does not give the values of b_0, b_i, b_{ij}, and b_z. They are given further below.) The mean squares opposite the coefficients in Table III show how much of the total variability (19.11620) may be accounted for by the corresponding coefficients.

The Lack of Fit mean square with 5 degrees of freedom should be examined first. It is compared with the mean square for Experimental Error with 4 degrees of freedom and not found to be significant at the 5 per cent level. This test shows that the second order model describes the response of hot-pressed density adequately, i.e., within the limits of experimental error. In other words, the truncated Taylor Series expansion is an acceptable approximation to $\eta = f(x_1, x_2, x_3)$.

The mean squares for Lack of Fit and Experimental Error were then combined to form the mean square for Pooled Experimental Error with 9 degrees of freedom. It is this estimate of experimental error which is used to test the significance of the mean squares for the coefficients in Table III and later on is used to compute the confidence intervals.

The tests of significance applied to the mean squares in Table III show that the contributions of all coefficients, except the two mixed quadratic coefficients, b_{12} and b_{13}, are significant at the 5 per cent level.

The estimates of the coefficients with their 95 per cent limits of error (which form the 95 per cent confidence intervals) are as follows:

$b_0 = 6.439 \pm .058$		
$b_1 = 0.165 \pm .039$	$b_{11} = -0.0306 \pm .0392$	$b_{12} = 0.0025 \pm .0503$
$b_2 = 0.890 \pm .039$	$b_{22} = 0.1382 \pm .0392$	$b_{13} = 0.0425 \pm .0503$
$b_3 = 0.314 \pm .039$	$b_{33} = 0.0482 \pm .0392$	$b_{23} = 0.1950 \pm .0503$
		$b_z = 0.2596 \pm .0650$

An apparent inconsistency needs explanation here. It may be seen that the 95 per cent limit of error for the coefficient, b_{11}, is greater than the magnitude of the coefficient itself. Yet the test of significance in Table III showed that the contribution of b_{11} was significant. This has happened because the mean square for b_{11} in Table III represents the contribution of b_{11} ignoring completely the contributions of b_{22} and b_{33}. The coefficient b_{11}, itself, however, is calculated by taking b_{22} and b_{33} into account. In other words, if β_{22} and β_{33} had not been included in the model the estimate of β_{11} would have had a magnitude larger than its limit of error.

Canonical Analysis

By translating the origin of the independent variables to the stationary point (i.e., to those coordinates which satisfy $\partial Y_c/\partial x_i = 0$, $i = 1, 2, 3$, where Y_c represents the equation of the model with b's replacing the β's) and by rotating the axes to eliminate the mixed quadratic terms, the fitted equation may be expressed by

$$Y_c - Y_s - b_z z = -0.0419\ X_1^2 - 0.0035\ X_2^2 + 0.2012\ X_3^2$$

In this form of the polynomial, Y_c and Z are defined as before; Y_s is the value calculated from the response equation at the stationary point and X_1, X_2, and X_3 are defined as follows:

$$X_1 = 0.849\ (x_1 + 7.33) + 0.247\ (x_2 - 7.33) - 0.468\ (x_3 + 14.87)$$
$$X_2 = 0.526\ (x_1 + 7.33) - 0.485\ (x_2 - 7.33) + 0.698\ (x_3 + 14.87)$$
$$X_3 = 0.054\ (x_1 + 7.33) + 0.839\ (x_2 - 7.33) + 0.542\ (x_3 + 14.87)$$

The numerical coefficients in the three equations above form the canonical vectors of the fitted second degree equation. The coefficients of X_1^2, X_2^2, and X_3^2 in the equation previous are the canonical roots.

The canonical form of the fitted equation shows that the response is essentially two-dimensional. That is, since the coefficient of X_2^2

is negligible (-0.0035), a good approximation would be

$$Y_c - Y_s - b_z\, z = -\,0.0419\, X_1^2 + 0.2012\, X_3^2$$

which involves only the variables X_1 and X_3. Now, this equation represents a minimax surface, in that any change in X_1 causes a decrease in the response while any change in X_3 causes an increase. To decrease the density of hot-pressed pellets one should move away from the stationary point along the X_1 axis in the factor space. Since X_1 is defined by

$$\begin{aligned} X_1 &= 0.849\,(x_1 + 7.33) + 0.247\,(x_2 - 7.33) - 0.468\,(x_3 + 14.87) \\ &= -2.54 + 0.849\,x_1 + 0.247\,x_2 - 0.468\,x_3 \end{aligned}$$

values of time, temperature, and load such that $x_1 < 0$, $x_2 < 0$, and $x_3 > 0$ will result in larger magnitudes of X_1 and thus cause greater decreases in hot-pressed density than other values of x_1, x_2, and x_3. Thus, lesser hot-pressed densities will obtain for times less than 356.7 seconds, temperatures less than 1300°C, and loads greater than 1500 psi. (See the table on page 4). A change in time has the greatest effect.

On the other hand, the greatest increases in hot-pressed densities are obtained by changing X_3. Since X_3 is defined by

$$\begin{aligned} X_3 &= 0.054\,(x_1 + 7.33) + 0.839\,(x_2 - 7.33) + 0.542\,(x_3 + 14.87) \\ &= 2.305 + 0.054\,x_1 + 0.839\,x_2 + 0.542\,x_3 \end{aligned}$$

larger magnitudes of X_3 and thus greater increases in density are obtained by choosing values of time, temperature, and load such that $x_1 > 0$, $x_2 > 0$, and $x_3 > 0$ rather than otherwise. This means time greater than 356.7 seconds, temperature greater than 1300°C, and loads larger than 1500 psi. For increases in density a change in temperature has the greatest effect.

These conclusions concerning the means of changing time, temperature, and load to obtain decreases or increases in hot-pressed density could be observed from Table I, of course. For example, a few paragraphs earlier it was said that $x_1 < 0$, $x_2 < 0$, and $x_3 > 0$ would result in decreases in density. In Table I there is an observation at $x_1 = -1$, $x_2 = -1$, and $x_3 = +1$; the hot-pressed density at this point is 5.56 g/cc, one of the smallest densities observed.

Similarly, $x_1 > 0$, $x_2 > 0$, $x_3 > 0$ was said to result in greater densities. In Table I, there is an observation at $x_1 = 1$, $x_2 = 1$, $x_3 = 1$ where the density was observed to be 8.10 g/cc, almost the largest of them all.

It is interesting to verify that the data support these conclusions from the canonical analysis but we have not taken full advantage of what has been learned. There is more to say than that $x_1 < 0$, $x_2 < 0$, and $x_3 > 0$ will result in lower densities of pellets. We may say instead that the greatest decreases in density may be obtained by changing x_1, x_2, and x_3 in the ratio -0.849: -0.247: 0.468. Similarly, the greatest increases in density may be obtained by changing x_1, x_2, and x_3 in the ratio 0.054: 0.839: 0.542. Since the coefficient of X_3^2 (0.2012) is larger than the absolute value of the coefficient of X_1^2, (-0.0419), increases in density are obtained with less change in X_3 than decreases are obtained from a change in X_1.

Graphical Description

Within the boundaries of the experimental design (20 - 900 secs, 1,000 - 1600°C, 0 - 3000 psi), the contours of constant hot-pressed density are shown in Figure 2. The contours are like curved sheets slanting down through the space of time, temperature and load. For smaller values of time and load the curvature is more pronounced. At the higher loads the sheets are almost flat.

The "sheet" closest to the back of the diagram represents a density of 8 g/cc from pellets of batch TH-3D. (It would represent a density of about 8.25 g/cc from pellets of the other batch.) Any combination of time, temperature, and load which could be plotted as a point on this sheet would result in a final hot-pressed density of pellet of 8 g/cc. The other contours may be interpreted similarly for densities of 7, 6, 5.5 and 5 g/cc proceeding from back to front.

SUMMARY

Hot-pressed density of ThO_2 pellets as a function of time, temperature, and load may be approximated adequately by the quadratic function.

$$Y_c = 6.439 + 0.165\, x_1 + 0.890\, x_2 + 0.314\, x_3 - 0.0306\, x_1^2 + 0.138\, x_2^2 + 0.0482\, x_3^2 + 0.0025\, x_1 x_2 + 0.0425\, x_1 x_3 + 0.195\, x_2 x_3 + 0.260\, z$$

in which Y_c is predicted density, x_1, x_2, and x_3 represent time, temperature, and load transformed by the equations on page 4 of this report and $z = -0.4$ or $+ 0.6$ as the ThO_2 is representative of batch Th-3D or batch Th-3B of powder.

The equation is useful only for times between 20 and 900 seconds, temperatures between 1,000 and 1,600°C and loads between 0 and 3,000 psi. Any attempt to use this equation beyond these ranges would not be reccommended. However, within these ranges of the independent variables, the final hot-pressed density may be predicted within adequate limits of error.

ACKNOWLEDGEMENT

The problem described here originated with Chester S. Morgan and Charles S. Yust of the Metals and Ceramics Division. The experiment was carried out under their direction. All credit for the successful performance of the experiment belongs to Morgan and Yust and their colleagues.

Table 1. Three-Factor Composite Design in Two Blocks

Design Variables				Response
Time (sec)	Temp. (°C)	Load (psi)	Material	Hot-pressed Density (g/cc)
118 (-1)	1484 (1)	581 (-1)	TH-3D (-0.4)	6.73
670 (1)	1485 (1)	581 (-1)	"	6.95
670 (1)	1116 (-1)	2419 (1)	"	5.94
118 (-1)	1116 (-1)	581 (-1)	"	5.36
670 (1)	1484 (1)	2419 (1)	"	8.10
118 (-1)	1484 (1)	2419 (1)	"	7.74
670 (1)	1116 (-1)	581 (-1)	"	5.54
357 (0)	1300 (0)	1500 (0)	"	6.37
357 (0)	1300 (0)	1500 (0)	"	6.34
357 (0)	1300 (0)	1500 (0)	"	6.31
357 (0)	1300 (0)	1500 (0)	"	6.33
118 (-1)	1116 (-1)	2419 (1)	"	5.56
900 (1.633)	1300 (0)	1500 (0)	TH-3B (0.6)	6.84
357 (0)	1000 (-1.633)	1500 (0)	"	5.51
20 (-1.633)	1300 (0)	1500 (0)	"	6.19
357 (0)	1300 (0)	1500 (0)	"	6.63
357 (0)	1300 (0)	1500 (0)	"	6.55
357 (0)	1300 (0)	0 (-1.633)	"	6.29
357 (0)	1600 (1.633)	1500 (0)	"	8.42
357 (0)	1300 (0)	3000 (1.633)	"	7.16

Table II. Preliminary Analysis of Variance

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square
Total	20	19.11620	
Mean	1	5.89698	
Between Blocks	1	0.32344	0.3234
Among Treatments			
In Block I	8	7.83261	0.9791
In Block II	6	5.05809	0.8430
Experimental Error			
In Block I	3	0.00188	0.0006
In Block II	1	0.00320	0.0032

Table III. Analysis of Variance According to the Second Order Model

Source of Variation	Degrees of Freedom	Sum of Squares*	Mean Square
Total	20	19.11620	
b_o	1		5.8970 S
Linear Terms			
b_1 (time)	1		0.3635 S
b_2 (temp.)	1		10.5708 S
b_3 (load)	1		1.3109 S
Quadratic Terms			
b_{11} after b_o	1		0.0247 S
b_{22} after b_o and b_{11}	1		0.2410 S
b_{33} after b_o, b_{11}, b_{22}	1		0.0307 S
Mixed Quadratic			
b_{12}	1		0.0001
b_{13}	1		0.0144
b_{23}	1		0.3042
Block Coefficient, b_z	1		0.3234 S
Lack of Fit	5	0.03059	0.0061
Experimental Error	4	0.00508	0.0013
Pooled Experimental Error	9	0.03567	0.0040

*The missing Sums of Squares are the same as the Mean Squares.

S opposite a Mean Square means that Mean Square is significant at the 5 per cent level.

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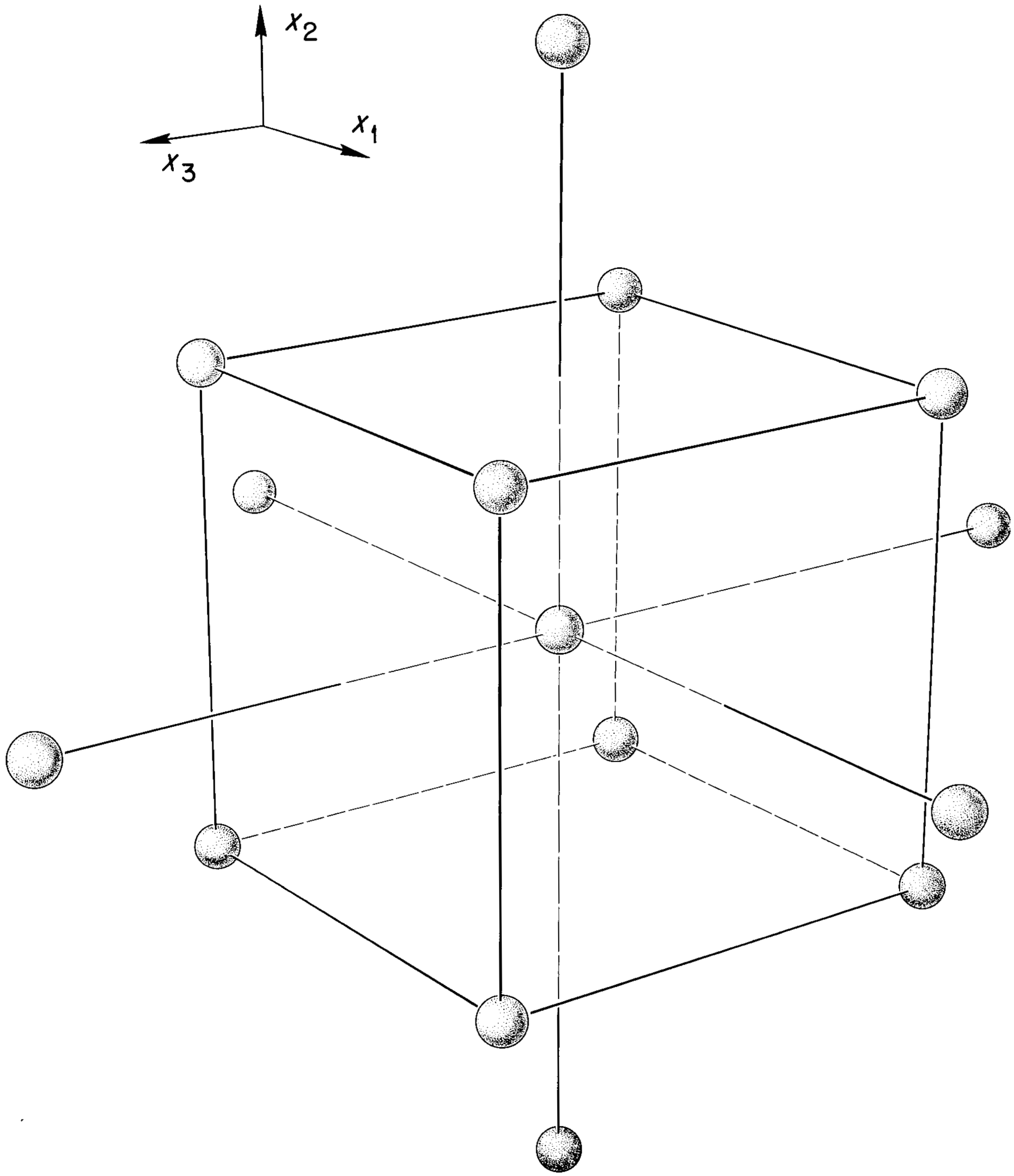

Fig. 1. Central Composite Design — Three Factors.

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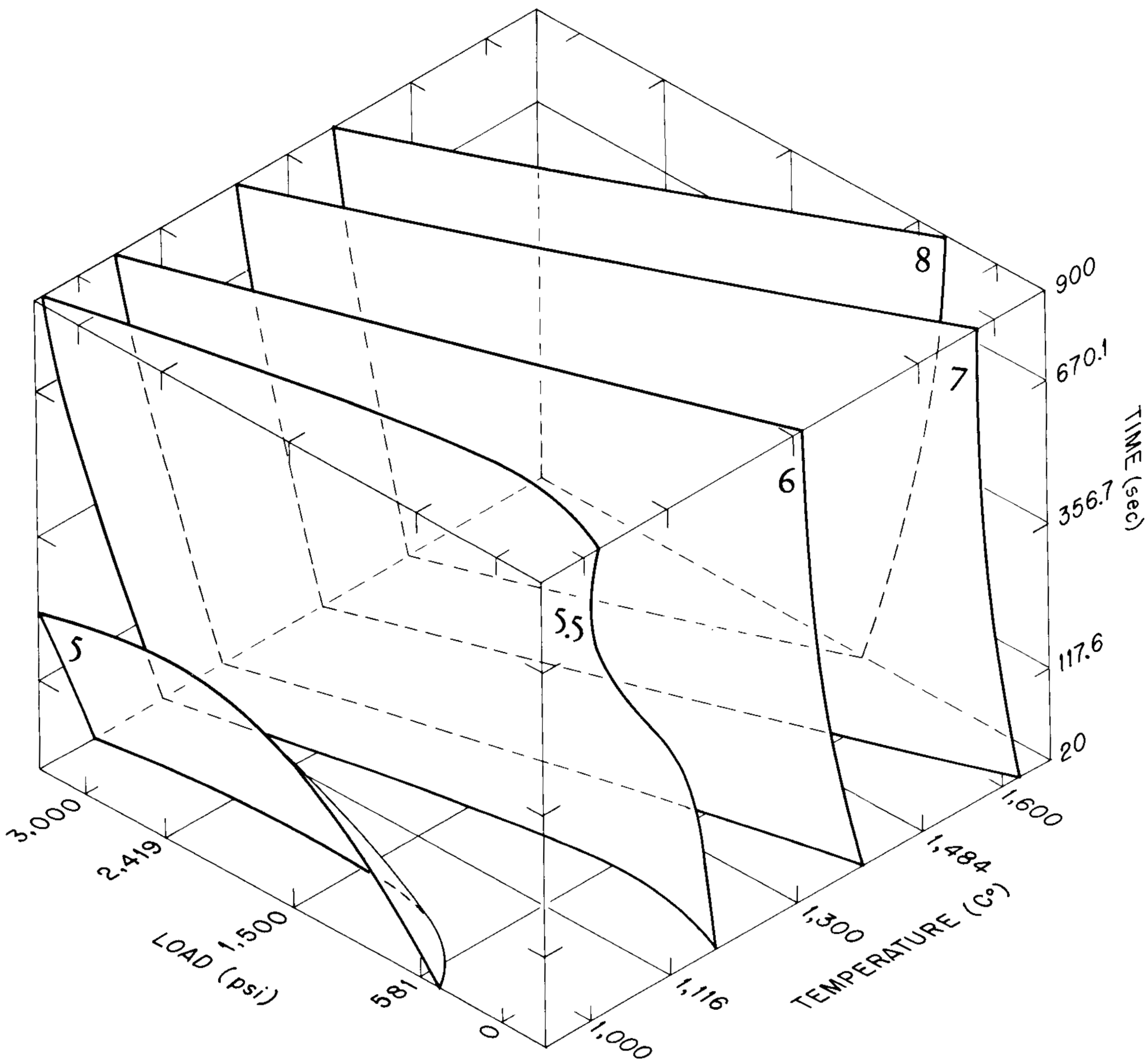

Fig. 2. Response Contours of Hot-Pressed Density.

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