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DISSOLUTION OF MIXED OXIDE FUEL AS A FUNCTION OF FABRICATION VARIABLES

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1.0 INTRODUCTION

This paper describes experiments that have been performed at the Hanford Engineering Development Laboratory in Richland, Washington to measure the dissolution properties of mixed oxide fuel fabricated using the three fast reactor fuel fabrication processes: mechanically blending, Sol Gel, and coprecipitation. Experiments were performed to measure both the completeness of fuel dissolution in nitric acid alone and the rate of fuel dissolution. The paper will primarily deal with completeness of dissolution of mechanically blended fuel pellets since that is where the most significant effects of fuel pellet fabrication conditions were noted. In addition, some data will be discussed which show the influence of fuel fabrication effects on the dissolution of irradiated mixed oxide fuel.

Fabrication and irradiation histories of mixed oxide reactor fuels are recognized as having an important effect on both the dissolution rate and completeness of fuel during reprocessing. Previous investigations[1-4] have shown that, in general, irradiation has a beneficial effect on dissolution of mixed oxide fuel. Investigations[5-8] have also shown the beneficial effect of certain fabrication conditions (e.g., high sintering temperature) on the dissolution properties of mixed oxide fuel.

In order to investigate the effect of fuel fabrication conditions on the dissolution properties of unirradiated mixed oxide fuel, a series of statistical, fractional-factorial experiments were performed. Six fuel fabrication conditions, shown in Table 1, were identified which could have an effect on the dissolution properties of the fuel. In setting the levels of the six variables, primary consideration was given to selecting conditions which would produce wide differences in fuel dissolution conditions. Thus, the final pellets were not always typical of acceptable fuel pellets. Only two levels of investigation were chosen for variables X_4, X_5 and X_6 to facilitate fabrication of the pellets. The levels were sufficiently seperated so that any effects due to the particular variable were easily identified; however, whether or not the effect was linear or curvilinear could not be determined.

TABLE 1

VARIABLES FOR DISSOLUTION EXPERIMENT

MECHANICALLY BLENDED, UO_2-PuO_2 FUEL

		Levels	Statistical Designation
X_1:	Source of PuO_2	burned metal	-1
		calcined nitrate	0
		calcined oxalate	1
X_2:	PuO_2 Content	15	-1
		20	0
		25	1
X_3:	Sintering Temperature, °C	1400	-1
		1550	0
		1700	1
X_4:	Sintering Time, hours	1	-1
		6	1
X_5:	Rate of Temperature Rise During Sintering, °C/hr	100	-1
		250	1
X_6:	Press Pressure, kpsi	25	-1
		50	1

The following fabrication parameters were held constant:

1) PuO_2 calcination temperature: 700°C
2) PuO_2 particle size: -325 mesh
3) UO_2: Eldorado ceramic grade
4) Blending conditions: wet process to provide good homogeneity for the small bath sizes
5) Ball Milling: 12 hours ball milling; -325 mesh
6) Binder type and percentage: 3% carbowax
7) Drying conditions: 4-5 hours at 70°C
8) Screening of mixed oxide: agglomeration for press feed to -20 mesh
9) Pre-slug conditions: no pre-slug
10) Sintering atmosphere: Dry Ar-8% H_2; less than 5 ppm H_2O

2.0 SUMMARY

Statistically controlled experiments were used to establish the effect of fuel fabrication conditions on nitric acid dissolution of mixed oxide fast reactor fuel. Dissolution experiments were performed on fuel from three different fuel fabrication processes: mechanically blending, Sol Gel, and coprecipitation.

Dissolution properties (i.e., fuel dissolubility and dissolution rate) of mechanically blended mixed oxide fuel were found to be very dependent on the six fuel fabrication variables studied in these experiments. In particular, fuel sintering temperature, source of PuO_2 (i.e., oxalate, nitrate, or burned metal derived PuO_2), and PuO_2 content of the fuel had major effects on fuel dissolution characteristics. Typical major effects were as follows: 1) as the sintering temperature was increased from 1400°C to 1700°C, pellet dissolution was more complete;* 2) pellets made from burned metal derived PuO_2 were more completely dissolved than pellets made

*Using a standard dissolution treatment of 12 hours in boiling 12M nitric acid.

from calcined nitrate derived PuO_2 which, in turn, were more completely dissolved than pellets made from calcined nitrate derived PuO_2; 3) as the PuO_2 content decreased from 25 w/o PuO_2 to 15 w/o PuO_2, pellet dissolution was more complete.

Preferential dissolution of uranium occurred in all the mechanically blended mixed oxide fuel pellets that were dissolved. Final residues typically were 75-90% PuO_2 and 10-25% UO_2.

Unirradiated mixed oxide fuel pellets made by the Sol Gel process were generally quite soluble in nitric acid. Dissolution was rapid and complete for most fabrication conditions studied. Incomplete dissolution of Sol Gel derived pellets caused by high calcination temperature was eliminated by high (1700°C) sintering temperature.

Unirradiated mixed oxide fuel pellets made by the coprecipitation process dissolved completely and rapidly in nitric acid for all fabrication conditions studied in these experiments.

Where fabrication conditions were directly comparable among the three condidate LMFBR fuel fabrication processes (i.e., mechanically blending, Sol Gel, and coprecipitation) fuel made by the coprecipitation process was more completely dissolved than fuel made by the Sol Gel process which, in turn, was more completely dissolved than fuel made by mechanically blending UO_2 and PuO_2 as shown below.

Addition of uncomplexed fluoride to nitric acid during fuel dissolution generally rendered all fuel samples completely dissolvable.

While fabrication variables had an effect on the initial rate of fuel dissolution, in the boiling 12M nitric acid used for these studies, 95 to 99 percent of the plutonium which was going to dissolve did so in the first hour of dissolution.

Irradiated mechanically blended mixed oxide fuel with known fuel fabrication conditions was also subjected to fuel dissolution tests. While irradiation was shown to increase completeness of plutonium dissolution, poor dissolubility due to adverse fabrication conditions (e.g., low sintering temperature) remained after irradiation.

3.0 EXPERIMENTAL

The same general experimental procedures were used for all dissolution experiments discussed in this report. All handling of mixed oxide powder, pellets, and solutions was done in standard plutonium glove boxes.

3.1 Statistical Considerations

A statistical approach to experimental design and interpretation of data was used throughout these studies. In particular, fractional factorial designs [9] (i.e., experimental designs that look at a fraction of all combinations of the variables being studied) were used to reduce the number of experimental observations necessary to completely characterize the system being studied. Combining the fractional factorial design with statistical methods of data analysis (e.g., multiple regression analysis and analysis of variance) resulted in mathematical equations that defined the primary effects and interactions of all the fabrication variables studied. Unbiased tests of significance for the factors were also obtained.

Statistical terms used in this report are defined in Appendix A

3.2 Dissolubility Measurements

Measurement of pellet dissolubility, i.e., the fraction of plutonium and uranium that dissolved in boiling nitric acid after a short period of time (<24 hours) was the main dissolution test used in these experiments. The procedure consisted of dissolving individual pellets (c.a. 0.2 in. in diameter x 0.2 in. in length; 1-1.5 g each) in 25ml of boiling 12M nitric acid for one, or, if necessary, two six-hour periods. After the second six-hour dissolution treatment any residue remaining was separated from the solution, dried, and weighed. The amount of residue, calculated as percent of original pellet, was a measure of the pellet dissolubility. When sufficient residue remained for accurate chemical analysis, the residue was dissolved in fresh 12M nitric acid-0.05M hydrofluoric acid and the resulting solution analyzed for plutonium and uranium. A minimum of two pellets was dissolved for each experimental test condition and the mean value for the amount of residue was used in the statistical analysis.

3.3 Dissolution Rate Measurement

The dissolution rate of a pellet (i.e., the amount of pellet dissolving in a specified time period) was determined for selected experiments by adding single pellets to 25 ml of boiling 12M nitric acid. After exactly 15 minutes dissolution the reaction was quenched by addition of cold water. The solution was immediately filtered using ashless filter paper and diluted to a known volume. Following filtration the undissolved powder and filter paper were added to 25 ml of fresh, boiling 12M nitric

acid and the procedure repeated until four different dissolution rate solutions had been generated, one each after 15, 60, 120 and 360 minutes dissolution. Following dilution of the four solutions to known volumes, the solutions were analyzed for plutonium and uranium. The amount of plutonium and uranium dissolved (or conversely, still undissolved) was then calculated from the accumulative total in the four solutions. The dissolution rates were normally reported as the percent of plutonium or uranium still undissolved as calculated from the amount of plutonium and uranium in the starting pellet. The final filtered residues were heated in a muffle furnace to remove the filter paper, then weighed as a check of the dissolution rate numbers. The residues were not analyzed for plutonium and uranium.

3.4 Apparatus

The dissolubility apparatus shown in Figure 1 was used throughout these experiments and consisted of specially fabricated glass five finger condensers fit with 24/40 ȝ dissolution tubes such that multiple pellets could be dissolved simultaneously. Three of the condensers were used for any given run.

4.0 RESULTS AND DISCUSSION

Three separate evaluations were completed to characterize the effect of fabrication processes on fuel dissolution. A comparison of the three fuel fabrication processes is shown schematically in Figure 2. Mechanically blending was the most thoroughly studied fuel fabrication process since it is the reference process for the Fast Flux Test Facility (FFTF)* fuel fabrication. Extensive dissolubility, dissolution rate, and residue solubility measurements were made on mechanically blended fuel, results of which were used in the design of the Sol Gel and coprecipitated mixed oxide fuel experiments. For Sol Gel and coprecipitated fuel, dissolubility experiments only were performed since, in general, the dissolution rate was fast and there was little, if any, residue after 12 hours treatment in boiling 12M nitric acid.

4.1 Mechanically Blended Mixed Oxide Fuel Studies

The fabrication variables shown previously in Table 1 were used in the mechanically blended fuel dissolution experiments. A 1/3 replicate (i.e., it looked at 1/3 of all possible interactions) of a full factorial experiment was selected for the statistical design. The design, defined to be

*The FFTF reactor is being constructed at Richland, WA by Westinghouse Hanford Company.

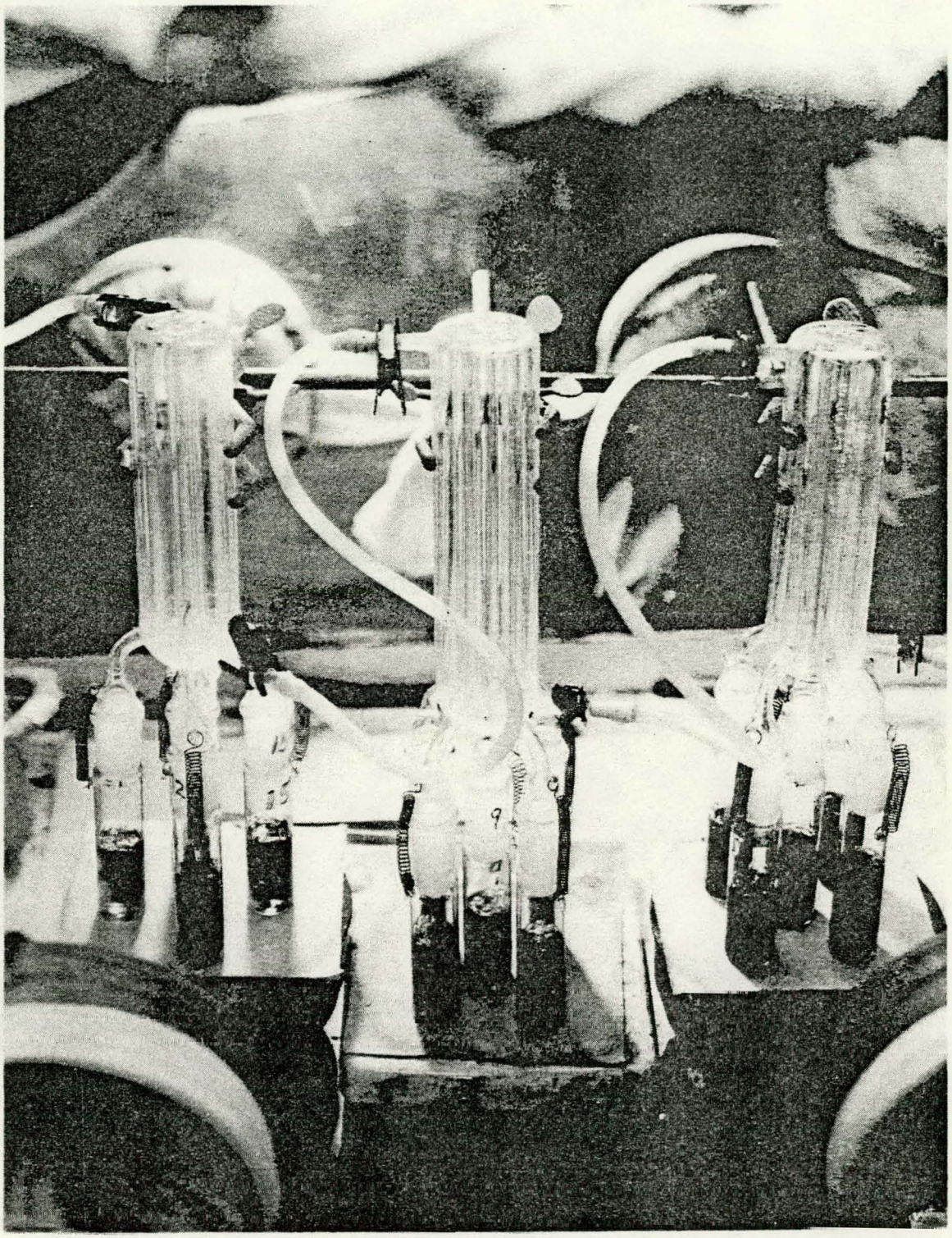

FIGURE 1. Dissolubility Apparatus

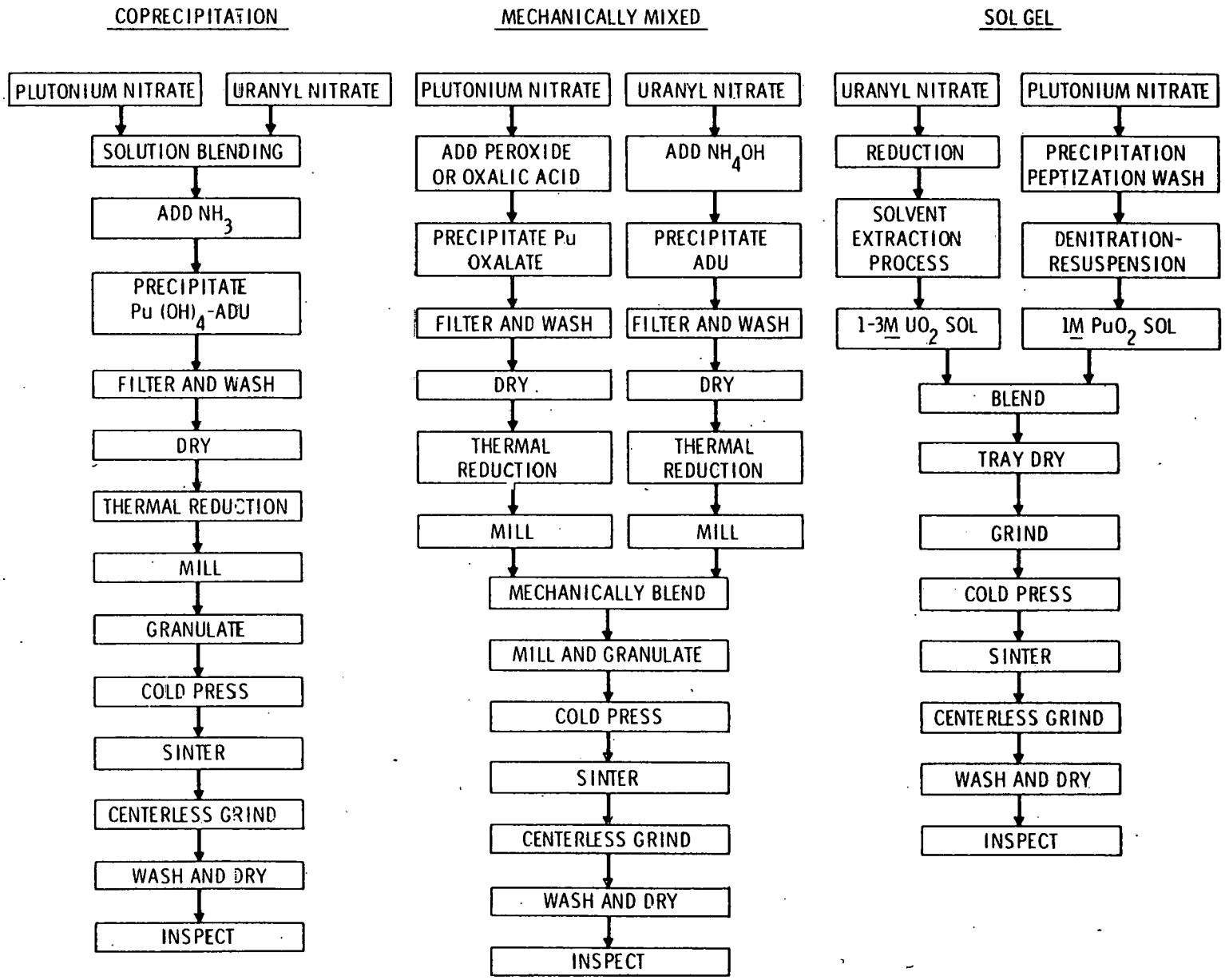

Figure 2. Flowsheets for $(U, Pu)O_2$ Pellet Fabrication.

combination of values of the six variables for each run, resulted in 72 treatment conditions or "cells", each cell representing a different combination of fuel pellet fabrication variables. About 12 pellets were fabricated for each particular cell. The variables used for each particular cell are shown in Appendix B.

4.1.1 Dissolubility Results

Dissolubility experiments were run on pellets from each of the 72 cells. Results of these runs were then analyzed statistically.

A full quadratic model, that is, one that considers all possible two factor interactions (e.g., X_1^2, X_1X_2, X_1X_3, etc.) of all six variables, was used in the first attempt at estimating the effect of each independent variable on dissolubility. After deleting the terms from the full quadratic model which were statistically insignificant and again estimating the parameters, the following equation resulted:

$$\begin{aligned} Y = {} & 4.86 + 0.53X_1 + 0.94X_2 - 2.24X_3 - 0.24X_4 \\ & + 0.75X_5 - 0.14X_6 - 1.87X_1^2 - 0.36X_3^2 \\ & - 0.37X_1X_2 + 0.15X_1X_5 - 0.51X_2X_3 - 0.35X_2X_4 \end{aligned} \qquad \text{(MB-1)}$$

X_1 Source of PuO_2
X_2 PuO_2 Content
X_3 Sintering Temperature
X_4 Sintering Time
X_5 Rate of Temperature Rise
X_6 Press Pressure

In the equation, Y is the weight percent undissolved and the X's are the statistical designations of the particular variable and are defined to run from -1 to +1. By inserting the appropriate values for the various X's, this equation can be used to give the predicted or expected weight percent undissolved. A negative percent undissolved would indicate that the pellet is completely soluble. The equation can also be used to calculate response curves which show the effect of going from one level to another within a given variable.

The relative dissolubility of a pellet can be estimated from fabrication variables within the range of those studied (but not exactly the same as used in this study) by substituting a fractional value into equation MB-1 for the

particular variable of interest. The fractional value would be directly proportional to the spacing within the variable and would have a value between -1 and +1. (For sintering temperatures of 1500°C and 1600°C, for example, the values of -0.33 and +0.33, respectively, would be substituted for X_3 in equation 1.)

The relative effect of each particular fabrication variable on dissolubility can be roughly estimated by comparing the coefficients in the equation. The relative order of decreasing effect was sintering temperature, source of PuO_2, PuO_2 content, rate of temperature rise during sintering, sintering time, and press pressure.

Since the equation as it stands is of limited direct use, a computer was used to calculate the predicted weight percent undissolved for a number of combinations of the X's. The series of curves given in the following sections was plotted from those calculated values and should be useful in depicting some of the relationships that exist. They do not represent all possible curves that could be drawn but rather represent selected curves that are useful in depicting trends that exist within a particular fabrication variable.

Source of PuO_2

The source of PuO_2 had a major effect on the dissolubility of mechanically blended, mixed oxide fuel as shown in Figure 3 for 15 wt% PuO_2 pellets. Mixed oxide pellets made from burned metal PuO_2 were more soluble than pellets made from either calcined oxalate or calcined nitrate PuO_2 at all three levels of sintering temperature and PuO_2 content investigated. Similar relationships were noted for dissolution of 20 and 25 wt% PuO_2 pellets as shown in Figures 4 and 5. The primary difference was that the curves were shifted toward lower dissolubilities (i.e., higher weight percent undissolved material) as the PuO_2 content increased. Source of PuO_2 produced the largest difference in dissolubility for the 15 wt% PuO_2 pellets.

PuO_2 Content

The PuO_2 content of the mixed oxide fuel also had a major influence on the dissolubility of the fuel as shown in Figure 6 for burned metal PuO_2. The curves shown in Figure 6 are the same as the lower curves shown in Figures 3, 4, and 5. In general, as the weight percent of PuO_2 increased, the dissolubility decreased for all three sintering temperatures and all three sources of PuO_2 investigated. The PuO_2 content produced the largest

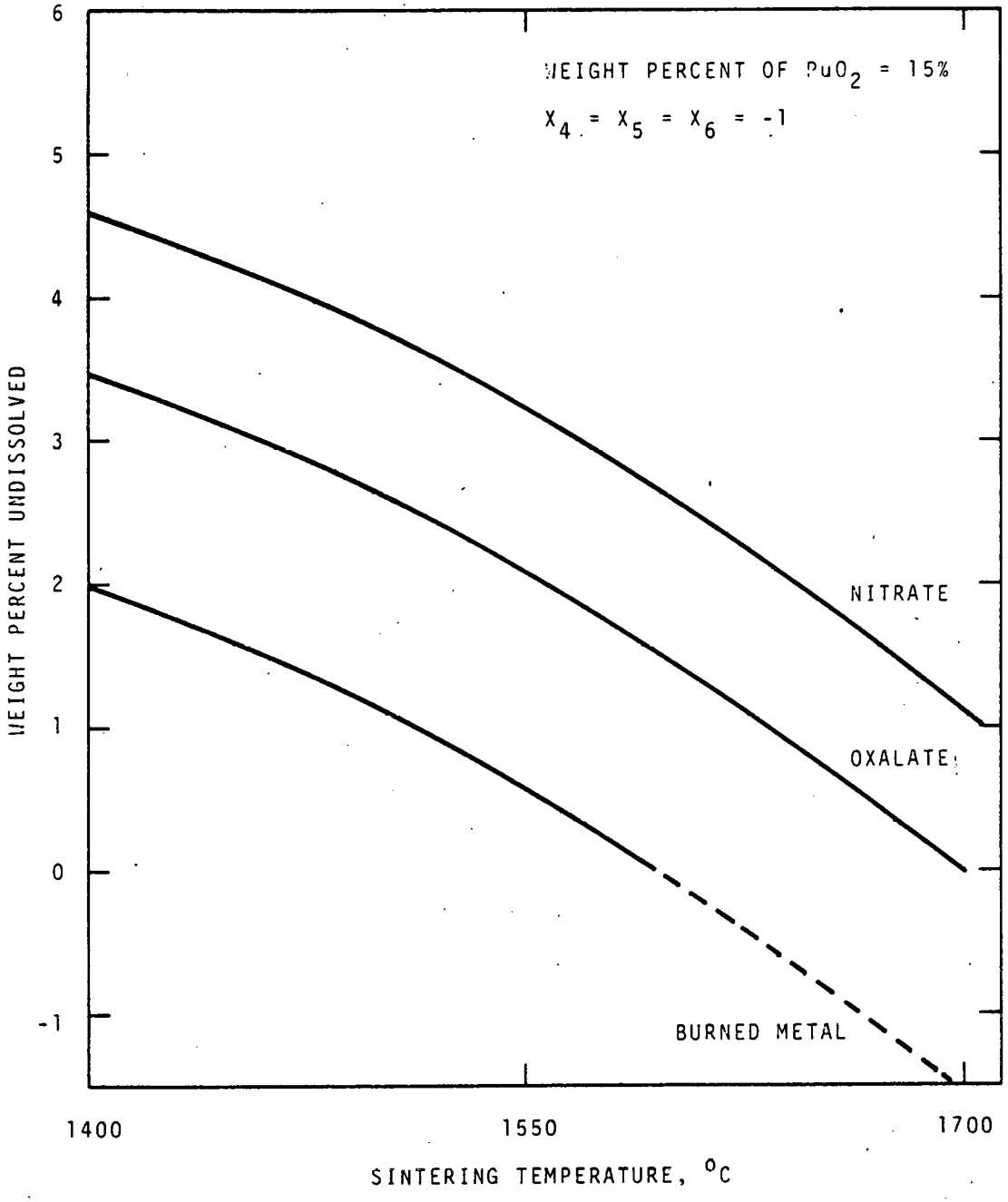

FIGURE 3 The Effect of Source of PuO_2 and Sintering Temperature on Dissolubility of 15 wt% PuO_2-UO_2 Fuel

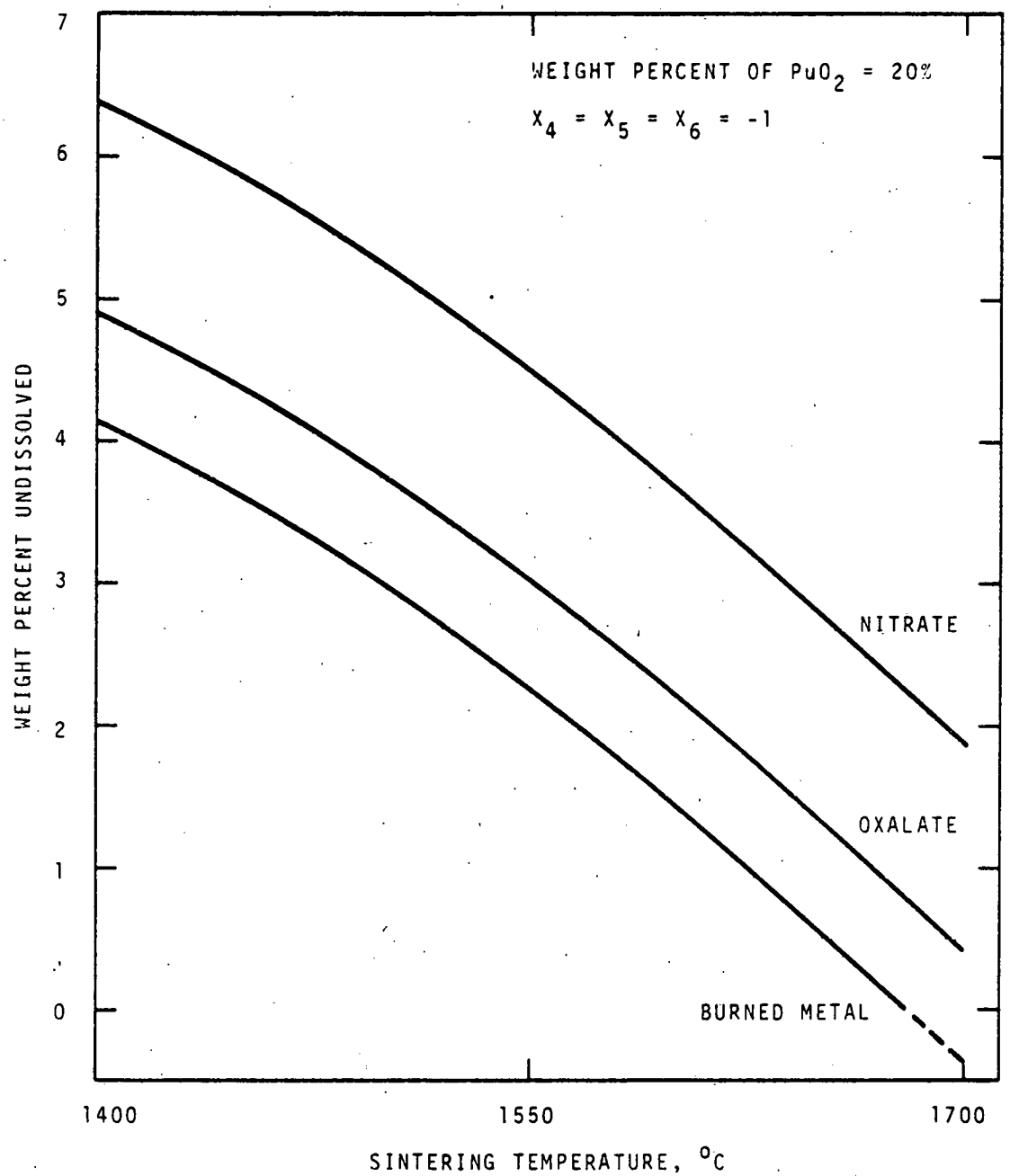

FIGURE 4 The Effect of Source of PuO_2 and Sintering Temperature on Dissolubility of 20 wt% PuO_2-UO_2 Fuel

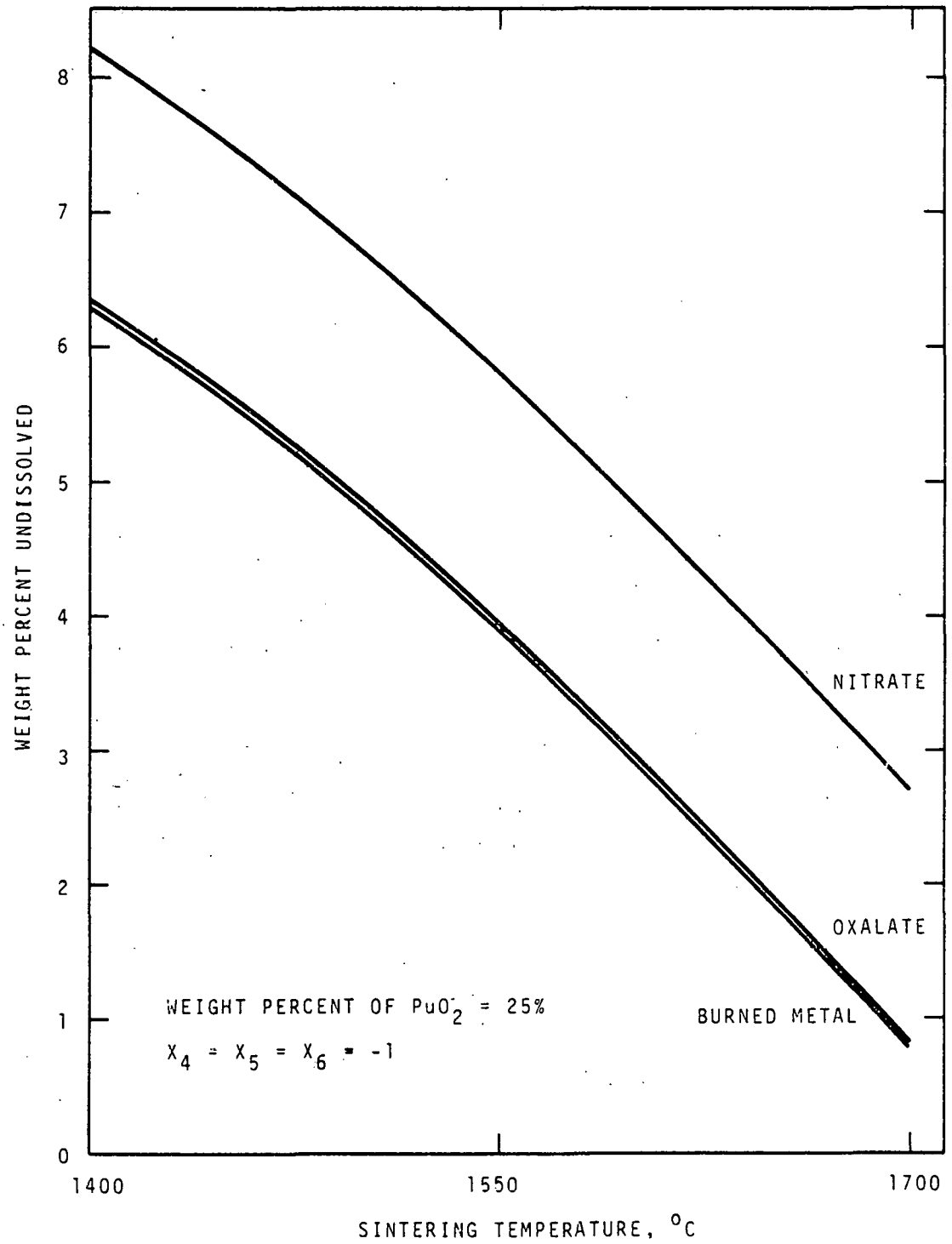

FIGURE 5 The Effect of Source of PuO_2 and Sintering Temperature on Dissolubility of 25 wt% PuO_2-UO_2 Fuel

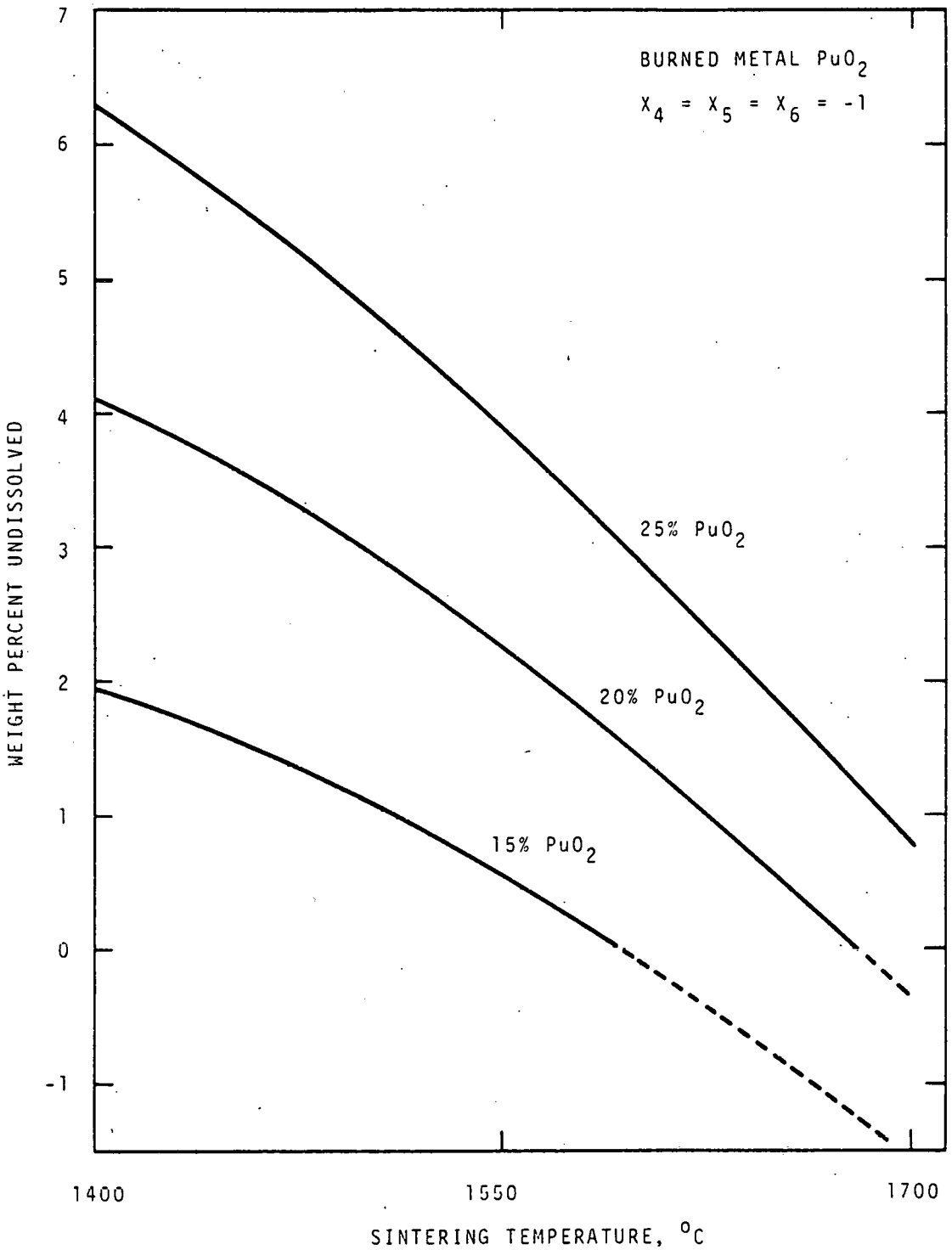

FIGURE 6 The Effect of PuO_2 Content and Sintering Temperature on Dissolubility of Burned Metal PuO_2-UO_2 Fuel

difference in dissolubility of burned metal PuO_2-UO_2 pellets. The dissolubility relationships were similar for calcined oxalate and calcined nitrate derived PuO_2.

Sintering Temperature

A third variable having a major effect on the dissolubility of the mixed oxide fuel was the sintering temperature. As the sintering temperature increased, the dissolubility of the pellets increased for all three sources of PuO_2 and for all three PuO_2 contents investigated. Typical dissolubility curves are shown in Figure 7 for calcined nitrate PuO_2. In general, the dissolubility of mixed oxide fuel increased by 3 to 5 percent when the sintering temperature was raised from 1400°C to 1700°C. The largest increase in dissolubility with an increase in sintering temperature was noted for the UO_2-25 wt% PuO_2 fuel pellets. This indicates that a high sintering temperature (e.g., 1700°C) is necessary to obtain good mixed crystal formation (i.e., solid solution) and a high degree of dissolubility in the 25 wt% PuO_2 fuel.

Sintering Time

Sintering time (i.e., the time at temperature or "soak time") was also found to have an effect on dissolubility but to a lesser degree than the three variables discussed previously. An increase in sintering time produced an increase in dissolubility except for the 15 wt% PuO_2 pellets. The combined effects of sintering time and sintering temperature are shown in Figure 8 for burned metal PuO_2-UO_2 fuel. (Note the reverse effect of sintering time for the 15 wt% PuO_2 fuel.) The magnitude of the effect of soak time is essentially the same at all three temperatures investigated. The largest effect of soak time on dissolubility occurs with the 25 wt% PuO_2 fuel. This is probably due to the relative degree of solid solution taking place during sintering and is consistent with results of earlier work at ORNL[3] where researchers found that as the concentration of PuO_2 increased, the time (and/or temperature) required for solid solution formation also increased. Longer soak times than 6 hours would undoubtedly increase the dissolubility of 20 and 25 wt% PuO_2 fuel even further.

Rate of Temperature Rise During Sintering

The rate of temperature rise during sintering was also found to have an effect on the dissolubility of mixed oxide fuels but to a lesser degree than

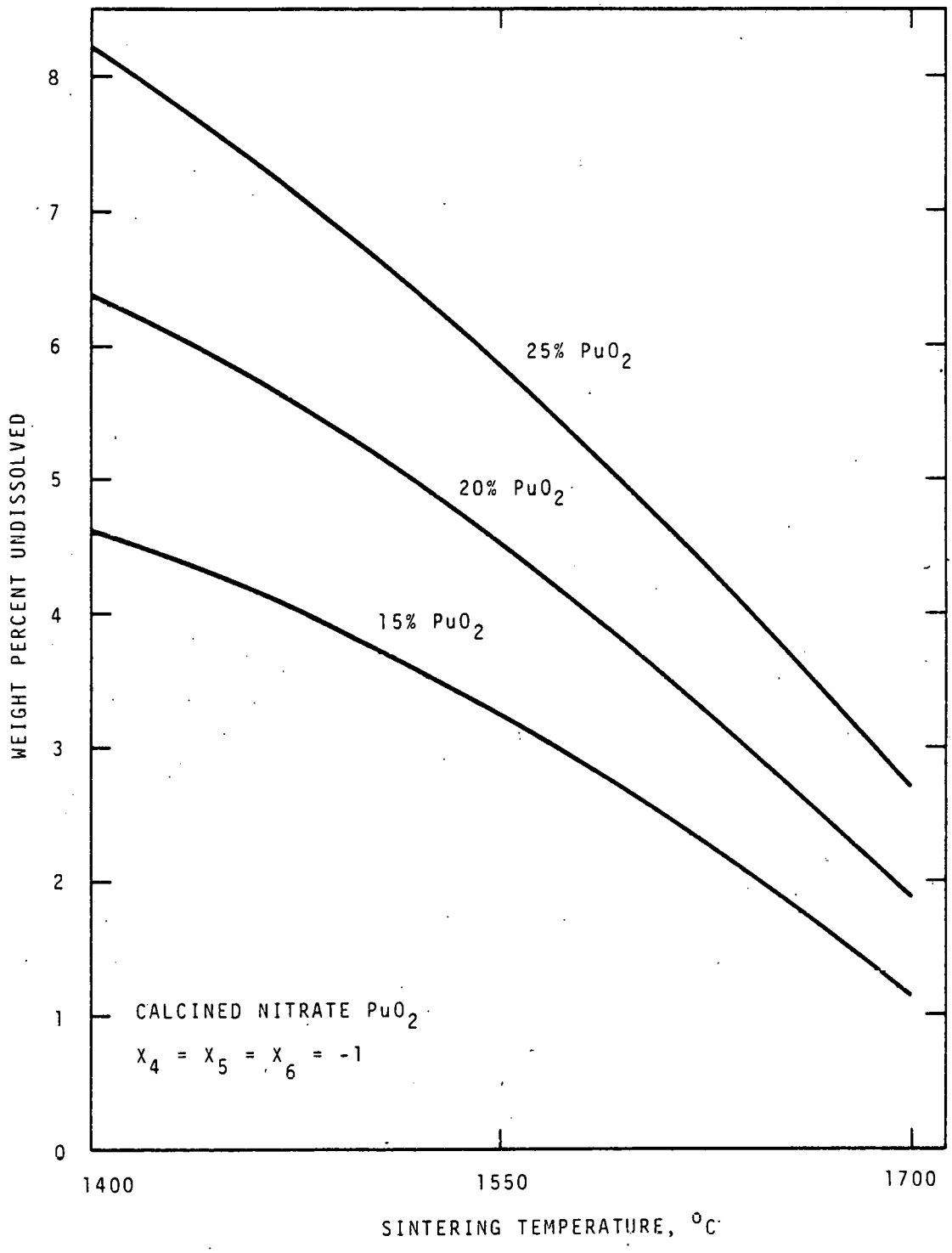

FIGURE 7 The Effect of PuO_2 Content and Sintering Temperature on Dissolubility of Calcined Nitrate PuO_2-UO_2 Fuel

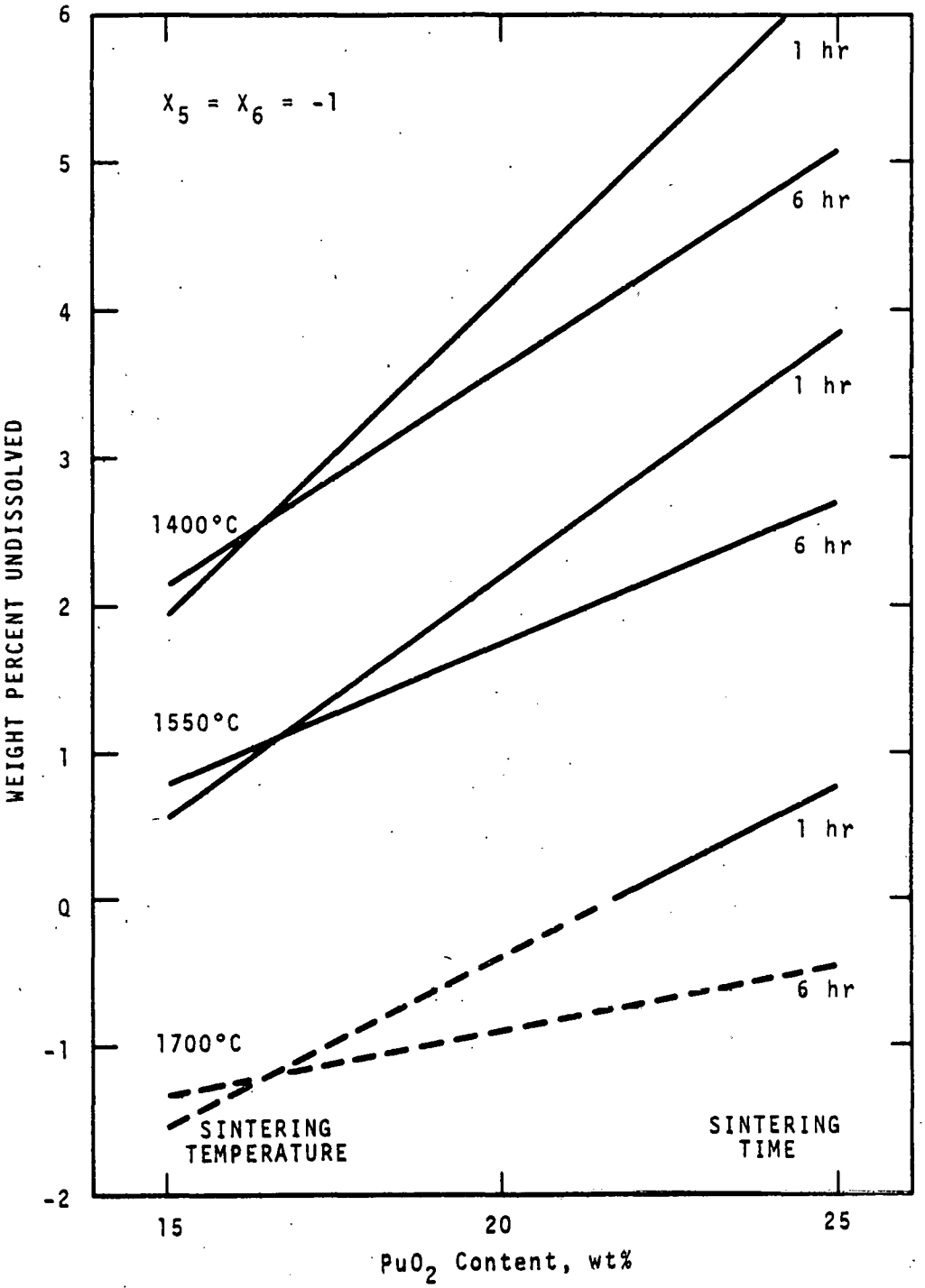

FIGURE 8 The Effect of Sintering Time, PuO_2 Content and Sintering Temperature on Dissolubility of Burned Metal PuO_2-UO_2 Fuel

source of PuO_2, PuO_2 content, and sintering temperature. In general, a slower rate of temperature rise during sintering favored increased dissolubility at all three sintering temperatures investigated and for all three sources of PuO_2 as shown in Figure 9 for fuel sintered at 1700°C. The relationships are similar for fuel sintered at 1550°C and 1400°C with the dissolubility curves being shifted to lower dissolubility. In general, the magnitude of the increase in dissolubility was between 1 and 2 wt% when the rate of temperature rise during sintering was lowered from 250°C/hr to 100°C/hr.

Pressing Pressure

The final variable that was evaluated in this experiment was the pressure used to press the blended oxide into green fuel pellets. The press pressure was found to have very little effect on dissolubility. In general, dissolubility of mixed oxide pellets was increased <0.5 wt% when the pellet pressing pressure was increased from 25,000 psi to 50,000 psi.

Accuracy of Statistical Model

To measure the accuracy of the model, a "goodness of fit" was prepared to compare the observed weight percent undissolved for the 72 observations as a function of the weight percent undissolved predicted by the model. Figure 10 shows the observed weight percent undissolved to be very close to that predicted. The standard deviation which expresses the scatter of these points about the line is ±0.53. Another way to express the adequacy of the model is in terms of the amount of the total variation of weight percent undissolved explained by the model. In this experiment, the multiple correlation coefficient was 0.976. Thus, the model used explained approximately 95% of the total variation (calculated by multiplying 100 times the square of the multiple correlation coefficient) which indicates that the model was very effective in accounting for the overall variation.

The standard deviation between pellets within cells was calculated to be 0.11 (weight percent undissolved). If experimental control were perfect, the standard deviation between cell averages would be about $0.11/\sqrt{2}$ or 0.08. In actual fact, the residual standard deviation, that is, the standard deviation expressing the scatter of data points about the predicted line, was observed to be 0.53. The difference reflects the combined effect of

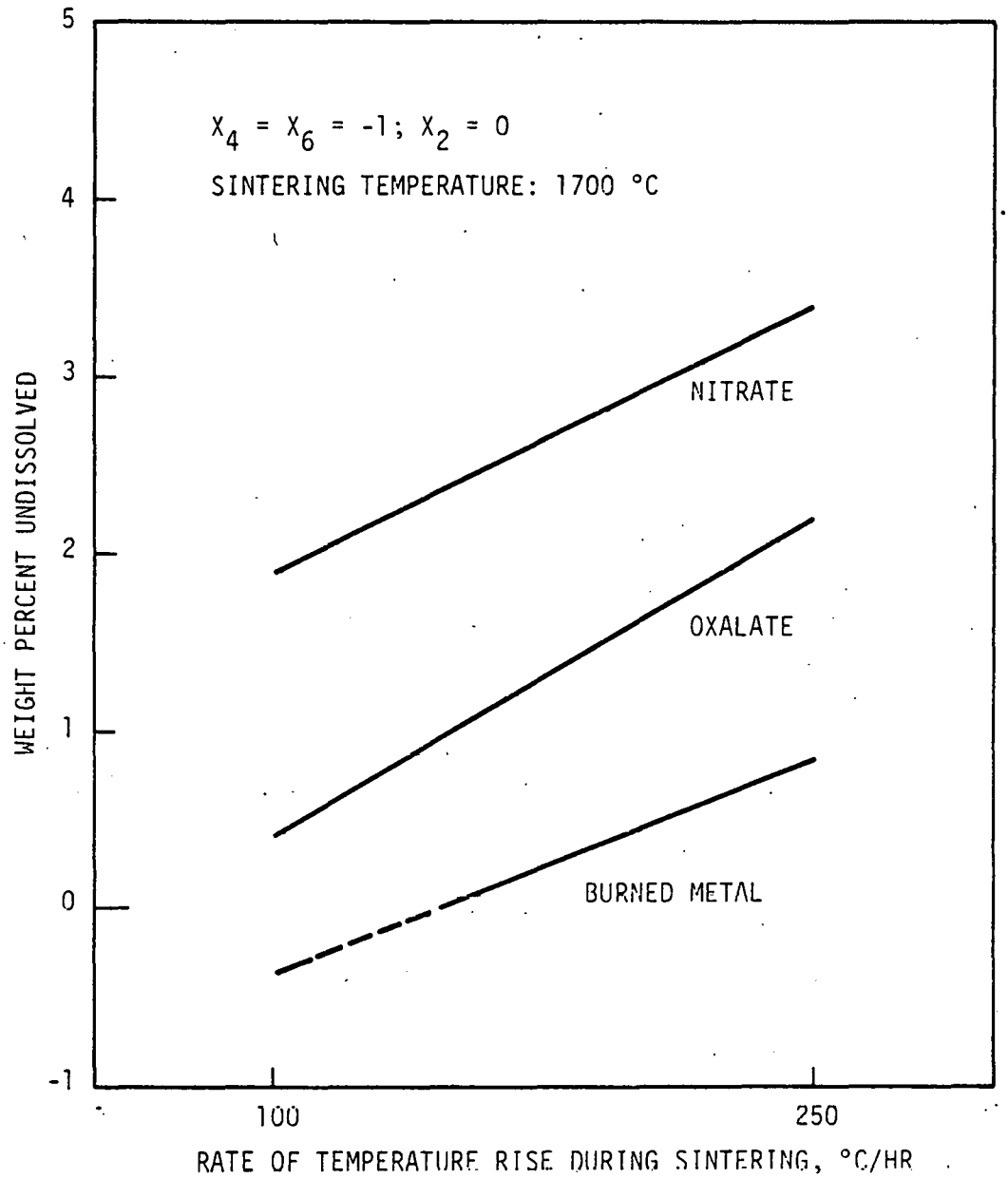

FIGURE 9. The Effect of Rate of Temperature Rise During Sintering and Source of PuO_2 on Dissolubility of Fuel Pellets Sintered at 1700°C

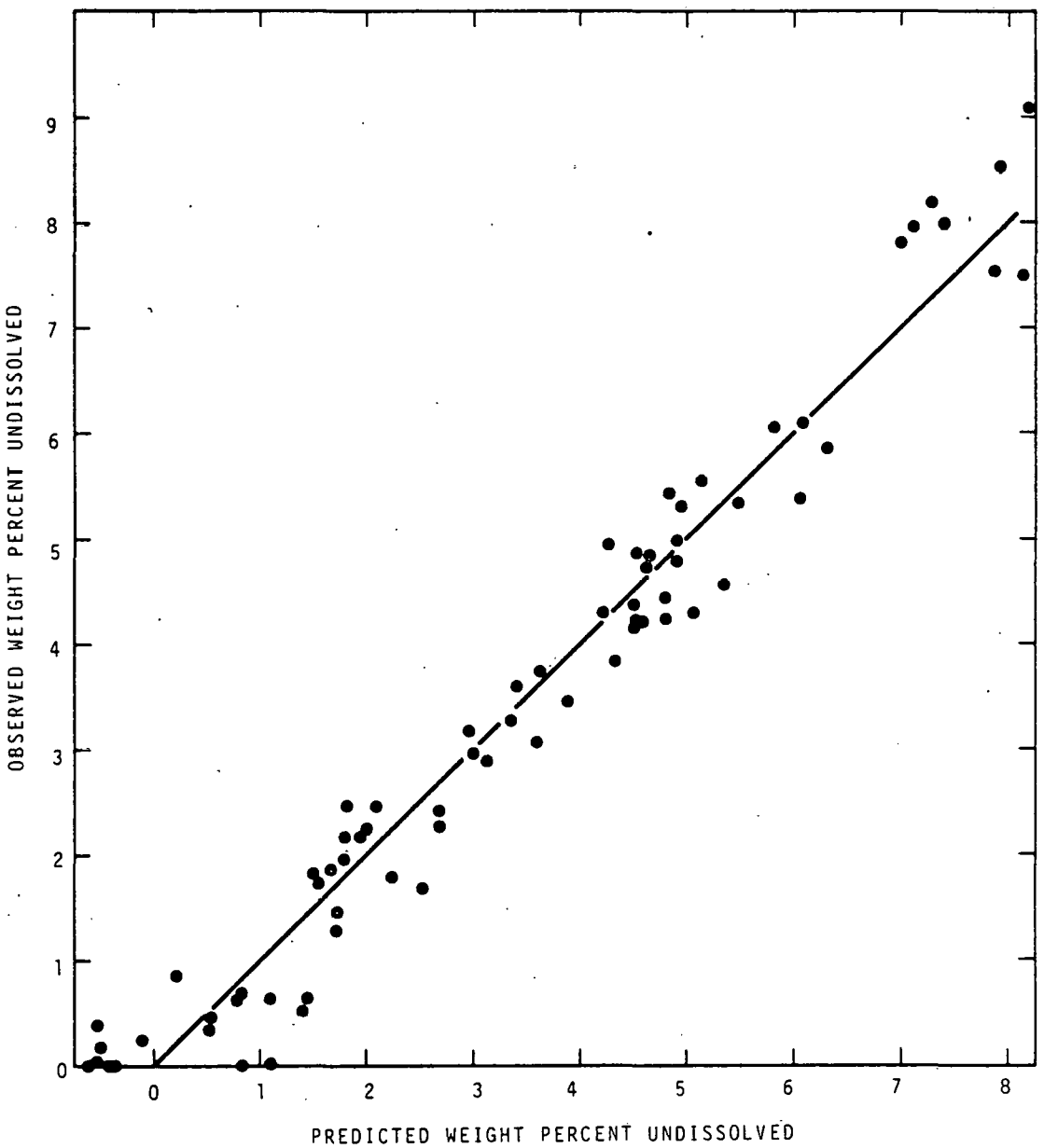

FIGURE 10 Observed Weight Percent Undissolved vs Predicted Weight Percent Undissolved

time-associated-undefined variables, possible inadequacies in the model, and possible difficulties in attaining the exact levels of the independent variables as specified. A residual standard deviation of 0.53 is considered to be very good in this type of experiment.

4.1.2 Dissolution Rate Results

In order to reduce the size of the dissolution rate experiment, a one-half statistical fraction of the original 72 cell experiment was run. A representative cross section of the full range of pellet dissolubility noted in the dissolubility experiment (i.e., 0 to 9.1 w/o of the pellet undissolved) was maintained for the dissolution rate experiment. The dissolution rate data are included in Appendix A for reference purposes.

Results of the dissolution rate experiment were about as expected and indicated that extensive dissolution rate data were probably not needed. In the boiling 12M nitric acid, 95 to 99 percent of the plutonium which was going to dissolve did so in the first hour. After dissolution for the first 15 minutes, the overriding effects of fabrication conditions on dissolution rate were essentially the same as noted previously for overall pellet dissolubility, i.e., conditions which increased dissolubility also increased rate of dissolution.

Specific trends were:

1. Increased sintering temperature produced the largest increase in dissolution rate, i.e. approximately a 22 percent reduction in the amount of residue left after 1 hour. High sintering temperatures produced lower plutonium dissolution rates during the first 15 minutes of dissolution. However, after one hour dissolution high sintering temperatures enhanced dissolution.
2. Burned metal derived PuO_2 dissolved faster than oxalate derived PuO_2 which dissolved faster than nitrate derived PuO_2.
3. The 15 w/o PuO_2 dissolved faster than 20 w/o PuO_2 which dissolved faster than 25 w/o PuO_2.
4. A lower rate of temperature rise during sintering increased the dissolution rate of plutonium.
5. A higher pressing pressure increased the dissolution rate of plutonium, however, only to a minor extent.
6. Sintering time had only a minor effect on plutonium dissolution rate with longer sintering times increasing the dissolution rate.

7. For the six fabrication variable investigated in this experiment, the following levels produced the maximum overall dissolution rate:

   $X_1 = -1$ (burned metal PuO_2)

   $X_2 = -1$ (15 w/o PuO_2)

   $X_3 = +1$ (1700°C sintering)

   $X_4 = +1$ (6 hr sintering)

   $X_5 = -1$ (100°C/hr temperature rise)

   $X_6 = +1$ (50 kpsi pressing pressure)

8. The following levels produced the minimum overall dissolution rate:

   $X_1 = 0$ (calcined nitrate PuO_2)

   $X_2 = +1$ (25 w/o PuO_2)

   $X_3 = -1$ (1400°C sintering)

   $X_4 = -1$ (1 hr sintering)

   $X_5 = +1$ (250°C/hr temperature rise)

   $X_6 = -1$ (25 kpsi pressing pressure)

In general, initial dissolution of the mixed oxide pellets was quite rapid followed by very slow dissolution after one hour. For example, on the average 88.7% of the plutonium that was going to dissolve did so during the first 15 minutes of dissolution. (The mean value was 90.0% with a high of 96.8% and a low of 68.1%.) Further, on the average 97.6% of the plutonium that was going to dissolve did so in the first hour. (The mean value was 98.0 with a high of 99.5% and a low of 94.6%.) Dissolution of the uranium was nearly quantitative during the first hour of dissolution with an average of 98.5% dissolving during that period. Typical dissolution rate curves are shown in Figure 11.

The dissolution rate data were statistically analyzed using standard statistical techniques for the four separate sample times and for all the rate data together. The dependent variable in the analysis (Y) was the amount of plutonium (expressed as w/o of original plutonium) that did not dissolve. The six independent process variables (X) and the level of each were shown in Table 1. The statistical equations resulting from these statistical analyzes are summarized in Appendix C.

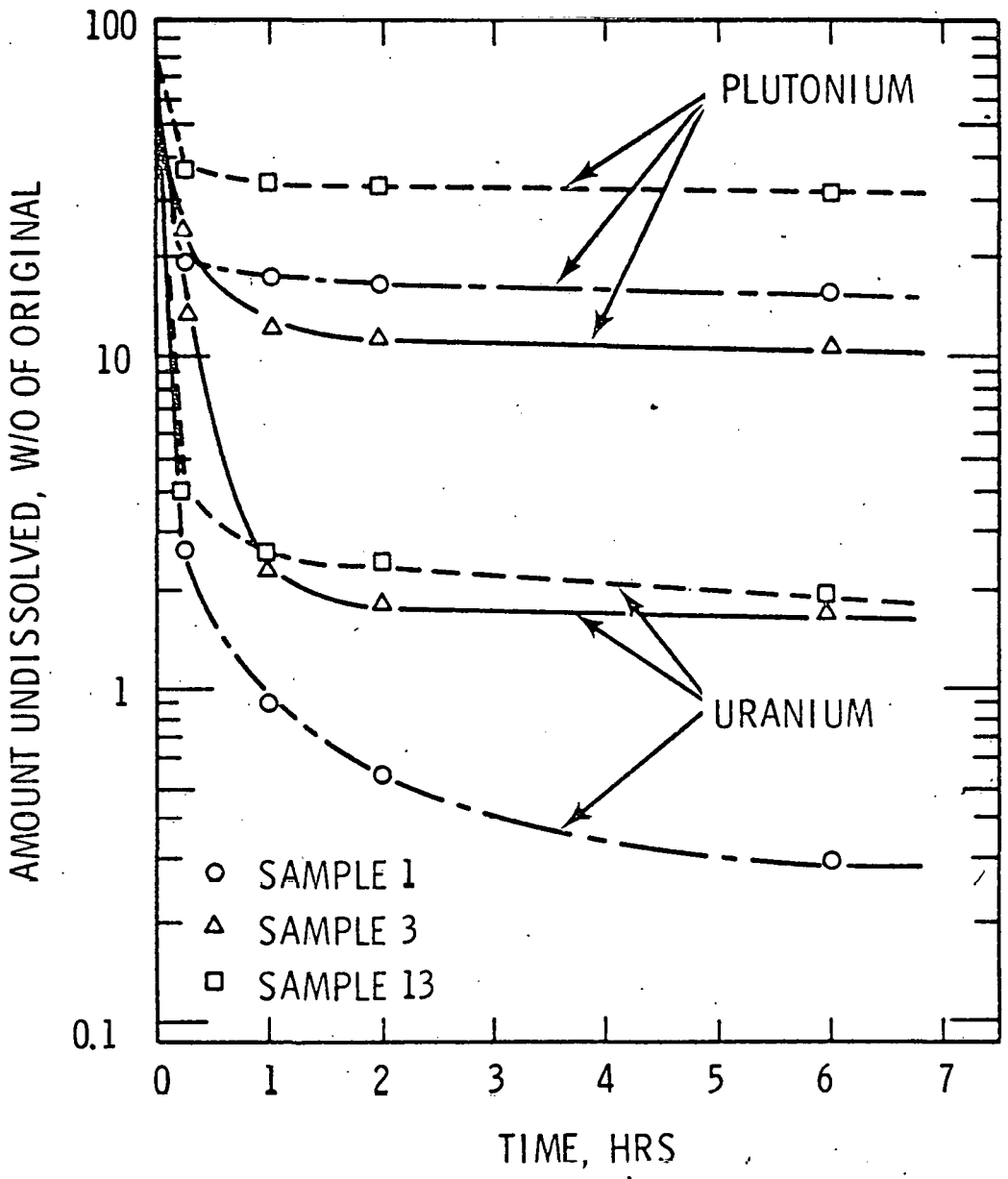

Figure 11. Typical Dissolution Rate Curves for Mechanically Blended Mixed Oxide Fuel in 12 M Nitric Acid.

4.1.3 Analysis of Residues

The residues remaining after dissolution were dissolved in 12M HNO_3-0.05M HF and the resulting solutions were analyzed for uranium and plutonium by X-ray fluorescence. Preferential dissolution of uranium was found to occur in every case. The ratio of plutonium oxide to uranium oxide in the final residues ranged from 3.9 to 14.0. The relationship between PuO_2/UO_2 ratio in the residues and pellet "weight percent undissolved" is shown in Figure 12 for 25 wt% PuO_2 pellets. The degree of preferential dissolution taking place was related directly to the amount of residue remaining in the sample.

The relationship between pellet weight percent undissolved and amount of starting PuO_2 undissolved is shown in Figure 12. In the worst case, nearly 40 weight percent of the original plutonium oxide in the pellet was still undissolved after 12 hours in boiling 12M nitric acid. Greater than 99 wt% of the original uranium dioxide dissolved in all but one sample. All data in Figure 13 were fit to the lines by the method of least squares. The relative positions of the three lines are exactly as expected and are very near to the positions of a calculated line if only plutonium oxide remained in the residues.

The amount of plutonium still undissolved after 12 hours in boiling 12 M HNO_3 was calculated from the amount of pellet undissolved and from the Pu/U ratio in the final residue. The following statistical equation was obtained for plutonium dissolution where Y is now the amount of original plutonium still undissolved and the X's are the statistical designation of the variables studied, Table 1, and are defined to run from -1 to +1:

$$Y = 20.86 + 2.76X_1 - 10.52X_3 - 0.84X_4 + 3.53X_5 - 8.71X_1^2 - 2.42X_1X_2 - 1.60X_2X_4 - 1.25X_2X_5 \qquad \text{(MB-2)}$$

4.2 Sol Gel Mixed Oxide Fuel Studies

The Sol Gel process is another candidate fabrication process for mixed oxide fuels and generally consists of blending UO_2 and PuO_2 sols together and drying them to a gel, grinding the resulting gel into a fine powder, calcining the powder, cold pressing it into pellets, then sintering the pressed pellets at high temperature in a reducing atmosphere.

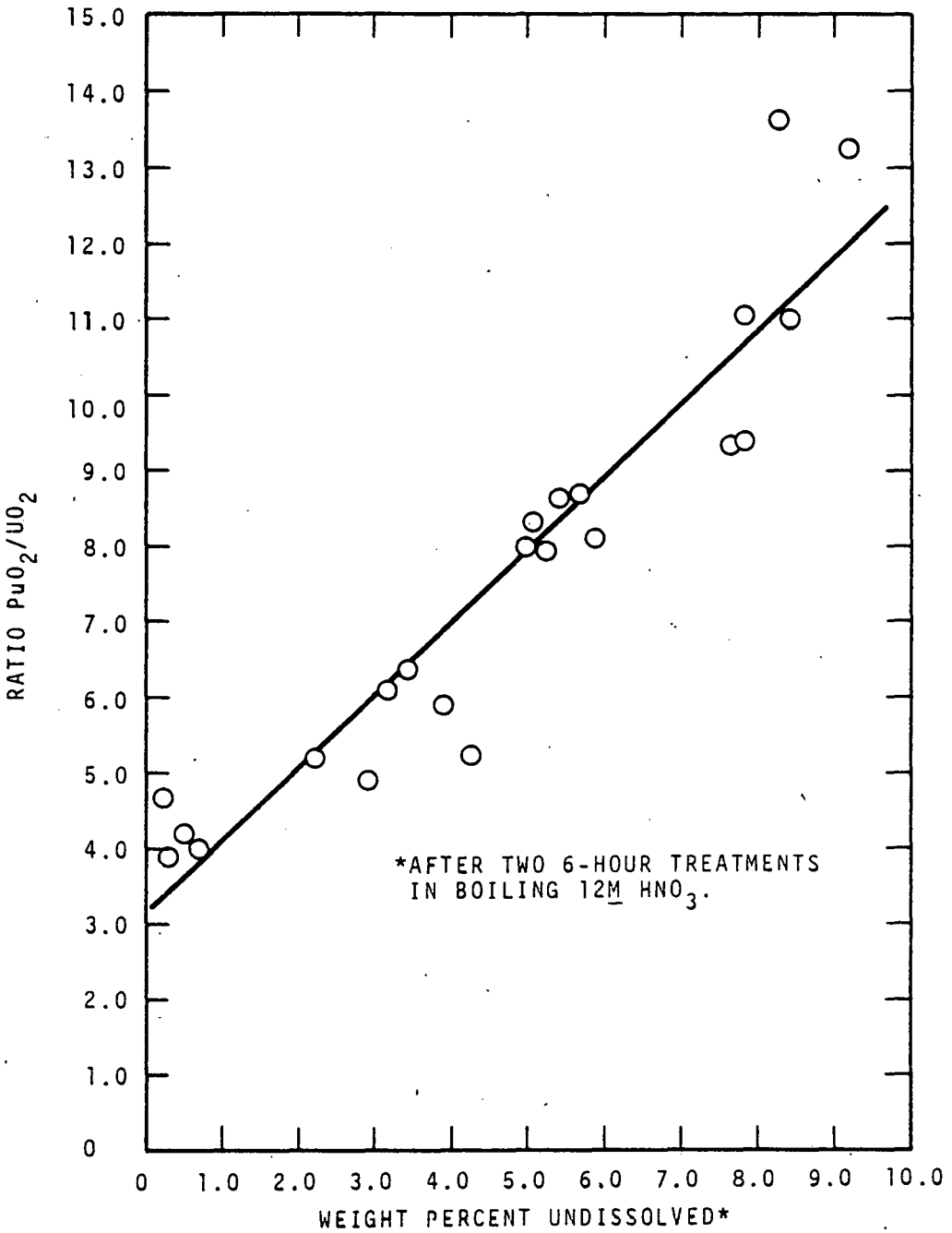

FIGURE 12 Ratio of PuO_2/UO_2 in Residue Versus Weight Percent Undissolved for 25 wt% PuO_2 Pellets

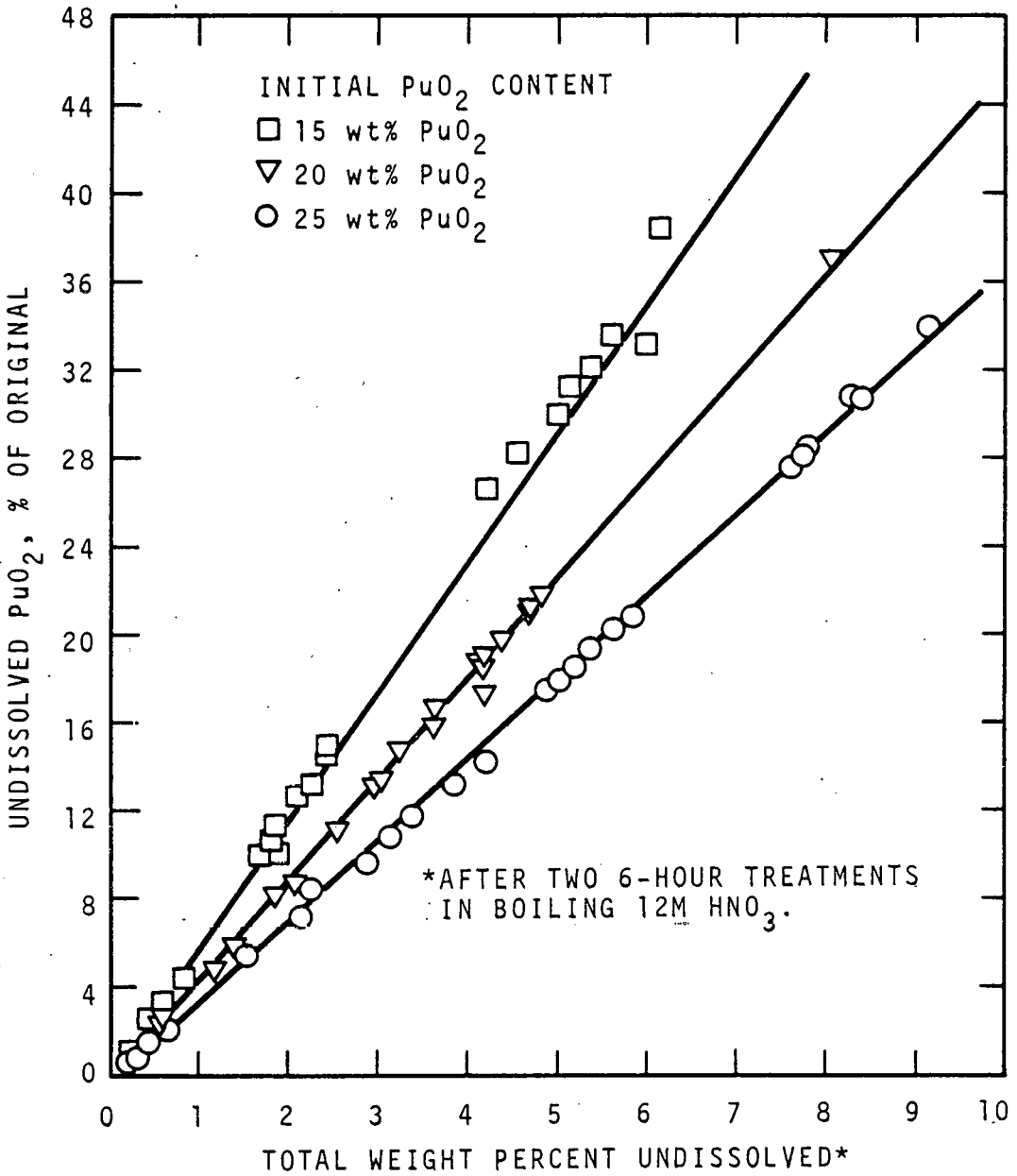

FIGURE 13 Total Weight Percent Undissolved Versus Weight Percent of PuO_2 Undissolved

Previous dissolution studies performed at ORNL on both unirradiated[10-12] and irradiated[12-14] Sol Gel mixed oxide pellets and microspheres indicate that, mixed oxide fuel prepared by the Sol Gel process dissolved quite readily in nitric acid alone, both before and after irradiation. The rate of dissolution and quantity of plutonium that dissolved increased slightly with irradiation[10]. Plutonium recoveries were normally quite high (> 99.8%) for dissolving both irradiated and nonirradiated Sol Gel Fuel[14,15].

The fabrication variables shown in Table 2 were selected for the statistical evaluation of the effect of fuel fabrication conditions on the dissolution properties of Sol Gel derived mixed oxide fuel. Amount of PuO_2, sintering temperature and rate of temperature rise during sintering were selected for evaluation since all three affected the dissolution properties of mechanically blended mixed oxide fuel. Calcination temperature, which affects sinterability and final density of the mixed oxide, was selected for evaluation because of its significance to Sol Gel fabrication processes. Sintering time and pellet pressing pressure, both of which were evaluated for mechanically blended fuels, were held constant in this experiment since they had only minor effects on dissolution of mechanically blended fuel. Source of PuO_2, also evaluated for mechanically blended fuel, was nitrate derived in this experiment. In the case where a variable was held constant, the level of the variable was fixed at one of the levels previously evaluated (e.g., sintering time and pellet pressing pressure were fixed at 1 hour and 25 kpsi, respectively).

The statistical design used in these experiments was a 2/3 fractional factorial design. This resulted in 36 treatment cells or conditions. The levels of the four independent variables for each of the 36 cells are shown in Appendix B. All pellets were fabricated at HEDL from nine batches of calcined powder starting material supplied by ORNL's Metal and Ceramics Division. About 12 pellets were fabricated for each cell. Only pellet dissolubility tests were run on this fuel material since, in general, the dissolution rate was fast and there was little, if any, residue after 12 hours treatment in boiling 12M nitric acid.

4.2.1 Dissolubility Results

Dissolubility experiments were run on pellets from each of the 36 treatment cells. Results of these runs were then analyzed statistically.

TABLE 2

VARIABLES FOR STATISTICAL FACTORIAL EXPERIMENT ON DISSOLUTION OF SOL GEL, MIXED OXIDE FUEL

Variable[a]	Levels	Statistical Designation
X_2: Amount of PuO_2, w/o	15	-1
	20	0
	25	1
X_3: Sintering Temperature, °C	1400	-1
	1550	0
	1700	1
X_4: Rate of Temperature Rise During Sintering, °C/hr	100	-1
	250	1
X_5: Calcination Temperature of Mixed Oxide, °C	500	-1
	600	0
	700	1

a. Variable X_1 was initially Process (i.e., Sol Gel or coprecipitation).

Statistical analysis of the dissolubility data from the Sol Gel mixed oxide fuel dissolution study indicated that the fabrication variables studied had only minor effects on dissolubility of the Sol Gel. A discussion of the influence that specific fabrication variables had on dissolubility is difficult since the effects were not the same for all combinations of PuO_2 content, sintering temperature, and calcination temperature. However, the following general statements can be made:

1. For 15 w/o PuO_2 Sol Gel fuel, the amount of undissolved residue decreased as the sintering temperature was increased from 1400°C to 1700°C. This was not uniformly true for the 20 and 25 w/o PuO_2 Sol Gel fuel.

2. For 15 and 20 w/o PuO_2 Sol Gel fuel, the amount of undissolved residue increased as the calcination temperature of the mixed oxide increased from 500°C to 700°C. Again, this was not uniformly true for the 25 w/o PuO_2 fuel.
3. The particular combination of low PuO_2 content (15 w/o), low sintering temperature (1400°C), and high calcination temperature (700°C) produced Sol Gel fuel with the largest amount of undissolved residue with nearly 2 w/o of the original fuel pellet remaining undissolved.
4. Most combinations of the fabrication variables studied yielded fuel that was almost completely dissoluble in nitric acid alone. This was seen by the fact that fuel from 29 of 36 Sol Gel fabrication cells had pellet residues of less than 0.1 w/o using our standard dissolubility procedure.

Dissolution results for one particular set of fabrication conditions (e.g., 25 w/o PuO_2, 1700°C sintering temperature, 100°C/hr rate of temperature rise during sintering, and a mixed oxide calcination temperature of 600°C) were highly variable with pellet residues of 10.81, 4.65, 7.94, and 3.80 w/o (average 6.80 w/o) obtained after 12 hours dissolution in the boiling 12M nitric acid. The final residue retained the cylindrical shape of the original pellet throughout dissolution (see Figure 14) and thus the final amount of residue appeared to be more a function of dissolution rate than of dissolubility. Additional tests showed the pellets to dissolve completely in the nitric acid after $\sim$ 25 hours dissolution. Actual dissolubility results from this particular cell were not used in the statistical analysis. Rather, an adjusted value calculated by taking the average value from three cells having the same fabrication variables for three of the four independent variables was used.

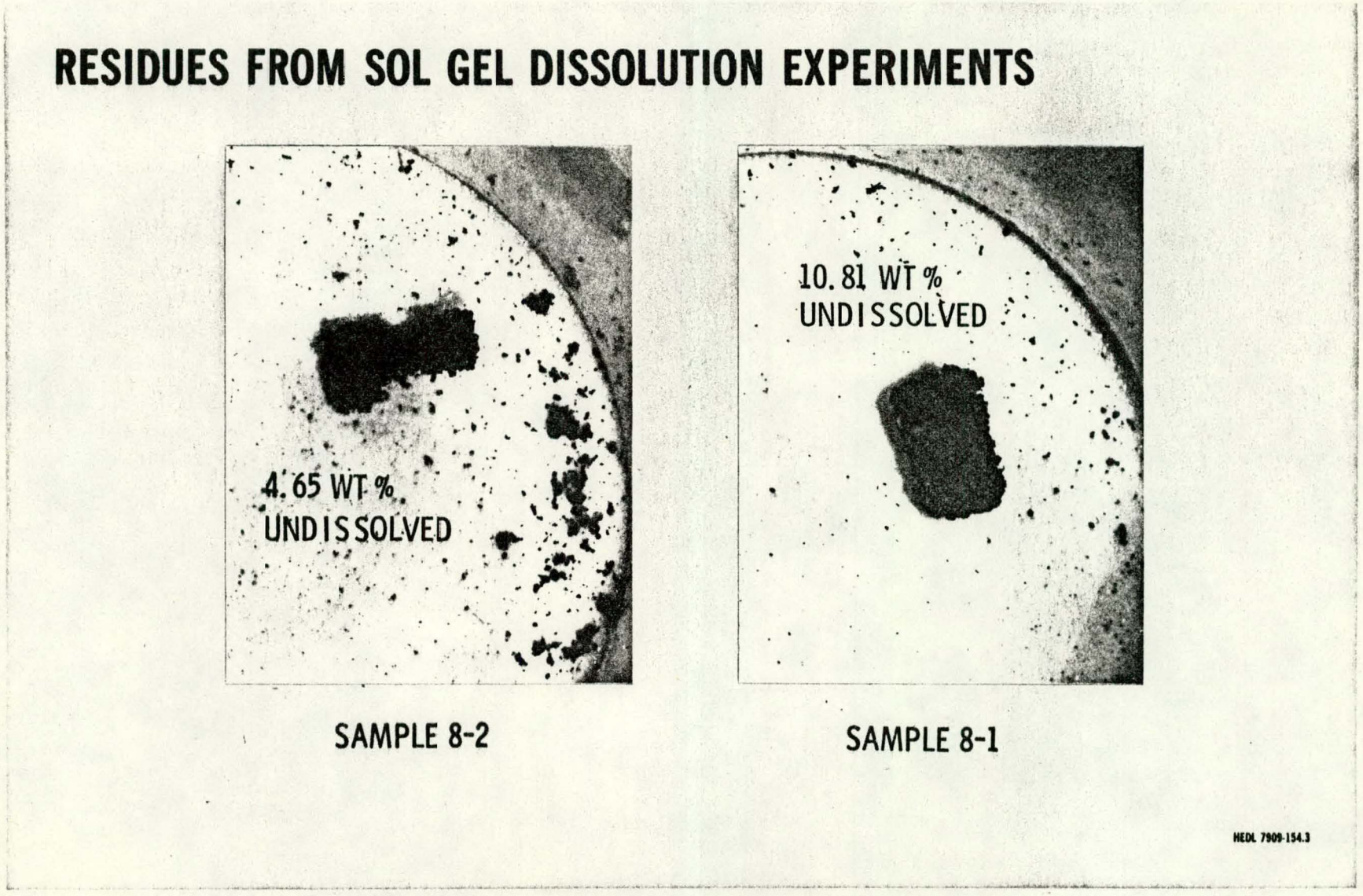

Figure 14: Residues from Sol Gel Dissolution Experiment, Cell Number 8.

A full quadratic model was used in the first attempt at estimation for each independent variable was the full quadratic model. After deleting the terms from the full quadratic model which were not statistically significant and reestimating the parameters the following equation resulted:

Model SG-2 - Value for experimental cell 8 = 0.062

$$Y = - 0.253X_2 - 0.239X_3 + 0.228X_5 + 0.232X_3^2 + 0.327X_2X_3 - 0.203X_2X_5 - 0.222X_3X_5 \qquad \text{(SG-2)}$$

X_1 Amount of PuO_2

X_2 Sintering Temperature

X_3 Rate of Temperature Rise During Sintering

X_4 Calcination Temperature of Mixed Oxide Fuel

In the equations, Y was the amount of undissolved pellet (calculated as w/o of original pellet) and the X's were the statistical designation of the particular variables (as shown in Table 2) and were defined to run from -1 to +1. When the appropriate values for the X's were inserted, the equations gave the predicted or expected amount of pellet residue.

The amount of the total variation in the dissolubility data explained by Model SG-2 was 85%. The standard deviation which expresses the scatter of the data points between the predicted and observed values was ± 0.225. The percentage of the variation in data explained by the model was somewhat misleading, however, since most of the variation was due to two or three relatively high dissolubility values which accounted for most of the variation in the data. The major problem of trying to fit data of this type to any statistical model was that most of the data points were very near zero. The few non-zero points tended to dominate the fitting process while the data points close to zero have little influence on the statistical model.

The relatively large residue of the 15 w/o PuO_2, high calcined, low sintered fuel (conclusion 3 above) may have been influenced by a longer time at temperature during the calcination cycle. Powder from one of the nine calcination temperature for 6-1/2 hours instead of 4 hours as per all other batches.[28] Powder from that particular batch was subsequently used to fabricate pellets for four different dissolution cells according to the characteristics shown in Table 3.

TABLE 3

Fabrication Variables of Fuel Pellets
Made From Calcination Batch C-32

Cell No	Amount of PuO_2, w/o	Sintering Temperature, °C	Rate of Temp Rise °C/hr	Calcine Temp, °C	Residue, w/o Undiss
3	15	1700	100	700	0.075
18	15	1400	100	700	1.97
21	15	1700	250	700	0.042
36	15	1400	250	700	2.12

It appears that the higher sintering temperature used in cells 3 and 21 was sufficient to override the adverse effect of high calcine temperature. Whether or not the longer soak time during calcination (i.e., 6 1/2 hours instead of 4 hours) of this particular batch of powder had further influenced dissolubility cannot be determined by these experiments and was discussed simply as a possible explanation. The actual effect of longer calcination time would have to be determined in separate experiments.

4.2.2 Dissolution Rate Results

Dissolution rate measurements were not made on the Sol Gel fuel. However, dissolution in general was very fast with pellets from most of the cells dissolving nearly completely in the first 6-hour dissolubility treatment. Some pellets disintegrated in the hot acid while others maintained their cylindrical shape throughout dissolution. Neither characteristic, however, produced a clear pattern relating to dissolution rate or dissolubility.

4.3 Coprecipitated Mixed Oxide Fuel Studies

The coprecipitated process is the third candidate fuel fabrication process for mixed oxide fuels. The process consists of precipitating plutonium and uranium from a properly mixed nitrate solution using ammonium hydroxide at controlled pH and temperature. The resulting plutonium hydroxide-ammonium diuranate coprecipitate is reduced in a hydrogen atmosphere at high temperature to yield a dioxide. The dioxide is pressed into pellets and then sintered at high temperature in a reducing atmosphere.

Previous dissolution studies performed on both irradiated[4,11,13,16,17] and unirradiated[3] coprecipitated mixed oxide fuel indicate that coprecipitated fuel was readily soluble in nitric acid alone. Pellets prepared by

coprecipitation were observed to dissolve slower than similar pellets made by the mechanically blending process.[3,18] The rate of dissolution increased with increasing nitric acid concentration.[3,14]

Fabrication variables evaluated in the coprecipitated mixed oxide fuel dissolution studies (shown in Table 4) were exactly the same as used for the Sol Gel dissolution studies in order to facilitate fabrication of the pellets and comparison of the dissolution results.

The experimental design was a 2/3 fraction factorial design. This resulted in 36 different fabrication cells or conditions. Levels for each of the four independent variables in all 36 cells are shown in Appendix B. All pellets were fabricated by HEDL following receipt of dried plutonium hydroxide-ammonium diuranate starting material from the Atlantic Richfield Hanford Company (ARHCO). The material was subsequently reduced, calcined, and pressed into pellets. The pellets were sintered with pellets from the identical Sol Gel fabrication batches. Approximately 12 pellets were fabricated for each cell in the statistical design. Only pellet dissolubility tests were run on the pellets.

4.3.1 Dissolubility Results

Dissolubility experiments were run on pellets from each of the 36 treatment cells. Results of these runs were analyzed statistically.

Statistical analysis of the dissolubility data from the coprecipitated mixed oxide fuel dissolution study showed that the particular fabrication variables studied had essentially no effect on the dissolubility of the coprecipitated mixed oxide fuel. This was seen by the fact that pellets from 31 of the 36 coprecipitated fuel fabrication cells had pellet residues of less than 0.1 w/o of the original pellet using our standard dissolubility procedure. The largest residue found was only 0.25 w/o of the original pellet.

The model employed in the first estimation for each independent variable was the full quadratic model. After deleting the terms from the full quadratic model which were not statistically significant and re-estimating the parameters the following equation resulted:

TABLE 4

VARIABLES FOR STATISTICAL FACTORIAL EXPERIMENT ON DISSOLUTION OF COPRECIPITATED MIXED OXIDE FUEL

Variable[a]	Levels	Statistical Designation
X_2: Amount of PuO_2, w/o	15	-1
	20	0
	25	1
X_3: Sintering Temperature, °C	1400	-1
	1550	0
	1700	1
X_4: Rate of Temperature Rise During Sintering, °C/hr	100	-1
	250	1
X_5: Calcination Temperature of Mixed Oxide, °C	500	-1
	600	0
	700	1

a. Variable X_1 was initially Process (i.e., Sol Gel or coprecipitation).

Model CP-1

$$Y = 0.059 + 0.014X_2 - 0.010X_4 + 0.031X_3^2 - 0.020X_2X_4 + 0.022X_2X_5 - 0.025X_3X_5 \quad \text{(CP-1)}$$

X_1 Amount of PuO_2

X_2 Sintering Temperature

X_3 Rate of Temperature Rise During Sintering

X_4 Calcination Temperature of Mixed Oxide Fuel

In the equation, Y was the amount of undissolved pellet (calculated as w/o of original pellet) and the X's were the statistical designations of the particular variables and were defined to run from -1 to +1. When the appropriate values for the various X's were inserted, the equation gave the predicted or expected amoung of undissolved pellet. As can be seen from the various coefficients, no one particular fabrication variable dominated dissolubility and the predicted amount of residue was small, regardless of the particular combination of fabrication variables. Predicted residues ranged from 0.01 w/o to 0.18 w/o using this particular statistical model.

The adequacy of the statistical model can be expressed in terms of the amount of the total variation in dissolubility data explained by the model. In this case the multiple correlation coefficient* was 0.66 which means that the model explained only about 44% of the variation.

The average standard deviation between pellets within cells was estimated to be 0.034. If experimental control was perfect, the expected standard deviation between cell averages would be about $0.034/\sqrt{3}$ or 0.020. In actual fact, the standard deviation between observed and predicted data points was ±0.043; the difference reflected the combined effect of time-associated-undefined variables, possible inadequacies in the model, and possible difficulties in attaining the exact levels of the independent variables as specified.

Although the statistical model explained only 44% of the variation in the dissolubility data and the standard deviation of ±0.043 was relatively high, the experiment did demonstrate that none of the four fabrication variables had an appreciable effect on dissolubility of mixed oxide fuel fabricated using the coprecipitation process. Thus, changes within the range of any of the four fabrication variables investigated produced no appreciable change in dissolubility of the coprecipitated fuel. Since pellet samples from almost all of the 36 experimental cells had such small

residues regardless of the particular combination of variables used, a general statistical model was difficult to derive, and, in fact, was probably not necessary.

4.3.2 Dissolution Rate Results

Dissolution rate measurements were not made on the coprecipitated mixed oxide fuel pellets. However, dissolution rates in general were observed to be very fast with fuel pellets from 30 of the 36 cells having no visible residue after two hours dissolution in boiling 12M nitric acid. The six remaining cells had only small residues (<0.1 w/o of the original pellet) at the end of 12 hours dissolution in boiling 12M nitric acid.

4.4 Comparison of Fuel Fabrication Processes

The fabrication variables evaluated in these studies were selected to facilitate direct comparison of dissolution characteristics of fuel made by the three condidate fabrication processes. In cases where variables were held constant, the variables were fixed at a level evaluated in the other experiments. Table 5 shows the comparison of variables used in the three dissolution experiments.

In general the Sol Gel and coprecipitated mixed oxide fuel pellets dissolved more completely than similarly fabricated mechanically blended fuel. This is shown graphically in Figure 15 for all three fuel fabrication procedures. Variables that were held constant in this particular comparison include the source of PuO_2 (nitrate), sintering time (1 hr.) rate of temperature rise during sintering (100°C/hr.), pressing pressure (25 kpsi), and the calcination temperature (700°C). The predicted dissolubility for 15 and 20 w/o PuO_2 mixed oxide fuel indicated that fuel made by the coprecipitation process dissolved more completely than fuel made by the Sol Gel process which, in turn, dissolved more completely than fuel made by the mechanically blending process. For 25 w/o PuO_2 mixed oxide fuel the order was Sol Gel more dissolvable than coprecipitated which was more dissolvable than mechanically blended fuel.

TABLE 5

Comparison of Related Fabrication Variables in the Mechanically Blended, Sol Gel, and Coprecipitated Mixed Oxide Fuel Dissolution Experiments

Variable	Mechanically Blended	Sol Gel	Coprecipitation
Source of PuO_2	Calcined Oxalate Calcined Nitrate Burned Metal	Nitrate	Nitrate
Amount of PuO_2, w/o	15 20 25	15 20 25	15 20 25
Sintering Temperature, °C	1400 1550 1700	1400 1550 1700	1400 1550 1700
Rate of Temperature Rise During Sintering, °C/hr	100 250	100 250	100 250
Sintering Time, hrs	1 6	1	1
Pellet Pressing Pressure	25 50	25	25
Calcination Temperature, °C	 700	500 600 700	500 600 700

4.5 Effect of Irradiation on Completeness of Fuel Dissolution

Previous studies[1-4] have shown, in general, that irradiation has a beneficial effect on dissolution of mixed oxide fuel. This beneficial effect has been attributed to formation of extensive mixed crystal solid solution in the fuel. Experiments were performed at HEDL to investigate the effect of irradiation on dissolution of mechanically blended mixed oxide fuel with known fabrication histories. For the studies, samples were selected which would enable direct comparison of differences between fabrication variables and how they might effect completeness of plutonium dissolution following irradiation of the fuel.

The procedure used in the tests consisted of leaching stainless-steel-clad fuel pieces (∿ one inch in length) for two six-hour periods in boiling 12M nitric acid. Following the leach cycle, any residue is filtered from the solution, dried, and weighed, then leached an additional 48 to 72 hours in hot 12M HNO_3-0.05M HF to recover any previously undissolved plutonium. The plutonium found in the fluoride leach solution

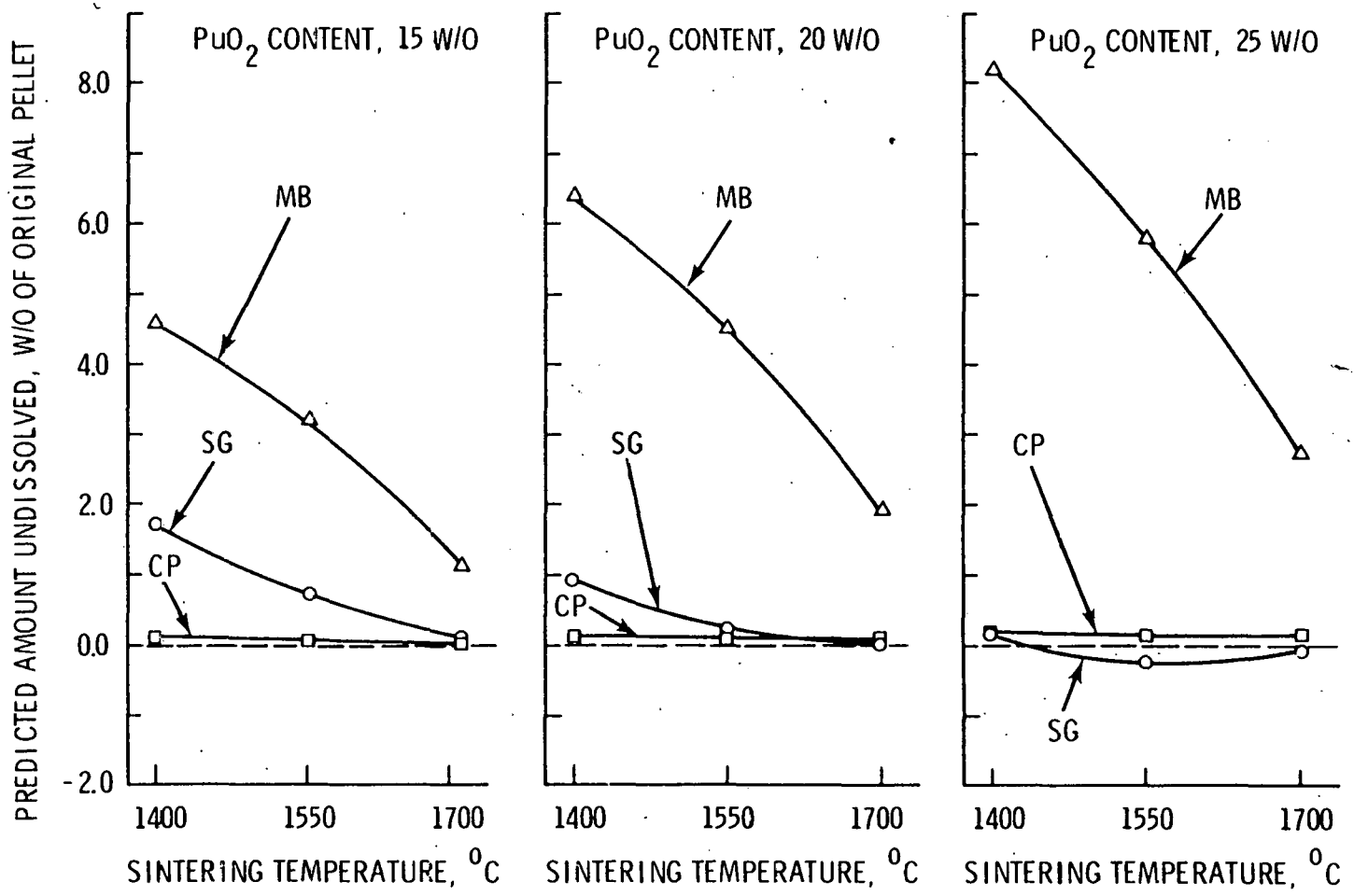

Figure 15. Effect of Sintering Temperature and PuO_2 Content on the Dissolubility of Unirradiated Mechanically Blended, Sol Gel, and Coprecipitated Mixed Oxide Fuel.

represents the nonsoluble plutonium in the irradiated fuel. Additional fluoride leaches of the residue were generally 10^{-2} to 10^{-3} lower in plutonium. Emission spectrographic analysis showed the residues after the fluoride leach consisted mainly of noble metals, in particular molybdenum, rhodium, ruthenium, and technetium. Plutonium was not detectable.

Results of the dissolution tests are summarized in Table 6. Several conclusions can be drawn from these data.

1. High burnups (up to 137,000 MWd/MT) produced no adverse effects on plutonium dissolubility (see samples BNW 1-3, 1-4, and 1-5).

2. Irradiation can be expected to increase plutonium dissolubility. However, comparison of dissolution results for similar nonirradiated fuel indicate that irradiation cannot be relied on to produce complete plutonium dissolubility on a routine basis (see samples PNL 3-27 and PNL 4-26).

3. Poor dissolubility of mechanically blended fuel due to adverse fuel fabrication conditions (e.g., low fuel sintering temperature) may carry through irradiation. Samples PNL 3-27 and PNL 4-26, for example (both with low sintering temperatures), had appreciable amounts of plutonium ($\sim$ 0.8 wt% of the original plutonium) still undissolved after 12 hours dissolution in boiling 12 M nitric acid. Dissolution of similar nonirradiated fuel samples produced low plutonium dissolubility using the same dissolution procedure.

4. Amount of fuel undissolved increased directly with fuel burnup. The increase was, however, due almost entirely to fission product buildup (see samples BNW 1-3, 1-4, and 1-5).

TABLE 6

SUMMARY OF HEDL DISSOLUTION EXPERIMENTS ON IRRADIATED FUEL[a]

IRRADIATION CONDITIONS					FABRICATION CONDITIONS[b]							DISSOLUTION		
Sample Number	Reactor	Fuel Burnup MWd/MT	Power Level, kW/ft	Centerline Temp, est °C	^{235}U	Sint Temp, °C	Sint Time, hrs	Source of PuO_2	Sint Density, % TD	Pellet O/M	Predicted Residue of Pu[c]	Pellet Residue w/o[d]	Pu in Residue[e] mg	Pu in Residue[e] w/o of Orig Pu
BNW 1-4	MTR	71,000	19.1	2700-2800	0.7	1680	6	Metal	94.75	1.94-1.96	No	0.05	0.14	0.02
BNW 1-3	MTR	113,500	16	2700-2800	0.7	1680	6	Metal	95.26	1.94-1.96	No	1.47	0.27	0.02
BNW 1-5	MTR	137,000	17.9	2700-2800	0.7	1680	6	Metal	96.36	1.94-1.96	No	1.86	0.06	<0.01
PNL X-1	EBR-II	4,200	5.3	1650	0.7	1600	8	Metal	91.30	1.98	Yes	0.01	0.63	0.05
PNL 59-5	GETR	10,000	7.5	1650-1750	0.7	1650	8	Metal	95.60	1.99-2.00	No	0.03	0.25	0.02
PNL 59-7	GETR	68,400	13.5	2200-2400	0.7	1650	8	Metal	95.60	1.99-2.00	No	0.34	0.21	0.02
PNL 3-23	EBR-II	26,000	5.3	1250-1350	0.7	1675	6	Oxalate	95.43	1.97	No	0.19	0.78	0.07
PNL 3-27	EBR-II	25,000	5.4	1450-1500	0.7	1500	6	Metal	88.77	1.97	Yes	0.52	11.3	0.78
PNL 4-1	EBR-II	40,450	9.4	1750-1850	45	1690	6	Oxalate	92.92	1.96	No	0.22	0.31	0.03
PNL 4-26	EBR-II	41,000	9.2	1700-1800	45	1450	6	Oxalate	90.08	1.97	Yes	0.50	9.9	0.82
PNL 4-34	EBR-II	38,600	8.3	1850-1950	45	1500	6	Metal	90.94	1.96	Yes	0.49	1.60	0.14
PNL 5-5	EBR-II	45,650	13.6	2350-2450	93	1675	6	Metal	92.15	1.96	No	0.37	1.42	0.11

a. All fuel is mechanically blended, 25 w/o PuO_2 fuel.

b. Conditions listed relate to previously studied conditions for unirradiated fuel. Other conditions include sintering in Ar-8% H_2, 1-3% Carbowax binder, 75-80°C/hr temperature rise during sintering.

c. Based on pervious data on unirradiated fuel (reference 4).

d. After two 6-hour treatments in boiling 12M HNO_3.

e. After 48-72 hours leaching in 12M HNO_3-0.05M HF.

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Appendix A

Statistical Terms Used in Report

Statistical Term	Definition
Statistical Model	A statistical model for an observation is a method of describing the observations in terms of parameters and random errors of observation. Example: $Y_i = \beta_0 + \beta_1 x_i + e_i$ where the x_i are known variates, the β values are unknown parameters and e_i is a random error.
Analysis of Variance	The analysis of the total variability of a set of data (measured by their total sum of squares) into components which can be attributed to different sources of variation.
Regression Analysis	The analysis of sets of paired data (X_1, Y_1), (X_2,Y_2),---and (X_n,Y_n) where the X's are constants and the Y's are values of random variables. The "method of least squares" fitting of data is an example of regression analysis.
Factorial Experiment	An experiment in which all levels of each factor (variable) are investigated in combination with all levels of every other factor.
Fractional Factorial Experiment	A statistically chosen fraction of a full factorial experiment.
Replicate	The individual repetition of an experiment.
Full Quadratic Model	A statistical model that looks at all possible two factor interactions of all the variables. For example, using variables X_1, X_2, X_3---X_n, this would include X_1^2, X_1X_2, X_1X_3, X_2^2, etc.-----
Multiple Correlation Coefficient	An indication of how well one variable can be predicted in terms of a linear combination of the other variables. It is given by the maximum correlation coefficient between the dependent variable and any linear combination of the independent variables. One hundred times $(mcc)^2$ gives the total amount of variation in data explained by a statistical model.
Standard Deviation	A measure of the variation of a set of data. The standard deviation(s) of a sample of size n is given by the square root of the sum of the squared deviations from the mean divided by n-1, i.e. $S = \sqrt{\Sigma (X-\overline{X})^2/n-1}$
Residual Variance	The part of the variability of the dependent variable which is attributed to chance or experimental error.
Residual Standard Deviation	A term calculated from the square root of the residual variance.

APPENDIX B

TABLE B-1

Levels of the Six Variables Used in Dissolution Experiment on Mechanically Blended Mixed Oxide Fuel

Cell	X_1	X_2	X_3	X_4	X_5	X_6	Cell	X_1	X_2	X_3	X_4	X_5	X_6
01	-1	-1	-1	-1	-1	-1	37	1	1	-1	1	-1	-1
02	-1	-1	-1	-1	-1	1	38	1	1	-1	1	-1	1
03	1	0	1	1	1	-1	39	0	1	0	-1	1	-1
04	1	0	1	1	1	1	40	0	1	0	-1	1	1
05	-1	1	1	1	-1	-1	41	0	-1	-1	1	-1	-1
06	-1	1	1	1	-1	1	42	0	-1	-1	1	-1	1
07	1	1	-1	-1	1	-1	43	-1	-1	0	-1	1	-1
08	1	1	-1	-1	1	1	44	-1	-1	0	-1	1	1
09	1	-1	1	1	-1	-1	45	0	0	0	-1	-1	-1
10	1	-1	1	1	-1	1	46	0	0	0	-1	-1	1
11	0	-1	-1	-1	1	-1	47	-1	1	-1	1	1	-1
12	0	-1	-1	-1	1	1	48	-1	1	-1	1	1	1
13	1	0	-1	-1	-1	-1	49	-1	-1	0	1	-1	-1
14	1	0	-1	-1	-1	1	50	-1	-1	0	1	-1	1
15	0	1	1	1	1	-1	51	1	-1	1	-1	1	-1
16	0	1	1	1	1	1	52	1	-1	1	-1	1	1
17	-1	0	-1	-1	1	-1	53	1	1	0	1	1	-1
18	-1	0	-1	-1	1	1	54	1	1	0	1	1	1
19	0	1	-1	-1	-1	-1	55	-1	0	1	-1	-1	-1
20	0	1	-1	-1	-1	1	56	-1	0	1	-1	-1	1
21	-1	-1	1	1	1	-1	57	0	0	1	-1	1	-1
22	-1	-1	1	1	1	1	58	0	0	1	-1	1	1
23	0	0	1	1	-1	-1	59	0	-1	0	1	1	-1
24	0	0	1	1	-1	1	60	0	-1	0	1	1	1
25	1	0	0	-1	1	-1	61	1	1	1	-1	-1	-1
26	1	0	0	-1	1	1	62	1	1	1	-1	-1	1
27	-1	1	0	-1	-1	-1	63	1	0	0	1	-1	-1
28	-1	1	0	-1	-1	1	64	1	0	0	1	-1	1
29	1	-1	-1	1	1	-1	65	-1	0	0	1	1	-1
30	1	-1	-1	1	1	1	66	-1	0	0	1	1	1
31	-1	0	-1	1	-1	-1	67	0	-1	1	-1	-1	-1
32	-1	0	-1	1	-1	1	68	0	-1	1	-1	-1	1
33	1	-1	0	-1	-1	-1	69	0	1	0	1	-1	-1
34	1	-1	0	-1	-1	1	70	0	1	0	1	-1	1
35	0	0	-1	1	-1	-1	71	-1	1	1	-1	1	-1
36	0	0	-1	1	1	1	72	-1	1	1	-1	1	1

APPENDIX B

TABLE B-2

Levels of the Four Variables Used in Dissolution Experiment on Sol Gel Mixed Oxide Fuel [a]

Cell	X_2	X_3	X_4	X_5
1	-1	-1	-1	-1
2	-1	0	-1	0
3	-1	1	-1	1
4	0	-1	-1	0
5	0	0	-1	1
6	0	1	-1	-1
7	1	0	-1	-1
8	1	1	-1	0
9	1	-1	-1	1
10	0	-1	-1	-1
11	0	0	-1	0
12	0	1	-1	1
13	1	-1	-1	0
14	1	0	-1	1
15	1	1	-1	-1
16	-1	0	-1	-1
17	-1	1	-1	0
18	-1	-1	-1	1
19	-1	-1	1	-1
20	-1	0	1	0
21	-1	1	1	1
22	0	-1	1	0
23	0	0	1	1
24	0	1	1	-1
25	1	0	1	-1
26	1	1	1	0
27	1	-1	1	1
28	0	-1	1	-1
29	0	0	1	0
30	0	1	1	1
31	1	-1	1	0
32	1	0	1	1
33	1	1	1	-1
34	-1	0	1	-1
35	-1	1	1	0
36	-1	-1	1	1

a. For simplicity the statistical designation (-1, 0, or +1) of the particular level has been used.

APPENDIX B

TABLE B-3

Levels of the Four Variables Used in Dissolution Experiment on Coprecipitated Mixed Oxide Fuel[a]

Cell	X_2	X_3	X_4	X_5
37	-1	-1	-1	-1
38	-1	0	-1	0
39	-1	1	-1	1
40	0	-1	-1	0
41	0	0	-1	1
42	0	1	-1	-1
43	1	0	-1	-1
44	1	1	-1	0
45	1	-1	-1	1
46	0	-1	-1	-1
47	0	0	-1	0
48	0	1	-1	1
49	1	-1	-1	0
50	1	0	-1	1
51	1	1	-1	-1
52	-1	0	-1	-1
53	-1	1	-1	0
54	-1	-1	-1	1
55	-1	-1	1	-1
56	-1	0	1	0
57	-1	1	1	1
58	0	-1	1	0
59	0	0	1	1
60	0	1	1	-1
61	1	0	1	-1
62	1	1	1	0
63	1	-1	1	1
64	0	-1	1	-1
65	0	0	1	0
66	0	1	1	1
67	1	-1	1	0
68	1	0	1	1
69	1	1	1	-1
70	-1	0	1	-1
71	-1	1	1	0
72	-1	-1	1	1

a. For simplicity the statistical designation (-1, 0, or +1) of the particular level has been used

APPENDIX C

Dissolution Rate Data for Mechanically Blended Fuel

Rate data for each sample time were evaluated using a full quadratic model (i.e., one that looks at all possible two factor interactions.) After deleting the terms from the full quadratic model which were not significant at each sample time and re-estimating the parameters, the following models resulted where Y was the w/o of undissolved plutonium and the X's were the statistical designations of the variables as shown in Table 2:

Model MB-3: 15 minutes dissolution

$$Y = 29.82 + 3.93X_1 + 5.69X_2 - 6.38X_3 + 4.92X_5 - 7.84X_1^2 + 4.24X_3^2 + 4.25X_2X_3 + 3.25X_3X_6 \quad \text{(MB-3)}$$

Model MB-4: 60 minutes dissolution

$$Y = 25.98 + 4.02X_1 + 2.22X_2 - 12.37X_3 - 1.07X_4 + 4.15X_5 - 0.95X_6 - 9.36X_1^2 - 1.83X_1X_2 - 1.03X_2X_4 - 1.18X_2X_5 \quad \text{(MB-4)}$$

Model MB-5: 120 minutes dissolution

$$Y = 24.93 + 3.95X_1 + 1.96X_2 - 12.44X_3 - 1.16X_4 + 3.92X_5 - 0.96X_6 - 9.20X_1^2 - 1.88X_1X_2 - 1.06X_2X_4 - 1.23X_2X_5 \quad \text{(MB-5)}$$

Model MB-6: 360 minutes dissolution

$$Y = 23.82 + 3.84X_1 + 1.73X_2 - 12.15X_3 - 1.17X_4 + 3.63X_5 - 0.91X_6 - 8.94X_1^2 - 1.85X_1X_2 - 1.08X_2X_4 - 1.37X_2X_5 \quad \text{(MB-6)}$$

Model MB-7: 60, 120, and 360 minutes dissolution

$$Y = 25.92 + 3.94X_1 + 1.97X_2 - 12.32X_3 - 1.13X_4 + 3.90X_5 - 0.94X_6 - 9.16X_1^2 - 1.85X_1X_2 - 1.06X_2X_4 - 1.26X_2X_5 - 0.34X_7 \quad \text{(MB-7)}$$

The dissolution rate data for all four sample times were evaluated together with time as a variable, again using a full quadratic model. The resulting statistical model (model MB-8) contained a time term (X_7) which equaled 0.25, 1, 2, or 6 hours.

Model MB-8: total dissolution cycle

$$Y = 36.83 + 4.02X_1 + 2.90X_2 - 10.87X_3 - 0.78X_4 + 4.16X_5 - 0.70X_6 - 8.76X_1^2 + 1.13X_3^2 - 1.64X_1X_2 + 1.67X_2X_3 - 1.07X_2X_4 - 1.28X_2X_5 + 0.99X_3X_4 + 1.08X_3X_6 - 19.33X_7 + 8.23X_7^2 - 0.90X_7^3 \quad \text{(MB-8)}$$

APPENDIX C

Table C shows the standard deviation, which expresses the scatter of the observed data when compared to the predicted values, for all six plutonium dissolution rate models. The table also give the multiple correlation coefficient and the percent of the total variation in amount of plutonium undissolved explained by the particular model. In all cases the final statistical models were very effective in accounting for the overall variation. The higher standard deviations for models MB-3 and MB-8 reflected the scatter in our data for the 15 minute rate samples. A "goodness of fit" plot of all of the observed data points vs the points as predicted by model MB-8 is shown in Figure C-1. The standard deviation of the points about the line was $\pm$ 4.25 with most of the scatter produced by the 15 minute rate data.

TABLE C

Statistical Accuracy of Models

	Model					
	MB-3	MB-4	MB-5	MB-6	MB-7	MB-8
Standard Deviations, ±%	4.67	3.05	2.98	3.00	2.69	4.25
Multiple Correlation Coefficient	0.916	0.972	0.973	0.970	0.977	0.944
Variation Explained by Model, %	83.9	94.6	94.6	94.1	95.4	89.1

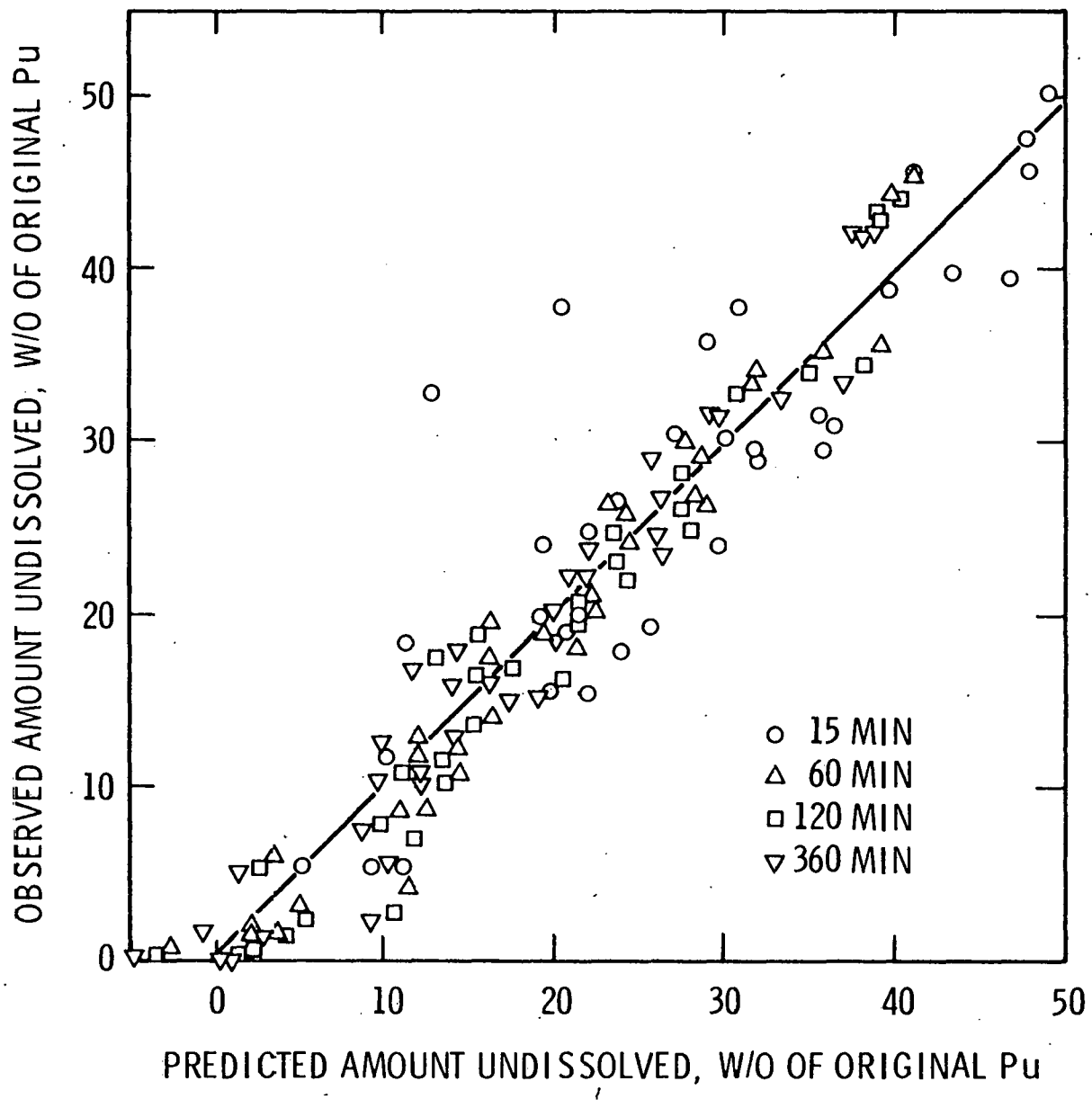

Figure C-1. Observed vs. Predicted Amount of Plutonium Undissolved (Model MB-8).