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DISSOLUTION OF UNIRRADIATED MECHANICALLY
BLENDED MIXED OXIDE FAST REACTOR FUEL^(a)

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ABSTRACT

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A statistical, fractional factorial experiment was performed to determine the effect of six fuel fabrication variables on the dissolubility of unirradiated, mechanically blended PuO_2 - UO_2 fuels. The six fabrication variables were source of PuO_2 , PuO_2 content, sintering temperature, sintering time, rate of temperature rise during sintering, and pellet pressing pressure. All six fabrication variables had some effect on pellet dissolubility with source of PuO_2 , PuO_2 content, and sintering temperature having major effects.

DISSOLUTION OF UNIRRADIATED MECHANICALLY BLENDED MIXED OXIDE FAST REACTOR FUEL

INTRODUCTION

This paper describes experiments that have been performed at HEDL and PNL to measure the dissolubility* of unirradiated, mechanically blended mixed oxide fast reactor fuel. Two significant histories of fast reactor fuels are recognized as having an important effect on the dissolution properties of the fuel. They are the fabrication history and the reactor history. Investigations of the effect of fabrication parameters on dissolution are important to establish what operations influence dissolubility and dissolution rate of the fuel and to what extent. Dissolubility data on unirradiated fuels provide the necessary base from which to assess the effects of irradiation time, temperature, and reactor flux upon dissolubility and dissolution rate of irradiated fast reactor fuel. The information will also be helpful for recycle of scrap materials from the fabrication process and for optimizing the overall fuel cycle.

In order to investigate the effect of fabrication variables on the dissolubility of unirradiated mechanically blended $\text{PuO}_2\text{-UO}_2$ fuels, a statistical, fractional-factorial experiment was performed.⁽¹⁾ The six independent variables shown in Table 1 were investigated. The dependent variable in the experiment was the weight percent of pellet that didn't dissolve.

EXPERIMENTAL

On the basis of previous work on dissolution of mixed oxide fuel, all six variables shown in Table 1 could have an effect on the dissolution properties of the fuel. In particular, temperature and time⁽²⁾ have been previously shown to strongly affect dissolution of mechanically blended 15 wt% PuO_2 fuel. In setting the levels of the six variables, primary consideration was given to procedures already in use or under consideration for FFTF fuels. 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 separated so that any effects due to the particular variable

* As used here, dissolubility refers simply to the fraction of plutonium and uranium which dissolves when the oxide fuel is exposed to boiling nitric acid for a short time [<24 hours].

were easily identified, however, whether or not the effect was linear or curvilinear could not be determined.

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: -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

A complete discussion of the choice of variables and their particular effects on the physical properties of mixed oxide pellets has been published.^(1,3)

The statistical design of the experiment was a 1/3 replicate (i.e., it looked at 1/3 of all possible interactions) of a full factorial experiment for three variables at three levels and three variables at two levels. The design, defined to be the 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 dissolubility procedure used in this experiment consisted of treating single fuel pellets (ca. 0.2 in. in diameter x 1/4 in. long; 1.5 g) with boiling 12M nitric acid for one or, if necessary, two 6-hour periods as shown in Figure 1. After the second 6-hour treatment any residue remaining was separated from the solution, dried, and weighed. The residue was then dissolved in fresh 12M HNO_3 -0.05M HF and the resulting solution analyzed for plutonium and uranium. Two or three pellets were dissolved for each cell

and the mean of the weight percent undissolved was used in the statistical analysis.

RESULTS

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 equation shown in Table 2 resulted.

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 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 2 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 3 and 4. 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 5 for burned metal PuO_2 . The curves shown in Figure 5 are the same as the lower curves shown in Figures 2, 3, and 4. 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 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 6 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 7 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⁽⁴⁾ 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 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 8 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.

DISCUSSION

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 9 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 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.

Density vs Dissolubility

A plot of sintered density vs dissolubility is shown in Figure 10 for all of the samples investigated in this dissolubility experiment. The data were evaluated by regression analysis to determine the relationship between weight percent undissolved and sintered density of the fuel pellets. The

model used in the analysis was of the form $Y = b_0 + b_1X$ where Y is the pellet density and X is the weight percent undissolved, b_0 is the intercept of the line on the Y axis and b_1 is the slope of the line. The estimates of b_0 and b_1 were 92.19 ± 0.51 and -0.562 ± 0.123 , respectively. The estimate of the slope (b_1) is significantly different from zero at the 0.05 level of significance and thus indicates that there is some correlation between sintered density and dissolubility.

Sintered density was also added as an independent variable to the quadratic model used in the original evaluation of the dissolubility data (see equation 1). The addition of sintered density as a variable, however, did not improve the model in the sense of reducing the residual standard error.

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 11 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 12 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.

Correlation of Microstructure and Physical Properties to Dissolubility

Micrographs have been (or will be) taken of pellets from all 72 cells at 10X, 250X, and 500X etched. The 500X etched micrographs will be used to

determine grain size within the pellets. The 10X and 250X micrographs will be used to observe differences in porosity (open vs closed, relative distribution) on a qualitative basis. In addition to the micrographs, some α -autoradiographs were taken of representative pellet batches and will be used to indicate homogeneity (non-quantitative) relative to other similar fabrication runs.

Possible correlation of dissolubility to actual physical properties of the pellets will be studied when characterization of all of the pellet batches is complete.

CONCLUSIONS

All six variables investigated in this experiment were shown to have an effect on the dissolubility of mixed oxide fuels. 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. The data provide good base line measurements from which to assess the effects, if any, of irradiation time, irradiation temperature and reactor flux upon dissolubility of fast reactor fuels as well as providing useful information concerning possible recycle of unirradiated fast reactor fuel materials.

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TABLE 1: VARIABLES FOR DISSOLUTION EXPERIMENT
MECHANICALLY BLENDED, UO₂-PuO₂ FUEL

	<u>Levels</u>	<u>Statistical Designation</u>
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

TABLE 2: DISSOLUBILITY EQUATION

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

- X₁ Source of PuO₂
 X₂ PuO₂ Content
 X₃ Sintering Temperature
 X₄ Sintering Time
 X₅ Rate of Temperature Rise
 X₆ Press Pressure

FIGURE 1 Dissolubility Apparatus

FIGURE 2 The Effect of Source of PuO_2 and Sintering Temperature on Dissolubility of 15 wt% PuO_2 - UO_2 Fuel

FIGURE 3 The Effect of Source of PuO_2 and Sintering Temperature on Dissolubility of 20 wt% PuO_2 - UO_2 Fuel

FIGURE 4 The Effect of Source of PuO_2 and Sintering Temperature on Dissolubility of 25 wt% $\text{PuO}_2\text{-UO}_2$ Fuel

FIGURE 5 The Effect of PuO_2 Content and Sintering Temperature on Dissolubility of Burned Metal PuO_2 - UO_2 Fuel

FIGURE 6 The Effect of PuO₂ Content and Sintering Temperature on Dissolubility of Calcined Nitrate PuO₂-UO₂ Fuel

FIGURE 7

The Effect of Sintering Time, Sintering Temperature, and PuO₂ Content on Dissolubility of Burned Metal PuO₂-UO₂ Fuel

FIGURE 8. The Effect of Rate of Temperature Rise During Sintering and Source of PuO_2 on Dissolubility of Fuel Pellets Sintered at 1700°C

FIGUPE 9 Observed Weight Percent Undissolved vs Predicted Weight Percent Undissolved

FIGURE 10 Relationship of Dissolubility to Pellet Density

FIGURE 11 Ratio of PuO₂/UO₂ in Residue Versus Weight Percent Undissolved for 25 wt% PuO₂ Pellets

FIGURE 12 Total Weight Percent Undissolved Versus Weight Percent of PuO_2 Undissolved

APPENDIX A

TABLE A-1

LEVELS OF THE SIX VARIABLES USED IN DISSOLUBILITY EXPERIMENT

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