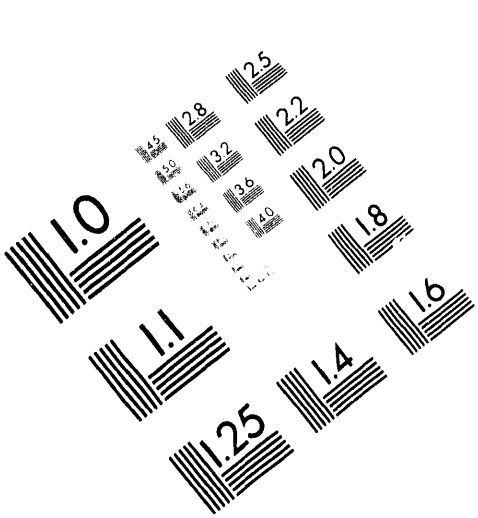

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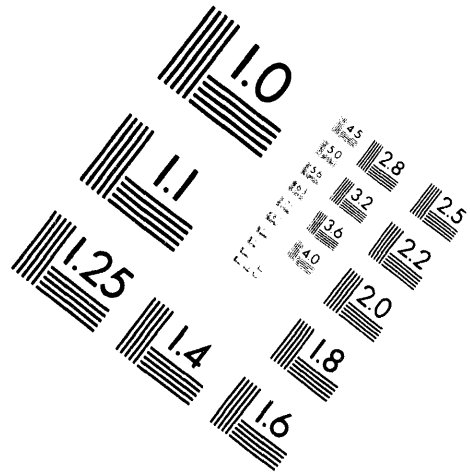

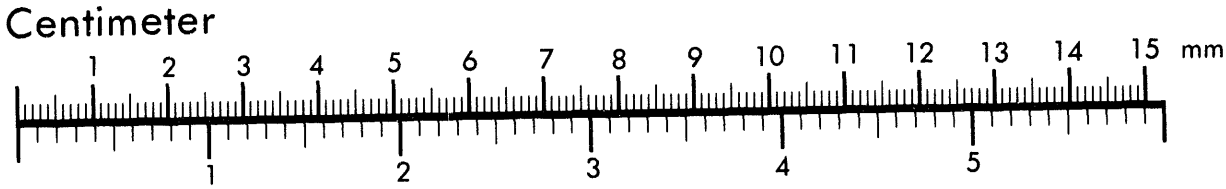

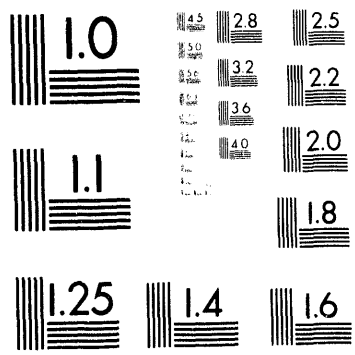

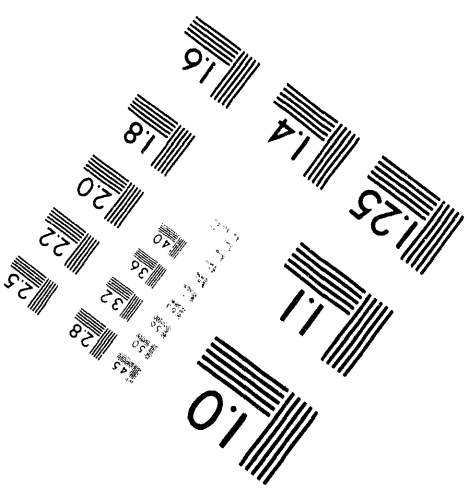

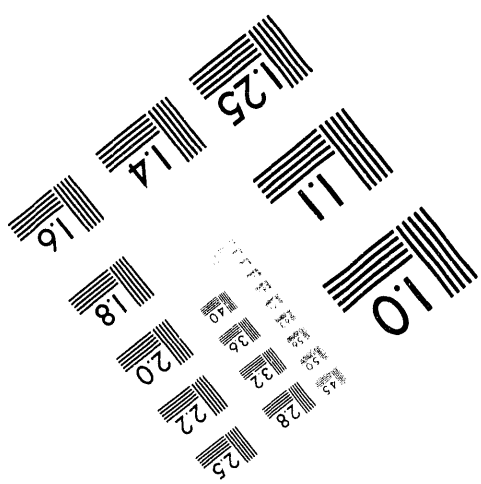

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MODELING OF UO_2 AQUEOUS DISSOLUTION OVER A WIDE RANGE OF CONDITIONS

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ABSTRACT

Previously it was not possible to predict reliably the rate at which spent fuel would react with groundwater because of conflicting data in the literature. The dissolution of the UO_2 spent fuel matrix is a necessary step for aqueous release of radioactive fission products. Statistical experimental design was used to plan a set of UO_2 dissolution experiments to examine systematically the effects of temperature (25-75°C), dissolved oxygen (0.002-0.2 atm overpressure), pH (8-10) and carbonate ($2\text{-}200\times10^{-4}$ molar) concentrations on UO_2 dissolution. The average uranium dissolution rate was 4.3 $mg/m^2/day$. The regression fit of the data indicate an Arrhenius type activation energy of 8750 cal/mol and a half-power dependence on dissolved oxygen in the simulated groundwater.

INTRODUCTION

Long-term, safe disposal of high level nuclear waste in an underground repository requires an understanding of the interaction of the waste form with its environment. Spent fuel dissolution and subsequent transport processes in groundwater are generally considered to be the main routes by which radionuclides could be released from a geological repository. Uranium dioxide is the primary constituent of spent nuclear fuel. The dissolution of the UO_2 spent fuel matrix is regarded as a necessary step for release of radioactive fission products.

At present it is not possible to predict reliably the rate at which spent fuel will react with groundwater because of conflicting data in the literature. There have been many studies of the dissolution of UO_2, spent fuel and uraninite in aqueous solutions [1, 2]. These investigations were under reducing and oxidizing conditions, and as a function of pH, oxygen fugacity, solution chemical compositions, and temperature. The conclusions are equivocal. This is due to the difference in experimental design and the diverse history of fuel samples. This ambiguity results from uncertainties regarding redox chemistry of uranium in both solution and solid phases, surface area measurements, and the possibility of precipitate formation. In addition, some previous studies were conducted under experimental conditions that were either unconstrained or which simulated complex repository conditions, making the results of such studies difficult to interpret [3].

The intrinsic dissolution kinetics of UO_2 were studied under a wide range of controlled conditions, using the single-pass flow-through method, which has been used successfully in the study of dissolution of glass and other minerals [4,5]. The advantage of this technique is that flow rates can be adjusted so that the UO_2 dissolves under conditions that are far from saturation with respect to precipitating phases. Consequently precipitation does not affect the measured uranium concentrations in solution. Under such conditions, the steady-state dissolution concentrations are directly proportional to the effective surface area of the sample [6].

The dissolution rates of uranium oxides are being measured under a variety of well-controlled conditions. The exact chemistry of groundwater in Yucca Mountain is not certain, but groundwater has typical constituents, such as carbonates, sulfates, chlorides, silicates, and calcium. These ions are seen in water taken from wells near Yucca Mountain, which have pH's of 8 or slightly higher. Of the anions commonly found in groundwater, bicarbonate is considered to be the most aggressive towards uranium and, as such, is a conservative surrogate for all anions in aggressive groundwater.

Consistent with previous studies, temperature, dissolved oxygen, pH and total carbonate composition were chosen as the important variables to be studied. What distinguishes this study is

the initial attempt to select wide ranges in variable settings, and to select a group of experiments that will allow later nonlinear modeling in all the variables, as well as allow measures of possible interactions between the variables, while minimizing the number of experiments necessary.

EXPERIMENTAL

Test Matrix

In order to test for nonlinear effects of the four variables on the dissolution rate and any interaction effects between the variables, a statistical experimental design approach was used to select the experiments to be performed and to reduce the number of required experiments. A model including nonlinear effects and interactions of all four variables has at least 15 terms. A set of experiments were selected to examine systematically the effects of temperature (25-75°C), dissolved oxygen (0.002-0.2 atm overpressure), pH (8-10) and carbonate ($2\text{-}200 \times 10^{-4}$ molar) concentrations on UO_2 dissolution. The high temperature was limited to 75°C, because temperatures nearer to 100°C induce considerably more experimental difficulties in an aqueous system. Later extrapolation of results near 100°C should not induce significant errors. The carbonate concentrations bracketed the typical groundwater concentration of 100 ppm. The oxygen pressure represented the atmospheric value and down two orders of magnitude to a minimally oxidizing atmosphere. The pH covered a value typical of groundwaters (pH=8) to very aggressive alkaline conditions.

A D-optimal design of 17 experiments was chosen using the RS/Discover computer program from BBN Software [7]. One experiment at middle values of the four variables was performed in triplicate to test the reproducibility of the experiments. The 17 different experiments were selected from a candidate set of the 81 different, possible combinations (3^4) of variable settings from the four variables at low, medium and high values. A three-level (use of mid-values) candidate set allows a test for nonlinearity in variable effects. The D-optimal approach reduced the number of experiments required by a classic factorial or fractional factorial design. These experiments are uniformly distributed over the 4-dimensional variable space. This set of nineteen experiments allows us to fit a fifteen-term second-order model discussed earlier. The extra degrees of freedom permit tests for experimental variability. If smaller models are satisfactory, the full set of 19 dissolution conditions and rates provides for higher confidence in the models.

Materials

The samples used in these dissolution experiments are polycrystalline UO_2 with a grain size of 1-10 mm. These samples contain dislocation substructures, i.e., low-angle grain boundaries. They are part of a very large batch produced and hand-picked in the early 1960's at Battelle Pacific Northwest Laboratories. Specimens from this batch were used at several laboratories to determine many of the reference physical properties of UO_2, such as melting point, thermal conductivity, hardness and electrical conductivity. The O/U ratio is 2.00 by coulometry after electrical conductivity measurements.

Leachants

The leachant solutions were made with sodium hydroxide, carbonate and bicarbonate. This combination allowed independent adjustment of the total carbonate and the pH required by our experimental design. The gas atmosphere above the buffer solutions consisted of various concentrations of carbon dioxide and oxygen in argon. The carbon dioxide was required for the correct carbonate/bicarbonate equilibrium. The gas and solution compositions were determined from calculations using EQ3/6 developed at this laboratory. The required gas compositions were purchased from traditional compressed gas suppliers. NIST traceable analyses were provided.

Equipment

The flowthrough system consisted of two similar designs. One style consisted of polymethylpentene cells with Teflon tubing and cell filters. These were used in the experiments at 20% oxygen. The polymeric components had been used extensively in glass leaching studies at our laboratory and are described elsewhere [3]. The second design used stainless steel tubing and cells, with the buffered leachants flowing via a gravity head of one to four feet. The metal cells were used in the subatmospheric oxygen experiments. Our earlier experiments with the plastic cells had shown that oxygen would readily diffuse through the Teflon tubing in or out of the system, making dissolved oxygen level control difficult.

RESULTS

The results of our experiments are shown in Table I. Our runs were performed as groups according to temperature and oxygen level. Cells at the same temperature were kept in one oven. In addition to replication experiments in the test matrix, three additional experiments, not in the original test matrix, were performed, because cells were available and the oven could accommodate them. These came from the seven remaining candidates at 75°C and 20% oxygen in the original 81-candidate set of the test matrix. Those additional runs are the final three (20-22) in Table I.

Column 1 of Table I gives a run identifier that is a shorthand for the nominal run conditions. For example, row 6 is U8LH75. This run was nominally at pH 8, low carbonate concentration ($2x10^{-4}$ mol/l), high oxygen overpressure (20%) and 75° C. The remaining columns give the measured and calculated data. The only measured logarithmic data form is pH.

Some of the original dissolution results did not seem correct and are being repeated. Run U10HL75 was originally very high. The oxygen level in the repeat run was monitored closely. The dissolution rate dropped by almost a factor of ten. Runs U8HH75 and U10HH75 also seem too high, and are being rerun as well.

Figures 1-4 are plots of the logarithm of the uranium dissolution rate in $mg/m^2/day$ as a function of respectively, inverse absolute temperature and logarithms of oxygen, total carbonate and hydrogen ion concentrations. Figure 5 is a boxplot that summarizes the statistics for the entire data set. The data are presented in logarithmic form because the classical chemical kinetic model can be analyzed easily in logarithmic form, and the original test matrices covered variable ranges of 100 in concentrations, making the logarithmic form easy to present.

The final analysis of the data is still ongoing, but some qualitative descriptions can be made. The data show the expected linear Arrhenius type dependence of the logarithmic dissolution rate on inverse temperature (Figure 1), with higher uranium dissolution rates at higher temperatures. A regression fit of these data gives a slope of -1910 K^{-1} or an activation energy of 8750 cal/mol. Using pH as a model, the oxygen and carbonate concentrations are expressed as pO_2 and pCO_3, the negative base10 logarithms. The oxygen concentrations are expressed in atmospheres of oxygen overpressure. The Henry's Law constant for dissolved oxygen is included in any fitting constant for the data. Increased levels of dissolved oxygen increase the uranium dissolution rate (see Figure 2). The slope of these data is 0.54, close to the half order dependence previously seen. The dissolution response to carbonate concentration is nonlinear, even in the log-log plot of Figure 3. The cause or importance of this is not yet clear. The effect of pH on the uranium dissolution rate shown in Figure 4 seems random. The data give some indication that increasing pH results in increased UO_2 dissolution. However, such an apparent effect is strongly influenced by two or three data points. Without these few points the effect of the pH on UO_2 dissolution would indeed look random.

The boxplot in Figure 5 shows several noteworthy features of the UO_2 data set. The mean uranium dissolution rate (DR) is 4.3 $mg/m^2/day$ (log DR=0.63). The interquartile region (IQR) is the difference in dissolution rate between the 75th and 25th percentile and is a measure of data spread. The median of the UO_2 dissolution rates is lower than the mean. This is because the mode or most frequently occurring rate is high.

Table 1. Experimental Test Matrix

Sample	TEMP. (deg C)	1/T (K)	CO3	pCO3	O2	pO2	H	pH	DISSOLUTION RATE (mg/m2.day)	Log DR
U9MM50	30.0	3.09E-03	2.00E-03	2.70	2.00E-02	1.70	1.32E-09	8.9	12.301	1.090
U9MM50	50.0	3.09E-03	2.00E-03	2.70	2.00E-02	1.70	1.66E-09	8.8	7.959	0.901
U9MM50	50.0	3.09E-03	2.00E-03	2.70	2.00E-02	1.70	1.41E-09	8.9	10.362	1.015
U8HH25	25.0	3.35E-03	2.00E-02	1.70	2.00E-01	0.70	1.95E-09	8.7	2.421	0.384
U10HH75	75.0	2.87E-03	2.00E-02	1.70	2.00E-01	0.70	4.57E-11	10.3	77.377	1.889
U8LH75	75.0	2.87E-03	2.00E-04	3.70	2.00E-01	0.70	8.13E-10	9.1	10.876	1.036
U10LH25	25.0	3.35E-03	2.00E-04	3.70	2.00E-01	0.70	1.05E-09	9.0	2.554	0.407
U8HL25	25.0	3.35E-03	2.00E-02	1.70	2.00E-03	2.70	1.00E-08	8.0	0.216	-0.666
U10HL75	75.0	2.87E-03	2.00E-02	1.70	2.00E-03	2.70	1.51E-10	9.8	9.000	0.954
U8LL75	75.0	2.87E-03	2.00E-04	3.70	2.00E-03	2.70	2.24E-09	8.7	0.511	-0.292
U10LL25	26.1	3.34E-03	2.00E-04	3.70	2.00E-03	2.70	4.79E-10	9.3	0.233	-0.633
U8LM25	25.8	3.34E-03	2.00E-04	3.70	2.00E-02	1.70	1.78E-08	7.8	0.120	-0.922
U10LM75	75.0	2.87E-03	2.00E-04	3.70	2.00E-02	1.70	2.19E-10	9.7	9.210	0.964
U10HM25	25.8	3.34E-03	2.00E-02	1.70	2.00E-02	1.70	7.24E-11	10.1	1.871	0.272
U8HM75	75.0	2.87E-03	2.00E-02	1.70	2.00E-02	1.70	3.02E-09	8.5	5.113	0.709
U10HL50	50.0	3.09E-03	2.00E-02	1.70	2.00E-03	2.70	1.41E-10	9.9	4.599	0.663
U9HH25	25.0	3.35E-03	2.00E-02	1.70	2.00E-01	0.70	4.07E-10	9.4	6.719	0.827
U10MH25	25.0	3.35E-03	2.00E-03	2.70	2.00E-01	0.70	5.13E-10	9.3	9.343	0.970
U9ML25	26.1	3.34E-03	2.00E-03	2.70	2.00E-03	2.70	1.05E-09	9.0	1.515	0.180
U10LH75	75.0	2.87E-03	2.00E-04	3.70	2.00E-01	0.70	2.95E-10	9.5	6.480	0.812
U9MH75	75.0	2.87E-03	2.00E-03	2.70	2.00E-01	0.70	2.51E-10	9.6	23.262	1.367
U8HH75	75.0	2.87E-03	2.00E-02	1.70	2.00E-01	0.70	3.16E-09	8.5	93.763	1.972

Figure 1. Log DR vs Inverse Temperature

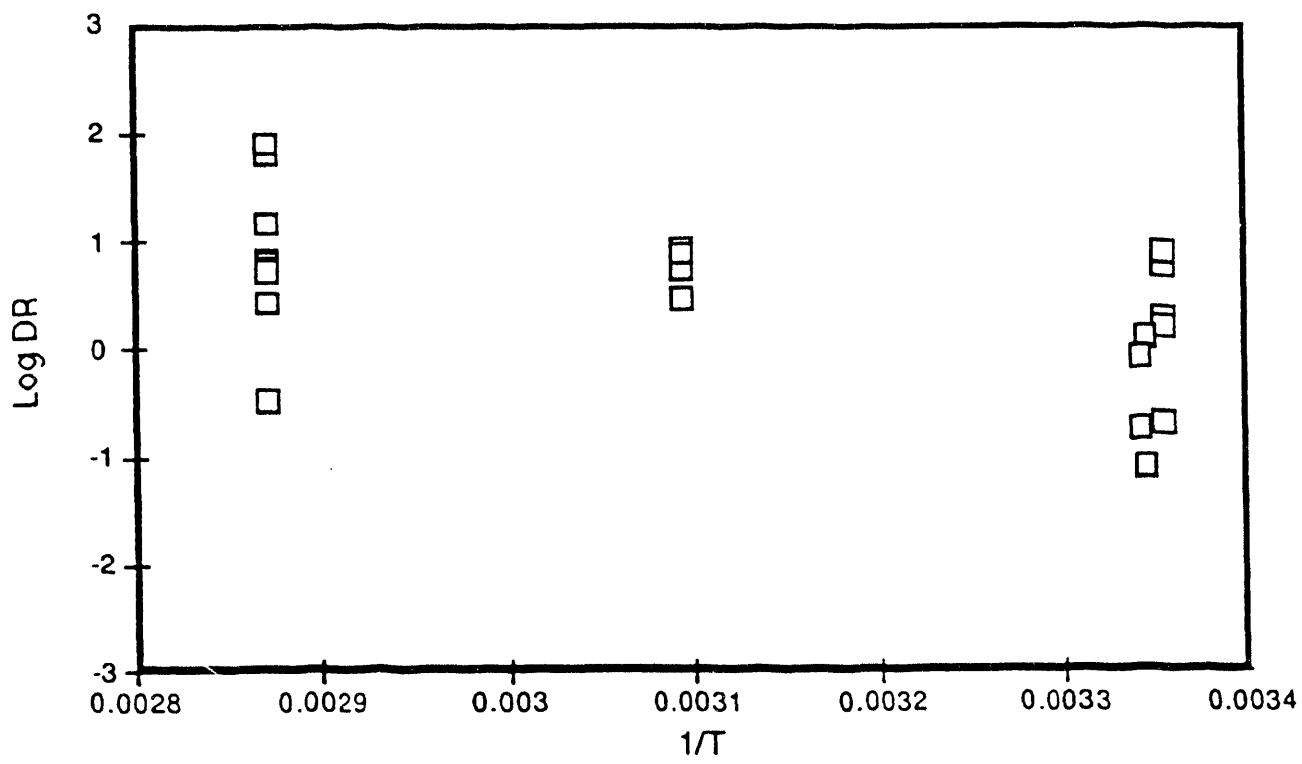


Figure 2. Log DR vs pO2

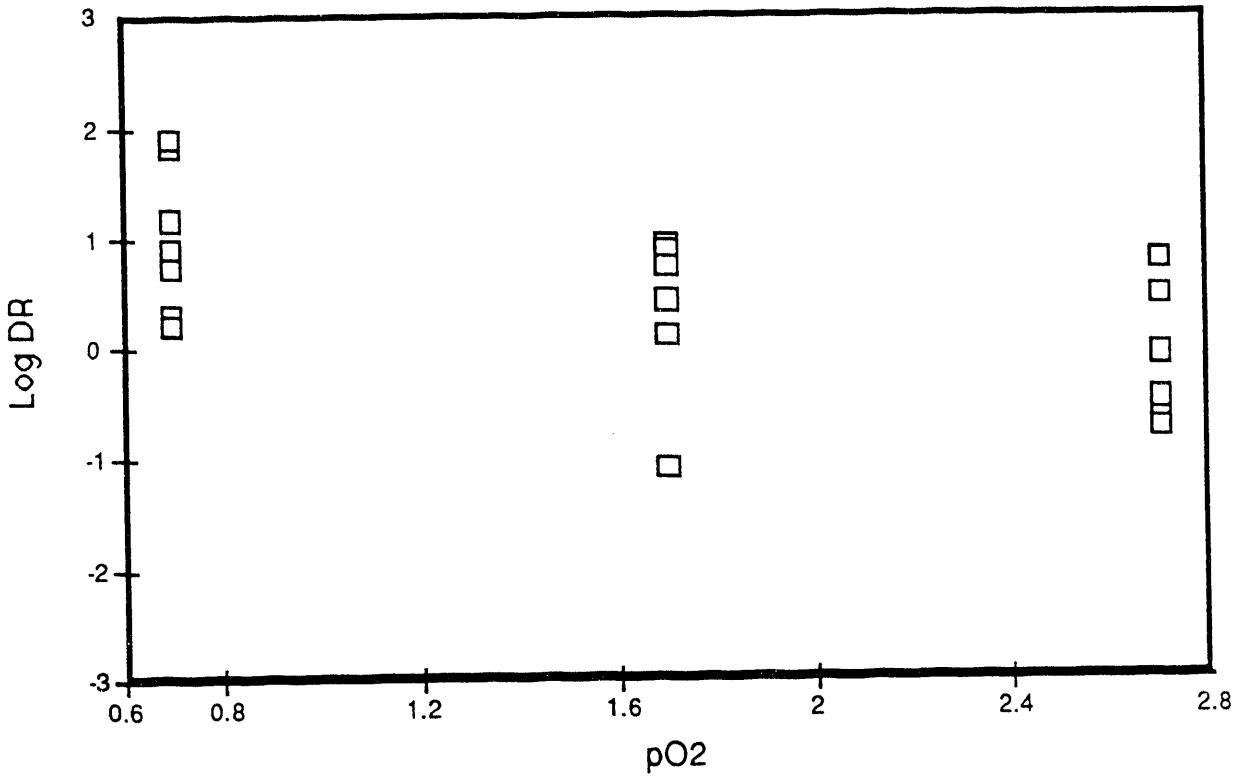


Figure 3. Log DR vs pCO3

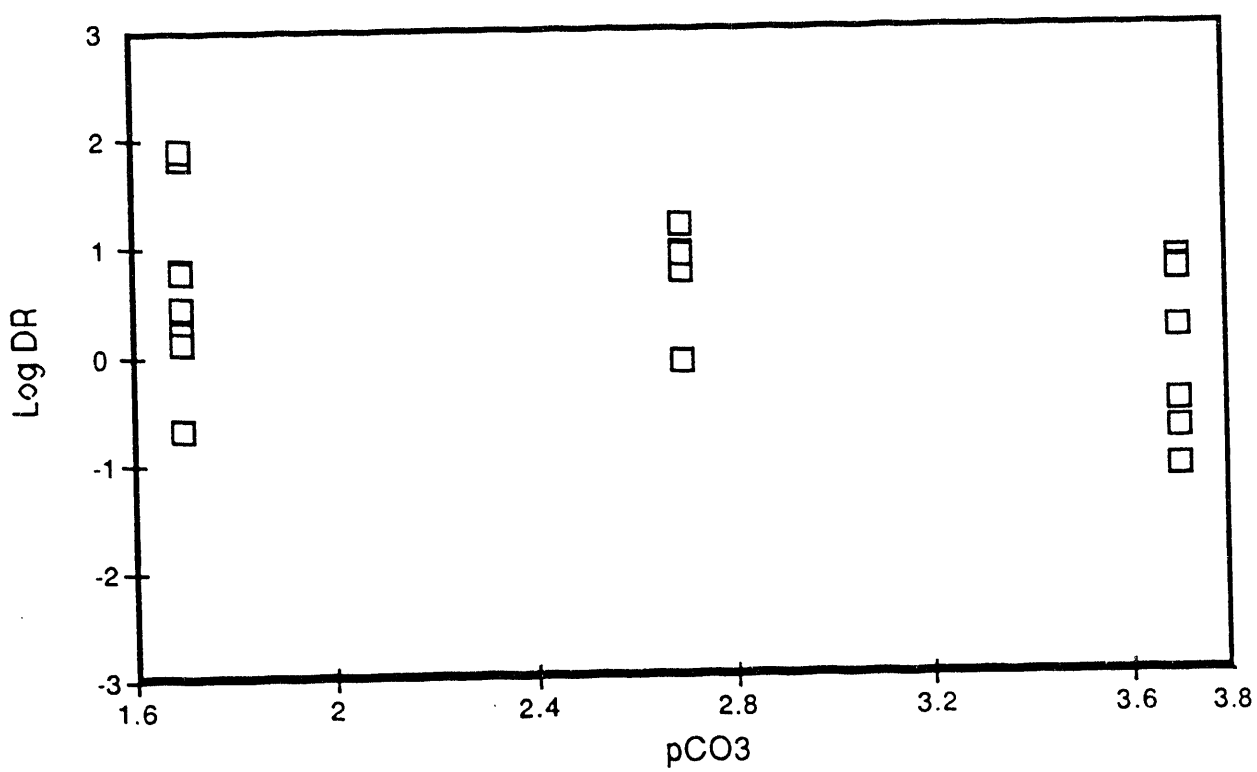


Figure 4. Log DR vs pH

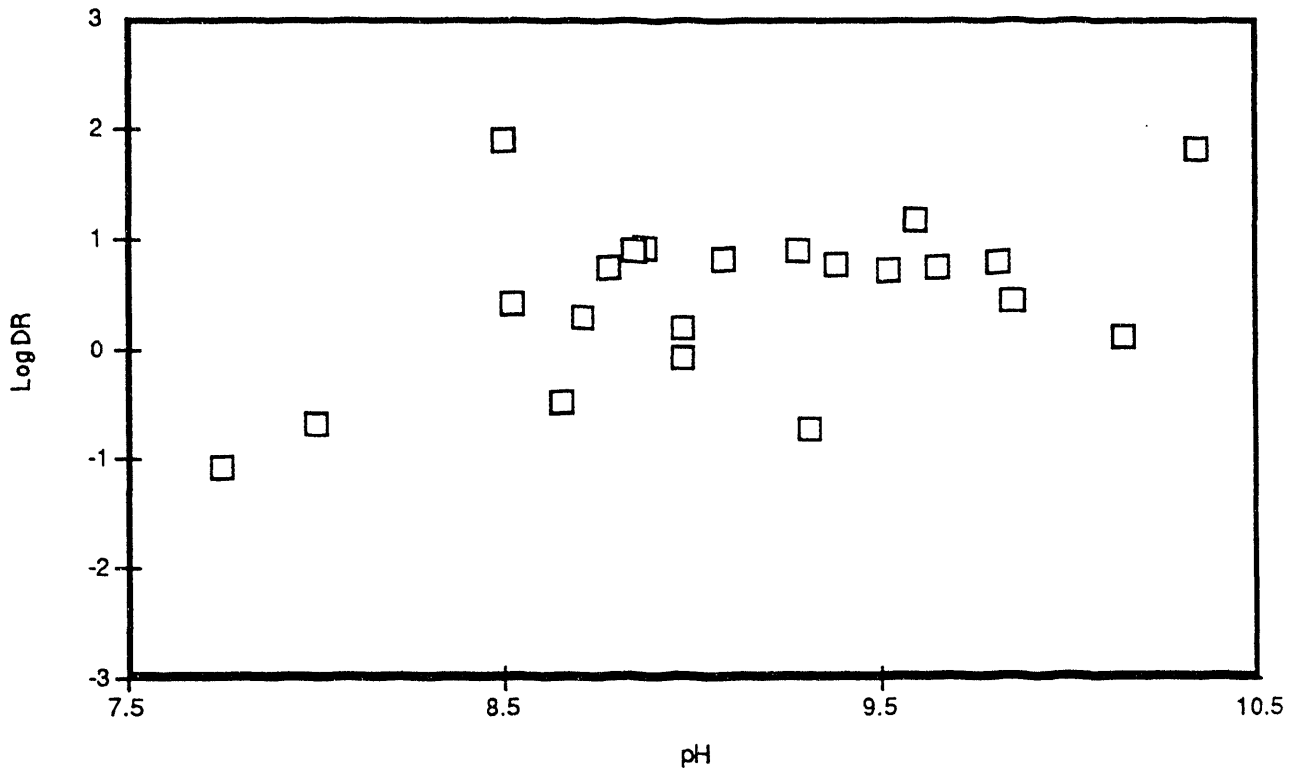
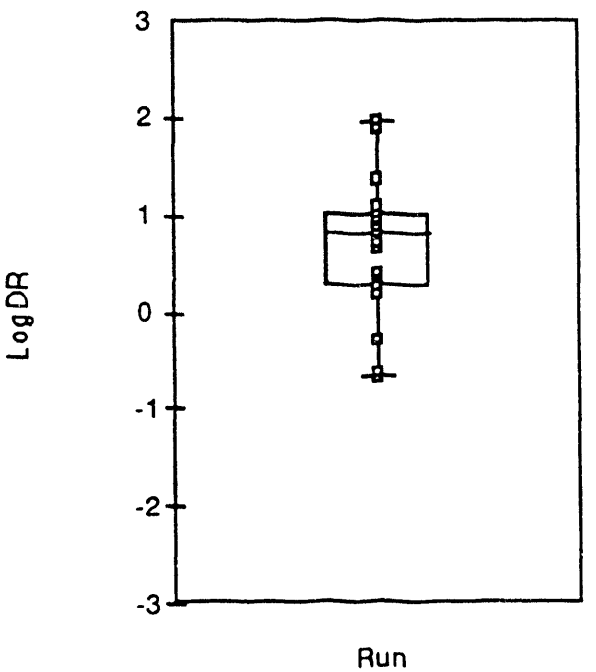


Figure 5. Dissolution Rate Distribution



A long-term study on samples of UO_2 powder from a common batch is being performed at Whiteshell Laboratories, Pinawa, Manitoba, Canada, Pacific Northwest Laboratories and at LLNL. Preliminary data exchanged between the three laboratories show room-temperature uranium dissolution rates between 1.4 and 4.1 $mg/m^2/day$ in a saline solution with 0.01 molar carbonate, 0.1 molar NaCl and at a pH of 8. A similar non-saline powder experiment at Livermore at 0.02 molar carbonate (U8HH-25) shows a dissolution rate of 2.25 $mg/m^2/day$, compared with 2.4 $mg/m^2/day$ under the same conditions in the UO_2 matrix discussed here. This is very good agreement between two different types of samples, different estimates of surface area and different techniques at three major laboratories.

Finally several approaches to dissolution modeling are being explored, including different model forms, as well as full and partial regressions that depend on some assumptions about the degree of variable dependency. There is no simple relationship between the thermodynamics and rates of chemical reactions. The classical observed chemical kinetic rate law for homogeneous reactions is one of the models being examined and takes the the following well-known general form [8]:

$$r = k[A]^a[B]^b[C]^c...T^t\exp(-E/RT),$$

where r is reaction rate, R is the gas constant, T is absolute temperature and A, B, C and additional letter variables represent concentrations (mol/L) of chemical species. This generalized form of the rate law is for homogeneous gas or liquid reaction systems. It does not take into consideration the possibly complex liquid-solid reaction at the UO_2 surface. Additional term(s) are needed to account for this element of the reaction, but are unknown at this time. The best regression fit of the current data to the classical rate law is:

$$DR(mg/m^2{\cdot}day) = 11.1{\cdot}[CO_3]^{0.27}[O_2]^{0.45}[H]^{-0.27}\exp(-7700/RT) \quad R^2=0.79.$$

The correlation coefficient of 0.79 indicates a significant lack of fit to this model, but fits to full fifteen-term empirical linear or logarithmic models are worse.

The inclusion of the additional T^t term outside the exponential term worsened the fit. As mentioned earlier, the log[CO_3] dissolution response is nonlinear. This is reflected in the carbonate portion of the multiple regression fit. Adding a nonlinear carbonate term improved the fit significantly, but cannot now be explained mechanistically.

Units of oxygen concentration [O_2] are atmospheres overpressure. The fits to either the pO_2 alone or within the full multivariate regression produce powers of 0.54 and 0.45 respectively, close to the half-power dependence on oxygen, explained by the simple dissociation reaction:

$$1/2O_2 = O$$

The activation energies obtained from the regression fit of logrithmic dissolution rate versus inverse absolute temperature (8750 cal/mol) and the full multivariate regression (7700 cal/mol) are similar. The activation energy of spent fuel under the same experimental conditions at 20% oxygen is 7100 cal/mol [9]. The development of other dissolution models may be required to obtain a mechanistic formulation.

A nearly identical dissolution study with spent fuel has been performed at Pacific Northwest Laboratories. The combined results of that study and the work discussed here will be reported in a future paper.

CONCLUSIONS

A statistical experimental design was used to plan a set of UO_2 dissolution experiments in order to examine systematically the effects of temperature (25-75°C), dissolved oxygen (0.002-0.2 atm overpressure), pH (8-10) and carbonate ($2\text{-}200\times10^{-4}$ molar) concentrations on aqueous UO_2

dissolution. The average dissolution rate was 4.3 mg/m^2/day. Plotted one-variable-at-a-time, the data have an Arrhenius type activation energy of 8750 cal/mol and a half-power (0.54) dependence on dissolved oxygen in the simulated groundwater. An activation energy from a multiregression fit to a classical chemical kinetic model is 7700 cal/mol. The oxygen dependence from that fit was again almost half-power at 0.45.

ACKNOWLEDGMENTS

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