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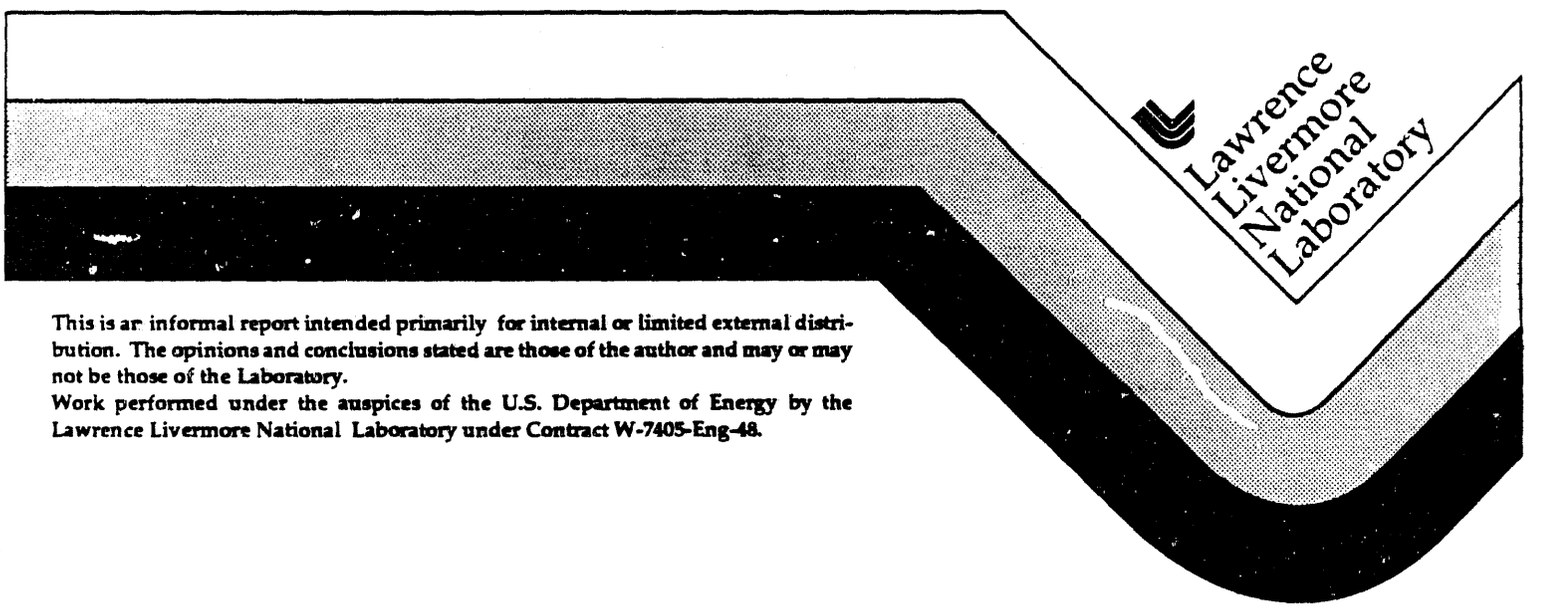

Prepared by Yucca Mountain Site Characterization Project (YMP) participants as part of the Civilian Radioactive Waste Management Program. The YMP is managed by the Yucca Mountain Site Characterization Project Office of the U.S. Department of Energy, Las Vegas, Nevada.

ESTIMATING THE TIME FOR DISSOLUTION OF SPENT FUEL EXPOSED TO UNLIMITED WATER

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ABSTRACT

The release of radionuclides from spent fuel cannot be precisely predicted at this point because a satisfactory dissolution model based on specific chemical processes is not yet available. However, preliminary results on the dissolution rate of UO_2 and spent fuel as a function of temperature and water composition have recently been reported. This information, together with data on fragment size distribution of spent fuel, are used to estimate the dissolution response of spent fuel in excess flowing water within the framework of a simple model. In this model, the reaction/dissolution front advances linearly with time and geometry is preserved. This also estimates the dissolution rate of the bulk of the fission products and higher actinides, which are uniformly distributed in the UO_2 matrix and are presumed to dissolve congruently.

We have used a fuel fragment distribution actually observed to calculate the time for total dissolution of spent fuel. A worst-case estimate was also made using the initial (maximum) rate of dissolution to predict the total dissolution time. The time for total dissolution of centimeter size particles is estimated to be 5.5×10^4 years at 25°C.

I. INTRODUCTION.

The Yucca Mountain Project of the U. S. Department of Energy is investigating the suitability of a site in the unsaturated zone at Yucca Mountain, NV, for a high-level nuclear waste repository.

Waste package analysts and designers have to understand the long term dissolution of waste form in groundwater to safely dispose of high level nuclear waste in an underground repository. The dissolution and transport processes in groundwater flow are generally considered to be the main route by which radionuclides could be released to the biosphere from a geological repository.

Many researchers have investigated the dissolution of UO_2, spent fuel and uraninite (a naturally occurring UO_2 mineral) in aqueous solutions, under either reducing or oxidizing conditions, and as a function of various other environmental variables. Experimental data on the dissolution rates of UO_2, spent fuel and uraninite have been reviewed by Amell and Langmuir,[1] Parks and Pohl,[2] Bruno et al,[3] and most recently by Grambow.[4]

Important variables considered in the many investigations were pH, temperature, oxygen fugacity, carbonate/bicarbonate concentrations and other reacting media. The dissolution data are very scattered, and vary as much as 6 orders of magnitude.[4] The dependence of the dissolution rates of UO_2, spent fuel and uraninite on these variables is not clear because of uncertainties regarding redox chemistry of uranium in solutions and in solid phases, secondary-phase formation, and surface area measurement. In addition, the previous studies were conducted under experimental conditions which were either inadequately controlled or which simulated complex repositorial conditions. The results of such studies are difficult to interpret. Several of these researchers have developed equations to correlate dissolution rates as a function of relevant variables.[5-8] However, none of the rate laws is universal, and inconsistencies or incompatibilities among the proposed laws are common.

Data indicate that UO_2 is easily oxidized to U_4O_9 and U_3O_7 in an air[9,10] and can be further oxidized to either U_3O_8[9,10,11] or schoepite, $UO_3 \cdot 2H_2O$.[12] The UO_2 surface oxidation may lead to higher leach rates because of possibly higher dissolution rates of U_3O_7, U_3O_8 or schoepite relative to that of UO_2[4] and because of the increase of surface area of the fuels due to surface cracking.

Discussion.

We are estimating a source term for liberation of radionuclides from spent fuel dissolving under conditions of temperature and water composition related to those anticipated for a potential repository at Yucca Mountain. This is done in the same spirit as estimates that have been made for repositories in Germany[13] and Sweden.[14] It is implicit in the following treatment that fission products are dissolved congruently with the UO_2 fuel matrix, except for those volatile species that have partially vaporized and that fraction that has migrated to near-surface grain boundaries and are possibly dissolved independent of the matrix dissolution. Most fission products and higher actinides are distributed throughout the UO_2 matrix, however.

Recent measurements on UO_2[15] and spent fuel (SF)[16] under comparable conditions have provided dissolution rates for UO_2 between 25°C and 85°C in waters of various composition and for SF in deionized water (DIW) at 25°C. These experiments were done in contact with air. The results are shown in figures 1 and 2. The rate of dissolution of SF in DIW at 25°C is 1.2-1.7 x 10^{-12} g cm^{-2} sec^{-1}. This is similar to the rate for UO_2 in DIW at 25°C at ~5 x 10^{-12} g cm^{-2} sec^{-1}. Given the great variability in other reported values[4] this is reasonable agreement. In fact, the observed dissolution rate for SF at 25°C is about the same as that of UO_2 in (DIW + Ca + Si), a simulation of ground water.[15]

A model for dissolution is used in which the dissolution front propagates linearly in time, much like a recently published model for the advance of the oxidation front during oxidation of UO_2 and spent fuel.[15-19] This implies that the particle geometry is retained. We can describe the change in characteristic dimension of a SF particle (a sort of "radius"), X as follows:

$$X(t) = X_o - \left(\frac{Q}{\rho}\right) t \quad , \qquad (1)$$

where
- $X(t)$ = the characteristic dimension as a function of time
- X_o = the original dimension (half of the actual size)
- t = time
- Q = dissolution rate per unit area
- ρ = density

The time for complete dissolution of a particle of original size X_o is then

$$t_\infty = \frac{X_o \rho}{Q} \qquad (2)$$

This dissolution time is proportional to size, of course, and for an ensemble of particles of different sizes, t_∞ for the ensemble is that for the largest particle.

Some data are available on the size distribution of spent fuel fragments.[20] These data are given for two different fuels but the distributions are quite similar. The aggregate of these two sets of data can be adequately described by the simplified distribution shown in Table I.

Table I

Approximate Size (cm) ($2X_o$)	Weight (Volume) Fraction
0.15	.02
0.25	.14
0.35	.29
0.50	.38
0.70	.17

Using the relationship of equation (1), we can calculate the time to dissolve a given weight (volume) fraction of an amount of SF as a function of time. For generality, we treat time as the dimensionless quantity t/t_∞, with t_∞ defined above. This is shown in figure 3 for the size distribution given in Table I*, and also for a single size with $X_o = 0.35$ cm. Here V_o and V(t) are the original volume of a particle and its volume at arbitrary time, respectively. The volume is proportional to the characteristic dimension

$$V_o = k X_o^3 \text{ and } V(t) = k X^3(t)$$

where k is a constant depending on shape. Since geometry is retained, as noted above,

*Each size was calculated separately and the time responses were added together.

$$\frac{V(t)}{V_o} = \left(\frac{X(t)}{X_o}\right)^3 = 1 - 3\left(\frac{Q}{X_o\rho}\right)t + 3\left(\frac{Q}{X_o\rho}\right)^2 t^2 - \left(\frac{Q}{X_o\rho}\right)^3 t^3, \qquad (3)$$

and the dissolution rate is $-\dfrac{d\left(\frac{V(t)}{V_o}\right)}{dt}$

Initially, i.e., $t \rightarrow 0$

$$\text{Rate } (t=0) = 3\left(\frac{Q}{X_o\rho}\right)$$

and the extrapolated time for total dissolution is

$$t_\infty^* = \frac{X_o\rho}{3Q} \qquad (4)$$

In figure 4 we show that the rate of dissolution relative to the initial rate varies with time for both the system with $X_o = 0.35$ cm and for the distribution of Table I.

The measured dissolution rates for UO_2[15] and spent fuel[16] allow us to calculate actual times for dissolution. As is evident from figure 3, the overall dissolution rate is greatest at early time and approaches zero as t_∞ is approached; therefore, as a conservative approximation, we have also calculated the total dissolution time extrapolated from the initial rate, t_∞^*. These times calculated for the size distribution in Table I are given in Table II. The actual dissolution rates used are derived from the bottom curve in figure 1. We chose this curve as most representative of the expected ground water. The rate equation used is

$$Q(t)\ (\text{g cm}^{-2}\ \text{sec}^{-1}) = 6.43 \times 10^{-9} \exp -\left(\frac{4740}{RT(K)}\right) \quad (\text{R is in cal/mole K}) \qquad (5)$$

Table II

Temperature (°C)	Dissolution Time (years)	
	t_∞^*	t_∞
25	8.0×10^3	5.5×10^4
85	2.2×10^3	1.5×10^4

Conclusions

These times are calculated for the case of bare fuel immersed in unlimited quantities of flowing water at flow rates sufficient to prevent any species from forming a saturated solution. Nonetheless, this estimate provides a "core" value on which to apply "credits" corresponding to features of realistic repository performance such as frequency of cladding and container failure, actual amounts of ground water and various transport rates, etc. Of course this "core" estimate is based on only one particular dissolution rate, as is discussed above. Future measurements of dissolution rate may change this value considerably. The estimates presented here ignore the possibility that grain boundary dissolution behaves differently than bulk SF dissolution.

Dissolution tests are now under way that are designed to define the mechanism of the dissolution process of UO_2 and SF in terms of oxidizing potential, temperature, pH and other water composition variables generally appropriate to a potential repository at Yucca Mountain. When these tests are completed, considerably more realistic estimates will be possible. These tests will also clarify the contribution of radionuclides from grain boundaries to the total dissolution rate.(16)

Figure Captions

1. Arrhenius plots of the dissolution rate of UO_2 in waters of various composition.[15]

2. The approach to steady-state of the dissolution rate of two spent fuel samples.[1] Experiments were done at 25°C using deionized water (DIW).

3. Calculation of the fractional dissolution in terms of dimensionless time, according to equation (3). Monodisperse refers to a single particle size.

4. Evolution of the normalized dissolution rate with time as the particle size decreases, according to equation (3).

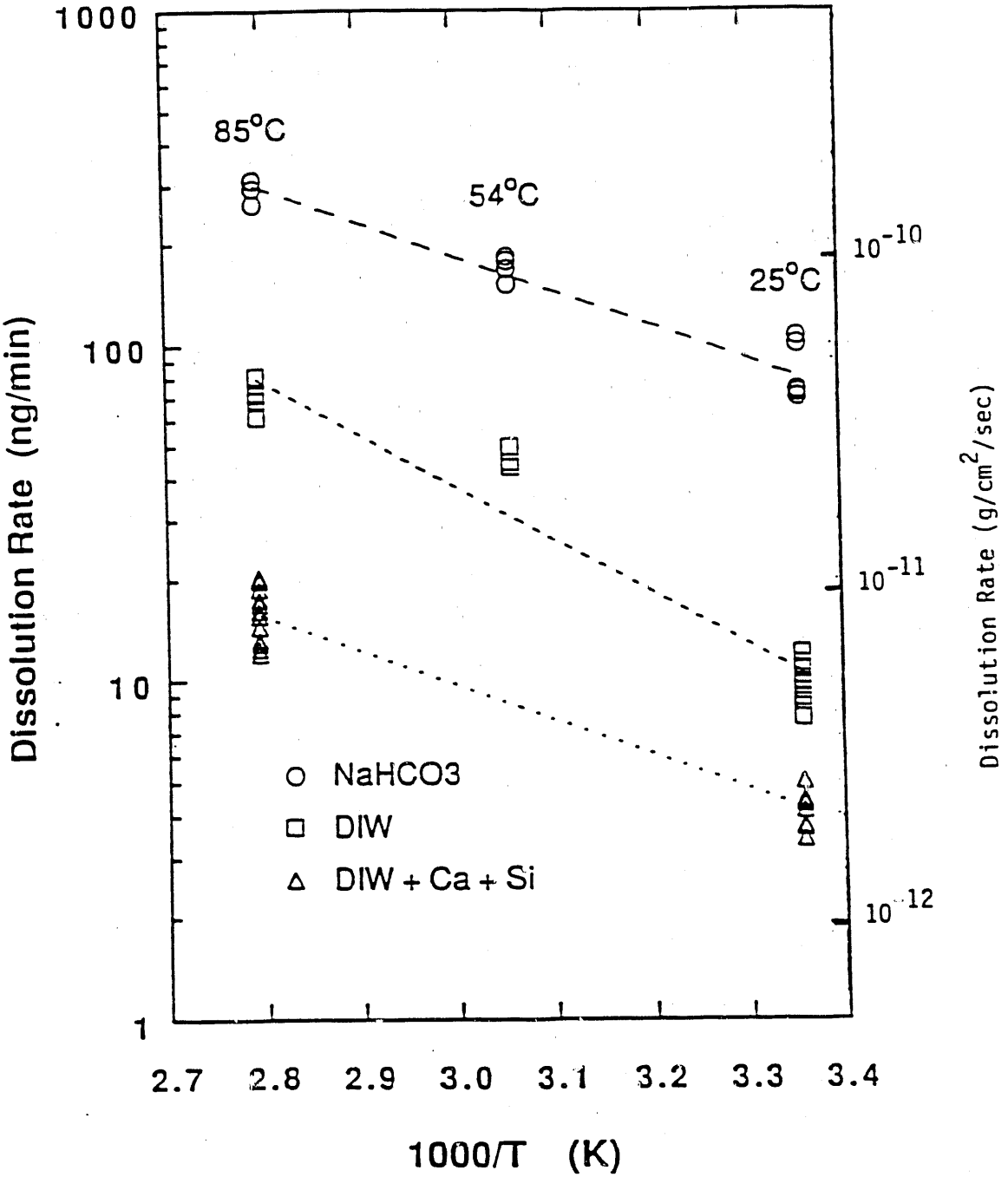

Figure 1. (from W. Gray and C. Wilson, ref. 15)

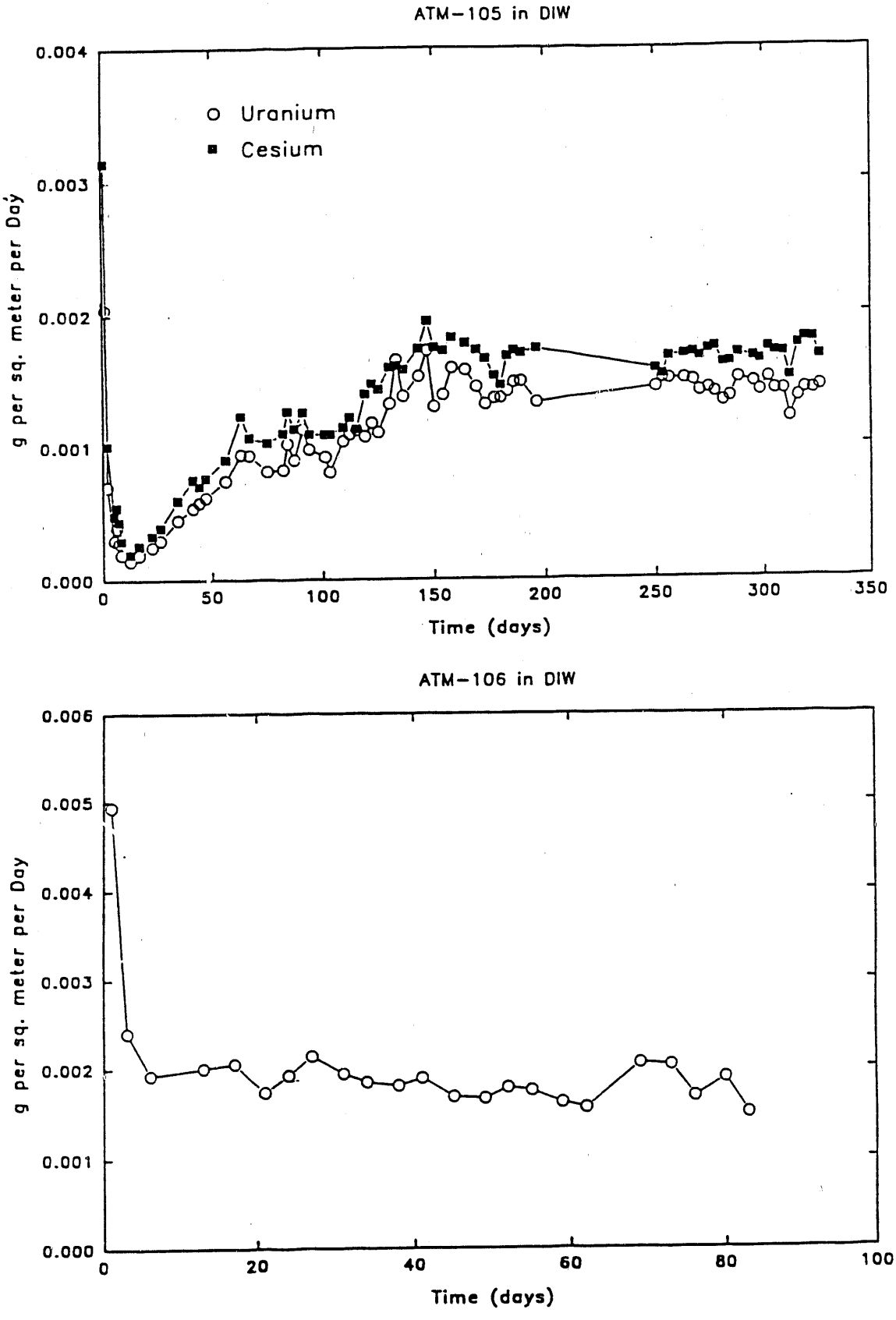

Figure 2. (from W. Gray and S. Strachan, ref. 16)

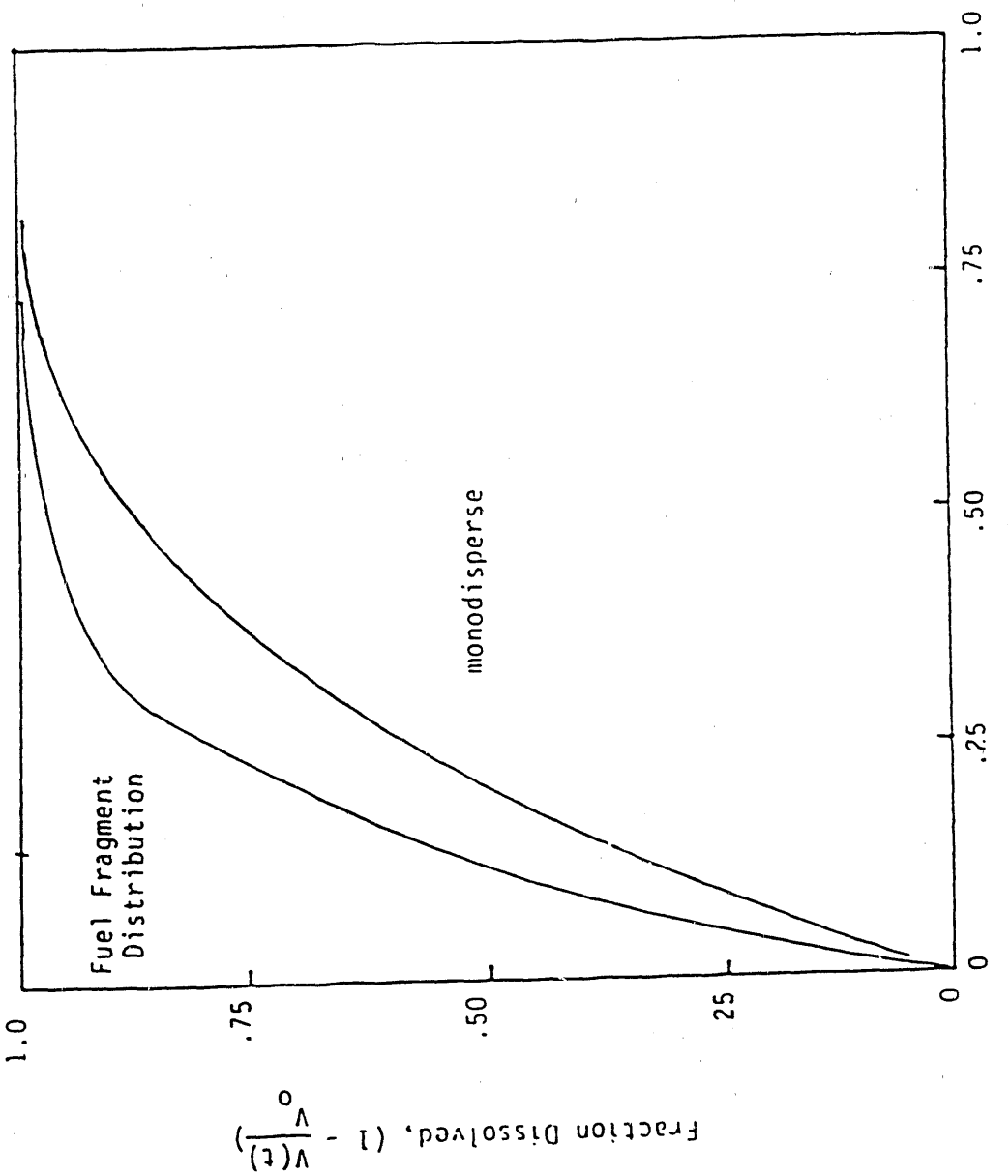
Fraction Dissolved, $(1 - \frac{V(t)}{V_o})$
1.0
.75
.50
25
0
0
.25
.50
.75
1.0
time, t/t_∞
monodisperse
Fuel Fragment Distribution

Figure 3

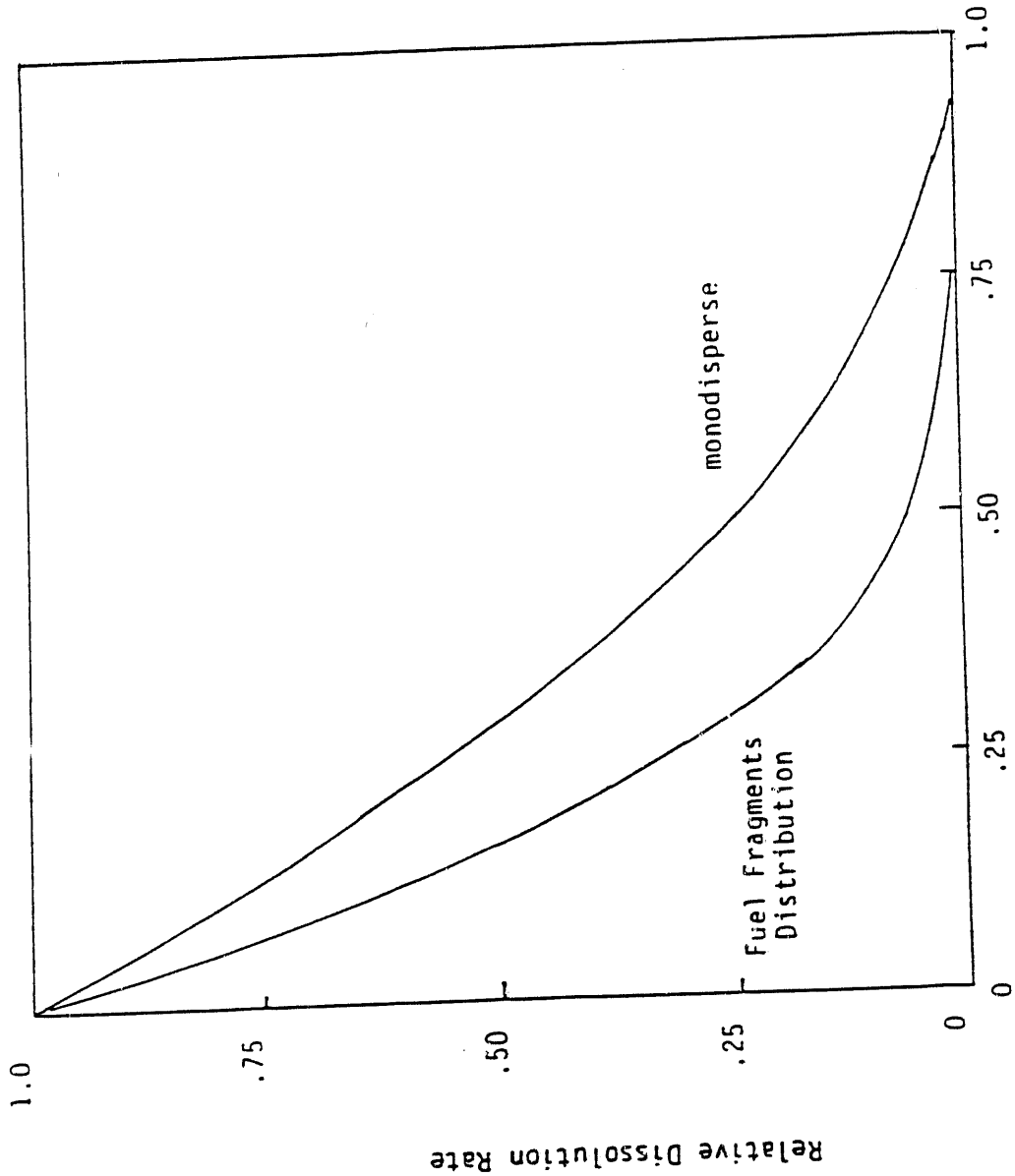
Relative Dissolution Rate
1.0
.75
.50
.25
0
0
.25
.50
.75
1.0
time, t/t_∞
monodisperse
Fuel Fragments
Distribution

Figure 4

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