Spent Nuclear Fuel
Intrinsic Dissolution Model
Overview

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Workshop on Significant Issues and Available Data
Waste Form Degradation and Radionuclide Mobilization
Expert Elicitation Project

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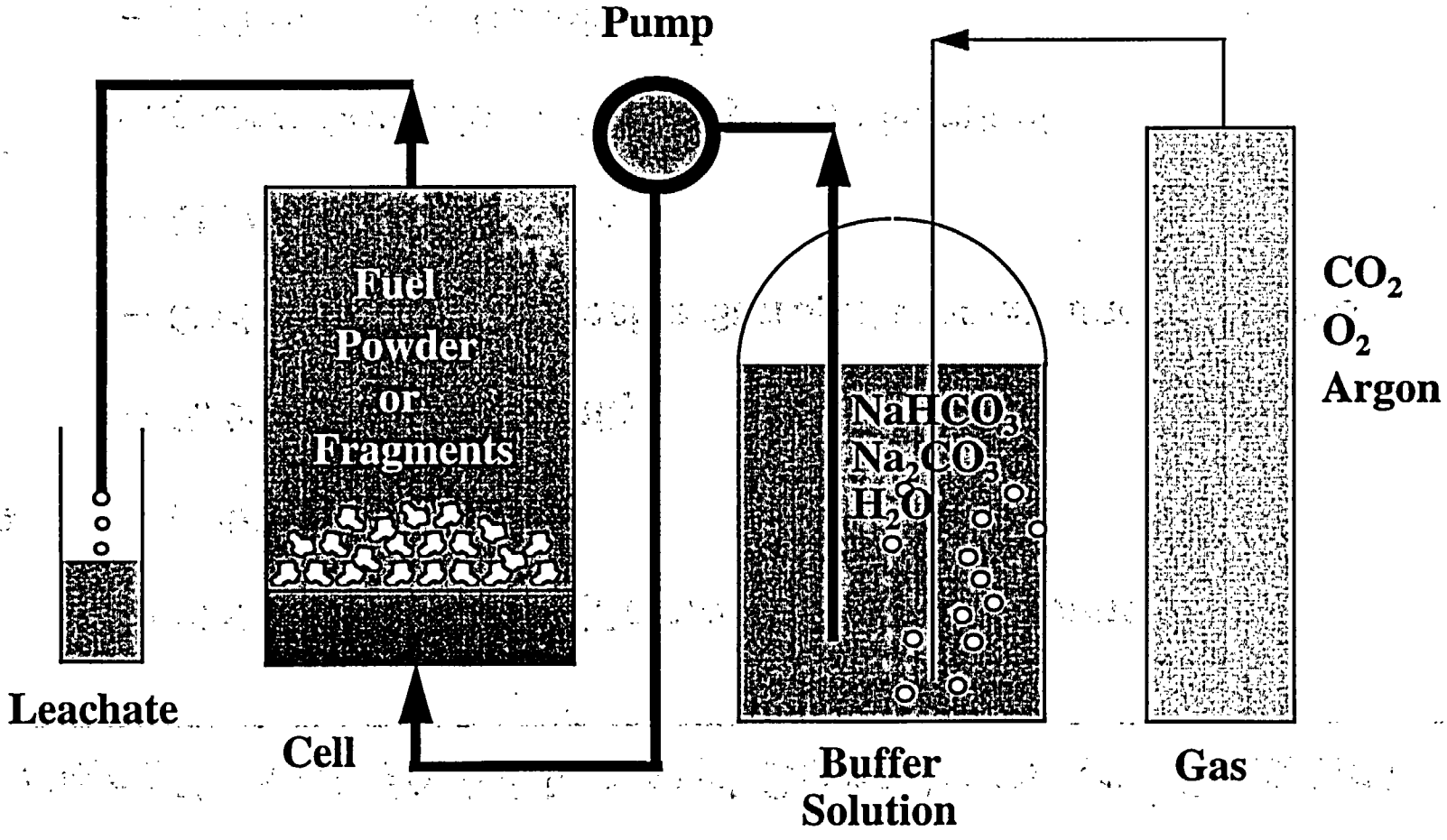
Legacy-20

Activity Purpose is Measurement of Spent Fuel Intrinsic Dissolution Rate in Aggressive Groundwater

- Quantify Effect of Groundwater Contacting Spent Fuel
  - Develop Data Set for Analysis and Modeling
- Develop a Bounding Intrinsic Dissolution Model
- Model Should Be Reliably Extrapolated
- Since Fuel Matrix is UO_2, Dissolution Differences Should be Due to Burnup Factors, e.g. Concentrations of Radionuclides in Spent Fuel
- Unirradiated UO_2 is Surrogate for Spent Fuel and Test of "Zero Burnup"

Measure Intrinsic Dissolution of UO_2 and Spent Fuel Using Flow-through Method



Selection of Variables and Conditions for Data Set

- Simulate Environment (Referenced to J-13 Groundwater)
  - Oxidizing
  - Groundwater Alkalinity
  - Carbonate as Aggressive Surrogate for Groundwater Ions
  - Elevated Temperature
- Long-term Conditions May Vary From Nominal
  - Pick Plausible Conditions
  - Wide-Range of Conditions
  - Be Aggressive for Conservatism

Aqueous Chemistry Based on J-13 Well Water Analysis

Table 2.1.3.5-2. J-13 Well Water Analysis

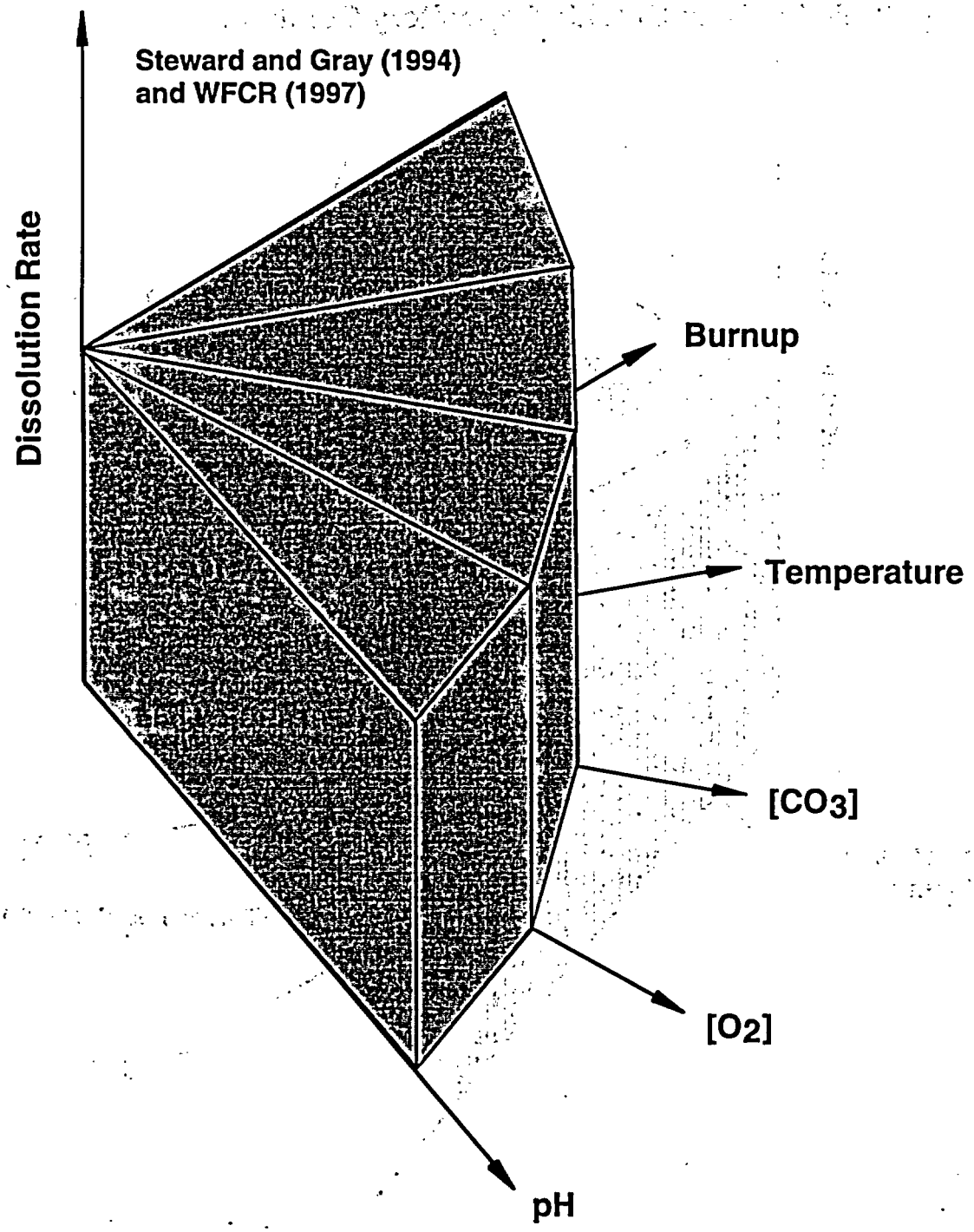
Component	Concentration (μg/ml)	Component	Concentration (μg/ml)
Li	0.042	Si	27.0
Na	43.9	F	2.2
K	5.11	Cl	6.9
Ca	12.5	NO_3	9.6
Mg	1.92	SO_4	18.7
Sr	0.035	HCO_3	125.3
Al	0.012		
Fe	0.006	pH	7.6

Selection of Experiments

- Bracket Conditions
  - Oxygen: 80 ppb to 8 ppm (0.2% to 20% gas phase)
  - pH: 8 to 10
  - Carbonate: 0.2 to 20 mmol/L
  - Temperature: 25 C to 75 C

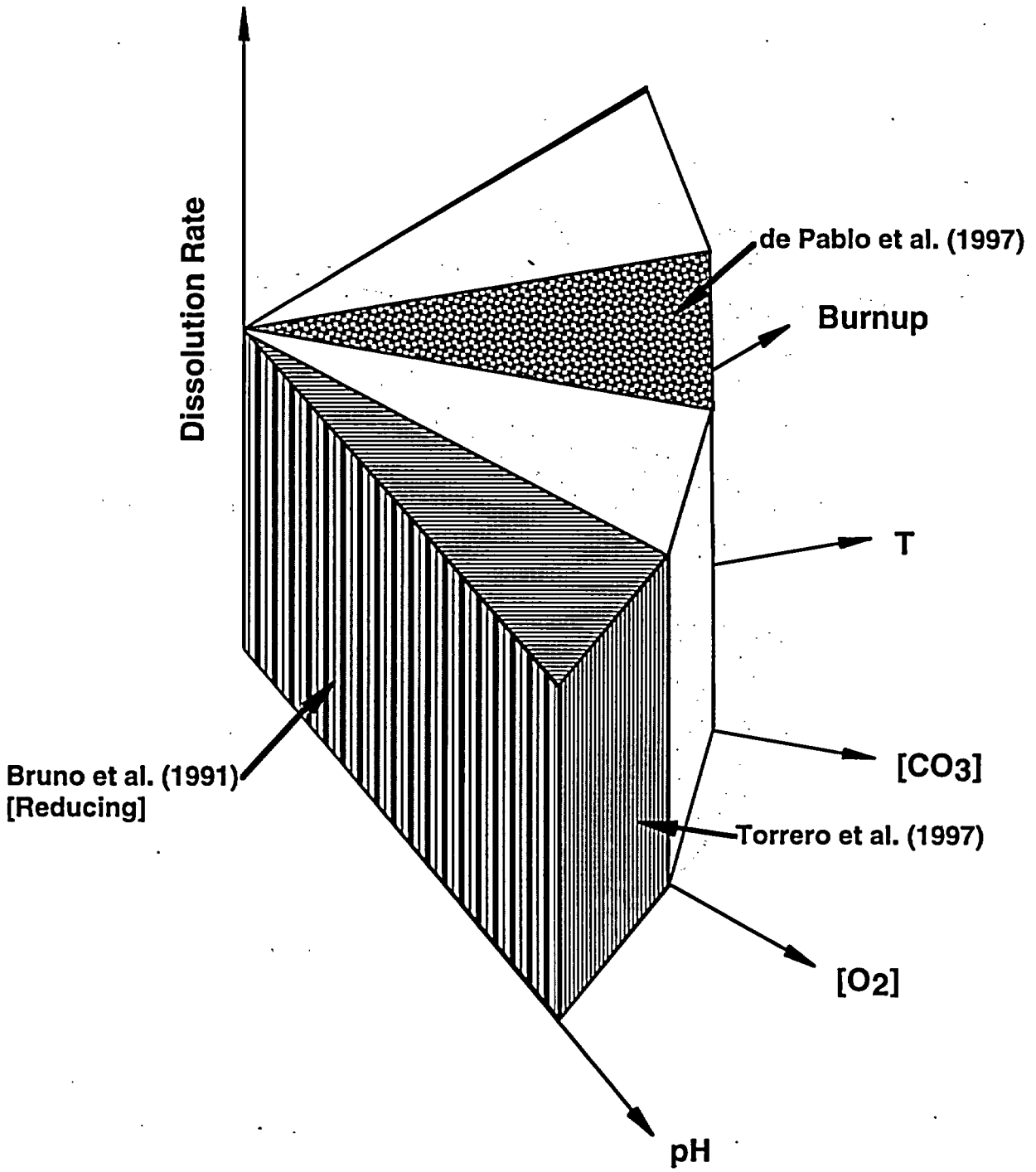
YMP Spent Fuel Dissolution Data Examine Five Variables Simultaneously

- Coupling of All Five Variables Studied



Two Other Published Data Sets Measure Only Two Variables at a Time on UO_2

- The Two Other Published Data Sets Cover Only Patterned Areas
- Some Reports Examined Only One Variable (e.g. pH at 25°C)
- Other Available Data Outside Repository Conditions



Statistical Experimental Design (DOE) Allows for Robust Multivariate Modeling

- Minimizes Experiments Needed to Fit Model Type
- More than One Variable Changes at a Time
- Picks Variable Settings that are Uniformly Distributed in the 'Experimental Space'
- Provides Regressible Dataset for Modeling
- Experimental Conditions are Independent
  - Assures Best Fits and Statistics
  - No Confounding
    - » Confusion of Variable Effects (e.g. carbonate)

19 Experiments Allowed for Full Second Order Model in All Variables

- Same Test Matrix Used for UO_2 (LLNL) and Spent Fuel (PNL) Studies
- SF Grains and Large Polycrystalline UO_2 Samples Used
- Replicates at Mid-Values Checked on Reproducibility
- Designs can add to Previous Designs or Data

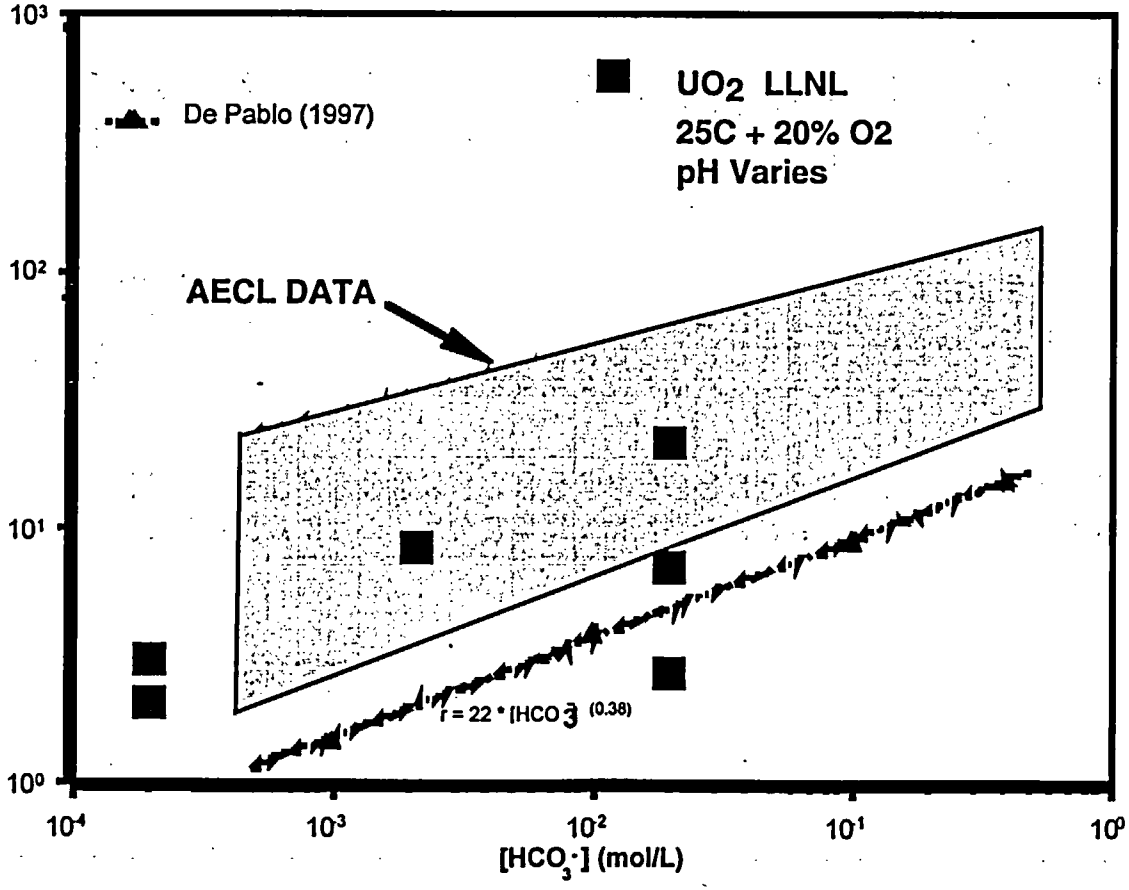
Current 49 Run Dissolution Data Set Has 25 SF Runs and 24 UO_2 Runs

BURNUP (MWd/kgU)	TEMP °C	CO3 (mol/L)	O2 (atm)	PH	Diss. Rate ($mg/m^2/d$)
0	25.00	0.019953	0.001995	8.00	0.215797
0	26.10	0.000200	0.001995	10.00	0.232558
0	26.10	0.001995	0.001995	9.00	1.515152
0	50.00	0.019953	0.001995	10.00	4.599407
0	75.00	0.019953	0.001995	10.00	5.610000
0	75.00	0.000200	0.001995	8.00	0.510915
0	25.80	0.000200	0.019953	8.00	0.119689
0	25.80	0.019953	0.019953	10.00	1.871345
0	50.00	0.001995	0.019953	9.00	12.300717
0	50.00	0.001995	0.019953	9.00	7.959093
0	50.00	0.001995	0.019953	9.00	10.361842
0	75.00	0.000200	0.019953	10.00	9.210299
0	75.00	0.019953	0.019953	8.00	5.113193
0	25.00	0.019953	0.199526	8.00	2.421000
0	25.00	0.000200	0.199526	10.00	2.554155
0	25.00	0.019953	0.199526	9.00	6.719085
0	25.00	0.001995	0.199526	10.00	9.342891
0	75.00	0.019953	0.199526	10.00	77.376698
0	75.00	0.000200	0.199526	8.00	10.876331
0	75.00	0.000200	0.199526	10.00	6.480447
0	75.00	0.001995	0.199526	9.00	23.262205
0	75.00	0.019953	0.199526	8.00	54.000000
30	19.00	0.000200	0.001995	10.00	0.507000
30	21.00	0.001995	0.001995	9.00	1.870000
30	23.00	0.019953	0.001995	8.00	2.830000
30	50.00	0.019953	0.001995	10.00	1.040000
30	74.00	0.019953	0.001995	10.00	0.693000
30	78.00	0.000200	0.001995	8.00	1.980000
30	25.00	0.019953	0.019953	10.00	2.050000
30	27.00	0.000200	0.019953	8.00	1.790000
30	74.00	0.019953	0.019953	10.00	4.750000
30	77.00	0.019953	0.019953	8.00	2.890000
30	78.00	0.000200	0.019953	10.00	1.490000
30	21.00	0.000200	0.199526	10.00	0.629000
30	22.00	0.019953	0.199526	8.00	3.450000
30	22.00	0.019953	0.199526	9.00	2.830000
30	22.00	0.001995	0.199526	10.00	2.040000
30	50.00	0.001995	0.199526	9.00	6.340000
30	50.00	0.001995	0.199526	9.00	7.050000
30	50.00	0.001995	0.199526	9.00	5.070000
30	74.00	0.019953	0.199526	10.00	14.200000
30	74.00	0.000200	0.199526	8.00	8.600000
31	25.00	0.020000	0.200000	8.00	3.100000
31	25.00	0.000200	0.200000	8.00	2.400000
31	50.00	0.002000	0.200000	9.00	7.000000
31	75.00	0.020000	0.200000	8.00	6.900000
31	75.00	0.000200	0.200000	8.00	9.700000
44	25.00	0.000200	0.200000	8.00	3.000000
50	22.00	0.020000	0.200000	8.00	1.500000

YMP/LLNL Multivariate UO_2 Dissolution Results Similar to Existing Carbonate Studies

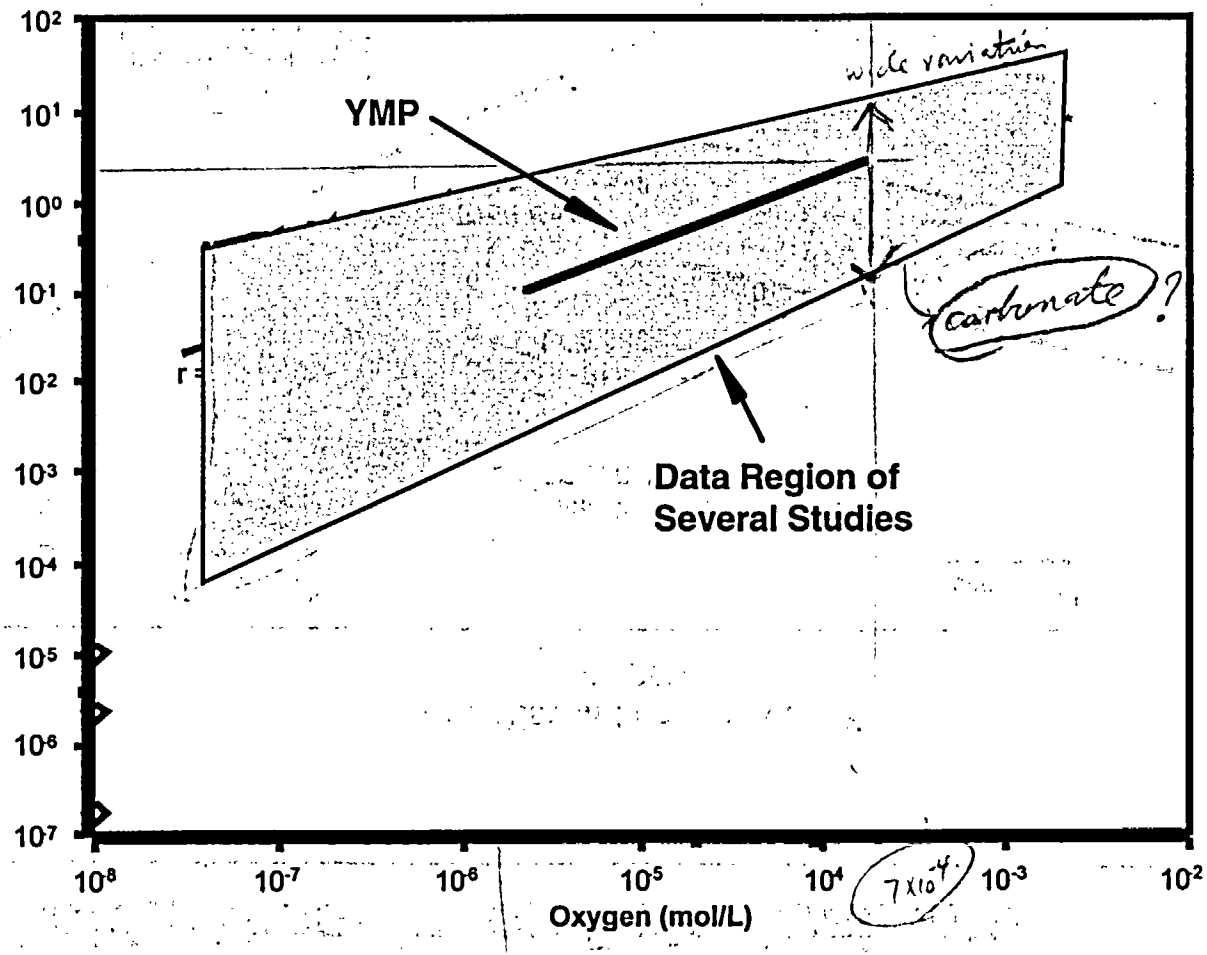
- pH Varies for YMP/LLNL Data Points

DRAFT

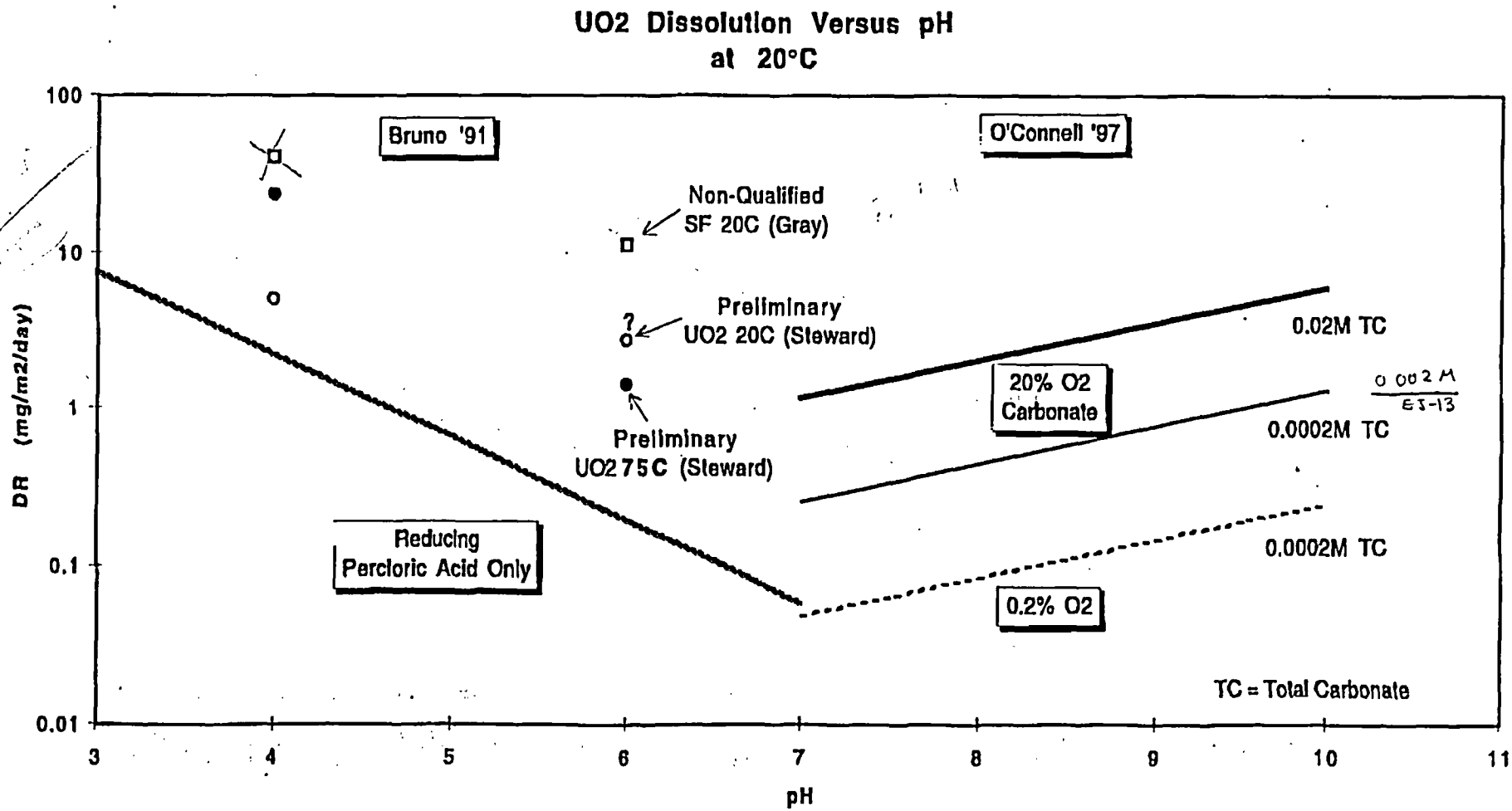


Data courtesy John Tait (AECL)

YMP/LLNL Multivariate UO_2 Dissolution Results Similar to Existing Oxygen Studies



Some Acidic Dissolution Data Available



25 Dissolution Experiments Performed on $UO_3 \cdot H_2O$ and U_3O_8

- Unirradiated $UO_3 \cdot H_2O$ and U_3O_8 Are Surrogates for Oxidized Spent Fuel
- 16 Experiments Required for Full Nonlinear Model in All Variables
- 9 Additional Runs Formed Complete Set of Hi/Lo Temperature Pairs
- Variable Ranges Same As UO_2
  - Temperature 25 to 75 °C
  - Carbonate 0.0002 to 0.02 Molar
  - pH 8 to 10

Dissolution Rates Increase in Higher Oxides and at Higher Carbonate and Temperature Levels

Comparison of Dissolution Rates at Boundary Conditions

pH	Carbonate (mol/L)	Oxygen (atm)	Temp °C	Spent Fuel* ATM-103	Dissolution Rate (mgU/m^2·day) UO_2	U_3O_8	$UO_3 \cdot H_2O$
8	0.0002	0.2	25		3.9	~5	~100
8	0.0002	0.2	50		5.4		
8	0.0002	0.2	75	8.6	11	~6	>200
8	0.02	0.2	25	3.5	2.4	19	~700
8	0.02	0.2	50		38		
8	0.02	0.2	75		54	~150	>1500
10	0.0002	0.2	25	0.63	2.5	0.8	>100
10	0.0002	0.2	50		3.1		
10	0.0002	0.2	75		6.5	~3	>150
10	0.02	0.2	25		20	21	~200
10	0.02	0.2	50		26		
10	0.02	0.2	75	14	77	~200	>1000

* From Walt Gray (PNNL)

Different Modeling Approaches Investigated

- Classical Chemical Kinetic Rate Law First Used
- Non-Equilibrium Thermodynamics Foundation of Later Formulations
  - Based on Energetics Across Solid-Liquid Surface
  - Onsager Form Works Near Equilibrium
  - Butler-Volmer Form Applies Under All Conditions--Intrinsic Dissolution is Far From Equilibrium

Classical Chemical Kinetic Rate Law

$$R = [A]^{\alpha}[B]^{\beta}[C]^{\gamma}[D]^{\delta}....e^{-\frac{E_a}{RT}}$$

Simple Form

$$R = \frac{\sum_j a_j \prod_{i,j} [X_i]^{\gamma_{ij}}}{\sum_m b_m \prod_{i,m} [X_i]^{\gamma_{im}}}$$

General Form

*Stumm and Morgan
"Aquatic Chemistry"

UO_2 and Spent Fuel Rates Have Different Oxygen Dependencies

- UO_2 Data Exhibited About Half-Order Oxygen Dependency at All Conditions
  - O_2 -> 2O or $1/2 \cdot O_2$ -> O
    - » Possibly Surface Oxygen Decomposition or Redox Coupling
- At 25°C Spent Fuel Rate was Almost Independent of Oxygen Concentration
- At 75°C Spent Fuel Reaction Orders Between 0.35 and 0.73 Observed

Only Spent Fuel Data Show Strong Temperature and Oxygen Interaction

- Classical Chemical Kinetic Rate Law:
  - Rate = $k[A]^a[B]^b[C]^c[D]^d... \exp(E_a/RT)$
- UO_2: $\log(D)\{mg/(m^2/day)\} = 4.824+0.275\log_{10}[CO_3]+ 0.448\log_{10}[O_2]-0.27\log_{10}[H]-1685/T$ $r^2=0.79$
- SF: $\log(D)\{mg/(m^2/day)\} = 9.234+0.142\log_{10}[CO_3]- 16.73\log_{10}[O_2]-0.140\log_{10}[H]-2133/T+ \boxed{6.81\log_{10}(T)\log_{10}[O_2]}$ $r^2=0.85$
- **Oxygen <--->Temperature Coupling May Be Radiolysis**

Regression Fits of 20% Oxygen Results Similar

- UO_2: $\log(D)\{mg/(m^2/day)\} = 4.650+0.274\log_{10}[CO_3] - 0.187\log_{10}[H]-1500/T$

  $r^2=0.79$

- SF: $\log(D)\{mg/(m^2/day)\} = 7.202+0.226\log_{10}[CO_3] - 0.091\log_{10}[H]-1628/T$

  $r^2=0.95$

- Without Oxygen Dependence Results are Similar

Onsager Form of Rate Equations for Regression

$$R = \left\{ A4 \cdot e^{\frac{A5}{T}} \right\} \cdot \left\{ 1 + A1 \cdot [CO_3] + A2 \cdot [O_2] + A3 \cdot [H^+] \right\} \cdot \left\{ A6 - R \cdot X4 \cdot log_{10}\left([CO_3] \cdot [O_2] \cdot [H^+] \right) \right\}$$

L_{ff} | $\mu_S - \mu_L$

$$R = \left\{ A4 \cdot e^{\frac{A5}{T}} \right\} \cdot \left\{ 1 + A1 \cdot [CO_3]^{A7} + A2 \cdot [O_2]^{A8} + A3 \cdot [H^+]^{A9} \right\} \cdot \left\{ A6 - R \cdot X4 \cdot log_{10}\left([CO_3] \cdot [O_2] \cdot [H^+] \right) \right\}$$

L_{ff} | $\mu_S - \mu_L$

- L_{ff} is an Onsager Coefficient
- No Onsager Form Worked Well

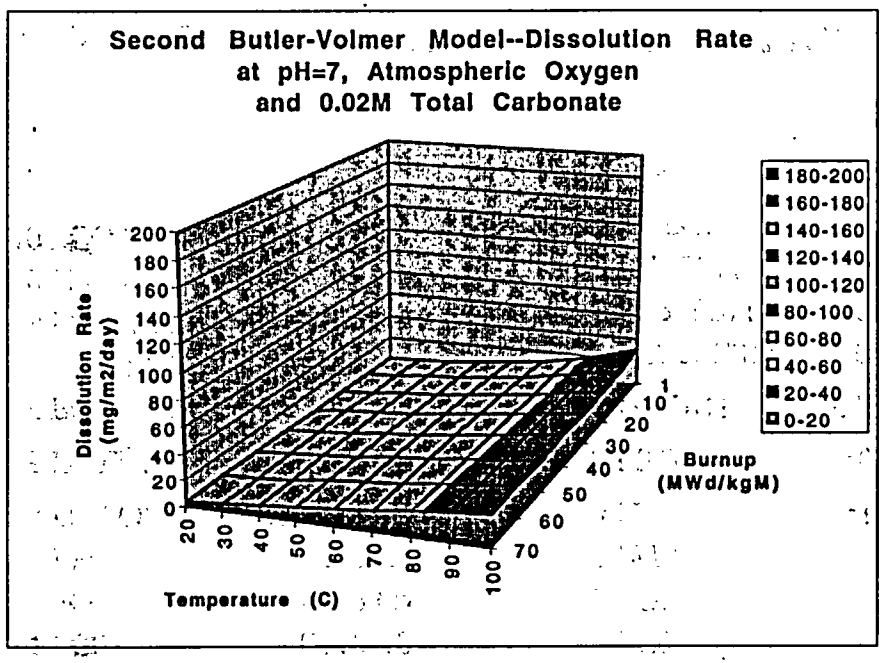
Two Forms of Butler-Volmer-Like Models Tested

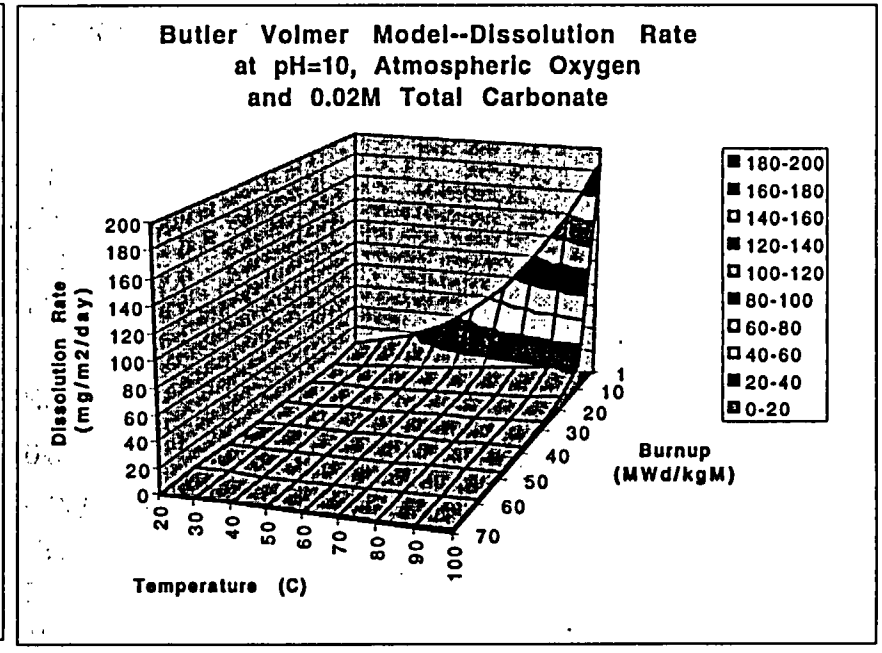
- First Butler-Volmer Form used Polynomials in the Bulk Concentration Variables of the Liquid and the Spent Fuel (Burnup)
  - Represented chemical potential and electrochemical functional terms
- Second Butler-Volmer Form Had Logarithmic Polynomials of Concentrations Representing the Chemical Potentials
  - Logarithmic Functions Correspond to Accepted Function Representations for Ideal and Non-Ideal Solid and Liquid Solutions

Second Form of the Butler-Volmer-Like Model Is Best

- First Non-Logarithmic Form is:
- $\ln(\text{Rate SF}) = a0 + a1 \cdot BU + a2 \cdot IT + a3 \cdot CO3 + a4 \cdot O2 + a5 \cdot H + a6 \cdot BU \cdot IT + a7 \cdot BU \cdot O2 + a8 \cdot BU \cdot H + a9 \cdot CO3 \cdot O2 + a10 \cdot CO3^2 + a11 \cdot O2^2 + a12 \cdot BU \cdot O2 \cdot IT$ <- Radiolysis Term
- Second Logarithmic Form is:
- $\ln(\text{Rate SF}) = a0 + a1 \cdot PCO3 + a2 \cdot PO2 + a3 \cdot PH + a4 \cdot PO2 \cdot IT + a5 \cdot LBU \cdot IT + a6 \cdot LBU \cdot PCO3 + a7 \cdot LBU \cdot PO2 + a8 \cdot LBU \cdot PH + a9 \cdot IT^2 + a10 \cdot PCO3^2$

Model Fits Existing Data and Extrapolates UO_2 Data Well





Comparison of latest model at pH=10 and extrapolated as well to pH=7

Model fits data well and extrapolates predictably, particularly for UO_2 (zero burnup)

Burnup shows little effect yet, but only 2 spent fuel data points are not at ~30 MWd/kgM burnup

Slightly Modified Intrinsic Dissolution Model Provided to PA Recently by Bill O'Connell

WFCR R1 Model		O'Connell 2 Model	
Term	Coeff. (a_i)	Term	Coeff. (a_i)
0 1	1.161868	0 1	0.5105
1 PC03	1.547418	1 PC03	-0.0767
2 PO2	-1.672304	2 PO2	-0.3242
3 PH	0.260294	3 PH	0.0531
4 IT*PO2	384.146973	4 IT	-1173.78
5 IT*LBU	584.818339	5 LBU	-0.1042
6 PCO3*LBU	0.147972	6 IT*LBU	561.3420
7 PO2*LBU	0.174971	7 PCO3*LBU	0.1092
8 PH*LBU	-0.285106	8 PO2*LBU	0.1440
9 IT**2	-3.727218E+05	9 PH*LBU	-0.3091
10 PCO3**2	-0.345209	10 IT*PO2	369.2896
		11 PCO3**2	-0.3531

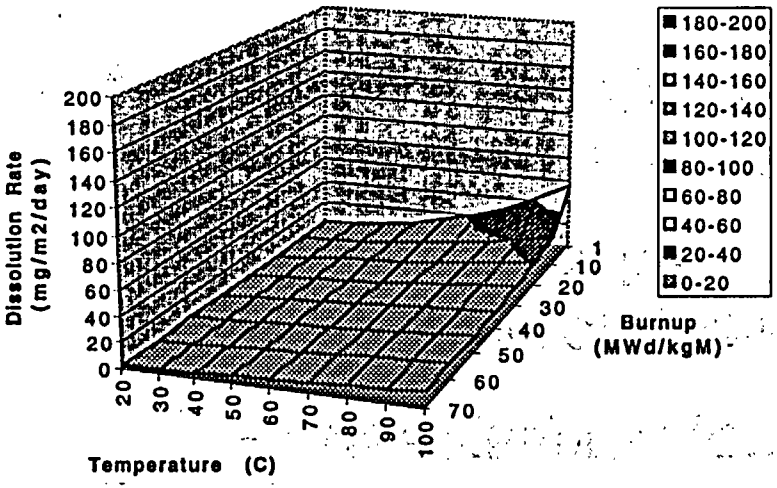
Differences:

1/T substituted for $(1/T)^2$: More Like Standard Form

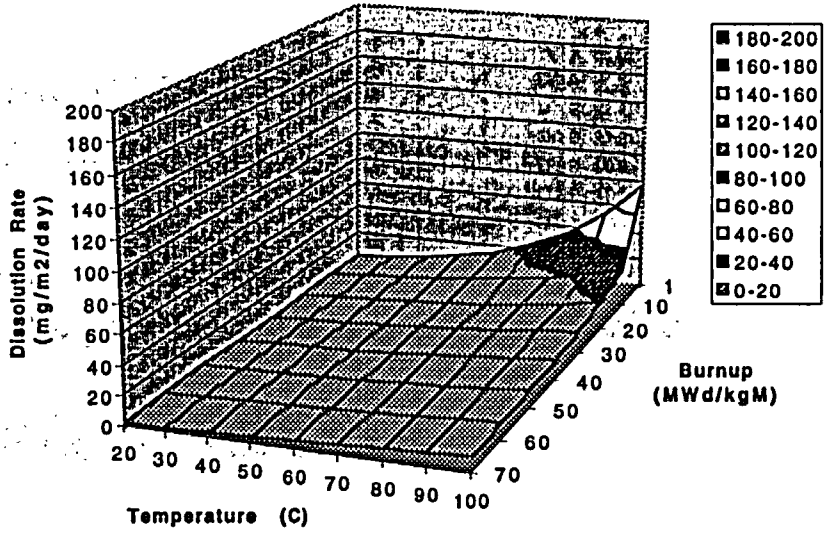
LBU Linear Term Added: Obeys Model Heirarchy
i.e. Every Variable Has Linear Term

WFCR and O'Connell Models Similar

Second BV Model--Dissolution Rate at pH=8, Atmospheric Oxygen and 0.02M Total Carbonate



Second O'Connell Model--Dissolution Rate at pH=8, Atmospheric Oxygen and 0.02M Total Carbonate



— O'Connell Model Yields Slightly Higher Dissolution Rate at Zero Burnup--UO2
Not Important Difference for Repository Conditions

Simpler Models Including Burnup Do Not Fit Well

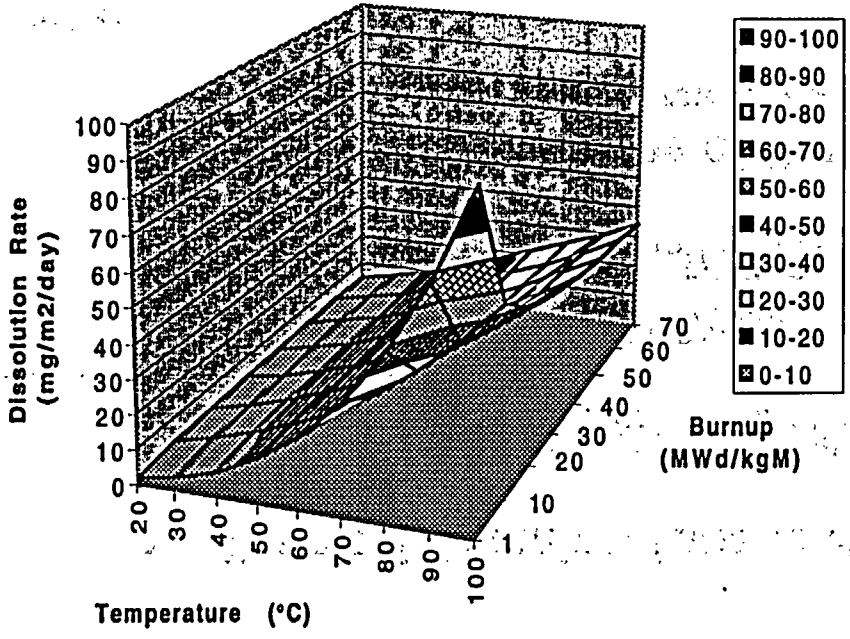
- Using Classical Chemical Kinetic Rate Law Gives a R^2 of only 0.60
  - Rate = $k[Bu]^a[O_2]^b[CO_3]^c[H^+]^d... \exp(E_a/RT)$
  - Using Solid Characteristic of Burnup in Homogeneous Rate Equation is Not Really Appropriate
- Data Currently Show Differences Between SF and UO_2-- Presumably Radiolysis (Burnup Differences)

AECL · 204-753-2311
Stewards 510-423-1767

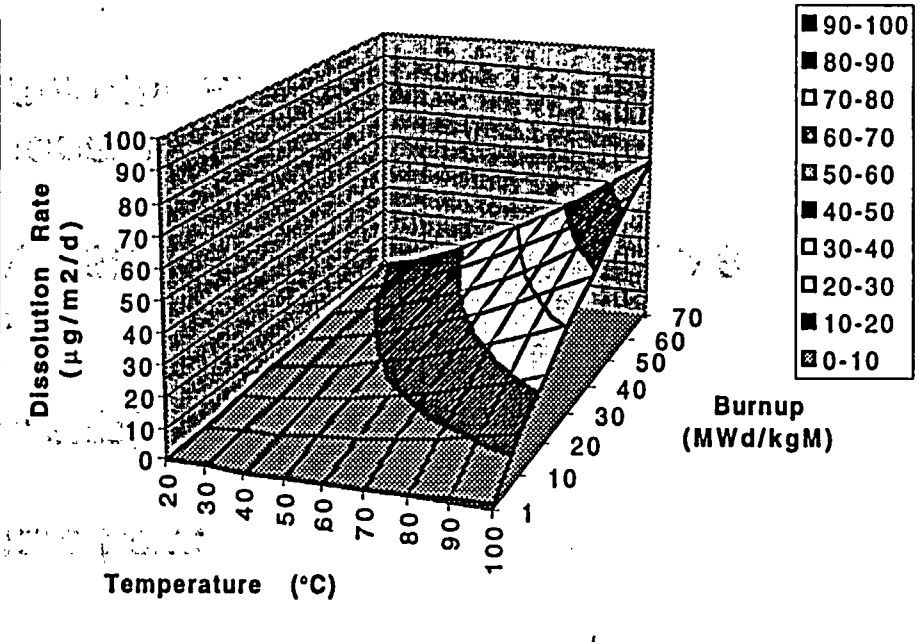
Model Can Be Applied to Technicium and Iodine

normalized?

Uranium Dissolution Rate [mg/m2/d]
pH=8, 0.001 M Carbonate, 0.2 atm O2



Technicium(99) Dissolution Rate [µg/m2/d]
pH=8, 0.001 M Carbonate, 0.2 atm O2



$T_c = 8.2 \times 10^3$ µg / µ-g

µg mJ

U_3O_8 Dissolution Exhibits a 20% Smaller Activation Energy Than UO_2

- Classical Chemical Kinetic Rate Law:
  - Rate = $k[A]^a[B]^b[C]^c[D]^d... \exp(E_a/RT)$
- U_3O_8: $\log_{10}(D)\{mg/(m^2/day)\} =$
  $7.95+0.649\log_{10}[CO_3]+0.106\log_{10}[H]-1333/T$ $r^2=0.88$
  - Interaction Terms of Carbonate With Temperature and pH Improve Fit Significantly => $r^2=0.95$
- U_3O_8: $\log_{10}(D)\{mg/(m^2/day)\} =$
  $6.93 + 0.649\log_{10}[CO_3] - 1307/T$ $r^2=0.86$
- UO_2: $\log_{10}(D)\{mg/(m^2/day)\} =$
  $5.83+0.334\log_{10}[CO_3]-0.157\log_{10}[H]-1685/T$ $r^2=0.83$

Classic Rate Law Fits U_3O_8 Data Well