U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD FULL BOARD MEETING

SUBJECT: DISSOLUTION TESTING OF SPENT FUEL

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Complexity of Spent-Fuel Dissolution Requires a Controlled Approach

- Results of previous data vary widely
- Semi-static tests allow precipitation; flow-through method does not
- Compare studies using UO_2 to spent fuel matrix dissolution
- Statistical experimental design is only way to understand effects of many variables on spent-fuel dissolution
  - Experimental design normally limits needed experiments to 32 and still understand variable interactions and confounding

Previous Data* Show > Million-Fold Variation in Dissolution Rate under Various Conditions

Controls are needed!!!

- UO_2 fuel matrix dissolution governs long-term soluble radionuclide release
- Bulk of fission product and actinide release controlled by UO_2 matrix dissolution rate
- Soluble radionuclides at gap and grain boundaries are released quickly

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* B. Grambow, SKB Technical Report 89-13, March 1989

UO_2 Fuel Matrix Dissolution Governs Long-term Soluble Radionuclide Release

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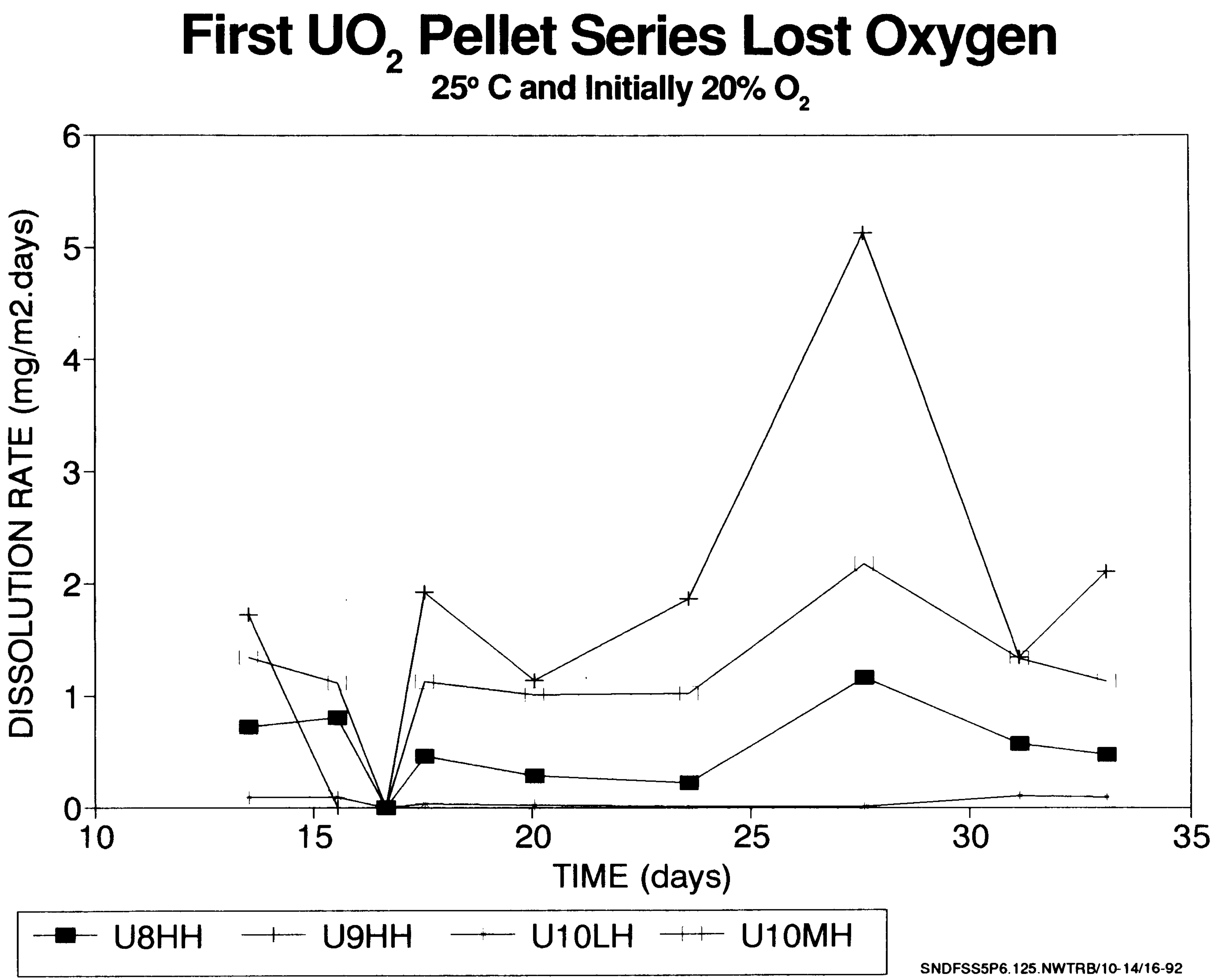
Flow-Through Method Overcomes Solubility Limitation

- High flow-rates prevent precipitate formation by staying in the unsaturated concentration regime
- First use on glass by Knause et al. at LLNL in 1986
- Refined at LLNL and PNL for glass and spent fuel

Knauss, K.G., and Wolery, T.J., Geochim. Cosmochim. Acta 50, 2481 (1986)

Measurements on UO_2 Dissolution are Important to Modeling

- Matrix dissolution can be defined
- Comparison with spent fuel will provide
  - Chemical effects of fission products on matrix behavior
  - Chemical effects of high radiation levels
  - Grain boundary dissolution of some fission products



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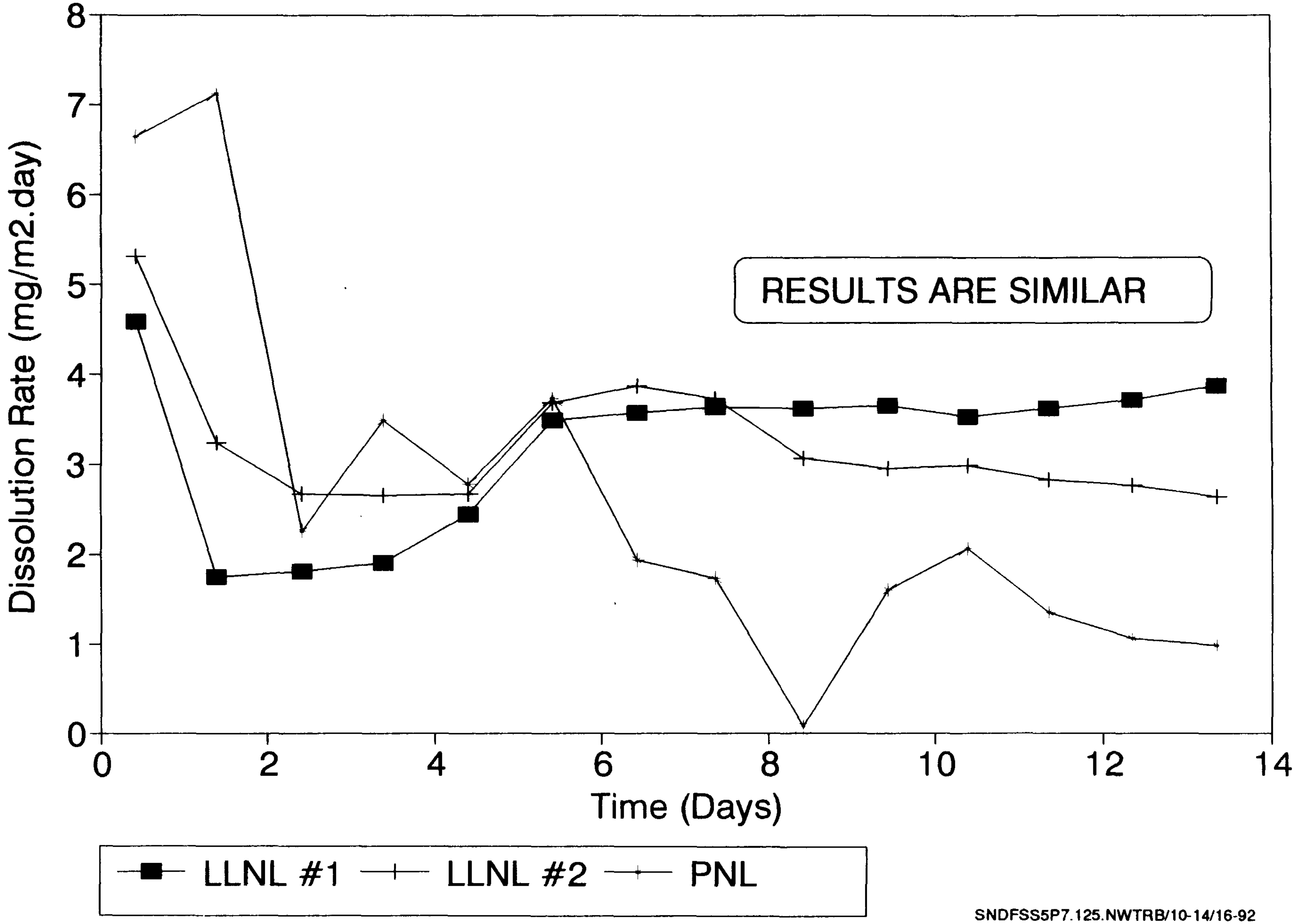
UO_2 Powder Runs for PNL & LLNL Cells

25° C, pH 8, 0.02 [CO_3], 0.2 O_2



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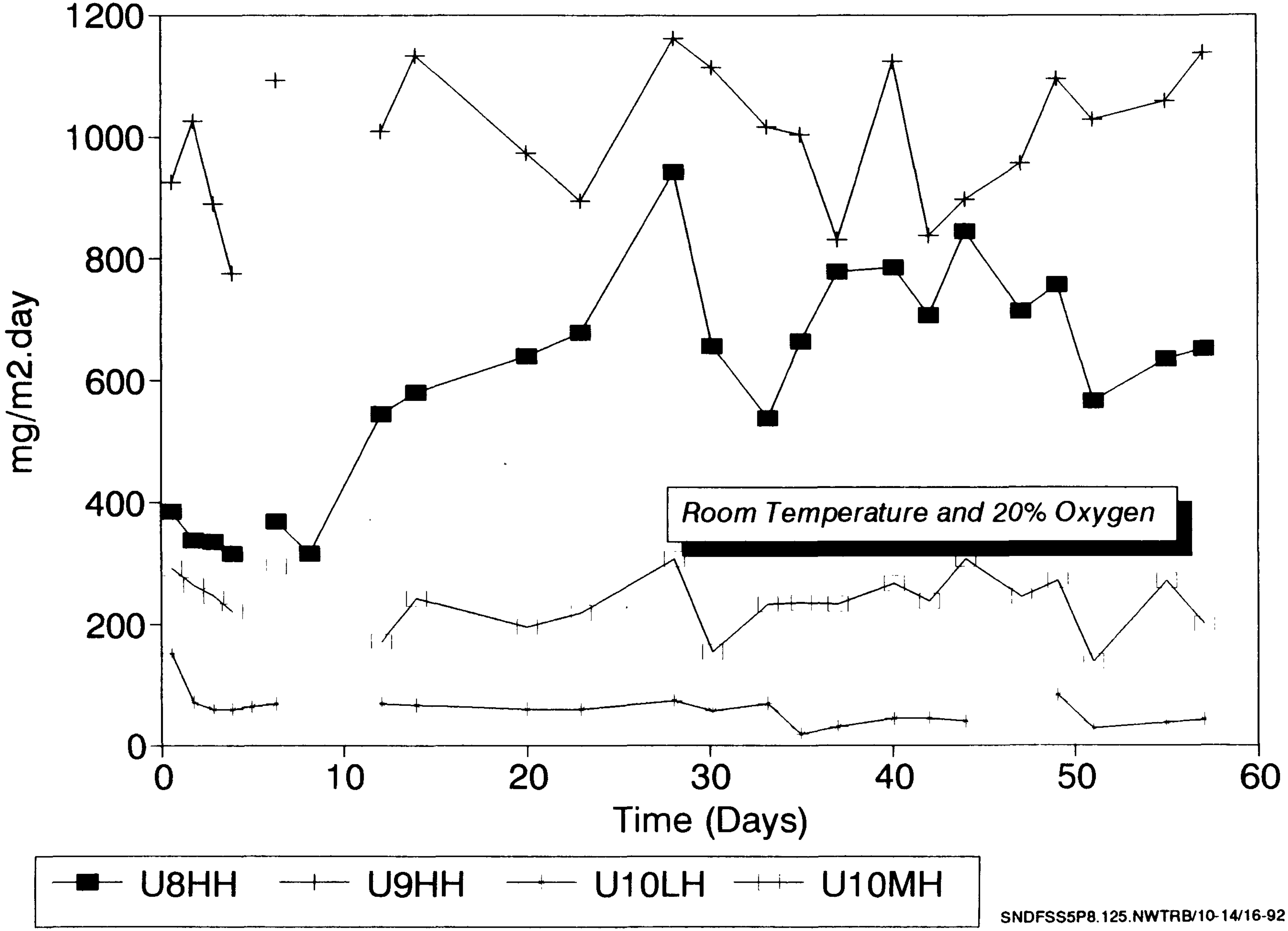
Surface Area may have Largest Effect

Pellet Fragments Cause High Dissolution



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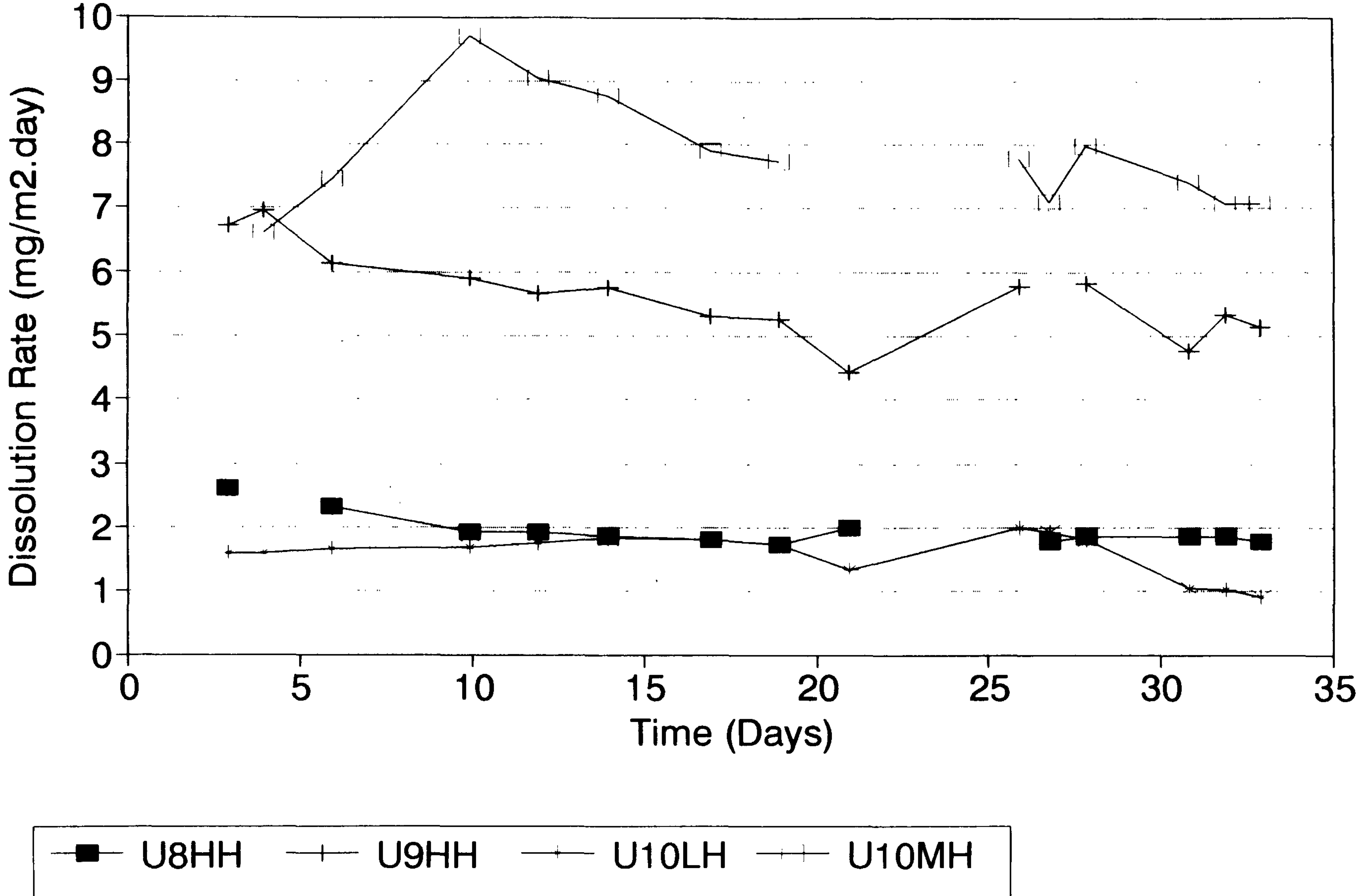
Polycrystalline Runs Gave Good Results

Room Temperature and 20% Oxygen



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Temperature and CO_3 Have Greatest Effect upon PNL Spent-Fuel Dissolution Data at 20% O_2

1. $[u] = 1.65 + 1.41 (\log[CO_3]) + 0.160T - 0.0341 (\log[H])$ r^2adj* = 0.963
2. $[u] = 1.97 + 1.41 (\log[CO_3]) + 0.160T$ r^2adj = 0.969
3. Full 6-term Quadratic Fit r^2 adj = 0.918
4. $\log [u] = 7.45 + 0.258 (\log[c]) + 0.142 (\log[H]) - 1550/T$ r^2adj = 0.843

- Simple two-term linear model (#2) gives best fit with data at 20% oxygen
- pH has little effect
- Desirable classic kinetic model gives poorer fit

* Adjusted correlation coefficient accounts for degrees of freedom in fit

W.J. Gray (PNL, H.R. Leider and S.A. Steward (LLNL), J. Nucl. Matls., (in press)

Averages of Current PNL and LLNL Dissolution Rates Show Smaller Variation than Historical Data

$0.0002 \text{ atm} \leq P(O_2) \leq 0.2 \text{ atm}; \; 8.0 \leq pH \leq 11.1$

[carbonate] (M) / Temp.(°C)	Rate ($mg/m^2 \cdot day$)		
	0.02	0.002	0.0002
25	2.9 ± 1.6 (0.8 to 5.6)	3.3 ± 3.3 (1.2 to 7.8)	0.8 ± 0.6 (0.2 to 1.6)
50		6.1	
75	11.5		8.6

UO_2 : large crystals, powder and pressed pellets (oxygen adjusted)

S.F. : powder

Indicated error is 1σ

Near-Term Plans

- Studies of expanded water chemistry and fuel attributes devised (10 variables)
- Existing test matrix (4 variables) used only carbonate as the reactive ion
- Additional major components of J-13 water will be tested
    - Si, Ca, SO_4, and Halide
- Reactor-type and fuel burnup level also explored
- UO_2 will be compared to different fuels with similar water chemistry

A Screening Study Will Determine Importance of the 10 Variables

- Statistical experimental design is used
- A fractional-factorial screening design with 32 experiments is sufficient to test importance of each variable
- A modeling design will be based on those screening results
  - This modeling design will take no more than 32 experiments, as well