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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: SPENT FUEL LEACHING: FLOW-THROUGH TESTS

PRESENTER: HERMAN R. LEIDER

PRESENTER'S TITLE AND ORGANIZATION: PHYSICAL CHEMIST
LAWRENCE LIVERMORE NATIONAL LABORATORY
LIVERMORE, CALIFORNIA

PRESENTER'S TELEPHONE NUMBER: (415) 422-9947

AUGUST 28-29, 1990

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WHY STUDY UO_2?

MEASUREMENTS ON UO_2 DISSOLUTION ARE IMPORTANT TO MODELING FOR SEVERAL REASONS

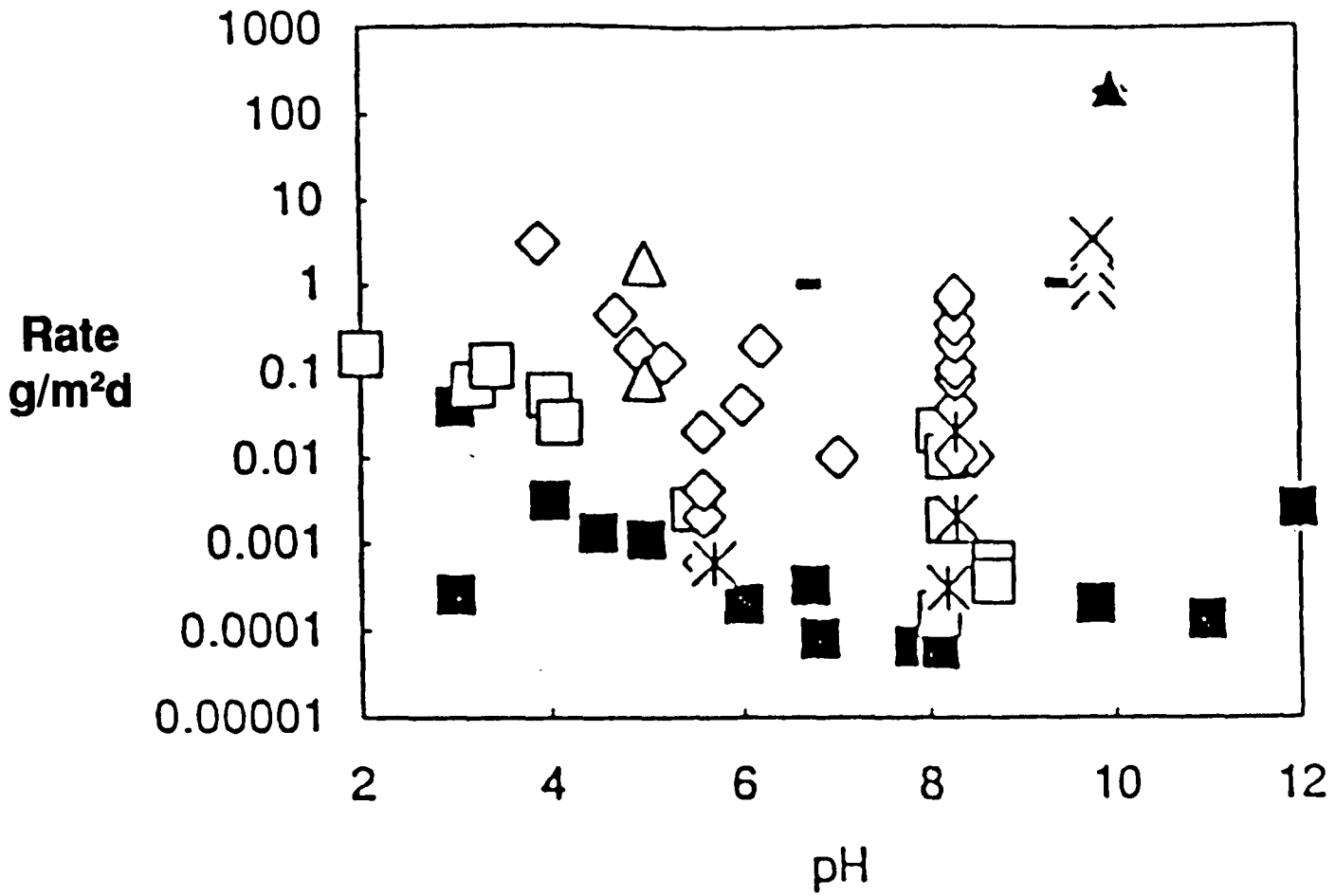
- MATRIX DISSOLUTION CAN BE DEFINED
- COMPARISON WITH DISSOLUTION BEHAVIOR OF SPENT FUEL (SF) WILL PROVIDE INFORMATION ABOUT
  - THE CHEMICAL EFFECTS OF FISSION PRODUCTS (FPs) (SEVERAL %) ON THE MATRIX BEHAVIOR
  - THE CHEMICAL EFFECTS OF HIGH RADIATION LEVELS
  - GRAIN BOUNDARY DISSOLUTION OF SOME FPs

DO WE NEED MORE EXPERIMENTS?

YES

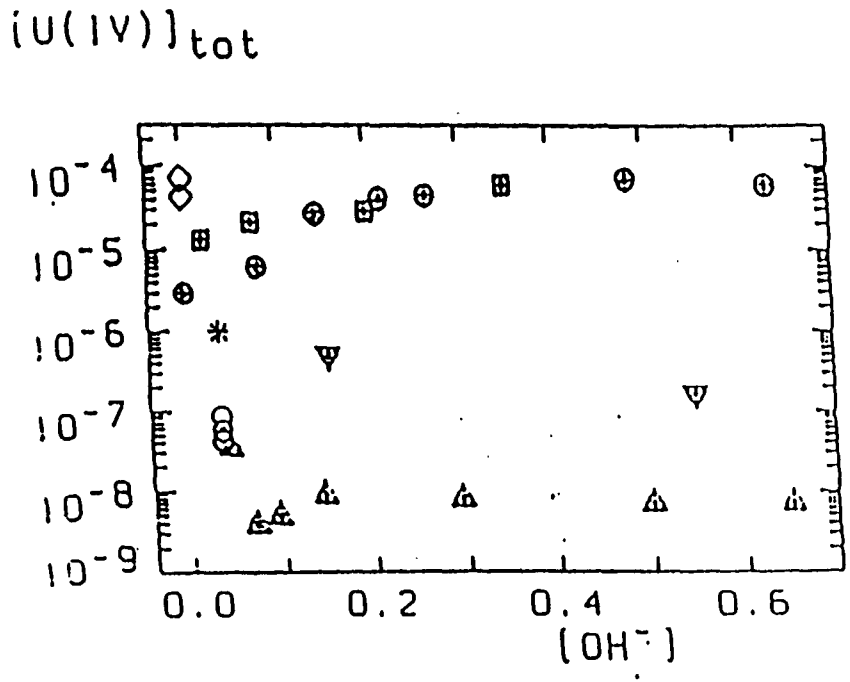
AVAILABLE DATA, ALTHOUGH AMPLE, ARE HIGHLY NON-REPRODUCIBLE, AND, IN ANY EVENT, ARE NOT EASY TO APPLY TO OUR NEEDS

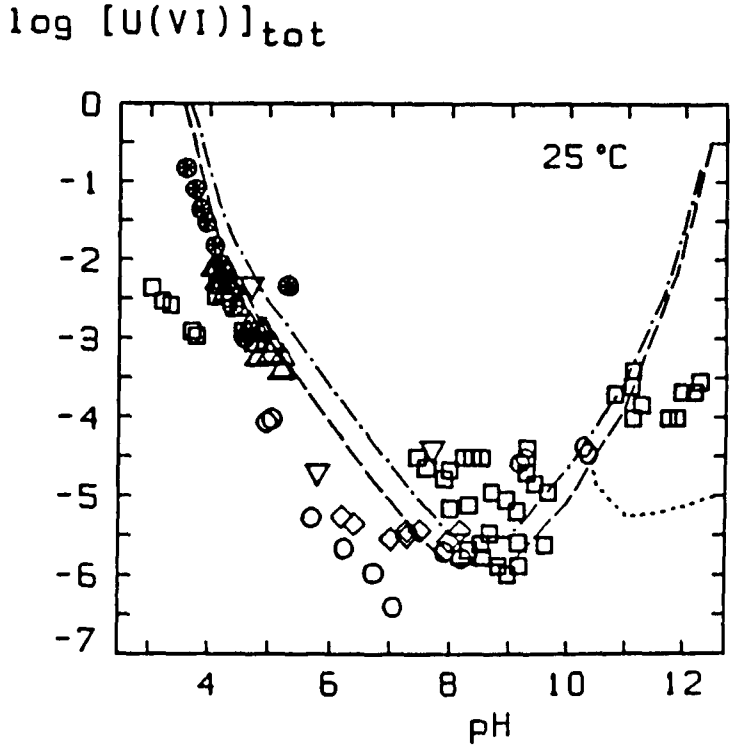
PUBLISHED DISSOLUTION RATES*



*BERND GRAMBOW, SKB TECHNICAL REPORT 89-13, MARCH, 1989

THE SOLUBILITIES OF THE OXIDES AND HYDROXIDES ARE ALSO UNCERTAIN*





* I. PUIGDOMENECH AND J. BRUNO, SKB TECHNICAL REPORT 88-21, OCTOBER, 1988

STATIC TESTS HAVE LIMITATIONS

- SATURATED STATIC, OR SEMI-STATIC DISSOLUTION TEST CAN GIVE INFORMATION ON DISSOLUTION RATE ONLY FOR VERY SOLUBLE SPECIES, LIKE Cs

- FOR ALL SPECIES WITH LIMITED SOLUBILITY (MOST), SATURATED STATIC TESTS WILL ONLY GIVE INFORMATION ON THE CONCENTRATION OF THE SATURATED SOLUTION

UNDERSATURATED FLOW-THROUGH TESTS COMPLEMENT STATIC TESTS

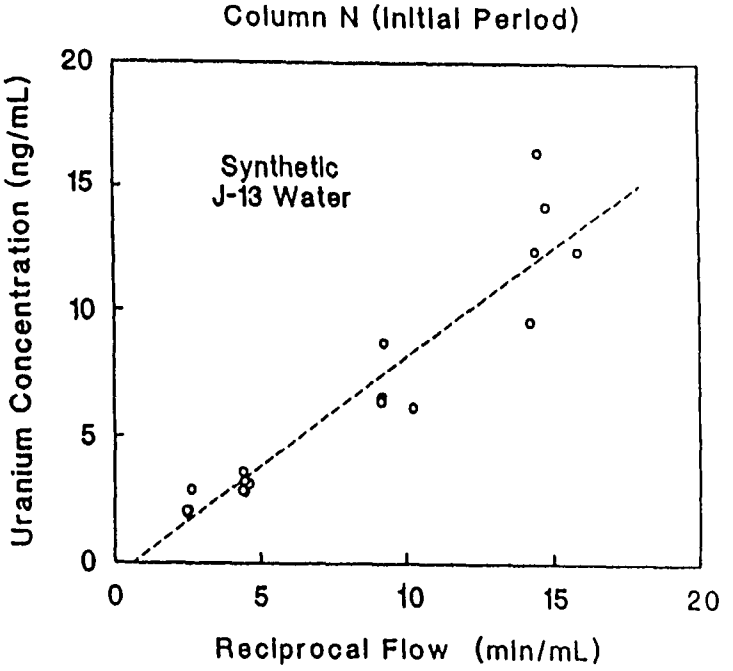
- UNDERSATURATED FLOW-THROUGH TESTS PRODUCE CONCENTRATIONS THAT CAN BE MEASURED BY ACCEPTED TECHNIQUES
- THIS IS TRUE FOR U AND Cs, AND HOPEFULLY, Sr. OTHER SPECIES WILL HAVE TO BE EXAMINED, AS WELL

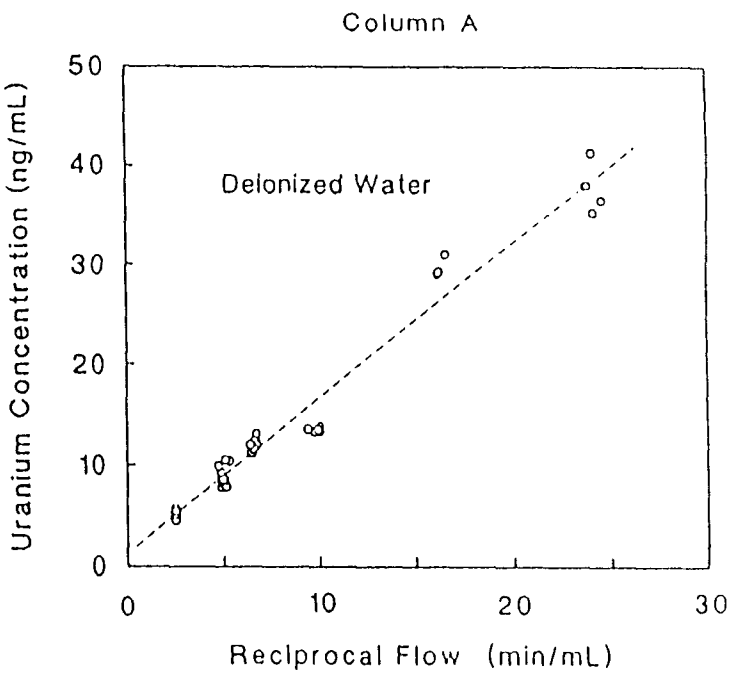
UNDERSATURATED FLOW-THROUGH TESTS

- IN THESE TESTS, THE CONCENTRATION OF SOLUTES IS KEPT FAR BELOW THE LEVELS THAT WOULD RESULT IN PRECIPITATION OF SECONDARY PHASES
- THE EXPERIMENTAL PHILOSOPHY AND FLOW-THROUGH APPARATUS IS ESSENTIALLY THE SAME AS THAT FOR THE ON-GOING GLASS DISSOLUTION STUDIES
- CONCENTRATION WILL (PROBABLY) BE INVERSELY PROPORTIONAL TO FLOW RATE. THE SLOPE OF SUCH A PLOT IS THE RATE OF DISSOLUTION
- SOLUBILITY IS MEASURED DIRECTLY AT THE POINT WHERE CONCENTRATION BECOMES INDEPENDENT OF FLOW RATE
- DISCONTINUOUS CHANGES IN DISSOLUTION RATE IN THE UNDERSATURATED REGIME INDICATE A CHANGE IN MECHANISM

FLOW-THROUGH TESTS ON UO_2*

URANIUM CONCENTRATION VS. RECIPROCAL FLOW





Dashed lines are least squares linear fit to the data
Linear relationship indicates undersaturated conditions
Test temperature 25 C

*C. WILSON & W. GRAY, PNL

WE WILL USE SIMPLIFIED SOLUTIONS

IN SIMPLIFIED EXPERIMENTS, ONLY [H^+], [HCO_3^-] AND [O_2] WILL BE PRESENT. THE SOLUBILITY-LIMITING PHASE WILL BE SCHOEPITE, $UO_3 \cdot 2\ H_2O$

UNDER REPOSITORY-LIKE CONDITIONS, OTHER SOLUBILITY-LIMITING PHASES WILL BE PRESENT AND WOULD COMPLICATE INTERPRETATION OF THE CHEMISTRY

THESE WILL INCLUDE:

URANOPHANE	$Ca(UO_2)_2\ (SiO_3OH)_2\ 5\ H_2O$
HAIWEEITE	$Ca(UO_2)_2\ Si_6O_{15}\ 5\ H_2O$
SODDYITE	$(UO_2)_2\ SiO_4\ 2\ H_2O$

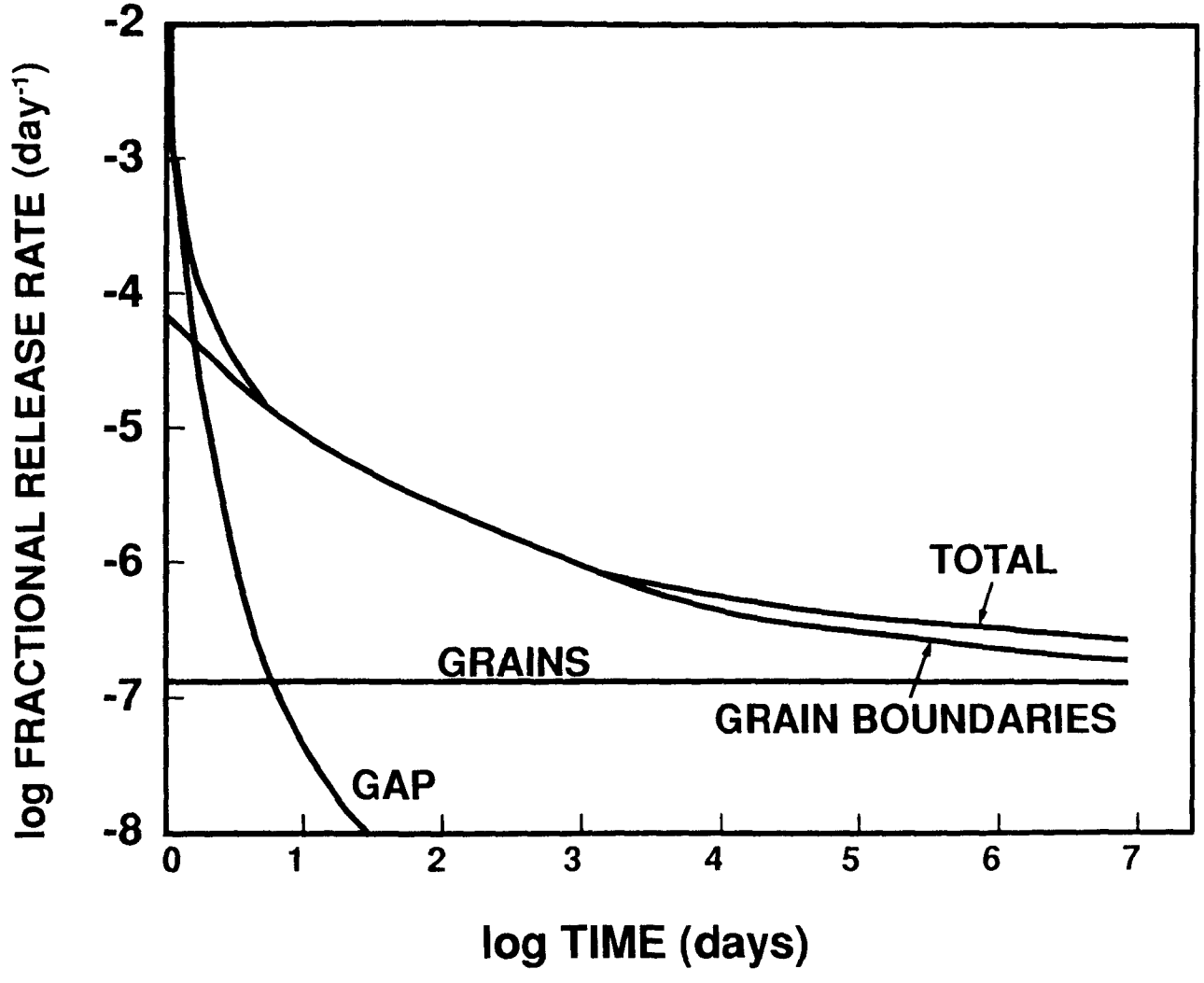
FISSION PRODUCT (FP) DISSOLUTION ARISES FROM THREE SOURCES IN SPENT FUEL (SF)

- THE GAP. RELEASED VOLATILES, SUCH AS Cs, I, ETC., FOUND ON SF SURFACES AND CLADDING. IMMEDIATELY AVAILABLE

- GRAIN BOUNDARIES (GB). THIS WILL CONSIST OF VOLATILES AND OTHER RADIONUCLIDES THAT ARE INSOLUBLE IN THE MATRIX. MAY OR MAY NOT COINCIDE WITH MATRIX DISSOLUTION

- THE MATRIX. CONGRUENT WITH UO_2 DISSOLUTION. ALL RADIONUCLIDES DISSOLVED OR FINELY DISPERSED IN THE MATRIX. THIS IS THE BULK OF THE FPs AND ACTINIDES

A SCHEMATIC VIEW OF SF DISSOLUTION*



*L.H. JOHNSON AND D.W. SHOESMITH, "RADIOACTIVE WASTE FORMS FOR THE FUTURE," W. LUTZE AND R.C. EWING, EDS., ELSEVIER (1988) P. 686

SOLID DISSOLUTION OF NON-DISSOCIATING SOLIDS

THE SIMPLEST MODEL IS BASED ON KINETIC THEORY

$$RATE = KDS (C_{sat} - C(t))$$

- K = PROPORTIONALITY CONSTANT
- D = DIFFUSION COEFFICIENT IN SOLUTION
- S = SURFACE AREA OF SOLID
- C_{sat} = SATURATED SOLUTION CONCENTRATION
- C (t) = INSTANTANEOUS SOLUTION CONCENTRATION

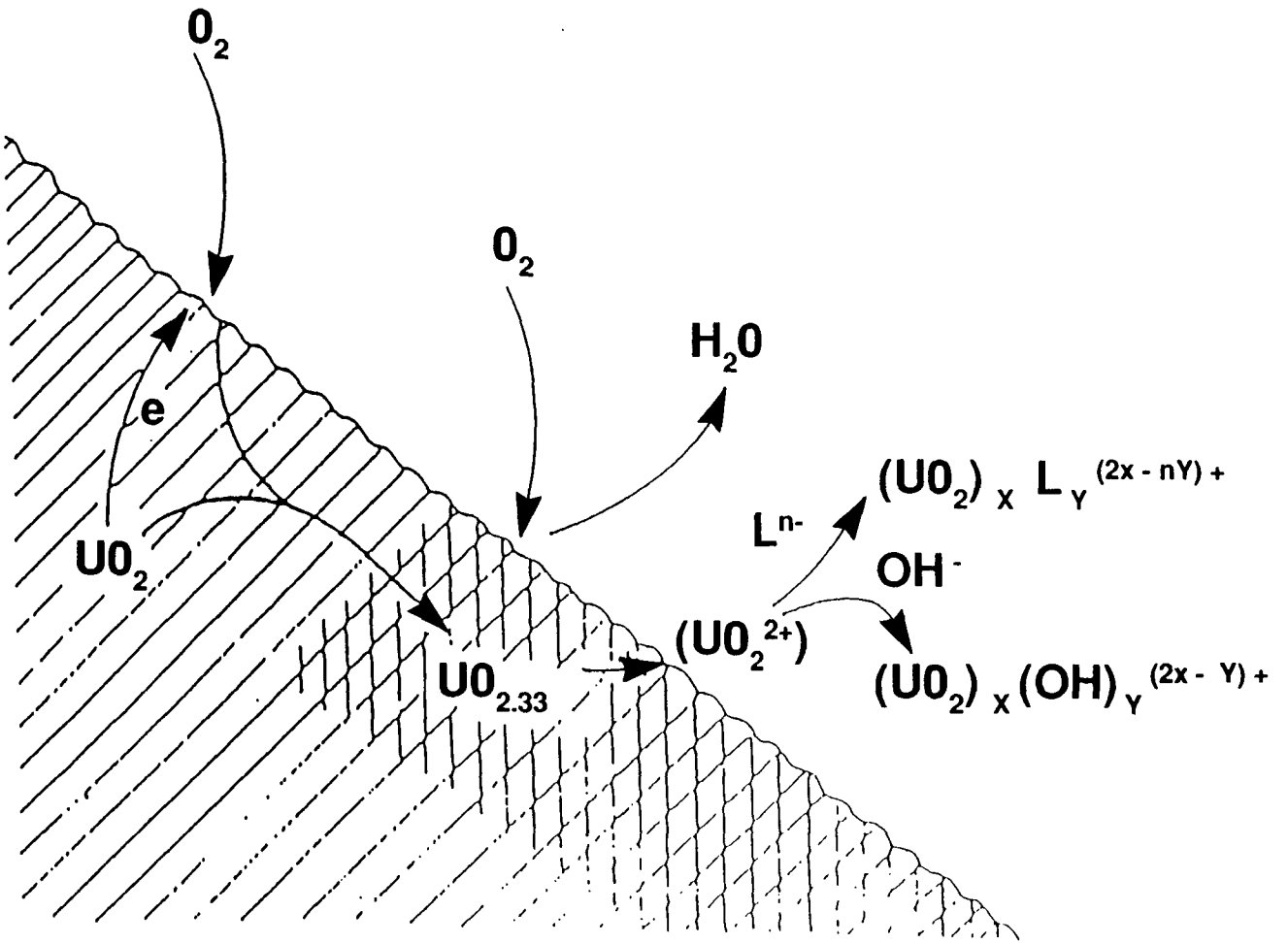
THE GENERAL VALIDITY OF THIS MODEL HAS BEEN AMPLY CONFIRMED. HOWEVER, SF AND UO_2 DISSOLUTION INVOLVES IONIC MATERIAL

CONSIDER THE (OVERLY) SIMPLE EQUATION

$$UO_{2(S)} + 2\ H_2O_{(aq)} \qquad U^{+4}_{(aq)} + 4\ OH^-_{(aq)}$$

IN THIS CASE SOLUBILITY AND DISSOLUTION RATE WILL BE STRONGLY AFFECTED BY pH. THE EQUATION INDICATES A 4th POWER DEPENDENCE ON [OH^-] AND THEREFORE ON [H^+]

A SCHEMATIC VIEW OF UO_2 (AND SF) DISSOLUTION*



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REACTIONS OF UO_2 IN OXIDATION AND DISSOLUTION

THERE ARE SEVERAL POSSIBLE RATE-DETERMINING PROCESSES IN SF AND UO_2 DISSOLUTION. (WE WILL REGARD PARTIALLY OXIDIZED UO_2 AS CONSISTING OF U^{IV} + U^{VI}). REPOSITORY CONDITIONS WILL BE OXIC.

REACTION			DEPENDENCE
$O_{2(g)}$	⇔	$O_{2(aq)}$	
$O_{2(aq)}$	⇔	$O_{2(ads)}$	
$O_{2(ads)}$	⇔	$O_{2(s)}$	
$O_{2(ads)}$	⇔	$2O_{(ads)}$	
$O_{(ads)}$	⇔	$O_{(s)}$	
$UO_{2(s)} + x/2\ O_{2(ads)}$	⇔	$UO_{2+x(s)}$	$P(O_2)$
$UO_{2(s)} + x/2\ O_{2(s)}$	⇔	$UO_{2+x(s)}$	$D(O_2) = K_1 \exp(-\Delta H1/RT)$

REACTIONS OF UO_2 IN OXIDATION AND DISSOLUTION

(CONTINUED)

REACTION		DEPENDENCE
$UO_{2(s)} + xO_{2(ads)}$	$UO_{2+x(s)}$	$P(O_2)^{1/2}$
$UO_{2(s)} + xO_{(s)}$	$UO_{2+x(s)}$	$D(O) = K_2 \exp(-\ H2/RT)$
$UO_{3(s)} + H_2O_{(aq)}$	$UO^{+2}_{2(aq)}\ 20H^{-1}_{(aq)}$	$[H^+]^2$
$UO_{3(s)} + 2\ HCO^{-1}_{3(aq)}$	$UO_2(CO_3)^{-2}_{2(aq)}\ H_20_{(aq)}$	$[HCO_3^-]^2$
$UO^{+2}_{2(aq)} + 2\ HCO^{-1}_{3(aq)}$	$UO_2(CO_3)^{-2}_{2(aq)}\ 2H^{+1}_{(aq)}$	$[HCO_3^-]^2, [H^+]^{-2}$

WE WILL USE A STATISTICAL APPROACH

WE HAVE USED "R/S DISCOVER", A COMMERCIAL COMPUTER PROGRAM, TO GENERATE AN EFFICIENT STATISTICAL EXPERIMENTAL DESIGN

- DETERMINATE - OPTIMAL
- QUADRATIC MODEL
- 15 TESTS PLUS 4 DUPLICATIONS

TEST MATRIX FOR THE UO_2 DISSOLUTION TESTS

NO.	TEMPERATURE (°C)	-log (Pco_2, atm)	-log (Po_2, atm)	pH
1	50	2.5	1.7	9
2	50	2.5	1.7	9
3	50	2.5	1.7	9
4	25	1.5	0.7	8
5	75	1.5	0.7	10
6	75	3.5	0.7	8
7	25	3.5	0.7	10
8	25	1.5	2.7	8
9	75	1.5	2.7	10
10	75	3.5	2.7	8
11	25	3.5	2.7	10
12	25	3.5	1.7	8
13	75	3.5	1.7	10
14	25	1.5	1.7	10
15	75	1.5	1.7	8
16	50	1.5	2.7	10
17	25	1.5	0.7	9
18	25	2.5	0.7	10
19	25	2.5	2.7	9

SF DISSOLUTION TESTS

- IDEALLY, SF FLOW-THROUGH DISSOLUTION TESTS WOULD USE THE SAME EXPERIMENTAL DESIGN. THIS WILL BE DONE WITHIN THE CONSTRAINTS ASSOCIATED WITH HOT CELL WORK

- SF TESTS WILL COVER A PART OF THE EXPERIMENTAL MATRIX SO AS TO DUPLICATE AS MANY OF THE UO_2 TESTS AS IS FEASIBLE

- SUCH PARTIAL MATRICES WILL ULTIMATELY BE USED TO EXAMINE SFs THAT REPRESENT THE FULL RANGE OF BURNUP AND OF FISSION GAS RELEASE

NOVEL TECHNIQUES FOR MEASURING DISSOLUTION

- SPECTRO-ELECTROCHEMISTRY USING OPTICAL PROBE BEAM DEFLECTION SPECTROSCOPY (R.E. RUSSO, LBL)
- SCANNING ATOMIC SCALE MICROSCOPY (W. SIEKHAUS AND M. BALOOCH, LLNL)

EXISTING SCANNING MICROSCOPY INSTRUMENTATION

- FOR ELECTRICALLY CONDUCTING SAMPLES
  - SCANNING TUNNELING MICROSCOPE OPERATING IN AIR OR WATER
  - ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE OPERATING IN ELECTROLYTES WITH POTENTIAL APPLIED
  - SCANNING TUNNELING MICROSCOPE OPERATING IN ULTRA HIGH VACUUM
- FOR ELECTRICALLY INSULATING SAMPLES
  - ATOMIC FORCE MICROSCOPE OPERATING IN AIR, WATER, OR OTHER FLUIDS

SUMMARY

- THE EXPERIMENTAL SYSTEM HAS BEEN THOROUGHLY TESTED AND FOUND TO BE SATISFACTORY
- SUITABLE DISSOLUTION SAMPLES ARE IN HAND. VERIFICATION OF THEIR PROPERTIES IS UNDERWAY
- START OF ACTUAL DISSOLUTION MEASUREMENT IS IMMINENT