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

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

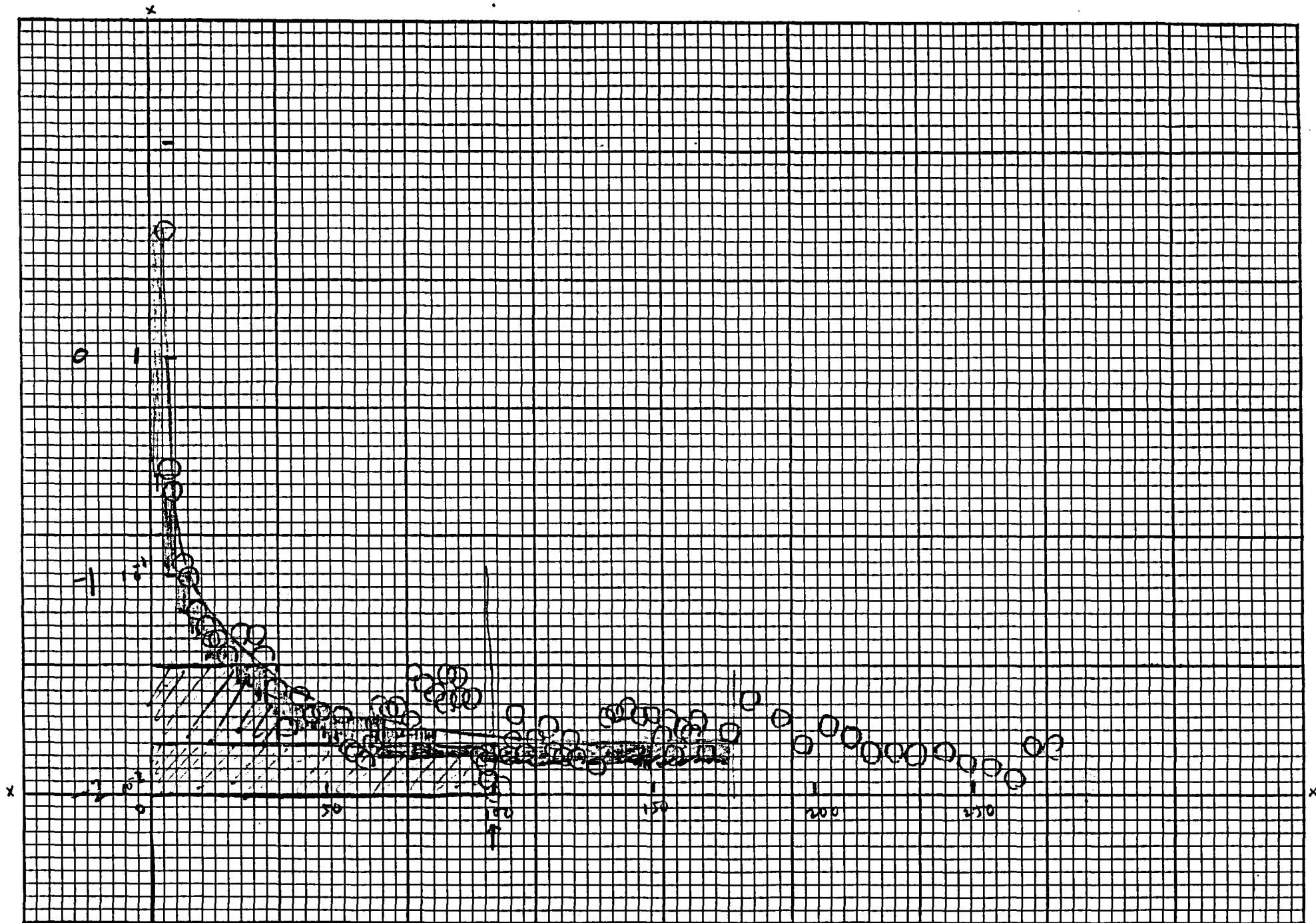**SUBJECT:**   **DISSOLUTION TESTING OF SPENT FUEL**

PRESENTER: **DR. WALTER J. GRAY**

PRESENTER'S TITLE
AND ORGANIZATION: **SENIOR SCIENTIST**
PACIFIC NORTHWEST LABORATORY (PNL)
RICHLAND, WASHINGTON

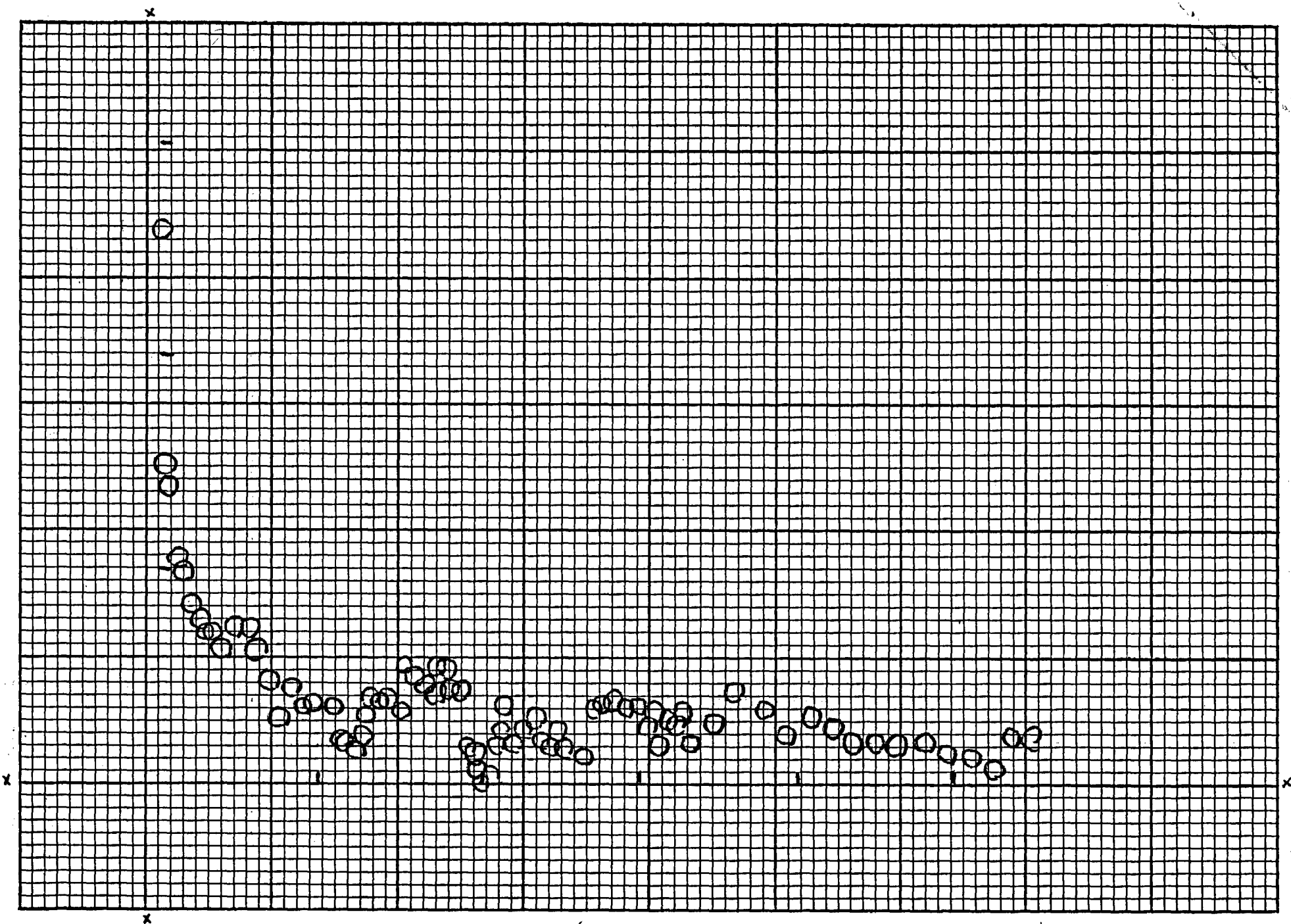**PRESENTER'S**
TELEPHONE NUMBER: **(509) 376-9693**

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OCTOBER 14 - 16, 1992

100 days $\frac{10.42}{17}$ = 0.613   -2   : -1.501   4.1×10

175-180 days $\frac{7.74}{17}$ = 0.455   -2   : -1.545 $2.9×10^{-2}$

100 days : 100 + 16.5×4 + 110 = 276   175~180 day : 276 + 19×4 = 352
276/26.5 = 10.42   352/45.5 = 7.74

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LAWRENCE LIVERMORE NATIONAL LABORATORY
(LLNL)
YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT
(YMP)
STATUS REPORT

April 1995

EXECUTIVE SUMMARY

WBS 1.2.1.5, Special Studies
1) J. Blink, ACD Project Engineer for Thermal Integration, prepared a white paper on thermal loading for the YMSCO Project Manager. The white paper provided background and a succinct problem definition.

WBS 1.2.2.1, Waste Package Coordination and Planning
1) R. Van Konynenburg of Lawrence Livermore National Laboratory coordinated an LLNL review of the draft Los Alamos National Laboratory report by C. Bowman and F. Venneri, entitled 'Underground Supercriticality from Plutonium and Other Fissile Material".

WBS 1.2.2.4.1, Spent Fuel
1) Two semi-static scoping dissolution tests at Pacific Northwest Laboratory (PNL) under Lawrence Livermore National Laboratory sponsorship were terminated. These tests of partially oxidized specimens of Turkey Point PWR spent fuel in J-13 well water were started in 1986 and last sampled in June 1990. Water chemistry and radionuclide analyses of the test solutions were completed. A preliminary evaluation of the results suggests that they are reasonably consistent with those from the first four years of the study, which were reported in 1990. The x-ray diffraction results, for some black powder that was not originally present in the fuel specimens, indicate the presence of UO_2 and U_4O_{9+x}, but no U_3O_8 or other uranium-bearing phases. The scanning electron microscope results showed that the powder consisted almost entirely of individual grains 10 to 30 μm in size. One of the specimens contained a few particles composed, in part, of U, Ca, and Si. It is clear that oxidation followed by long exposure to J-13 well water so weakened the grain boundaries of these spent fuel specimens that they can now be easily fragmented into individual grains. However, it would be premature to assume that similar behavior might be possible under repository conditions. For one thing, the oxidation was rather severe: exposure to air at 250°C for 45 and 116 hours, respectively, for the two specimens. Whether unoxidized fuel, or fuel oxidized at lower temperatures, would show a similar weakening of grain boundaries after long-term exposure to water has not yet been established.

2) Two irradiated PWR fuels, ATM-103 and ATM-106, are being tested at Argonne National Laboratory under Lawrence Livermore National Laboratory sponsorship, in three types of unsaturated tests (high drip rate, low drip rate, and vapor). The fuel in the tests has undergone 31 months of reaction at 90°C. The leachate was sampled and a fuel

Table 12. Average Unprecipitated Fractions (%) for Unsaturated High Drip-Rate versus Saturated Tests

	U	Pu	Am	Cm	Cs
ATM-103 (275 d)[a]	50	40	50	70	98
ATM-103 (100 d)[b]	N.A.[c]	59	<1	2	96
ATM-106 (275 d)[a]	20	50	10	30	60
ATM-106 (100 d)[b]	N.A.	2	2	1	94
Wilson (540 d)[d]	10	5	3	3	85

[a]This is total time for first two test intervals.
[b]Fourth test interval.
[c]N.A. = not yet available.
[d]Reference 12; bare fuel for three test periods at 85°C.

Table 13. Maximum Fraction (%) for Unsaturated High Drip-Rate versus Saturated Tests

	U	Pu	Am	Cm	Cs
ATM-103 (275 d)[a]	1(-5)	1(-6)	6(-4)	7(-3)	6(-4)
ATM-103 (100 d)[b]	N.A.	9(-5)	1(-3)	4(-3)	2(-2)
ATM-106 (275 d)[a]	5(-5)	3(-5)	9(-5)	2(-4)	1(-3)
ATM-106 (100 d)[b]	N.A.	1(-5)	4(-5)	1(-4)	2(-2)
Wilson (540 d)[c]	1(-4)	1(-4)	2(-4)	4(-5)	1(-2)
Werme[d]	1(-4)	---	---	---	8(-3)

[a]This is total time and total fractions for first two test intervals.
[b]Fourth test interval.
[c]Reference 12; bare fuel for three test periods at 85°C.
[d]Reference 10.

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ANL-94/42

Yucca Mountain Project – Argonne National Laboratory Annual Progress Report, FY 1994

by J. K. Bates, J. A. Fortner, P. A. Finn, D. J. Wronkiewicz,
J. C. Hoh, J. W. Emery, E. C. Buck, and S. F. Wolf

1995

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TABLE 3
Rates of Dissolution, and Precipitation and Convection in J-13 Well Water (Eqs. 3–4)

	Dissolution Rate (Flow-through Tests)		Dissolution Rate (Electrochemical Tests)	Rates of Precipitation and Convection (Semi-static Tests)	
	25°C	85°C	25°C	25°C	85°C
Uranium	$(0.3 \sim 1.2) \times 10^{-6}$ g/day [a](70)	[b](91)	$(10^{-8} \sim 10^{-3})$ g/day [c](74,75)	$\sim 1.5 \times 10^{-6}$ g/day [d](15)	$\sim 8.8 \times 10^{-6}$ g/day [d](15)

[a]Dissolution rates were normalized over the surface area of 205 cm^2 to compare with those from immersion tests. Dissolution rates for 20–250 days are used.

[b]Direct measurements were not made at 85°C in J-13 well water containing approximately 2×10^{-3} M bicarbonate ions and other constituents. Indirect data were obtained in pure carbonate/bicarbonate solutions. Approximately 3.4 and 21.3 times the dissolution rates increased by raising temperature from 23–75°C in 2×10^{-2} and 2×10^{-4} M carbonate/bicarbonate solutions, respectively, without minor pH corrections.

[c]Dissolution rates are from UO_2 tests in chloride solutions. Values vary significantly, depending on corrosion potentials under various oxidizing conditions, including the radiation effects.

[d]Cycle 2 tests for 180 days were corrected, based on Tc-99 releases, to exclude any undissolved fuel grains from the stripping process of the altered layer on SF surfaces. Cycle 2 tests were retests of first-cycled samples that had been placed in new leachant, after removing the altered layer.

Flow-through test results with the J-13 well water at 85°C are not available. Therefore, values measured in two different carbonate/bicarbonate solutions are given in Table 3 for an indirect comparison.

Using a constant dissolution rate in Table 3, and approximately 10 g/cm^3 of SF density (15), the SF matrix of approximately 0.03 mm at 25°C and approximately 0.2 mm at 85°C of the SF matrix will dissolve within 10,000 years. If each grain is exposed and dissolved, the radionuclide release will be facilitated because of the small size of each grain. For instance, Wilson suggested intergranular attack near SF surfaces (15,77). If SF is subjected to groundwater drip conditions, the groundwater chemistry in an aqueous film on SF surfaces may be altered (63,65). Additionally, the role of backfill in the alteration of groundwater chemistry is largely unknown. Considering a) that the average size of SF particles is in the order of mm (15,78); b) that the average grain size is in the order of 10 μm (35,78); c) the regulatory limit of C-14, 0.1 Ci/MTHM (3); and total inventory of C-14 in the SF matrix, 0.53 Ci/MTHM (8–11), the aforementioned 0.2 mm dissolution of the SF matrix can be significant.

Contrary to the aforementioned postulate of linear time law, there is a possibility that non linear time law may govern the SF matrix dissolution in a geological period. For the aforementioned postulate of linear time law, the amount of precipitated uranium determined in immersion tests has appeared to be the same as that of uranium dissolved in flow-through tests. However, there are uncertainties about the amount of precipitated materials. For example, the analyzed precipitated materials could have been comprised of undissolved fuel grains from the stripping process of the altered layer on the SF surfaces (15). The real amount of precipi-

tated materials could have been smaller. Similar arguments can be made for radiolysis effects. Then, the dissolution of SF matrices could have slowed down gradually as the altered layer became an effective (aqueous or solid-state) diffusion barrier as time elapses. In the presence of diffusion barriers, radionuclide releases are likely to slow down significantly, during long-term SF performance.

Because detailed mechanisms for diffusion-barrier effectivensss are not well-understood, we present a phenomenological description of the diffusion-limited kinetics of the SF matrix dissolution, as

$$R_{dis,d} = kS \, (t + a)^{-\frac{1}{n}}, \qquad [5]$$

where S and t represent surface area of the dissolving phase and time respectively; k, a, and n are constants; and n is an integer. In many problems of diffusion-limited kinetics, we expect $n = 2$; however, the various geometries involved are likely to result in other n values, too. For instance, precipitated materials on SF surfaces may vary the surface "S" in a time-dependent manner. This will lead to the effective n value other than 2 (e.g., $n = 3$ or 1). Assuming that Eq. 5 represents the dissolution rates of SF matrices, we conducted a sample calculation for the long-term dissolution of the SF matrix. We took the transient data of flow-through tests (70) showing a gradual decrease of the dissolution rates of SF matrices. Fitting the transient data to Eq. 5 with $n = 2$ determined k and a values. The numerically determined Eq. 5 was extrapolated to a geological period. The extrapolated values of the amount of the dissolved SF matrix were far less (by

Pergamon

ORIGINAL CONTRIBUTION

LONG-TERM C-14 SOURCE TERM FOR A HIGH-LEVEL WASTE REPOSITORY

Tae M. Ahn
U.S. Nuclear Regulatory Commission, Washington, DC 20555-0001, U.S.A.

ABSTRACT. This paper evaluates the possibility of long-term Carbon-14 (C-14) releases from spent fuels and containers in the anticipated environments of the proposed Yucca Mountain high-level waste repository. Long-term degradation mechanisms of spent fuel matrices, cladding, and containers are evaluated. Under dry conditions, formation of higher oxides, such as U_3O_8, may lead to significant C-14 releases from the spent fuel matrix. It is unclear whether there will be significant C-14 releases from lower oxidation to $UO_{2.4}$ or from the unoxidized matrix. Under aqueous dissolution conditions, C-14 releases from the spent fuel matrix can be significant. Under aqueous dissolution or dry conditions, it is unlikely that there will be significant C-14 releases from cladding, unless severe localized corrosion takes place. In considering containers and cladding as metallic barriers, we discuss qualitatively various factors governing total C-14 containment inside metallic barriers. C-14 releases can be delayed, even by the formation of small through-wall pits in metallic barriers. Although we do not have completely definitive information yet, it is clear that the spent fuel matrix, cladding, and containers can serve as important barriers to C-14 releases from waste packages in a repository environment.

INTRODUCTION

Currently, the United States has one proposed repository site for high-level nuclear waste (HLW). The proposed site is Yucca Mountain, in the southwestern corner of the Nevada Test site (1); following are characteristics of the site: a) the static water level at Yucca Mountain is approximately 530 m below the surface; b) the host rock is a densely welded, devitrified tuff, with some lithophysal cavities; c) the rock is estimated to contain approximately 5% water, by volume, with a porosity of approximately 12%; and d) the repository horizon is fractured with an average fracture density, 0.8–3.9 fractures per meter. Currently, it is planned that the repository be located in a horizon above the water table. Among the advantages of locating a reposi-

tory in this so-called unsaturated zone is less severe corrosion of waste packages, because of the small amount of water. The current planning is that only two forms of U.S. HLW may go into a tuff repository—spent fuel (SF), from commercial light-water nuclear reactors (LWRs), and HLW glass. The HLW glass is a borosilicate glass containing high levels of fission products from reprocessing commercial SF and from liquid HLW accumulated from three defense installations.

The U.S. Department of Energy (DOE) is responsible for the safe disposal of HLW in Yucca Mountain. DOE's disposal implementation is under the licensing authority of the U.S. Nuclear Regulatory Commission and the applicable environmental standards of the U.S. Environmental Protection Agency (EPA). Current rules mandate:

1. that substantially complete containment of radionuclides within the waste packages be ensured for the first 300–1000 years after the emplacement of waste packages and that the release of any radionuclide from the engineered barrier system (EBS) be controlled so as not to exceed 1 part per 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years after permanent closure (i.e., 10 CFR 60.113, Nuclear Regulatory Commission (NRC)

Transmit Confirmation Report

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No.            :    007
Receiver       :    915093769781
Transmitter    :    NRC/NMSS/DWM
Date           :        May 14'97    14:41
Time           :    03'24
Mode           :        Norm
Pages          :    09
Result         :    OK
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UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

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* * * * * * * * * *

1. __Walter Gray__   FAX #: __509-376-9781__
   LOCATION: __PNL__   VERIFY: _____

2. _____/_____   FAX #: _____/_____
   LOCATION: _____/_____.   VERIFY: ____/_____

Walter:

In the report, dissolution rates in J-13 well water and in carbonate solution are the same. The attached is a selected data base from your NWTRB presentation

Tae

NUMBER OF PAGES __8__   PLUS COVER SHEET

FROM: __T. Ahn,_____

PHONE: __301-415-5812__   MAIL STOP: _____

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

NUCLEAR WASTE TECHNICAL REVIEW BOARD
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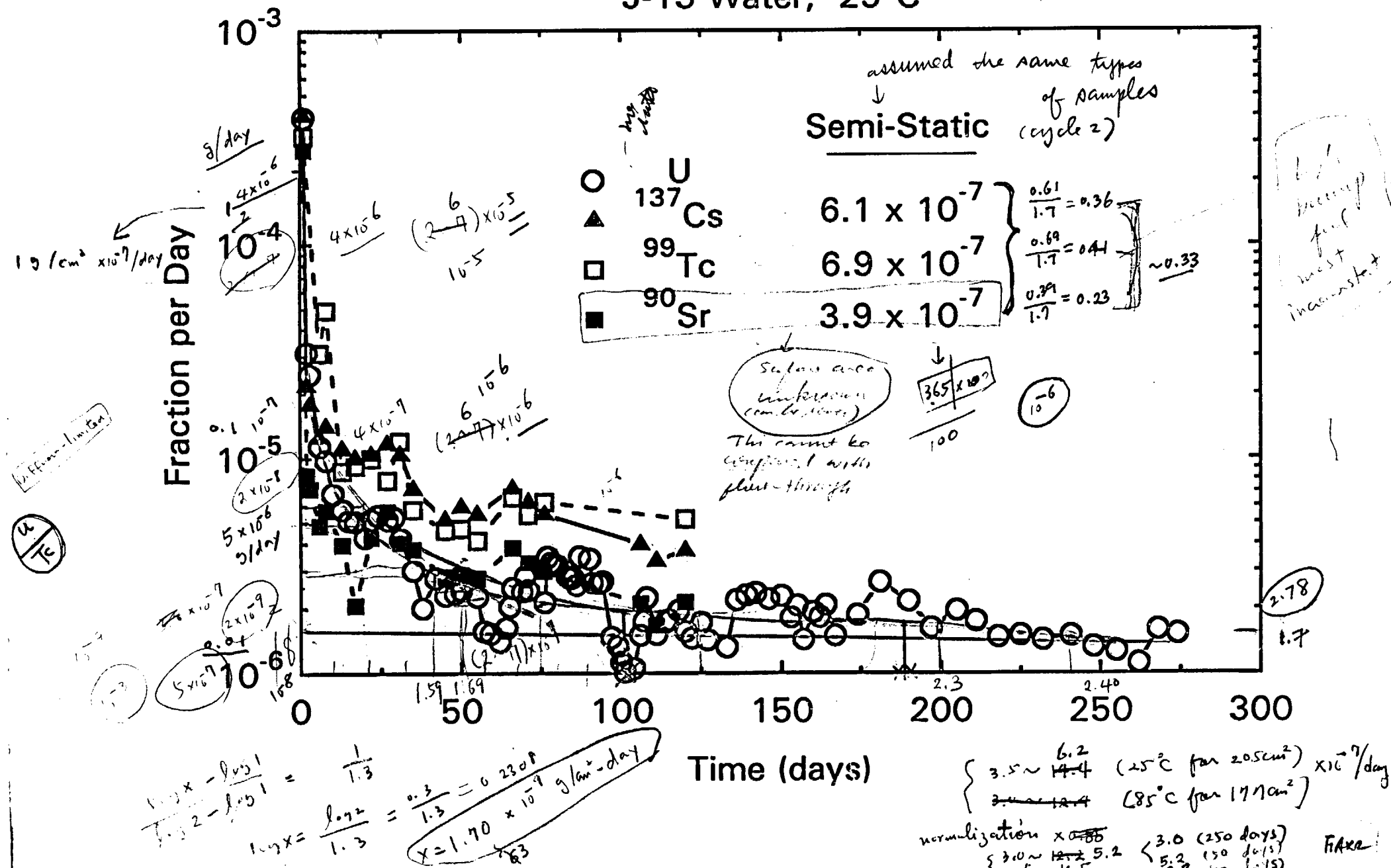**SUBJECT:** **DISSOLUTION TESTING OF SPENT FUEL**

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PRESENTER'S TELEPHONE NUMBER: (509) 376-9693

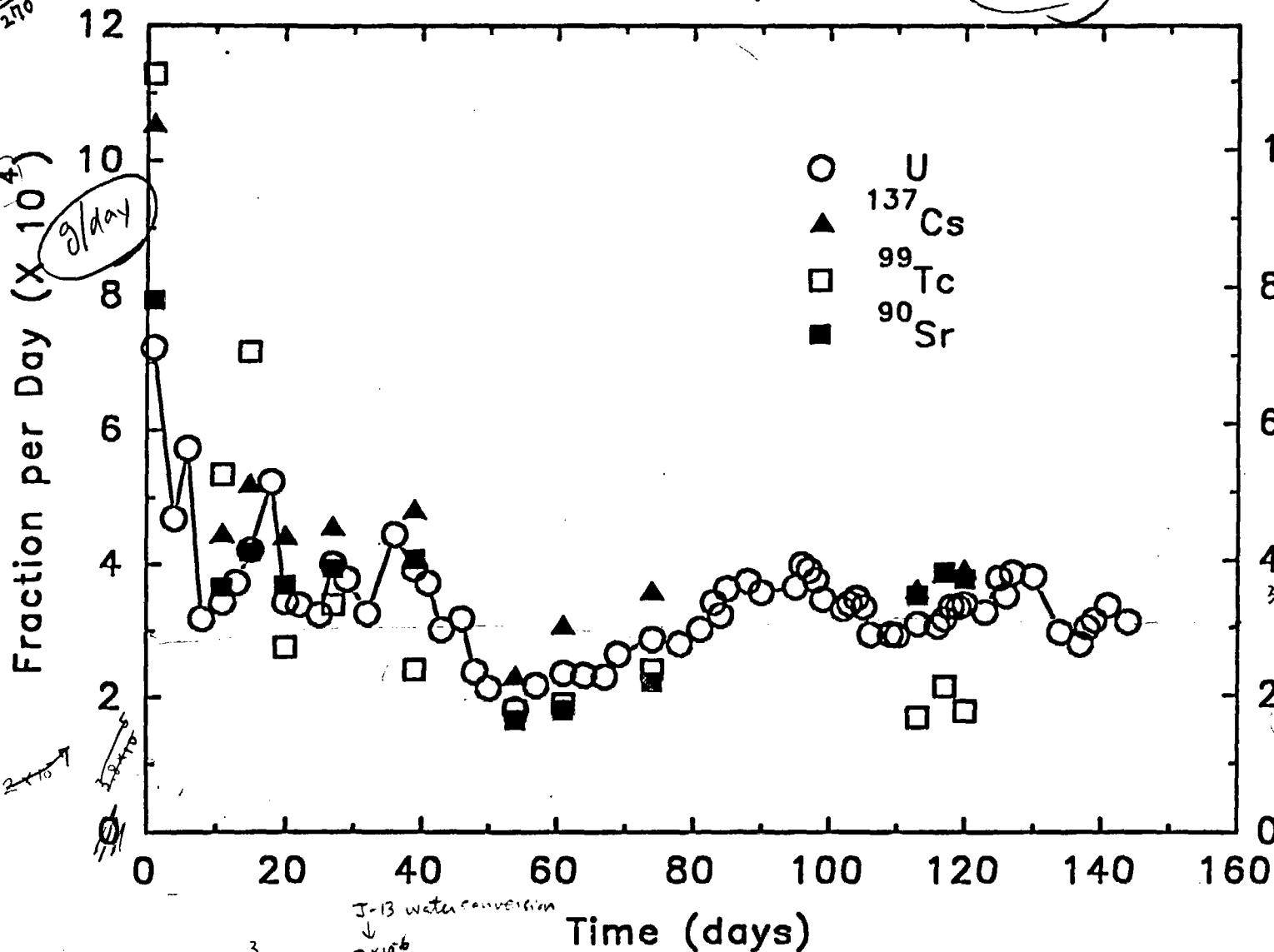**PLAZA SUITE HOTEL • LAS VEGAS, NEVADA**
OCTOBER 14 - 16, 1992

FULL

Spent Fuel Dissolution Rates
J-13 Water, 25°C

assumed the same types
↓   of samples
Semi-Static (cycle 2)
_____

		Semi-Static	
O	U		
▲	^{137}Cs	6.1×10^{-7}	$\frac{0.61}{1.7} = 0.36$
☐	^{99}Tc	6.9×10^{-7}	$\frac{0.69}{1.7} = 0.41$
■	^{90}Sr	3.9×10^{-7}	$\frac{0.39}{1.7} = 0.23$

~0.33

Y axis: Fraction per Day — 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}

X axis: Time (days) — 0, 50, 100, 150, 200, 250, 300

Surface area unknown (controlled)

This cannot be compared with flow-through

$\frac{365 \times 10^{2}}{100}$

10^{-6}

2.78

1.7

2.3   2.40

g/day
$\frac{4 \times 10^{-6}}{2}$

4×10^{-6} $(\frac{6}{2.7}) \times 10^{-5}$ 10^{-5}

$1 \, g/cm^2 \times 10^{-7}/day$

$0.1 \, 10^{-7}$

diffusion-limited

2×10^{-6}

5×10^{-6} g/cm

4×10^{-7} $\frac{6}{2.7} \times 10^{-6}$ $(\frac{6}{2.7}) \times 10^{-6}$

$\frac{U}{Tc}$

$\frac{76}{10^{-7}}$ 2×10^{-9}

2.04 5×10^{-7}

$(\frac{2}{9.7}) \times 10^{-6}$

1.59 1.69

$\frac{\log x - \log 1}{\log 2 - \log 1} = \frac{1}{1.3}$

$\log x = \frac{\log 2}{1.3} = \frac{0.3}{1.3} = 0.230 \beta$

$x = 1.70 \times 10^{-9} \, g/cm^2-day$

$\{ 3.5 \sim \frac{6.2}{14.4} \,(25°C \text{ for } 20.5 cm^2) \} \times 10^{-7}/day$

$\{ (85°C \text{ for } 177 cm^2)$

normalization $\times$

$\{ 3.0 \sim 5.2 \, \{ 3.0 \,(250 \text{ days})$
$5.3 \,(150 \text{ days})$

FIXER

Dissolution Rate of Fuel Grains

20 mM Carbonate, pH = 8, 25°C

$$NLi = \frac{C_i}{F_i \cdot (SA/V)}$$

$$F_i = \frac{238}{238+32} = \frac{238}{270} = 0.881$$

Fraction per Day (X 10⁴) → written as Fraction per Day ($\times 10^4$)

g/day

g/day

6

U Normalized Rate (mg/m²/day) → U Normalized Rate ($mg/m^2/day$)

Legend:
- O U
- ▲ ^{137}Cs
- □ ^{99}Tc
- ■ ^{90}Sr

$\frac{10^{-3} g / 10^4 cm^2}{10^{-7} g / cm^2}$ $10^{-4} cm/day$

3.91

3.65 × 10⁶

3.65 × 10⁻²

2.00

10^{-6} 2×10^{6}

J-13 water conversion

$3 \times 10^{-7} g / cm^2 \times \frac{cm^3}{11 g} \times (\frac{2 \times 10^6}{3 \times 10^4})$

$\rightarrow 1.8 \times 10^{-10} cm/day$ for 10,000 years : $1.8 \times 10^{-10} \times 10^4 \times 3.65 \times 10^2 = 6.6 \times 10^{-3} cm$

6.57×10^{-6}

6.57×10^{-3}

1 mm

fraction

Time (days) — axis 0 to 160
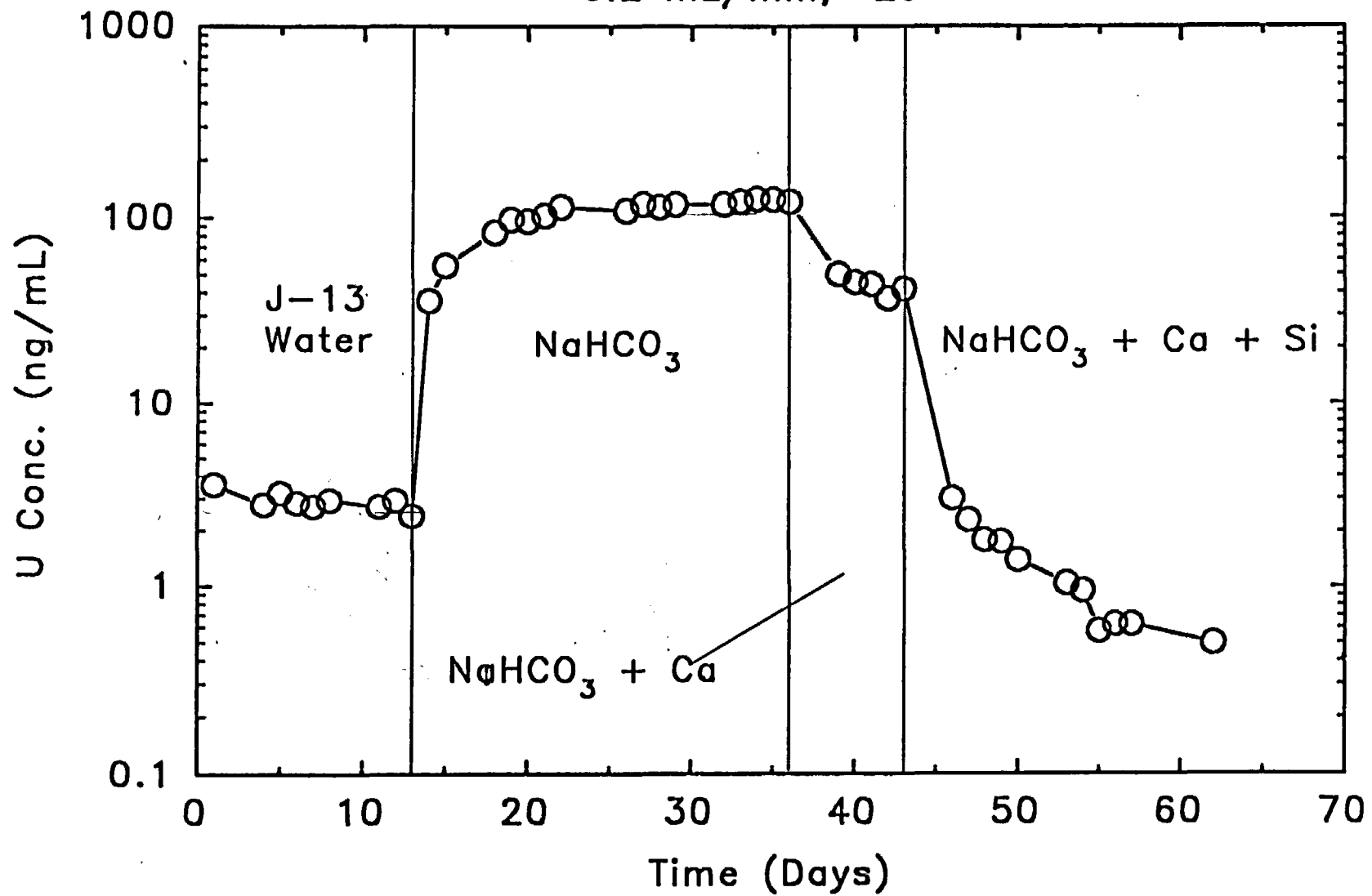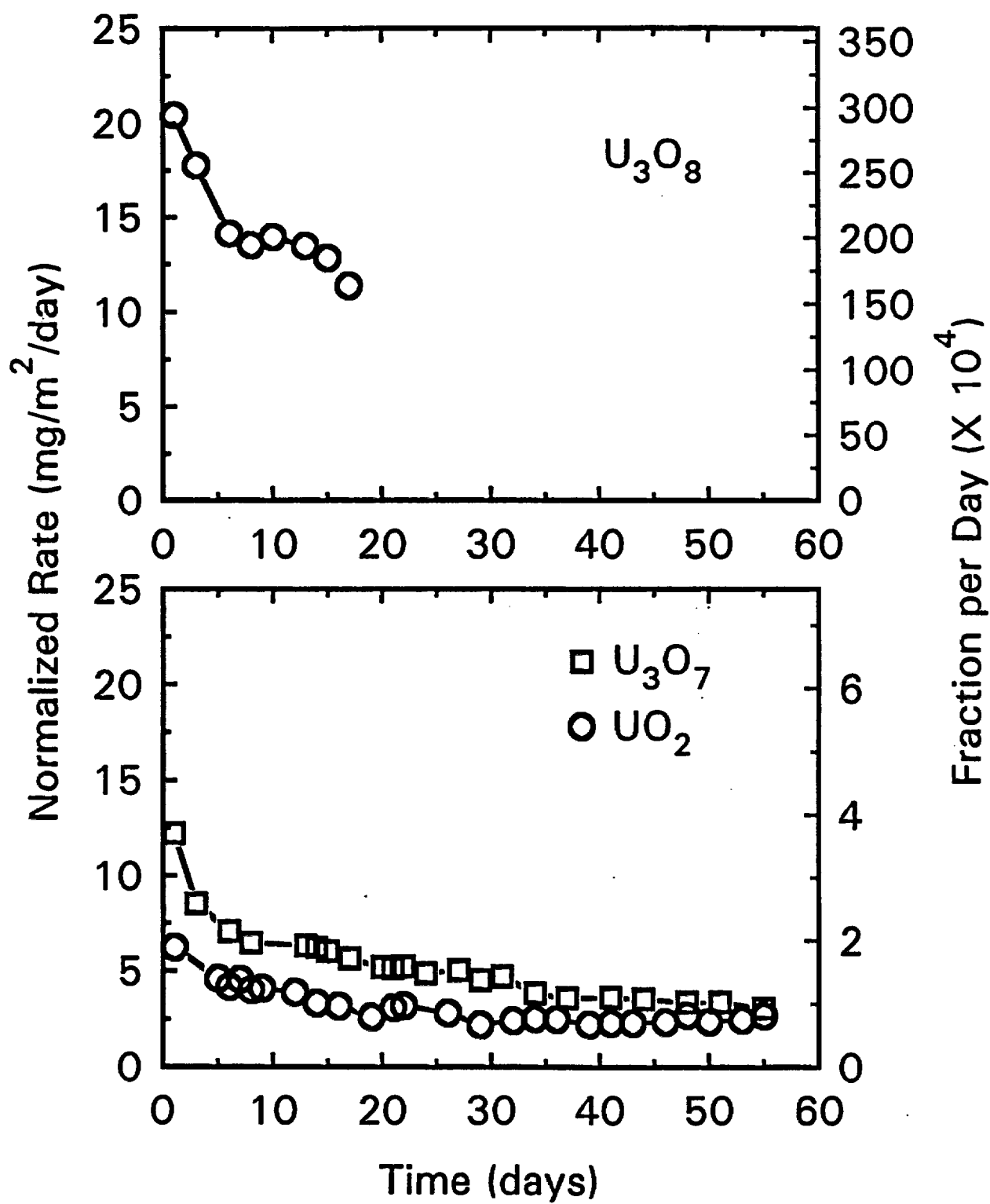
Spent Fuel Dissolution Rates
J-13 Water, 25°C

assumed the same types
of samples
(j.f. 2)

↓

Semi-Static

○	U	
▲	^{137}Cs	6.1×10^{-7}
□	^{99}Tc	6.9×10^{-7}
■	^{90}Sr	3.9×10^{-7}

$\frac{0.61}{1.7} = 0.36$

$\frac{0.69}{1.7} = 0.41$

$\frac{0.39}{1.7} = 0.23$

~0.33

y-axis: Fraction per Day

10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}

x-axis: Time (days)

0, 50, 100, 150, 200, 250, 300

FAX

Dissolution Rate of Fuel Grains
20 mM Carbonate, pH = 8, 25°C

$$\dot{z} = \frac{C_i}{\dot{R}_i \cdot (SA/V)}$$

$$\frac{238}{238+32} = \frac{238}{270} = 0.881$$

Legend:
- ○ U
- ▲ ^{137}Cs
- □ ^{99}Tc
- ■ ^{90}Sr

Y-axis (left): Fraction per Day ($\times 10^4$)
Y-axis (right): U Normalized Rate ($mg/m^2/day$)
X-axis: Time (days)

GAX3
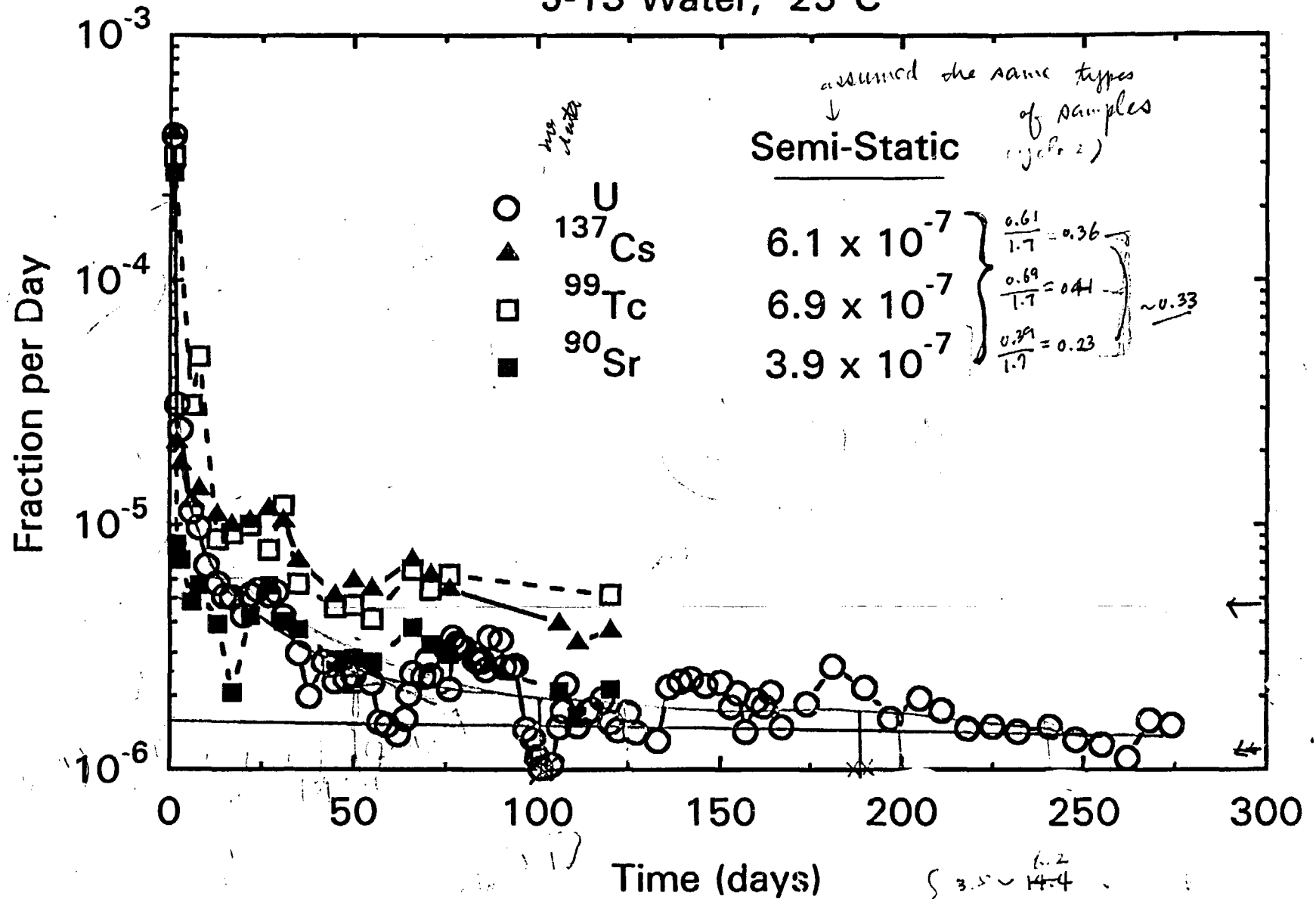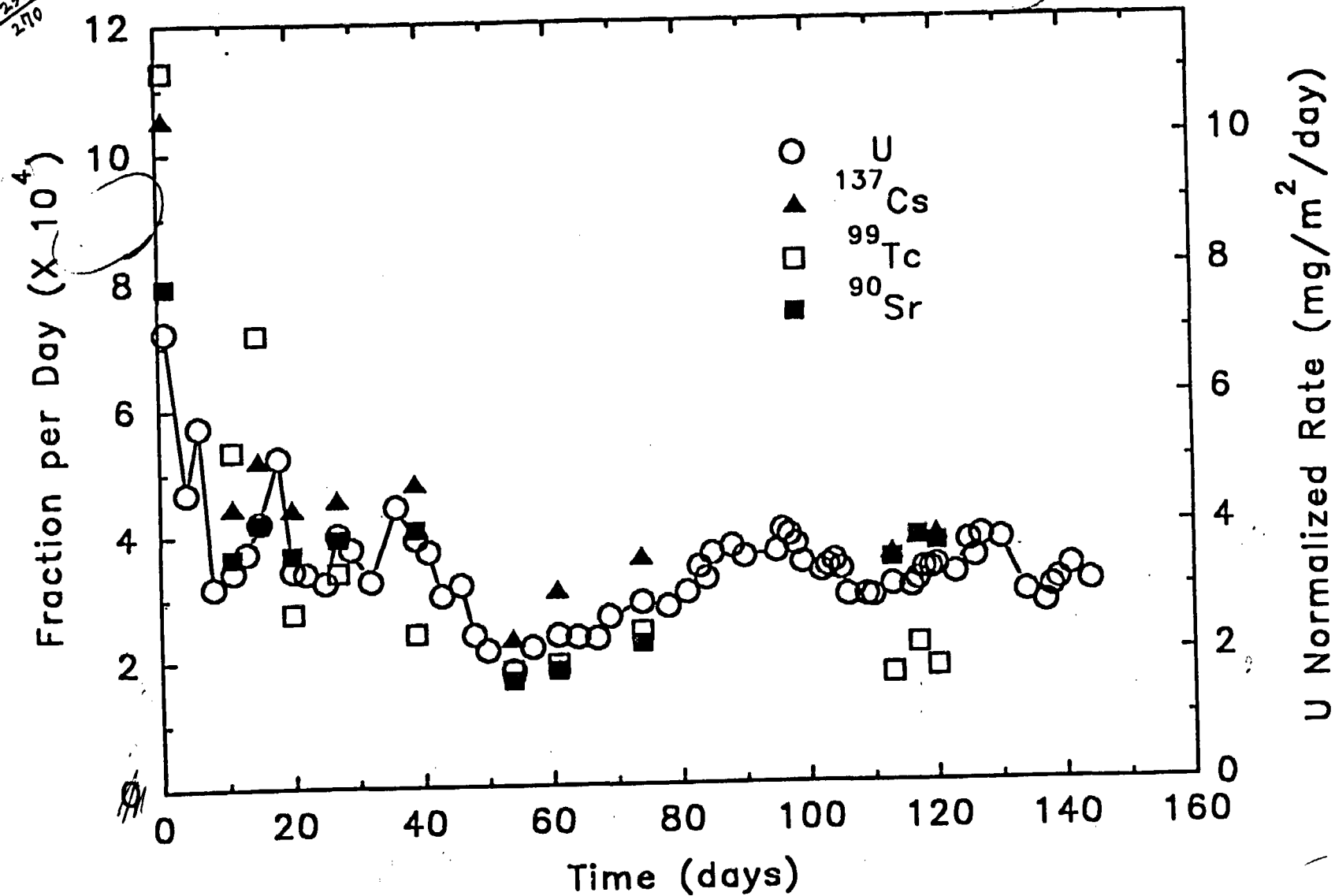
Flow–Through Test with UO$_2$
0.2 mL/min, 25°C

Dissolution Rate of Unirradiated Specimens
20 mM NaHCO$_3$, pH = 8
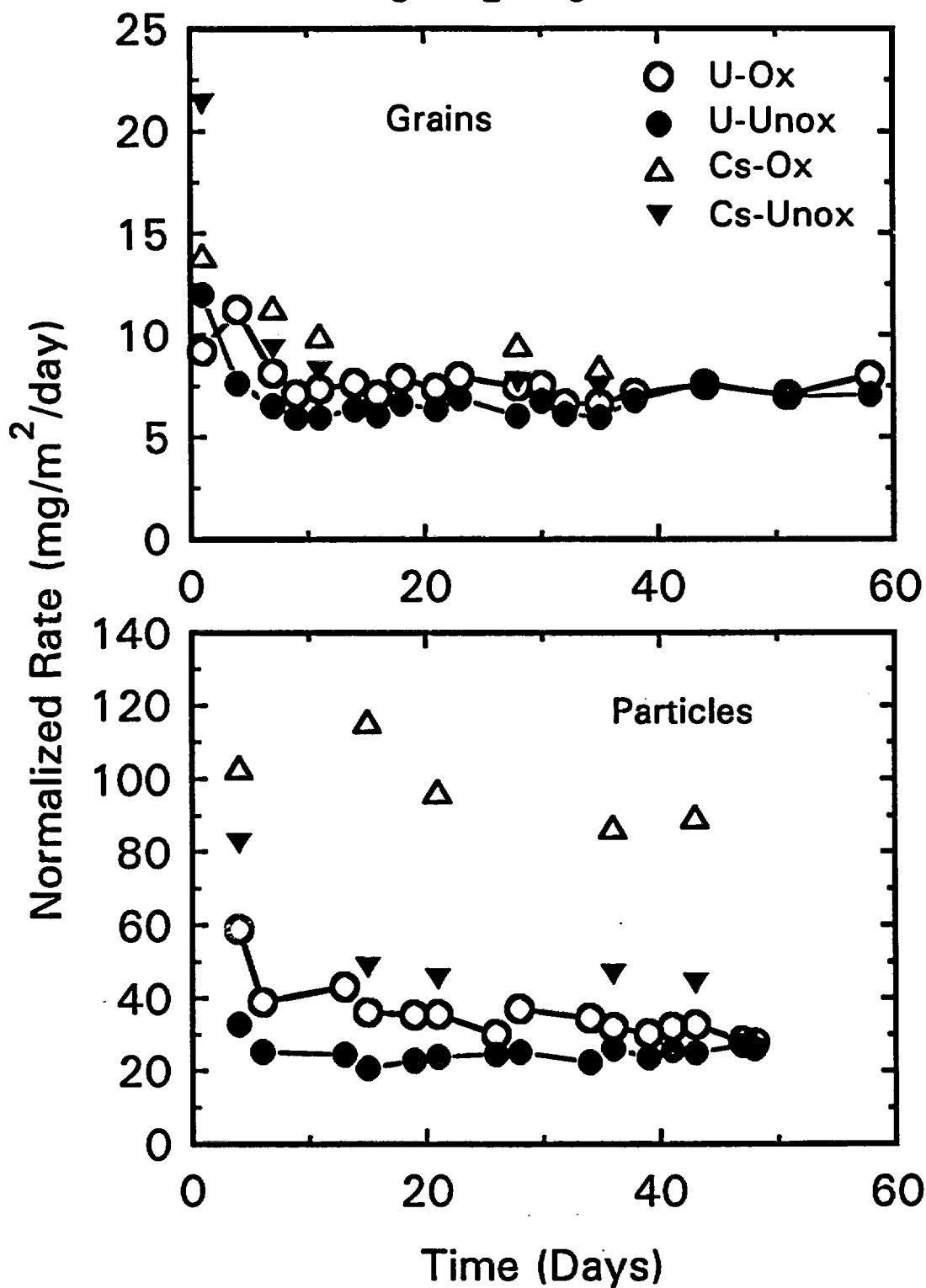
U Dissolution Rate
20 mM NaHCO$_3$, pH = 8

Legend:
- ■ Spent Fuel
- ○ UO$_2$

Y-axis: U Normalized Rate (mg/m^2/day)

X-axis: Time (days)

ŪAx6
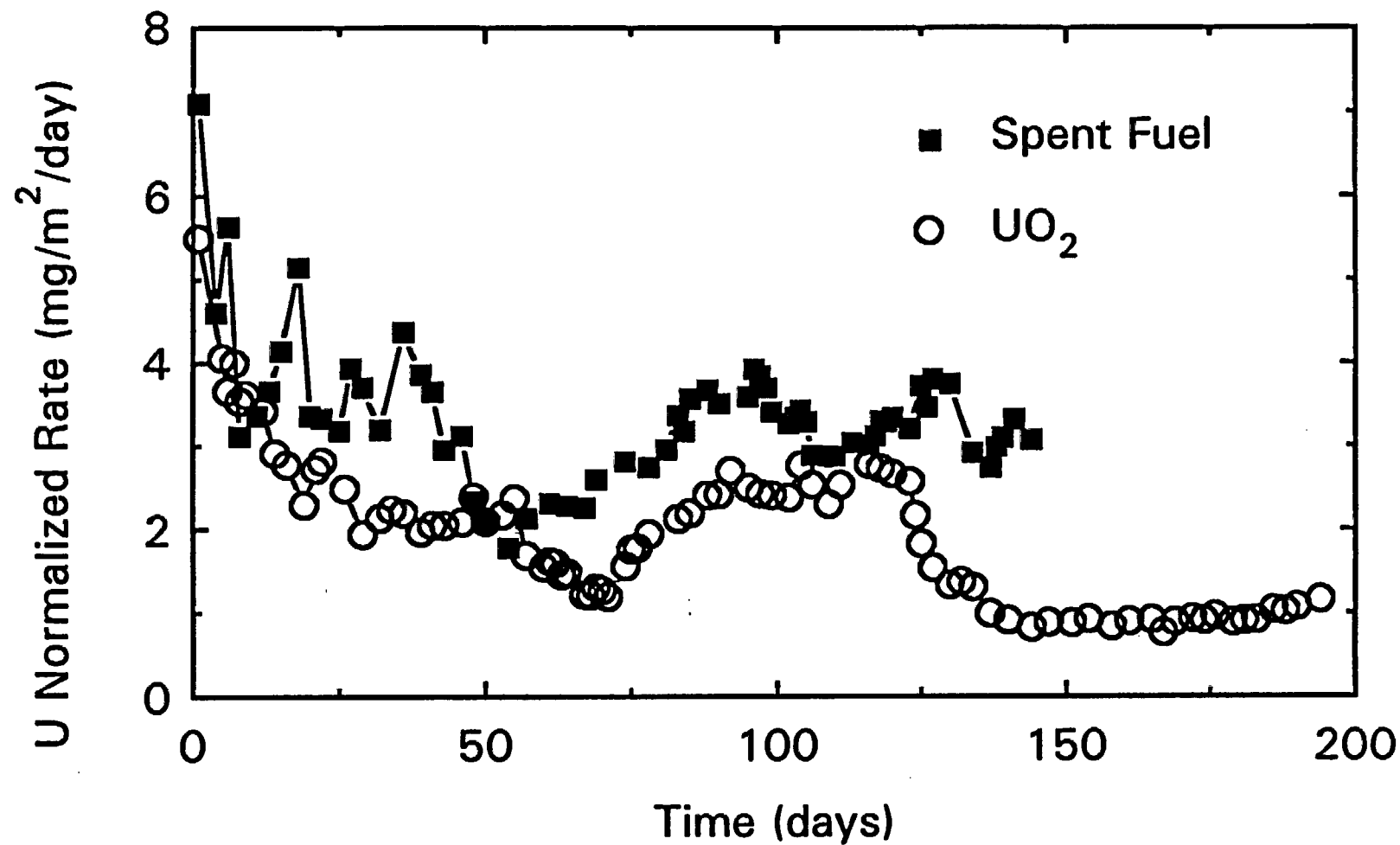
Dissolution Rate of Unirradiated Specimens
0.2 mM Na$_2$CO$_3$, 0.2% Oxygen, pH = 10

$\square$ U$_3$O$_7$

$\bigcirc$ UO$_2$

Normalized Rate (mg/m^2/day)

Time (days)
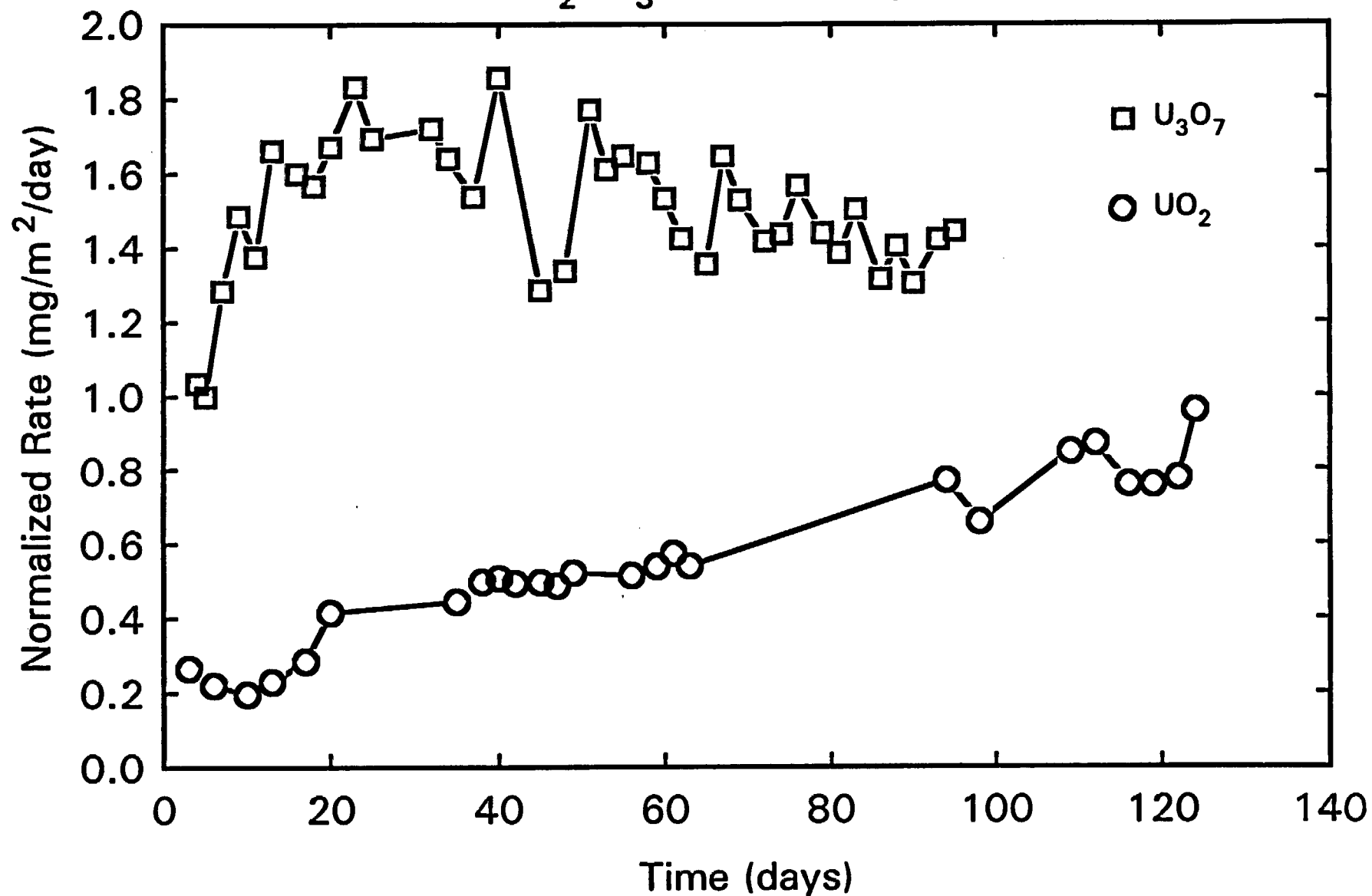
Spent Fuel Dissolution Rates
2 mM NaHCO$_3$/Na$_2$CO$_3$, pH = 9, 50°C

OVERALL OBJECTIVE

Provide experimental source-term data and models that can be used to help predict the potential for release of radionuclides from a repository in the unlikely event that spent fuel is contacted by groundwater.

BACKGROUND

- Over 98% of the 1000-year radioactive inventory in spent fuel is Am and Pu.

    * Release will be controlled by solubility (or possibly colloidal transport).

- Release of soluble radionuclides (^{99}Tc, ^{135}Cs, ^{129}I) will be controlled by two separate mechanisms because of the heterogeneous nature of spent fuel.

    * Rapid release of Cs and I (0.1 to 20% of total inventories) from gap and grain boundaries.

    * Long-term release of soluble radionuclides contained within the UO_2 matrix of spent fuel will be controlled by the dissolution rate of that matrix.

PWR Spent Fuel Radionuclide Inventories at 1,000 Years

Radionuclide	Half-Life (years)	1,000-Year Activity (% of Total)	Cumulative Activity (%)
^{241}Am	432	51.3	51.3
^{243}Am	7,380	1.8	53.1
^{240}Pu	6,570	27.4	80.5
^{239}Pu	24,100	17.5	98.0
^{242}Pu	375,800	0.10	98.1
^{238}Pu	88	0.06	98.1
^{99}Tc	213,000	0.75	98.9
^{135}Cs	2,300,000	0.020	
^{129}I	15,700,000	0.0018	

Soluble Fission-Product Release from UO_2 Fuel in Water Under Oxidizing Conditions
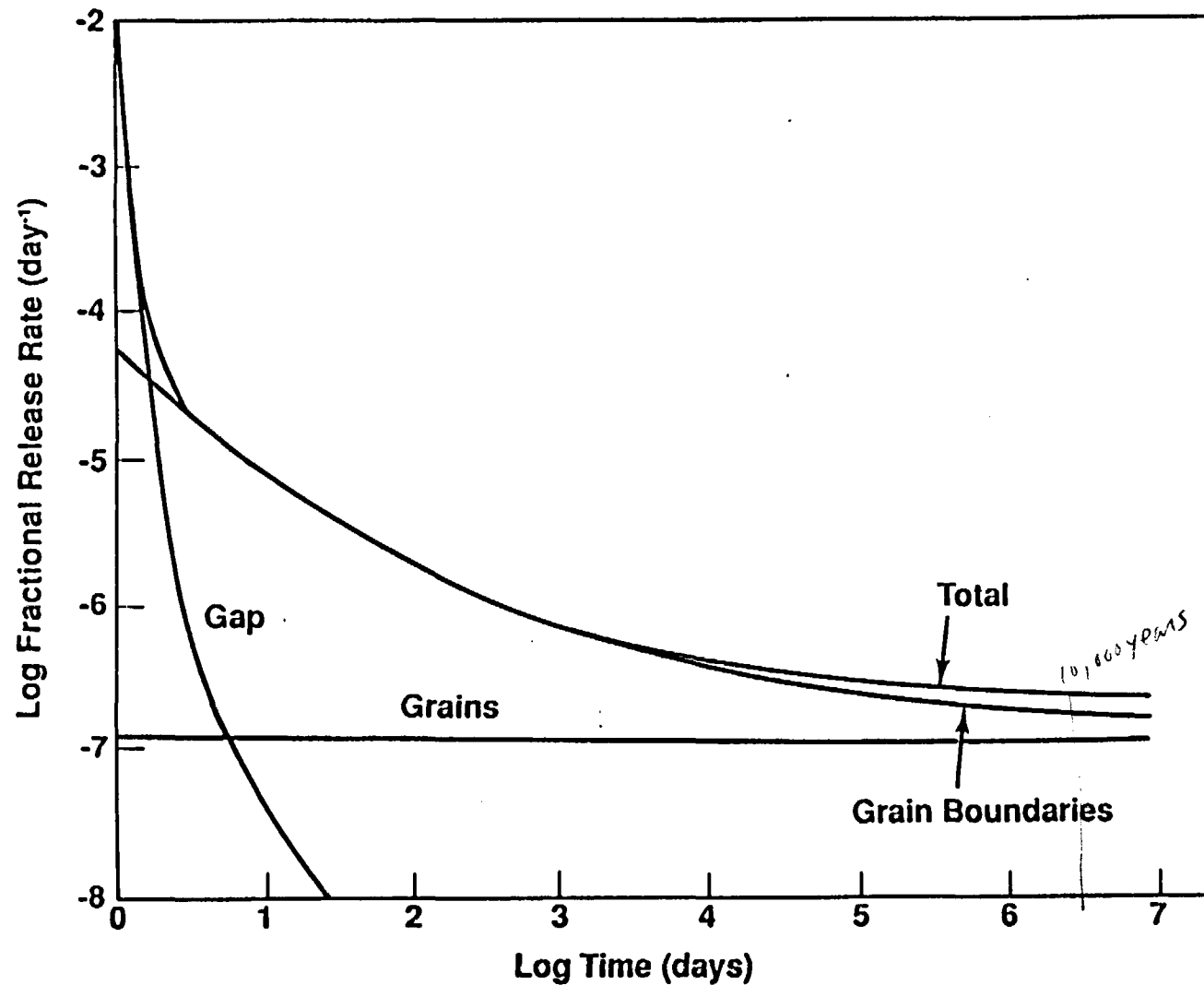
L. H. Johnson, N. C. Garisto, and S. Stroes-Gascoyne, in Waste Management '85, Vol. 1--High-Level Waste, pp. 479-482.

DATA NEEDS/MOTIVATION

- Thermodynamic data for key solid/solution reactions involving low-solubility radionuclides.

  * These radionuclides constitute most of the activity in spent fuel, and solubility will control their release unless colloids make an important contribution.

- Experiments to determine the nature and importance of actinide-bearing colloids.

- Gap inventories and grain-boundary inventories of soluble radionuclides.

  * YMP assumes immediate dissolution of gap and grain-boundary inventories upon contact by water--inventories must be measured.

DATA NEEDS/MOTIVATION (Continued)

- Demonstration that spent fuel matrix dissolves congruently.

  * YMP assumes matrix dissolution controls dissolution of soluble radionuclides--this needs verification.

- Kinetics of spent fuel matrix dissolution as a function of water chemistry and fuel condition.

  * Spent fuel dissolution mechanism is poorly understood.

  * The effect of prior oxidation on dissolution is unknown.

  * A better understanding of these factors is needed to predict the long-term release of soluble radionuclides.

ACCOMPLISHMENTS FY 1987 - 1992

- Completed three series of semi-static spent fuel dissolution tests; the first in deionized water; the second and third in J-13 water.

  * Results are documented in HEDL-TME 84-30, PNL-7169 and PNL-7170

- Developed methods for:

  * Preparing separated fuel-grain specimens, thus exposing grain boundaries and allowing inventories of radionuclides concentrated therein to be measured.

  * Conducting flow-through dissolution-rate measurements.

- Measured gap and grain-boundary inventories of Cs, Tc, and Sr -- only two different fuels tested to date.

- Showed that spent fuel grains dissolve nearly congruently -- only three different fuels tested to date.

- Showed importance of Si and Ca in test solutions.

Summary of Results for Artificially Defected Cladding

- ^{137}Cs concentrations 2 to 4 times lower from defected rods compared to bare fuel tests.

- ^{99}Tc concentrations 20 to 40 times lower from defected rods compared to bare fuel tests.

- Actinide concentrations 100 to 1000 times lower from defected rods compared to bare fuel tests.

Annual Release Rates at 25°C in J-13 Water
as Fraction of 1,000-Year Inventories

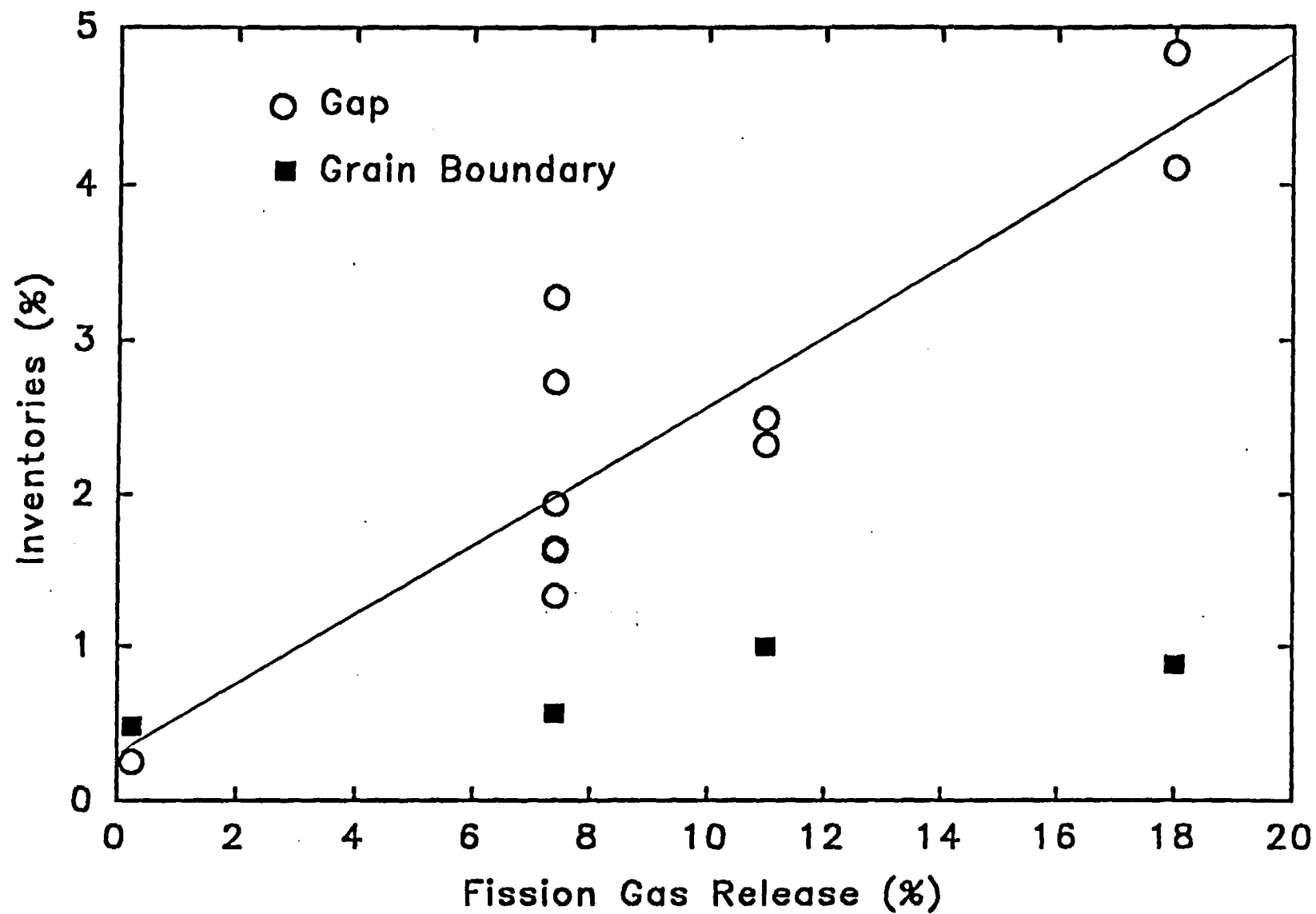| Actinide	log(Release Rate)[*]
U	-8.6
Np	-8.8
Pu	-9.0
Am	-9.1

---

[*]   Assumes water flow rate of 20 L/Yr per waste package containing
3140 kg of 33 MWd/kgM PWR fuel.

$Pu\ (239 + 240)$ $7.44 \times 10^2 \mu Ci/g \times 3.14 \times 10^6 g = 23.4 \times 10^2 Ci$

$5 \times 10^2 Ci \quad (20\%)$

$\dfrac{100 Ci/MTHM}{\times 10^4\ years\ \times 10^{-9}}$

check

Cs Gap and Grain Boundary Inventories

Tc & Sr Gap and Grain Boundary Inventories

Spent Fuel Dissolution Testing

Sample/Waste Collection

Specimen Column

Controlled- Flow Pump

Feed Water Container

Gas Cylinder Fixed O_2, CO_2 Concentration
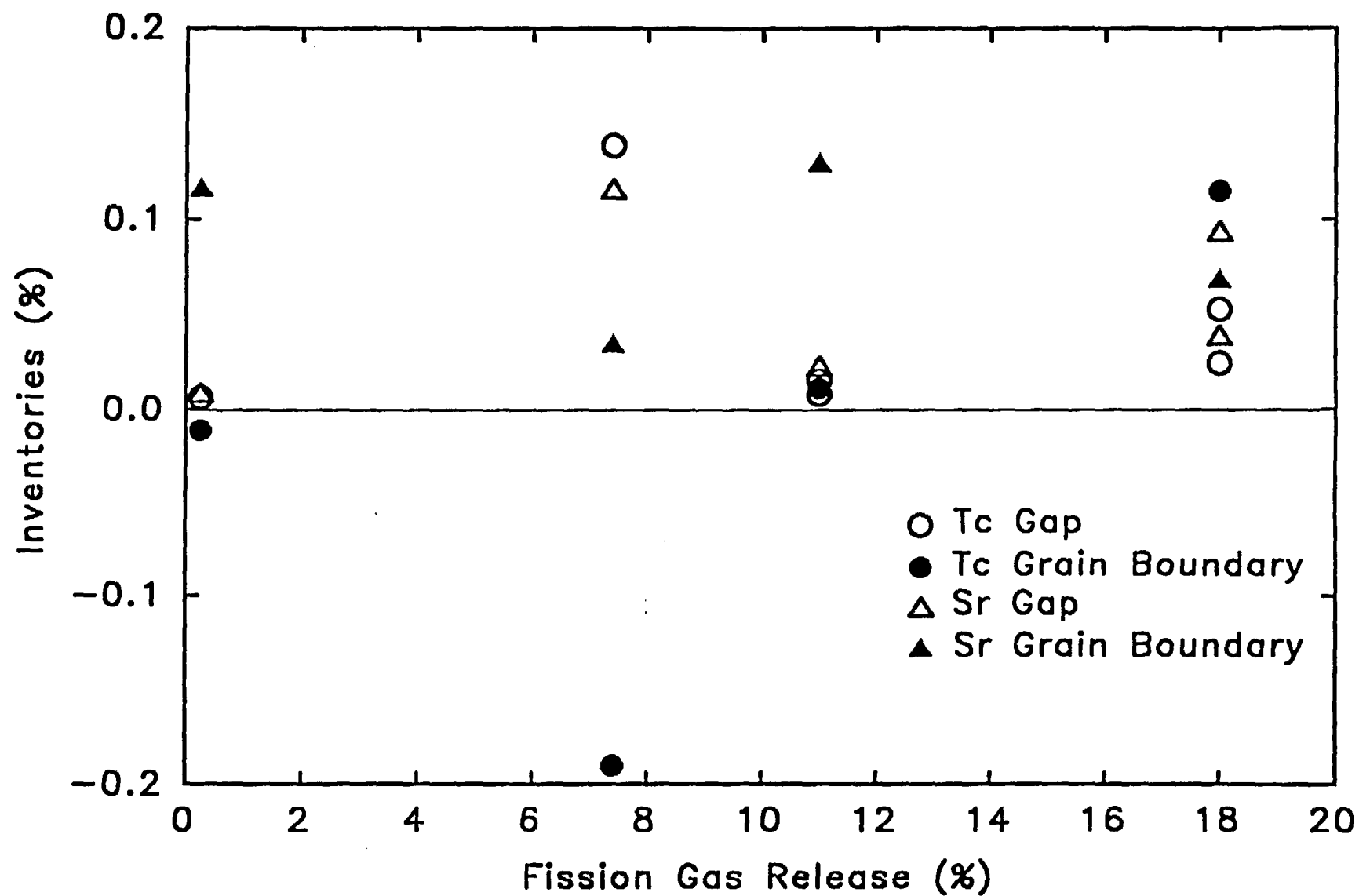
Radiochemical Analyses:
- U by Laser Fluorimetry
- [137]Cs by Direct Gamma Counting
- [90]Tc and ^{90}Sr by Chemical Separation Followed by Beta Counting
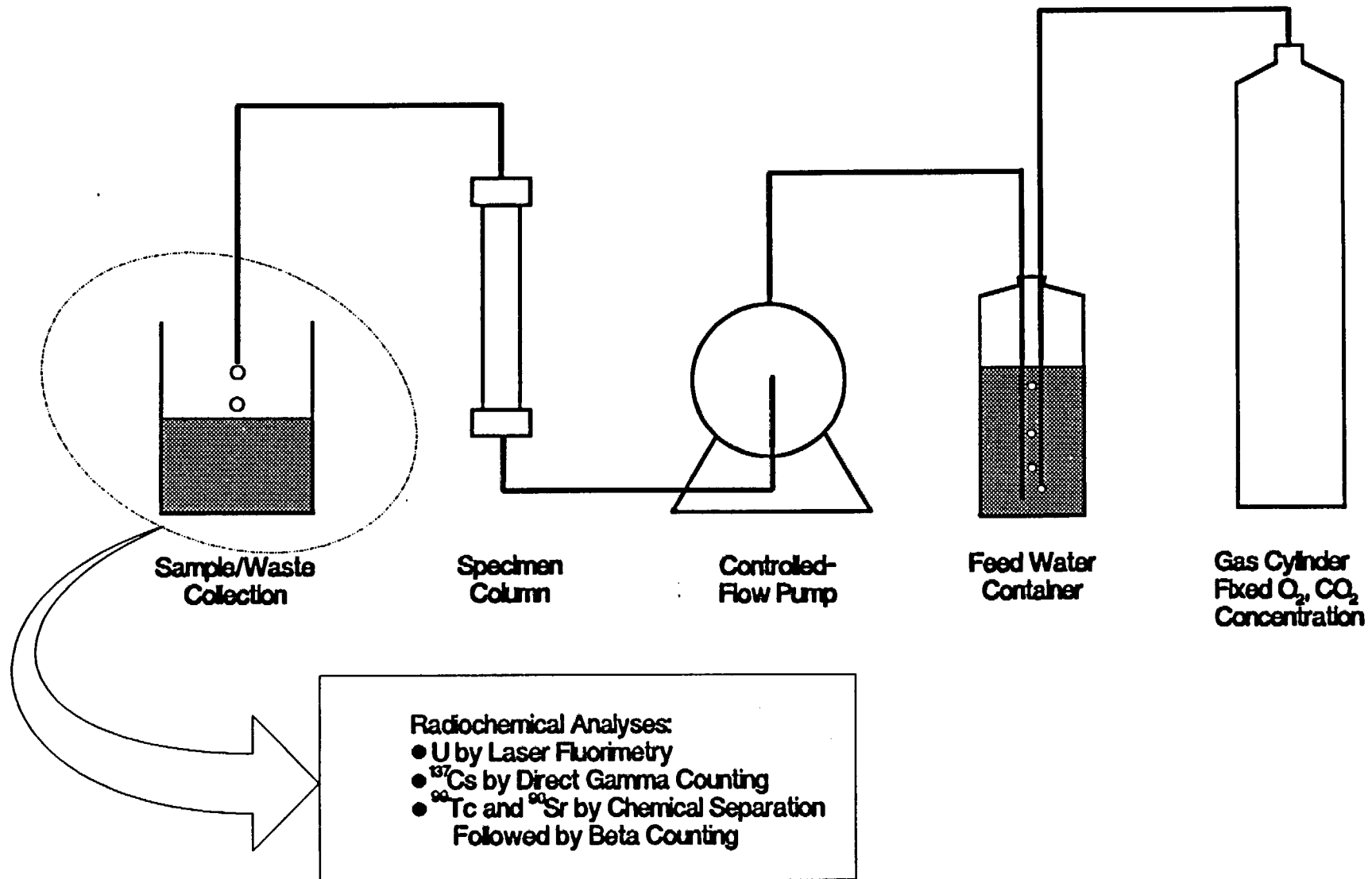
Flow Rate Data for Fuel Grains
20 mM Carbonate, pH = 8, 25°C

Y-axis: U Conc. (ng/mL)

X-axis: 1/Flow (min/mL)

$500 \times 10^{-9} \times 144$

$= 7.2 \times 10^{-5}$

$\frac{1}{10}$ mL/min

$= \frac{1}{10} \times 60 \times 24$

$= 144$ mL/day

0.1 mL/min

6 mL/hr

144 mL/day

52.6 L/365
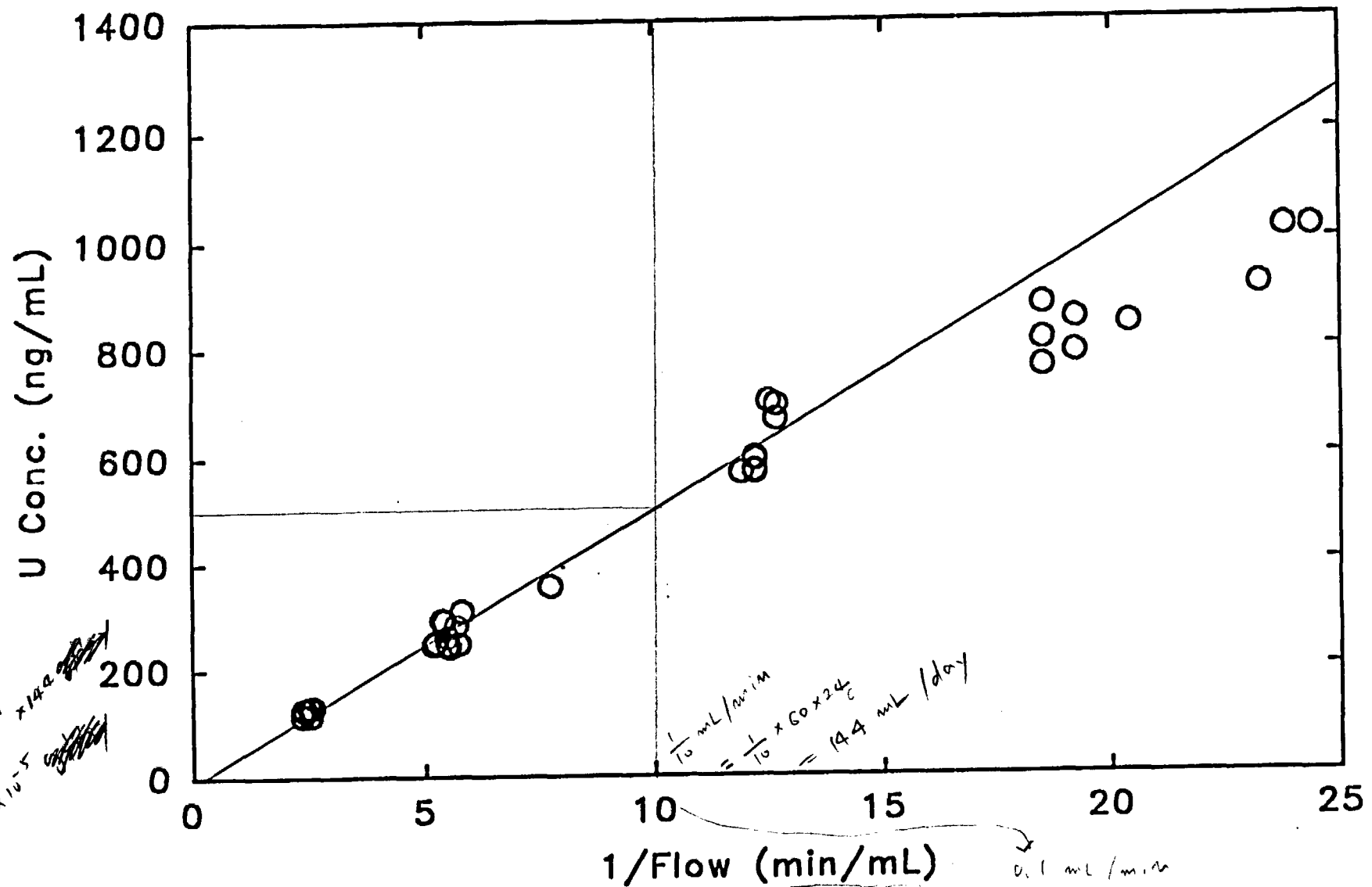
ACCOMPLISHMENTS '87 - '92 (Continued)

● Developed dissolution test matrix (UO_2 at LLNL; spent fuel at PNL) to investigate:

    * temperature (25 to 75°C)
    * carbonate/bicarbonate concentration (2×10^{-4} to 2×10^{-2} $\underline{M}$)
    * pH (8 to 10)
    * oxygen fugacity (20% to 0.2%)

ACCOMPLISHMENTS '87 - '92 (Continued)

- For a limited number of fuels and test conditions, showed that dissolution rates of unirradiated UO_2 and spent fuel up to burnup of 50 MWd/kgM are roughly equal.

- For one fuel and one test condition, showed that dissolution rates of spent fuel oxidized to U_4O_{9+x} ($UO_{2.4}$) are roughly equal to those of unoxidized fuel.

- For one test condition, showed that dissolution rates of unirradiated UO_2 and U_3O_7 are roughly equal.

- For one test condition, showed that dissolution rates of unirradiated U_3O_8 are much higher than UO_2.

- For one fuel and one test condition, demonstrated that flow-through fractional dissolution rates are not substantially different from those in semi-static tests.

SUMMARY OF ACCOMPLISHMENTS

- Showed that solubility constraints are likely to limit release of actinides (over 98% of total activity) to far less than 1 part in 100,000 per year unless colloids make an important contribution.

- Developed method for measuring grain-boundary inventories and showed, for the two fuels tested, that the inventories of Cs, Sr, and Tc are quite small.

- Developed method for measuring the dissolution rate of the UO_2 matrix in spent fuel and demonstrated (only 3 fuels) that it dissolves congruently.

- For a very limited number of fuels and test conditions, showed that oxidation (up to $UO_{2.4}$ and U_3O_7) and burnup (unirradiated up to 50 MWd/kgM) have little effect on dissolution rates under the conditions tested.

SUMMARY OF ACCOMPLISHMENTS (Continued)

- For a single fuel and test condition, showed that dissolution rates in flow-through tests are not substantially different from those observed in semi-static (more repository relevant) tests.

- Showed that the presence of Si or Ca in test solutions has an important influence on dissolution rates.

- Embarked on systematic test program to determine the effects of various parameters on the dissolution rate of the UO_2 matrix of spent fuel.

GOALS FOR FY-1993 AND BEYOND

1) Generate thermodynamic data for key solid/solution reactions involving low-solubility radionuclides.

2) Work to identify solid phases that control the solubilities of the actinides under expected repository conditions.

3) Develop experiments to determine the nature and importance of actinide-bearing colloids.

GOALS (Continued)

4) Gap and grain-boundary inventory measurements.

- Extend measurements to a variety of fuels to correlate inventories with other fuel parameters such as burnup and fission gas release.

5) Flow-through dissolution-rate measurements.

- Measure dissolution rates for spent fuel oxidized beyond $UO_{2.4}$.

- Measure dissolution rates for oxidized spent fuel under other water chemistry test conditions. Also test additional oxidized fuels.

- Complete current test matrix with UO_2 and spent fuel.

- Expand test matrix to include Si, Ca, and waste package corrosion products.

- Extend measurements to gadolinia fuels and fuels with very high burnup.

PUBLICATIONS

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C. N. Wilson and H. F. Shaw, "Experimental Study of the Dissolution of Spent Fuel at 85°C in Natural Ground Water." <u>Sci. Basis for Nucl. Waste Management X</u>. Vol. 84, ed. J. K. Bates and W. B. Seefeldt, pp. 123-130. Materials Research Society, Pittsburgh, PA, 1987.

C. N. Wilson, "Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests." <u>Sci. Basis for Nucl. Waste Management XI</u>. Vol. 112, ed. M. J. Apted and R. E. Westerman, pp. 473-483. Materials Research Society, Pittsburgh, PA, 1988.

C. N. Wilson, <u>Results from NNWSI Series 2 Bare Fuel Dissolution Tests</u>, PNL-7169, Pacific Northwest Laboratory, Richland, WA, 1990.

C. N. Wilson, <u>Results from NNWSI Series 3 Spent Fuel Dissolution Tests</u>, PNL-7170, Pacific Northwest Laboratory, Richland, WA, 1990.

C. N. Wilson and W. J. Gray, "Effects of Water Composition on the Dissolution Rate of UO$_2$ Under Oxidizing Conditions." <u>High Level Radioactive Waste Management Proceedings of the First International Conference</u>. pp. 1431-1436. American Nuclear Society, Inc. La Grange Park, Il, 1990.

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C. N. Wilson and W. J. Gray, "Measurement of Soluble Nuclide Dissolution Rates from Spent Fuel." Sci. Basis for Nucl. Waste Management XIII. Vol. 176, ed. V. M. Oversby and P. W. Brown, pp. 489-498. Materials Research Society, Pittsburgh, PA, 1990.

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W. J. Gray and D. M. Strachan, "UO_2 Matrix Dissolution Rates and Grain-Boundary Inventories of Cs, Sr, and Tc in Spent LWR Fuel." Sci. Basis for Nucl. Waste Management XIV. Vol. 212, ed. T. A. Abrajano, Jr. and L. H. Johnson, pp. 205-212. Materials Research Society, Pittsburgh, PA, 1991.

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W. J. Gray, L. E. Thomas, and R. E. Einziger, "Effects of Air Oxidation on the Dissolution Rate of LWR Spent Fuel." To be presented at the XIV International Symposium on the Scientific Basis for Nuclear Waste Management, November 30 - December 4, 1992 in Boston, MA.