See file pocket 6 for enclosure 5

NRC-NNWSI PROJECT WASTE PACKAGE MEETING SUMMARY
July 23-24, 1985

WM Record File 102

WM Project 11
Docket No.
PDR ✓
LPDR ✓

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rec'd 8/30/85

Lawrence Livermore National Laboratory
Livermore, CA 94550

Attendees

A list of attendees and their organizational affiliations is attached as Enclosure 1.

Background/Facts

An agenda is attached as Enclosure 2. Copies of the viewgraphs used in the NNWSI presentations and in the NRC presentations are attached as Enclosures 3 and 4 respectively.

Observations

The NRC had the following observations:

1. The NNWSI waste package development program has made notable progress in a number of areas since the last NNWSI-NRC waste package meeting, which was held in October, 1983. Among the areas where progress is especially evident are the types of corrosion experiments on the container materials (but see observation 4 regarding the materials being tested), which may potentially lead to the necessary mechanistic understanding of the corrosion processes.

2. The overall strategy that will enable the NNWSI waste package to be part of a successful license application for a geological repository has not yet been defined; hence, although much good research is being done, it appears to be very preliminary - scoping and screening - rather than focused toward specific licensing concerns. Furthermore, the efforts of individual investigators appear to be largely independent of each others' activities: there seems to be a lack of integration in the program. The NRC suggests that the following steps need to be taken promptly:

   - The NNWSI define their waste package design bases and explain the rationale for selecting those bases;

   - The NNWSI define the range or envelope of environmental parameters which are to be used for testing;

   - The NNWSI then identify the data and develop the test plans needed to demonstrate that the waste package design will be capable of meeting the applicable NRC and EPA regulations. These test plans should include methods and models to allow extrapolation from short-term tests to 300-1000 years.

3. As mentioned in the first observation, the conceptual design bases have not been specified and need to be promptly. When this is done, the emphasis should be on making the specified bounding conditions sufficiently conservative that the design envelope will encompass the waste package environment as it is better and better defined by newly gathered field data. If this is not done, the license application may be significantly delayed while testing of a modified waste package design is carried out.

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4. Despite NRC concerns expressed during the 1983 NNWSI/NRC workshop, the NNWSI continues to treat austenitic stainless steels as the reference canister materials. Given the problems of austenitic stainless steels with respect to failure mechanisms such as pitting, stress corrosion cracking, and transgranular stress corrosion cracking, in particular in chloride environments, the NRC believes that the NNWSI is extremely unlikely to be at a point by the time of license application submittal, to convince the NRC that an austenitic stainless steel waste package will meet the Part 60 containment performance objective. Serious consideration should be given to changing the emphasis from austenitic stainless steels to materials such as high-Ni alloys, which have fewer well-documented failure mechanisms.

5. The NNWSI strategy for extrapolation from short-term results to long-term containment has not been delineated. The NRC suggests that elements of such an endeavor should include testing of a conservative design based upon an understanding of plausible failure mechanisms given the waste package environment, followed by post-emplacement confirmatory testing.

6. The suggestion voiced by the NNWSI that there may not be enough water in the waste package environment for chloride-related corrosion to be a problem is based upon the USGS's current estimate of 1 mm/yr groundwater flux in the unsaturated zone. The NRC considers such an approach non-conservative and likely to jeopardize the success of the DOE's license application. The 1 mm/yr flux estimate is not well-established at this time (see NRC comments on the Yucca Mountain Draft Environmental Assessment for a detailed discussion of this point). Furthermore, the amount and effects of chloride-bearing steam are presently unknown.

7. The NRC is concerned about the ability of the NNWSI to validly extrapolate spent fuel dissolution results to long time intervals. Given the variability in spent fuel rods of the same type, and different behaviors of spent fuel rods of different types, it is essential that the NNWSI expand their test matrix such that it embraces enough samples to develop a supportable data base.

The NNWSI had the following observations:

1. Agendas for future meetings should not be so ambitious. Need to allow more time for discussions; will encourage more participation. Complex agendas involve too many people.

2. NNWSI recognizes the need for an integrated project wide position on quantitative design basis (including environmental conditions) for the waste package. This design basis will also guide the formulation of scenarios for the PAP.

3. No specific guidance was received in relation to implications of an MRS on the NNWSI waste package design. The current status of the MRS studies preclude obtaining any guidance regarding possible scenarios or role.

4. NNWSI appreciates the statement of rationale with respect to "excluded materials" i.e., free liquids, combustible materials, and chemically reactive materials. Prior to this meeting, it appeared that the NRC had not considered "water-logged" fuel in this requirement.

5. NNWSI agrees with the NRC comments regarding the need for complete QA records for all aspects of primary License Application Data and the need for appropriate statistical analysis of these data bases.

6. Waste Acceptance Criteria issues will be addressed by the recently DOE Headquarters directed Waste Acceptance Process and Committee.

7. NNWSI understands that the NRC has taken an action item to provide Generic guidance on the intent of the Part 60 role provisions for analysis of performance under expected and unanticipated conditions. DOE/HQs said they would pursue this on a Generic basis with the NRC.

8. NRC reviewed their presentation on a numerical interpretation of "Substantially Complete Containment." DOe/HQ will encourage the formulation of a technical position on this subject by the NRC.

9. Hydrothermal Analysis of Waste Package environment is in progress. The effect of these results on the waste package thermal analysis will be evaluated in the future.

10. Structural Analysis failure criteria (1-D 40% plastic) was questioned. Application of triaxial, large deformation properties will be evaluated.

11. Some NRC representatives indicated strong skepticism of successfully demonstrating that any austenitic stainless steel can be shown to meet the containment requirement. Their concern is based upon the large number of containment limiting corrosion mechanisms and uncertainties in the credible environmental conditions surrounding the waste package. They suggested NNWSI consider the highly Ni based materials in order to eliminate some of these mechanisms.

12. NNWSI recognizes the need for a more thorough analysis of the possible mechanisms for concentrating ionic species in water which may contact the container following rehydration of the near field environment and to determine the maximum credible concentrations.

Agreements

1. The NRC and NNWSI reached a mutual understanding that explosive, pyrophoric, and chemically reactive materials and free liquid allowable in the waste package is restricted in 10 CFR Part 60 to amounts that can be demonstrated not to compromise the integrity of the waste package. Hence, the presence of these materials in a waste package, e. g., water in spent fuel rods, would be permissible if an analysis can establish that conservatively estimated quantities of these materials which may be present is nonthreatening to the integrity of the waste package.

2. The meeting was successful in meeting the objectives established beforehand by the NRC and the NNWSI.

Open Items

Much of the spent fuel dissolution test data, plans, calculations, and models presented by the NNWSI at this meeting have not been published. The NRC proposes that a future meeting be organized on this specific topic after the NRC has had an opportunity to provide the NNWSI with a detailed review of this material following its publication.

The NRC will provide the NNWSI with a detailed review of the NNWSI's recently published report on the "unsaturated test."

The NRC will provide the NNWSI with guidance on the emphasis that should be placed on the analysis of performance under anticipated and unanticipated conditions required in 10 CFR Part 60 relative to that to be placed on the 10 CFR Part 60 performance objectives.

Vern Witherill
Waste Management Project Office
DOE/NV
July 25, 1985

Newton K. Stablein
Division of Waste Management
US NRC
July 25, 1985

Enclosure 1

Rec'd w/ ltr. rec'd 8/30/85 - Attendees

Attendees
NNWSI/NRC WASTE PACKAGE MEETING
July 23, 1985

Mark Frei	US DOE/HQ
Michael Valentine	US DOE/LV
Vern Witherill	US DOE/LV
Kang Ku Wu	US DOE/SRPO
Cesar Sastre	Brookhaven National Laboratory
Don Schweitzer	Brookhaven National Laboratory
Peter Soo	Brookhaven National Laboratory
Terry Sullivan	NRC/Brookhaven National Laboratory
Daniel Van Rooyen	Brookhaven National Laboratory
Kenneth W. Stephens	NRC/Aerospace
Linda A. Kovach	NRC
Tim Johnson	NRC
Tom Jungling	NRC
Michael McNeil	NRC
King Stablein	NRC
Everett Wick	NRC
Ed Escalante	National Bureau of Standards
C. G. Interrante	National Bureau of Standards
Gary K. Jacobs	Oak Ridge National Laboratory
A. D. Kelmas	Oak Ridge National Laboratory
Susan K. Whatley	Oak Ridge National Laboratory
John K. Bates	Argonne National Laboratory
S. J. Basham	Battelle-ONWI
Paul McConnell	Fracture Control Corp.
R. P. Anantatmula	Rockwell/BWIP
Denny Jones	University of Nevada, Reno
Evelyn Gause	Weston
Lyn Ballou	Lawrence Livermore National Laboratory
Denny Becker	Lawrence Livermore National Laboratory
John Dronkers	Lawrence Livermore National Laboratory
Bob Glass	Lawrence Livermore National Laboratory
William Glassley	Lawrence Livermore National Laboratory
Linda Hansen	Lawrence Livermore National Laboratory
Dan McCright	Lawrence Livermore National Laboratory
Bill O'Connell	Lawrence Livermore National Laboratory
Virginia Oversby	Lawrence Livermore National Laboratory
Larry Ramspott	Lawrence Livermore National Laboratory
Michael Revelli	Lawrence Livermore National Laboratory
Edward Russell	Lawrence Livermore National Laboratory
Bonnie Smith	Lawrence Livermore National Laboratory

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Enclosure 1

Attendees
NNWSI/NRC WASTE PACKAGE MEETING
July 24, 1985

Mark Frei	US DOE/HQ
Michael Valentine	US DOE/LV
Vern Witherill	US DOE/LV
Kang Kun Wu	US DOE/SRPO
Cesar Sastre	Brookhaven National Laboratory
Don Schweitzer	Brookhaven National Laboratory
Peter Soo	Brookhaven National Laboratory
Terry Sullivan	NRC/Brookhaven National Laboratory
Daniel Van Rooyen	Brookhaven National Laboratory
Kenneth W. Stephens	NRC/Aerospace
Linda A. Kovach	NRC
Tim Johnson	NRC
Tom Jungling	NRC
Michael McNeil	NRC
King Stablein	NRC
Everett Wick	NRC
Ed Escalante	National Bureau of Standards
C. G. Interrante	National Bureau of Standards
John Griess	Oak Ridge National Laboratory
Gary K. Jacobs	Oak Ridge National Laboratory
A. D. Kelmas	Oak Ridge National Laboratory
John K. Bates	Argonne National Laboratory
S. J. Basham	Battelle-ONWI
Paul McConnell	Fracture Control Corp.
R. P. Anantatmula	Rockwell/BWIP
Denny Jones	University of Nevada, Reno
Evelyn Gause	Weston
Roger Aines	Lawrence Livermore National Laboratory
Lyn Ballou	Lawrence Livermore National Laboratory
Denny Becker	Lawrence Livermore National Laboratory
John Dronkers	Lawrence Livermore National Laboratory
William Glassley	Lawrence Livermore National Laboratory
Linda Hansen	Lawrence Livermore National Laboratory
Dan McCright	Lawrence Livermore National Laboratory
Bill O'Connell	Lawrence Livermore National Laboratory
Virginia Oversby	Lawrence Livermore National Laboratory
Larry Ramspott	Lawrence Livermore National Laboratory
Michael Revelli	Lawrence Livermore National Laboratory
Edward Russell	Lawrence Livermore National Laboratory
Bonnie Smith	Lawrence Livermore National Laboratory

Enclosure 2

AGENDA

NNWSI/NRC WASTE PACKAGE MEETING

July 23-24, 1985
Building 123 - Conference Room A
Lawrence Livermore National Laboratory

Tuesday, July 23

8:30 - Introductions
- NRC Participants
- DOE & LLNL Participants
- Others

8:45 - Meeting Objectives & Agenda Overview
- NRC Objectives
- DOE/LLNL Objectives
- Agenda Overview and Arrangements

9:00 - Update on Package Design Concepts - E. Russell
- Alternative Emplacement Geometries
- Spent Fuel Internal Configurations
  - Thermal and Structural Analyses
- WV/DWPF Containers

10:00 - Potential Implications of MRS on NNWSI - L. Ballou
- Packaging Options
- Storage and Transportation Considerations

10:45 - Break

11:00 - Part 60.135(b) Excluded Materials - NRC
- Discussion of NRC Intent
- Rationale for Implementing Criteria

12:00 - Lunch - LLNL Cafeteria

1:00 - Container Material Testing - D. McCright
- Introduction and Overview
- NNWSI Environmental Conditions
  - Anticipated Conditions and Uncertainties
- Candidate Materials
  - Austenitic Stainless Steels and Copper Alloys
- Conceptual Corrosion Models

3:00 - Break

3:15 - Material Testing - Continued

- General and Localized Corrosion Testing
- Stress Corrosion Testing
- Planned Testing and Schedules

4:45 - Adjourn

Wednesday, July 24

8:30 - Waste Form Testing - Spent Fuel - V. Oversby
- Approach to Testing & Results to Date
  - Isotopes of Concern
  - Release Rates
  - Cladding Degradation
  - Fuel Oxidation

10:00 - Break

10:15 - Spent Fuel - Continued
- Modeling of Release Mechanisms
  - Comparison with Performance Objectives
- Planned Testing
- Discussion of Fuel Population
  - Proposed Test Matrix - Test Materials
  - Adequacy of Sampling

12:00 - Lunch - LLNL Cafeteria

1:00 - Waste Form Testing - Glass - V. Oversby
- Unsaturated Testing
  - Procedure Development
  - Results to Date
  - Planned Testing
- Supporting Tests and Experiments
- Modeling of Release Mechanisms

2:30 - Break

2:45 - Reliability Considerations
- Discussion of NRC Approach to Interpretation of "substantially complete"
- Approach to Reliability for Containment

3:30 - Summary and Development of Minutes

4:45 - Adjourn

Note to Attendees:

This meeting will be held on the LLNL site. To reach the Laboratory from the San Francisco Area, proceed east on I-580 past Livermore to the Vasco Rd. exit; south to East Ave.(2+miles); east .1 miles to entrance. Enter Bldg. 123 (Auditorium) just north of West Badge Office. Visitor parking is limited, park in any non-carpool space in the main West Lot.

Enclosure 3

Vugraphs

NNWSI/NRC Waste Package Meeting

July 23, 1985

U.S. DEPARTMENT OF ENERGY

OCRWM

Nevada Nuclear Waste Storage Investigations PROJECT

OGA

WASTE FORM TESTING

- SPENT FUEL -

VIRGINIA OVERSBY

APPROACH TO TESTING AND RESULTS TO DATE

ISOTOPES OF CONCERN

RELEASE RATES

CLADDING DEGRADATION

FUEL OXIDATION

PERFORMANCE OBJECTIVES SET DOWN IN 10 CFR 60 REGULATIONS

1. FOR THE FIRST 300 TO 1000 YEARS AFTER CLOSURE, CONTAINMENT OF THE RADIONUCLIDES SHALL BE SUBSTANTIALLY COMPLETE.

2. FOR THE PERIOD FOLLOWING THE CONTAINMENT PERIOD, THE RELEASE RATE OF RADIONUCLIDES FROM THE ENGINEERED BARRIER SYSTEM SHALL BE CONTROLLED SO THAT RELEASE IS LIMITED TO LESS THAN 1 PART IN 100,000 OF THE 1000 YEAR INVENTORY OF ACTIVITY PER YEAR.

ENVIRONMENTAL PROTECTION AGENCY REQUIREMENTS

RELEASE OF RADIONUCLIDES TO THE ACCESSIBLE ENVIRONMENT MUST BE LESS THAN THE LIMITS PRESCRIBED BY THE EPA. THESE ARE LISTED ON A NUCLIDE SPECIFIC BASIS, AND ARE MET AUTOMATICALLY FOR ALL NUCLIDES EXCEPT AM AND PU ISOTOPES IF RELEASE RATES ARE LESS THAN ONE PART IN 100,000 PER YEAR FROM THE ENGINEERED BARRIER SYSTEM.

APPENDIX A - TABLE FOR SUBPART B

TABLE 1 - RELEASE LIMITS FOR CONTAINMENT REQUIREMENTS
(Cumulative Releases to the Accessible Environment for 10,000 Years After Disposal)

Radionuclide	Release Limit per 1000 MTHM or other unit of waste (curies)
Americium-241 or -243	100
Carbon-14	100
Cesium-135 or -137	1000
Iodine-129	100
Neptunium-237	100
Plutonium-238, -239, -240, or -242	100
Radium-226	100
Strontium-90	100
Technetium-99	10000
Thorium-230 or -232	10
Tin-126	1000
Uranium-233, -234, -235, -236, or -238	100
Any other alpha-emitting radionuclide with a half-life greater than 20 years	100
Any other radionuclide with a half-life greater than 20 years that does not emit alpha particles	1000

PWR SPENT FUEL ASSEMBLY RADIONUCLIDE INVENTORIES AT 1000 YEARS[a]

RADIONUCLIDE[b]	% OF TOTAL 1000-YEAR ACTIVITY	CUMULATIVE %
Am-241	51.84	51.84
Am-243	1.75[c]	53.59
Pu-240	26.87	80.46
Pu-239	17.37	97.83
Pu-242	0.10	97.93
Pu-238	0.06	97.99
Tc-99	0.77	98.76
Ni-59	0.252	
Ni-63	0.021	
Zr-93	0.181	
Nb-94	0.074	
C-14	0.076[d]	
U-234	0.113	
U-238	0.018	
U-236	0.015	
Np-237	0.058	
Sn-126	0.045	
Se-79	0.023	
Cs-135	0.022	
Sm-151	0.013	
Pd-107	0.006	
I-129	0.0018	

[a] BASED ON ORIGEN DATA REPORTED IN ORNL/TM-6006[2] FOR 33,000 MWd/MTM BURNUP PWR ASSEMBLY.
[b] RADIONUCLIDES WITH 1000-YEAR ACTIVITY LESS THAN ^{129}I OR HALF-LIFE LESS THAN 1 YEAR OMMITED.
[c] INCLUDES ACTIVITY OF ^{239}Np DAUGHTER PRODUCTS.
[d] ^{14}C ACTIVITY MAY VARY CONSIDERABLY DEPENDING ON AS-FABRICATED NITROGEN IMPURITIES.

HEDL 8503-151.1

PWR SPENT FUEL ASSEMBLY
RADIONUCLIDE RELEASE per 1000 MTIHM

Nuclide	Inventory at 1000 y Curies	Total Release at 1×10^{-5}/y Curies	EPA DRAFT 5 Cumm. Limit	Ratio Adjusted	Decay
Am-241	9.3E+05	8.4E+03	1.0E+02	84	yes
Am-243+d	3.1E+04	2.8E+03	1.0E+02	28	no
Pu-240	4.8E+05	4.3E+04	1.0E+02	434	no
Pu-239	3.1E+05	2.8E+04	1.0E+02	280	N/I
Pu-242	1.8E+03	1.6E+02	1.0E+02	1.6	N/I
Pu-238	1.1E+03	2.2E+00	1.0E+02	0.02	yes
Tc-99	1.4E+04	1.2E+03	1.0E+04	0.12	N/I
Ni-59	4.5E+03	4.1E+02	1.0E+03	0.41	N/I
Ni-63	3.8E+02	6.0E-01	1.0E+03		yes
Zr-93	3.2E+03	2.9E+02	1.0E+03	0.29	N/I
Nb-94	1.3E+03	1.2E+02	1.0E+03	0.12	N/I
C-14	1.4E+03	7.4E+01	1.0E+02	0.74	yes
U-234	2.0E+03	1.8E+02	1.0E+02	1.8	N/I
U-238	3.2E+02	2.9E+01	1.0E+02	0.29	N/I
U-236	2.7E+02	2.4E+01	1.0E+02	0.24	N/I
Np-237	1.0E+03	9.4E+01	1.0E+02	0.94	N/I
Sn-126	8.1E+02	7.3E+01	1.0E+03	0.07	N/I
Se-79	4.1E+02	3.7E+01	1.0E+03	0.04	N/I
Cs-135	3.9E+02	3.6E+01	1.0E+03	0.04	N/I
Sm-151	2.3E+02	4.3E-01	1.0E+03		yes
Pd-107	1.1E+02	9.7E+00	1.0E+03	0.010	N/I
I-129	3.2E+01	2.9E+00	1.0E+02	0.029	N/I
Total	1.79E+06				

Decay Adustments: N/I = not important, half life over 10000 years
For short half lives, release calculated by
Total = (.00001*2T)*Inventory at 1000 y

For C-14, release estimated using 0.6*Inventory for 9000 y

Candidates for Sorption, Solubility, or Isotope Exchange Control

Element	Factor to reduce ratio to 0.05
Americium	1680
Plutonium	8680
Technetium	2.4
Nickel	8.2
Zirconium	5.8
Niobium	2.4
Carbon	14.8
Uranium	36
Neptunium	18.8
Tin	1.4

BASIS FOR RELATING LABORATORY MEASUREMENTS TO NRC - EPA REQUIREMENTS

1. DETERMINE ANNUAL RELEASE RATE FROM WASTE FORM.

2. MODEL RESULTS FROM RELEASE RATE TESTING TO ALLOW EXTRAPOLATION TO LONGER TIMES.

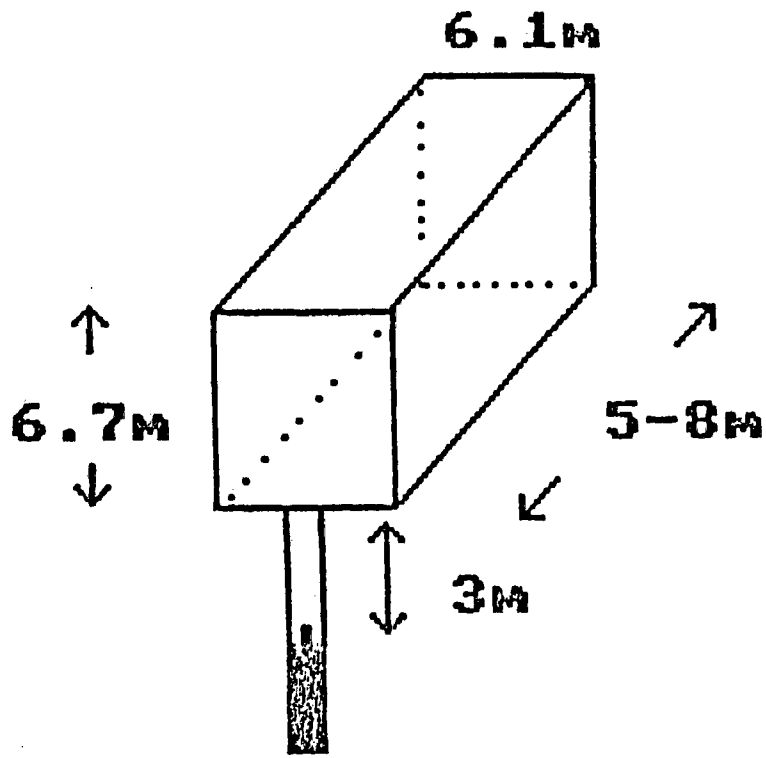
3. IF RESULT FROM STEP 2 SHOWS RELEASE IS ALWAYS LESS THAN 1 PART IN 10^5 PER YEAR, NRC REQUIREMENT IS MET.

4. IF NRC REQUIREMENT IS MET, THE EPA REQUIREMENT IS MET AT THE BOUNDARY OF THE ENGINEERED BARRIER SYSTEM FOR ALL NUCLIDES EXCEPT AM-241, AM-243, PU-239, PU-240, PU-242.

5. DO SORPTION STUDIES ON PU, AM AND NP TO DETERMINE THE DISPERSION AND RETARDATION OF THOSE NUCLIDES ALONG THE PATH TO THE ACCESSIBLE ENVIRONMENT.

6. MODEL TRAVEL PATH AND TRAVEL TIMES FOR WATER PLUS SORPTION RESULTS FOR AM, PU AND NP TO SHOW THAT EPA REQUIREMENTS ARE MET.

Vertical Emplacement



Open area per package - average

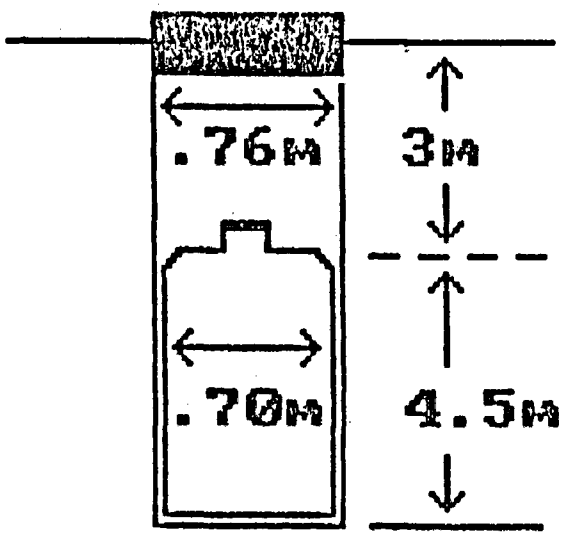
$40\ м^2$

Water volume to open area per yr.

Influx rate	Volume per year
1мм/yr	40 l
2мм/yr	80 l
8мм/yr	320 l

For 1 мм/yr infiltration rate, water volume directly to borehole is 0.5 l/yr.

Water to Fuel Ratio



Void volume per hole

1800 l

Fuel weight per pkg

3140 kg UO_2

R = 1.74 kg/l of water

if borehole full

Ratio for experiments:

Turkey Point, DIW	R = 0.16 kg/l
Turkey Point, J-13	R = 0.11 kg/l
H.B.Robinson, J-13	R = 0.33 kg/l

THREE PART SOURCE TERM for SPENT FUEL

1. Elements controlled by matrix dissolution, such as U, Pu, Am, Np.

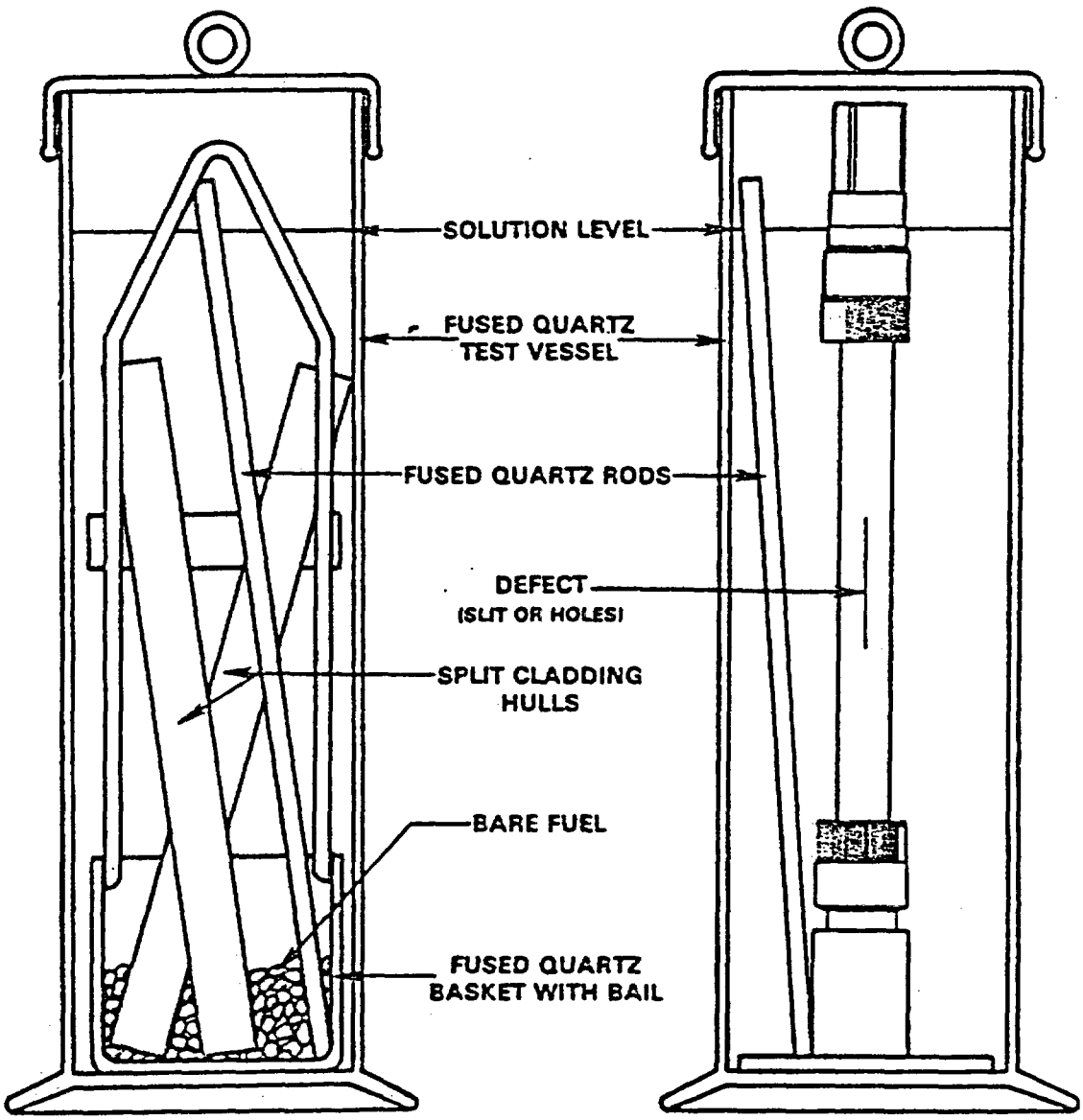
2. Elements present in the pellet cladding gap. Release will be immediate upon breach of cladding for gases and nearly immediate upon contact with water for others such as Ts, Cs, I.

3. Elements that can be released into air without water present, such as C-14 from metal parts.

TEST METHODS

- SEMI-STATIC LEACH TESTS USING SPENT FUELS WITH VARIOUS INDUCED CLADDING DEFECTS OR STATES OF DEGRADATION WHICH MAY OCCUR DURING LONG TERM NNWSI REPOSITORY STORAGE
- MEASURE RADIONUCLIDE RELEASE
  - PERIODIC SOLUTION SAMPLES (UNFILTERED, 0.4 μm FILTERED, AND 18Å FILTERED)
  - FUSED QUARTZ ROD SAMPLES
  - TEST VESSEL AND APPARATUS 8M HNO_3 STRIP SAMPLES
  - RINSE SAMPLES
  - RADIOCHEMISTRY: pH, U, $^{239+240}Pu$, ^{241}Am, ^{244}Cm, ^{237}Np, ^{99}Tc, ^{14}C, ^{129}I (NAA), AND GAMMA SPECTROMETRY (^{137}Cs,...)
- POST-TEST SAMPLE ANALYSES
  - RADIOMETALLURGY
  - ELECTRON MICROSCOPY

TEST APPARATUS



BARE FUEL TEST

DEFECTED AND UNDEFECTED CLADDING TESTS

TEST SPECIMENS

- BARE FUEL WITH SPLIT CLADDING
- SLIT DEFECT, 150 μm WIDE BY 2 cm LONG
- HOLE DEFECTS, TWO LASER DRILLED HOLES ~200 μm DIAMETER
- UNDEFECTED ROD SEGMENTS

SPECIMENS WERE PREPARED FROM 12.7 cm LONG PWR SPENT FUEL ROD SEGMENTS

HEDL 8408-186.11

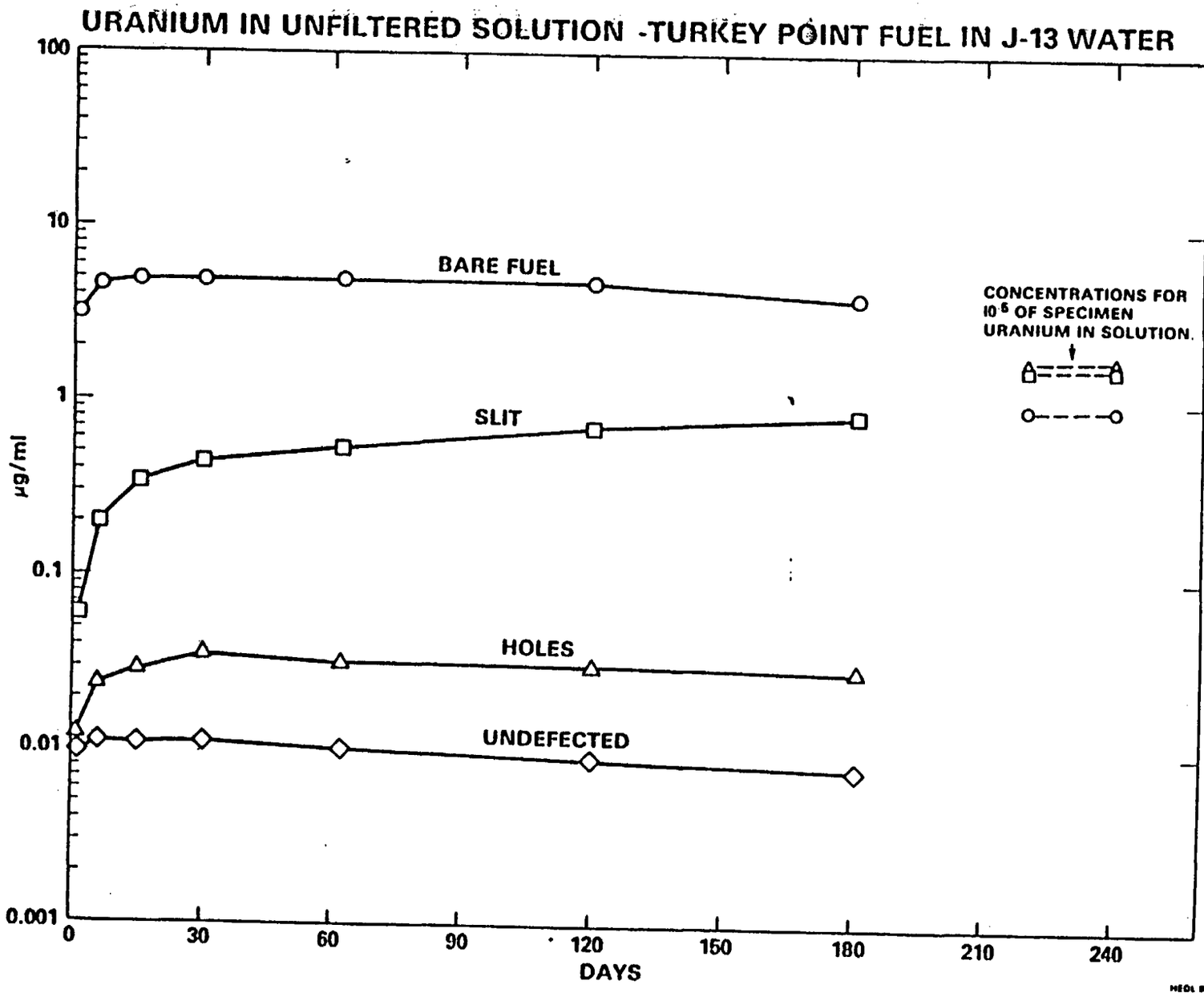
TEST SERIES

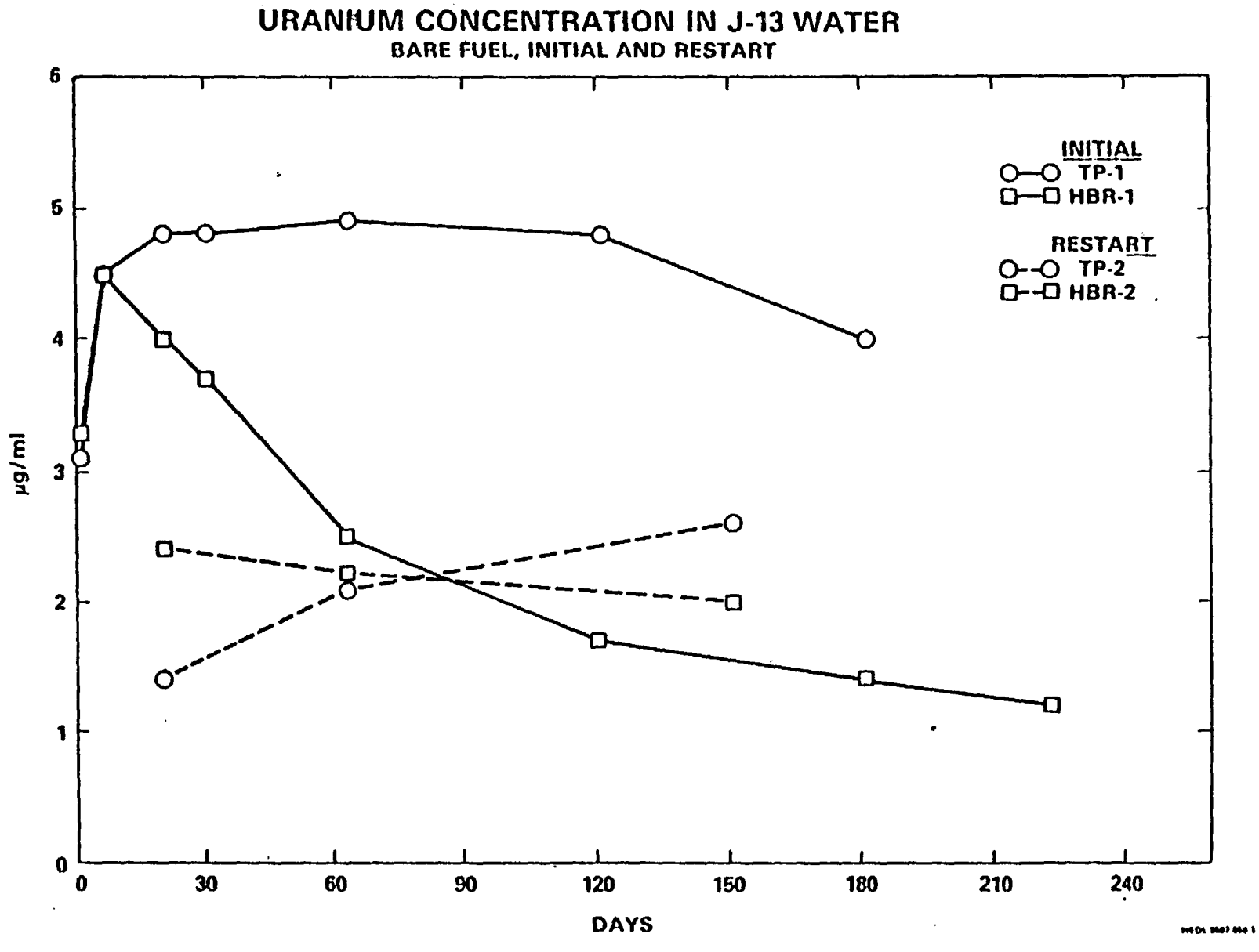
- SERIES 1 – TURKEY POINT FUEL IN DEIONIZED WATER (25°C), RUN ~250 DAYS, RESTARTED IN FRESH DEIONIZED WATER AND RUN FOR 128 DAYS.
- SERIES 2A – H.B. ROBINSON FUEL IN J-13 WELL WATER (25°C), RUN 223 DAYS, RESTARTED IN FRESH J-13 WELL WATER ON JANUARY 23, 1985.
- SERIES 2B – TURKEY POINT FUEL IN J-13 WELL WATER (25°C), RUN 181 DAYS, RESTARTED IN FRESH J-13 WELL WATER ON FEBRUARY 6, 1985.
- SERIES 3 – H.B. ROBINSON FUEL IN J-13 WELL WATER AT 70-90°C, START JUNE 1985.
- SERIES 4 – USE PARTIALLY OXIDIZED SPENT FUEL, START IN FY-1986.
- FUTURE TESTS
  - DIFFERENT FUELS, SUCH AS BWR AND HIGH FISSION GAS RELEASE FUEL
  - INCLUDE TUFF ROCK

CHARACTERISTICS OF H.B. ROBINSON UNIT 2 AND TURKEY POINT UNIT 3 FUELS

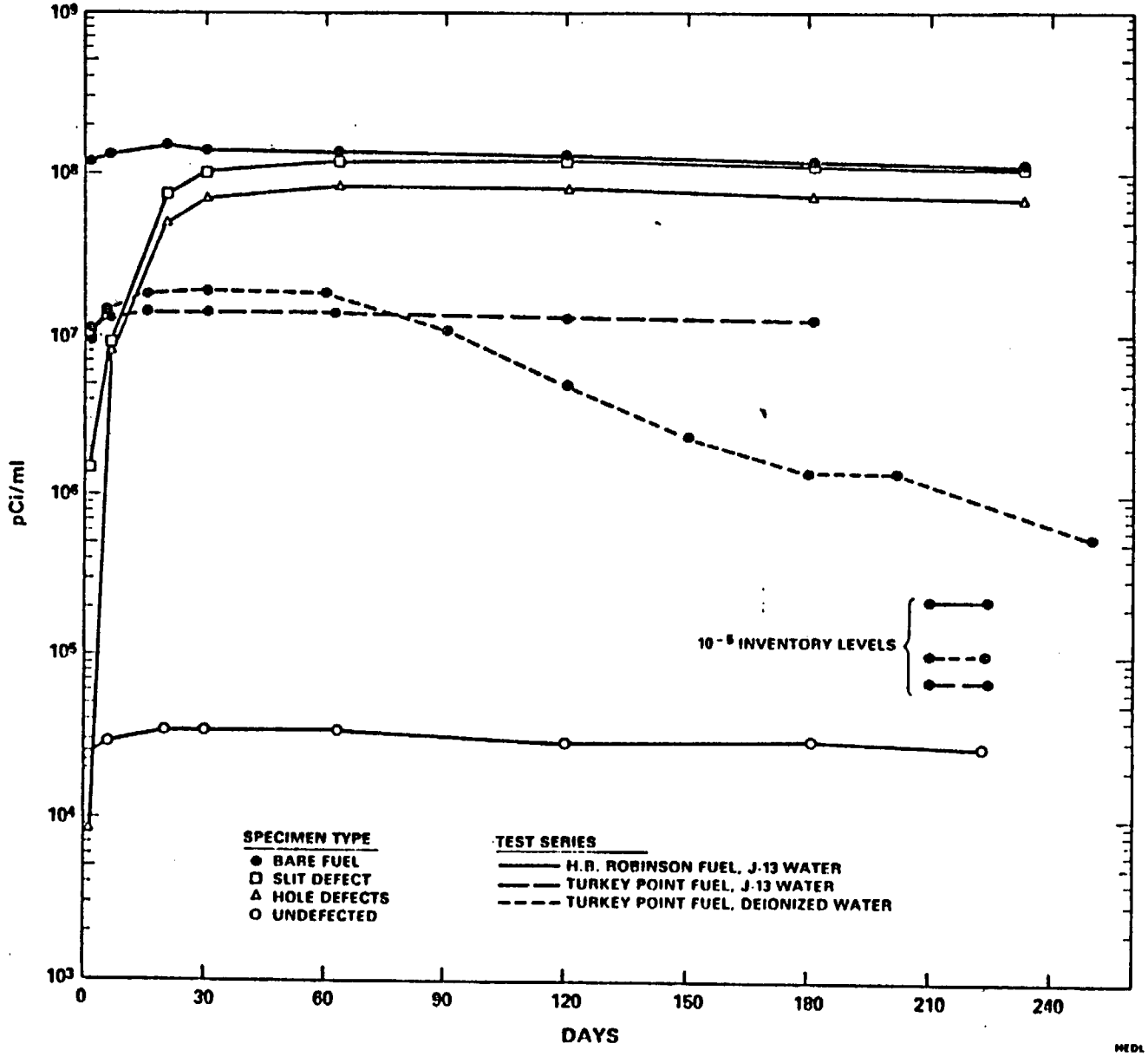
CHARACTERISTIC	H.B. ROBINSON	TURKEY POINT
FUEL TYPE	PWR 15 x 15	PWR 15 x 15
DISCHARGED	MAY, 1974	NOVEMBER, 1975
ESTIMATED BURNUP	31 MWd/kgM	27 MWd/kgM
FISSION GAS RELEASE	~0.2%	~0.3%
INITIAL ENRICHMENT	2.55 wt% ^{235}U	2.559 wt% ^{235}U
INITIAL PELLET DENSITY	92% TD (UO_2)	92% TD (UO_2)
ROD DIAMETER	10.7 mm	10.7 mm
CLADDING	ZIRCALOY-4	ZIRCALOY-4
SPECIMEN SECTION LENGTH	5 INCHES	5 INCHES
SPECIMEN FUEL LENGTH	5 INCHES	2-3 INCHES

HEDL 8503-151.2


URANIUM IN UNFILTERED SOLUTION -TURKEY POINT FUEL IN J-13 WATER
100
10
1
0.1
0.01
0.001
µg/ml
BARE FUEL
SLIT
HOLES
UNDEFECTED
CONCENTRATIONS FOR
10⁻⁵ OF SPECIMEN
URANIUM IN SOLUTION.
0
30
60
90
120
150
180
210
240
DAYS


URANIUM CONCENTRATION IN J-13 WATER
BARE FUEL, INITIAL AND RESTART
INITIAL
TP-1
HBR-1
RESTART
TP-2
HBR-2
µg/ml
0
1
2
3
4
5
6
0
30
60
90
120
150
180
210
240
DAYS

^{137}Cs IN UNFILTERED SOLUTION



HEDL 8502 297 2

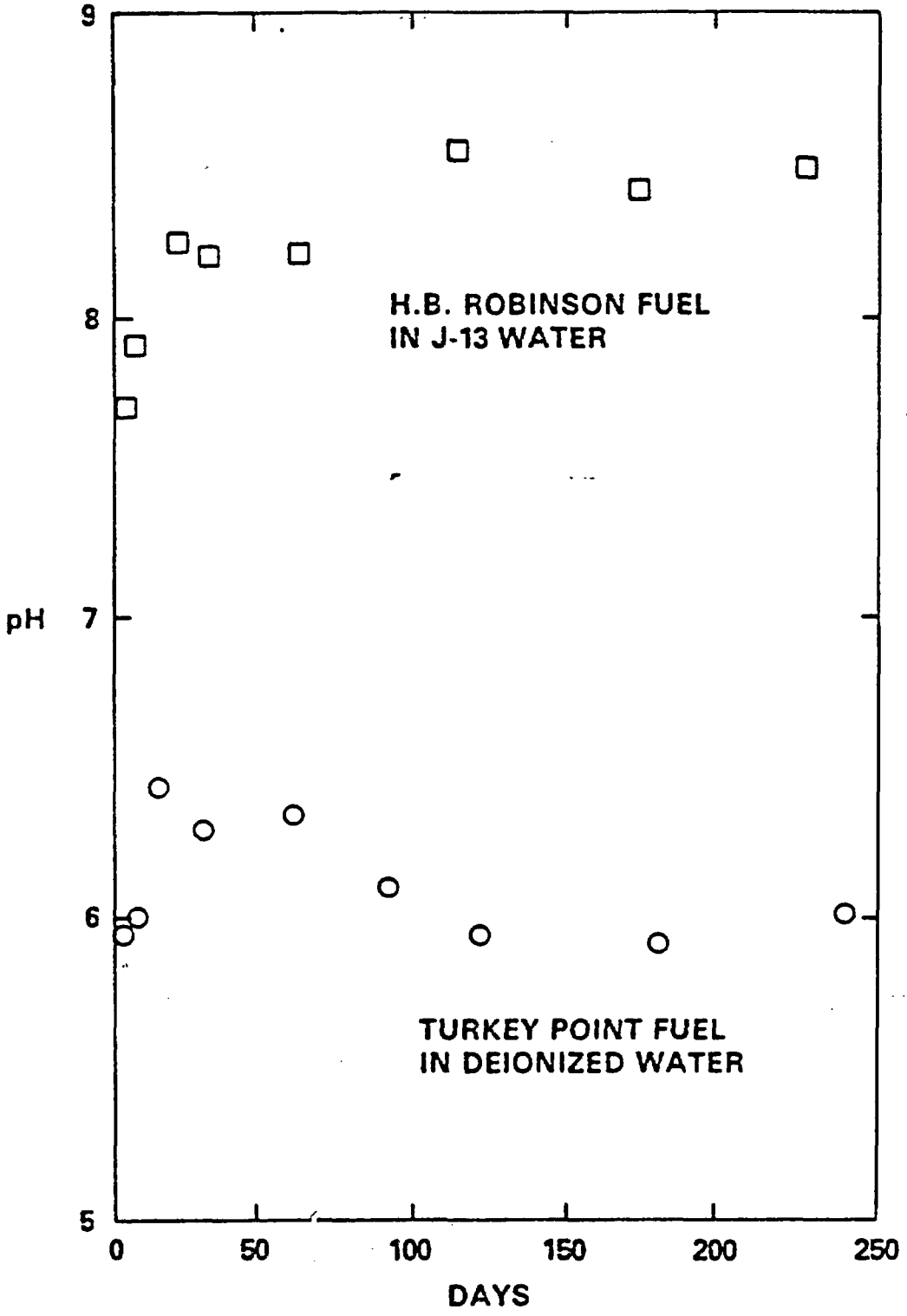
SOLUTION CHEMISTRY* FOR THE H.B. ROBINSON BARE FUEL TEST IN J-13 WATER

	STARTING J-13 WATER	30 DAYS	120 DAYS	223 DAYS
pH	7.2	8.2	8.5	8.5
Al	0.11	0.09	0.10	< 0.08
Ca	15.0	12.7	12.1	12.3
Fe	--	0.21	0.15	0.08
K	5.5	4.5	2.8	2.2
Mg	2.1	1.8	2.1	2.0
Mo	--	0.26	0.21	0.20
Na	49.5	41.6	44.5	45.5
Sr	--	--	--	0.06
Si	31.9	24.5	26.2	32.7
Cl	7.3	7.8	7.3	7.6
F	2.7	2.4	2.1	2.2
PO_4	2.8	--	--	--
NO_2	--	--	~0.5	~0.6
NO_3	8.7	7.4	8.1	8.3
SO_4	18.8	18.8	18.6	18.5
CO_3	118.0	--	120.0	118.0

*UNITS IN μg/ml, 0.4 μm FILTERED.

HEDL 8503-151.11

pH IN BARE FUEL TESTS



HEDL 8502 021.11

EFFECTS OF FILTRATION ON 223-DAY J-13/HBR AND 202-DAY DIW/TP BARE FUEL TEST SOLUTION SAMPLES

	SERIES	UNFILTERED	0.4 μm	18A
URANIUM (μg/ml)	J-13/HBR	1.2	1.2	1.2
	DIW/TP	0.3	0.003	0.002
$^{239+240}Pu$ (pCi/ml)	J-13/HBR	112	75	26
	DIW/TP	2240	2180	1810
^{241}Am (pCi/ml)	J-13/HBR	286	151	3.6
	DIW/TP	9860	1430	97
^{244}Cm (pCi/ml)	J-13/HBR	410	231	0.9
	DIW/TP	21,100	2860	163
^{99}Tc (pCi/ml)	J-13/HBR	450	490	450
	DIW/TP*	2250	2250	2200

*250 DAY SOLUTION SAMPLE

HEDL 8503-151.3

H.B. ROBINSON FUEL IN J-13 WATER URANIUM RELEASE DATA (μg)

	BARE FUEL	SLIT DEFECT	HOLE DEFECTS	UNDEFECTED
Σ SOLUTION SAMPLES	211	4.3	0.50	1.26
Σ ROD SAMPLES	34	0.3	0.17	0.19
FINAL SOLUTION [U (μg/ml)]*	300 (1.2)	23.8 (0.095)	1.50 (0.006)	3.25 (0.013)
STRIP	2700	1.5	0.60	0.60
RINSE	550**	1.8	0.60	0.27
Σ ABOVE	3795	31.7	3.37	5.57
DIVIDED BY 10^{-5} INV.	5.42	0.044	0.0047	0.008

*UNFILTERED 223-DAY FINAL SOLUTION URANIUM CONTENT IN μg/ml GIVEN IN PARENTHESES.
**0.4 μm FILTERED

HEDL 8503-151.6

Table 1: Uranium release data for Turkey Point Fuel in J-13 water. All units in micrograms U except for fractional release.

	Bare Fuel	Slit Defect	Hole Defects	Undefected
Total Solns.	350.5	35.8	2.26	0.76
Total Rods	15.4	0.5	0.19	0.10
Final Soln.	1000	212.5	7.25	2.00
Water Rinse	366	10.2	0.60	0.60
Acid strip	960	15.9	2.70	0.30
Total	2691.9	274.9	13.0	3.8
Fractional	11.67	0.65	0.03	0.011

RELEASE DATA FOR H.B. ROBINSON BARE FUEL IN J-13 WATER (nCi)

	$^{239+240}Pu$	^{241}Am	^{244}Cm	^{99}Tc
Σ SOLUTION SAMPLES	42.9	93.9	125.0	~24
Σ ROD SAMPLES	56.2	125.1	138.2	0.6
FINAL SOLUTION	27.9	71.5	102.5	112.5
STRIP	4054.1	9600.0	8970.0	28.4
RINSE*	253.8	532.0	564.6	18.6
Σ ABOVE	4434.9	10,422.5	9900.3	183.6
DIVIDED BY 10^{-5} INV.	7.04	7.76	6.54	20.2

*RINSE SOLUTION 0.4 μm FILTERED.

HEDL 8503-151.6

Table 2: Bare Fuel release data for Turkey Point Fuel in J-13 water. All units in nanocuries except for fractional release.

	Pu-239+Pu-240	Am-241	Cm-244	Tc-99	Cs-137
Total Solns.	63	138	138	8	1.0E+06
Total Rods	22	42	38	n.m.	2.7E+03
Final Soln.	114	243	250	53	3.1E+06
Water Rinse	63	111	104	11.6	7.9E+05
Acid strip	1140	2180	1610	6.1	1.4E+05
Total	1401	2714	2140	79	5.0E+06
Fractional Release, parts in 100,000	7.30	6.87	7.44	29.7	295

^{129}I MEASURED IN J-13/HBR SOLUTION SAMPLES

TEST	DAYS	^{129}I (pCi/ml)*	$+10^{-5}$ INVENTORY**
BARE FUEL	63	0.52	5.6
	223	0.72	7.5
SLIT DEFECT	63	0.29	3.0
	223	0.38	4.0
HOLE DEFECTS	63	0.0019	0.020
	223	0.0050	0.053
UNDEFECTED	63	0.0060	0.064
	223	0.0054	0.057

*AVERAGE FOR 2 REPLICATE SAMPLES MEASURED BY NEUTRON ACTIVATION ANALYSIS.
**(pCi/ml) (250 ml)/(10^{-5} OF SPECIMEN INVENTORY).

HEDL 8603-151.4

TEST	DAYS	^{14}C (nCi)
BARE FUEL	63	5.0
	223	6.5
SLIT DEFECT	63	3.3
	223	14.0
HOLE DEFECTS	63	1.4
	223	24.0
UNDEFECTED	63	5.5
	223	5.0

SPECIMEN INVENTORY ESTIMATED AT 28 μCi IN THE FUEL AND 10 μCi IN THE CLADDING BASED ON SINGLE SPECIMEN ANALYSIS.

HEDL 8504-089.1

SLIDE 14. ^{14}C Measured in J-13/HBR Solution.

Table 4: Summary of fractional release data for all sample types. Units are parts in 100,000 of the inventory in the test specimen. DIW/TP = Turkey Point fuel in deionized water (Wilson, 1985). J-13/HBR = H. B. Robinson fuel in J-13 water (Wilson and Oversby, 1985).

Nuclide	Series	Bare Fuel	Slit	Holes	Control
Uranium	J-13/HBR	5.63	0.05	0.005	0.009
	J-13/TP	11.7	0.65	0.030	0.011
	DIW/TP	21.2	0.07	0.032	0.010
239 + 240 Pu	J-13/HBR	7.04	0.01	0.003	0.002
	J-13/TP	7.30	0.11	0.022	0.006
	DIW/TP	22.4	0.20	0.042	0.021
241 Am	J-13/HBR	7.76	0.01	0.002	0.003
	J-13/TP	6.87	0.12	0.023	0.004
	DIW/TP	17.2	0.15	0.019	0.005
244 Cm	J-13/HBR	6.54	0.01	0.001	0.002
	J-13/TP	7.44	0.13	0.026	0.005
	DIW/TP	21.5	0.35	0.026	0.006
237 Np	J-13/HBR	<6.4	<2.5	---	---
	J-13/TP	<7.4	<3.4	---	---
	DIW/TP	18	0.2	---	---
137 Cs	J-13/HBR	739	633	400	0.18
	J-13/TP	295	137	7.6	0.13
	DIW/TP	230	110	50	0.04
99 Tc	J-13/HBR	19.9	2.4	<1.5	---
	J-13/TP	29.7	<13.7	<2	---
	DIW/TP	152	8.1	---	---

WASTE FORM TESTING

SPENT FUEL

- CONTINED -

MODELING OF RELEASE MECHANISMS COMPARISON
WITH PERFORMANCE OBJECTIVES

PLANNED TESTING

DISCUSSION OF FUEL POPULATION

PROPOSED TEST MATRIX - TEST MATERIALS

ADEQUACY OF SAMPLING

ASSUMPTIONS FOR RELEASE RATE CALCULATIONS

1. Carbon-14 release begins as soon as air enters container.

   Two release rates: Initial pulse of about 0.2% of inventory will be controlled by rate of container breach.

   Further release is controlled by Zircaloy and spent fuel oxidation and dissolution rates.

2. Cesium-135 release rate will consist of 2 components.

   Gap-grain boundary release, approximated by the fission gas release for the fuel.

   Use 0.5% gas release and cladding breach rate of 0.1% per year.

   Bulk of inventory will have release rate controlled by the matrix dissolution rate.

3. Technetium and iodine.

   Some inital preferential release, but less than that for cesium. For initial model use cesium release rate as upper bound for Tc and I.

4. Activation products.

   Controlled by the dissolution rate of the matrix (Zircaloy, Inconel, Stainless steel)

5. All other elements.

   Controlled by the dissolution rate of the UO_2 matrix

CALCULATION OF MATRIX DISSOLUTION RATE

MODEL ASSUMPTIONS

1. Dissolution Rate controlled by Uranium solubility of 5 ppm.

   Basis: Ambient temperature spent fuel dissolution in J-13 water.

2. Semi-Static dissolution conditions with 40 liters of fresh water replacing same volume of Uranium-saturated water each year.

   Basis: Infilitration rate of 1 mm/y, Vertical emplacement geometry. All water reaching open area collects in emplacement hole.

3. Fuel to water ratio is 1.7 kg/l.

   Basis: Emplacement hole does not drain, All open volume in hole fills with water.

RESULTS

Initial Dissolution

1.74 Kg fuel/liter of water

Dissolution - 5 mg of UO_2/liter of water

Years to fill void volume = 1800 l/ 40 l per year

= 45 years

Rate = 5 mg/1.74 kg in 45 years

6.4E-08 per year

Subsequent dissolution

40 liters of water per year

3140 kg UO_2 per package

Rate = (5 mg/l * 40 l) / 3140 kg

6.4E-08 per year

CESIUM RELEASE RATE CALCULATION

MODEL ASSUMPTIONS

1. Following cladding breach, the release rate is 0.5% for the first year and decreases by 1 order of magnitude per year until the matrix dissolution rate of 6×10^{-8} per year is reached.

2. Cladding breach rate is 0.1% per year.

RESULTS

First year - $0.001 \times 0.005 = 5 \times 10^{-6}$ per year

Second year - $0.001 \times 0.005 + 0.001 \times 0.0005 = 5.5 \times 10^{-6}$ per year

Third year - $0.001 \times 0.005 + 0.001 \times 0.0005 + 0.001 \times 0.00005 =$

5.55×10^{-6} per year

Etc.

Release rate will be about 5.55×10^{-6} per year until all cladding is breached. (Under the model assumptions, this will take 1000 years). Then rate will drop to the matrix dissolution rate.

IMPLICATIONS OF A RELEASE RATE OF 1 PART IN 10,000,000 PER YEAR

PWR SPENT FUEL ASSEMBLY RADIONUCLIDE RELEASE per 1000 MTIHM

Nuclide	Inventory at 1000 y Curies	Total Release at 1E-07/y Curies	EPA DRAFT 5 Cumm. Limit	Ratio	Decay Adjusted
Am-241	9.3E+05	8.4E+01	1.0E+02	1	yes
Am-243+d	3.1E+04	2.8E+01	1.0E+02	2.83E-01	no
Pu-240	4.8E+05	4.3E+02	1.0E+02	4	no
Pu-239	3.1E+05	2.8E+02	1.0E+02	3	N/I
Pu-242	1.8E+03	1.6E+00	1.0E+02	1.61E-02	N/I
Pu-238	1.1E+03	2.2E-02	1.0E+02	2.15E-04	yes
Tc-99	1.4E+04	1.2E+01	1.0E+04	1.24E-03	N/I
Ni-59	4.5E+03	4.1E+00	1.0E+03	4.07E-03	NON-FUEL
Ni-63	3.8E+02	6.0E-03	1.0E+03		yes
Zr-93	3.2E+03	2.9E+00	1.0E+03	2.92E-03	N/I
Nb-94	1.3E+03	1.2E+00	1.0E+03	1.19E-03	N/I
C-14	1.4E+03	7.4E-01	1.0E+02	7.36E-03	yes
U-234	2.0E+03	1.8E+00	1.0E+02	1.82E-02	N/I
U-236	3.2E+02	2.9E-01	1.0E+02	2.91E-03	N/I
U-236	2.7E+02	2.4E-01	1.0E+02	2.42E-03	N/I
Np-237	1.0E+03	9.4E-01	1.0E+02	9.36E-03	N/I
Sn-126	8.1E+02	7.3E-01	1.0E+03	7.27E-04	N/I
Se-79	4.1E+02	3.7E-01	1.0E+03	3.71E-04	N/I
Cs-135	3.9E+02	3.6E-01	1.0E+03	3.55E-04	N/I
Sm-151	2.3E+02	4.3E-03	1.0E+03		yes
Pd-107	1.1E+02	9.7E-02	1.0E+03	9.69E-05	N/I
I-129	3.2E+01	2.9E-02	1.0E+02	2.91E-04	N/I
Total	1.79E+06		Sum minus Am+Pu	0.052	

Candidates for Sorption, Solubility, or Isotope Exchange Control

Element	Factor to reduce ratio to 0.05
Americium	20
Plutonium	80

TEST SERIES FOR DETERMINING THE CONTROL OF RELEASE RATE FROM SPENT FUEL WHICH IS CONTAINED IN ZIRCALOY WITH MINOR DEFECTS

COMPLETED: (25°C)

- DETERMINE THE RELATIVE RELEASE RATE FROM BARE FUEL VS. FUEL IN ZIRCALOY CLADDING WITH PIN HOLE AND SLIT DEFECTS IN DEIONIZED WATER.

IN PROGRESS:

- CONDUCT CORROSION TESTS IN YUCCA MOUNTAIN GROUNDWATER TO DETERMINE THE DEGRADATION RATE OF THE DEFECTS IN CLADDING (90°C).
- CONDUCT RELATIVE RELEASE RATE TESTS IN REFERENCE GROUNDWATER (25°C).
- DETERMINE OXIDATION RATE FOR SPENT FUEL UNDER REPOSITORY CONDITIONS.

TEST SERIES FOR DETERMINING THE CONTROL OF RELEASE RATE FROM SPENT FUEL WHICH IS CONTAINED IN ZIRCALOY WITH MINOR DEFECTS

PLANS:

- DETERMINE DEPENDENCE OF RELEASE RATE ON FUEL TO WATER RATIO.
- INVESTIGATE RELEASE RATE FROM BWR AND HIGH GAS RELEASE FUEL RODS.
- CONDUCT CORROSION TESTS OF ZIRCALOY UNDER CONDITIONS RELEVANT TO INTACT CONTAINMENT BARRIER WITH WATERLOGGED FUEL PIN.
- CONDUCT TESTS AT HIGHER TEMPERATURES TO DETERMINE VARIATION OF RELEASE RATE WITH TEMPERATURE.
- CONDUCT STRESS CORROSION CRACKING TESTS ON IRRADIATED ZIRCALOY CLADDING.
- CONDUCT RELEASE RATE TESTS USING OXIDIZED SPENT FUEL.

WHY STUDY SPENT FUEL OXIDATION?

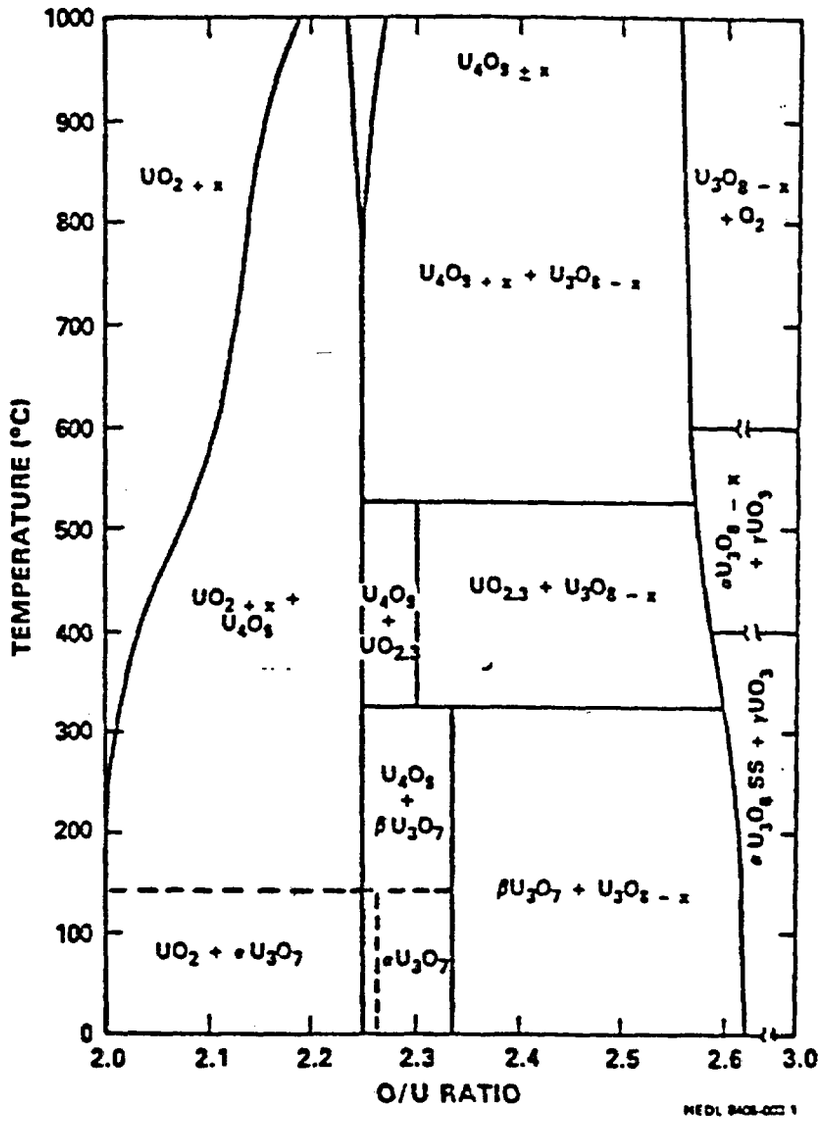
$$UO_2 \longrightarrow U_4O_9 \longrightarrow U_3O_7 \longrightarrow U_3O_8 \longrightarrow UO_3$$

- UO_2 WILL OXIDIZE TO UO_3 UNDER TUFF REPOSITORY CONDITIONS GIVEN ENOUGH TIME
- LOWER DENSITY U_3O_8 FORMATION CAN SPLIT CLADDING AND EXPOSE MORE FUEL TO GROUNDWATER
- HIGHER OXIDES OF UO_2 MAY LEACH FASTER THAN UO_2

HEDL 8602-032.7

OUTSTANDING QUESTIONS

- RATE OF OXIDE FORMATION AND MIXTURE OF PHASES AS FUNCTION OF TIME AND TEMPERATURE
- OXIDATION MECHANISMS OPERATIVE AT REPOSITORY TEMPERATURES
- EFFECT OF HUMIDITY AND FUEL VARIABILITY ON LONG-TERM, LOW-TEMPERATURE MECHANISMS
- RADIOLYSIS EFFECTS IN MOIST INERT HIGH TEMPERATURE ATMOSPHERES

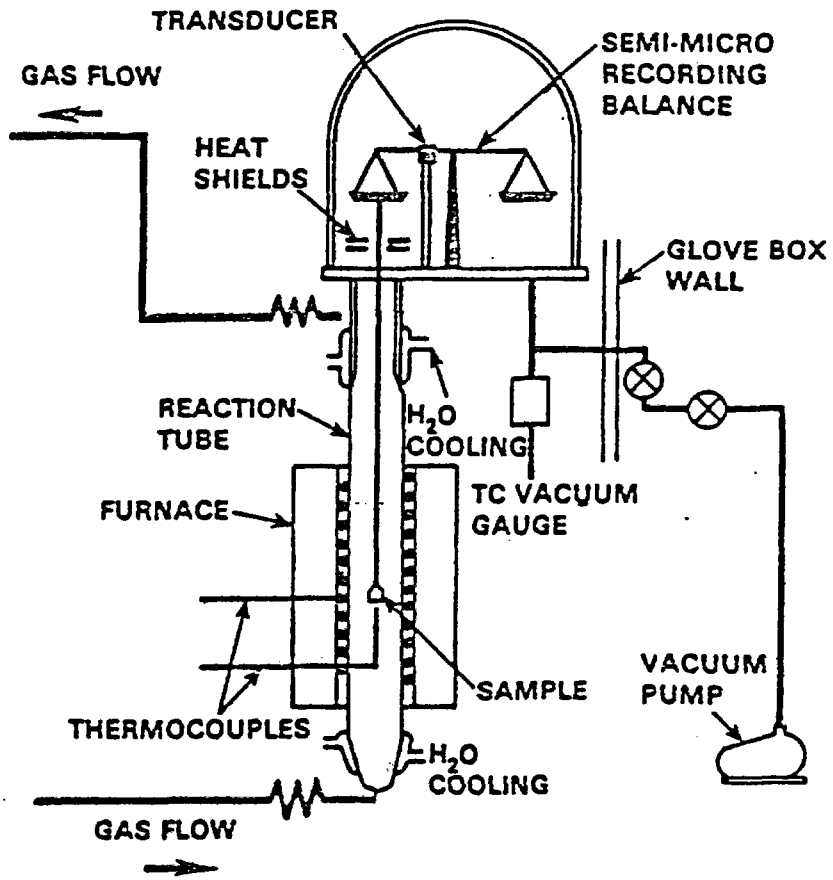


RE 1. Phase Diagram for Uranium-Oxygen System Adapted from References 15 and 16.

POSSIBLE OXIDATION MECHANISM

- GRAIN BOUNDARY DIFFUSION
- BULK DIFFUSION
- NUCLEATION AND GROWTH
- CRITICAL OXIDE LAYER THICKNESS
- MANY OTHERS

TGA SYSTEM



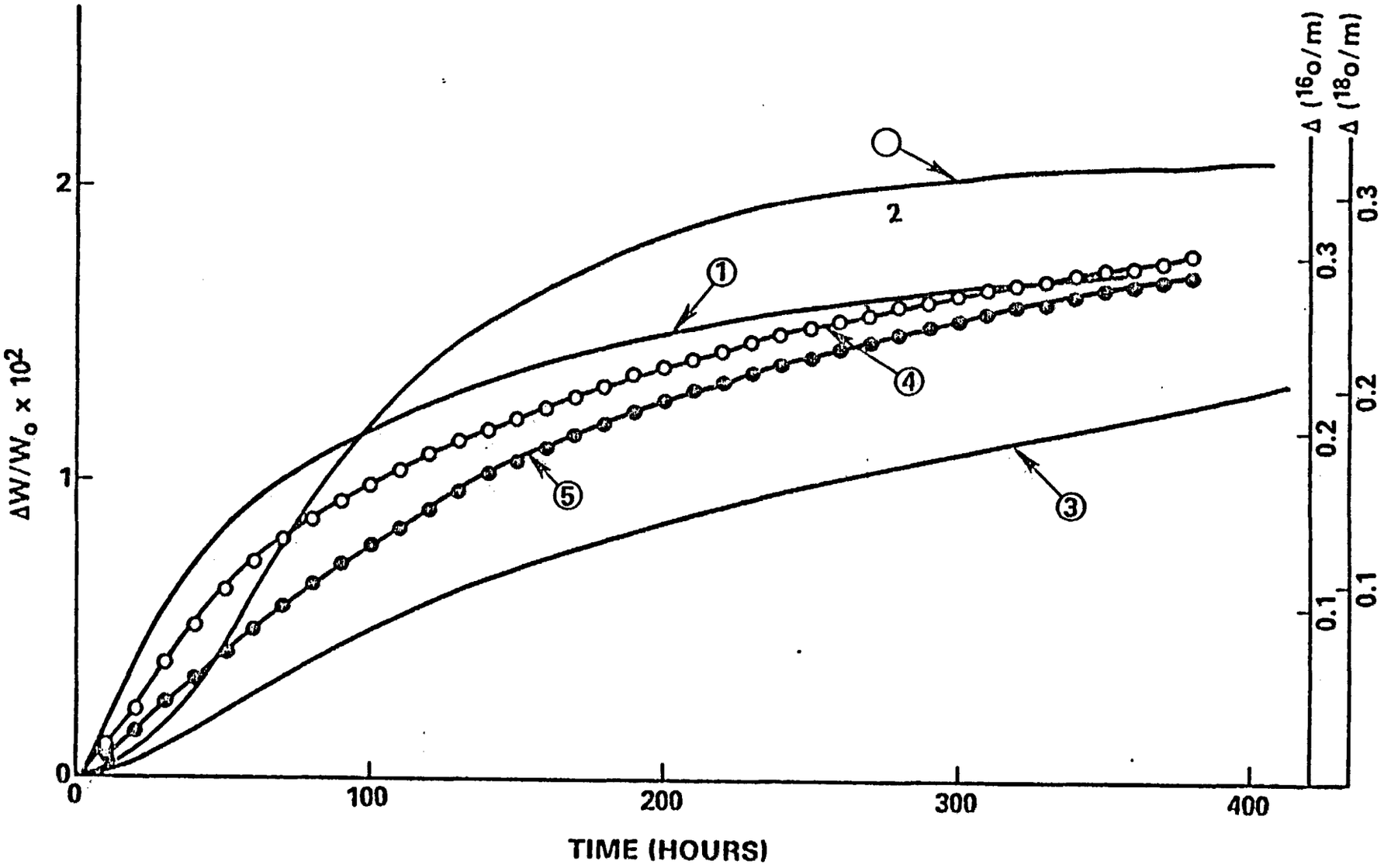
HEDL 8502-032.9

TABLE 3
TEST PARAMETERS

	RUN I	RUN II	RUN III	RUN IV	RUN V
TEMPERATURE (°C)	225	224	200	225	225
DURATION (hrs)	356	408	737	387	428
ATMOSPHERE	AIR	AIR	80% N_2 + 20% $^{18}O_2$	AIR	AIR
DEW POINT (°C)	14.5	14.5	14.5	−69.8	14.5
FUEL IDENTIFICATION*	G7-27-2	I9-24-1	I9-24-2	G7-14-3-1	G7-14-3-2
INITIAL WEIGHT (mg)	195.2	228.5	227.6	214.6	211.5
SAMPLE CONDITION	PULVERIZED FUEL	SINGLE FRAGMENT	SINGLE FRAGMENT	TWO FRAGMENTS	FOUR FRAGMENTS

*G7, I9 REFER TO THE FUEL ROD IDENTIFICATION

TGA TEST SAMPLE WEIGHT CHANGES



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EXAMINATION TECHNIQUES

- CERAMOGRAPHY
- SEM
- X-RAY DIFFRACTION
- ELECTRON MICROPROBE
- ION MICROPROBE
- GAS ANALYSIS

HEDL 8502-032.5

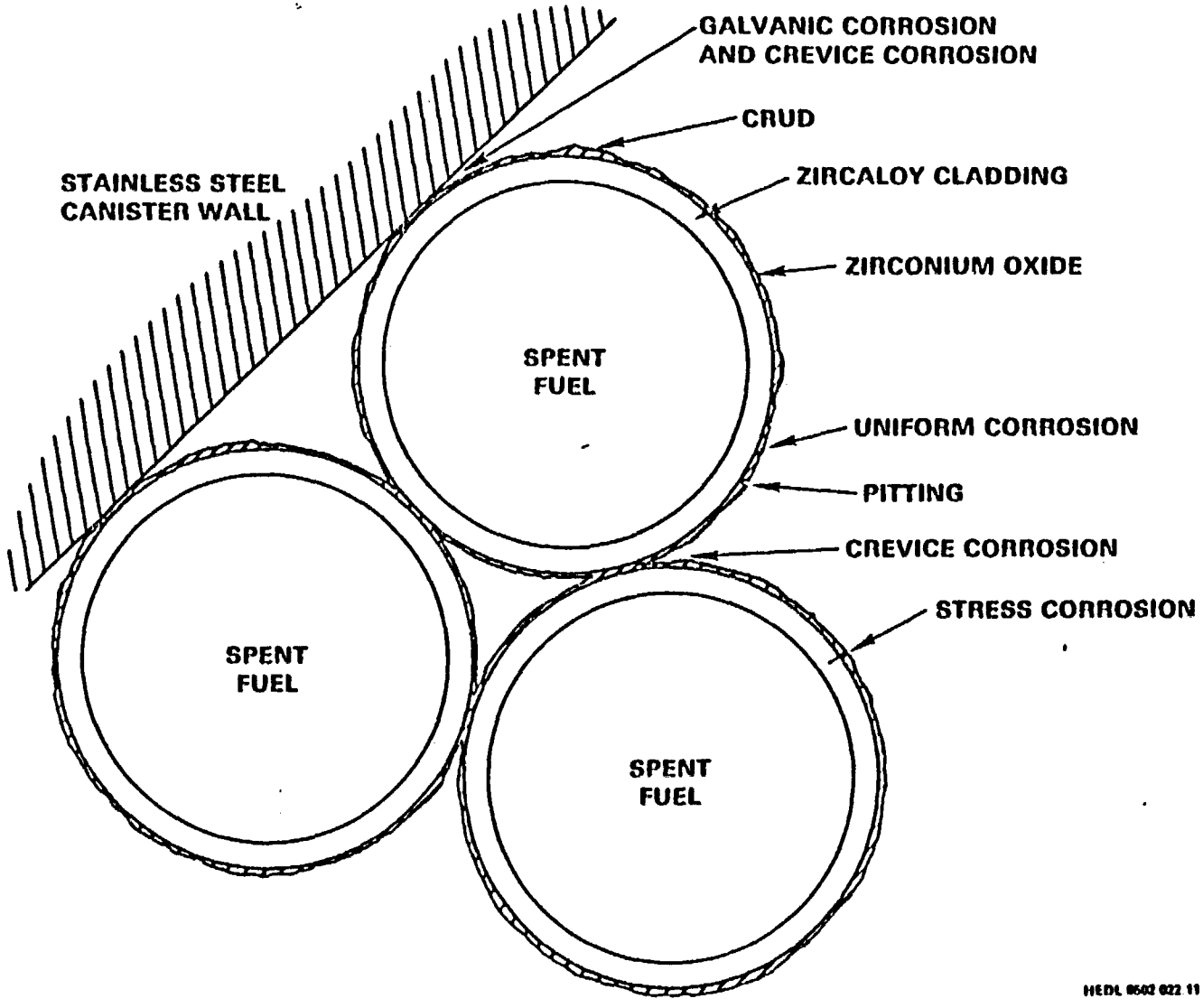
PRELIMINARY CONCLUSIONS FROM INITIAL TGA TESTING

- TGA SYSTEM SUFFICIENTLY STABLE FOR OXIDATION STUDIES
- SIZE OF SAMPLE DOES NOT APPEAR CRITICAL. GRAIN BOUNDARY DIFFUSION OPENS MOST GRAIN SURFACES TO OXIDIZING ATMOSPHERE
- 3 TO 16,000 ppm MOISTURE CONTENT OF AIR HAS ONLY MINOR EFFECT ON SHORT-TERM OXIDATION RATES

ZIRCALOY CLADDING CORROSION

H.D. SMITH

WESTINGHOUSE HANFORD COMPANY



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OBJECTIVES

- IDENTIFY ACTIVE CORROSION PROCESSES ON ZIRCALOY SPENT FUEL CLADDING UNDER TUFF REPOSITORY CONDITIONS
- ESTABLISH CORROSION RATES (OR UPPER BOUNDS) FOR POTENTIAL CORROSION PROCESSES. FOR SCC, STRESS INTENSITY FACTOR THRESHOLD VALUES ARE TO BE DETERMINED.

OVERVIEW OF APPROACH

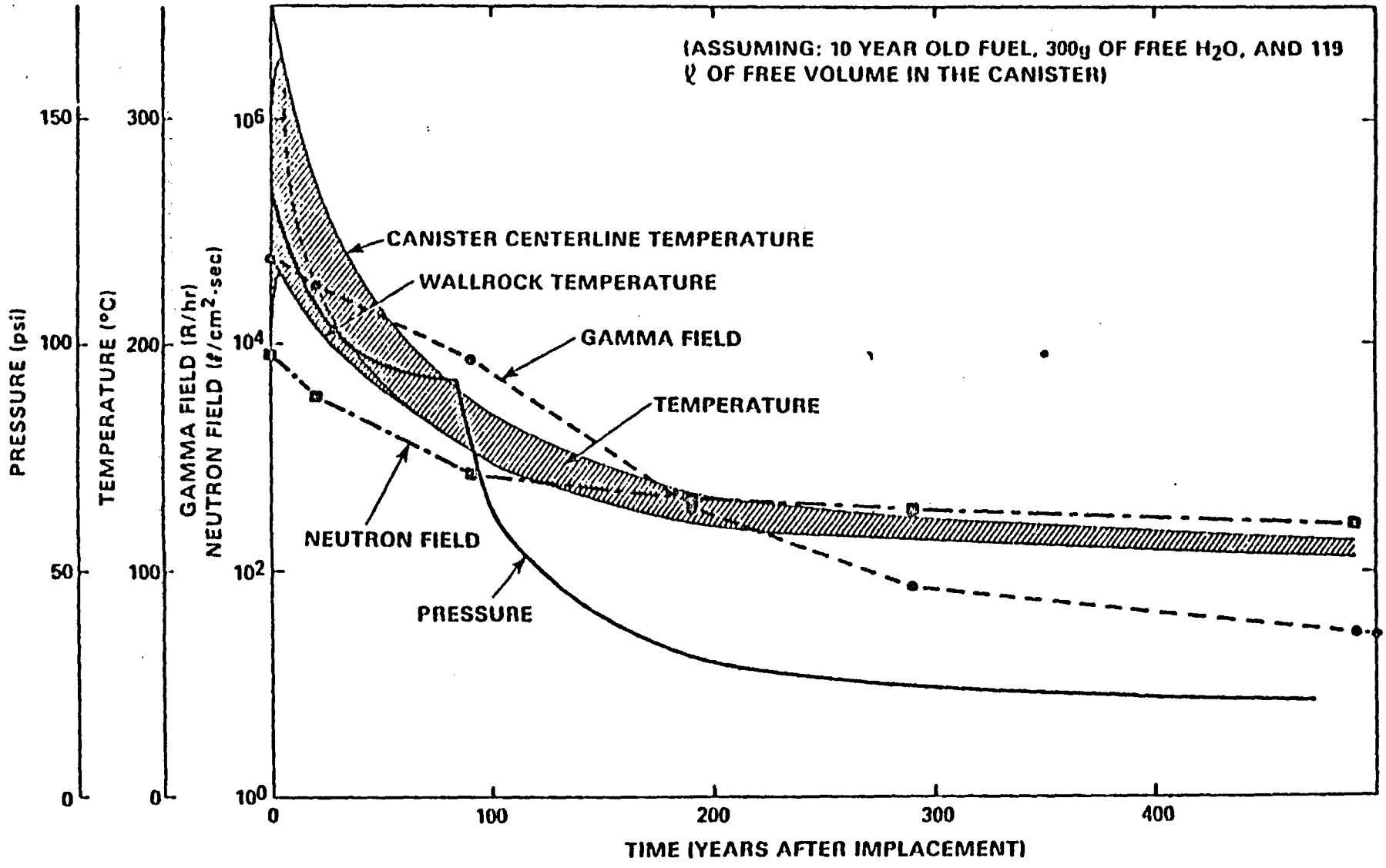
I. ANALYZE ENVIRONMENTAL TIME LINE OF THE REPOSITORY FOR CRITICAL CORROSION ENVIRONMENTS.

II. IDENTIFY POTENTIAL CORROSION MECHANISMS.

III. DEVELOP BASIC EXPERIMENTS TO EVALUATE CLADDING CORROSION IN THE CRITICAL ENVIRONMENTS.

IV. PLAN AND IMPLEMENT EXPERIMENTAL PROGRAM TO EVALUATE CORROSION IN THE CRITICAL REPOSITORY ENVIRONMENTS.

EXPECTED - RADIATION - PRESSURE - TEMPERATURE - TIME RELATIONS IN A TUFF REPOSITORY



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CORROSION ENVIRONMENTS

	PERIOD I	PERIOD II	PERIOD III
APPROXIMATE CORROSION PERIOD (YRS)	~0 TO 90	~90 TO 1,000	1,000 TO 10,000 AND BEYOND
TEMPERATURE (°C)	175-350	95-175	AMBIENT – 95
γ-FIELD (R/hr)	$5 \times 10^3 - 3 \times 10^4$	$4.0 - 5 \times 10^3$	4.0
η-FIELD (n/cm^2-sec)	$9.3 \times 10^2 - 4 \times 10^3$	250-930	250
POTENTIAL CANISTER INTERNAL PRESSURE (psi)	120-135	15-120	15
ENVIRONMENT AT CLADDING SURFACE	GAS	GAS AND LIQUID H_2O	GAS AND LIQUID H_2O
RELATIVE CORROSIVITY	LEAST	MOST	MOST

HEDL 8501-227.3

CORROSION TEXT MATRIX

		PWR	BWR	OTHER*
PERIOD II	EXTERNAL SCC	P	L	L
	ELECTROCHEMICAL	P	P	L
PERIOD III	EXTERNAL SCC	P	L	L
	ELECTROCHEMICAL	P	P	L

* – ~5% OF SPENT FUEL RODS ARE CLAD WITH STAINLESS STEEL

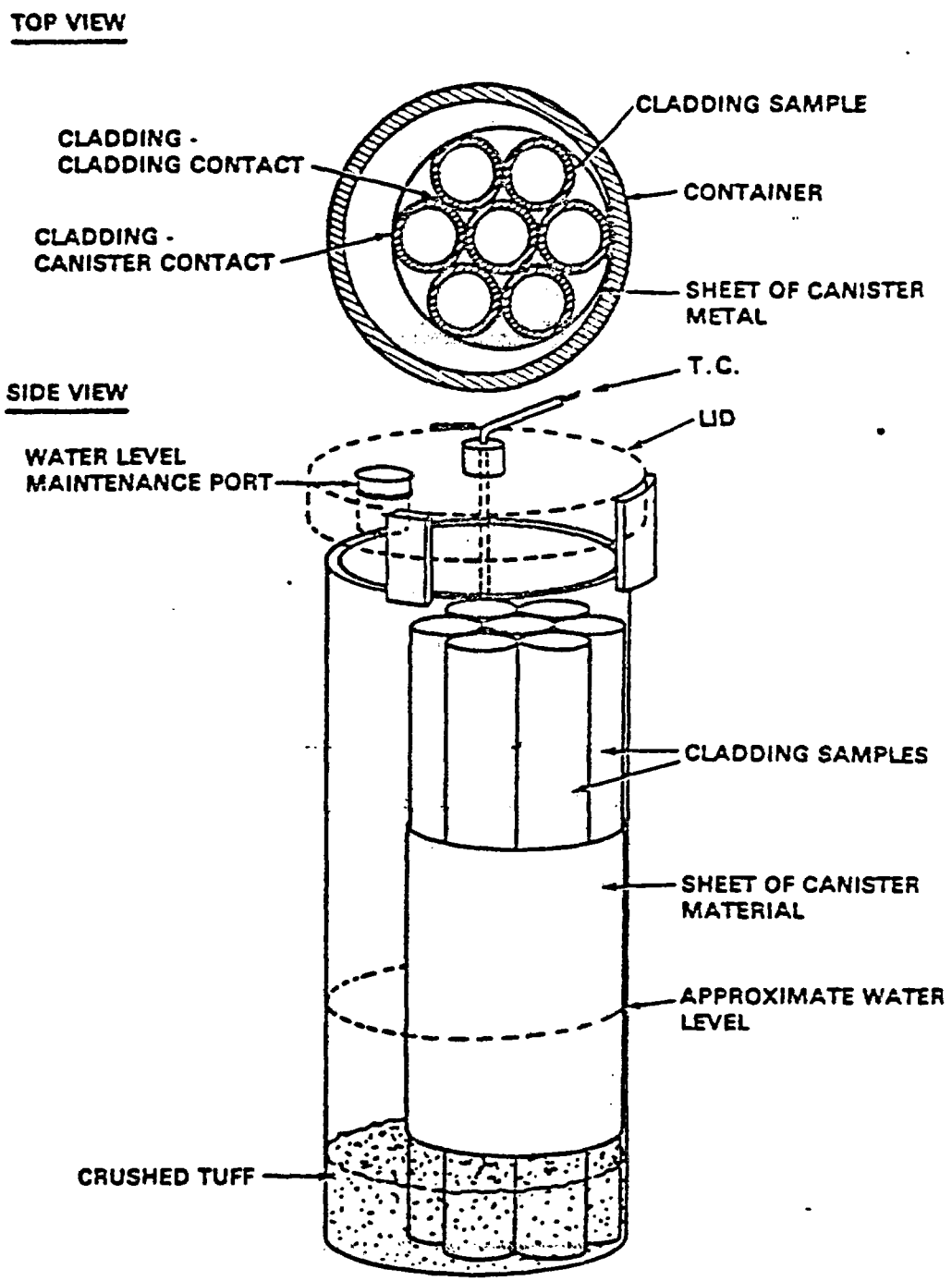
HEDL 8502-022.1

PLANNED CORROSION EXPERIMENTS

ELECTROCHEMICAL

1. SCOPING EXPERIMENT
   - EXPOSE DEFUELED CLADDING TO PERIOD III ENVIRONMENT
   - PRODUCE BASELINE DATA, REFINE TECHNIQUE
2. PERIOD III ENVIRONMENT
   - EXPOSE FUELED CLADDING
3. PERIOD II ENVIRONMENT
   - EXPOSE FUELED CLADDING USING AUTOCLAVE

CORROSION CELL (NOT TO SCALE)



HEDL 8502-022.9

ELECTROCHEMICAL CORROSION SCOPING TEST RESULTS

- 2 MO., 6 MO. TEST COMPLETE
- CHEMICAL DATA
  - pH
  - CONDUCTIVITY
  - IONIC SPECIES
- MACROSCOPIC APPEARANCE
- MICROSCOPIC ELALUATION TO DATE
  - EXPOSED MATERIAL – SEM
  - UNEXPOSED MATERIAL – SEM/STEM

  } IDENTIFY CORROSION BY COMPARISON
- CONCLUSIONS (TO DATE)
  - WITHIN THE LIMITS OF DETECTABILITY, NO CORROSION HAS BEEN OBSERVED

HEDL 8602-022.4

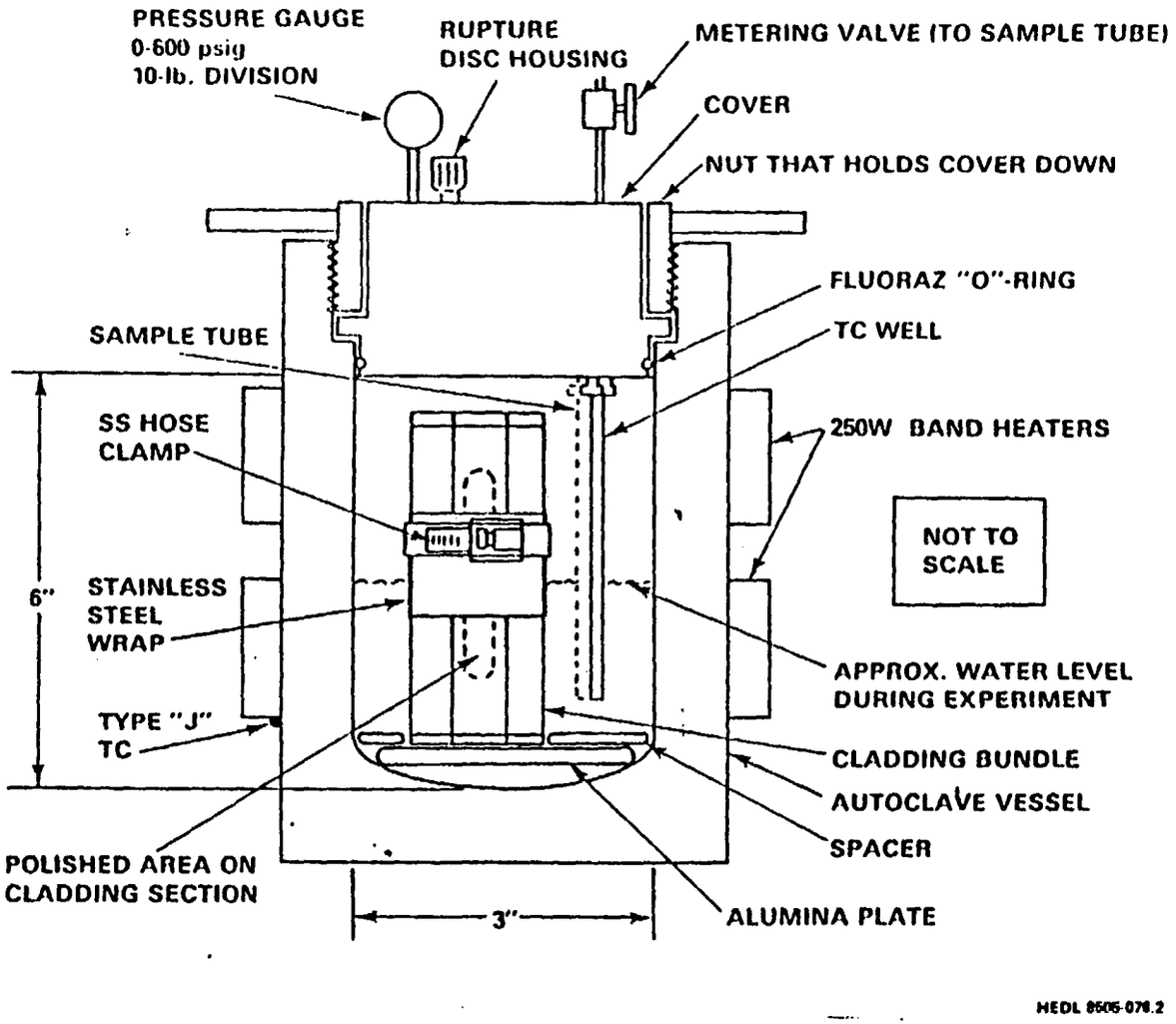


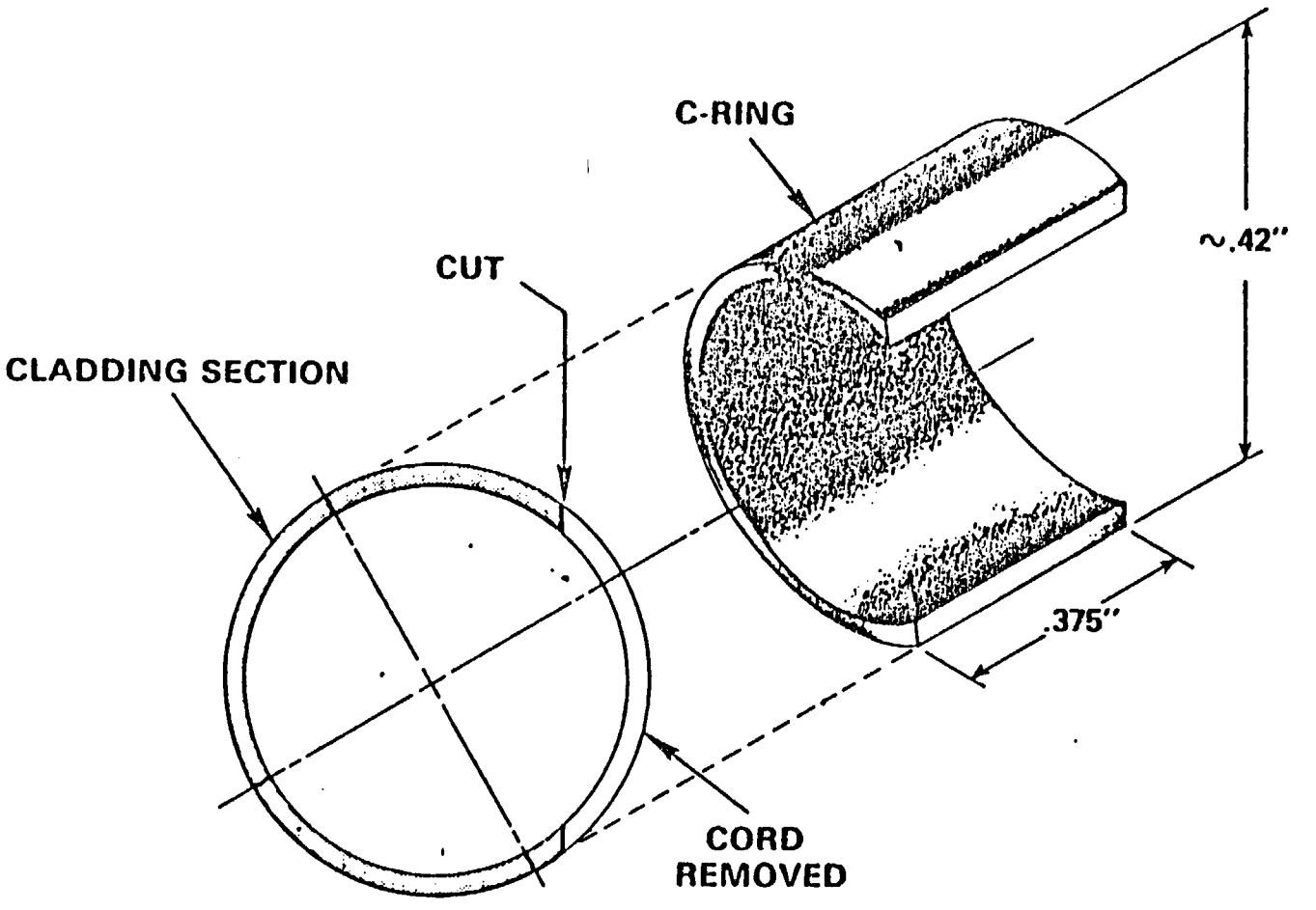
FIGURE 5. Schematic Cross Section of the Autoclave with the Spent Fuel Cladding Bundle in Place.

PLANNED CORROSION EXPERIMENTS

STRESS CORROSION CRACKING

1. SCOPING EXPERIMENT
   - STRESS DEFUELED CLADDING IN PERIOD III ENVIRONMENT
   - PRODUCE BASELINE DATA USING "C-RING" SYSTEM
2. PERIOD III ENVIRONMENT
   - EXPOSE PRESSURIZED FUELED CLADDING
3. PERIOD II ENVIRONMENT
   - EXPOSE PRESSURIZED FUELED CLADDING USING AUTOCLAVE

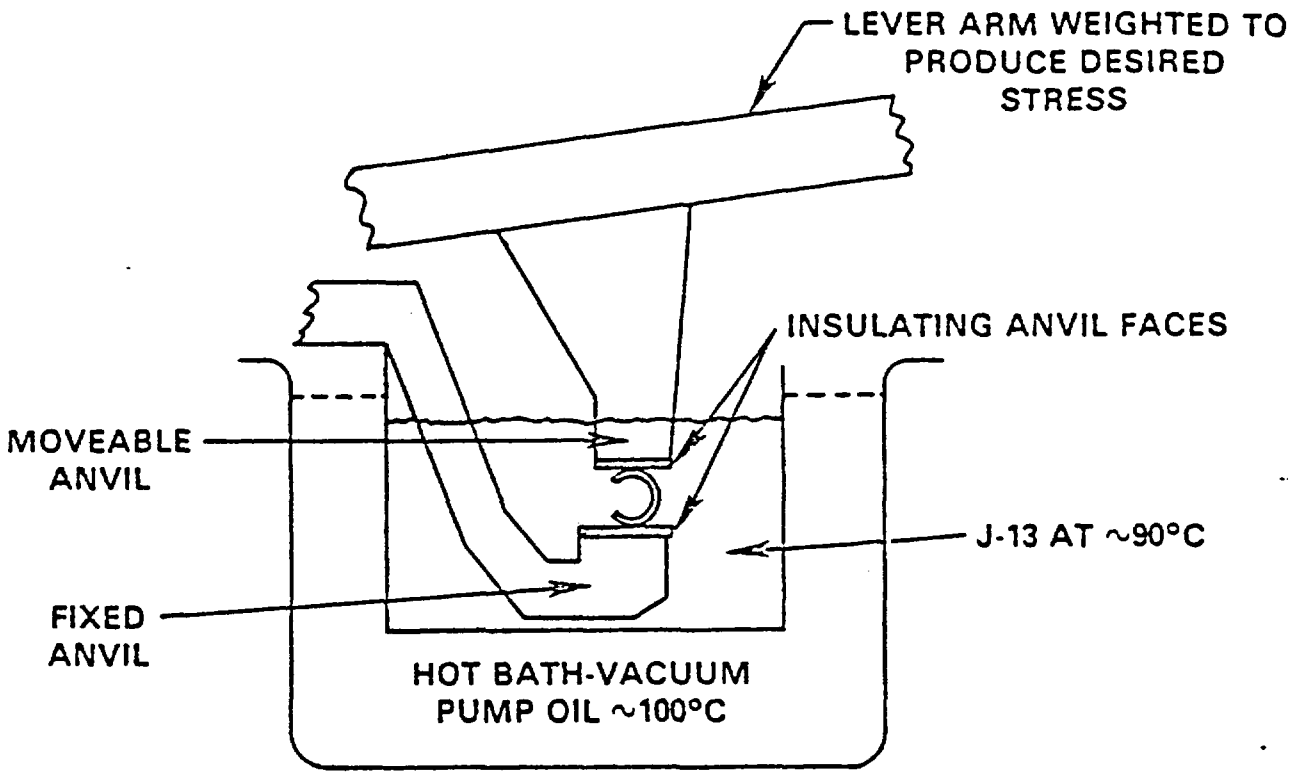
"C-RING" CLADDING SPECIMEN



HEDL 8604 005.1

FIGURE 3. Cladding "C-ring" Specimen.

"C-RING" STRESS CORROSION CRACKING EXPERIMENT



HEDL 8411-008

FIGURE 2. Schematic Cross Section of the Water Tank of the "C-ring" Stress Corrosion Cracking Scoping Experiment Apparatus with the Anvils in Position Stressing a "C-ring" Specimen.

U.S. DEPARTMENT OF ENERGY

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Nevada Nuclear Waste Storage Investigations PROJECT

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NNWSI PROJECT/NRC WASTE PACKAGE TECHNICAL MEETING

UPDATE ON DESIGN, FABRICATION, PROTOTYPE TESTING (WBS 2.2.4)

EDWARD W. RUSSELL

JULY 23, 1985

KEY SITE ENVIRONMENTAL CHARACTERISTICS TO THE OVERALL DESIGN APPROACH

- THE PROPOSED REPOSITORY HORIZON IS LOCATED IN THE UNSATURATED ZONE SEVERAL HUNDRED FEET ABOVE THE WATER TABLE IN A RELATIVELY STRONG ROCK THAT DOES NOT EXHIBIT SIGNIFICANT CREEP PROPERTIES AT PLANNED REPOSITORY TEMPERATURES.

- THE ANTICIPATED FLUX OF WATER MIGRATING FROM THE SURFACE TOWARD THE WATER TABLE IS EXTREMELY SMALL (<1 MM/YEAR), WITH THE PRINCIPAL FLOW OCCURRING IN THE ROCK MATRIX.

- THE WATER CHEMISTRY IS EXPECTED TO BE REASONABLY BENIGN; THE PH IS 7-8 AND THE IONIC STRENGTH IS LOW. THE PRINCIPAL DISSOLVED SOLIDS ARE BICARBONATES AND THE CHLORIDE CONCENTRATION IS A FEW PPM.

GIVEN THIS ENVIRONMENT, SEVERAL WASTE PACKAGE DESIGN PARAMETERS ARE SUGGESTED

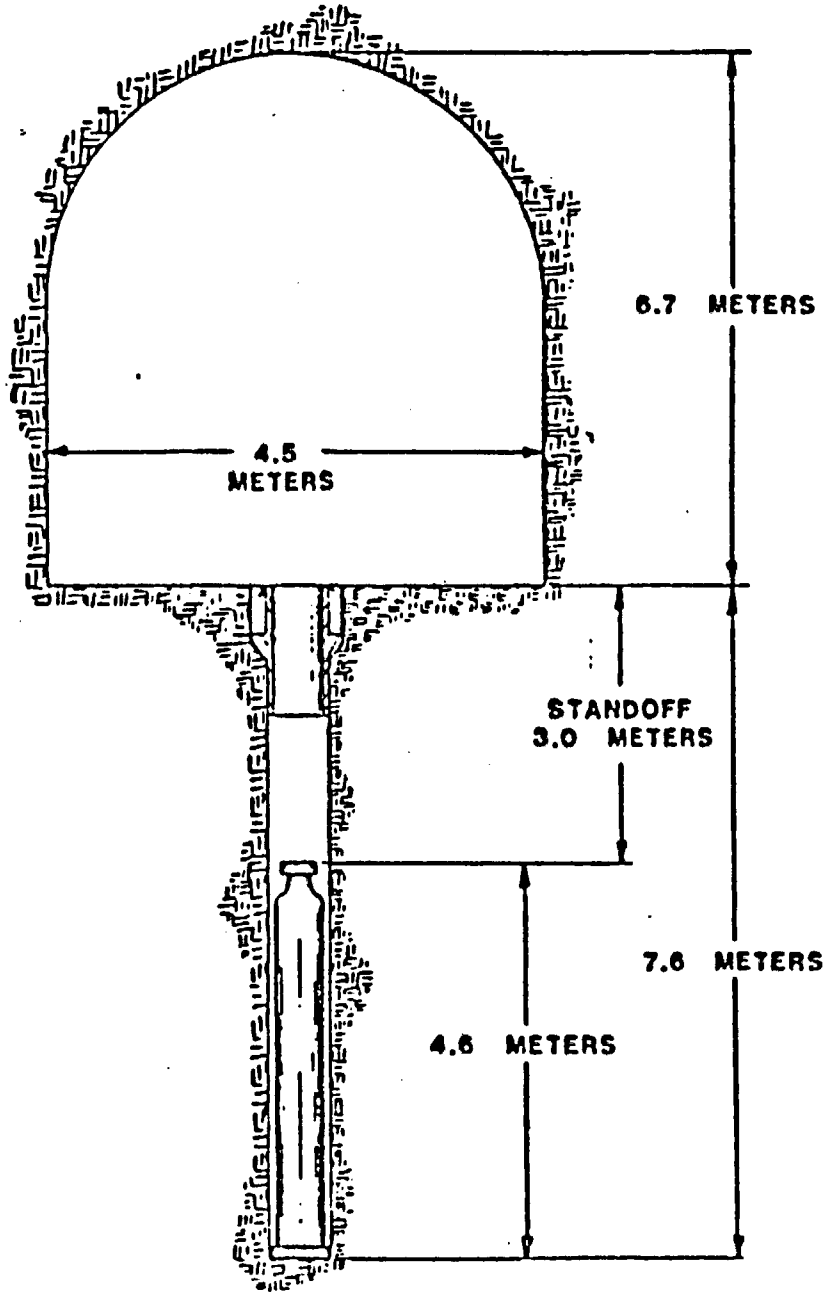
- THE LONG-LIFE DISPOSAL CONTAINER IS NOT REQUIRED TO RESIST SIGNIFICANT EXTERNAL HYDROSTATIC OR LITHOSTATIC PRESSURE LOADS.

- THE LOW WATER FLUX WILL RESULT IN A NEARLY DRY LOCAL ENVIRONMENT AROUND THE CONTAINER AS LONG AS THE ROCK TEMPERATURE EXCEEDS ABOUT 100°C. THE CORRODING FLUID IS STEAM OR HUMID AIR DURING THIS PERIOD.

- AFTER THE LOCAL TEMPERATURE DECLINES TO <100°C, LIQUID WATER CAN AGAIN CONTACT THE CONTAINER, BUT ONLY IN LIMITED AMOUNTS THE WATER CHEMISTRY IS COMPATIBLE WITH CORROSION RESISTANT MATERIALS SUCH AS AUSTENITIC STAINLESS STEELS.

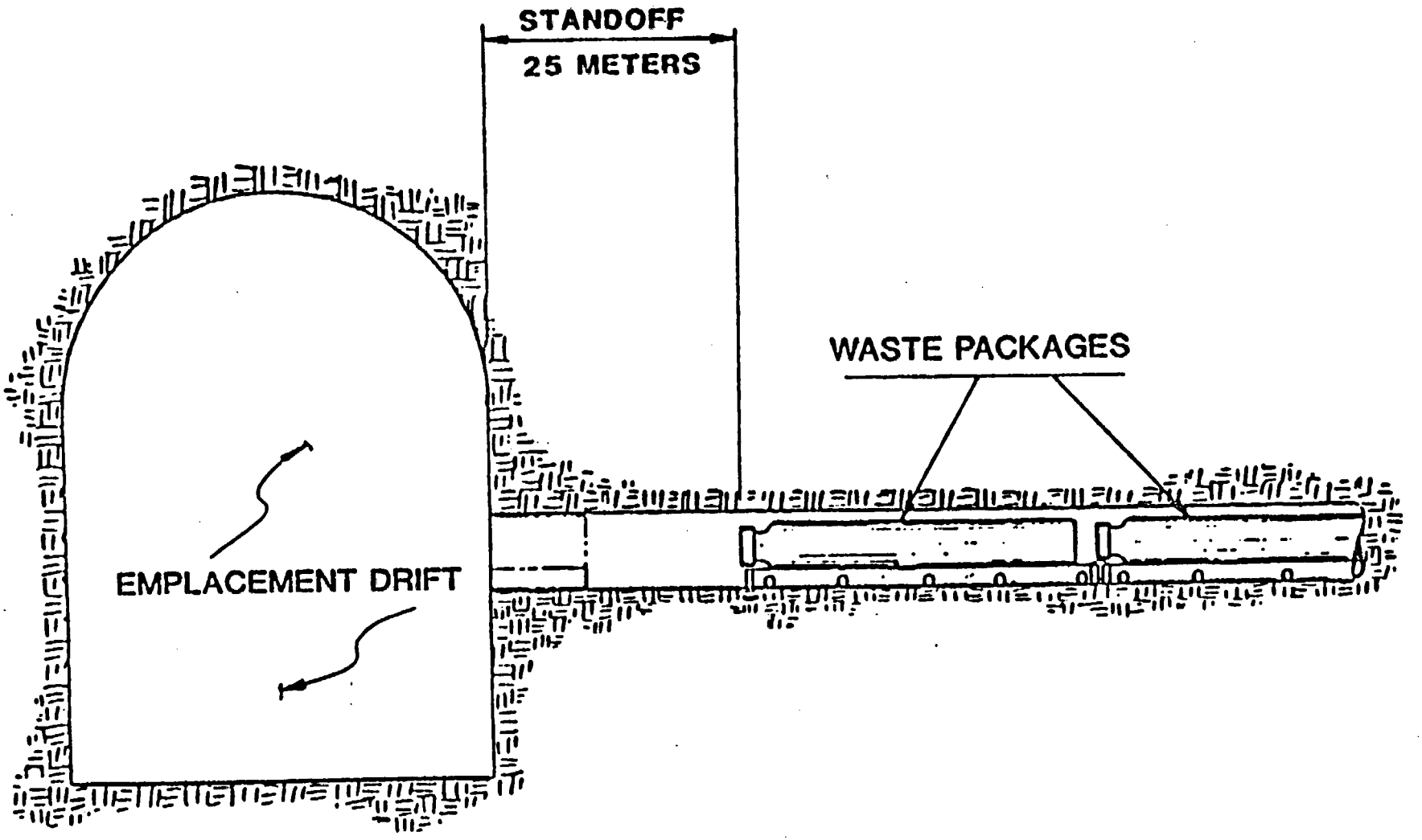
REFERENCE VERTICAL EMPLACEMENT DRIFT AND BOREHOLE CONFIGURATION

(SNL84-2242, DRAFT).



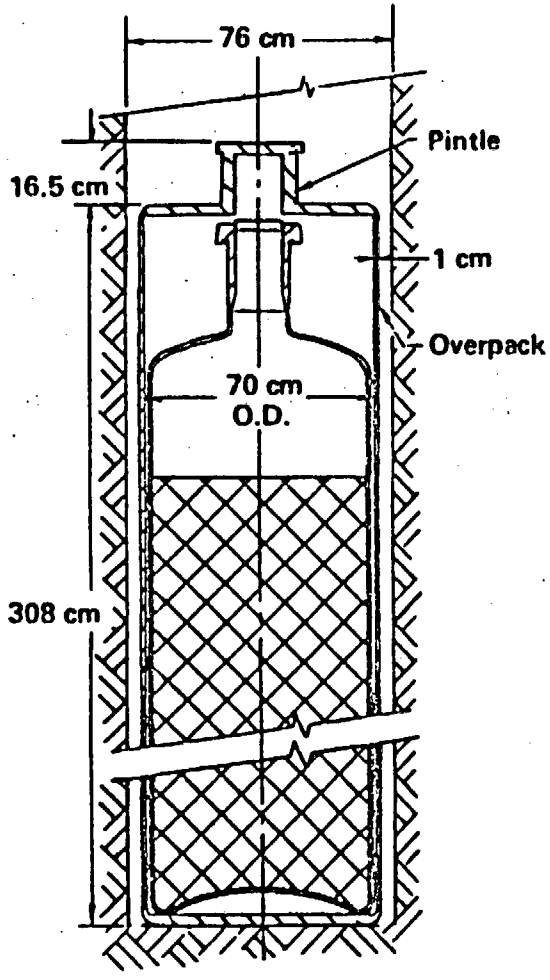
HORIZONTAL EMPLACEMENT DRIFT AND BOREHOLE CONFIGURATIONS

(SNL84-2242, DRAFT)

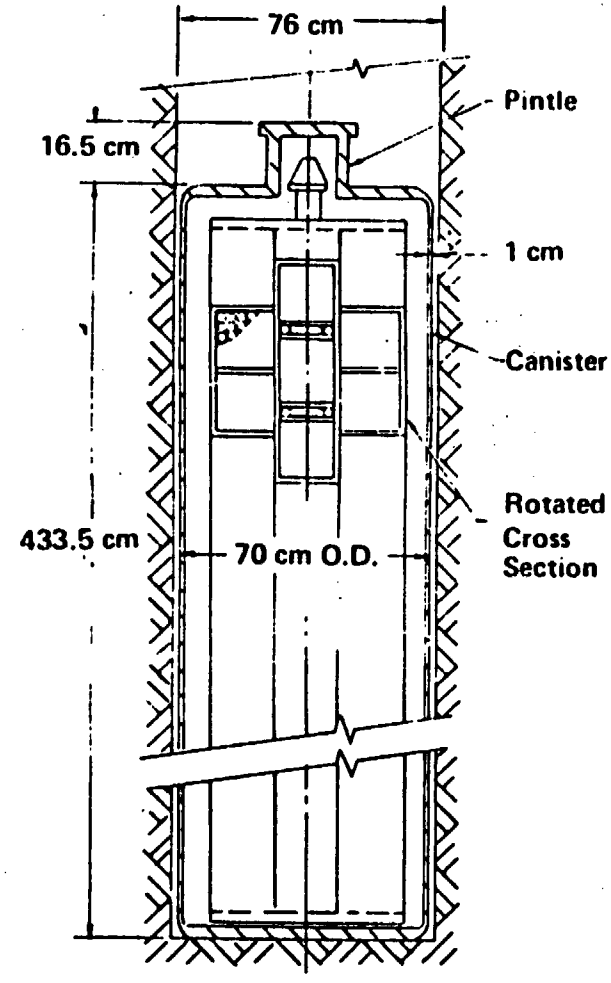


CONCEPTUAL DESIGN REPORT (UCRL-53595)

REFERENCE DESIGNS (NOVEMBER, 1984)



WV/DHLW (defense high-level waste) package emplaced in vertical borehole

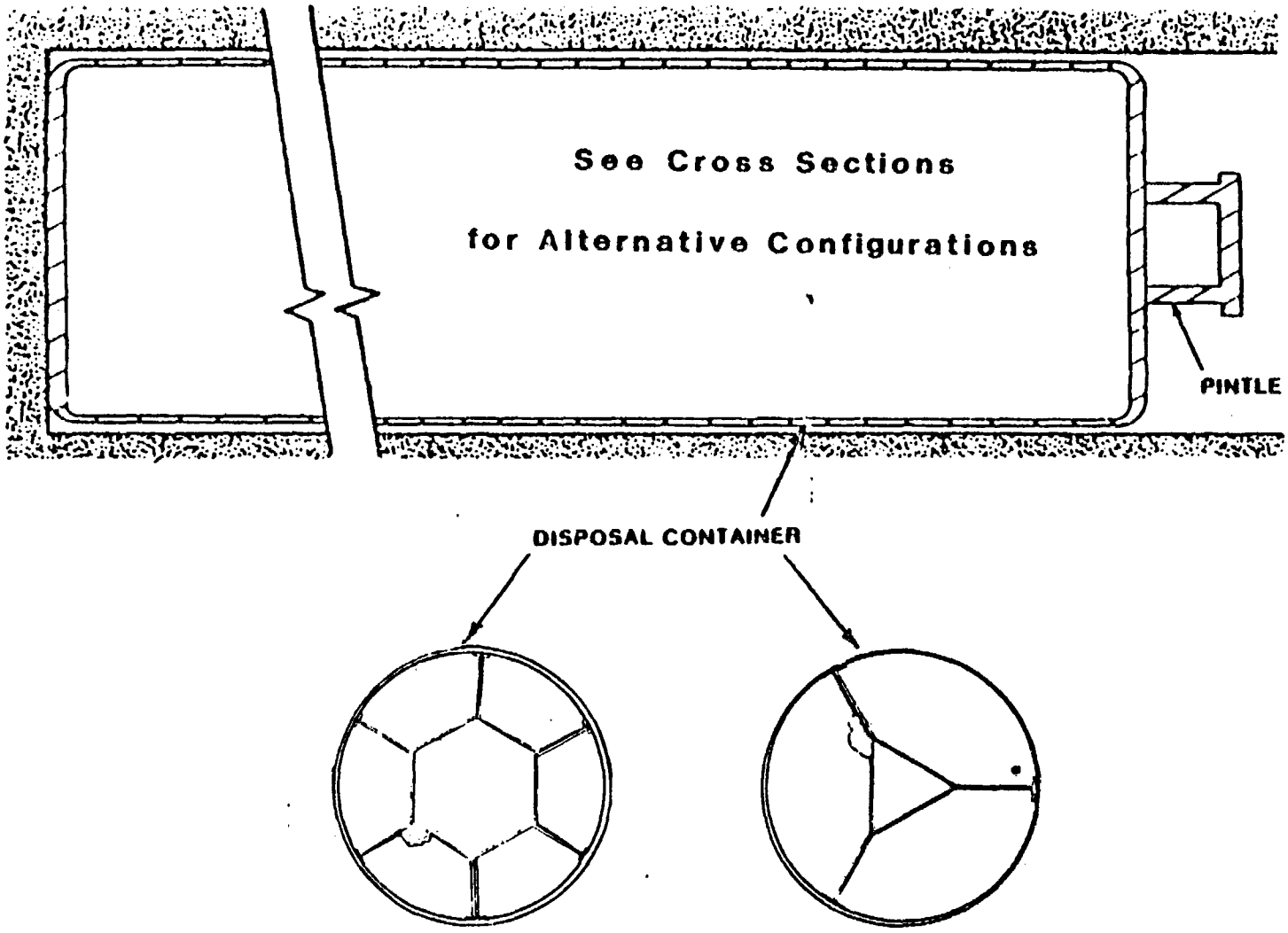


BWR (boiling water reactor) spent fuel waste package emplaced in vertical borehole PWR same except for 3 holes instead of 7.

SINCE NOVEMBER, 1984, DESIGN STUDIES HAVE BEEN UNDERWAY PREPARATORY TO THE FORMAL INITIATION OF THE ADVANCED CONCEPTUAL DESIGN PHASE.

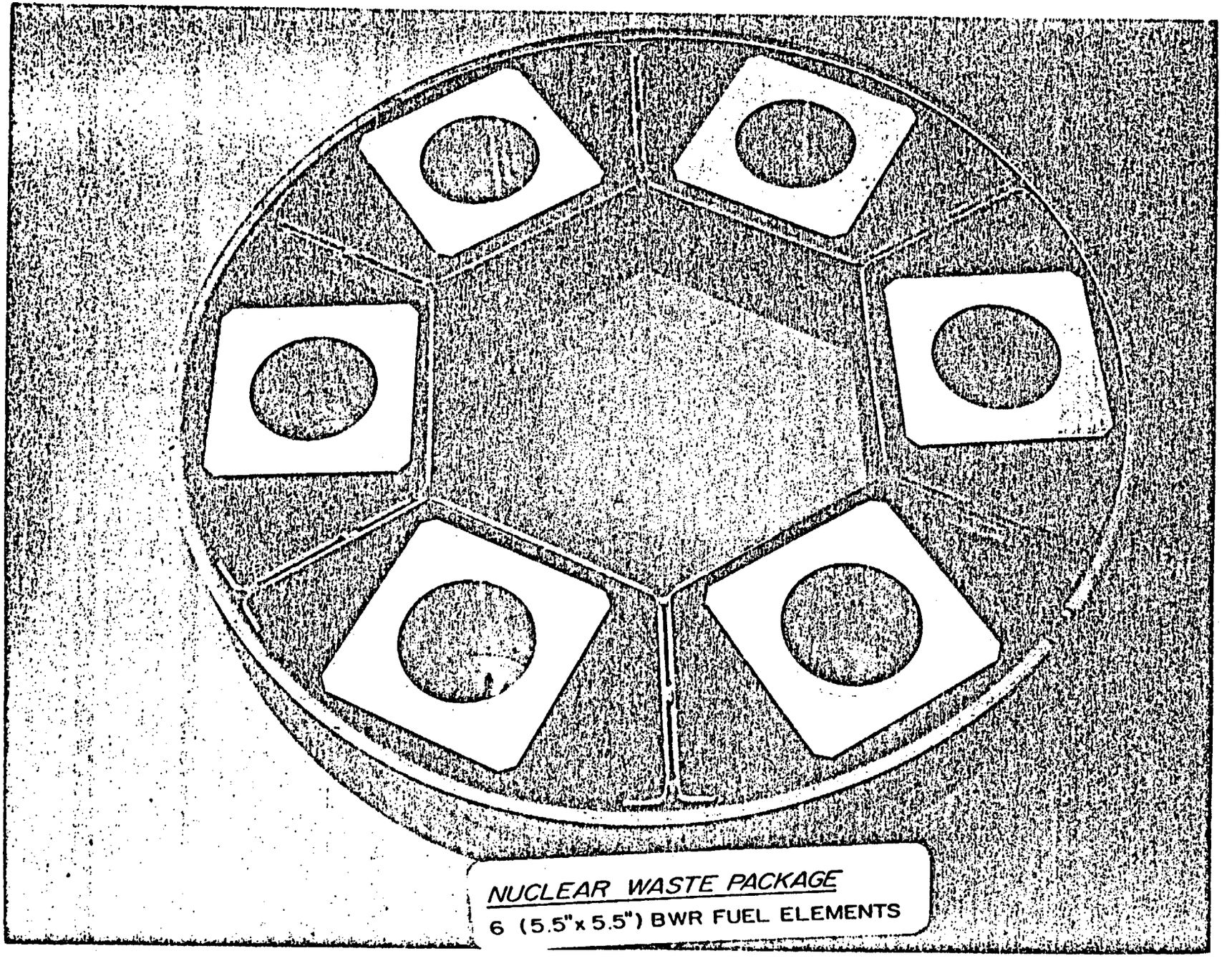
THE ADVANCED CONCEPTUAL DESIGN CRITERIA (UCID-20449) WHICH IS UNDERGOING HEADQUARTERS' REVIEW, IS THE PREREQUISITE TO INITIATION OF THIS DESIGN PHASE.

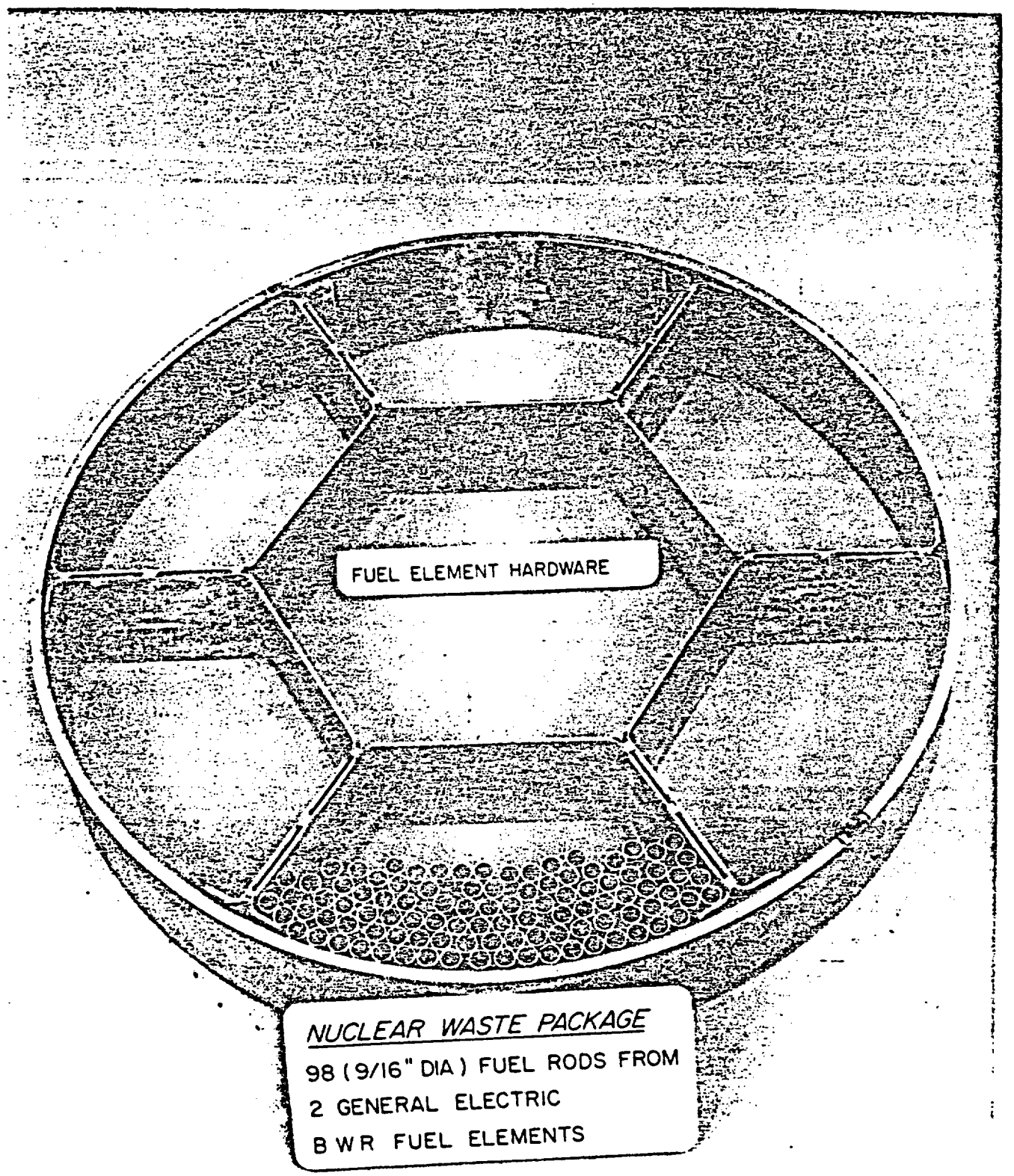
Waste Package Design Studies for Spent Fuel

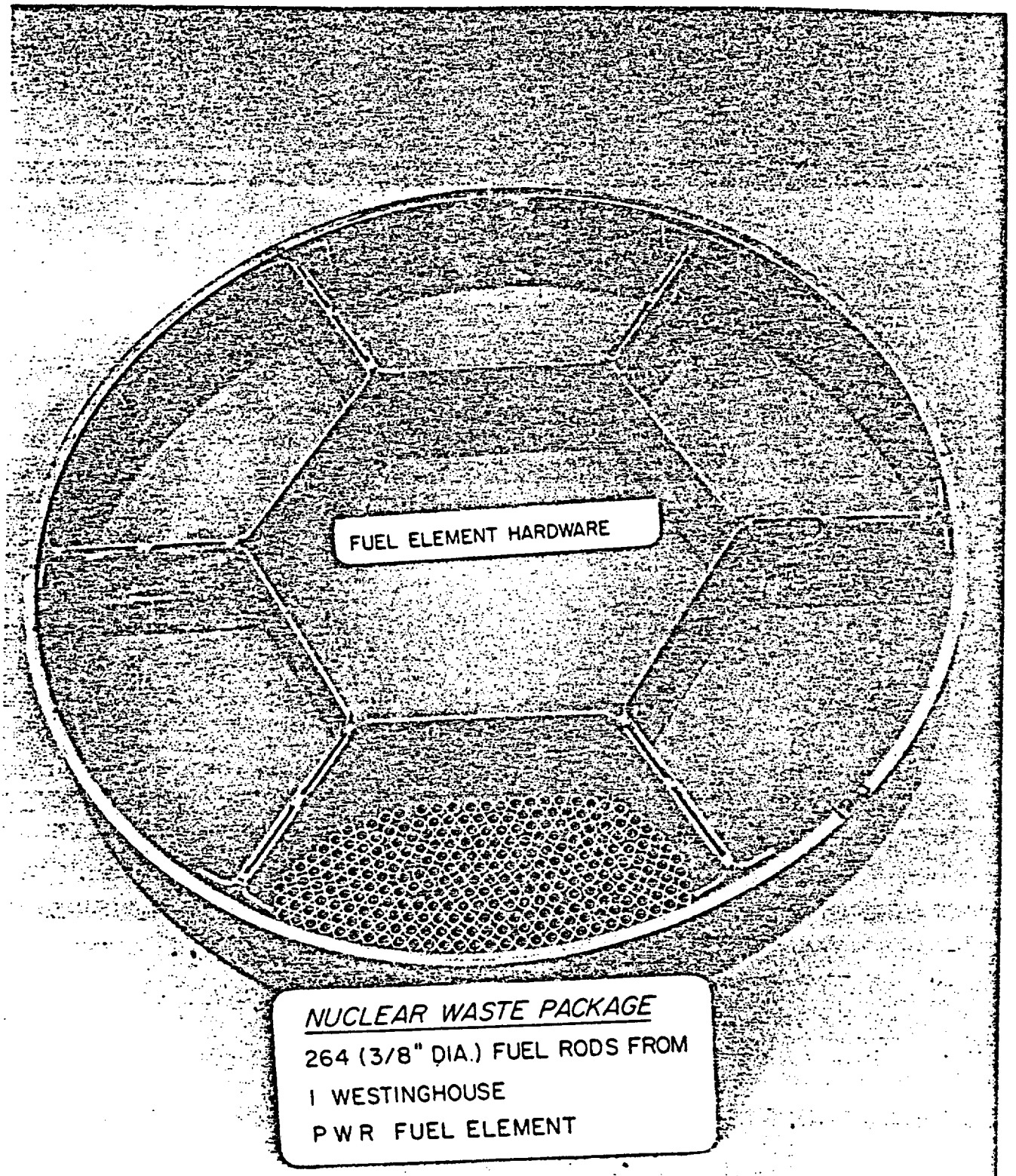


cross section
of disposal container
for BWR spent fuel

cross section
of disposal container
for PWR spent fuel


NUCLEAR WASTE PACKAGE
6 (5.5"x 5.5") BWR FUEL ELEMENTS


FUEL ELEMENT HARDWARE
NUCLEAR WASTE PACKAGE
98 (9/16" DIA) FUEL RODS FROM
2 GENERAL ELECTRIC
BWR FUEL ELEMENTS


FUEL ELEMENT HARDWARE
NUCLEAR WASTE PACKAGE
264 (3/8" DIA.) FUEL RODS FROM
1 WESTINGHOUSE
PWR FUEL ELEMENT

COST-EFFECTIVENESS CONSIDERATIONS

- MINIMIZE THE QUANTITY OF PREMIUM MATERIAL REQUIRED.
- MINIMIZE COMPLEX FORMING OR JOINING OPERATIONS, ESPECIALLY THOSE TO BE CONDUCTED REMOTELY (HOT CELL OPERATIONS).
- MINIMIZE THE NEED FOR CLOSE FABRICATION TOLERANCES.
- MINIMIZE THE NUMBER OF DESIGNS REQUIRED TO ACCOMMODATE THE VARIOUS WASTE FORMS AND CONFIGURATIONS.

A POTENTIALLY SIGNIFICANT DESIGN FEATURE IS A COMMON DIAMETER OF THE BASIC CONTAINER

- ELIMINATES MULTIPLE SETS OF SURFACE AND UNDERGROUND HANDLING EQUIPMENT
- PERMITS STANDARDIZATION OF EMPLACEMENT HOLE AND LINER SIZES.

BUT, OPTIMIZATION OF CONTAINER TEMPERATURE HISTORIES AND TRANSPORTATION CONSIDERATIONS COMPATIBLE WITH POSSIBLE MRS OPERATING SCENARIOS MAY INVOLVE A SMALLER DIAMETER CONTAINER FOR SPENT FUEL (THAN FOR WV/DWPF PACKAGE).

STRUCTURAL ANALYSIS

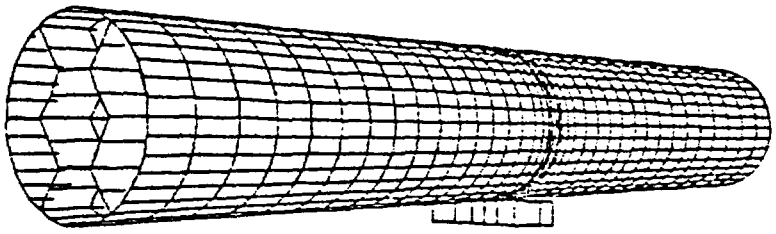
- TO DETERMINE IF REGULATORY REQUIREMENTS WILL BE MET UNDER NORMAL AND ACCIDENT CONDITIONS; STRUCTURAL ANALYSIS MUST ADDRESS LARGE DEFORMATION, INELASTIC STATIC AND DYNAMIC RESPONSES OF THE DISPOSAL CONTAINER TO PLAUSIBLE REPOSITORY OPERATING SCENARIOS.

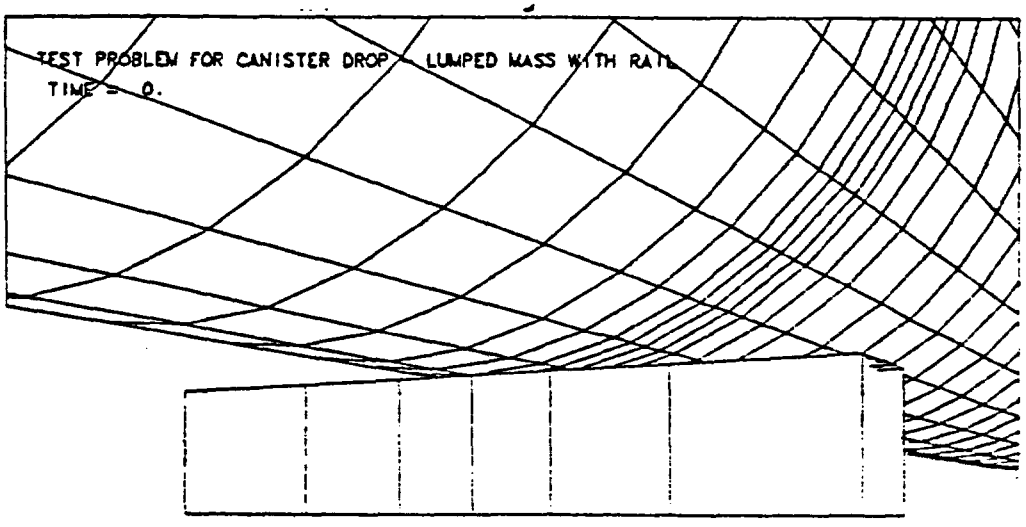
- DYNA3D, A THREE-DIMENSIONAL FINITE ELEMENT COMPUTER CODE (J. O. HALLQUIST, 1982), IS BEING USED.

SPENT FUEL DISPOSAL CONTAINER DESIGN STUDY

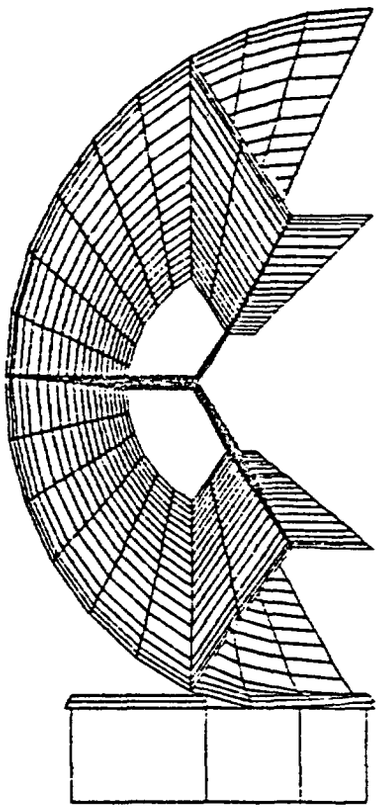
FULLY LOADED HORIZONTALLY ORIENTATED CONTAINER (66-CM DIAMETER) DROPPED 7 FEET ONTO A MILD STEEL SQUARE TUBE (4 IN X 1/4 IN WALL). THE TUBE AXIS AT RIGHT ANGLES TO THE CONTAINER AXIS, WITH IMPACT OCCURRING AT THE CONTAINER MIDPOINT.

TEST PROBLEM FOR CANISTER DROP - LUMPED MASS WITH RAIL
TIME = 0.

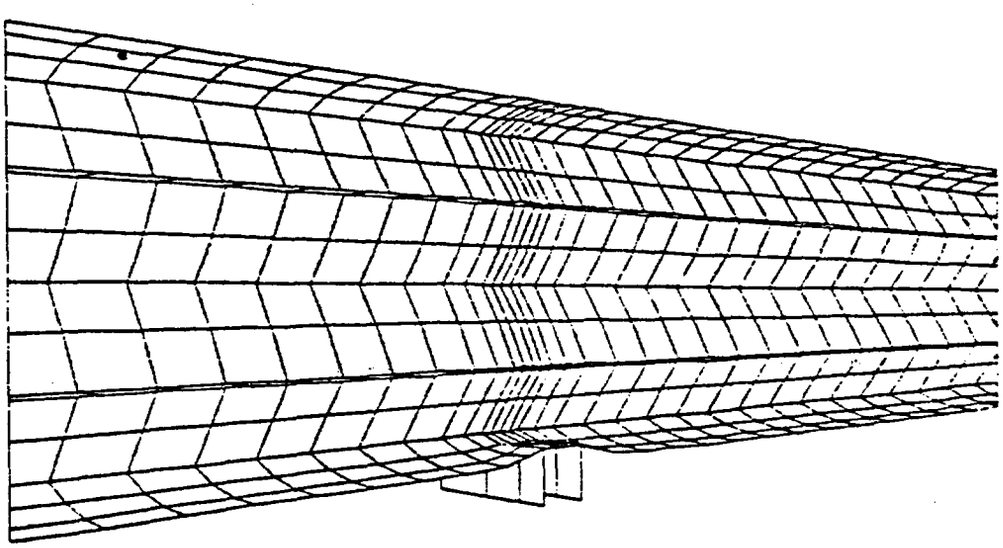




TEST PROBLEM FOR CANISTER DROP - LUMPED MASS WITH RAIL
TIME = 5.00000E-03

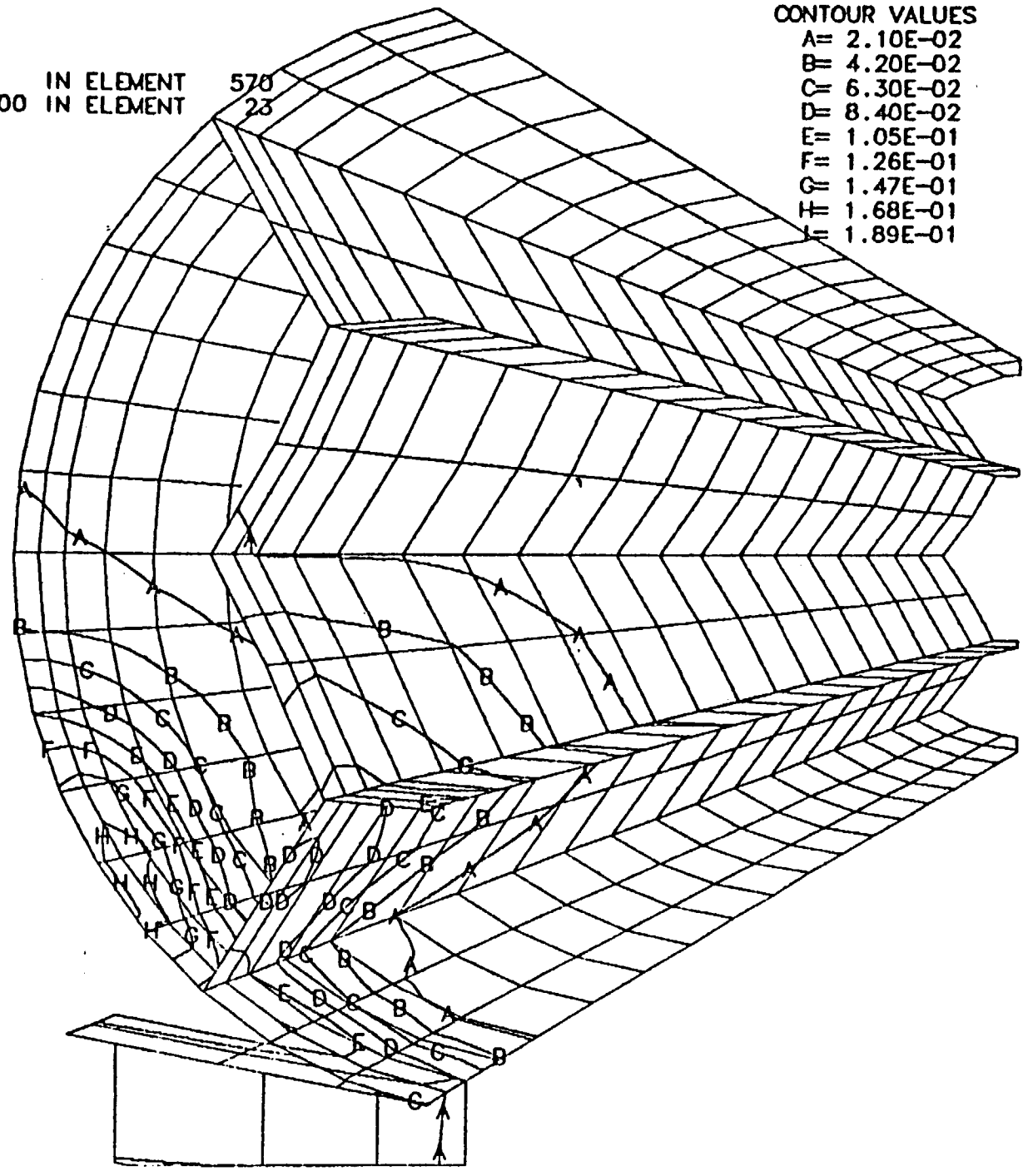


TEST PROBLEM FOR CANISTER DROP - LUMPED MASS WITH RAIL
TIME = 5.00000E-03



CASK DROP ON RAIL

MIN= 0. IN ELEMENT 570
MAX= .210E+00 IN ELEMENT 23



OUR RESULTS INDICATE THAT FAILURE PROBABLY WILL NOT OCCUR FOR THE AFOREMENTIONED HARSH ACCIDENT-SCENARIO SIMULATION.

FUTURE STRUCTURAL MODELING WILL INVOLVE INCORPORATING MORE DETAIL TO THE INTERNAL COMPARTMENTATION AND UPDATING OUR DESIGN TO REFLECT CURRENT MRS OPERATING SCENARIOS.

U.S. DEPARTMENT OF ENERGY

OCRWM

Nevada Nuclear Waste Storage Investigations PROJECT

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THERMAL ANALYSES OF SPENT FUEL WASTE PACKAGES

WERNER STEIN

23 JULY 1985

PRESENTATION WILL DISCUSS:

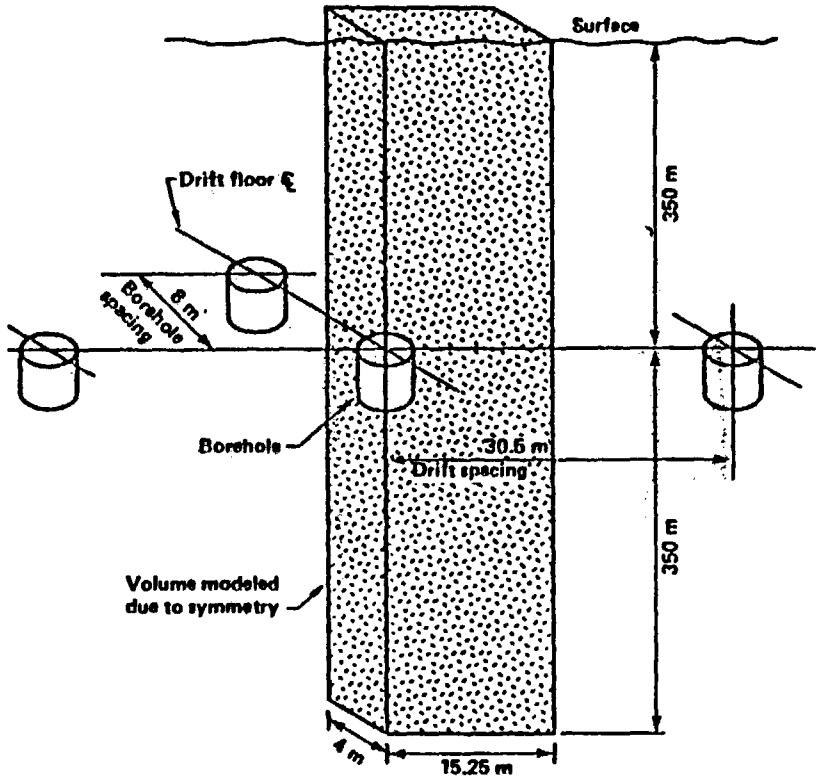
- CURRENT APPROACH
- PREVIOUS APPROACH
- ANALYSIS RESULTS FOR CURRENT DESIGN

THERMAL ANALYSES ARE NECESSARY TO PREDICT:

- PEAK SPENT FUEL CLADDING TEMPERATURE
  - NOT EXCEED 350°C
- CONTAINER WALL TEMPERATURE
  - PREDICT CORRODING FLUID STATE
- TUFF SURROUNDING TEMPERATURES
  - HYDROLOGIC BEHAVIOR

WASTE PACKAGE GEOMETRY & EMPLACEMENT

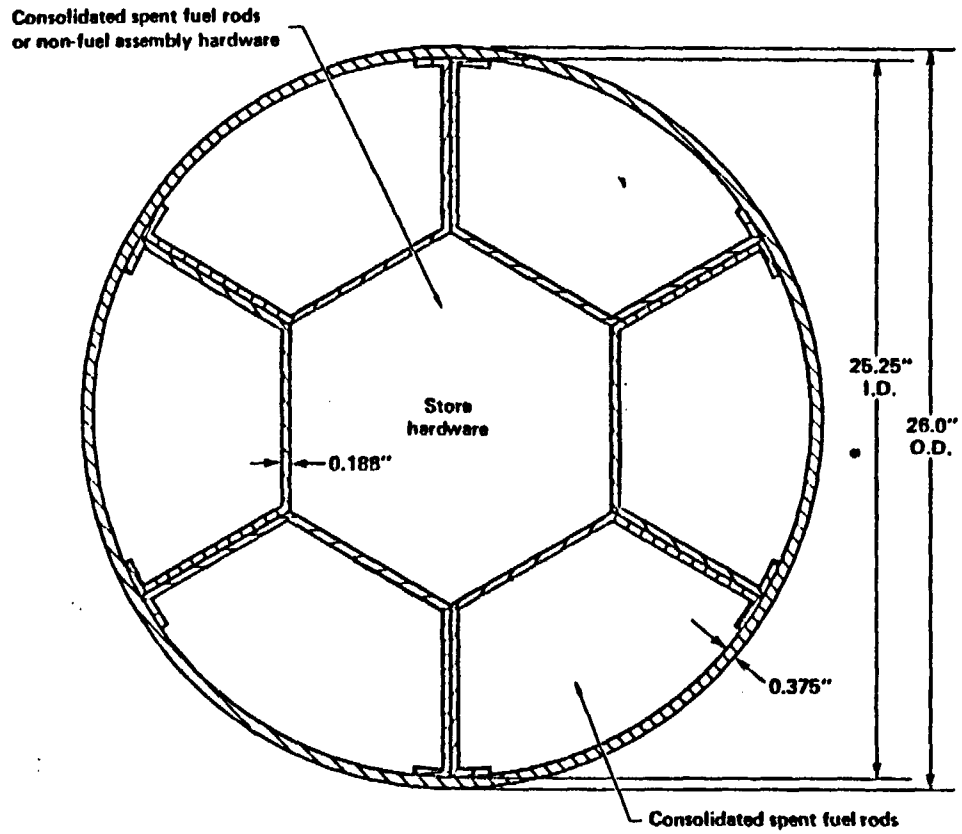
- 350 M BURIAL DEPTH
- VERTICALLY IN DRIFT FLOOR
  - 8 M CANISTER PITCH
  - 30 M DRIFT SPACING
- 25°C AMBIENT TUFF TEMPERATURE
  - GRADIENT-NEGLIGENT EFFECT



REPOSITORY LAYOUT FOR VERTICAL CONTAINER EMPLACEMENT.

CURRENT DISPOSAL CONTAINER DESIGN STUDY

- 66 CM DIAMETER
- INNER COMPARTMENTS
  - SIX ALONG CAN WALL
- CENTRAL REGION
  - STORE FUEL RODS OR NON-FUEL HARDWARE


Consolidated spent fuel rods
or non-fuel assembly hardware
Store
hardware
0.188"
25.25"
I.D.
26.0"
O.D.
0.375"
Consolidated spent fuel rods

THERMAL MODELING APPROACH

- PREVIOUS MODEL APPROACHES USED 2-D MODEL WITH A:
  - MODIFIED MESH TO ACCOUNT FOR 3-D
    - "HOURGLASS MODEL"
  - RESULTED IN HIGHER BOREHOLE WALL TEMPERATURE
  - APPROACH REPLACED BY CURRENT, IMPROVED TECHNIQUE
- TWO PARTS TO CALCULATIONS
  - 3-D MODEL OF BOREWALL & SURROUNDING TUFF
    - HEAT SOURCE INSIDE BOREHOLE
    - OBTAIN BOREHOLE WALL TEMP. HISTORY
  - 2-D MODEL OF CONTAINER INSIDE BOREHOLE
    - APPLY 3-D MODEL WALL TEMPERATURE HISTORY AS A BOUNDARY CONDITION
    - 3-D CALCULATION SHOWS THAT 2-D MODEL IS SATISFACTORY

3-D MODEL OF TUFF

- TACO-3D COMPUTER CODE (W. E. MASON, SAND83-8212)
  - FINITE ELEMENT MESH
  - REQUIRES DATA FOR SOIL
    - DENSITY
    - THERMAL CONDUCTIVITY
    - SPECIFIC HEAT

- TUFF THERMAL PROPERTIES VARY WITH TEMPERATURE
  - BELOW 100°C - 80% WATER SATURATED
  - ABOVE 100°C - DRY TUFF CONDITIONS
  - PROPERTIES FROM SNL KEYSTONE 6310-85-1

3-D MODEL OF TUFF

- 25°C AMBIENT TUFF TEMPERATURE
- HEAT SOURCE INSIDE BOREHOLE VOLUME
  - POWER VARIES WITH DECAY CURVE
    - ISOTROPIC MATERIAL OF HIGH CONDUCTIVITY TO RESULT IN UNIFORM BOREHOLE WALL TEMPERATURE

2-D MODEL OF WASTE PACKAGE

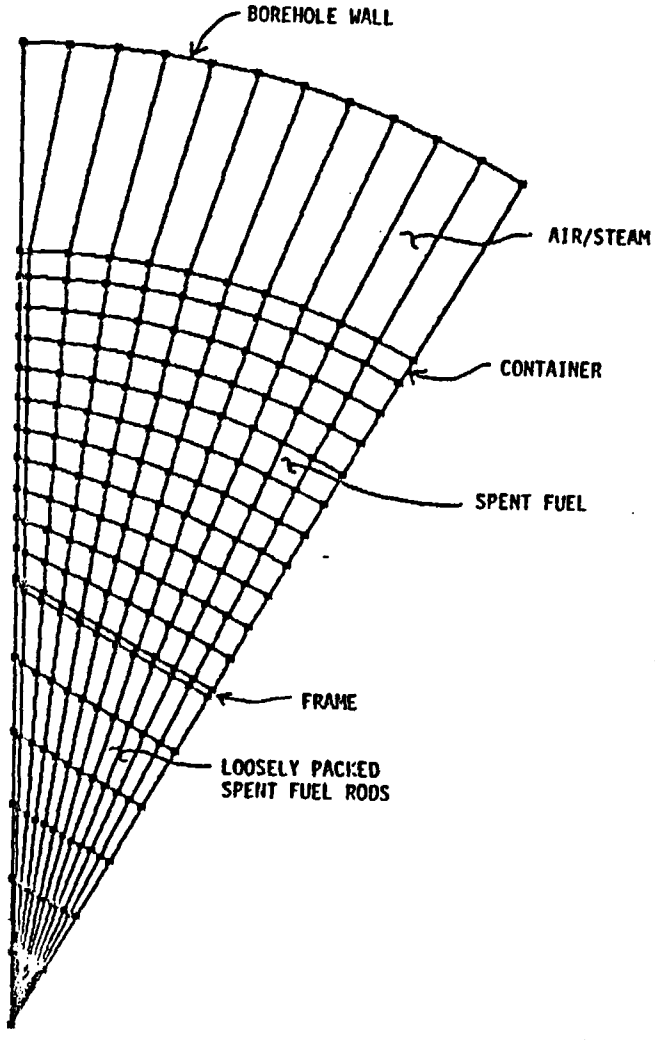
- TACO2D COMPUTER CODE (P. J. BURNS, UCID-17980)
- TEMPERATURE DEPENDENT THERMAL PROPERTIES
- APPLY 3-D MODEL TEMPERATURE BOUNDARY CONDITION
- MODEL THE SPENT FUEL, INTERNAL FRAME, & AIR SPACES
- SPENT FUEL MODELED AS AN ISOTROPIC MATERIAL
  - EQUIVALENT THERMAL CONDUCTIVITY
    - R. L. COX, ORNL-5239
      - BASED ON ANALYSIS

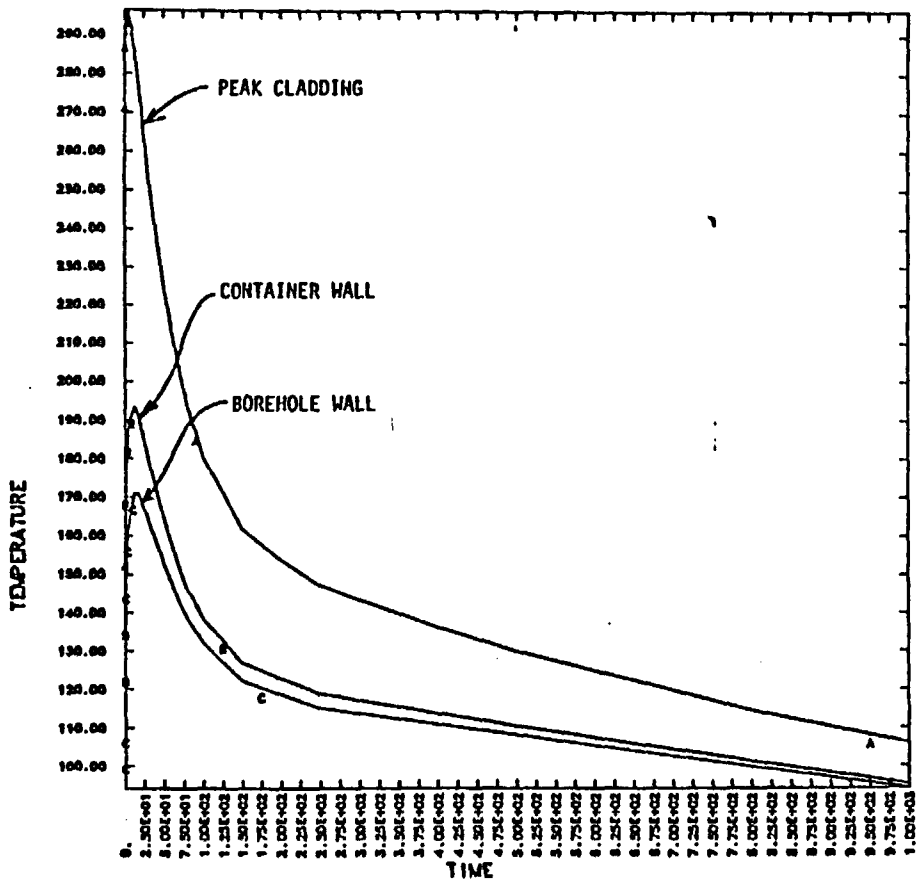
SPENT FUEL CONDUCTIVITY

- RECENT REPORT BY BATELLE SHOWS CONDUCTIVITY IS HIGHER THAN GIVEN BY COX.
  - EPRI NP-3764
    - BASED ON ANALYSIS
- PRELIMINARY EXPERIMENTAL VERIFICATION OF BATELLE ANALYSES ARE GOOD.
  - MAY RESULT IN LOWERING PEAK CLADDING TEMPERATURE BY $\sim 30^{\circ}C$

ANALYTICAL RESULTS FOR A DESIGN STUDY

- 60 CM CONTAINER
- 3610 WATTS DECAY POWER
  - 10 YEAR OUT-OF-CORE FUEL
  - 19 ASSEMBLIES BWR FUEL
- 8 M CAN PITCH & 100 FT DRIFT PITCH
- MESH AS SHOWN
- PEAK CLADDING TEMPERATURE IS 296°C
  - PEAK CONTAINER TEMP. IS 193°C
  - PEAK BORE HOLE TEMP. IS 171°C


BOREHOLE WALL
AIR/STEAM
CONTAINER
SPENT FUEL
FRAME
LOOSELY PACKED
SPENT FUEL RODS


PEAK CLADDING
CONTAINER WALL
BOREHOLE WALL
TEMPERATURE
TIME
A
B
C

FUTURE WORK

- SMALLER DIAMETER WASTE PACKAGE
- MODIFICATION OF INNER STRUCTURE COMPATIBLE WITH MRS OPERATING SCENARIOS AS THEY DEVELOP.
- EFFECTS OF SPENT FUEL AGE (5-25 YEARS OUT OF REACTOR).
- EFFECTS OF HIGHER BURN-UP SPENT FUEL.

U.S. DEPARTMENT OF ENERGY

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Nevada Nuclear Waste Storage Investigations PROJECT

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CONTAINER MATERIAL TESTING PRESENTATION
AT NNWSI/NRC WASTE PACKAGE MEETING

JULY 23, 1985

INTRODUCTION, ENVIRONMENT, CANDIDATE MATERIALS, CORROSION MODELS

R. D. MCCRIGHT

LOCALIZED CORROSION TESTING, IRRADIATION EFFECTS, ELECTROCHEMICAL TESTING

R. S. GLASS

STRESS CORROSION TESTING, METALLURGICAL PHASE STABILITY, ALLOY EFFECTS

M. C. JUHAS

SUMMARY, FUTURE PLANS, SCHEDULES

R. D. MCCRIGHT

ELEMENTS OF 10CFR60 WHICH PERTAIN DIRECTLY TO CONTAINER MATERIAL SELECTION AND PROCESS SPECIFICATION

REQUIREMENT	MATERIAL PROPERTIES AFFECTED
1. CONTAIN THE WASTE FOR 300-1000 YEARS	1. OVERALL CORROSION/OXIDATION RESISTANCE OF CONTAINER MATERIAL; "WELDABILITY" OF CONTAINER MATERIAL TO ACHIEVE HIGH-INTEGRITY WELD.
2. MAINTAIN RETRIEVABILITY FOR 50 YEARS AFTER EMPLACEMENT	2. COMPATIBILITY OF CONTAINER MATERIAL AND BOREHOLE LINER MATERIAL.
3. NO COMPROMISE OF LONG-TERM PERFORMANCE FROM EXPECTED TRANSPORTATION, HANDLING, EMPLACEMENT, SEISMIC LOADS	3. MECHANICAL PROPERTIES, E.G., YIELD STRENGTH, TENSILE STRENGTH, IMPACT STRENGTH.
4. SURVIVE "DROP TEST" (FALL 2X HEIGHT ON UNYIELDING SURFACE AT MINIMUM ANTICIPATED TEMPERATURE)	4. IMPACT STRENGTH AT "LOW TEMPERATURES".
5. SURVIVE "FIRE TEST" (30 MINUTES AT 800°C)	5. "HIGH TEMPERATURE" YIELD STRENGTH.

ADDITIONAL DESIRABLE WASTE PACKAGE DESIGN FEATURES

- USE STANDARDIZED COMPONENTS WHENEVER POSSIBLE
- EMPHASIZE SIMPLICITY AND EASE OF FABRICATION
- BE TECHNICALLY CONSERVATIVE
- USE CONVENTIONAL MATERIALS AND FABRICATION TECHNIQUES
- BE COMPARABLE WITH ALL WASTE PROCESSING, TRANSPORTATION, AND EMPLACEMENT OPERATIONS
- BE COST EFFECTIVE WITHOUT COMPROMISING DESIGN REQUIREMENTS
- USE COMMON CONTAINER DIAMETERS AND LENGTHS FOR VARIOUS WASTE FORMS WHEN POSSIBLE

ENVIRONMENTAL PARAMETERS IMPORTANT TO CORROSION

1. Physical State of Corrosion Medium
2. Composition
3. Temperature
4. Pressure
5. pH
6. Oxygen Potential
7. Flow Rate
8. Radiation

EXPECTED INITIAL ENVIRONMENT
(BEFORE WASTE EMPLACEMENT)

1. PHYSICAL STATE OF FLUID MEDIUM-

   TWO-PHASE, MOIST AIR-LIQUID WATER, 65 ± 19% SATURATION.

2. COMPOSITION

   A. SOLID

   ROCK - WELDED, DEVITRIFIED TUFF WITH ABOUT 14% POROSITY AND NUMEROUS FRACTURES.

   MINERALS - QUARTZ, CRISTOBALITE, FELDSPARS, AND OTHERS.

   CHEMICAL COMPOSITION (R. A. ZIELINSKI, USGS-OFR-83-480):

OXIDE	APPROX. WT. %
SiO_2	75.2
Al_2O_3	12.4
K_2O	4.8
Na_2O	3.1
Fe_2O_3	1.8
CaO	0.5
MgO	0.2
TiO_2	0.1
MnO	0.06
LOSS ON IGNITION	1.0
TOTAL	99.16

EXPECTED INITIAL ENVIRONMENT
(CONT'D.)

2. COMPOSITION (CONT'D.)

B. GAS — AIR (100% REL. HUMIDITY)

C. LIQUID — VADOSE WATER WITH DISSOLVED SOLIDS AND GASES.

J-13 WELL WATER -
(IC, ICP-OES, & TECHNICON AUTOANALYZER)

SPECIES	(MG/L)	mM
HCO_3	125	2.0
SO_4	19	0.20
NO_3	9.6	0.15
CL	6.9	0.19
F	2.2	0.12
NA	44	1.9
CA	12.5	0.31
K	5.1	0.13
MG	1.9	0.08
SI	27.0	0.96

DISSOLVED GASES (ASSUMED SATURATED):

N_2	0.4
O_2	0.2
CO_2	0.01

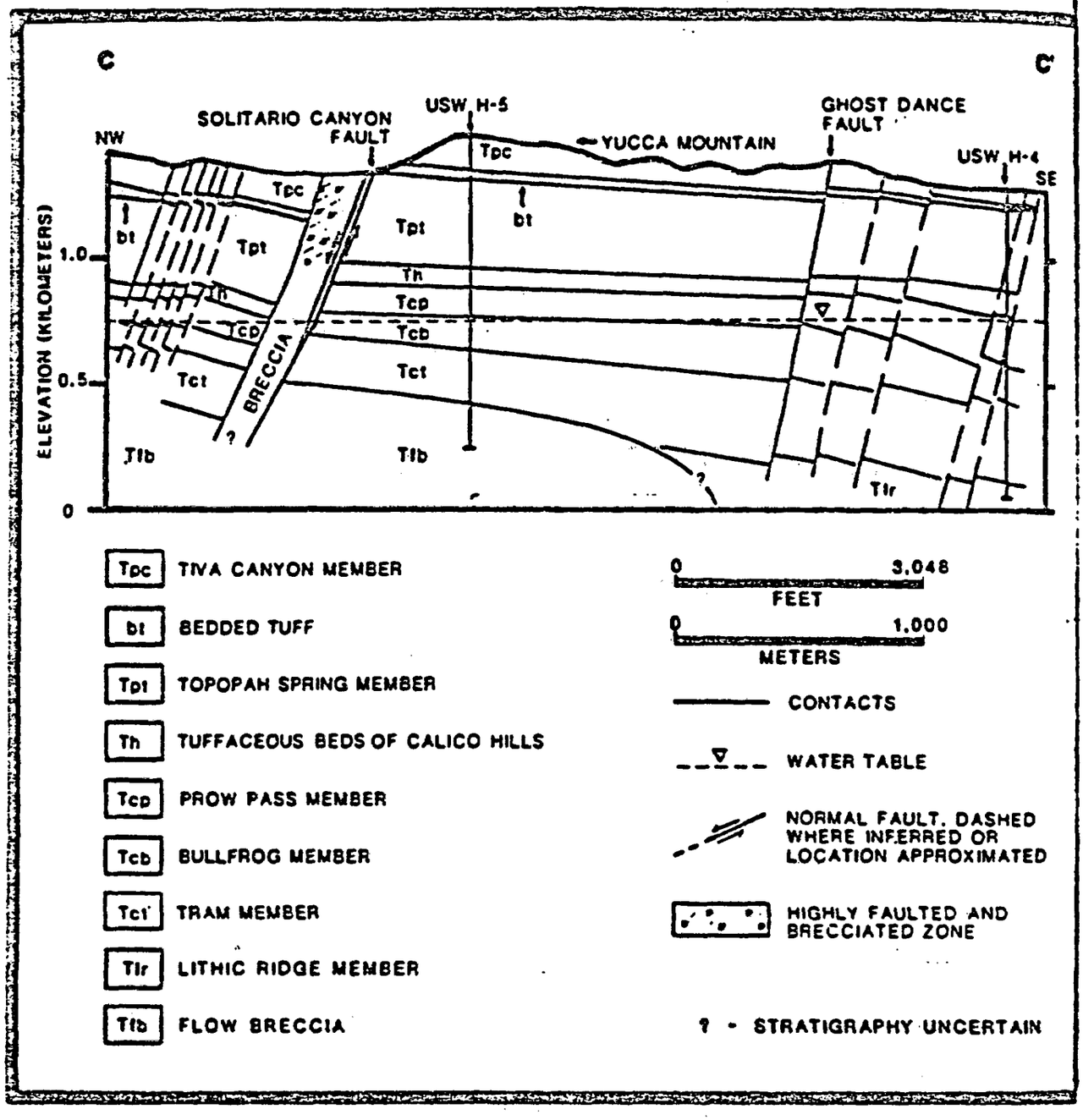


Figure 3-7. Northwest-southeast geologic cross section through drill holes USW H-5 and USW H-4, showing current interpretation of fault characteristics. See Figure 3-6 for approximate location of C-C' on geologic map. Modified from Scott and Bonk (1984).

EXPECTED INITIAL ENVIRONMENT
(CONT'D.)

3.	TEMPERATURE	29°C
4.	PRESSURE	0.1 MPA (ATMOSPHERIC)
5.	pH	NEUTRAL TO SLIGHTLY ALKALINE
6.	REDOX CONDITION	OXIDIZING (AIR PRESENT)
7.	WATER INFILTRATION RATE	LESS THAN 1 MM/YEAR
8.	GAMMA DOSE RATE	ABOUT 10^{-4} RAD/HOUR (BACKGROUND)

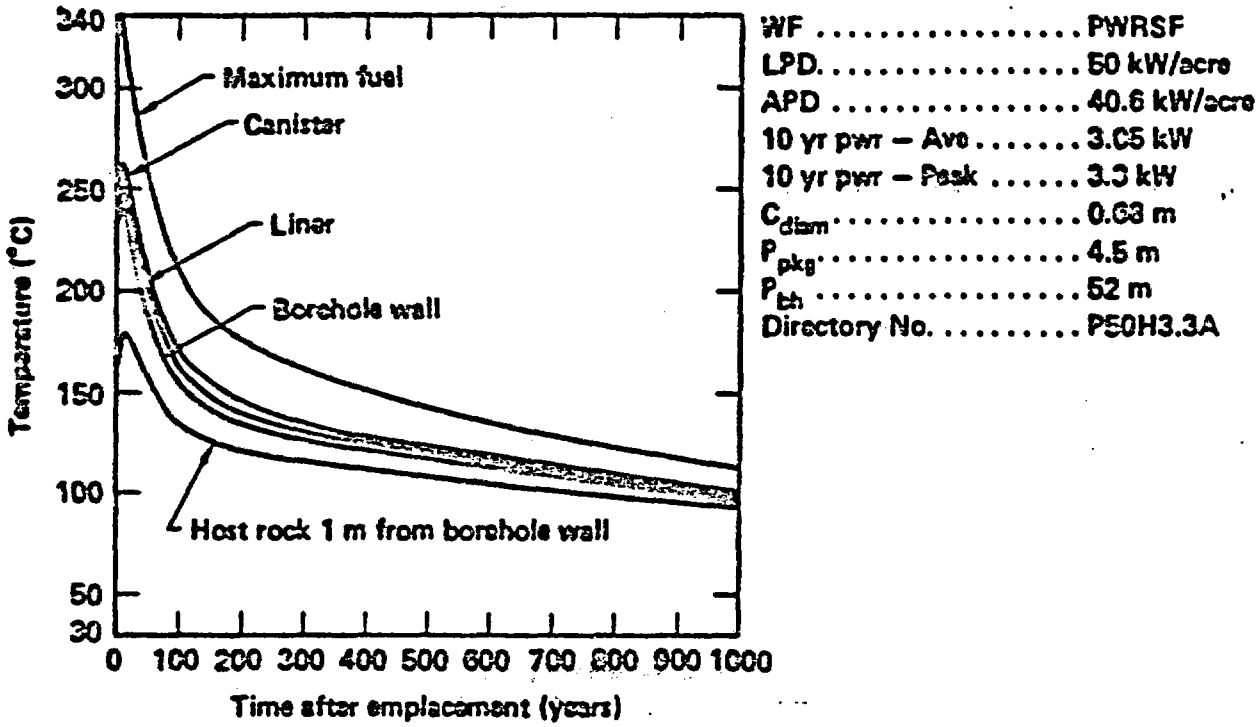


Figure 15. Temperature histories of waste package components and host rock for horizontally emplaced preconsolidated (boxed) PWR spent fuel (case 22).

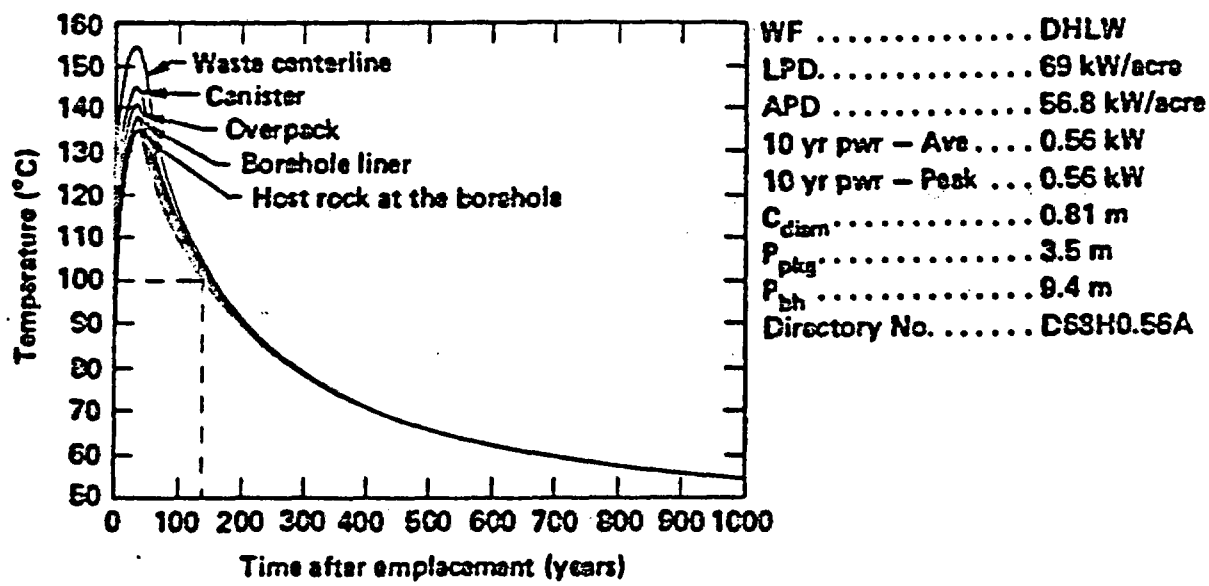


Figure 16. Temperature histories of waste package components and host rock for horizontally emplaced WV/DHLW canister (case 2).

THERMAL AND PHYSICAL CHANGES EXPECTED TO BE CAUSED BY WASTE EMPLACEMENT

1. TEMPERATURE OF PACKAGE SURFACE WOULD RISE TO A MAXIMUM AFTER 9 TO 40 YEARS AND WOULD THEN DECREASE.

2. PEAK TEMPERATURE WOULD NOT EXCEED 270°C.

3. BOILING POINT IS ABOUT 95°C AT REPOSITORY ELEVATION.

4. NO LIQUID WATER COULD EXIST NEAR PACKAGES FOR OVER 100 YEARS FOR DEFENSE WASTES AND FOR OVER 1,000 YEARS FOR 10-YEAR-OLD SPENT FUEL.

5. CORROSION MEDIUM WOULD BE SINGLE-PHASE AIR-STEAM MIXTURE FOR AT LEAST 100 YEARS FOR DEFENSE WASTES AND FOR THE ENTIRE CONTAINMENT PERIOD FOR INITIALLY YOUNG SPENT FUEL.

6. AFTER THE 95°C ISOTHERM MOVED BACK TO PACKAGES, CONDENSATION COULD PRODUCE SOME LIQUID WATER NEAR THEM, AND INFILTRATION OF VADOSE WATER COULD RESUME. A TWO-PHASE AIR-WATER MEDIUM COULD EXIST.

WHEN LIQUID WATER RETURNS, HOW MIGHT ITS COMPOSITION DIFFER FROM THAT OF THE INITIAL GROUNDWATER, AS A RESULT OF THERMAL PROCESSES?

1. POSSIBLY HIGHER CONCENTRATION OF THE MORE SOLUBLE SPECIES, BECAUSE OF RE-SOLUTION WITH LESS WATER OR BECAUSE OF DISTILLATION.

2. HIGHER SiO_2 CONCENTRATION (PERHAPS BY A FACTOR OF 2).

3. HIGHER pH, BECAUSE CO_2 WOULD BE DRIVEN OFF, AND INORGANIC CARBON EQUILIBRIUM WOULD SHIFT. (PRESENCE OF GROUT WOULD ALSO TEND TO INCREASE pH.)

4. LOWER CA AND MG CONCENTRATIONS, BECAUSE OF RETROGRADE SOLUBILITIES OF THEIR CARBONATES.

5. <u>POSSIBLE</u> CONSEQUENCES FOR CORROSION:
   - A. HIGHER HALIDE ION CONCENTRATIONS (DETRIMENTAL)
   - B. LOWER "BENIGN" ION CONCENTRATIONS (DETRIMENTAL)
   - C. HIGHER pH (BENEFICIAL)
   - D. DEPOSITION OF CARBONATES ON PACKAGE SURFACE (COULD BE EITHER BENEFICIAL OR DETRIMENTAL)

WHAT ARE "ATTRACTIVE" CANDIDATE METALS?
WHAT ARE THEIR ADVANTAGES/LIMITATIONS?

- CARBON STEELS
- ALLOY STEELS
- 400 STAINLESS STEELS, HIGH Cr FERRITIC
- 300 STAINLESS STEELS
- HIGH NICKEL STAINLESS STEELS
- NICKEL-BASE ALLOYS
- Ti AND Ti-BASE ALLOYS, ZIRCONIUM
- Cu-BASE ALLOYS

BASIS FOR SELECTION OF AUSTENITIC STAINLESS STEELS FOR REFERENCE CONTAINER MATERIALS IN CONCEPTUAL DESIGN

- EXCELLENT CORROSION/OXIDATION RESISTANCE IN AIR, IN STEAM, AND IN NON-SALINE, NEAR-NEUTRAL PH WATER (FOR EXAMPLE, J-13 WELL WATER) IN THE TEMPERATURE RANGE EXPECTED IN A TUFF REPOSITORY.
- EXCELLENT FRACTURE TOUGHNESS (RESISTANCE TO IMPACT LOADS) -- CONTAINERS READILY HANDLED AND EMPLACED IN THE REPOSITORY.
- READILY FABRICATED AND WELDED - MANY CHOICES FOR PROCESSES -- PROCESSES CAN BE EASILY ACCOMMODATED IN REMOTE HANDLING FACILITIES.

REFERENCE AND ALTERNATIVE CONTAINER MATERIALS FOR TUFF REPOSITORY -- CONCEPTUAL DESIGN LEVEL

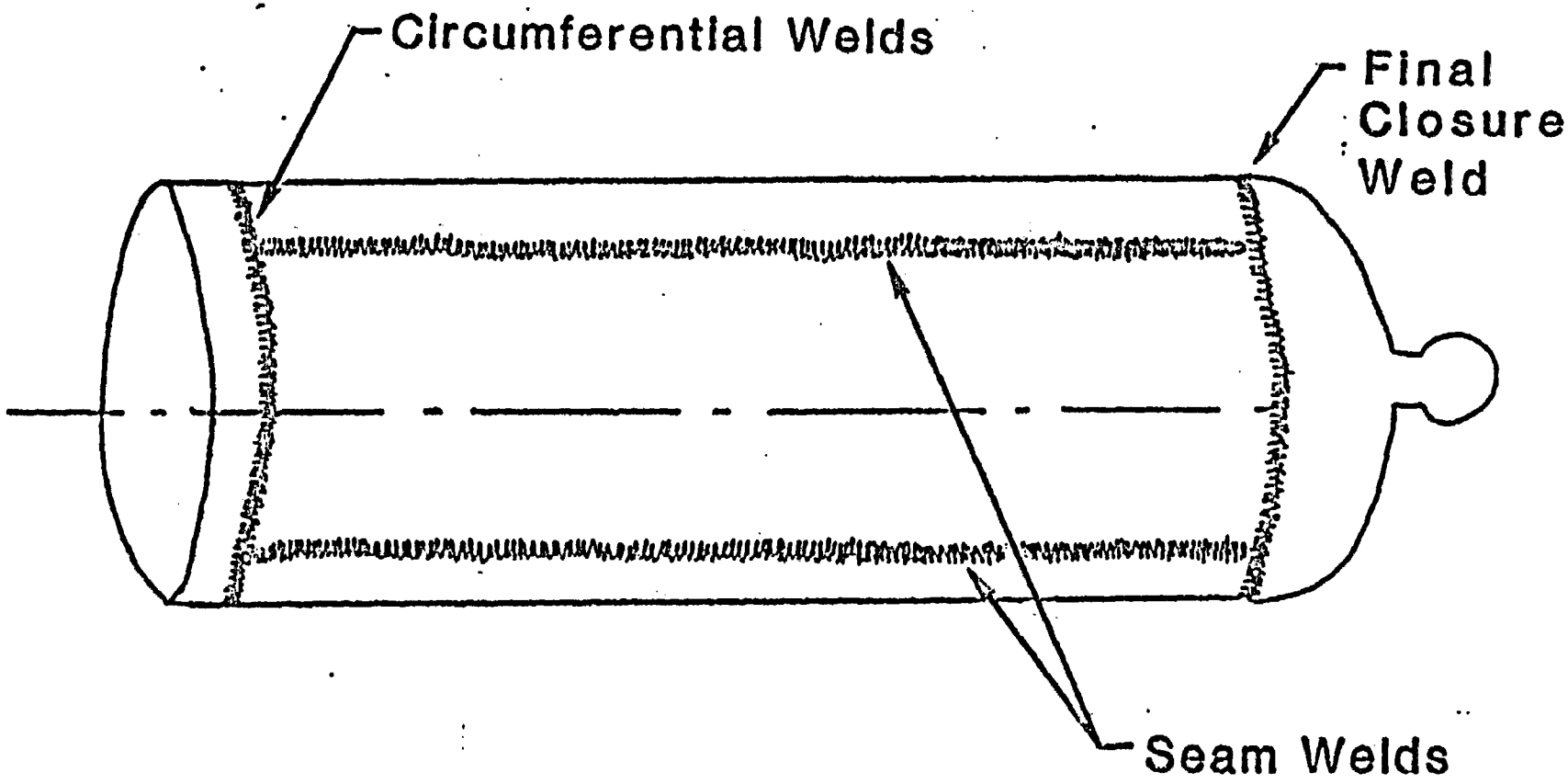
- AUSTENITIC STAINLESS STEELS SERVE AS REFERENCE MATERIALS, PARTICULARLY:
  - TYPE 304L STAINLESS STEEL - MOST TESTING SO FAR HAS BEEN FOCUSED ON THIS MATERIAL AS THE REFERENCE GRADE
  - TYPES 316L, 321 STAINLESS STEEL AND HIGH-NICKEL ALLOY 825 - THESE ALTERNATIVE GRADES ARE MORE RESISTANT TO SPECIFIC LOCALIZED/STRESS-ASSISTED FORMS OF CORROSION
- COPPER AND COPPER BASE ALLOYS SERVE AS AN ALTERNATIVE ALLOY SYSTEM TO THE STAINLESS STEELS

POSSIBLE NON-UNIFORM CORROSION DEGRADATION MODES IN AUSTENITIC STAINLESS STEELS CAN BE PLACED INTO TWO CAUSATIVE CATEGORIES

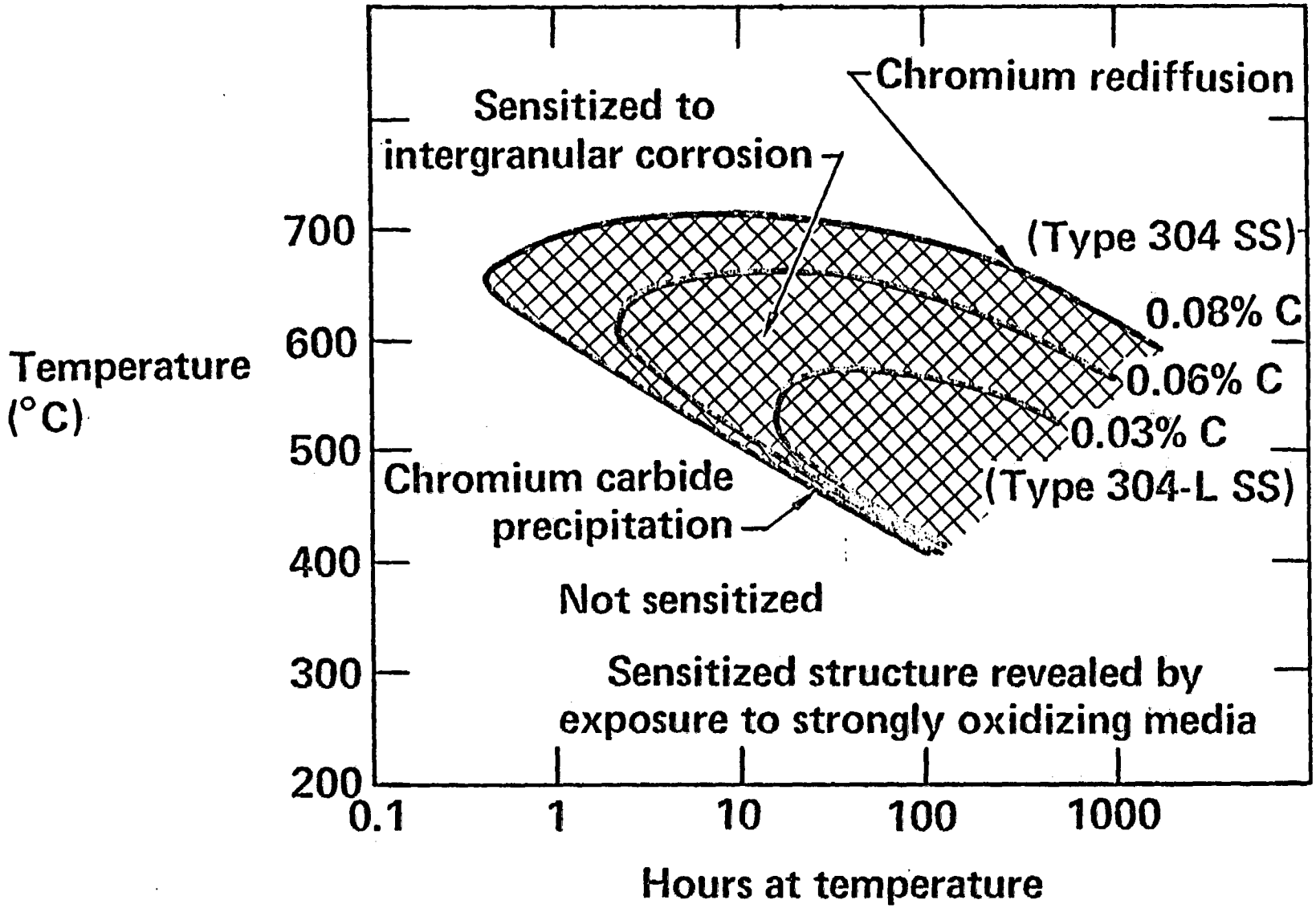
- DEGRADATION MODES CAUSED BY A "SENSITIZED MICROSTRUCTURE" WHICH DEVELOPS FROM PROCESSING OR STORING THE CONTAINER AT AN ELEVATED TEMPERATURE.
  - RESULT COULD BE INTERGRANULAR CORROSION OR INTERGRANULAR STRESS CORROSION CRACKING.
- CONTACT OF THE CONTAINER WITH AN AQUEOUS ENVIRONMENT WHICH IS SIGNIFICANTLY MORE CONCENTRATED IN ELECTROLYTES THAN IS J-13 WELL WATER.
  - RESULT COULD BE PITTING OR CREVICE CORROSION, OR TRANSGRANULAR STRESS CORROSION CRACKING.

THESE POSSIBILITIES ARE ADDRESSED IN THE NEXT GROUP OF SLIDES.

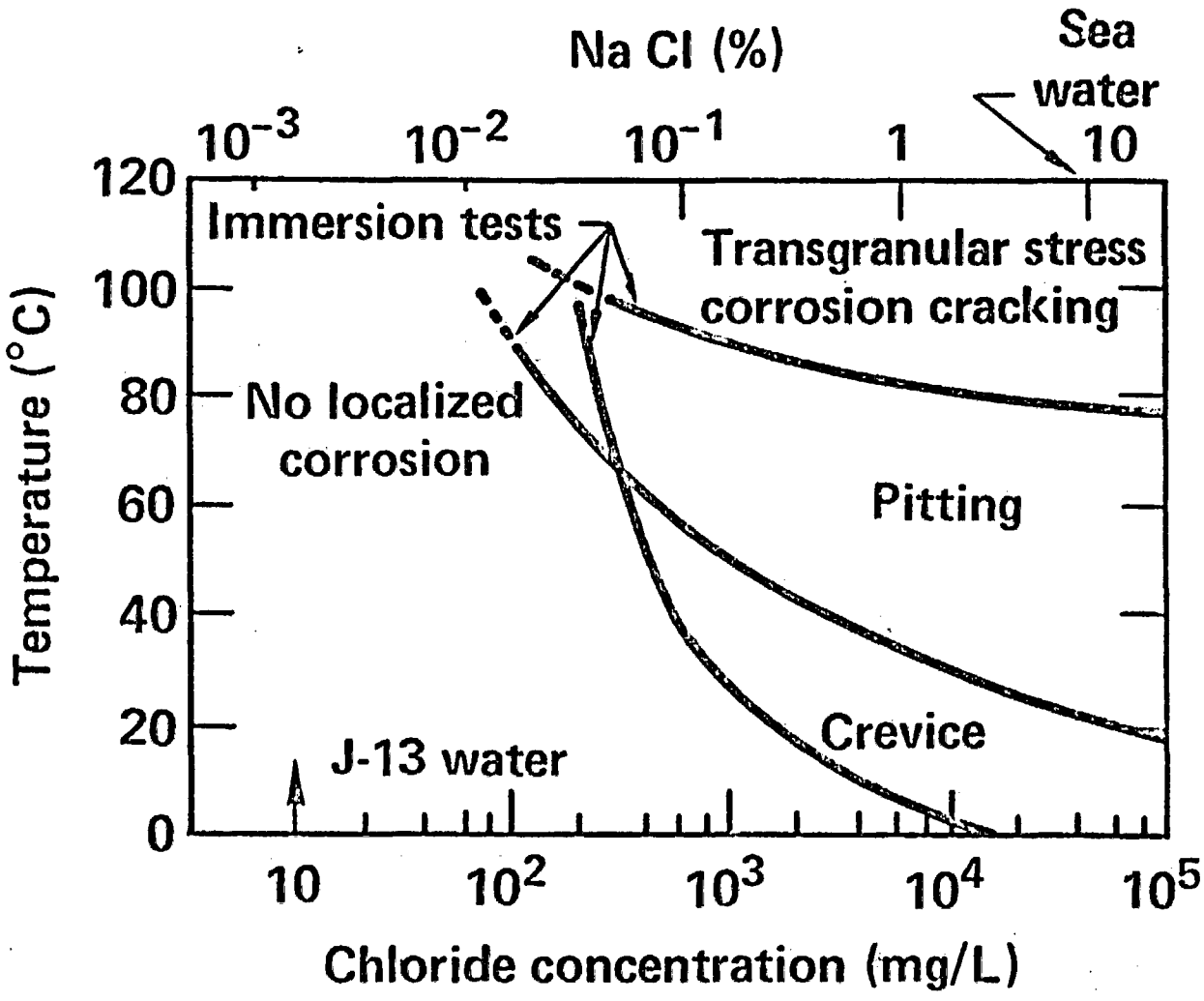
LOCATIONS OF WELDS IN PROTOTYPE WASTE CONTAINER



Time–temperature–sensitization curves indicate chromium carbide formation



Localized corrosion of type 304 stainless steel in water as a function of temperature and chloride concentration



GROWTH OF LOCALIZED ATTACK AREAS EXPECTED TO FOLLOW EQUATIONS

$$\text{LOG } P = K_0 + K_1 \text{ LOG } (CL^-) + K_2 \text{ LOG } (F^-) + K_3 \text{ LOG } (FE^{+++}) + \ldots$$
$$- K_4 \text{ LOG } (NO_3^-) - K_5 \text{ LOG } (SO_4^{--}) - K_6 \text{ LOG } (OH^-) - \ldots$$

$$P = K\,T^{1/3}$$

WHERE P = PIT DEPTH

T = TIME

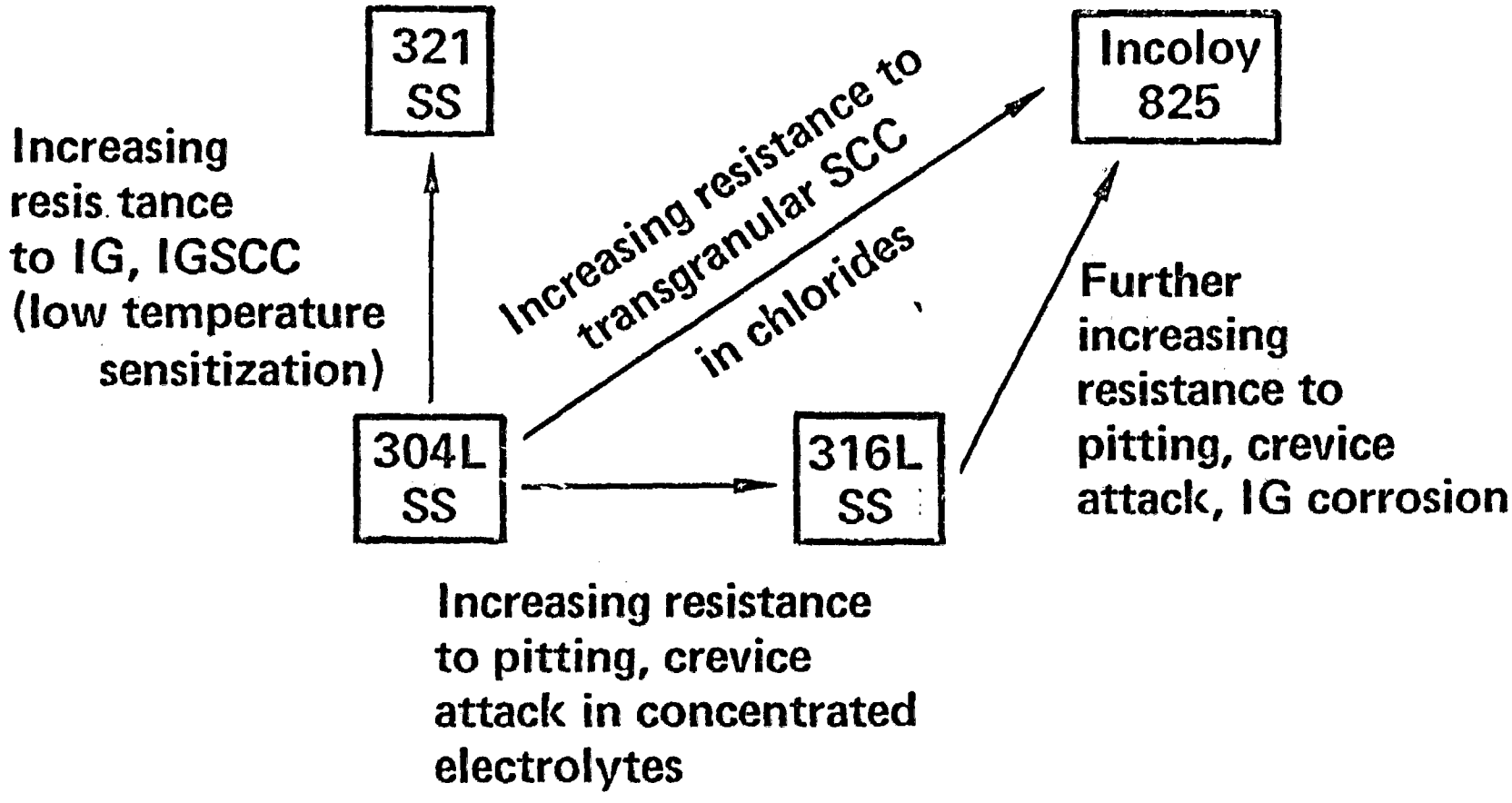
K'S DEPEND ON ALLOY COMPOSITION, TEMPERATURE, ETC.

Alloy composition for reference and alternative canister and overpack materials

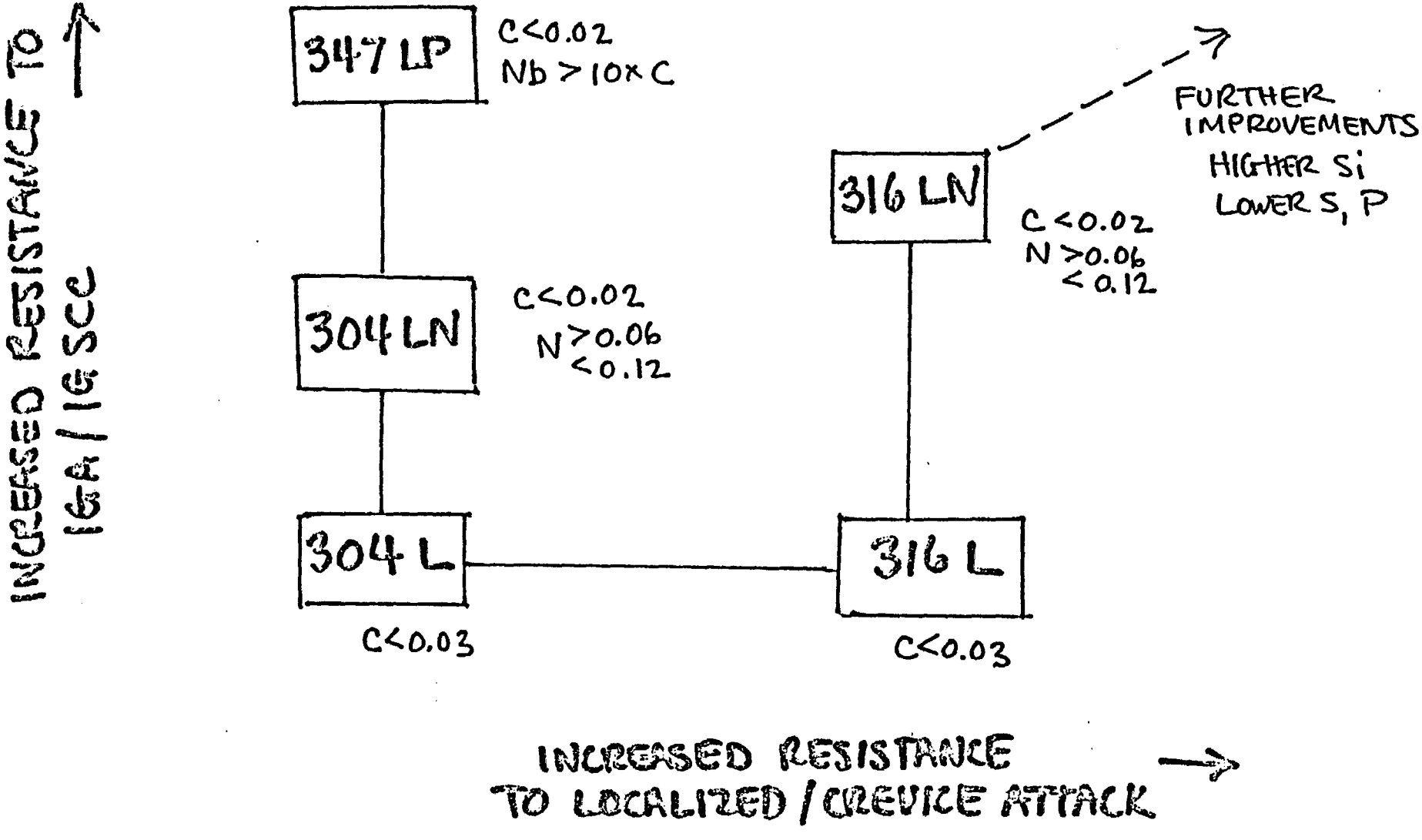
Chemical composition (weight per cent)

Common alloy designations	Carbon (max)	Manganese (max)	Phosphorus (max)	Sulfur (max)	Silicon (max)	Chromium (range)	Nickel (range)	Other elements
304L	0.03	2.0	0.045	0.03	1.0	18-20	8-12	N: 0.1 max
316L	0.03	2.0	0.045	0.03	1.0	16-18	10-14	Mo: 2.0-3.0 N: 0.1 max
321	0.08	2.0	0.045	0.03	1.0	17-19	9-12	Ti: 5 X C min
825	0.05	1.0	not specified	0.03	0.5	19.5-23.5	38-46	Mo: 2.5-3.5 Ti: 0.6-1.2 Cu: 1.5-3.0 Al: 0.2 max

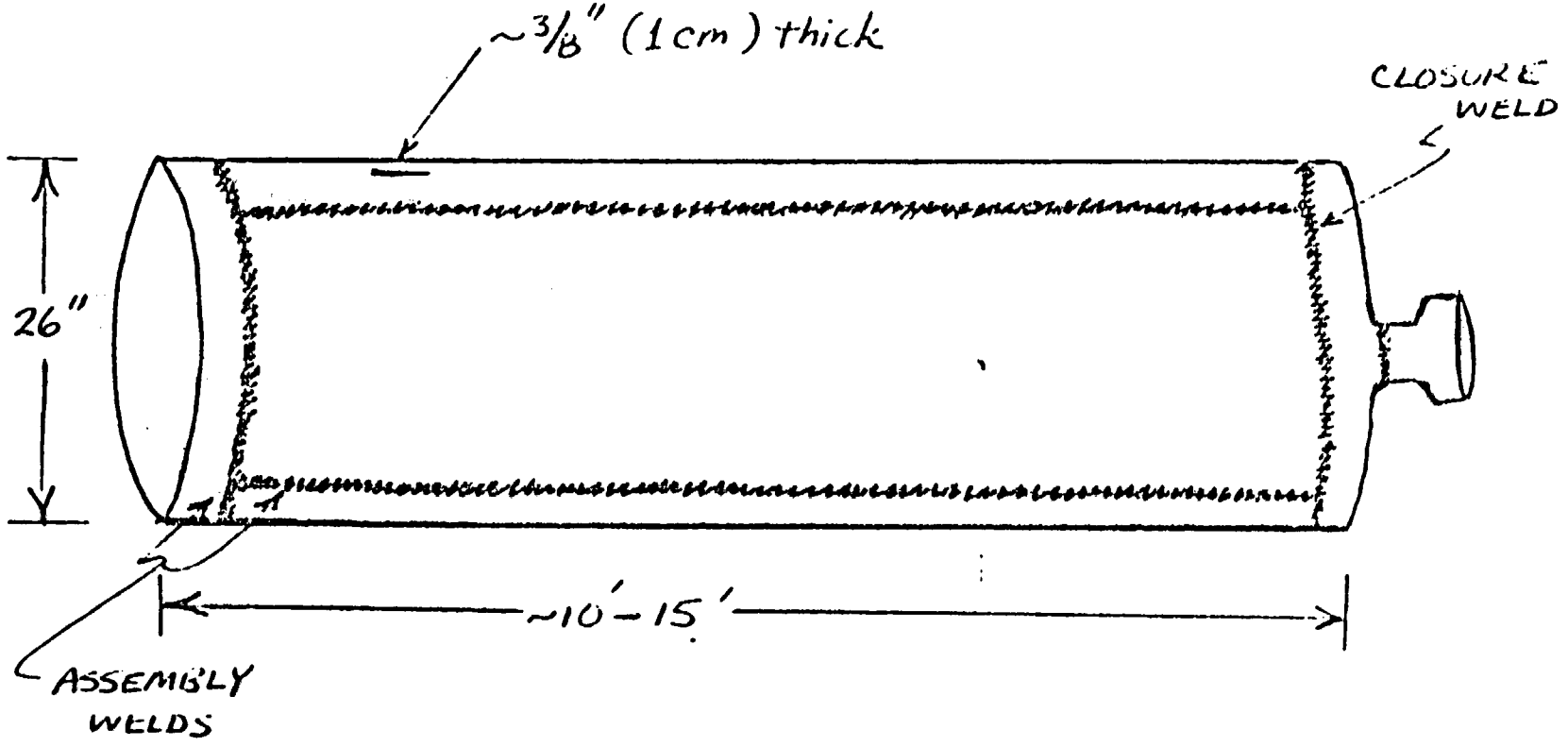
Alloy selection to solve localized/stress corrosion problems with stainless steel



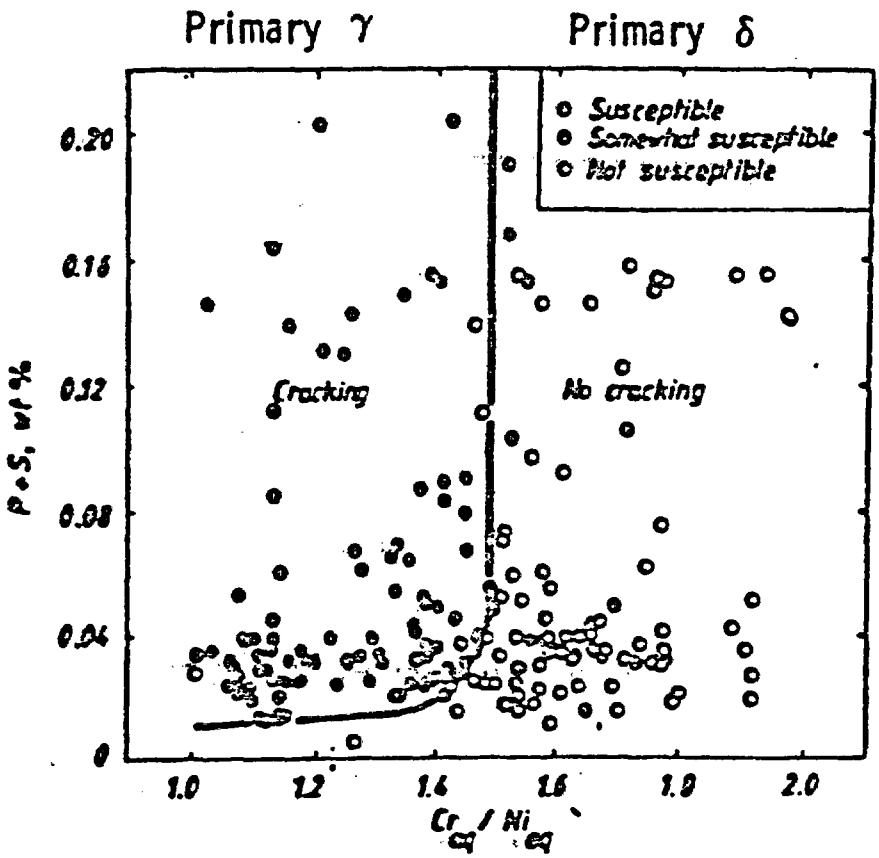
ADJUSTMENTS TO BASIC 18CR-8NI COMPOSITION CAN MARKEDLY IMPROVE CORROSION RESISTANCE



NNWSI CONCEPTUAL DESIGN WP CONTAINERS



Cracking Susceptibility of Austenitic Stainless Steels



CONTAINER CLOSURE WELD PRESENTS TECHNICAL CHALLENGES

- INTEGRITY OF WELD (CRACKS, POROSITY, PENETRATION)
- ADVERSE EFFECT OF HEAT AFFECTED ZONE (HAZ) ON CONTAINER PERFORMANCE

RESTRAINTS IN MAKING CLOSURE WELD

- WELD, POST-WELD INSPECT REMOTELY
- PRECLUDE POST-WELD HEAT TREATMENTS, STRESS RELIEFS

CONSIDERATIONS

- HOMOGENEITY
- DEPTH OF PENETRATION
- H.A.Z. (SIZE, GRADIENT)

POSSIBLE WELD PROCESSES

- GAS METAL ARC (GMA)
- GAS TUNGSTEN ARC (GTA)
- GTA + GMA
- RESISTANCE
- ELECTRON BEAM
- LASER BEAM
- PLASMA ~~BEAM~~ ARC
- FRICTION / INERTIA

Table 7-8. General corrosion rates of candidate austenitic stainless steels and stainless alloys in J-13 water at different temperatures

ALLOY	TEMP (°C)	TIME (HRS)	CORROSION RATE (um/yr)[a] Avg.	Std Dev.
304L	50	11,512	0.133	0.018
316L	50	11,512	0.154	0.008
317L	50	11,512	0.225	0.010
321	50	11,512	0.166	0.007
347	50	11,512	0.185	0.019
825	50	11,512	0.211	0.013
304L	80	11,056	0.085	0.001
316L	80	11,056	0.109	0.005
317L	80	11,056	0.104	0.010
321	80	11,056	0.043	0.008
347	80	11,056	0.085	0.007
825	80	11,056	0.109	0.012
304L	100	10,360	0.072	0.023
316L	100	10,360	0.037	0.011
317L	100	10,360	0.030	0.007
321	100	10,360	0.030	0.008
347	100	10,360	0.056	0.011
825	100	10,360	0.049	0.019

a Average and standard deviation of three replicate samples of each alloy at each test temperature.

Table 7-9. Corrosion rates of candidate stainless steels and alloys in steam

Material	Corrosion Rate[a] (um/yr) in 100°C Saturated Steam (10,456 Hours)	Corrosion Rate[a] (um/yr) in 150°C Unsaturated Steam (3,808 Hours)
304L	0.102	0.071
316L	0.099	0.064
317L	0.211	0.081
321	0.081	0.102
347	0.091	0.122
825	0.102	0.030

a (average of three replicate specimens of each alloy in each condition)

Corrosion Test Results for Room Temperature Irradiated and Non-Irradiated 304L Coupons (3750 Hrs Exposure)

304L Stainless Steel Material Condition	J-13 Water Environment (28°C)	Corrosion Rates (μm/yr) Vessel A (Irradiated)	Vessel B (Non-Irradiated)
Solution Annealed	Rock + Water	Average: 0.0811*	0.242**
		Range: 0.0690-0.0951	0.215-0.272
		St'd Deviation: 0.00959	0.0201
Solution Annealed	Water	Average: 0.151	0.285
		Range: 0.0817-0.299	0.138-0.451
		St'd Deviation: 0.0734	0.118
Sensitized***	Rock + Water	Average: 0.123	0.249
		Range: 0.111-0.142	0.165-0.322
		St'd Deviation: 0.0114	0.0522
Sensitized	Water	Average: 0.116	0.283
		Range: 0.092-0.142	0.203-0.452
		St'd Deviation: 0.0470	0.0980

* Averages of 6 coupons in each set.

** Maximum localized penetration measured = 0.010 μm in 8760 hours (appx. 1 year).

*** "Sensitizing" heat treatment: 1 hour at 650°C.

NNWSI COPPER TEST PLAN

COPPER DEVELOPMENT ASSOCIATION (CDA) - INTERNATIONAL COPPER RESEARCH ASSOCIATION (INCRA) RECOMMENDED LIST OF ALLOYS

ALLOY	DESCRIPTOR	COMMENTS
CDA 102	OXYGEN FREE, HIGH-CONDUCTIVITY PURE COPPER	LOW STRENGTH, EXCEEDINGLY DUCTILE MATERIAL, REFERENCE MATERIAL FOR SWEDISH KBS SPENT FUEL CONTAINER PROGRAM IN GRANITE.
CDA 613	ALUMINUM BRONZE	MORE CORROSION RESISTANT THAN CURE CU IN OXIDIZING ENVIRONMENTS.
CDA 715	70/30 CUPRONICKEL	PROBABLY MOST CORROSION RESISTANT CU-BASE ALLOY IN OXIDIZING ENVIRONMENTS.

TECHNICAL ISSUES ON USE OF CU AND CU-BASE ALLOYS AS NUCLEAR WASTE CONTAINER MATERIALS FALL INTO THREE GENERAL CATEGORIES

1. COMPATIBILITY OF CU/CU ALLOYS WITH GEOCHEMICAL ENVIRONMENT
   - RADIATION INDUCED GENERAL CORROSION (EFFECTS OF NITRATE, AMMONIA, HYDROGEN PEROXIDE)
   - LOCALIZED CORROSION (PITTING, CREVICE, SELECTIVE LEACHING OF ALLOYS)
   - STRESS CORROSION (RADIATION INDUCED EFFECTS OF AMMONIA)

2. COMPATIBILITY OF CU/CU ALLOYS WITH PROCESSES PROPOSED FOR FABRICATING AND CLOSING NUCLEAR WASTE CONTAINERS
   - LOWER STRENGTH METALS/ALLOYS, THICKER CONTAINERS
   - WELDABILITY OF COPPER, ESPECIALLY IN THICK SECTIONS
   - ALTERNATIVE FABRICATION TECHNOLOGIES, I.E., HOT ISOSTATIC PRESSING

3. COMPATIBILITY OF CU/CU ALLOYS WITH OTHER COMPONENTS IN WASTE PACKAGE
   - GALVANIC EFFECTS BETWEEN CU AND ZIRCALOY CLADDING (SF)
   - GALVANIC EFFECTS BETWEEN CU AND STAINLESS STEEL POUR CANISTER (DHLW)
   - EFFECTS OF COPPER CORROSION PRODUCTS ON GLASS AND ON SPENT FUEL LEACHING

FORMS OF CORROSION TO CONSIDER IN EVALUATING CU/CU ALLOY CONTAINER

- GENERAL CORROSION IN STEAM, IN J-13 WATER, WITH AND WITHOUT GAMMA RADIATION FIELD
- LOCALIZED CORROSION (PITTING AND CREVICE ATTACK)
- SELECTIVE LEACHING OF THE ALLOYS
- STRESS CORROSION CRACKING OF THE ALLOYS

EXPECTATIONS:

- CORROSION RATE FOR PURE CU WILL INCREASE WITH THE CONCENTRATION OF OXIDIZING SPECIES IN THE ENVIRONMENT
- CDA 613, CDA 715 SHOULD BE MORE RESISTANT IN THE OXIDIZING ENVIRONMENTS
- LOCALIZED, STRESS CORROSION BEHAVIOR DIFFICULT TO PREDICT WITHOUT SOME EXPERIMENTAL WORK - ACTIVE/PASSIVE BEHAVIOR, RADIATION-INDUCED CHANGES IN THE ENVIRONMENT

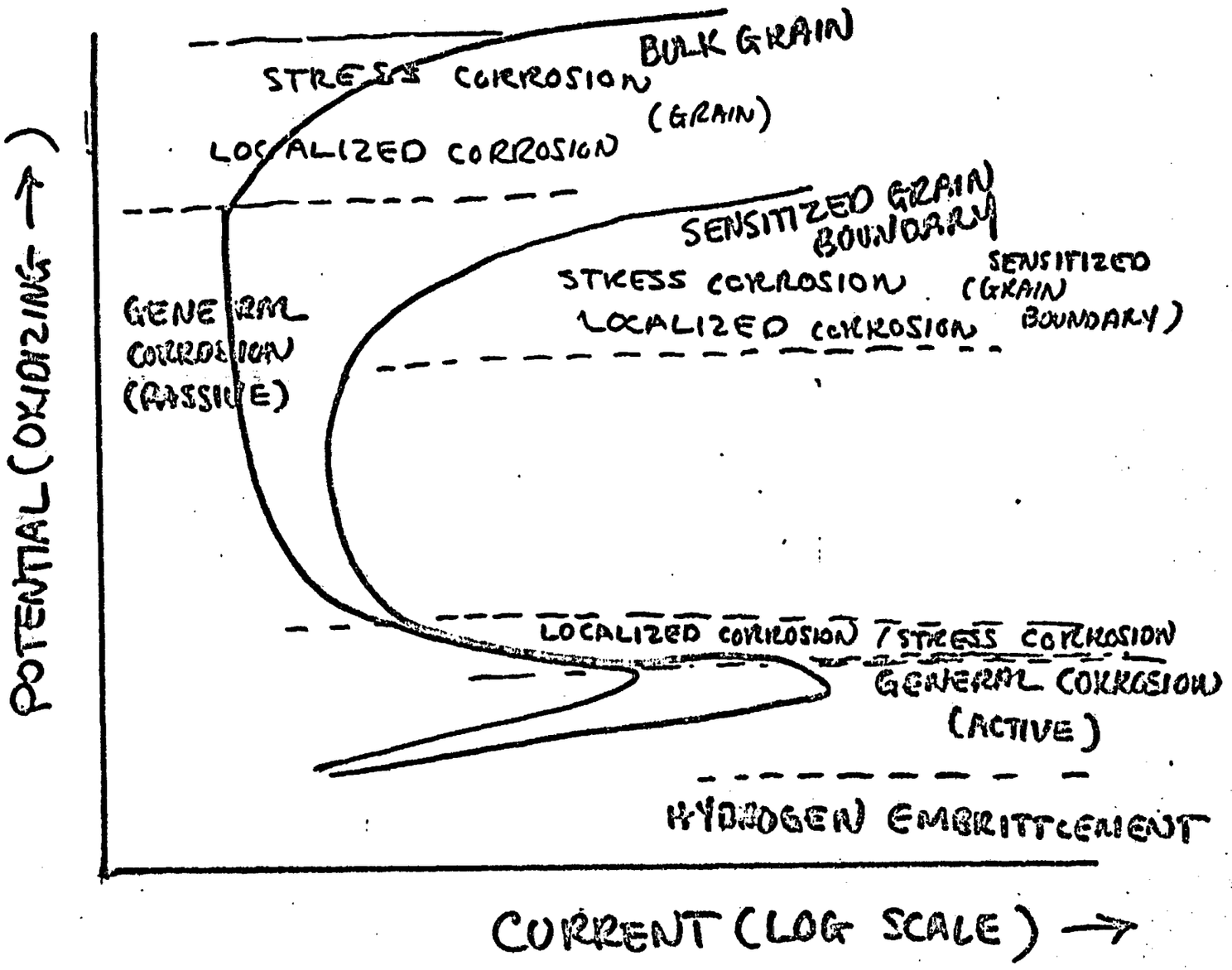
CORROSION SURVEY TESTS

- EMPHASIS ON TESTING IN IRRADIATED ENVIRONMENTS RELEVANT TO THE TUFF GEOPHYSICAL AND GEOCHEMICAL ENVIRONMENT
- EMPHASIS ON CDA 102, CDA 613, AND CDA 715
- BEGIN EXPOSURE TESTS OF STRESSED AND UNSTRESSED SPECIMENS IN APPROPRIATE IRRADIATED AND NON-IRRADIATED ENVIRONMENTS
- TO ACQUIRE AS MUCH DATA IN AS TIMELY A WAY AS POSSIBLE, WE PLAN TO CONDUCT A LARGE NUMBER OF ELECTROCHEMICAL INVESTIGATIONS
- SOME ELECTROCHEMICAL INVESTIGATIONS IN GAMMA RADIATION FIELD, SOME IN SIMULATED RADIOLYZED ENVIRONMENTS
- ELECTROCHEMICAL TECHNIQUES USEFUL FOR GENERAL CORROSION MEASUREMENTS, PREDICTIONS ON PASSIVE FILM STABILITY AND BREAKDOWN, MODELING OF PERFORMANCE BASED ON CORROSION POTENTIALS

DESIGN CONSIDERATIONS

- MAY REQUIRE THICKER CONTAINER SECTIONS WITH COPPER/COPPER ALLOYS
- LOWER YIELD STRENGTH, CORROSION ALLOWANCE FOR POSSIBLY HIGHER GENERAL CORROSION RATE
- RADIATION SHIELDING EFFECT OF HEAVIER SECTION - LITTLE OVER TWO INCHES OF COPPER WOULD REDUCE GAMMA DOSE RATE BY FACTOR OF TEN
- DESIGN SURFACE FACILITIES FOR HANDLING AND CLOSURE WELD OF SPENT FUEL PROCESSES FOR WELDING THICK CONTAINERS

CORROSION MODEL DERIVES FROM ELECTROCHEMICAL POTENTIAL



METAL BARRIER SUB-TASK ORGANIZATION

- ONE WORK BREAKDOWN STRUCTURE (WBS) ELEMENT, BUT WE MAINTAIN TWO ACCOUNTS (STAINLESS STEEL, COPPER) FOR THE TWO PARALLEL EFFORTS

- NO FORMAL ORGANIZATION BELOW SUB-TASK LEVEL, BUT IDENTIFY "AREAS" FOR EACH PRINCIPAL INVESTIGATOR

- MAINTAIN SUB-CONTRACTS (FY85)

<u>STAINLESS STEEL</u>

PNL (WESTERMAN) - SCC IN RADIATION FIELD/SLOW STRAIN RATE TESTS

SRI (MACDONALD) - CORROSION PERFORMANCE MODELING BASED ON CHANGES OF CORROSION POTENTIALS

<u>COPPER</u>

WESTINGHOUSE, HANFORD (KNECHT) - CORROSION SURVEY IN RADIATION FIELD

UNIV. OF MINNESOTA (SMYRL) - ANALYSIS OF RADIATION-INDUCED CORROSION PROCESSES

CDA (LYMAN) - OVERALL INDUSTRIAL SUPPORT ADVISORY

HOW WILL METAL BARRIER TEST DATA BE USED TO DEMONSTRATE ACHIEVEMENT OF "SUBSTANTIALLY COMPLETE" CONTAINMENT

- NEED TO FORMULATE PLAN/STRATEGY FOR THIS DEMONSTRATION
- PLAN TO SHOW SIGNIFICANCE OF INTERPRETING CORROSION DATA WHICH IS OFTEN GENERATED FROM SEVERE AND AGGRESSIVE CONDITIONS
- PLAN TO SUGGEST WAYS FOR FUTURE DATA ACQUISITION AND HOW TO PRESENT THESE DATA

SOME THOUGHTS ON ITEMS IN THE DEMONSTRATION PLAN

- PHENOMENA WHICH CAN COMPROMISE CONTAINMENT OBJECTIVE OCCUR ABOVE "CRITICAL THRESHOLDS"
  - MICROSTRUCTURAL
  - ENVIRONMENTAL
  - MECHANICAL

- NEED TO DETERMINE PROBABILITY OF EXCEEDING THESE THRESHOLDS, LOCALLY OR IN BULK

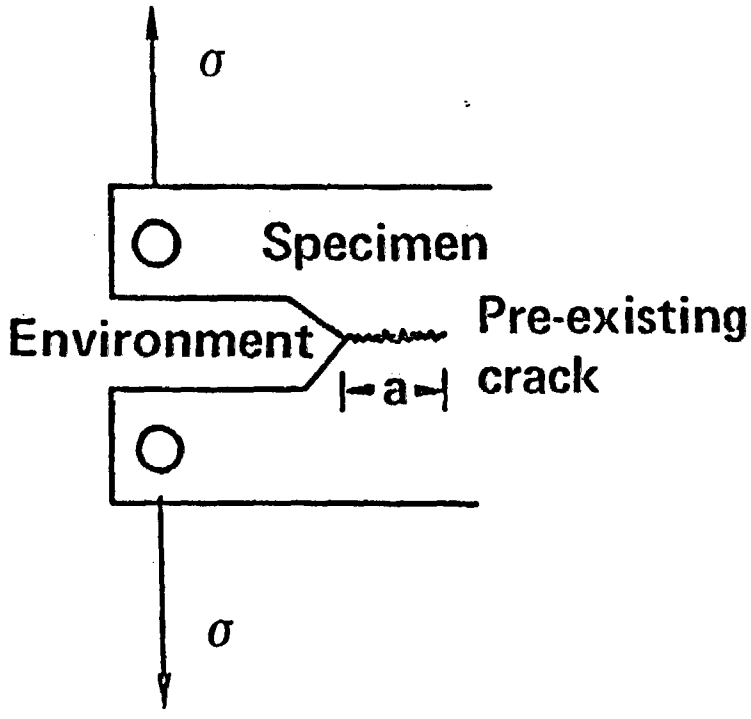
<u>EXAMPLES:</u>

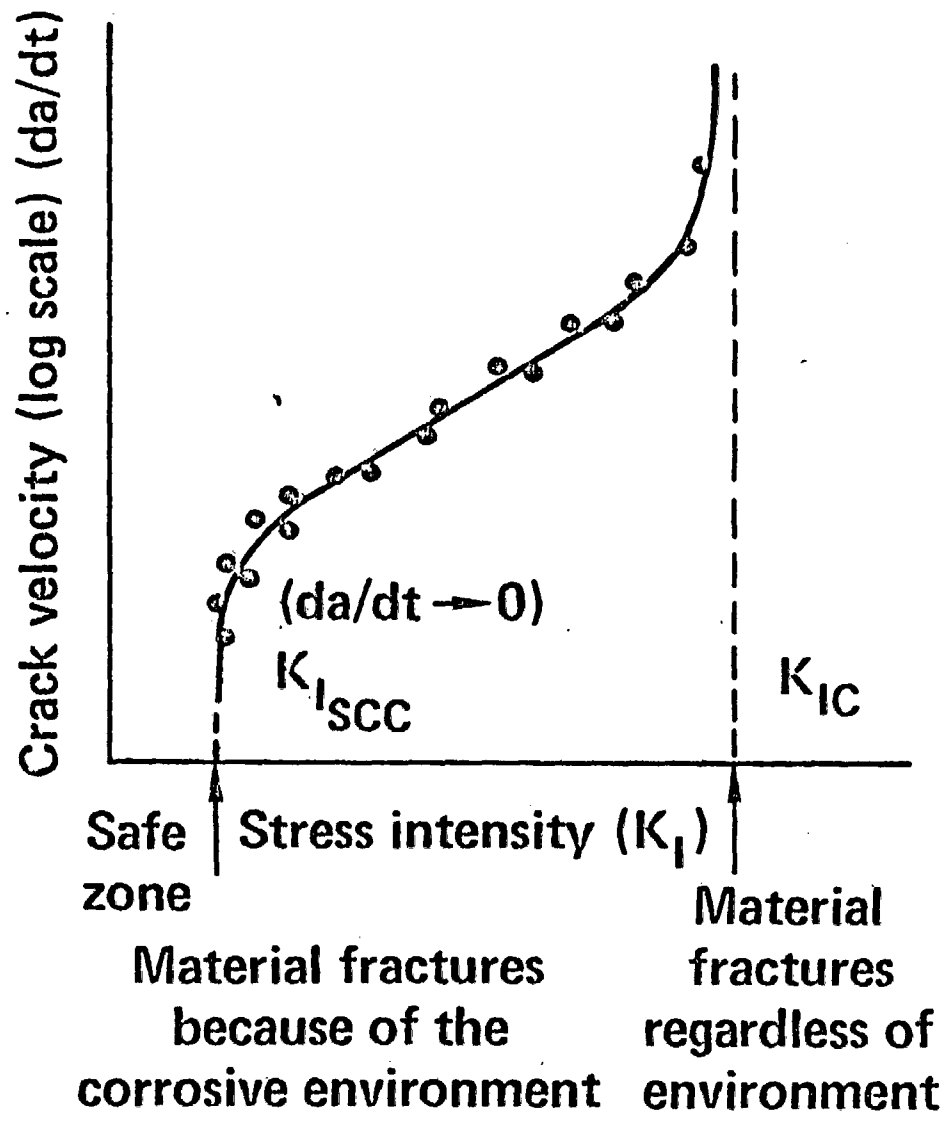
<u>MICROSTRUCTURAL</u> - NUMBER OF GRAIN BOUNDARIES THAT WILL SENSITIZE, IN WHAT TIME, SURFACE AREA AFFECTED, NUMBER OF CONTAINERS AFFECTED

<u>ENVIRONMENTAL</u> - AMOUNT AND STATISTICAL DISTRIBUTION OF WATER ENTERING WP ENVIRONMENT, DISTRIBUTION ON CONTAINER SURFACE, RESIDENCE TIME, IONIC CONTENT OF WATER, CHANGES OF IONIC CONTENT WITH TIME IN THERMAL AND RADIATION FIELDS

<u>MECHANICAL</u> - MAGNITUDE OF STRESS, STRESS DISTRIBUTION, FABRICATION/WELDING DEFECTS (SIZE, DISTRIBUTION), STRESS-INDUCED CHANGES IN MICROSTRUCTURE

Use fracture mechanics test methods to predict stress corrosion crack propagation rate

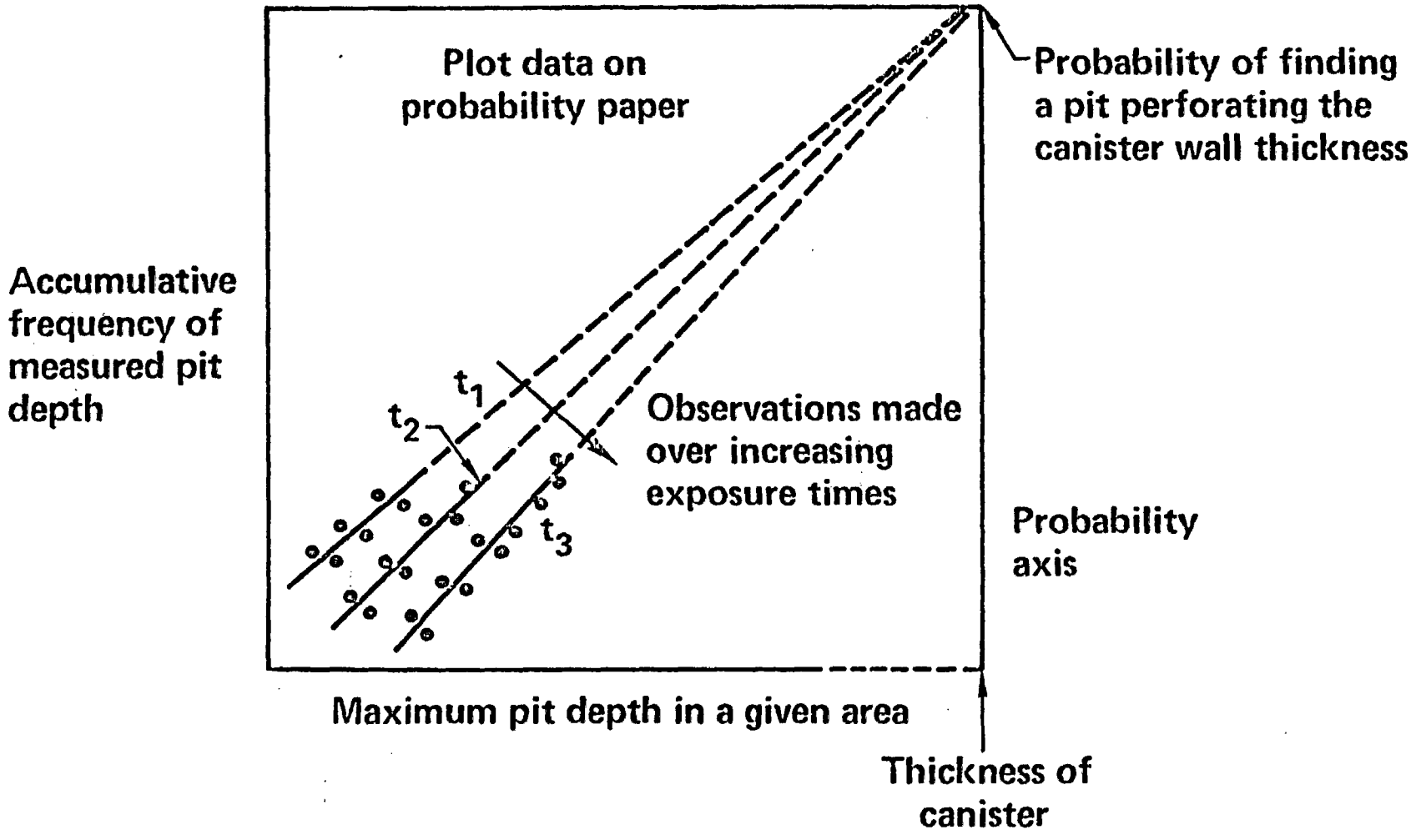




Stress intensity = K_I

$K_I = \sigma\sqrt{\pi a}\, f$ (geometry)

Use extreme value statistics to predict pitting penetration



APPROXIMATE GAMMA RAY DOSE RATES AT CANISTER SURFACE (5 YR. DECAY)

		RADS/HR.
1.	DEFENSE HIGH LEVEL WASTE (BAXTER, SRP, 1982)	5×10^3
2.	COMMERCIAL SPENT FUEL (WILCOX & VAN K., UCRL-53159, 1981)	1×10^4
3.	COMMERCIAL HIGH LEVEL WASTE (SLATE ET AL., PNL-3838, 1981)	2×10^5

FOR COMPARISON:

1.	NATURAL RADIOACTIVITY IN EARTH'S CRUST	2×10^{-4}
2.	MINIMUM OBSERVED DOSE RATE FOR "NOTICEABLE" INCREASE IN CORROSION RATE OF IRON IN HUMID AIR IN 100-HOUR TEST. (BYALOBZHESKII, 1970)	4×10^3
3.	TYPICAL ^{60}Co FACILITY	UP TO 10^7
4.	CORE OF OPERATING REACTOR	$>10^9$

Calculated Dose Rates in Climax Spent Fuel Test

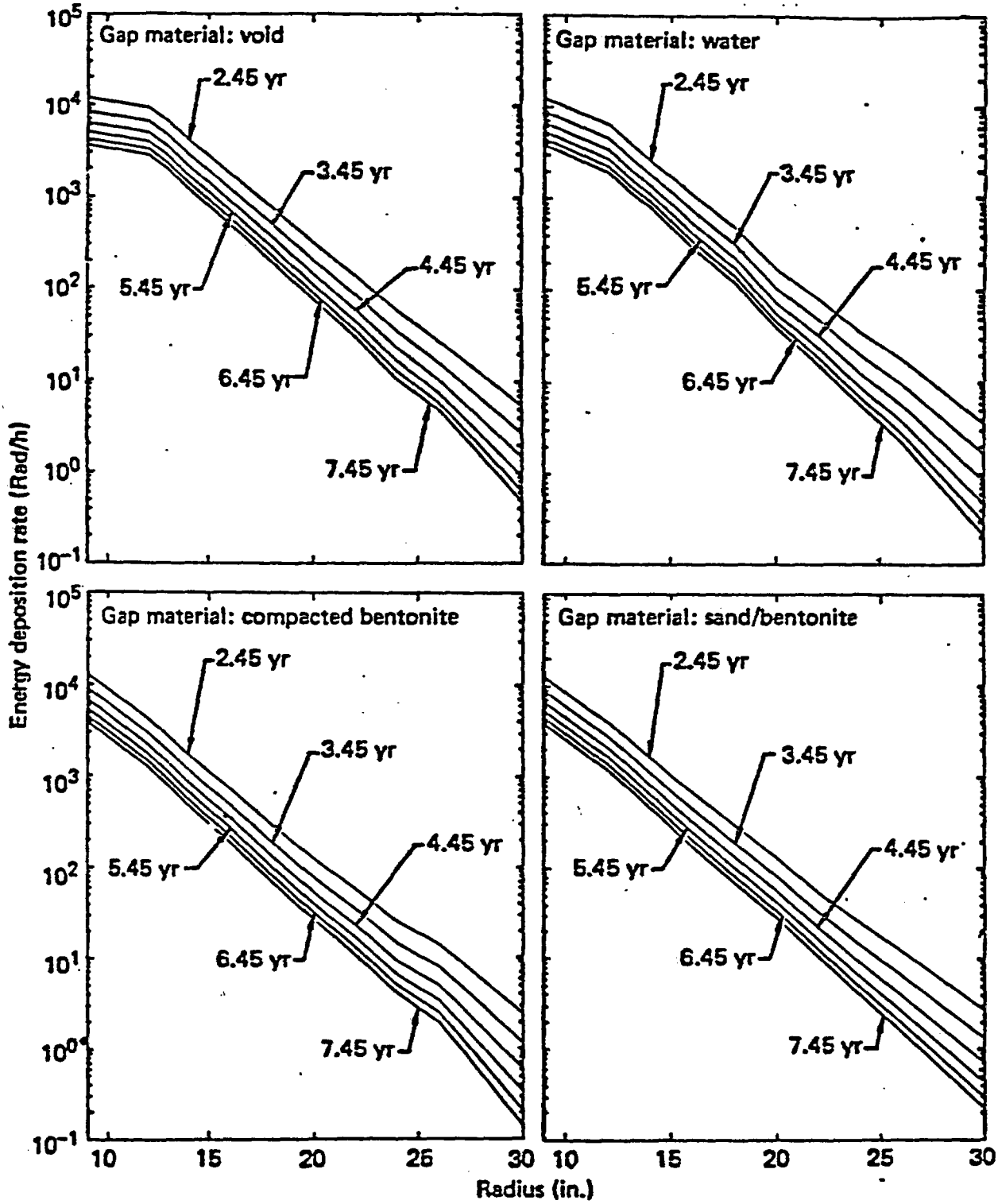


FIG. 5. The absorbed dose rate (rad/h to granite) outside the iron liner as a function of radius from the center line of the fuel assembly. The values plotted are averages over the central 2.44 m (8 ft) of the fuel assembly. The gap between the liner and the granite was assumed to be VOID, or filled with WATER or COMPACTED BENTONITE or a SAND/BENTONITE mixture, as shown in the legends of the plots. The parameter is time elapsed since discharge of fuel from reactor.

(from UCRL-53159)

RADIATION - CHEMICAL EFFECTS EXPECTED

I. SINGLE-PHASE, GASEOUS, WATER VAPOR AND AIR SYSTEMS.

A. PURE WATER VAPOR

1. SMALL STEADYSTATE CONCENTRATIONS OF H_2, O_2, AND H_2O_2.

2. H_2O_2 IS UNSTABLE, AND BOTH CU AND FE ARE CATALYSTS FOR DECOMPOSITION.

3. SCAVENGING COULD CAUSE RADIOLYSIS TO PROCEED, BUT PRODUCTION RATE TOO SMALL TO PRODUCE SIGNIFICANT GENERAL CORROSION. POSSIBLE DEGREE OF HYDROGEN EMBRITTLEMENT OF HOLE LINERS AND PACKAGES REMAINS TO BE DETERMINED.

4. EFFECTS OF H_2O_2 ON STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN <u>DRY</u> STEAM NOT YET KNOWN.

RADIATION - CHEMICAL EFFECTS EXPECTED
(CONT'D.)

B. AIR - WATER VAPOR MIXTURES

1. STABLE PRODUCTS OF RADIOLYSIS WOULD BE NITRIC ACID (HNO_3) AND NITROUS OXIDE (N_2O) AT TEMPERATURES UP TO ABOUT 120°C. TRANSIENTS: O_3 AND N_2O_5.

2. NITRIC ACID DECOMPOSES ABOVE THIS TEMPERATURE:

$$2\ HNO_3 \rightarrow 2\ NO_2 + H_2O + 1/2\ O_2$$

3. UP TO ABOUT 135°C,

$$2\ NO_2 \rightleftharpoons N_2O_4$$

4. ABOVE 150°C,

$$2\ NO_2 \rightleftharpoons 2\ NO + O_2$$

IN ADDITION,

$$NO + NO_2 \rightleftharpoons N_2O_3$$

5. GASES COULD MIGRATE IN REPOSITORY TO COOLER AREAS AND DISSOLVE IN LIQUID WATER, FORMING HNO_3 AND HNO_2. N_2O WOULD PROBABLY BE INERT AND BUILD UP.

6. H^+ WOULD EXCHANGE WITH Na^+, K^+, AND Ca^{++} FROM FELDSPARS, FORMING CLAYS AND BUFFERING THE SOLUTION IN THE SLIGHTLY ALKALINE REGION.

7. NO_2 COULD CHAIN REACT WITH Cu (OR Fe):

$$2\ Cu + NO_2 \rightarrow Cu_2O + NO$$

$$2\ NO + O_2 \rightarrow 2\ NO_2.$$

8. OXIDATION WOULD PROBABLY BE UNIFORMLY DISTRIBUTED. EXTENT REMAINS TO BE DETERMINED.

RADIATION - CHEMICAL EFFECTS EXPECTED
(CONT'D.)

II. TWO-PHASE, AIR-GROUNDWATER SYSTEM:

1. DOSE RATE WOULD BE MUCH LOWER WHEN THIS EXISTED.

2. MAIN EFFECT - PRODUCTION OF NO_x AND HNO_3 IN GAS PHASE AND DISSOLUTION IN LIQUID PHASE, FORMING HNO_3 AND HNO_2 IN SOLUTION.

3. FOR A SEALED SYSTEM (BURNS ET AL., 1982),

$$N = 2\, C_0 R\, [1 - \exp(-1.45 \times 10^{-5}\, GDT)]$$

WHERE N IS CONC. OF HNO_3 (M)

C_0 IS INITIAL CONC. OF N_2 IN AIR (M)

R IS RATIO OF VOL. OF AIR TO VOL. OF WATER

G IS THE YIELD (= 1.9)

D IS THE DOSE RATE (MRAD/HOUR)

T IS THE TIME (HOURS).

4. NOTE IMPORTANCE OF R, FOR EXAMPLE WITH LARGE AIR VOLUME AND WATER FILM ON METAL.

RADIATION - CHEMICAL EFFECTS EXPECTED
(CONT'D.)

II. TWO-PHASE, AIR-GROUNDWATER SYSTEM (CONT'D.):

5. IN THE WATER PHASE, THE IRRADIATION WOULD PRODUCE OH, e_{AQ}^-, H_2O_2, H, H_2, AND HO_2 AS PRIMARY PRODUCTS.

6. WITH DISSOLVED O_2 AND NEUTRAL OR ALKALINE pH, e_{AQ}^-, H, AND HO_2 WOULD BE CONVERTED TO O_2^-, LEAVING H_2 AND THE OXIDIZING SPECIES (O_2, H_2O_2, OH, AND O_2^-) IN SOLUTION.

7. IF OXIDIZABLE METAL (E.G. FE OR CU) WERE PRESENT, H_2 WOULD SURVIVE. OTHERWISE, IT WOULD BE OXIDIZED.

8. THE N_2O WOULD PROBABLY BE REDUCED TO N_2 BY e_{AQ}^- IN THE WATER.

9. FOR WATER IN CONTACT WITH TUFF, ION EXCHANGE AND BUFFERING WOULD OCCUR, LEAVING ALKALI NITRATES AND NITRITES IN THE SOLUTION.

RADIATION - CHEMICAL EFFECTS EXPECTED
(CONT'D.)

II. TWO-PHASE, AIR-GROUNDWATER SYSTEM (CONT'D.):

10. FOR WATER NOT IN CONTACT WITH TUFF, pH COULD MOVE INTO ACID REGION, PARTICULARLY WITH LARGE R VALUE AND THERMAL GRADIENT, TO GIVE PREFERENTIAL DEPOSITION OF ACID IN SMALL REGIONS ON SURFACES OF PACKAGES.

11. AUTOCATALYTIC OR CHAIN-TYPE REACTIONS OF HNO_3 ON Cu AND Fe COULD MAKE SMALL AMOUNTS OF ACID MORE SIGNIFICANT.

12. COMBINED EFFECTS OF HNO_3, HNO_2, AND H_2O_2 ON STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS UNDER "WET" CONDITIONS NEED TO BE ASSESSED.

13. IRRADIATION OF AERATED BICARBONATE SOLUTIONS CAN PRODUCE OXALIC ACID, $(COOH)_2$. NEAR 100°C, THIS HAS A SIGNIFICANT VAPOR PRESSURE, AND IT DOES NOT DECOMPOSE UNTIL ABOUT 160°C. AT LOWER TEMPERATURES, IT SHOULD PRECIPITATE AS CALCIUM OXALATE. FORMIC ACID FORMS UNDER LOW pH CONDITIONS, BUT APPARENTLY NOT IN AERATED, ALKALINE SOLUTIONS. (DISPLACEMENT IRRADIATION OF SOLID CARBONATES AND BICARBONATES, FOLLOWED BY DISSOLUTION, HAS ALSO BEEN REPORTED TO YIELD FORMIC AND OXALIC ACIDS, AS WELL AS GLYOXYLIC AND GLYCOLLIC ACIDS.)

CONCLUSIONS

1. WE EXPECT A GASEOUS, OXIDIZING, STEAM-AIR ENVIRONMENT DURING AT LEAST A SIGNIFICANT PORTION OF THE REQUIRED CONTAINMENT PERIOD FOR MOST OF THE PACKAGES. IN THIS ENVIRONMENT, THE RADIOLYTICALLY-GENERATED SPECIES OF CONCERN ARE H, H_2, H_2O_2, AND NO_x.

2. AFTER COOLING, A TWO-PHASE, AIR-GROUNDWATER SYSTEM COULD EXIST. ALTHOUGH THE DOSE RATE WOULD GENERALLY BE MUCH LOWER AT THIS TIME, RADIOLYTIC PRODUCTION OF HNO_2, HNO_3, AND H_2O_2 COULD BE IMPORTANT, PARTICULARLY IF DEPOSITION WERE CONCENTRATED IN SMALL REGIONS OF THE PACKAGE SURFACES.

3. DISSOLVED HALIDE IONS COULD BECOME MORE CONCENTRATED THAN IN THE ORIGINAL GROUNDWATER.

4. THE IMPORTANCE OF CARBOXYLIC ACIDS REMAINS TO BE DETERMINED.

Corrosion Considerations for Nuclear Waste Disposal in a Tuff Geologic Repository — Corrosion Rates and Mechanisms for Container Materials

R. S. GLASS

NUCLEAR WASTE STORAGE IN TUFF

* Austenitic stainless steels are prospective candidates for long-term (300-1000 yrs) high-level waste encapsulation.

1. What are potential long-term degradation mechanisms (pitting, crevice, SCC)?

2. What are effects of gamma radiolysis on corrosion rates/mechanisms?

Results from electrochemical experiments:

1. Accurate and quick in-lab experiments for assessing environmental stabilities of materials under a wide range of conditions — corrosion rates from Tafel extrapolation, linear polarization resistance, ac impedance

2. Anodic polarization curves — characterize response of a system to external perturbation (i - E relationship) — regions of active corrosion, passivity, pitting

3. Occluded cell experiments — crevice corrosion resistance

4. Detail models for corrosion mechanisms — long-term predictability

What is corrosion?

Anodic (corrosion) process, $M \rightarrow M^{+n} + ne^-$

Cathodic (reduction) process, $2H^+ + 2e^- \rightarrow H_2$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$i_{meas} = i_{corr} - i_{redn} = 0$ at E_{corr}

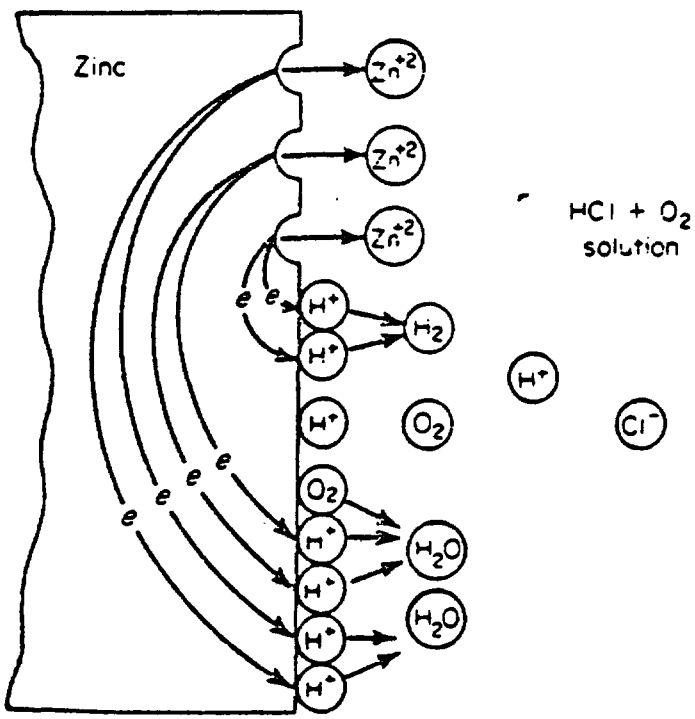


Fig. 2-4. Electrochemical reactions occurring during corrosion of zinc in aerated hydrochloric acid.

Eight forms of corrosion:

1. Uniform
2. Galvanic
3. Crevice corrosion
4. Pitting
5. Intergranular corrosion
6. Selective leaching
7. Erosion corrosion
8. Stress corrosion

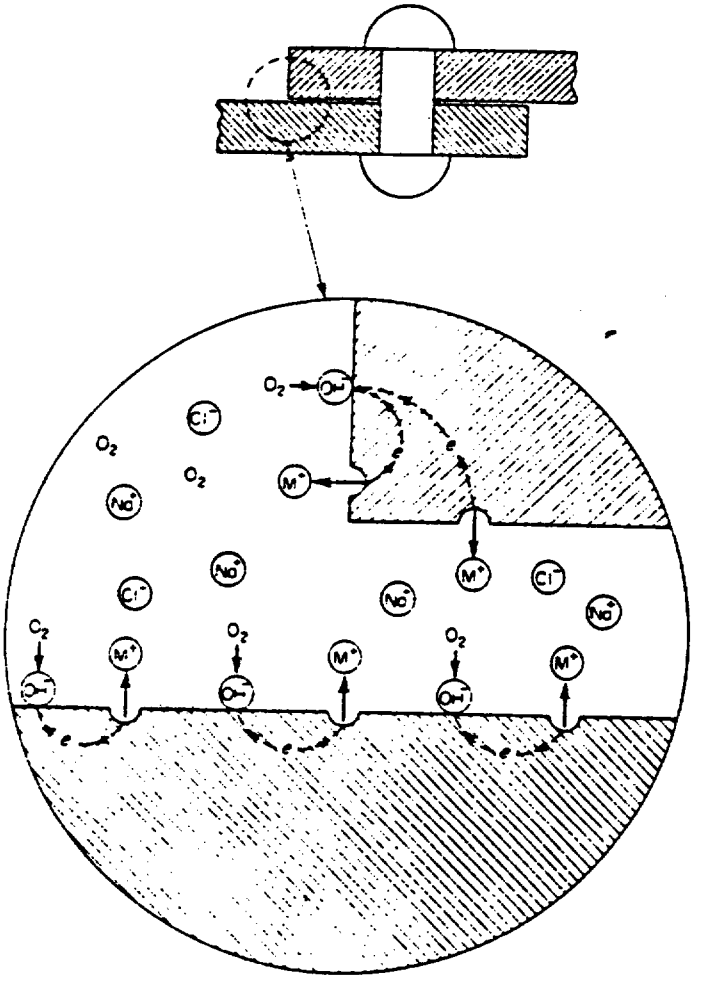


Fig. 3-9. Crevice corrosion—initial stage.

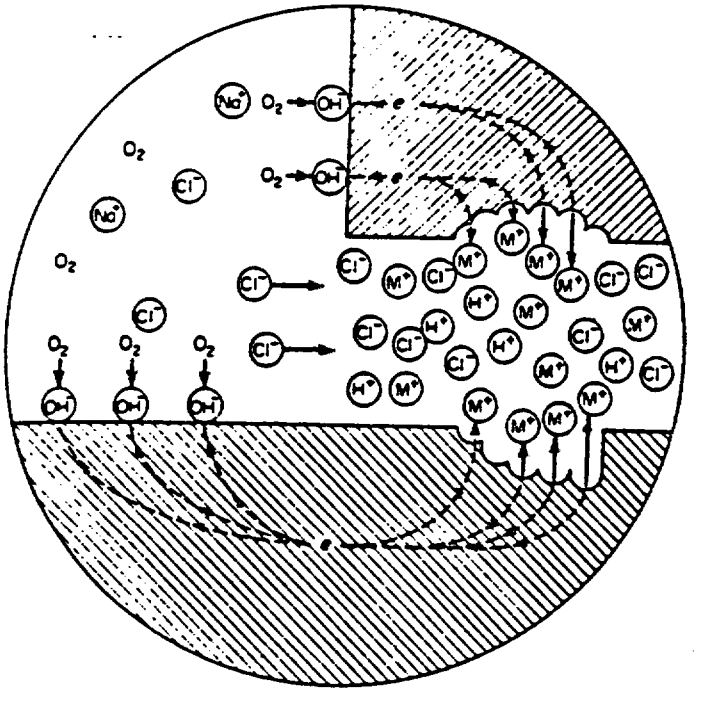


Fig. 3-10. Crevice corrosion—later stage.

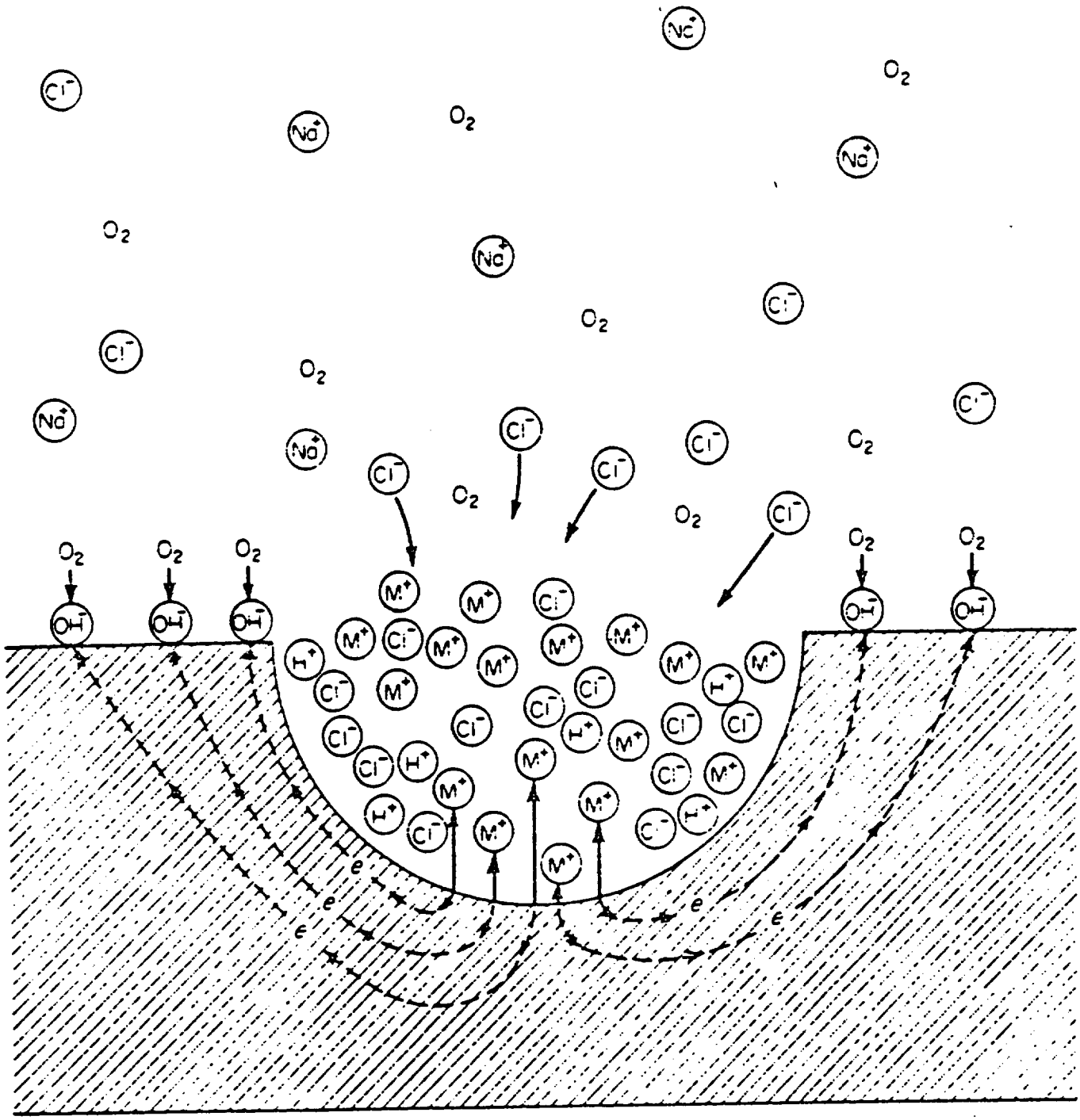


Fig. 3-19. Autocatalytic processes occurring in a corrosion pit.

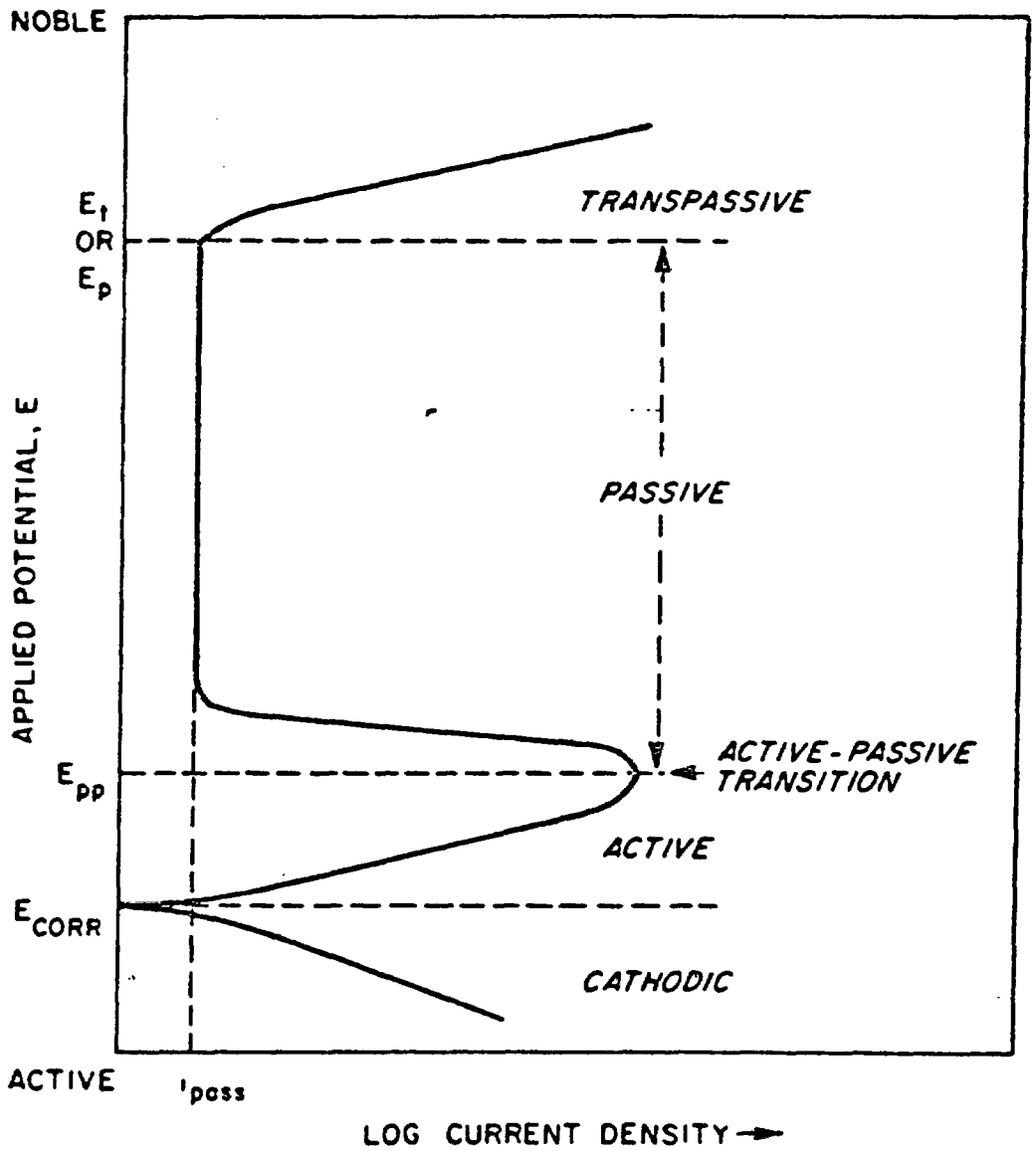


Figure 3-3. A schematic polarization curve for a stainless steel in a sulfuric acid solution.

1. GENERAL ELECTROCHEMICAL BEHAVIOR OF AUSTENITIC STAINLESS STEEL ALLOYS IN J13 AND RELATED ENVIRONMENTS.

2. COMPARATIVE BEHAVIOR OF L AND LN AUSTENITIC STAINLESS STEEL ALLOYS AND EFFECT OF ALLOY "CLEANLINESS."

3. GAMMA RADIATION EFFECTS ON THE ELECTROCHEMISTRY OF AUSTENITIC STAINLESS STEELS IN AQUEOUS MEDIA.

4. ELECTROCHEMISTRY OF COPPER ALLOYS IN J13 AND RELATED ENVIRONMENTS.

5. GAMMA RADIATION EFFECTS ON COPPER ALLOYS IN J13.

Radiation effects on the corrosion process

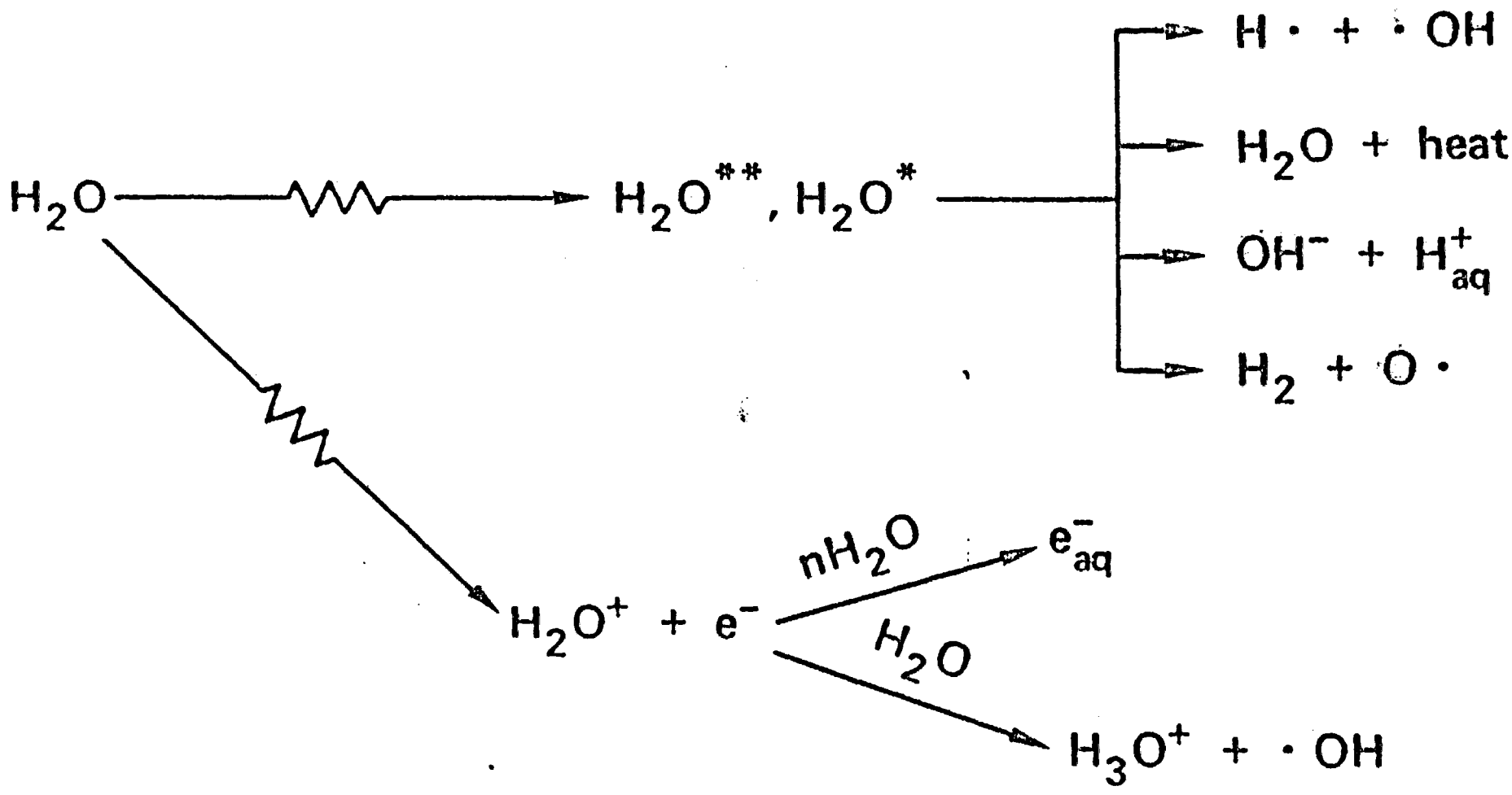
- On the metal itself
- On the protective oxide layer
- On the corrodant itself (the chemical environment)

TABLE 1. Measured Analyses of the Electrode Materials

	Composition (wt%)												
Alloy	C	Mn	P	S	Si	Ni	Cr	Mo	Co	Ti	Cu	Cb	N
304L	.022	1.55	.024	.025	.63	9.26	18.31	.36	.16	.002	.46	.01	.072
316L	.02	1.71	.033	.014	.56	10.29	16.51	2.07	.10	--	.28	--	.054

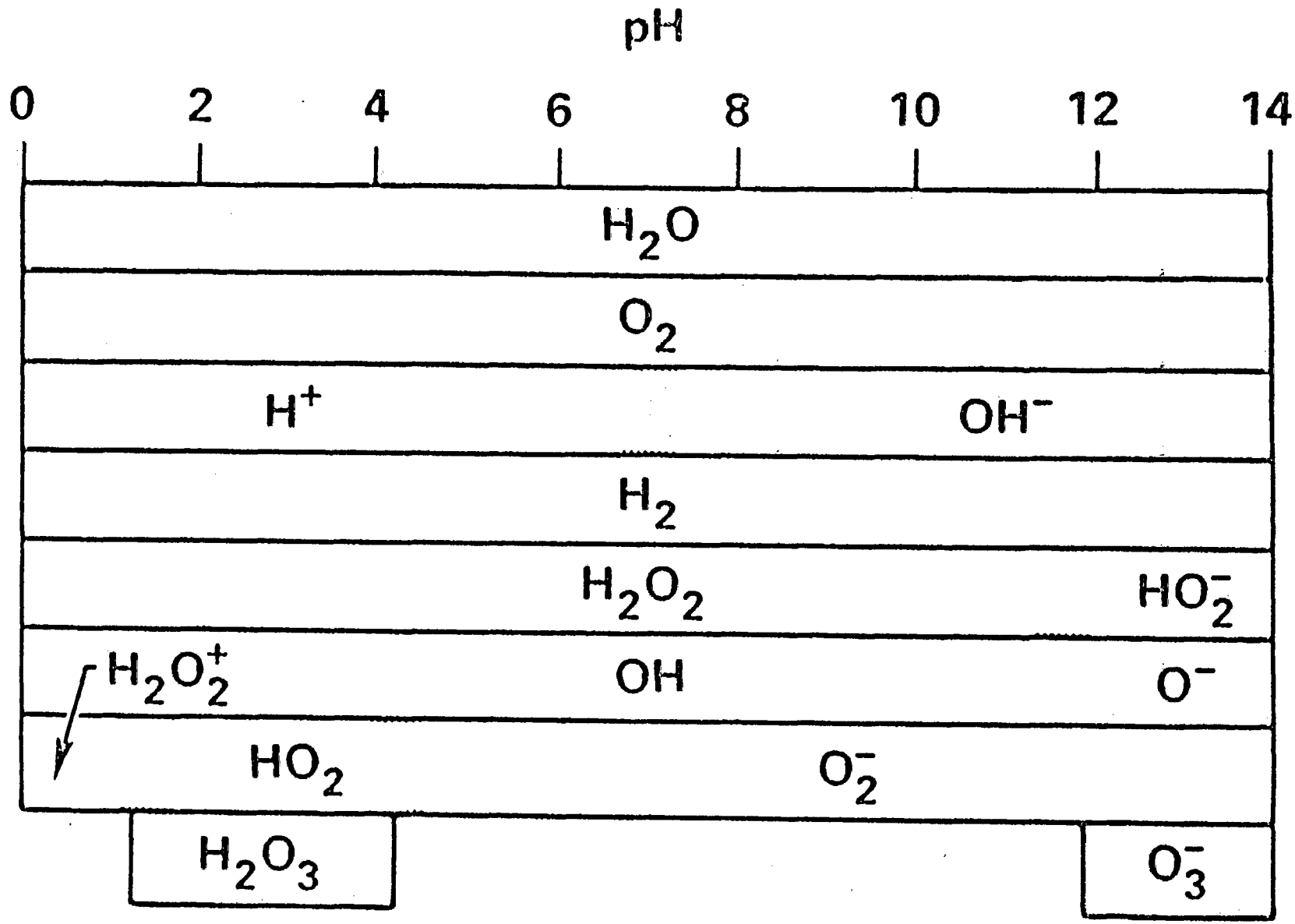
TABLE 2. Composition of J-13 water (average of 6 samples, by OES-ICP and IC), ppm

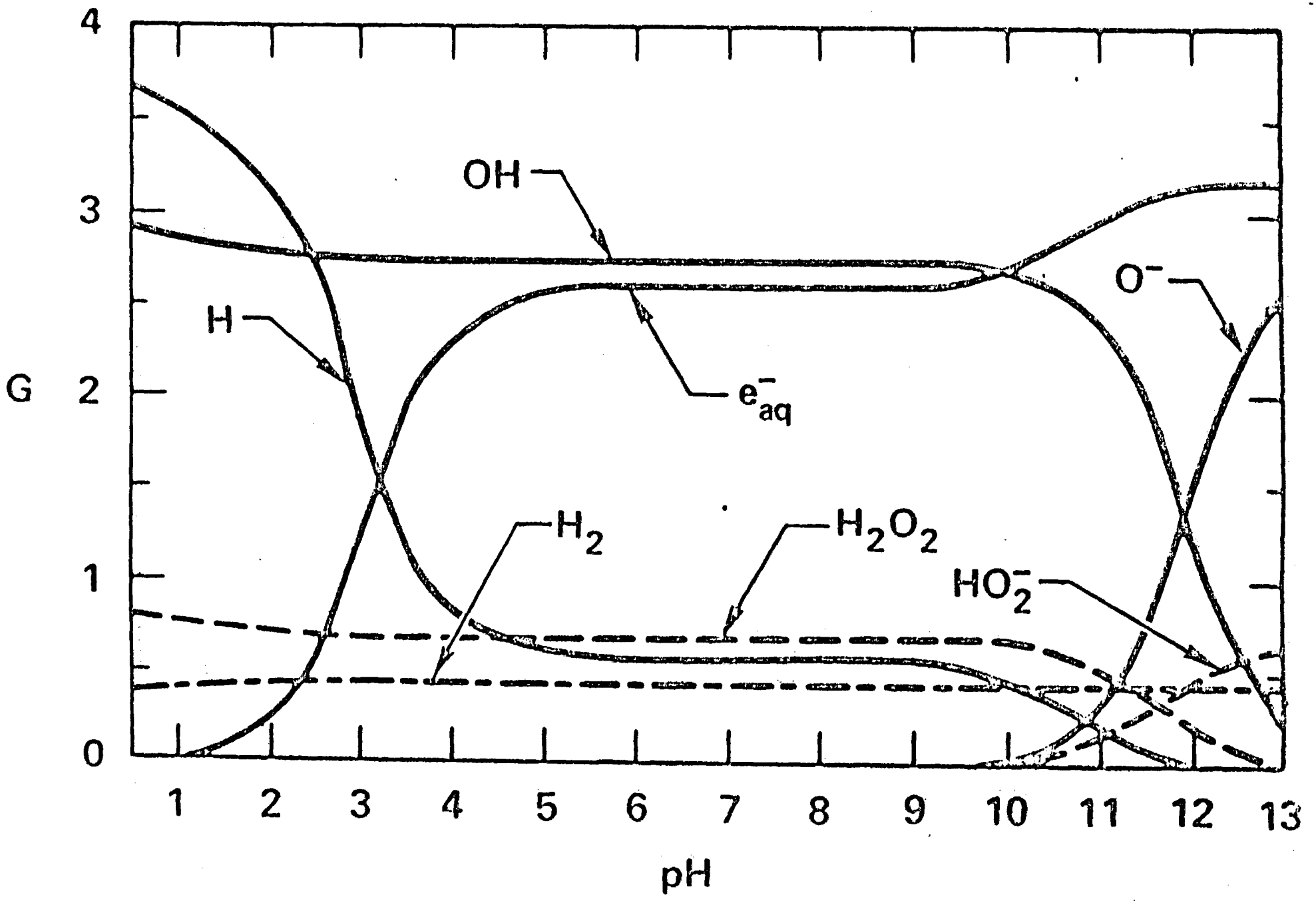
Al	<0.020	Si	27.0 ± 0.1
As	<0.060	Sr	0.054 ± 0.005
B	0.11 ± 0.01	U	<0.084
Be	0.003	V	0.011 ± 0.001
Cd	<0.003	Zn	<0.008
Co	<0.003	Ca	13.0 ± 0.1
Cu	<0.003	K	5.5 ± 0.3
Fe	<0.004	Mg	1.92 ± 0.01
Li	0.044 ± 0.001	Na	43.4 ± 0.3
Mn	<0.0005	Cl^-	7.1 ± 0.3
Mo	0.013 ± 0.002	F^-	2.4 ± 0.1
Ni	<0.008	NO_3^-	9.1 ± 0.2
P	<0.124	$SO_4^=$	18.5 ± 0.1
Pb	0.022 ± 0.003	HCO_3^-	132 ± 6
Se	<0.100		



$$H_2O \rightsquigarrow H\cdot, \cdot OH, e^-_{aq}, H_3O^+, H_2, H_2O_2, OH^-, O_2, O_2^-$$

Species in water containing dissolved oxygen, 10^{-8} sec after irradiation




G
4
3
2
1
0
OH
H
e^-_{aq}
O^-
H_2
H_2O_2
HO_2^-
1
2
3
4
5
6
7
8
9
10
11
12
13
pH

Radical and molecular product yields in irradiated water and water vapor

Radiation	pH	G_{-H_2O}	G_{H_2}	$G_{H_2O_2}$	$G_{e^-_{aq}}$	G_H	G_{OH}	G_{HO_2}
Water vapor								
x or γ-rays, electrons		8.2	0.5	0	(G_{e^-} = 3.0)	7.2	8.2	
Liquid water								
γ-rays and fast electrons with energies in the range 0.1 to 20 MeV	0.46	4.45	0.40	0.78	0	3.65	2.90	0.008[a]
	3-13	4.08	0.45	0.68	2.63	0.55	2.72	0.026[b]

Estimated steadystate concentrations of species in oxygen-saturated J-13 water irradiated at 3.3×10^6 rad/hr

Species		Estimated concentration (moles/liter)
HCO_3^-	(measured value)	2×10^{-3}
O_2	(air-saturated solution)	3×10^{-4}
H_2O_2	(1/3 of O_2 conc)	1×10^{-4}
OH^-	(assuming pH = 8)	1×10^{-6}
O_2^-	(assumed $\alpha \sqrt{\text{dose rate}}$)	1×10^{-7}
HO_2	(= $[H^+][O_2^-]/10^{-4.88}$)	1×10^{-10}
H^+	(assuming pH = 8)	1×10^{-8}
OH	(assumed $\alpha \sqrt{\text{dose rate}}$)	2×10^{-9}
H_2	(assumed $\alpha \sqrt{\text{dose rate}}$)	3×10^{-9}
e_{aq}^-	(assumed $\alpha \sqrt{\text{dose rate}}$)	3×10^{-11}
H	(assumed $\alpha \sqrt{\text{dose rate}}$)	2×10^{-11}
HO_2^-	(assumed $\alpha \sqrt{\text{dose rate}}$)	4×10^{-12}

Reactions producing H_2O_2:

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Reactions destroying molecular products:

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2$$

$$e^-_{aq} + H_2O_2 \rightarrow OH^- + \cdot OH$$

$$H\cdot + H_2O_2 \rightarrow H_2O + \cdot OH$$

$$H_2 + \cdot OH \rightarrow H_2O + H\cdot$$

$$e^-_{aq} + O_2 \rightarrow O_2^-$$

$$H + O_2 \rightarrow HO_2$$

$$HO_2 \rightleftharpoons H^+ + O_2^-$$

$$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2$$

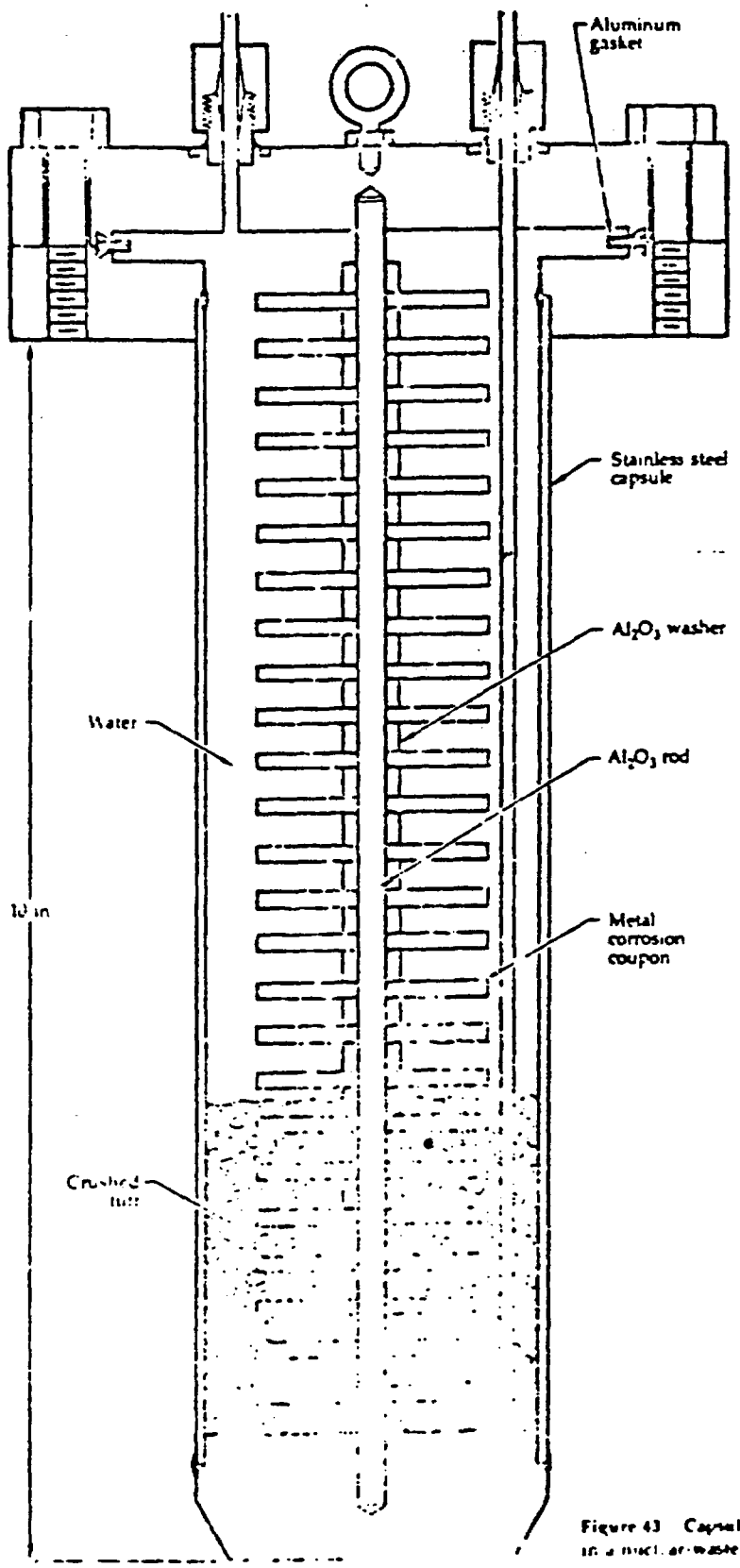


Figure 43 Capsule used to study the corrosion of metals in a nuclear-waste-repository environment.

Corrosion Test Results for Room Temperature Irradiated and Non-Irradiated 304L Coupons (8760 Hrs Exposure)

304L Stainless Steel Material Condition	J-13 Water Environment (28°C)	Corrosion Rates (μm/yr) Vessel A (Irradiated)	Vessel B (Non-Irradiated)
Solution Annealed	Rock + Water	Average: 0.0811*	0.242**
		Range: 0.0690-0.0951	0.215-0.272
		St'd Deviation: 0.00959	0.0201
Solution Annealed	Water	Average: 0.151	0.285
		Range: 0.0817-0.299	0.138-0.451
		St'd Deviation: 0.0734	0.118
Sensitized***	Rock + Water	Average: 0.123	0.249
		Range: 0.111-0.142	0.165-0.322
		St'd Deviation: 0.0114	0.0522
Sensitized	Water	Average: 0.116	0.283
		Range: 0.092-0.142	0.203-0.452
		St'd Deviation: 0.0470	0.0980

* Averages of 6 coupons in each set.

** Maximum localized penetration measured = 0.010 μm in 8760 hours (appx. 1 year).

*** "Sensitizing" heat treatment: 1 hour at 650°C.

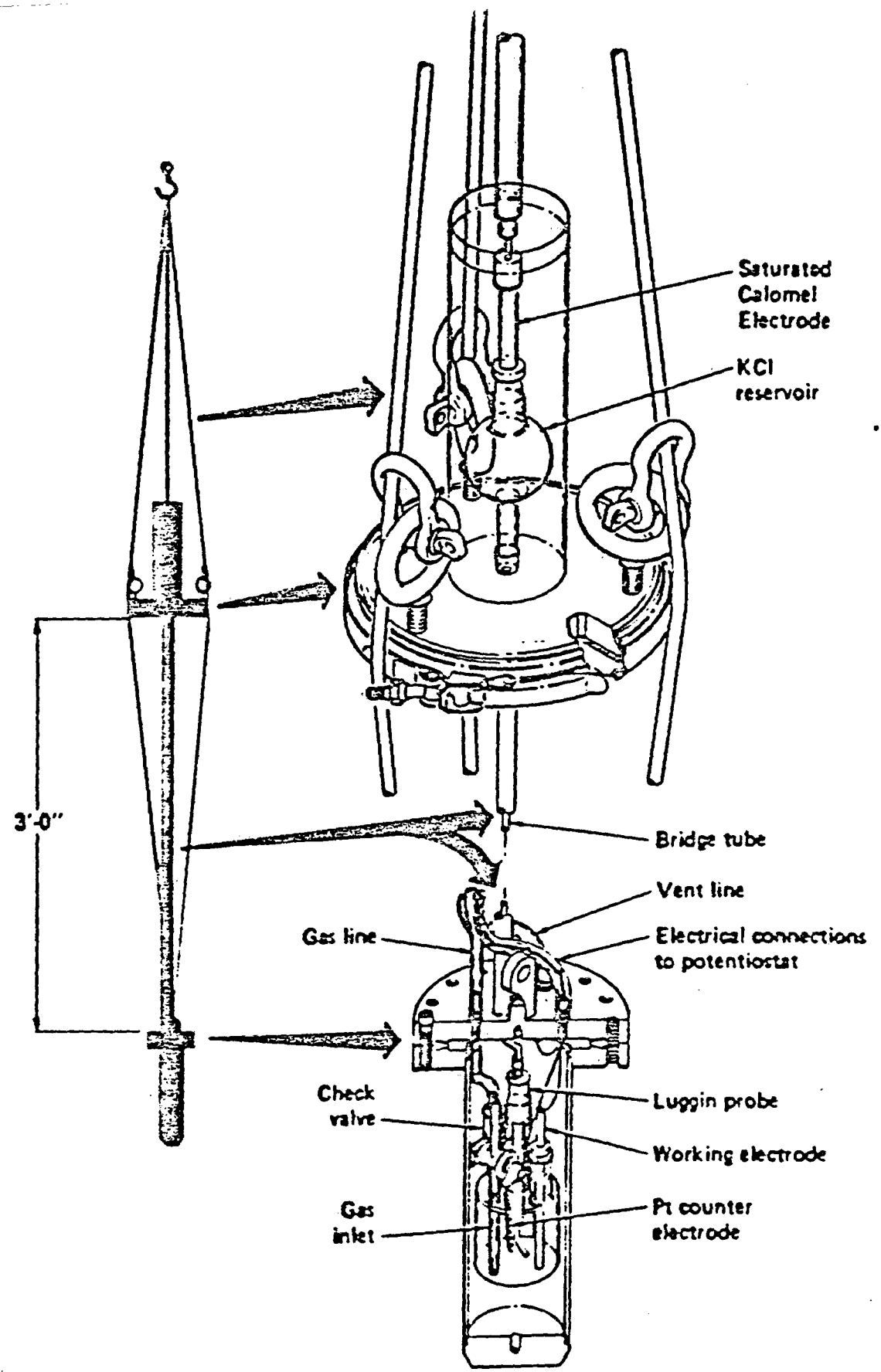


Figure 1: Schematic of the electrochemical cell used in this work. Details are provided in the text.

Figure 2: Corrosion potential behavior for 316L stainless steel in 10X concentrated J-13 well water under gamma irradiation. The solution was not exposed to irradiation prior to initiation of the first "on/off" irradiation cycle.

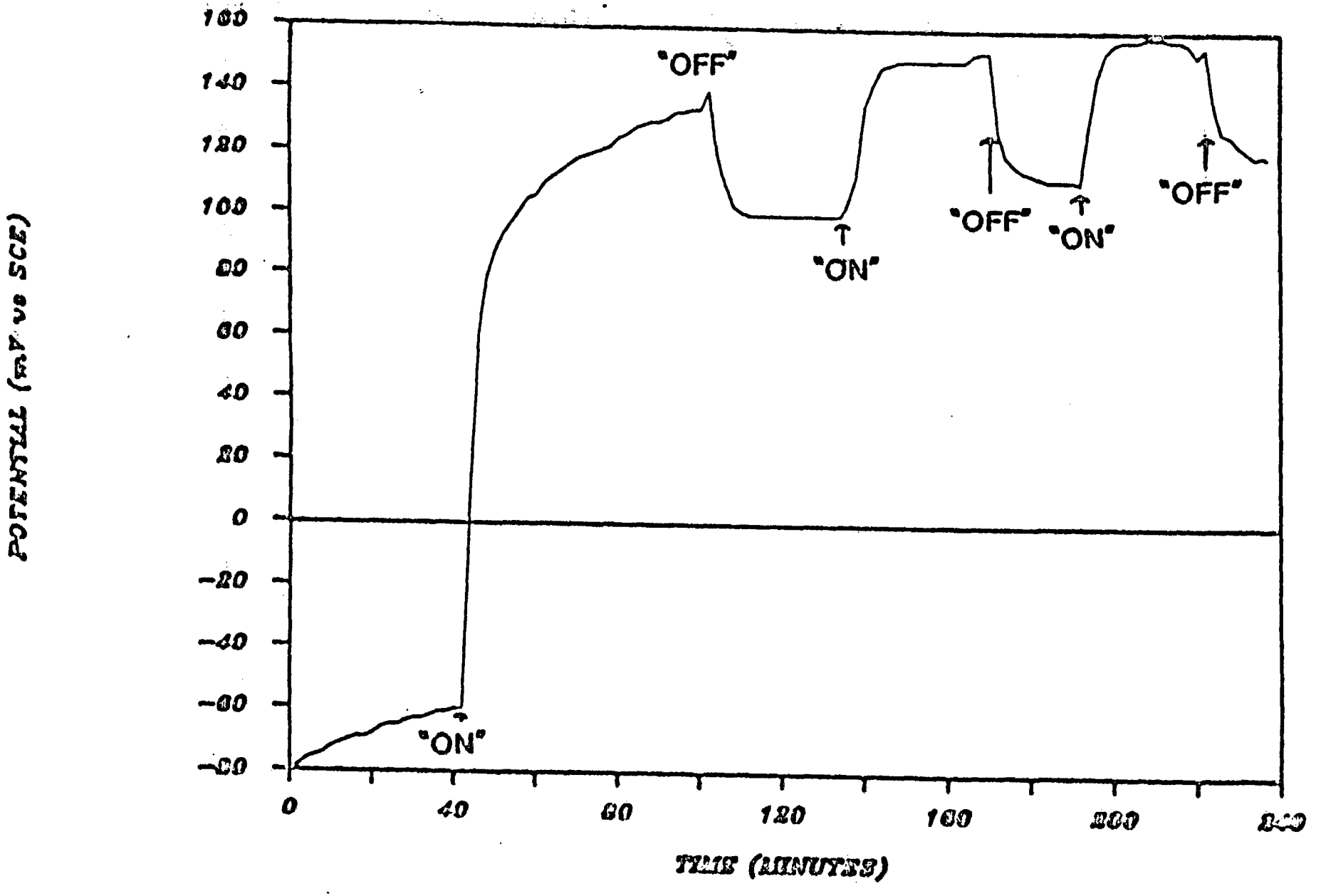


TABLE 3. Possible Redox Reactions in Gamma-Irradiated Solutions

$H_2O + e^- \rightleftarrows e^-_{aq}$	$H_2O_2 + H^+ + e^- \rightleftarrows H_2O + OH$
$H^+ + e^- \rightleftarrows H\ (aq)$	$HO_2^- + H_2O + 2e^- \rightleftarrows 3OH^-$
$OH\ (aqs) + e^- \rightleftarrows OH^-$	$HO_2^- + H_2O + e^- \rightleftarrows 2OH^- + OH$
$OH + H^+ + e^- \rightleftarrows H_2O$	$O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2$
$HO_2 + H^+ + e^- \rightleftarrows H_2O_2$	$O_2 + 2H_2O + 2e^- \rightleftarrows H_2O_2 + 2OH^-$
$O^- + e^- \rightleftarrows OH^-$	$O_2 + H_2O + 2e^- \rightleftarrows HO_2^- + OH^-$
$HO_2 + 2H^+ + 2e^- \rightleftarrows H_2O + OH$	$2H^+ + 2e^- \rightleftarrows H_2$
$O_2^- + H_2O + e^- \rightleftarrows HO_2^- + OH^-$	$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^-$
$O_2 + H^+ + e^- \rightleftarrows HO_2$	$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$
$O_2 + e^- \rightleftarrows O_2^-$	$O_2 + 2H_2O + 4e^- \rightleftarrows 4OH^-$
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	

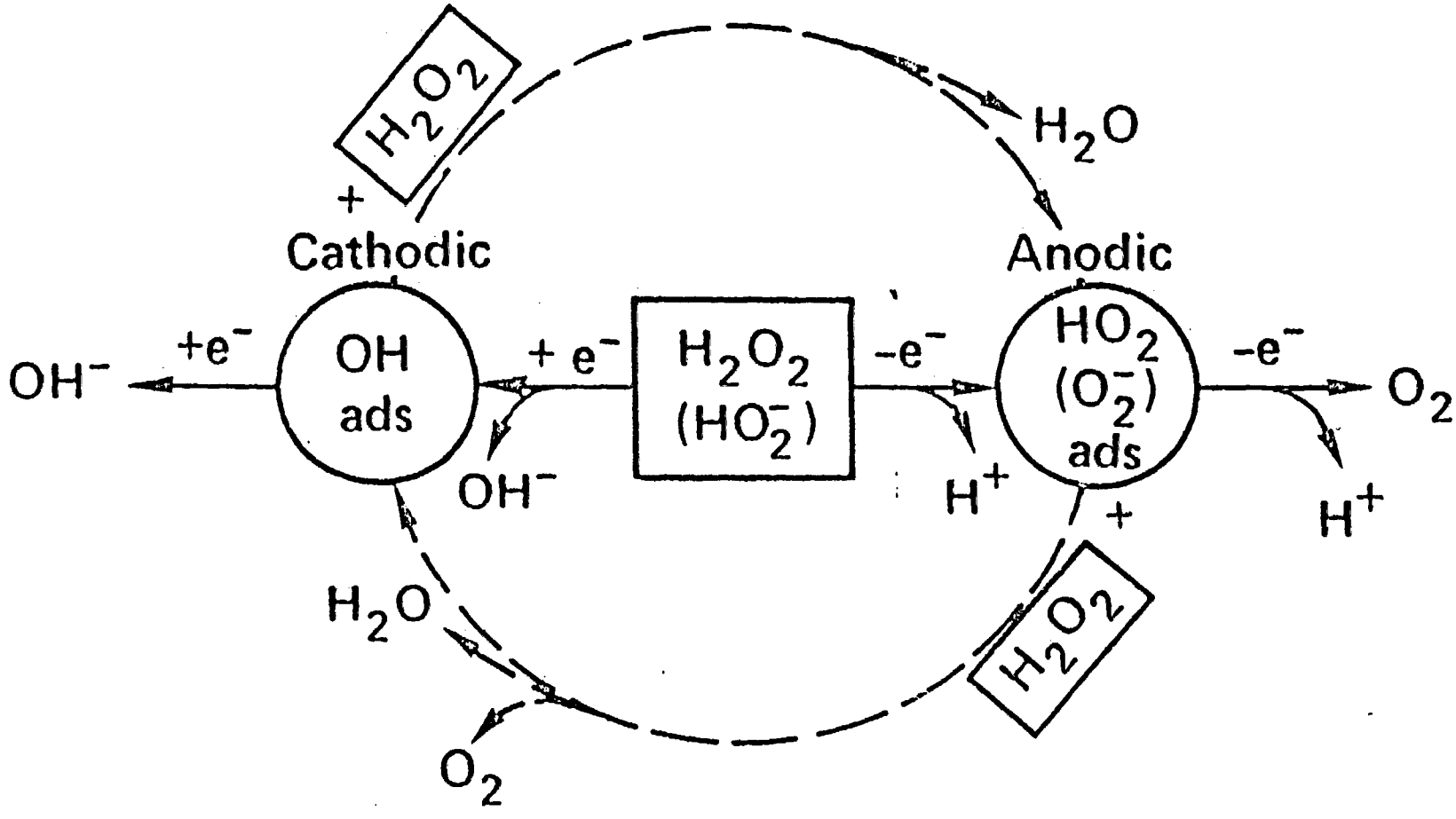
$$\bullet OH\ (aq) \rightarrow \bullet OH_{ads}$$

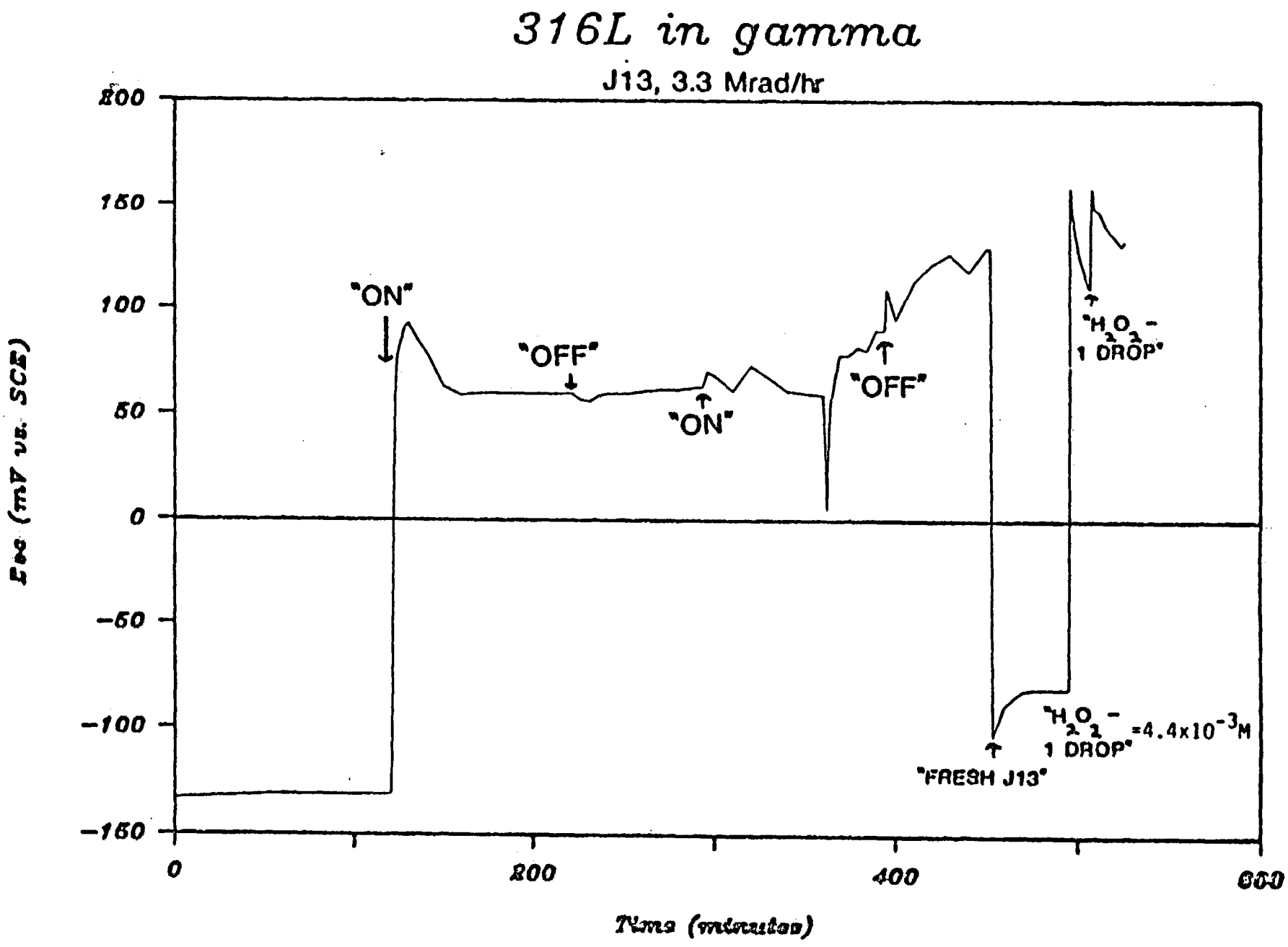
$$H_2O_2\ (aq) \rightleftarrows 2OH_{ads}$$

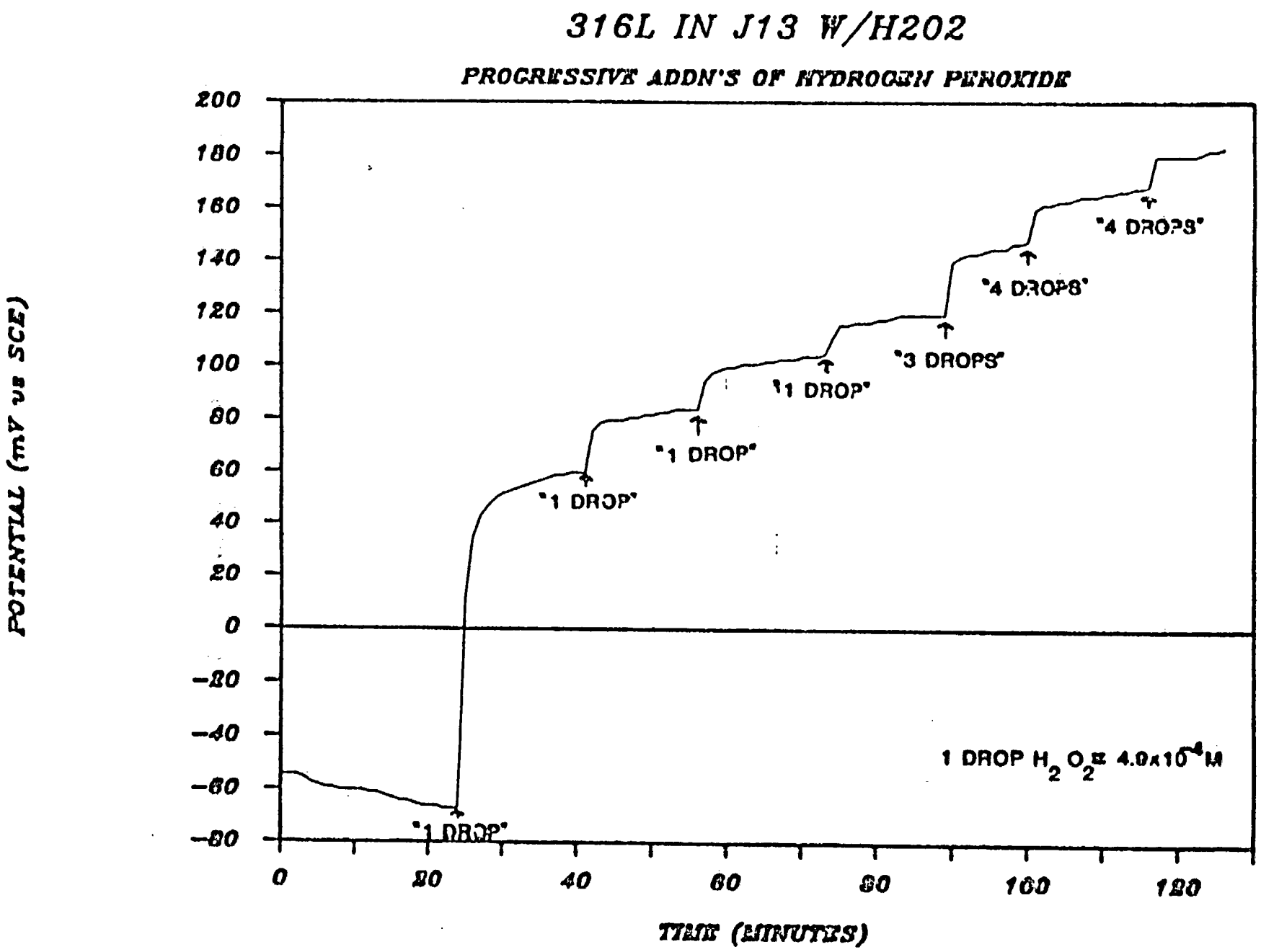
$$\bullet OH_{ads} + e \rightleftharpoons OH^-$$

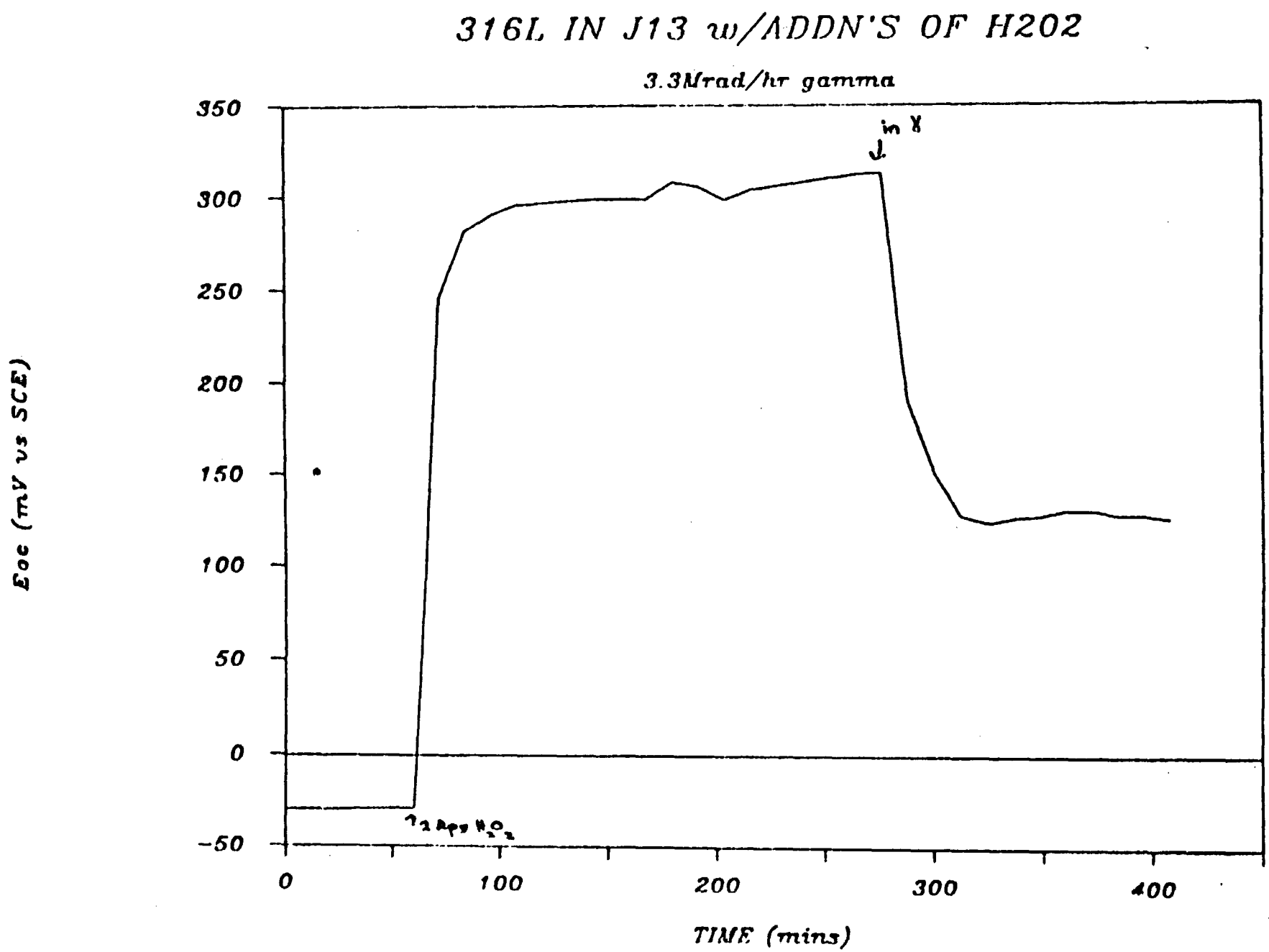
$E_{oc,Pt}$ = 0.594 - 0.059 pH, volts vs SCE at 25°C, independent of $[H_2O_2]$ to 10^{-6} M

at pH = 7, E = 0.181V at $(a_{OH})_{sat}$


H_2O_2
+
Cathodic
H_2O
Anodic
OH^-
$+e^-$
OH
ads
$+ e^-$
H_2O_2
(HO_2^-)
$-e^-$
HO_2
(O_2^-)
ads
$-e^-$
O_2
OH^-
H^+
H^+
+
H_2O
H_2O_2
O_2


316L in gamma
J13, 3.3 Mrad/hr
200
150
100
50
0
-50
-100
-150
Eco (mV vs. SCE)
"ON"
"OFF"
"ON"
"OFF"
"FRESH J13"
"H2O2 - 1 DROP"
"H2O2 - 1 DROP" =4.4x10-3M
0
200
400
600
Time (minutes)


316L IN J13 W/H202
PROGRESSIVE ADDN'S OF HYDROGEN PEROXIDE
POTENTIAL (mV vs SCE)
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
"1 DROP"
"1 DROP"
"1 DROP"
"1 DROP"
"3 DROPS"
"4 DROPS"
"4 DROPS"
1 DROP H_2O_2 ≈ 4.0×10^{-4} M
0
20
40
60
80
100
120
TIME (MINUTES)


316L IN J13 w/ADDN'S OF H202
3.3Mrad/hr gamma
in γ
Eoc (mV vs SCE)
350
300
250
200
150
100
50
0
-50
0
100
200
300
400
TIME (mins)

Cathodic reactions (neutral to basic):

$$OH\ (ads) + e^- \rightleftharpoons OH^-$$

$$O_2 + 2H_2O + 4\,e^- \rightleftharpoons 4OH^-$$

small, $$O_2^- + H_2O + e^- \rightleftharpoons HO_2^- + OH^-$$

very small, $$HO_2^- + H_2O + 2\,e^- \rightleftharpoons 3OH^-$$

Anodic reactions:

$$Fe \rightleftharpoons Fe^{+2} + 2\,e^-$$

$$Cr \rightleftharpoons Cr^{+3} + 3\,e^-$$

$$Ni \rightleftharpoons Ni^{+2} + 2\,e^-$$

Small, higher pH
$$OH^- + H_2O_2 \rightleftharpoons O_2 + 2H_2O + 2\,e^-$$
$$HO_2^- + OH^- \rightleftharpoons O_2 + H_2O + 2\,e^-$$

Oxidations of Fe^{+2} by radiolysis products:

$$\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$$

$$HO_2 + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \bullet OH$$

$$H\bullet + Fe^{2+} \rightarrow Fe^{3+}H^-$$

$$Fe^{3+}H^- + H^+ \rightarrow Fe^{3+} + H_2$$

$$2Fe(OH)_2 + H_2O_2 \rightarrow 2FeOOH + 2H_2O$$

$$xMe + yOH \longrightarrow Me_x (OH)_y$$

$$xMe + yHO_2 \longrightarrow Me_x O_{1.5y}\ 0.5\,y\ H_2O$$

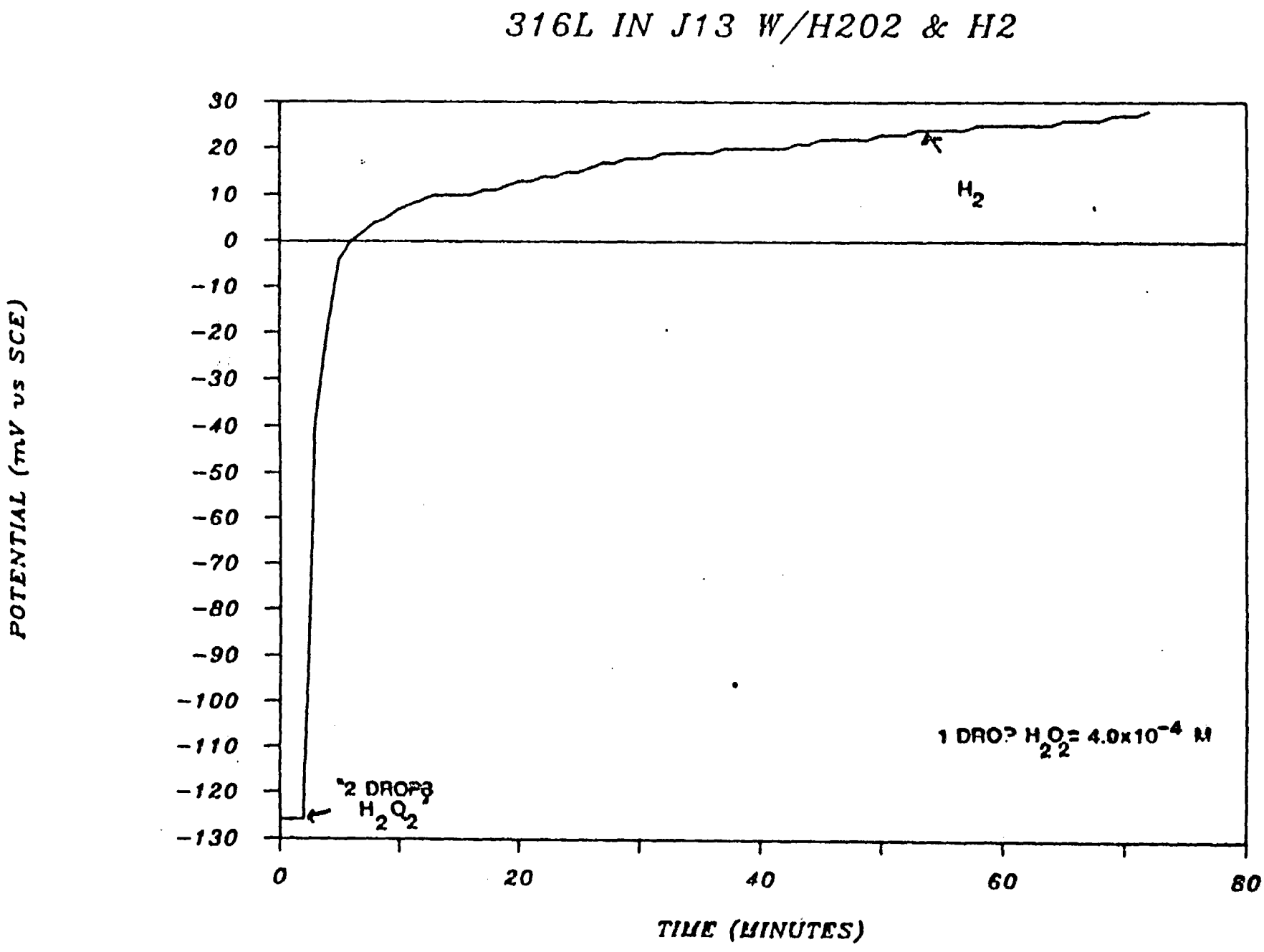
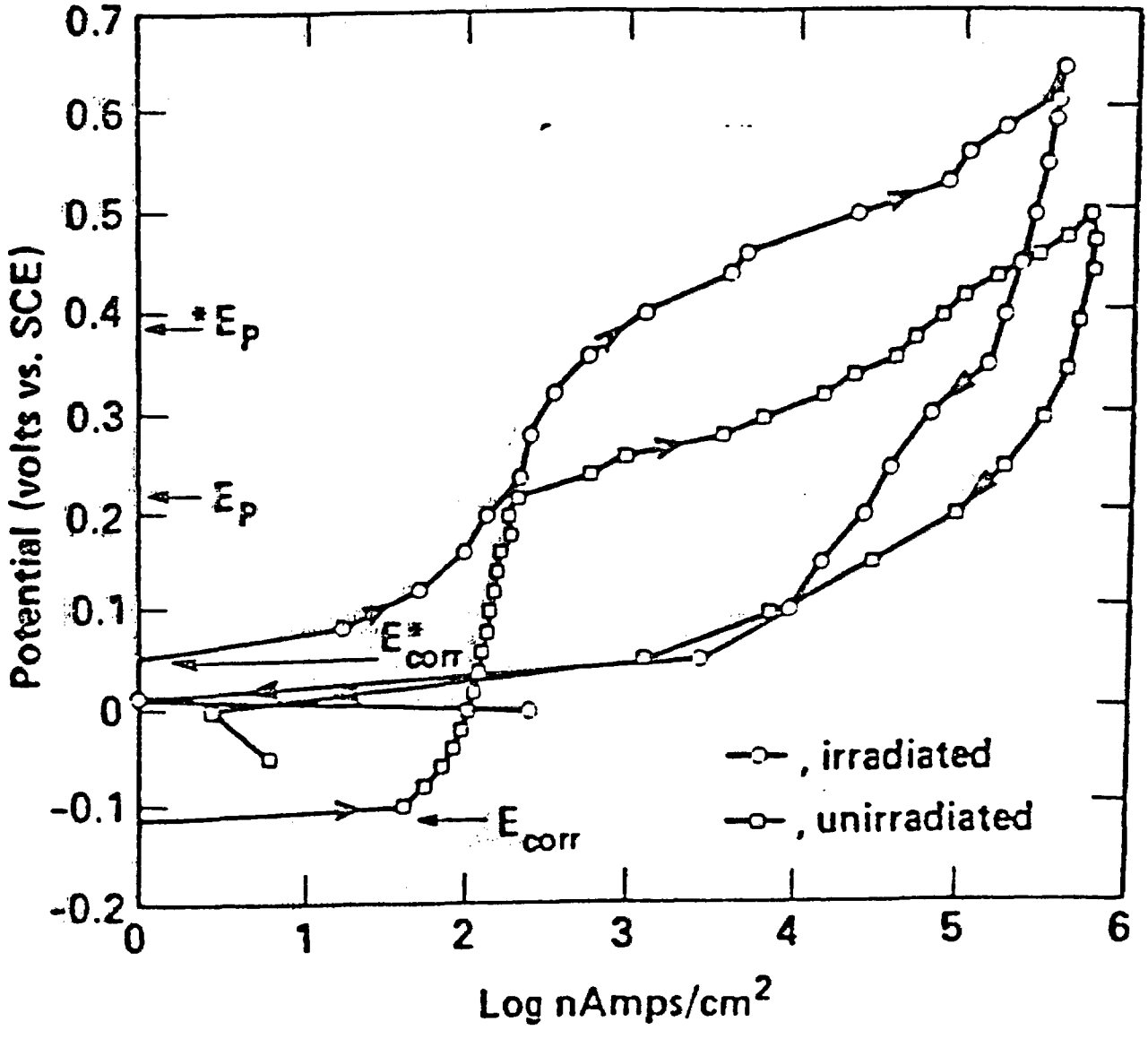

316L IN J13 W/H202 & H2
POTENTIAL (mV vs SCE)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
0
20
40
60
80
TIME (MINUTES)
H2
1 DROP H2O2= 4.0x10-4 M
2 DROPS H2O2

Figure 11: Comparison of the potentiostatic anodic polarization behavior for 316L stainless steel in 650 ppm Cl^- solution in deionized water with and without gamma irradiation. The polarization curves were scanned anodically starting from the corrosion potential in each case. Upon reaching the anodic limit, the scans were reversed to more negative potentials. In this figure, E_{corr} and E_p represent values of the corrosion potential and pitting potential, respectively, for the unirradiated case. The corresponding values for the irradiated experiment are indicated on the figure as $*E_{corr}$ and $*E_p$.



CONCLUSIONS:

1. Gamma radiation increases the oxidizing nature of the environment (H_2O_2); preliminary evidence suggests the oxide film changes are negligible.

2. $OH(ads) + e^- = OH^-$ may be an important equilibrium (analogy to Pt); situation complex.

3. Positive potential shifts appear generic to austenitic steels and electrolytes related to J13.

4. Equilibrium processes responsible for for Ecorr shifts occur in near-surface solution layers.

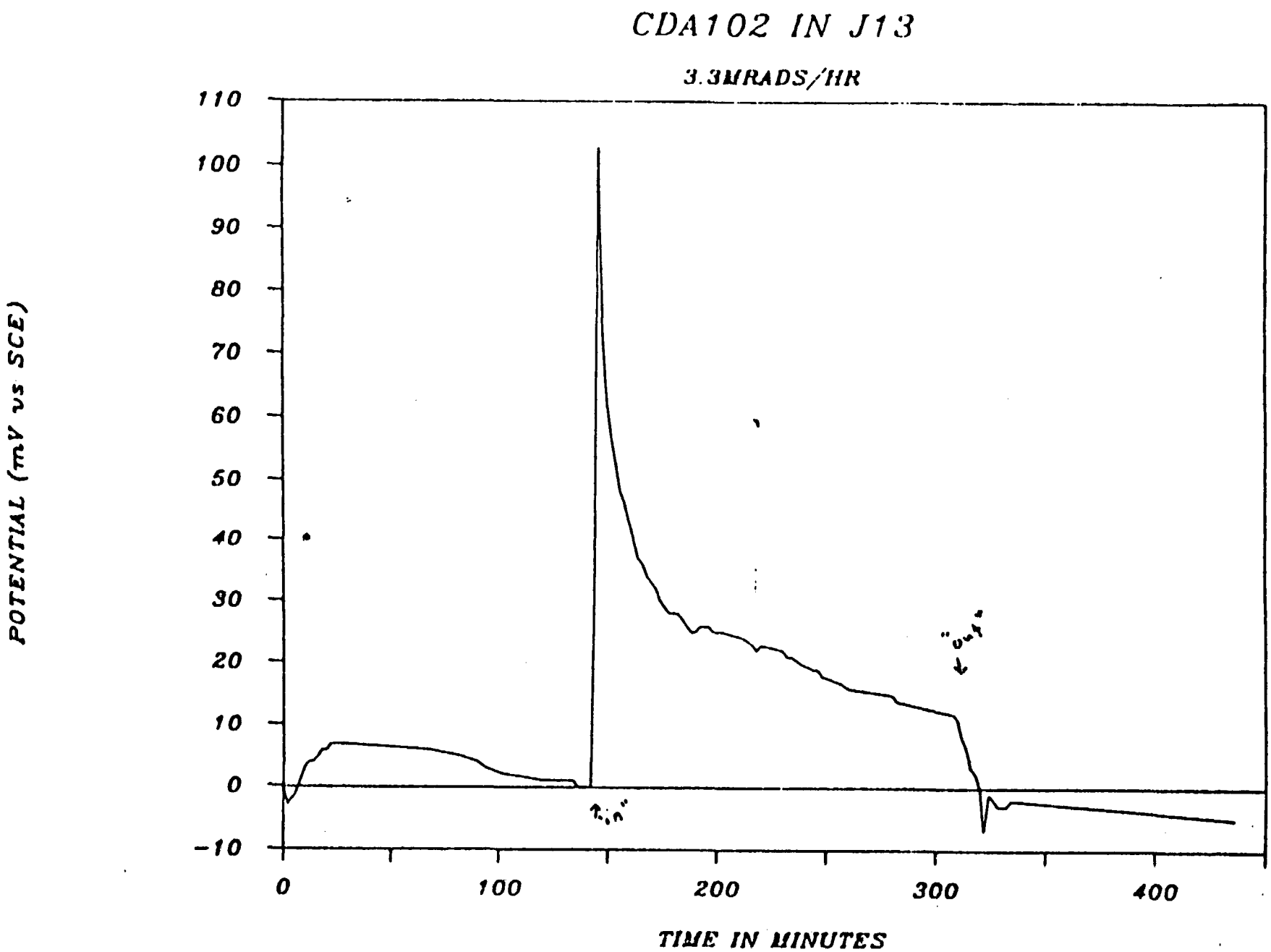
5. Ecorr of stainless steels is more sensitive to H_2O_2 than bulk H_2.

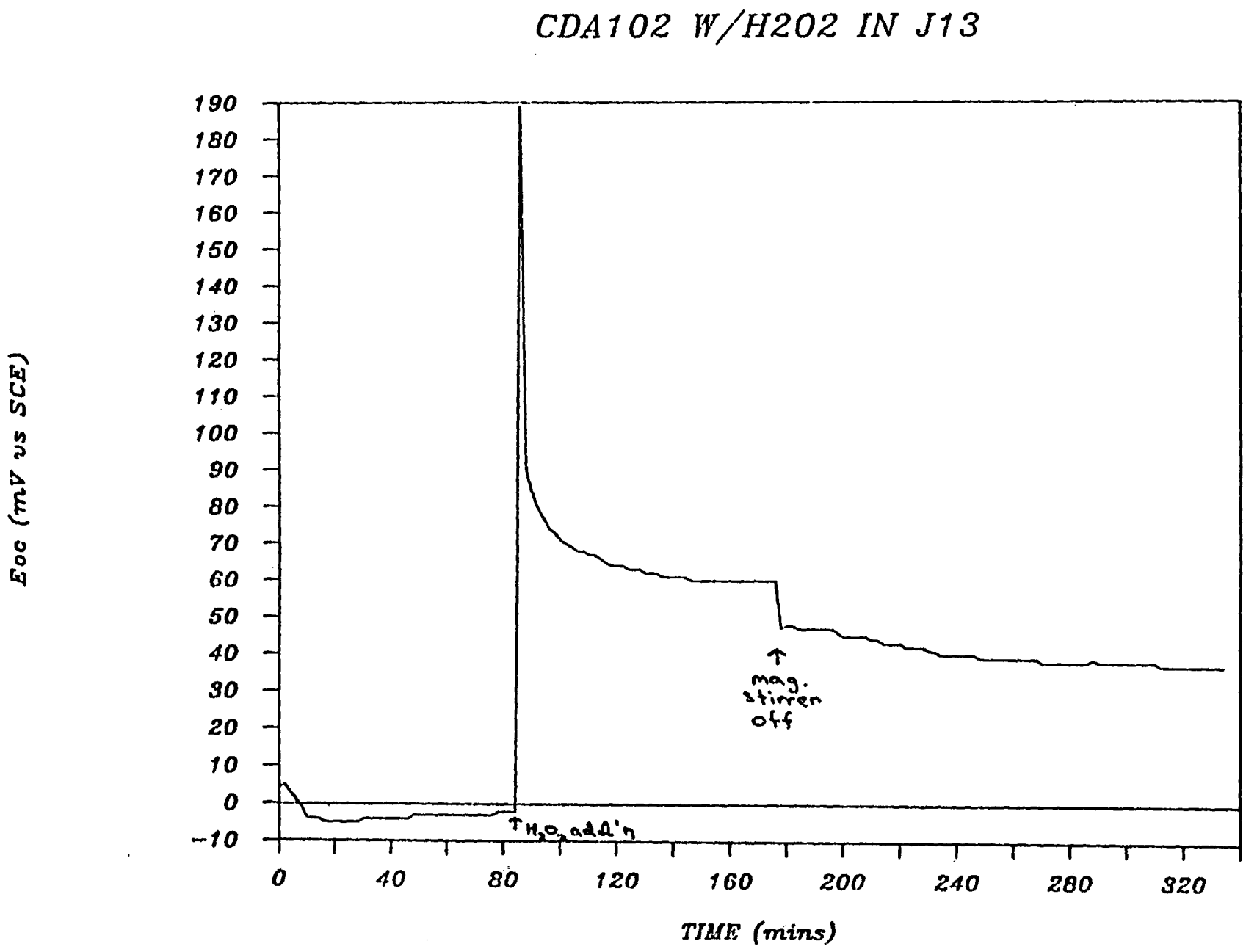
6. Preliminary results suggest radiation does not increase pitting susceptibility.

5. GAMMA RADIATION EFFECTS ON COPPER ALLOYS IN J13.

Measured analyses of copper alloys

Alloy	Elemental composition (wt %)							
	Cu	Ni	Al	Mn	Sn	Fe	Zn	Other
CDA 102	99.95	–	–	–	–	–	< 0.001	Pb < 0.001; Cd < 0.001 S < 0.0018; Hg <0.0001 P < 0.003
CDA 613/614	90.82	0.05	6.75	0.16	0.20	2.46	0.01	Pb < 0.01; Co < 0.01
CDA 715	69.18	29.60	–	0.51	–	0.53	0.07	Pb - 0.01; P - 0.002; C - 0.04; S - 0.01


CDA102 IN J13
3.3MRADS/HR
POTENTIAL (mV vs SCE)
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
100
200
300
400
TIME IN MINUTES


CDA102 W/H2O2 IN J13
Eoc (mV vs SCE)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
40
80
120
160
200
240
280
320
TIME (mins)
H2O2 add'n
mag. stirrer off

Sample	Exp. duration (h)	Date	Soln. vol.(ml)	Sample area	$[H_2O_2]$, μM
Blank	2.20	8/17/84	∿100	N/A	139.00
CDA102	355.00	3/8/85	25	30.91	6.00
316L	"	"	27	30.70	135.00
Blank	"	"	25	N/A	139.00
CDA102	164.00	4/15/85	25	30.95	37.00
316L	"	"	27	30.60	187.00
Blank	"	"	25	N/A	132.00

CATALYTIC AUTODISSOLUTION OF COPPER:

$$Cu \rightleftharpoons Cu^{+} + e^{-}$$

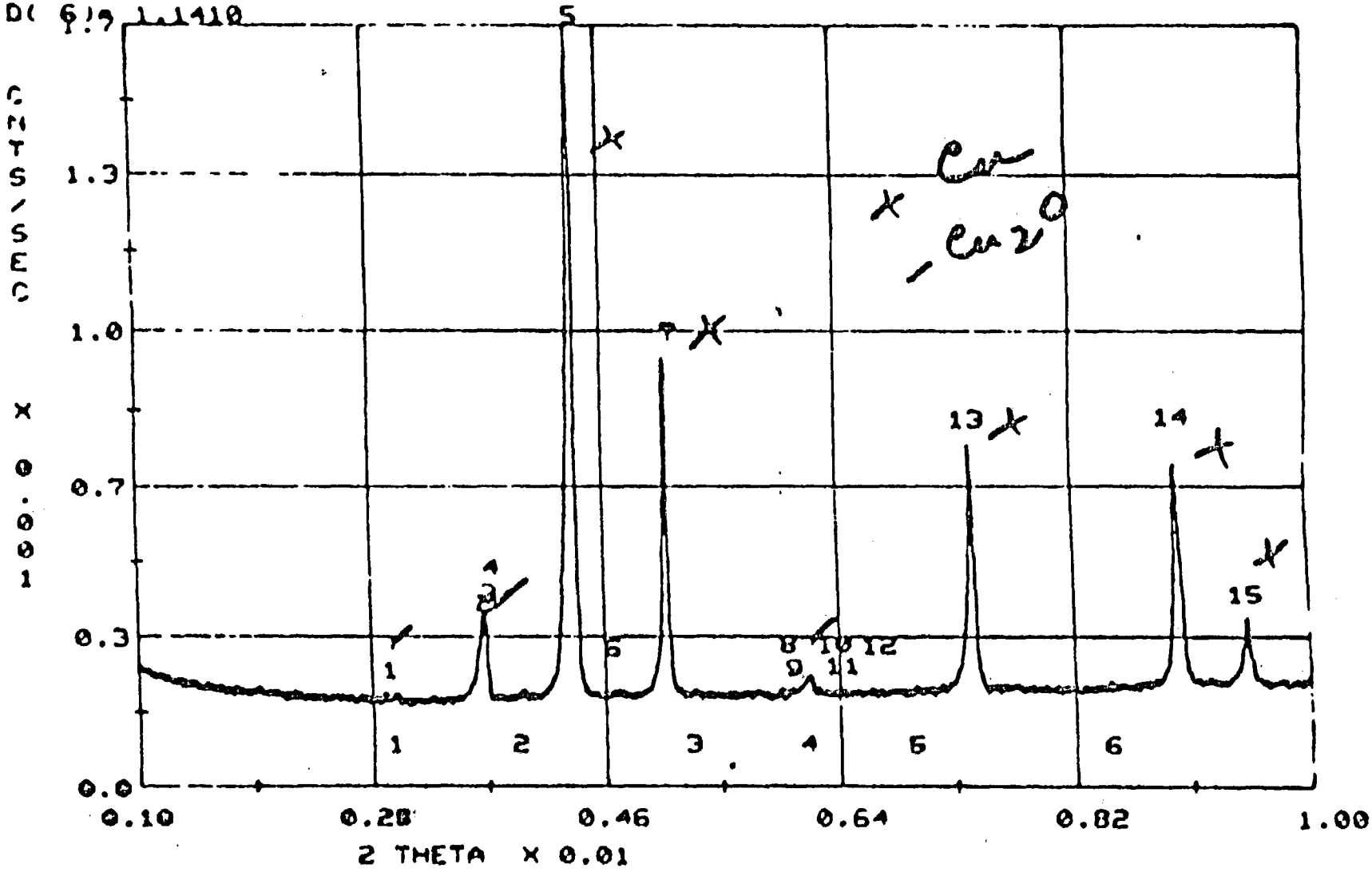
$$Cu^{+2} + e^{-} \rightarrow Cu^{+}$$

WITH Cu^{+2}, ACTING AS AN OXIDANT BEING GENERATED FROM:

$$Cu^{+} + H_2O_2 \rightarrow Cu^{+2} + OH + OH^{-}$$

$$Cu^{+} + OH \rightarrow Cu^{+2} + OH^{-}$$

4021 4-17-85 DIFF CAR CDA 102 CU ROD J13 WELL H20 162 HRS
INITIAL 2THETA= 10.000 DELTA 2THETA= 0.040 TIME INTERVAL= 4.00SEC
ISM= 7 IBKG= 0 0 TGKA2= TGDSP=CU ND2= 7 SENS.= 2.0 NUM= 1 IPF=5
D(1)= 2.9847 D(2)= 2.2759 D(3)= 1.7312 D(4)= 1.5024 D(5)= 1.3423
D(6)= 1.1410



$$H_2O + N_2 + 2.5O_2 \rightarrow HNO_3$$

LONG-TERM TEST CONDITIONS:

1. 150°C air/steam, 1×10^5 R/hr
2. 95°C liquid/vapor, 1×10^5 R/hr

1, 3, 6, 9, 12 .. month exposures —
wt. loss, crevice and "tear drop"
specimens for all copper materials

W-PROGRAM:

1.0 Electrochemistry of Copper in Aqueous Solutions
- 1.1 Kinetics studies in bulk electrolyte to identify reactions and processes (impedance and rotating disk experiments)
- 1.2 Modeling of impedance under thin films
- 1.3 Modeling of electrodissolution and corrosion under thin films of electrolyte

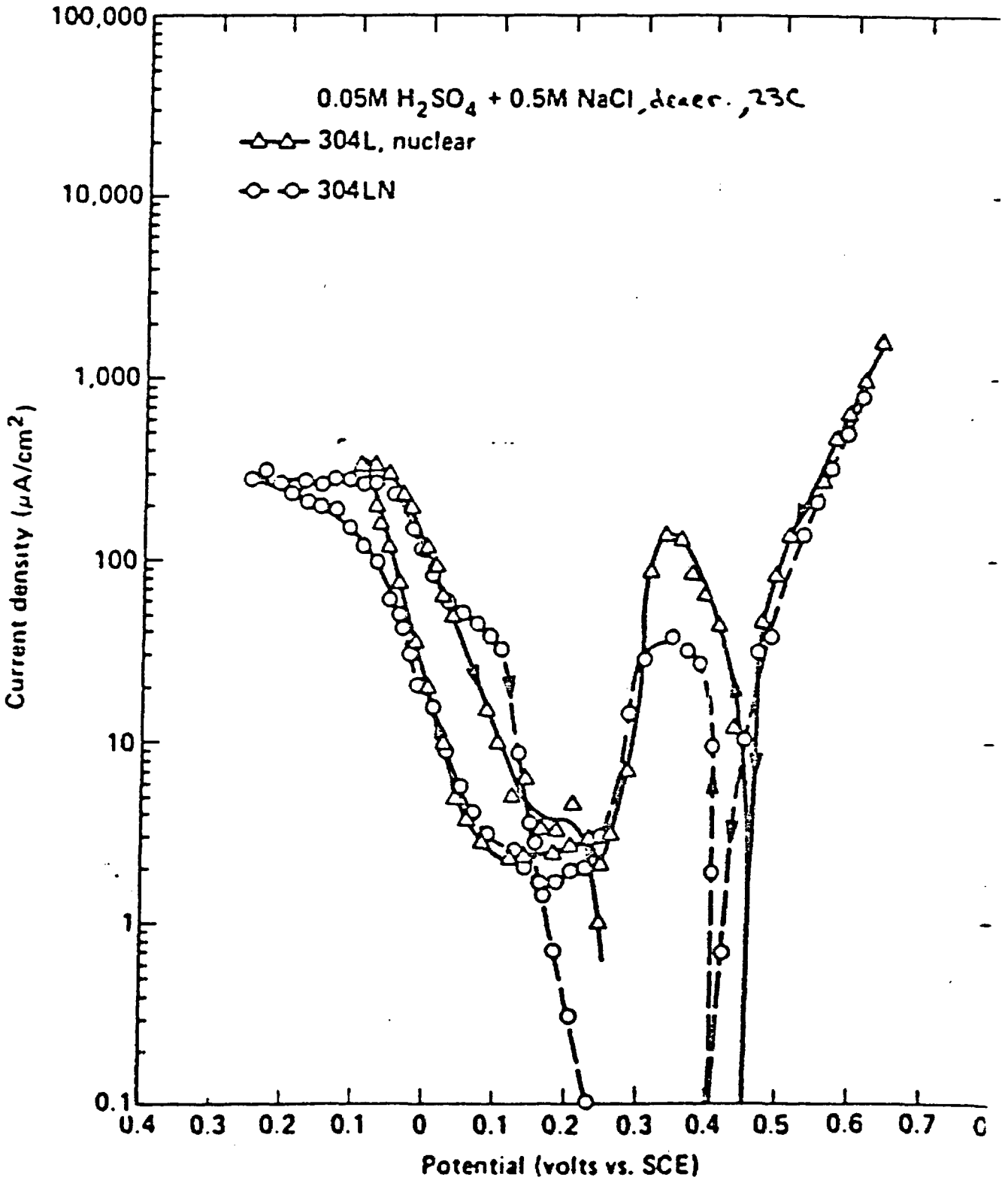
2.0 Electrochemistry of Copper in Irradiated Environments
- 2.1 Cathodic process investigation, in gamma field and in simulated irradiated environments
- 2.2 Modeling of radiolysis products build up in moisture films (electrolyte films)

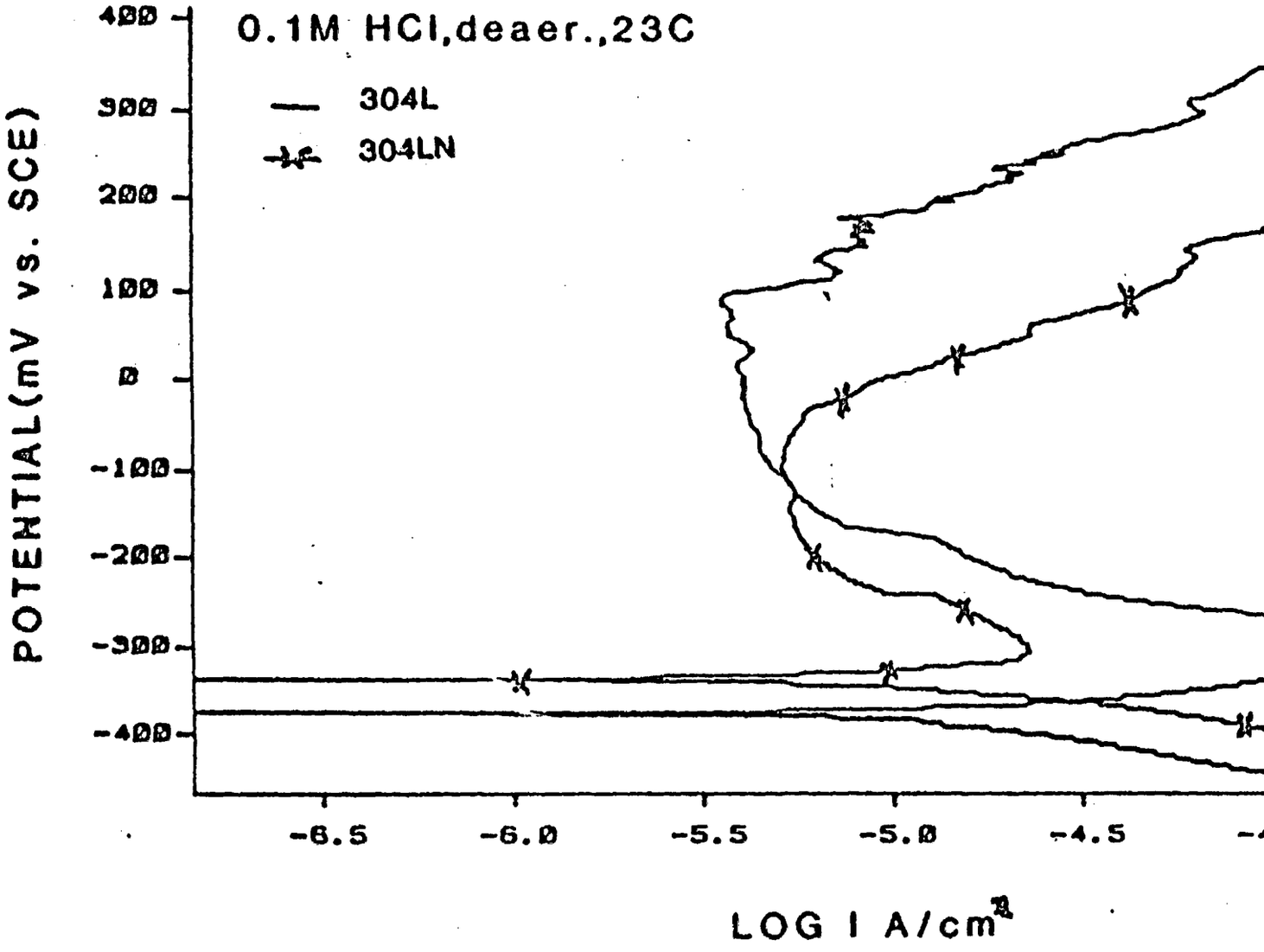
3.0 Photoelectrochemical Measurements on Copper Alloy Surfaces
- 3.1 Imaging of oxide layers on copper alloy surfaces
- 3.2 Imaging of oxide layers under thin electrolyte films

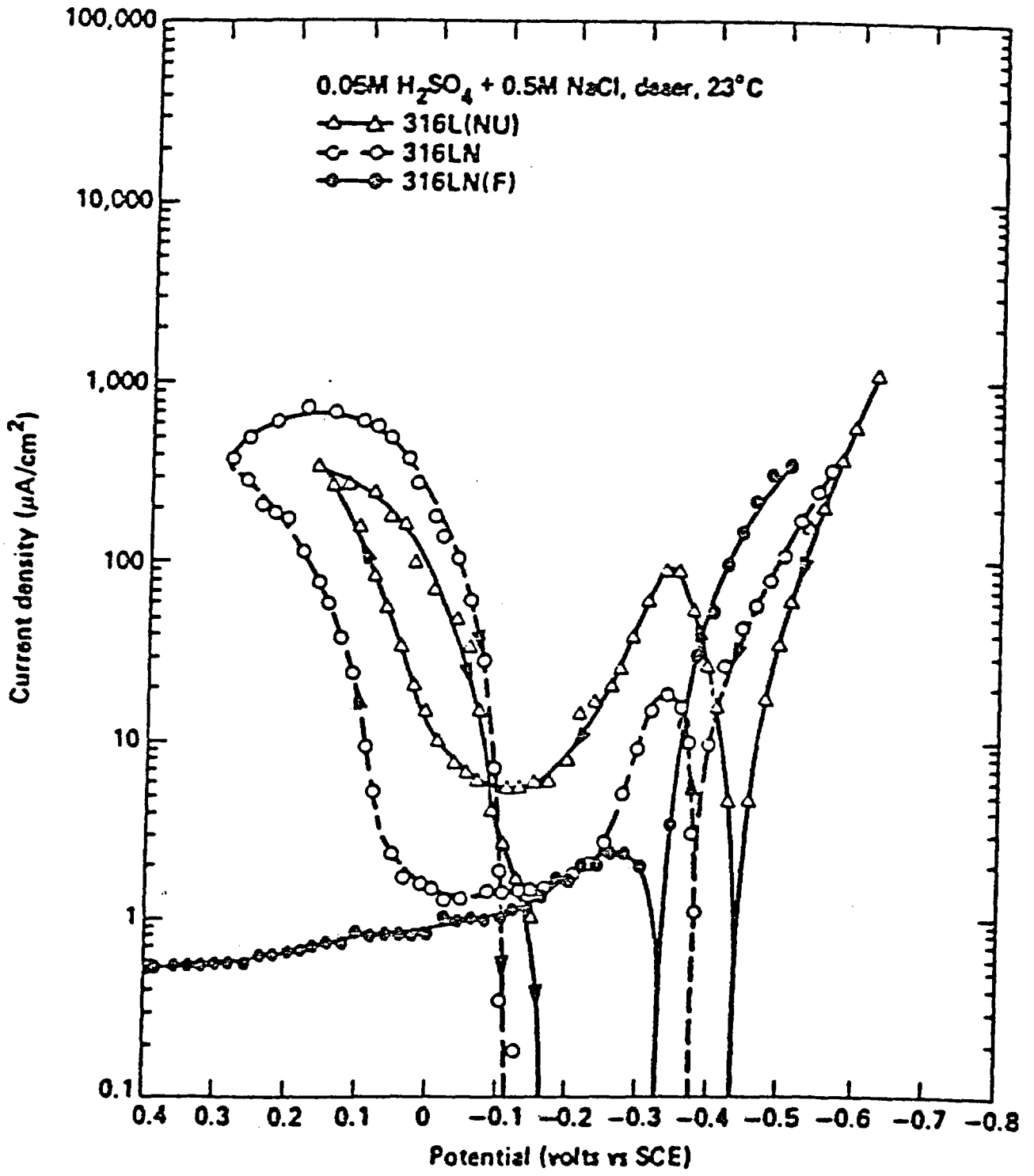
2. COMPARATIVE BEHAVIOR OF L AND LN AUSTENITIC STAINLESS STEEL ALLOYS AND EFFECT OF ALLOY "CLEANLINESS."

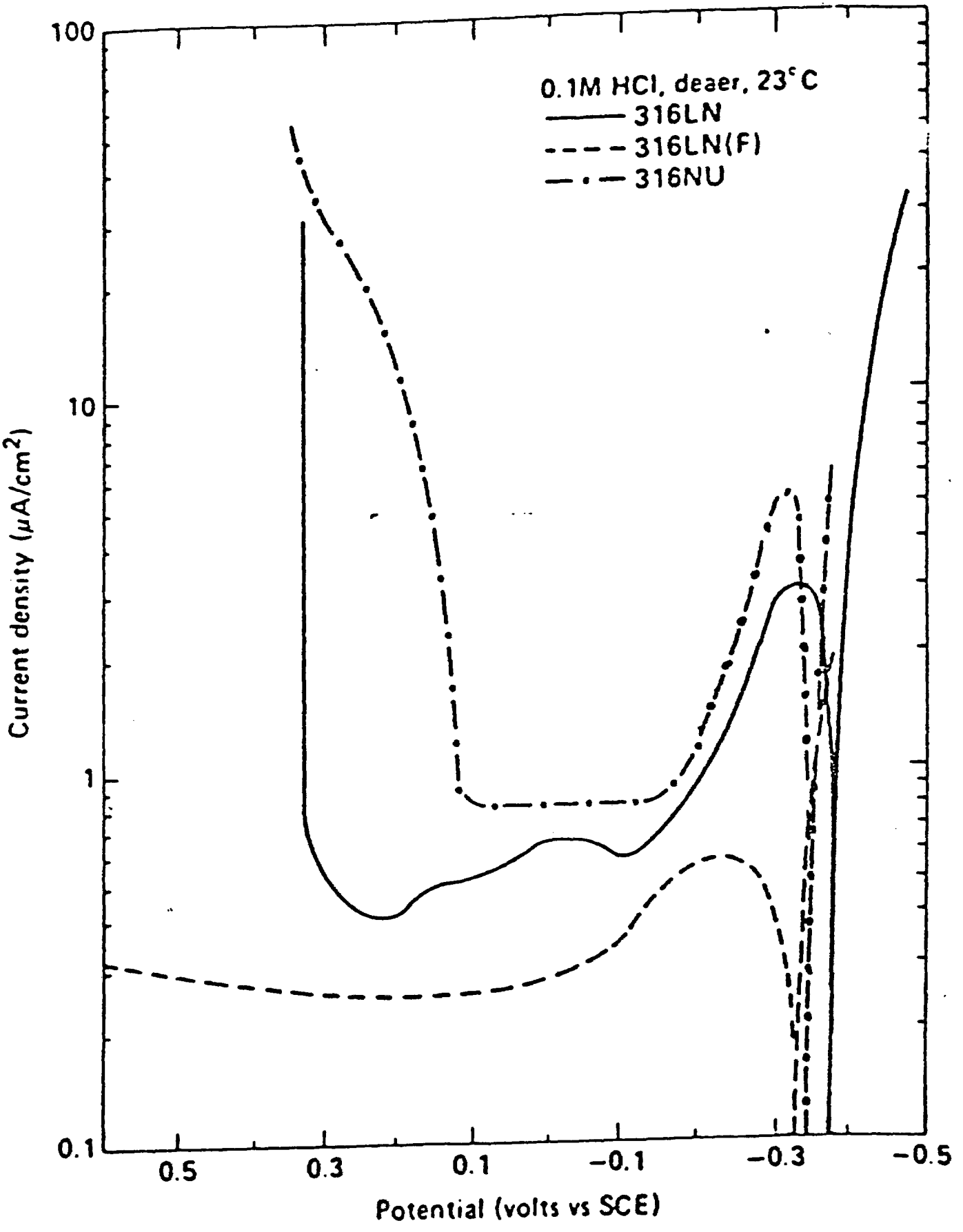
TABLE 1. Analyses of Alloys Used

	Elements											
Alloy	C	Mn	P	S	Si	Co	Cu	Ni	Cr	Mo	W	OTHER
304L	0.017	1.39	0.025	0.015	0.40	0.08	0.43	9.51	18.29	0.23	0.04	bal-
304L (NU)	0.011	1.73	0.031	0.004	0.34	0.12	0.20	9.01	18.30	0.41	0.08	bal-
304LN	0.025	1.10	0.016	0.007	0.45	0.19	0.14	9.28	18.36	0.24	0.16	bal-
316L (NU)	0.020	1.71	0.033	0.014	0.56	0.10	0.28	10.29	16.51	2.07	0.05	bal-
316LN	0.015	1.66	0.030	0.006	0.55	0.19	0.29	10.60	16.70	2.15	0.11	bal-
316LN (F)	0.017	1.61	0.028	0.003	0.50	-------	0.24	11.40	17.60	2.80	0.11	bal-


0.05M H_2SO_4 + 0.5M NaCl, deaer., 23C
304L, nuclear
304LN
Current density ($\mu A/cm^2$)
100,000
10,000
1,000
100
10
1
0.1
0.4
0.3
0.2
0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Potential (volts vs. SCE)


0.1M HCl,deaer.,23C
304L
304LN
POTENTIAL(mV vs. SCE)
400
300
200
100
0
-100
-200
-300
-400
-6.5
-6.0
-5.5
-5.0
-4.5
LOG I A/cm²


0.05M H_2SO_4 + 0.5M NaCl, deaer, 23°C
316L(NU)
316LN
316LN(F)
Current density (μA/cm²)
100,000
10,000
1,000
100
10
1
0.1
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
−0.8
Potential (volts vs SCE)


0.1M HCl, deaer, 23°C
316LN
316LN(F)
316NU
100
10
1
0.1
Current density (μA/cm²)
0.5
0.3
0.1
−0.1
−0.3
−0.5
Potential (volts vs SCE)

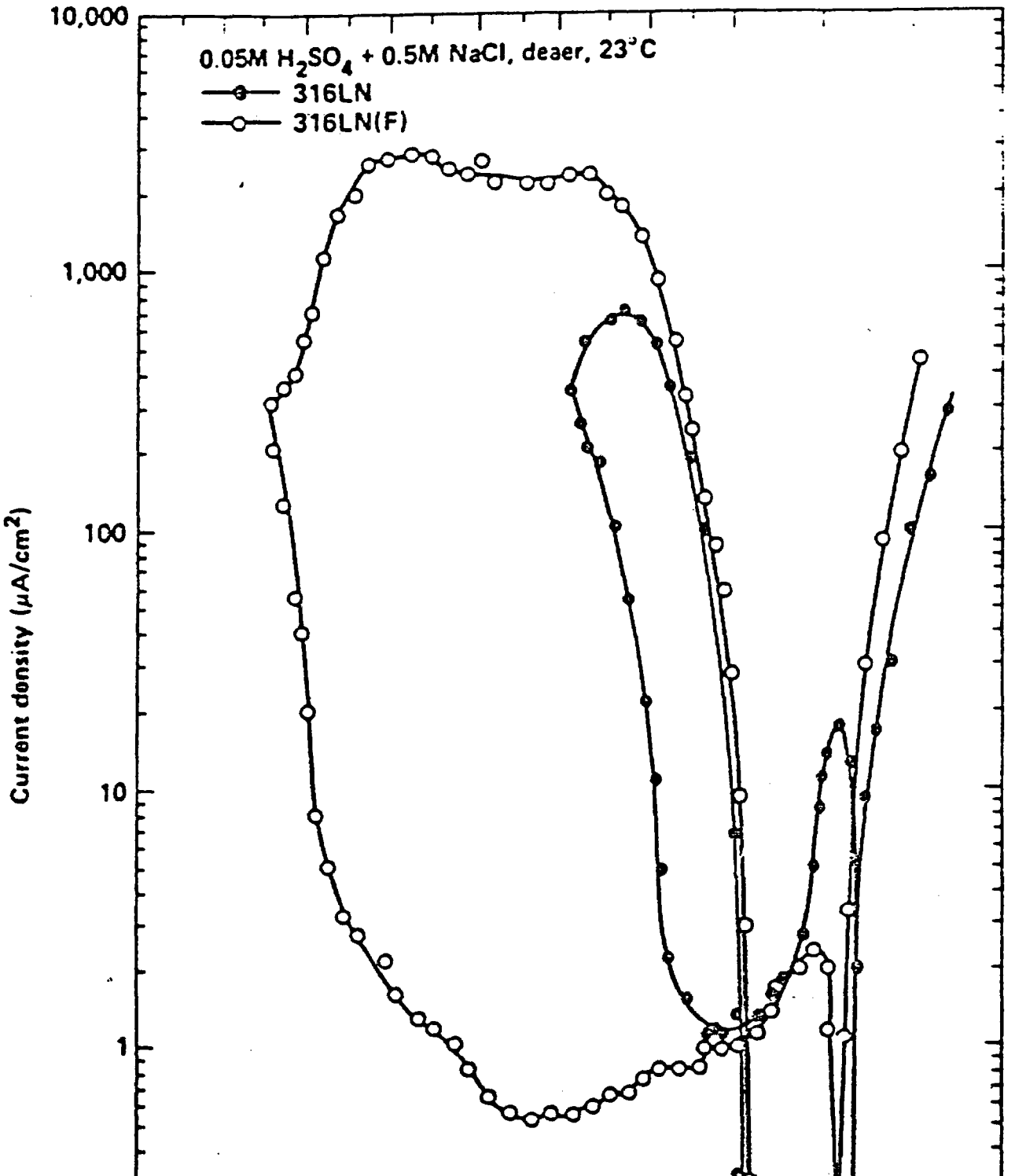
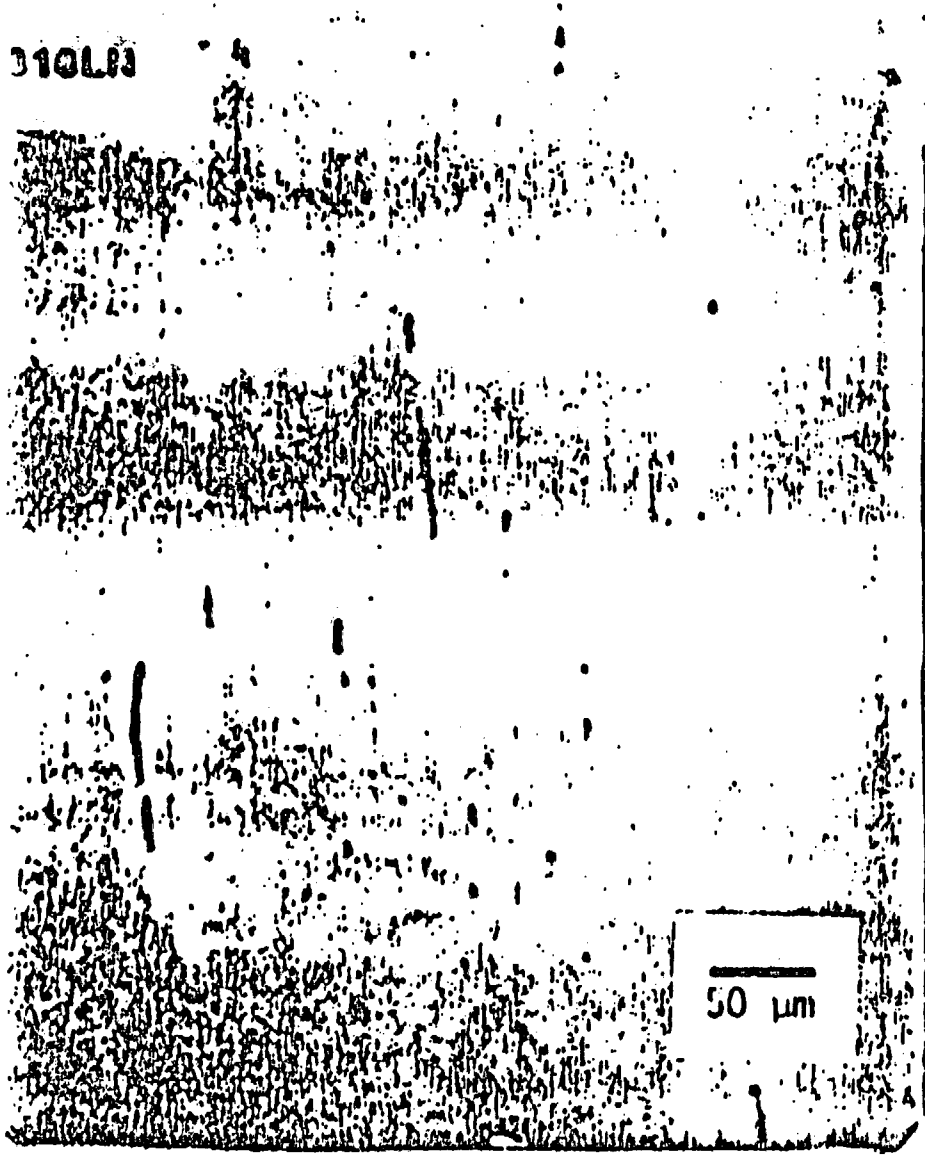
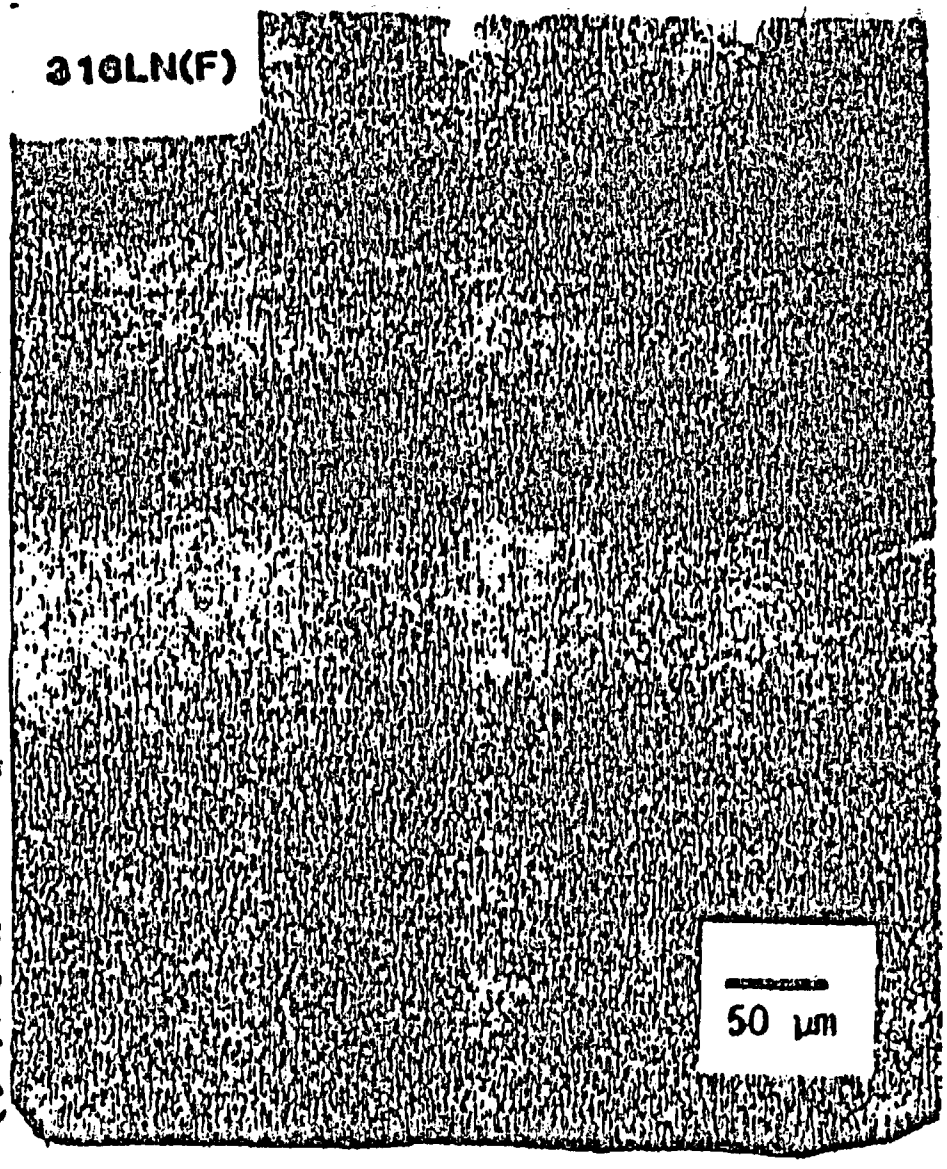
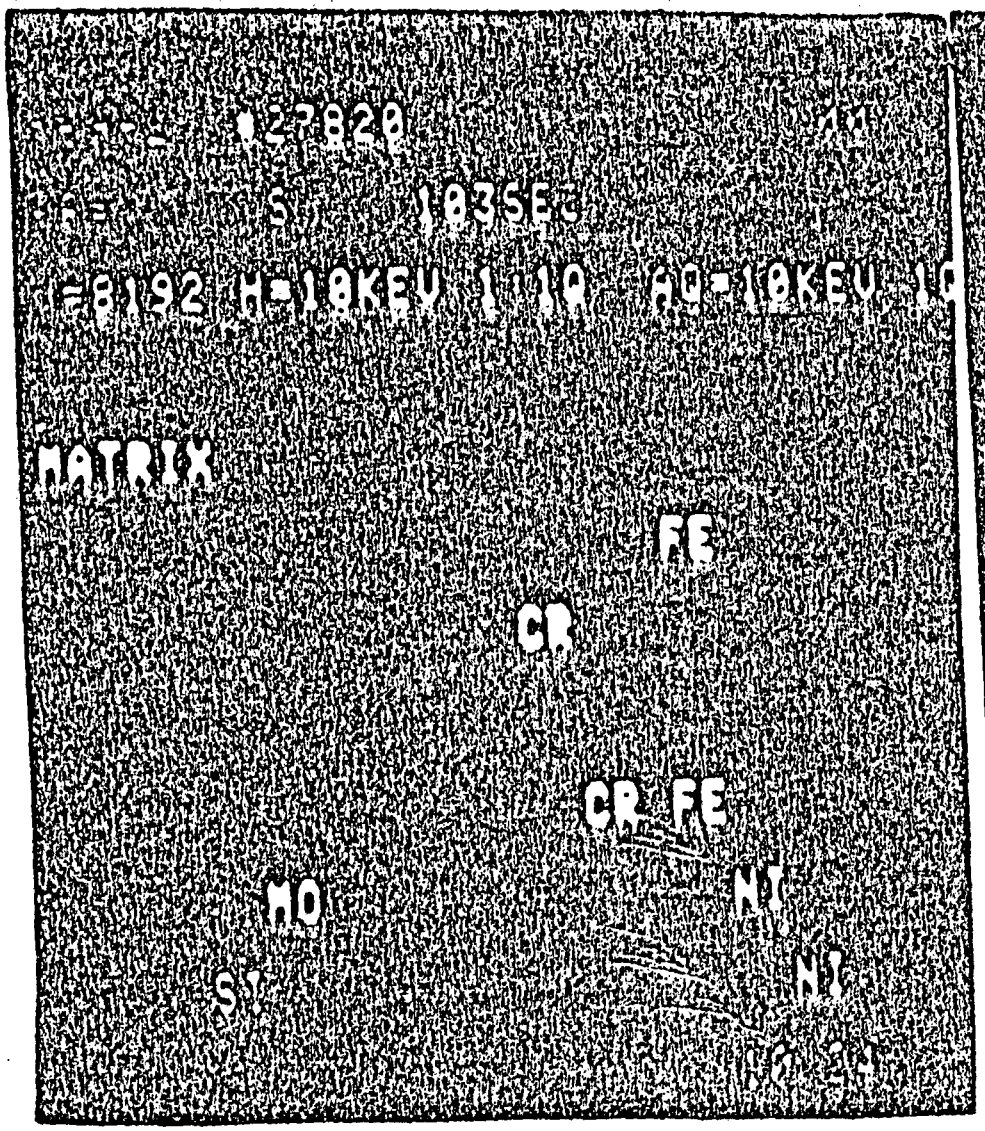

0.05M H_2SO_4 + 0.5M NaCl, deaer, 23°C
316LN
316LN(F)
Current density (μA/cm²)
10,000
1,000
100
10
1

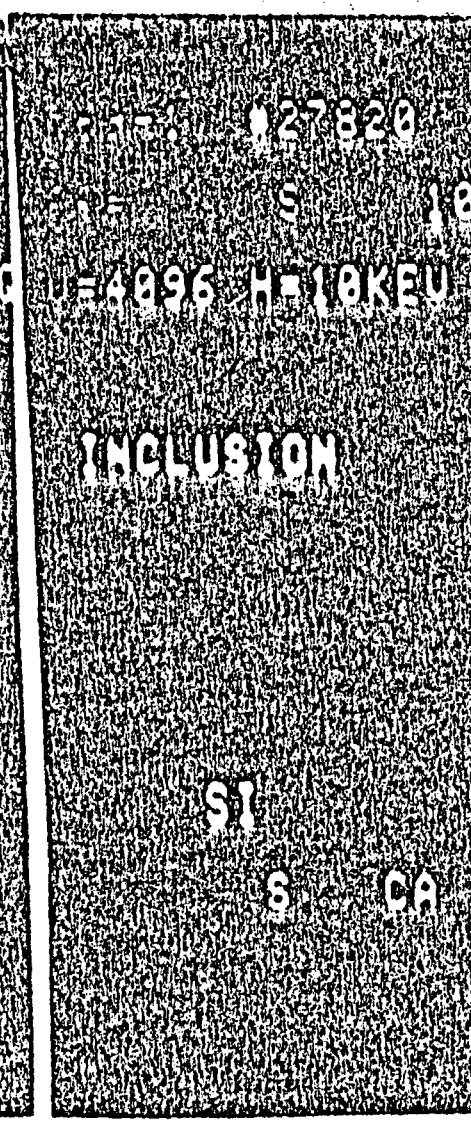
TABLE 1. Analyses of Alloys Used

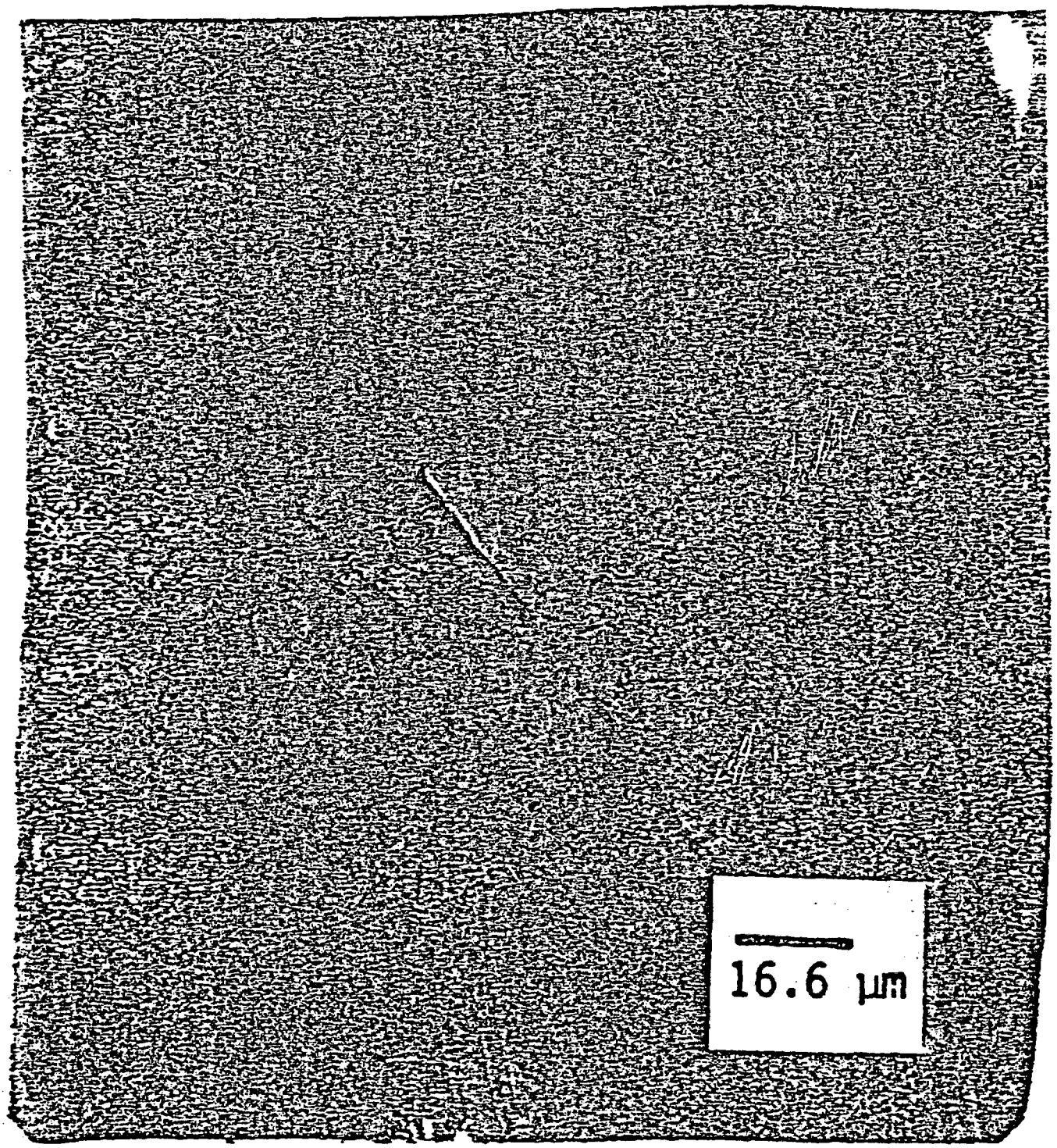
	Elements											
Alloy	C	Mn	P	S	Si	Co	Cu	Ni	Cr	Mo	N	OTHE
316L (MU)	0.02	1.71	0.033	0.014	0.56	0.10	0.28	10.29	16.51	2.07	0.05	bal
316LN	0.02	1.66	0.030	0.006	0.55	0.19	0.29	10.60	16.70	2.15	0.11	bal
316LN (F)	0.02	1.61	0.028	0.003	0.50	-------	0.24	11.40	17.60	2.80	0.11	bal


316L
50 μm

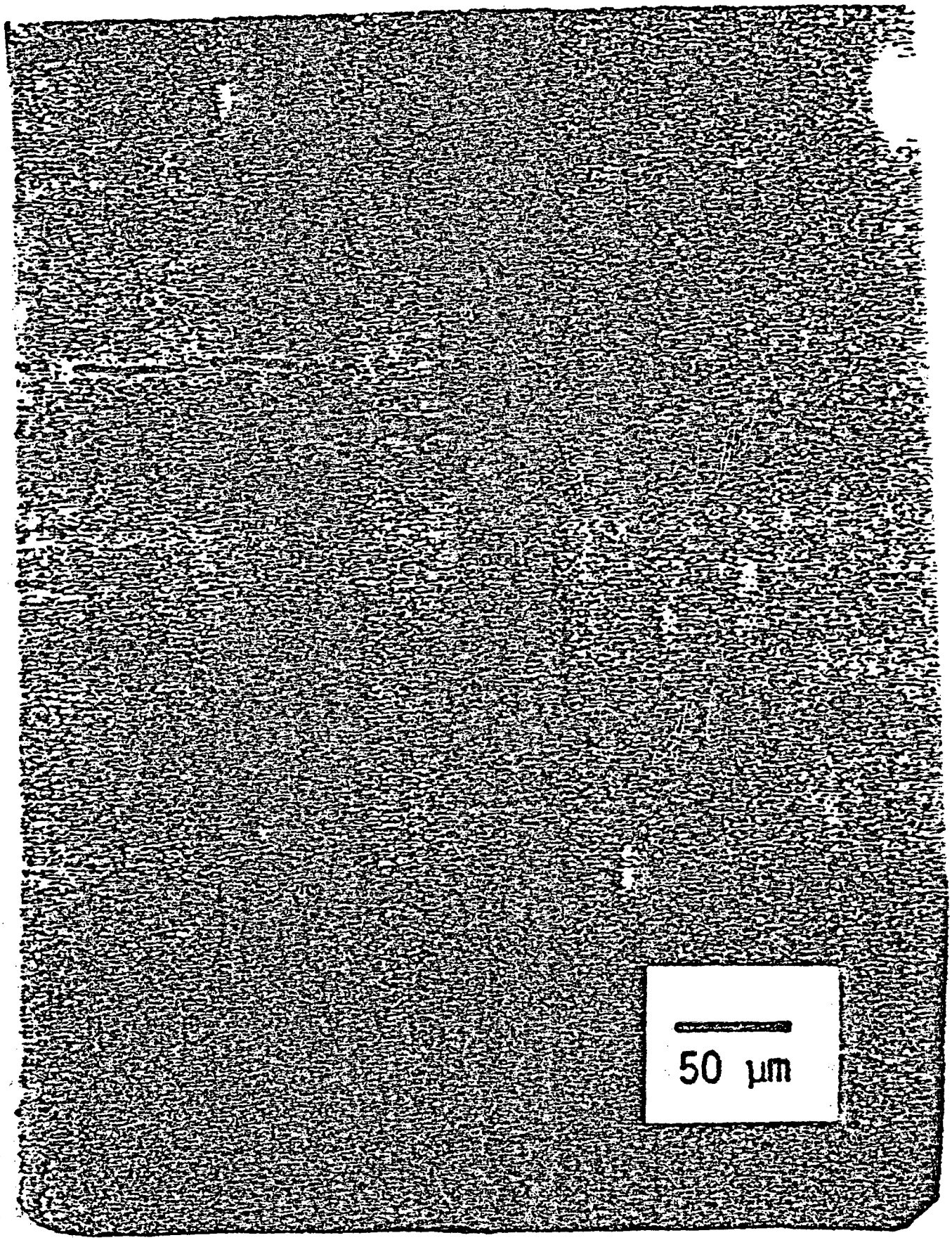

316LN(F)
50 μm


MATRIX
FE
CR
CR FE
MO
NI
S
NI


INCLUSION
SI
S
CA



310LN-INCLUSION PITTING

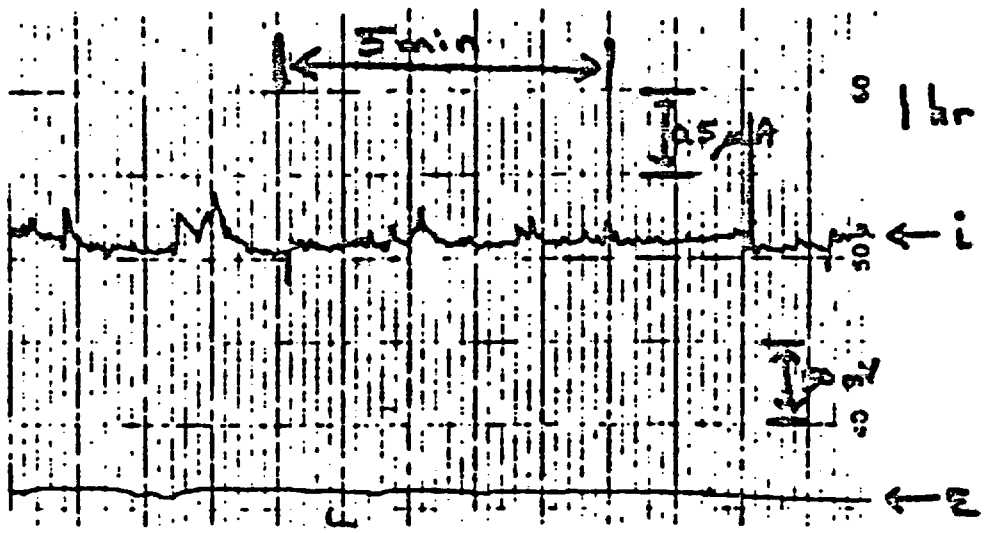


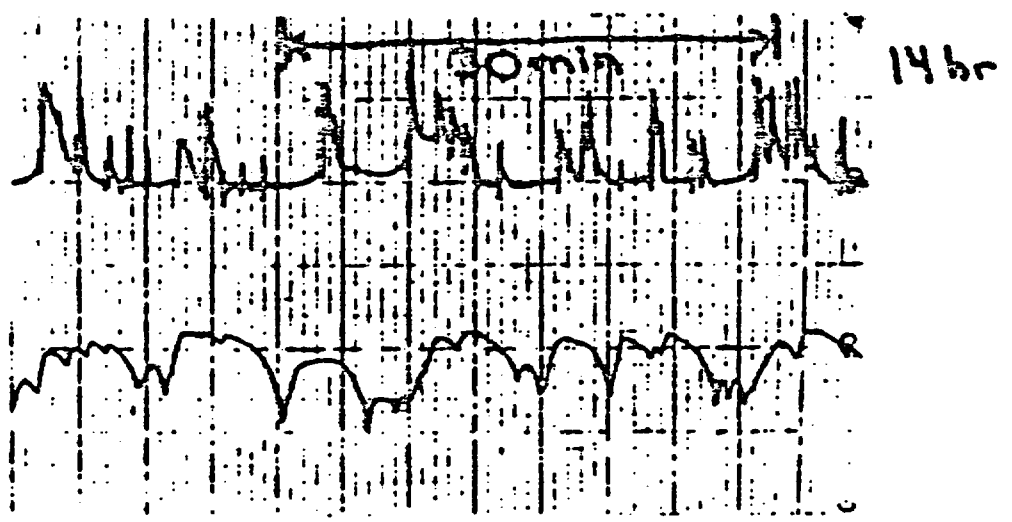
316LN(F)-FERRITE ETCH

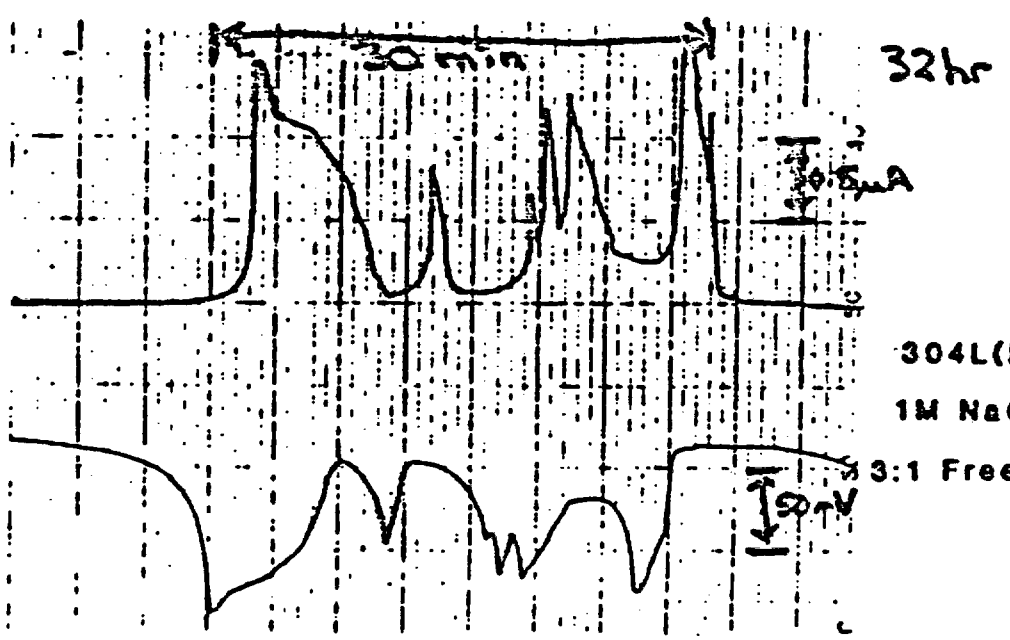
Boiled Coupon (Teflon Spacer) Crevice

Corrosion Tests in 10,000 mg/l Cl^- at 35°C, 54 days

Alloy	Sample	% rel. wt. loss	% area attacked
304L	1	0.0157	7.4
	2	0.0137	7.2
	3	0.0131	8.6
	ave.	0.0142	7.7
304LN	1	0.0047	2.1
	2	0.0078	5.1
	3	0.0054	3.5
	ave.	0.0059	3.5
316L	1	0.0076	1.2
	2	0.0060	2.1
	3	0.0041	0.6
	ave.	0.0059	1.3
316LN	1	0.0105	2.5
	2	0.0098	3.5
	3	0.0103	4.7
	ave.	0.0102	3.6



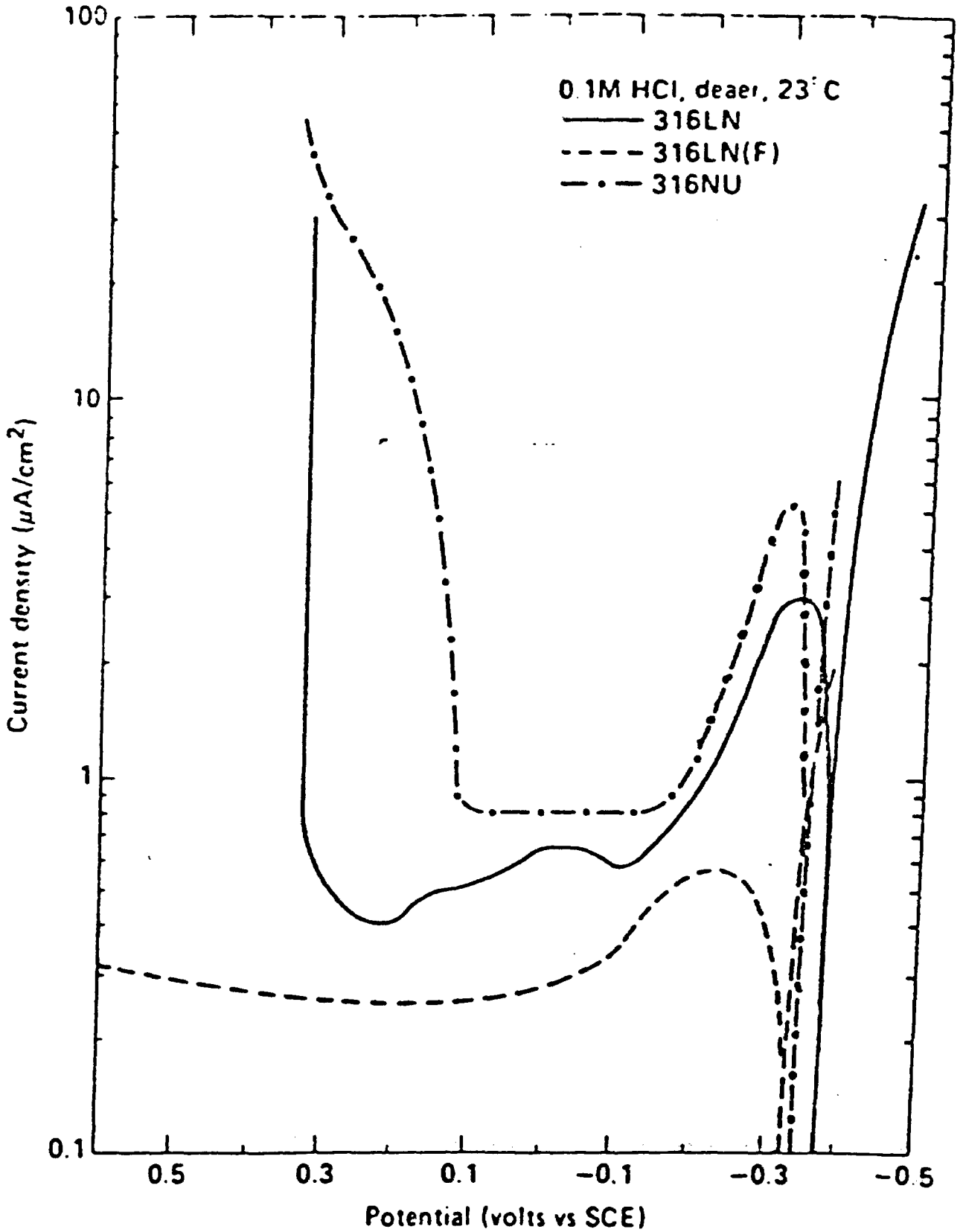


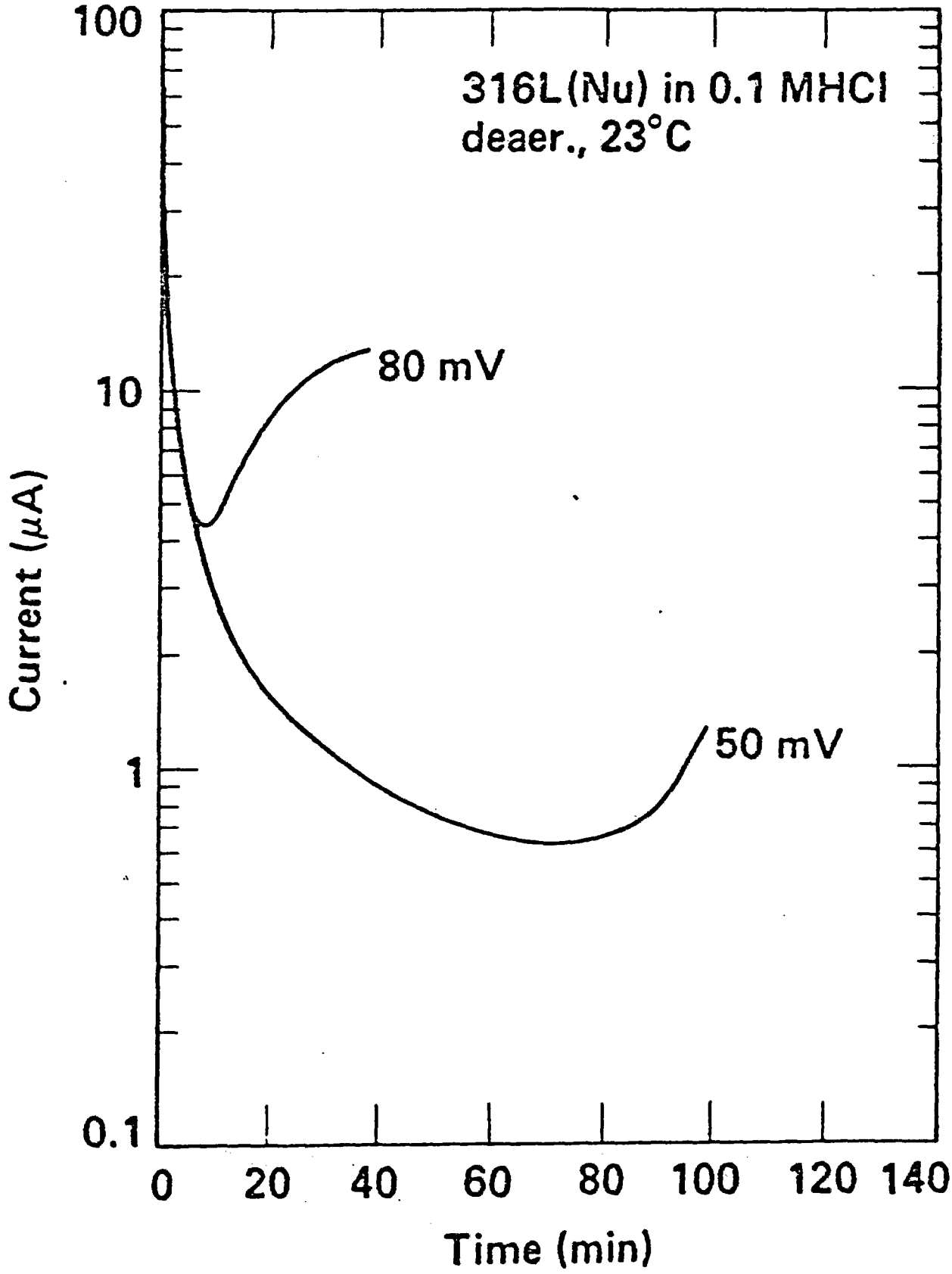


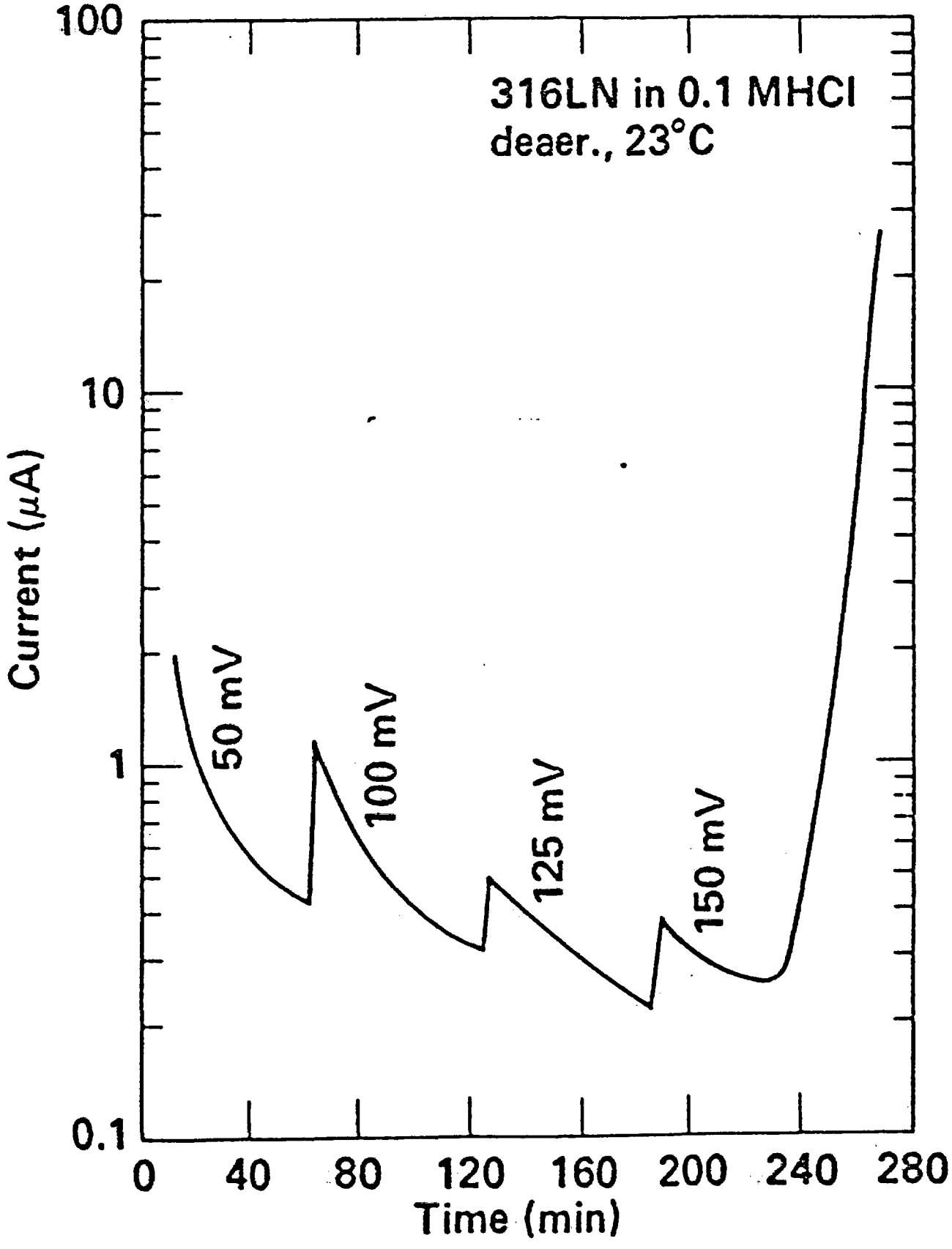
304L(NU)/ZRA

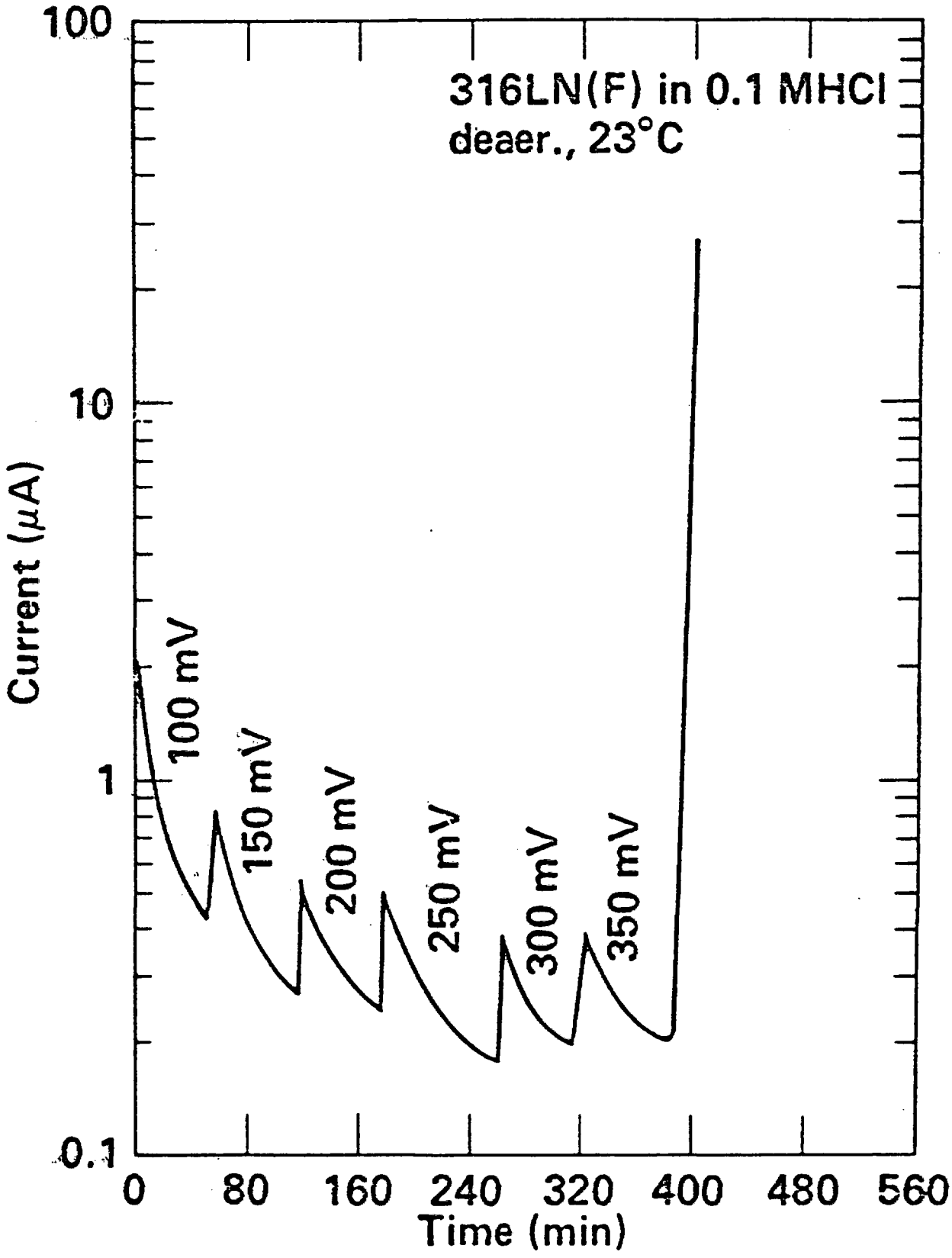
1M NaCl, pH 4, 50C

3:1 Free-to-Crevice Ratio


0.1M HCl, deaer, 23°C
316LN
316LN(F)
316NU
100
10
1
0.1
Current density (μA/cm²)
0.5
0.3
0.1
−0.1
−0.3
−0.5
Potential (volts vs SCE)

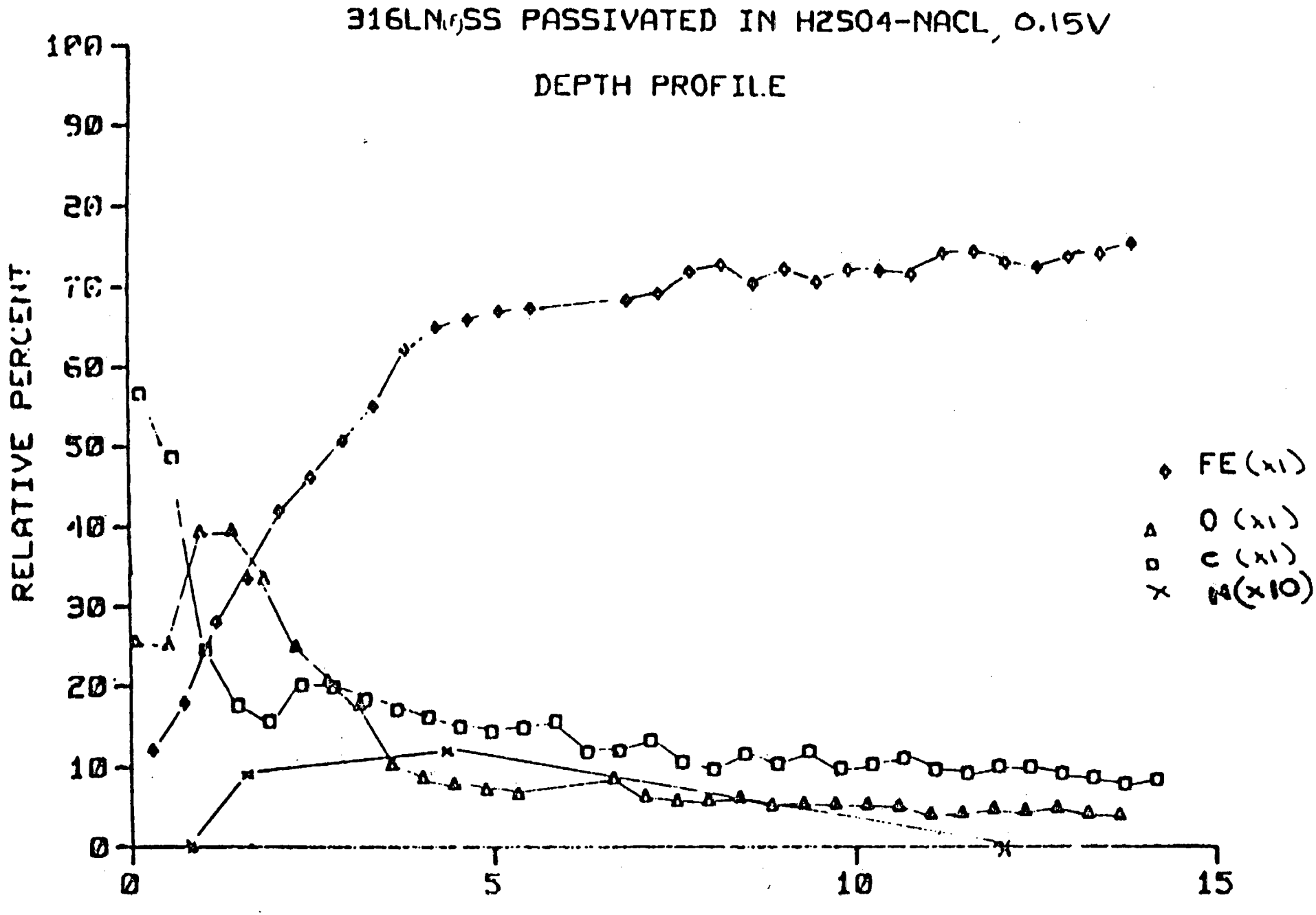

316L(Nu) in 0.1 MHCl
deaer., 23°C
80 mV
50 mV
100
10
1
0.1
Current (μA)
0
20
40
60
80
100
120
140
Time (min)


316LN in 0.1 MHCl
deaer., 23°C
100
10
1
0.1
Current (μA)
50 mV
100 mV
125 mV
150 mV
0
40
80
120
160
200
240
280
Time (min)


316LN(F) in 0.1 MHCl
deaer., 23°C
100
10
1
0.1
Current (μA)
100 mV
150 mV
200 mV
250 mV
300 mV
350 mV
0
80
160
240
320
400
480
560
Time (min)

Critical Potentials for Crevice Corrosion in 0.1M H

Alloy	E_{crit} (mV vs. SCE
304L	-20 to 0
304LN	20 to 40
316L(NU)	50 to 80
316LN	125 to 150
316LN(F)	300 to 350



Corrected 25A/MIN

Conclusions:

1. Differences in localized corrosion resistance exist between L and LN steels

   Generally, 316LN(F) > 316LN > 316L > 304LN $\gtrless$ 304L
   a. Increased nitrogen
   b. Small variations in other alloying constituents
   c. "Cleanliness"

2. With regard to the enhancement of corrosion resistance, 316LN appears to show a more marked improvement with respect to 316L than (relatively) 304LN does with respect to 304L. Synergism between Mo and N?

3. Not all commercial 316LN stainless steels are created equal. "Small" increase in N, Ni, Mo and Cr coupled with fewer inclusions leads to dramatic improvement.

Future Work

1. Continue γ radiation studies -

    a. Higher temperature electrochem
    b. Crevice effects
    c. Ex-situ modeling-stressed samples with impressed potential; SRI
    d. Long-term exposure testing - LLNL, HEDL, Univ. Minn.

2. Localized corrosion - both copper and alloys, and stainless steels - effect of minor variations in alloying constituents; "cleanliness"

3. AC impedance studies in thin films - LLNL, Univ. Minn.

N.N.W.S.I.

"SCC and other metallurgical concerns with austenitic stainless steels"

Mary C. Juhas

June 1985

WHAT ABOUT PHASE STABILITY?

- LOW TEMPERATURE SENSITIZATION (LTS)
- SIGMA PHASE
- EFFECTS OF COLD WORK

WHAT CAUSES THESE MICROSTRUCTURAL CHANGES?

WE MUST SEPARATE MICROSTRUCTURAL CHANGES INTO...

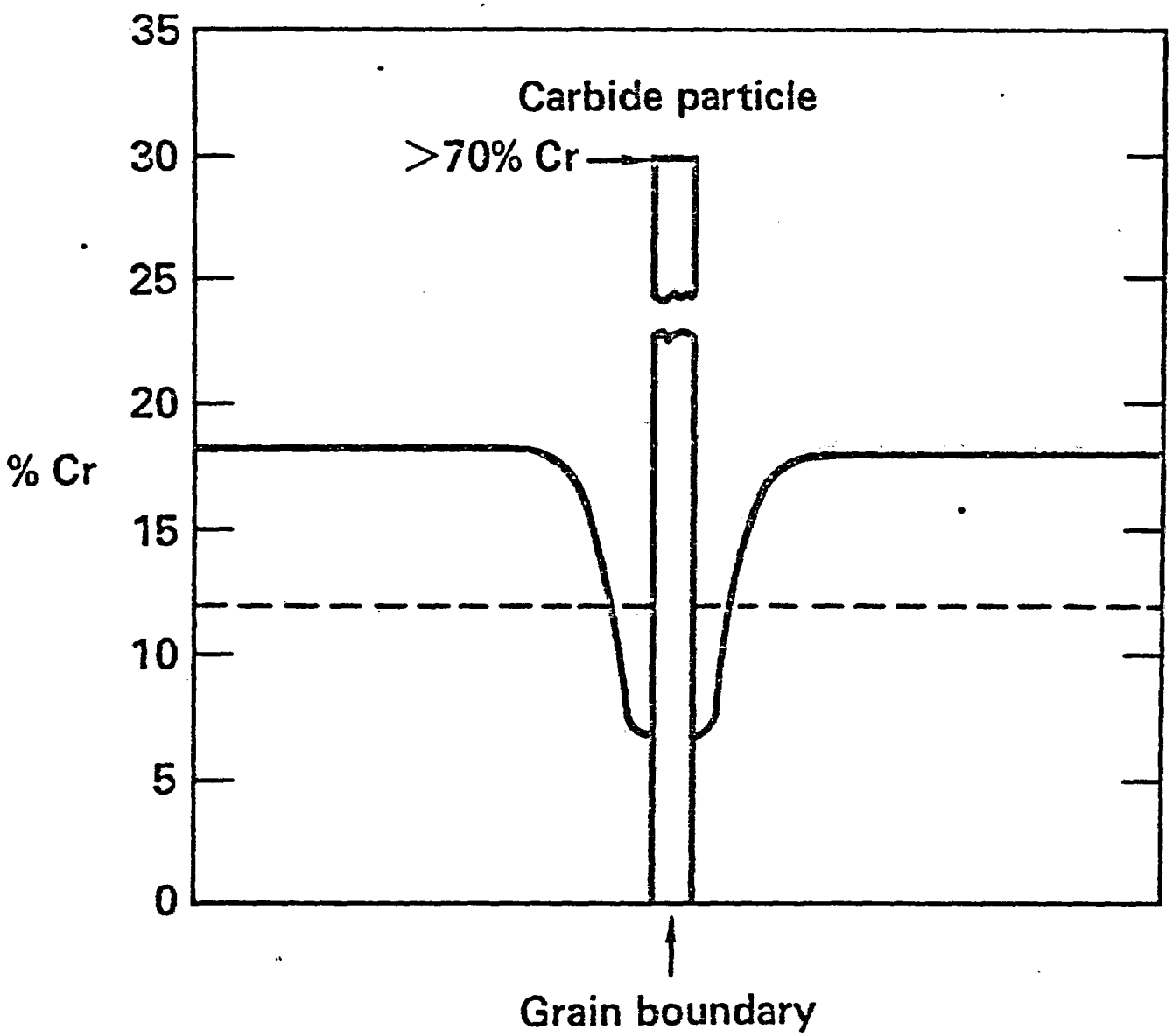
- o LONGTERM
- o SHORTERM

...AND ADDRESS THE QUESTIONS,

HOW DO WE TEST FOR THESE CHANGES IN THE LABORATORY?

CAN SOME PROCESSES BE ACCELERATED?

WHAT IS THE SMALLEST DETECTABLE MICROSTRUCTURAL FEATURE THAT WOULD ALERT US OF THE ONSET OF SCC?

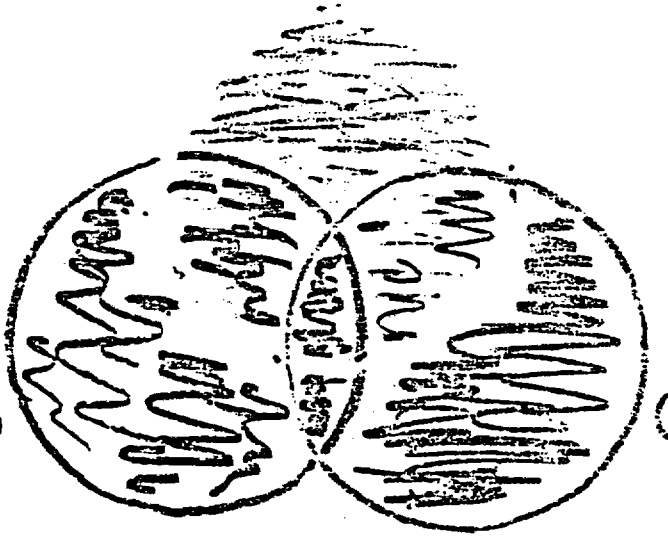


Schematic section through the boundary of two austenite grains of an 18-8 stainless steel. A carbide particle $(CrFe)_{23}C_6$ is precipitated at the boundary.

SEVERE ENVIRONMENTAL CONDITIONS AND A HIGHLY SUSCEPTIBLE MICROSTRUCTURE ARE IMPOSED INITIALLY TO ASSESS MATERIAL RESPONSE.

J-13 WATER/STEAM
CRUSHED TUFF
GAMMA RADIATION

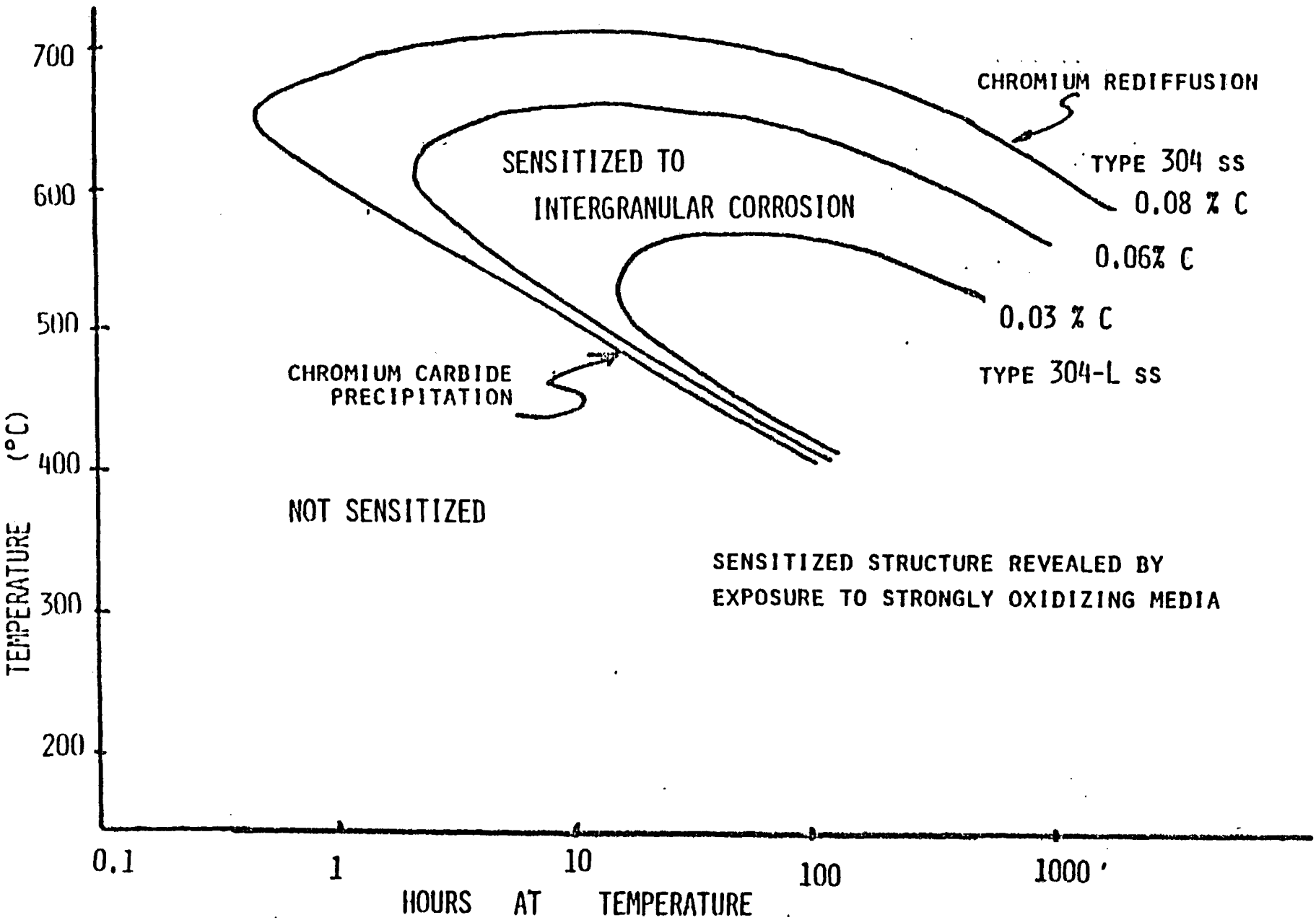
SENSITIZED



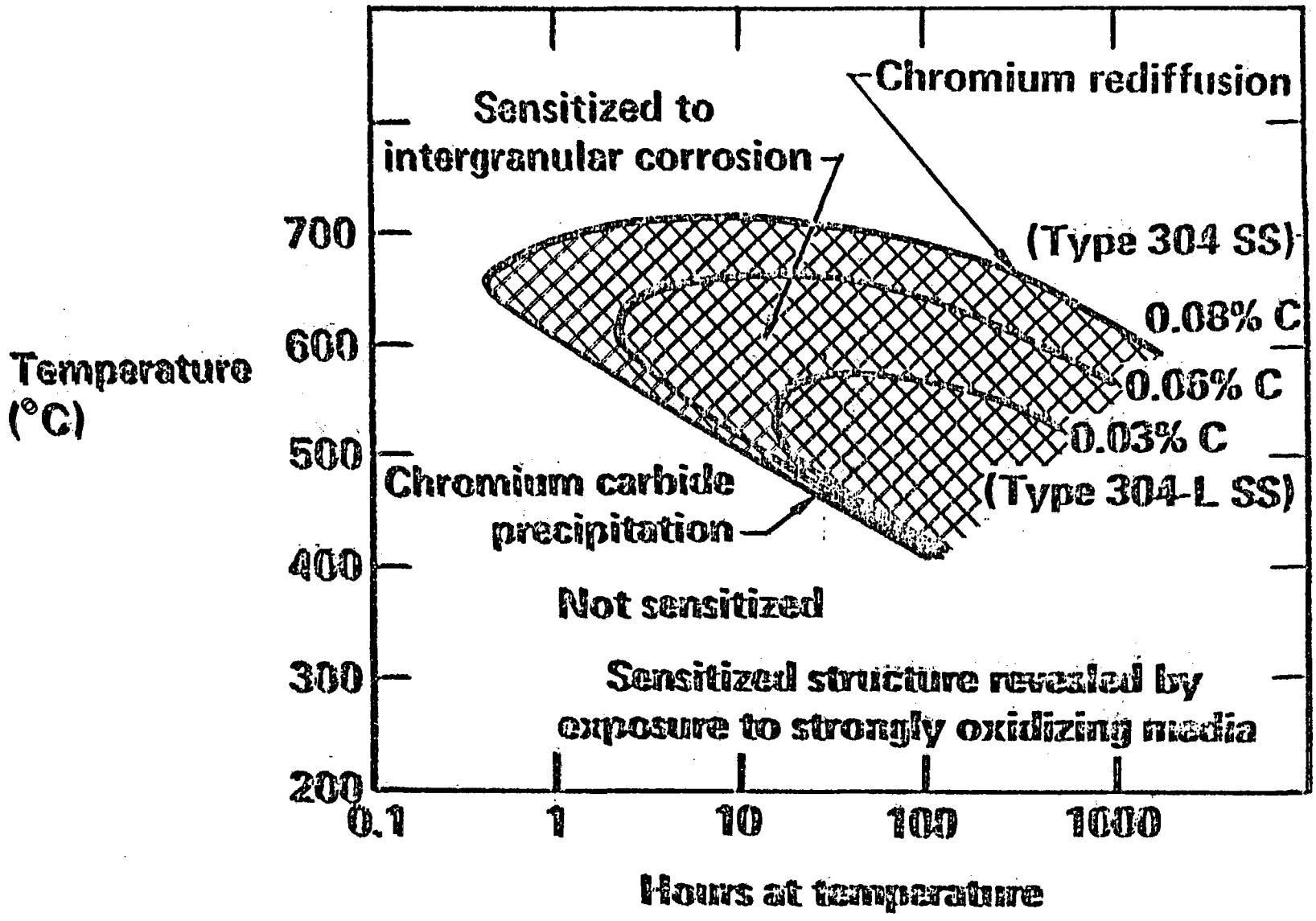
WELDED

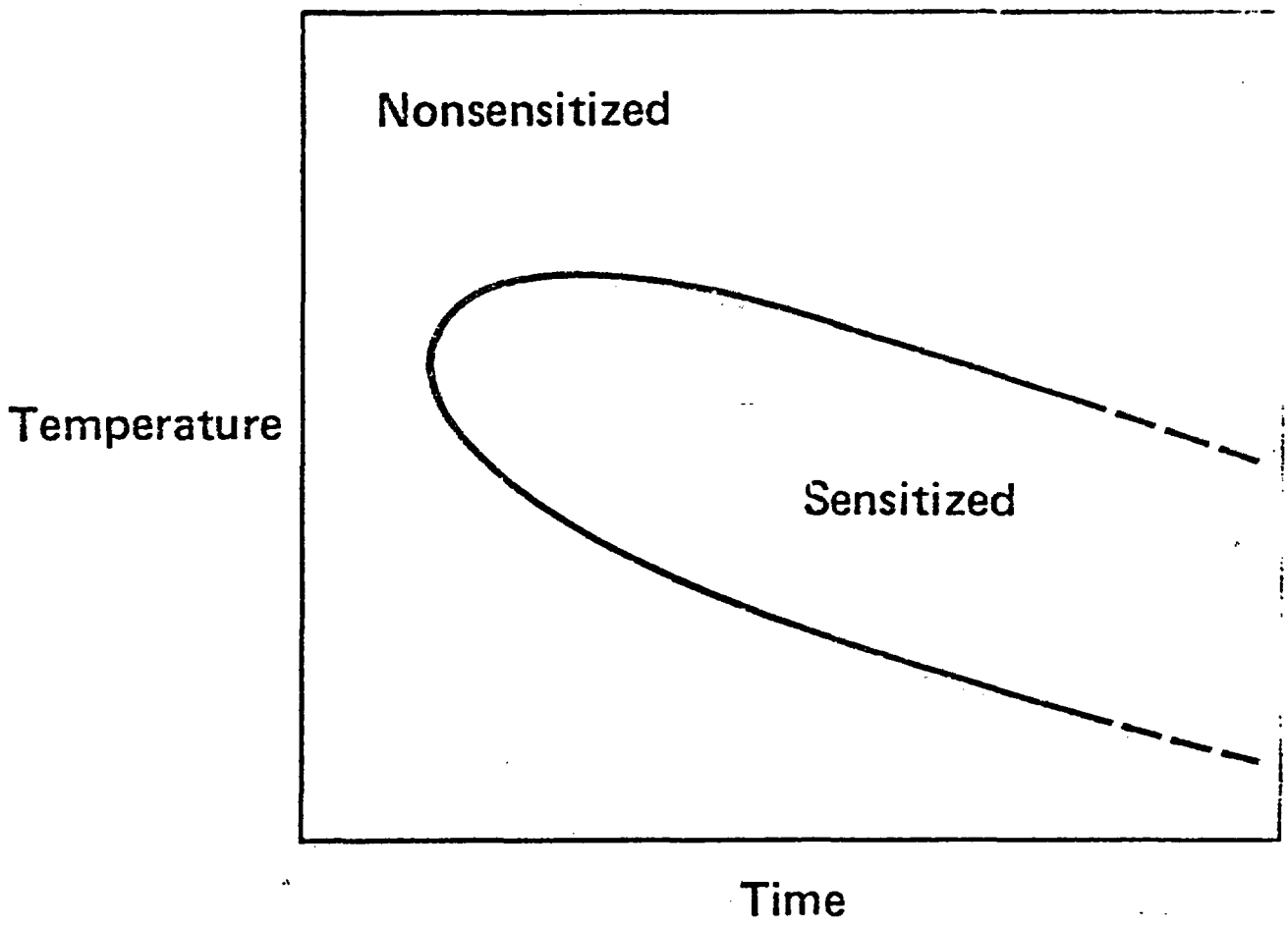
COLD-WORKED

TIME - TEMPERATURE - SENSITIZATION CURVES INDICATE CHROMIUM CARBIDE FORMATION

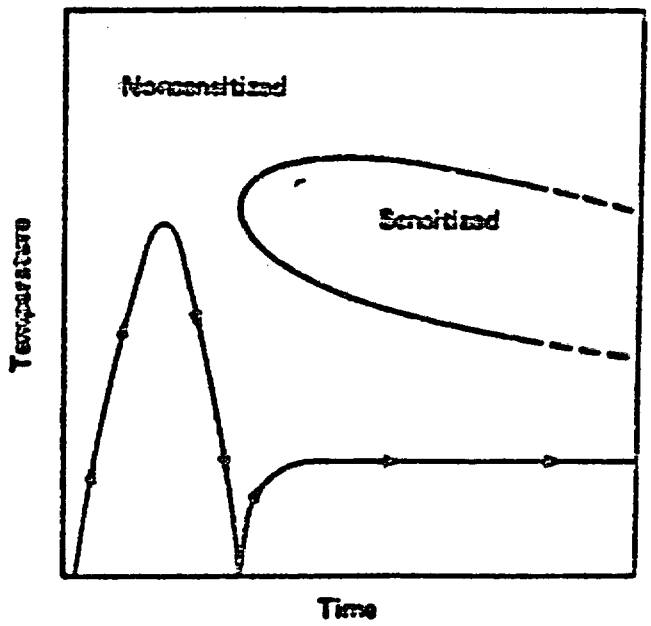


Time—temperature—sensitization curves indicate chromium carbide formation



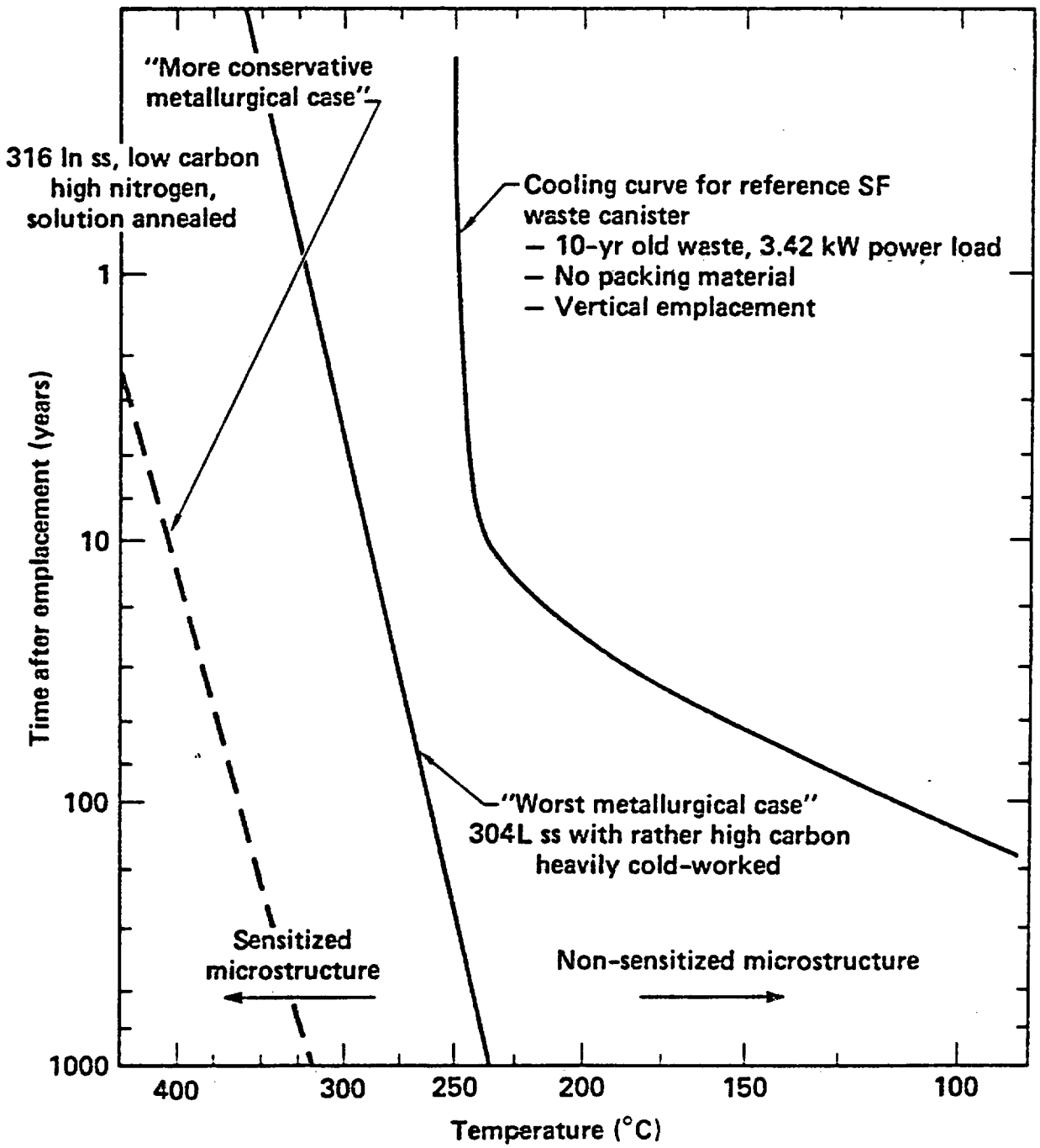


Schematic time, temperature, sensitization (TTS) diagram

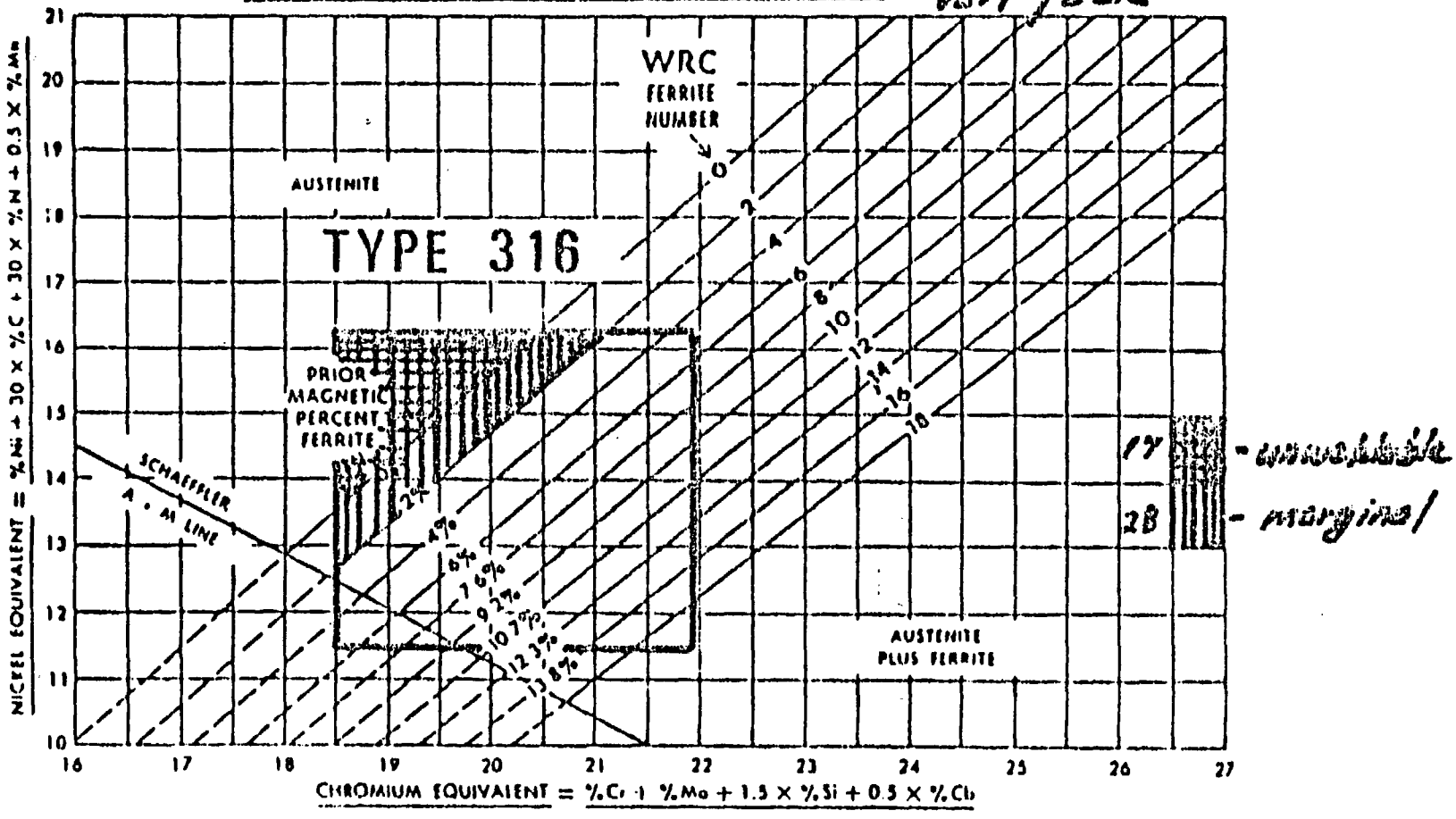


Low temperature sensitization (LTS) occurs when carbides are nucleated by a brief high temperature exposure followed by holding at temperatures below the TTS curve

Analysis of canister thermal history and long-term sensitization in stainless steel indicates that canister will not sensitize



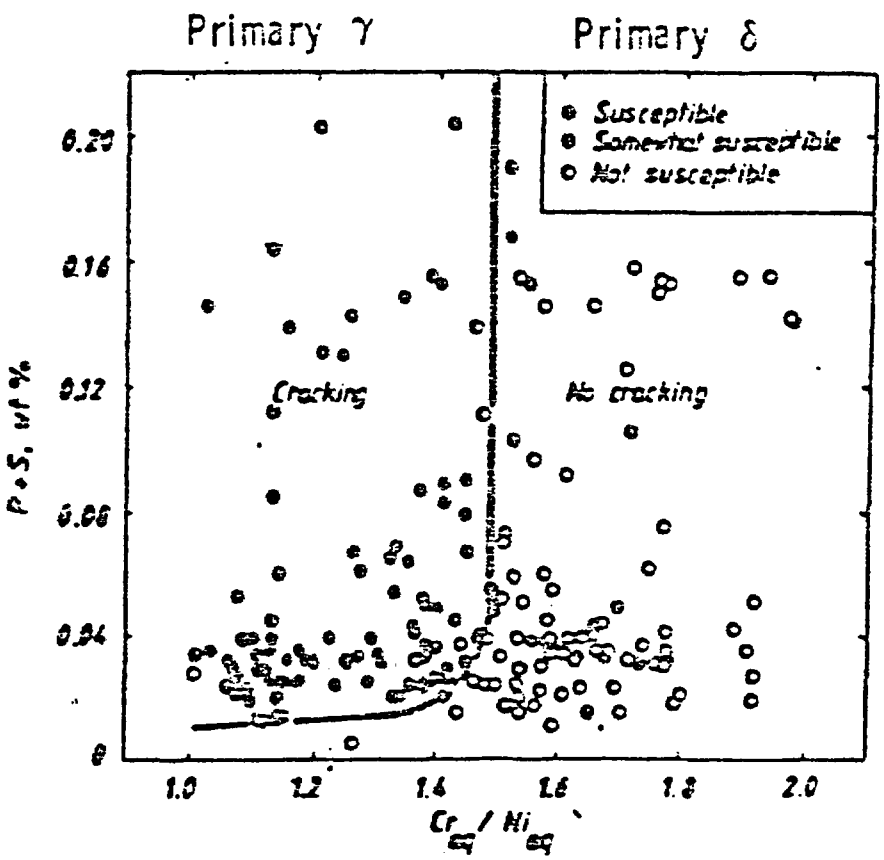
CONSTITUTION DIAGRAM FOR STAINLESS STEEL WELD METAL



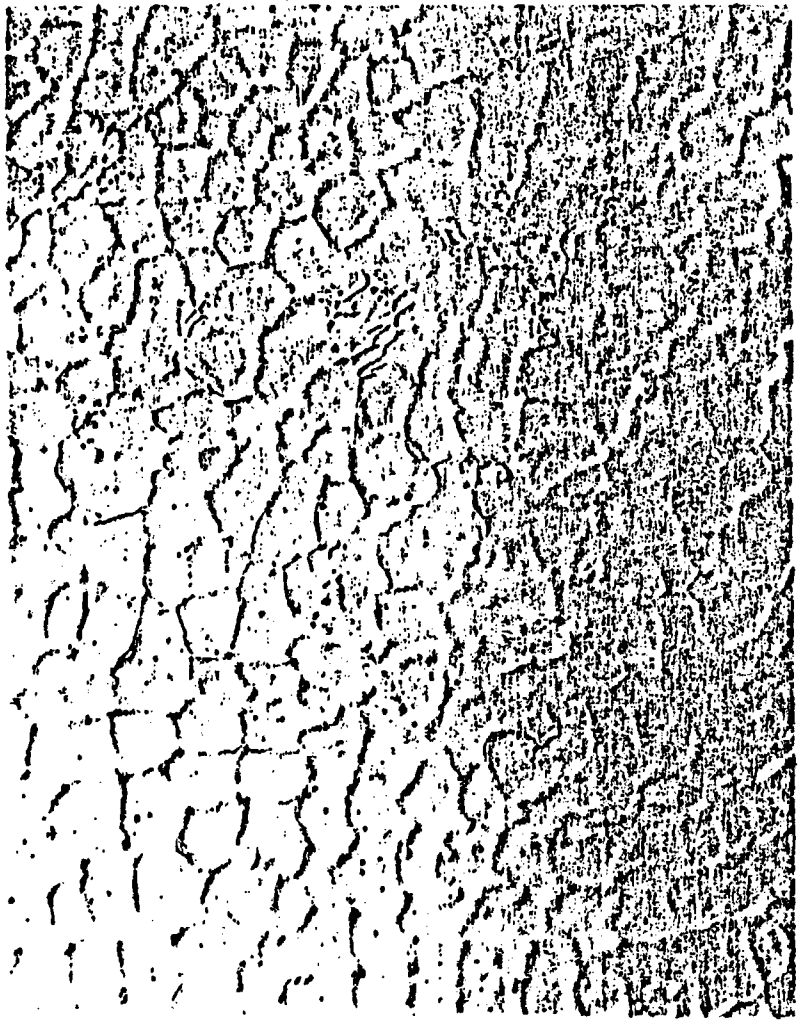
Cr	Ni	Mo	Mn	Si	N	C	P
16.0-18.0	10.0-14.0	2.0-3.0	1.5-2.0	0.3-0.7	0.110 max	0.015-.030	.045 max.

S
.006 max

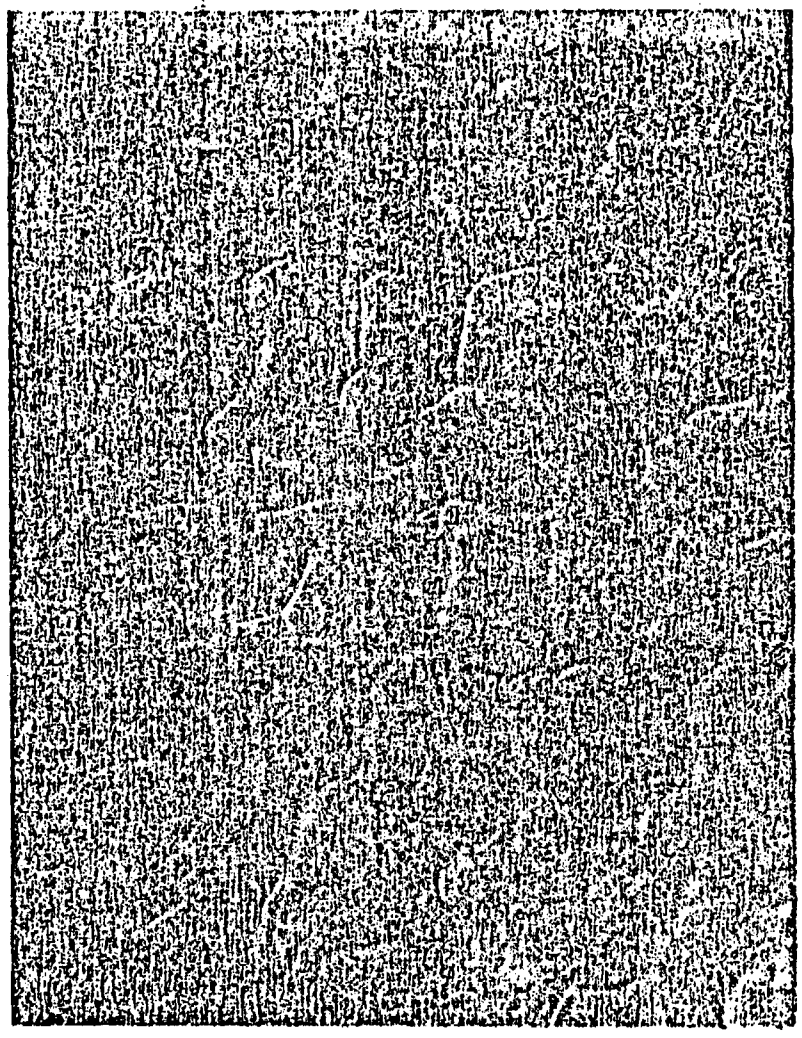
Cracking Susceptibility of Austenitic Stainless Steels



E316L-15 WITH CONTROLLED FERRITE



20 μ



10 μ

Note δ-ferrite at cell boundaries

SCC tests now underway:

- BOIL DOWN

  Periodic wet/dry environment to concentrate ionic species on specimen surface.

- BENT BEAM

  Used as a screening device to detect relative susceptibility to SCC.

- SSR - SLOW STRAIN RATE

  Determines amount of environmental degradation induced by the testing conditions.

- U-BEND

  Used to augment the effects of localized deformation and stress on a sensitized microstructure.

- SLOW CRACK GROWTH

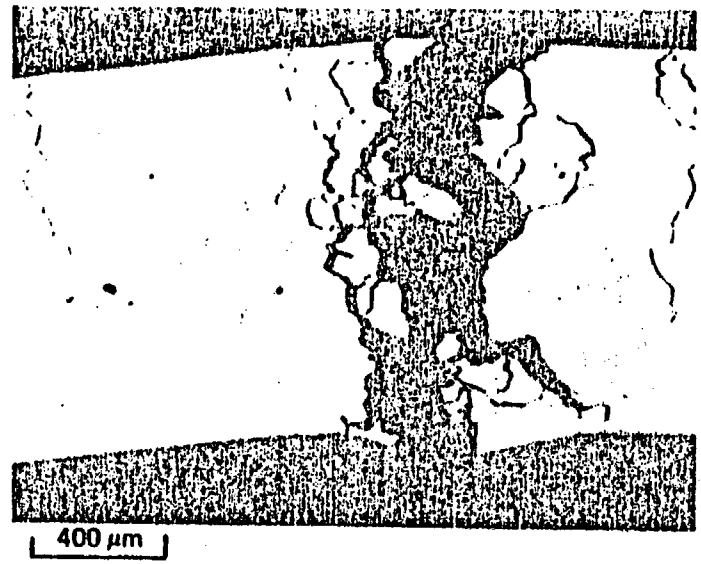
  Predicts crack growth rate at fixed stress levels.

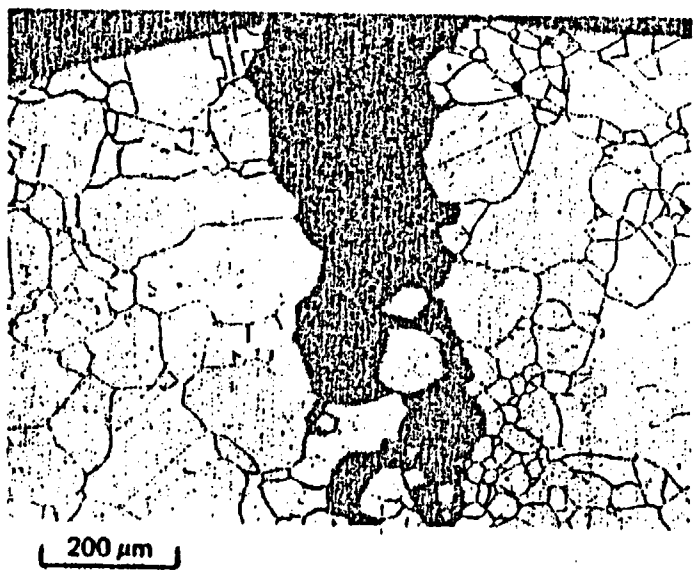
Stress Corrosion Cracking Test Results from U-Bend Specimens Exposed to Irradiated J-13 Water, Crushed Tuff Rock, and Water Vapor.

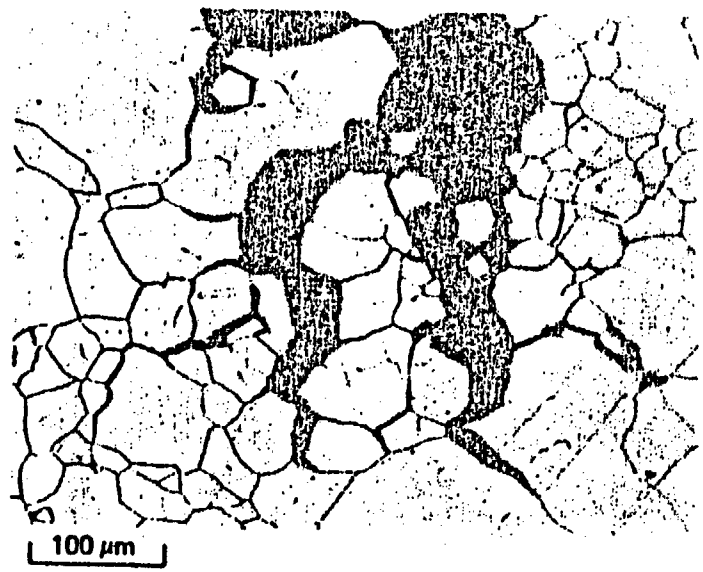
No. of Specimens Cracked/No. of Specimens Tested

Material	Environment					
	50°C (6×10^5 rads/hr)			90°C (3×10^5 rads/hr)		
	Rock + Water	Rock + Vapor	Vapor	Rock + Water	Rock + Vapor	Vapor
304	0/4	0/4	2/4	0/4	3/4	1/4
304L	0/4	0/4	0/4	0/4	0/4	0/4

304 U-BEND SPECIMENS
SOL'N ANNEALED (15 MIN. @ 1050°C)
AND SENSITIZED (24 HRS @ 600°C)
TESTED IN J-13 WATER AND CRUSHED
TOPOPAH SPRING TUFF ROCK AT
50°C, 6 x 10^5 RAD/HR.







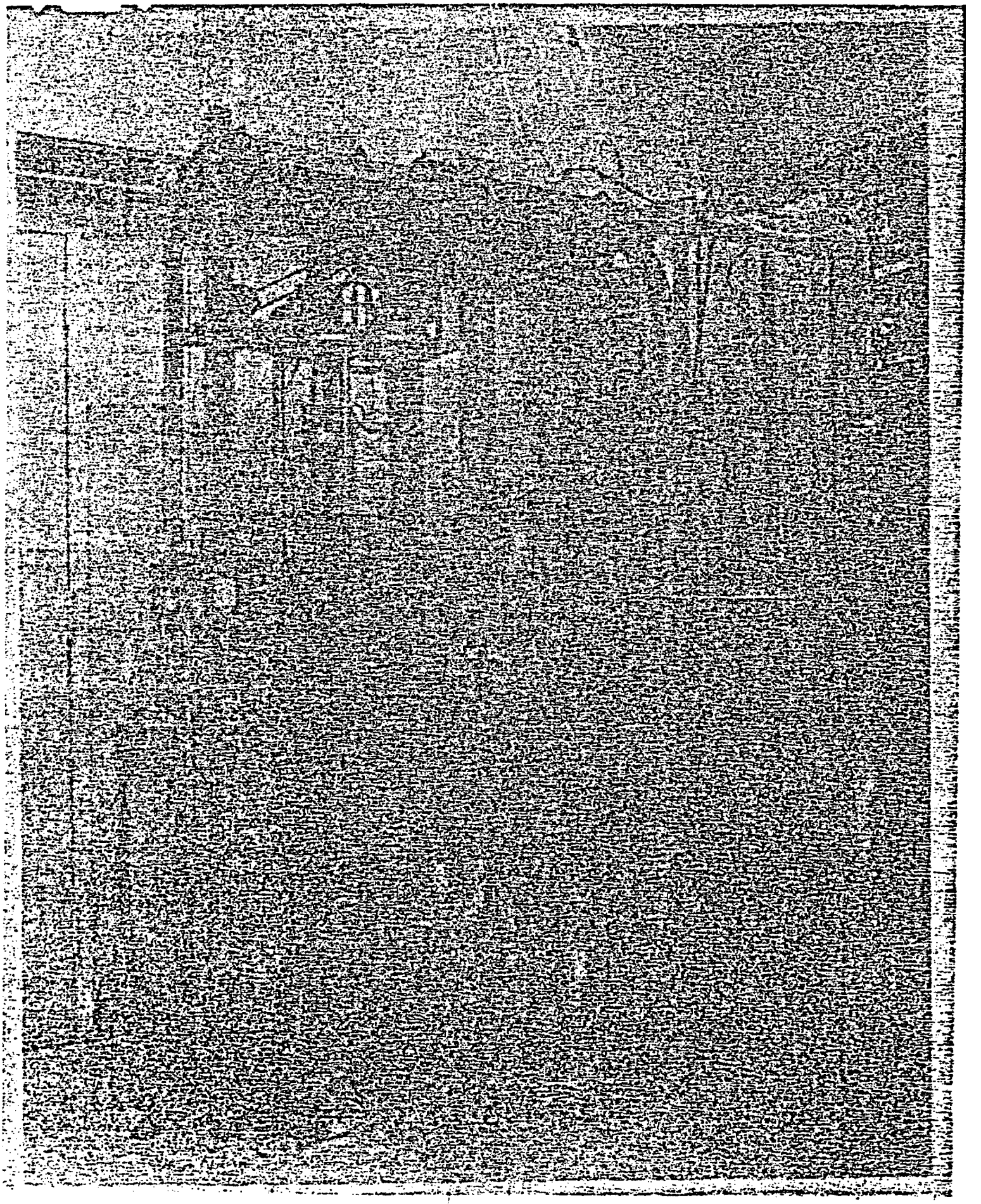


TABLE 3. Compositions of Steel Plate Used in SSR Tests

304 STAINLESS STEEL

Alloy Element, percent

N	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Co
0.0480	0.054	1.44	0.019	0.009	0.39	18.07	8.20	--	--	--

YS: 47.3 ksi (326 MPa)
TS: 89.4 ksi (617 MPa)
El: 57.3%

304L STAINLESS STEEL

Alloy Element, percent

N	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Co
--	0.024	1.65	0.031	0.012	0.42	18.12	9.52	--	--	--

YS: 42.4 ksi (292 MPa)
TS: 81.1 ksi (559 MPa)
El: 58.5%

Results of Slow Strain Rate Tests of 304 Stainless Steel at 150°C

Mill Annealed Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi	FAILURE MODE
Air	10^{-4}/s	80.2	48.0	37.4	74.4	ductile
Air	2×10^{-7}/s	76.5	45.0	35.9	76.6	
J-13[1]	10^{-4}/s	77.9	47.0	36.1	75.3	
J-13	10^{-4}/s	79.6	46.0	36.3	74.9	
J-13	2×10^{-7}/s	75.7	50.0	33.5	77.5	
J-13	2×10^{-7}/s	76.4	47.0	35.1	77.0	

Solution Annealed and Sensitized Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi	
Air	10^{-4}/s	72.2	50.6	21.9	68.0	ductile
Air	10^{-4}/s	66.5	51.5	26.0	68.8	"
J-13	10^{-4}/s	75.5	53.5	23.5	68.8	"
J-13	10^{-4}/s	74.9	51.0	23.5	69.0	"
J-13	2×10^{-7}/s	50.9	-[2]	22.0	70.1	I.G.
J-13	2×10^{-7}/s	26.4	-[3]	20.7	64.5	I.G.

1 Air-sparged J-13 well water.
2 Not determined.
3 Broke at gage mark.

Results of Slow Strain Rate Tests of 304L Stainless Steel at 150°C

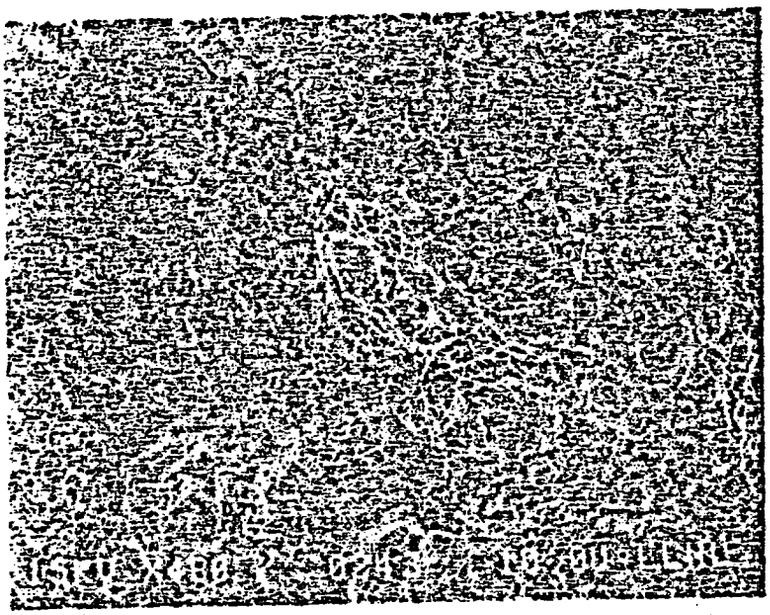
Solution Annealed Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi
J-13[1]	10^{-4}/s	80.5	54.0	25.8	68.4
J-13	10^{-4}/s	73.4	52.0	27.1	68.2
J-13	2×10^{-7}/s	68.7	48.0	28.4	67.7
J-13	2×10^{-7}/s	72.9	46.3	25.7	68.2

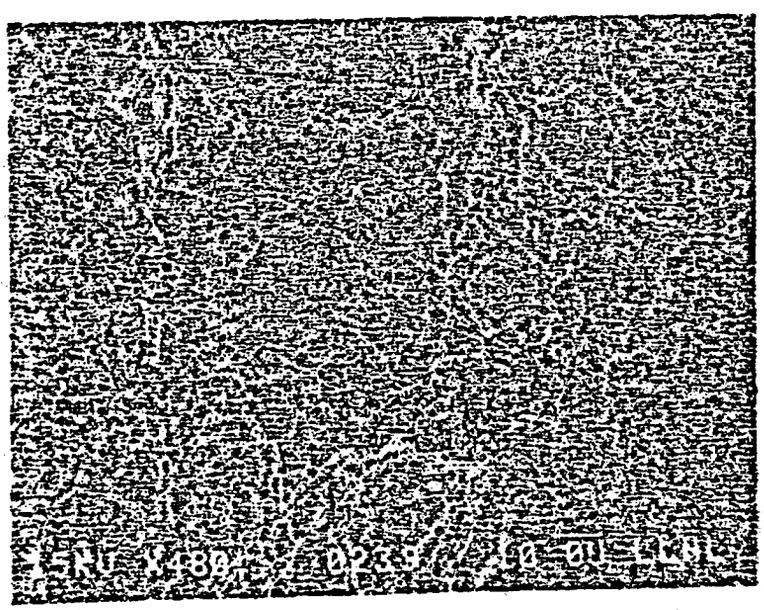
Solution Annealed and Sensitized Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi
Air	10^{-4}/s	73.7	49.0	29.4	68.6
J-13	10^{-4}/s	72.2	49.6	-[2]	-[2]
J-13	10^{-4}/s	74.8	51.6	29.6	69.1
J-13	2×10^{-7}/s	76.0	49.0	26.6	68.5
J-13	2×10^{-7}/s	70.4	48.0	27.2	68.8

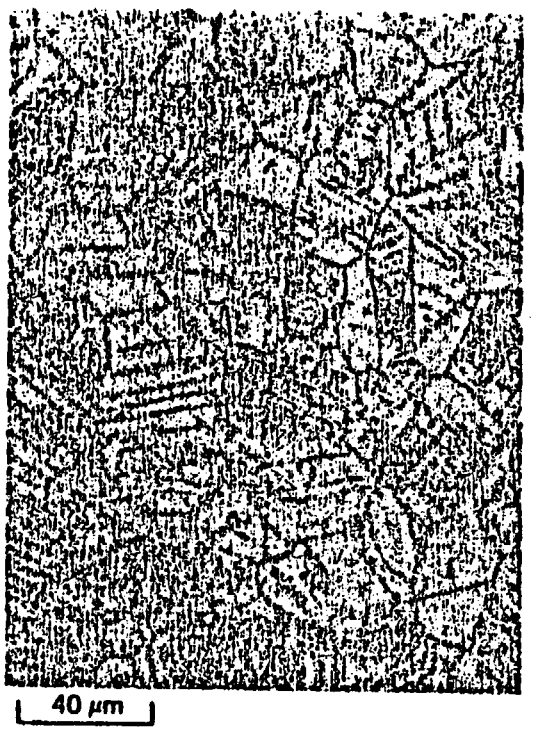
1 Air-sparged J-13 well water.
2 Not determined.



FRACTOGRAPH OF 304L SLOW STRAIN RATE SPECIMEN TESTED AT 150°C IN AIR.
STRAIN RATE = 1×10^{-4}/s. YS = 29.4 KSI UTS = 68.8 KSI ELONG = 49%

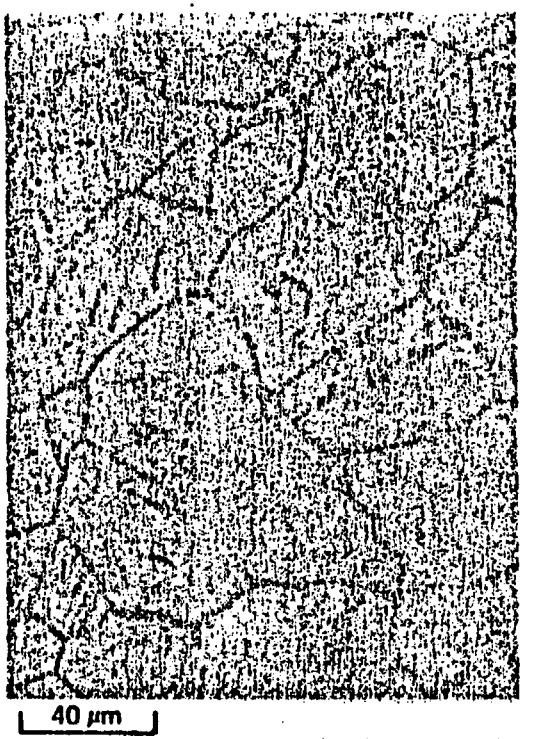


304L SLOW STRAIN RATE SPECIMEN TESTED AT 150°C IN J-13 WELL WATER.
YS = 29.6 KSI UTS = 69.1 KSI ELONG = 51.6%

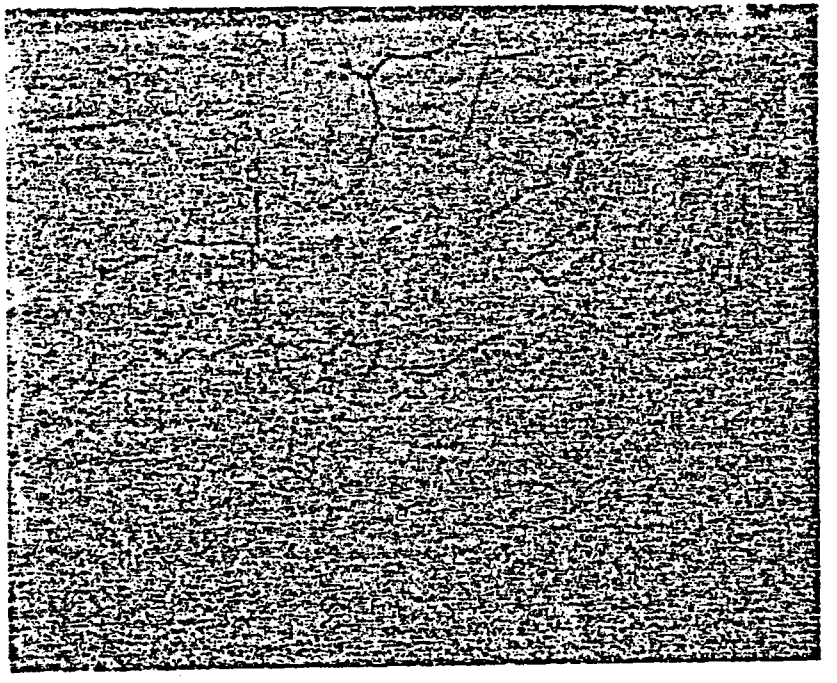


304: 20% COLD-WORKED
700°C FOR 1 WEEK

304L: 20% COLD-WORKED
700°C FOR 1 WEEK

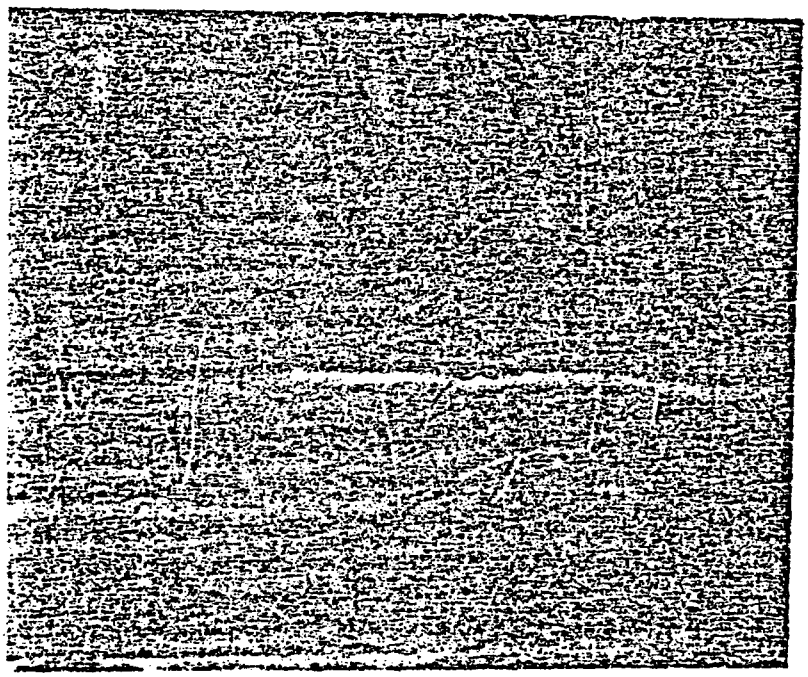


316L: 20% COLD-WORKED
700°C FOR 1 WEEK



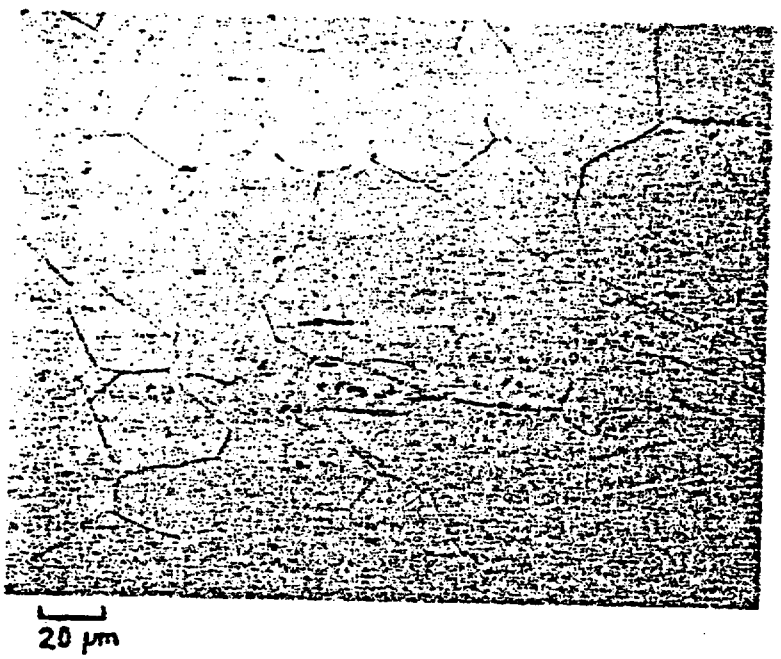
20 μm

316L 15 min @ 1000°C, AC / 1 day @ 250°C, WQ
(013A)

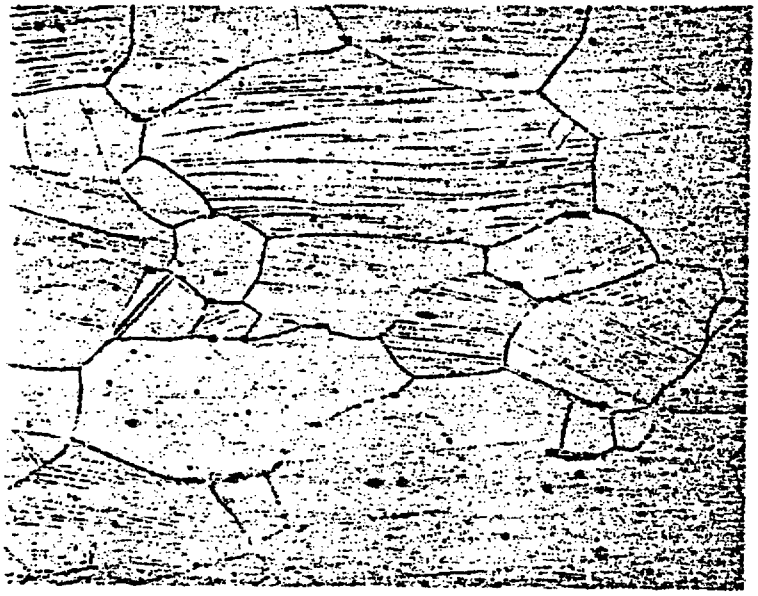


20μm

316L 20% CW / 15 min @ 1000°C, AC / 1 day @ 250°C, WQ
(016A)

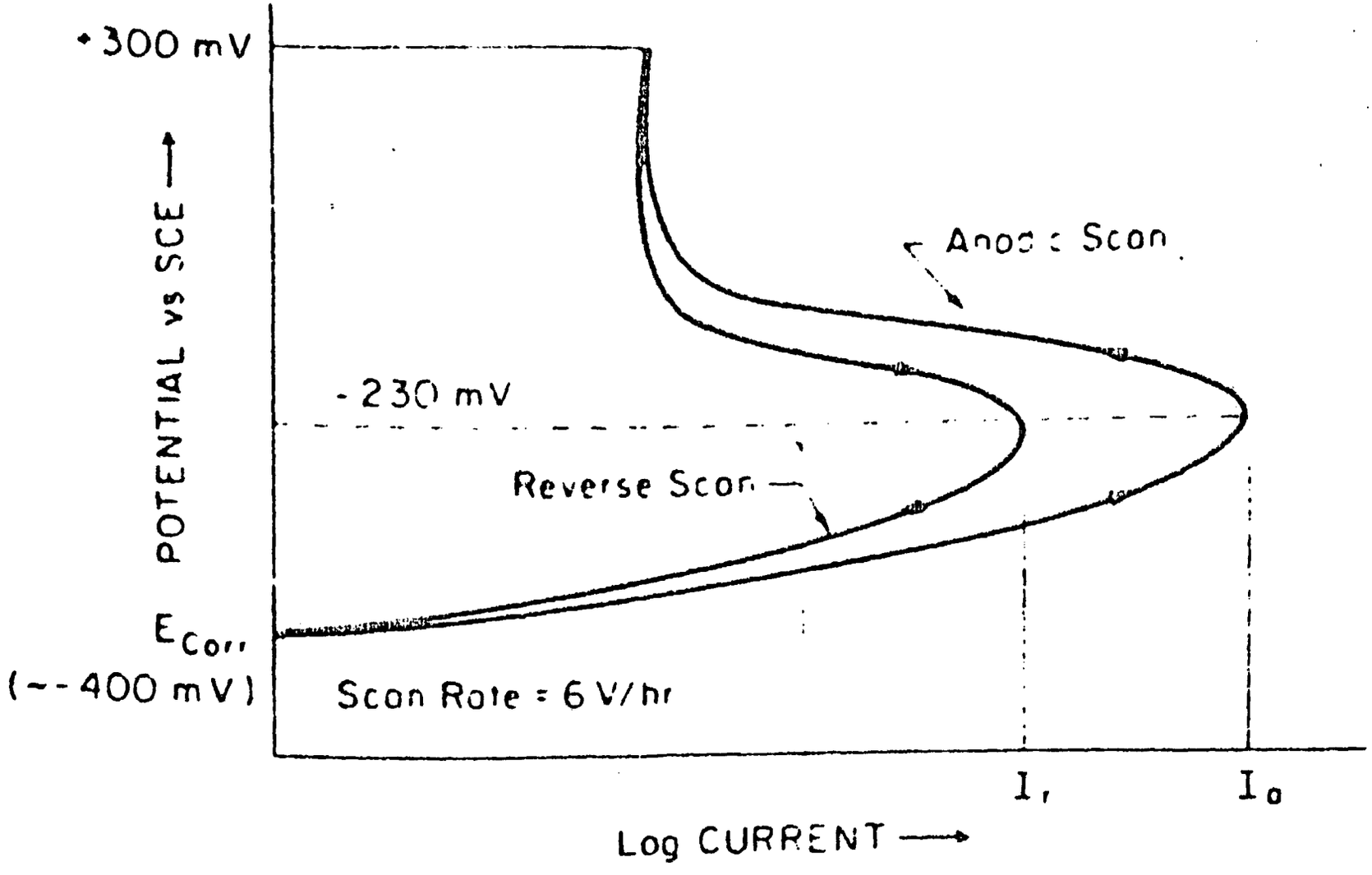


316L 15 min @ 1000°C, WQ / 1 wk @ 250°C, WQ
(007A)



20 μm

316L 20% CW/ 15 min @ 1000°C, WQ / 1 wk @ 250°C, WQ
(011A)



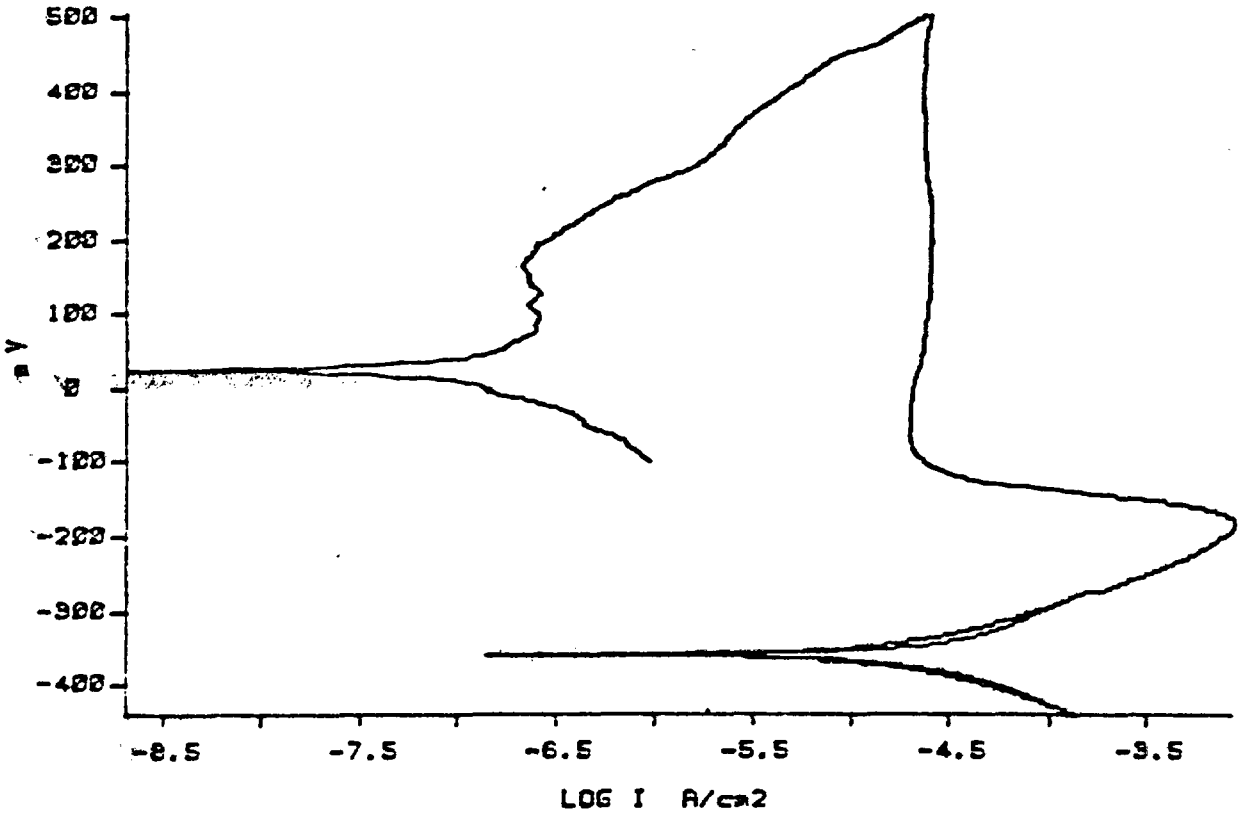
IHI-DOS RATIO TEST

Ratio = I_r / I_o

MODEL 351
CORROSION MEASUREMENT SYSTEM

001B
20 JUN 1985

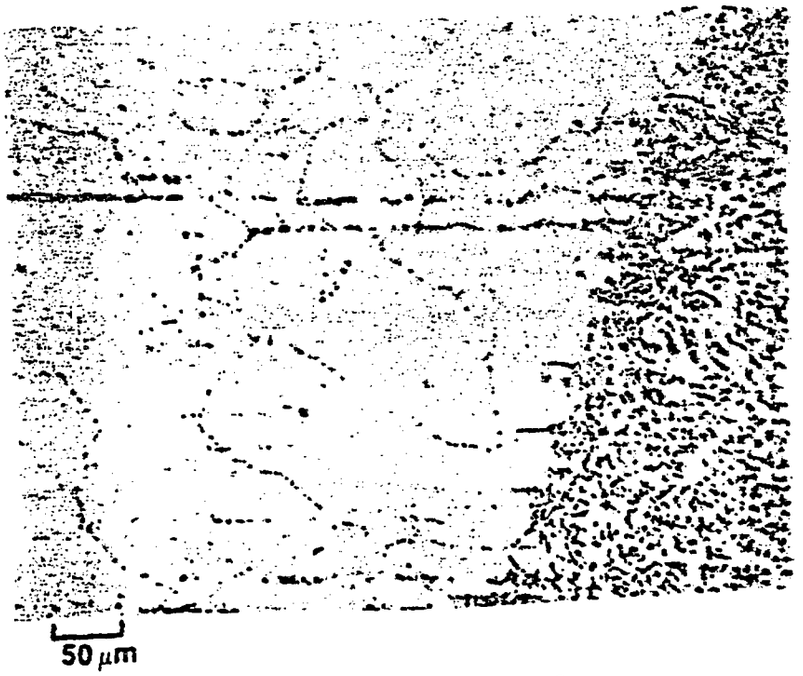
COMMENT:
316L 15MIN-1000C WQ 1DAY-250C WQ .5M H2SO4 .01M KSCN



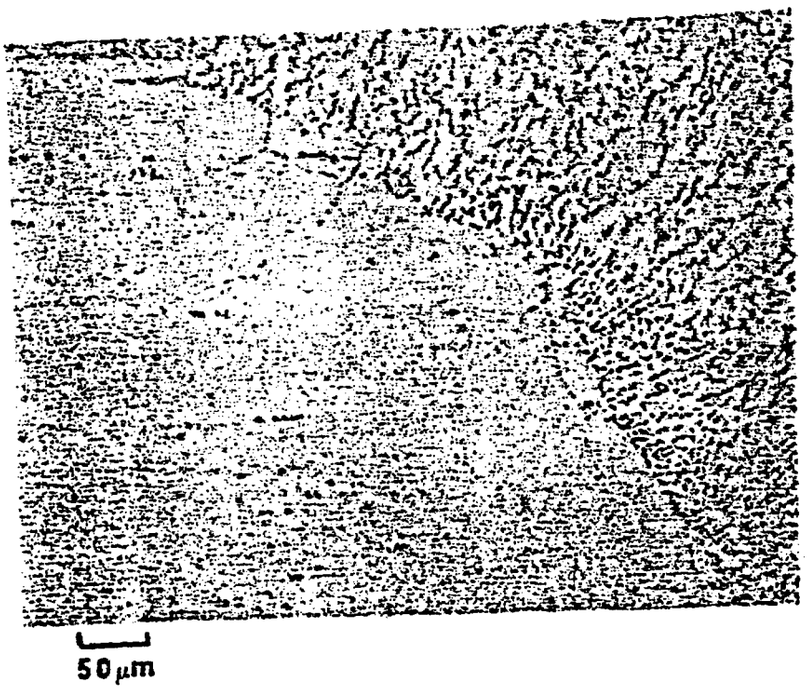
CYCLIC POLARIZATION

DATE CREATED	20 JUN 1985		DATE RAN	20 JUN 1985	
IR COMP	= DISABLED		ANODIC-BETA	= 0.098	
VERTEX DELAY	= 0 SEC		CATHODIC-BETA	= 0.103	
VERTEX I	= PASS		Ecorr	= -0.342	
VERTEX E	= 500 mV		E[I=0]	= -0.358	
FINAL E	= -100 mV		Icorr	= 22.1 E-6	
INITIAL E	= -100 mV ~ Ec		CORR RATE	= 10.1 E0	MPY
INITIAL DELAY	= 120 SEC		$I_a = 10^{-3.073}$	= 8.452×10^{-4} A/cm²	
SCAN RATE	= 1.67 mV/SEC		$I_r = 10^{-6.593}$	= 2.60×10^{-7} A/cm²	
EQUIV WEIGHT	= 27.93 g/EQUIV		I_r/I_a	= .000302	
DENSITY	= 7.98 g/cm3				
AREA	= 1 cm2				

EG&G
PRINCETON APPLIED RESEARCH



316L Weld 8hrs @ 800°C, WQ / 1 wk @ 750°C, WQ



3 hrs @ 800°C, WQ / 24 hrs @ 750°C, WQ

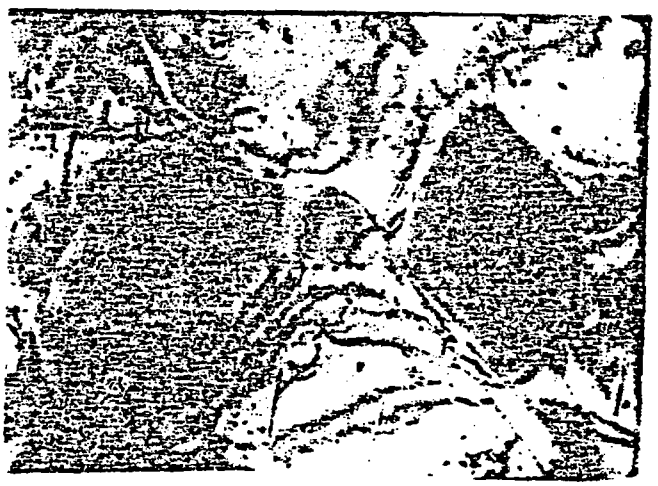
316L Weld

8 hrs @ 800°C
1 wk @ 750°C

$M_{23}C_6$ & some Sigma

5 μm

Sigma phase

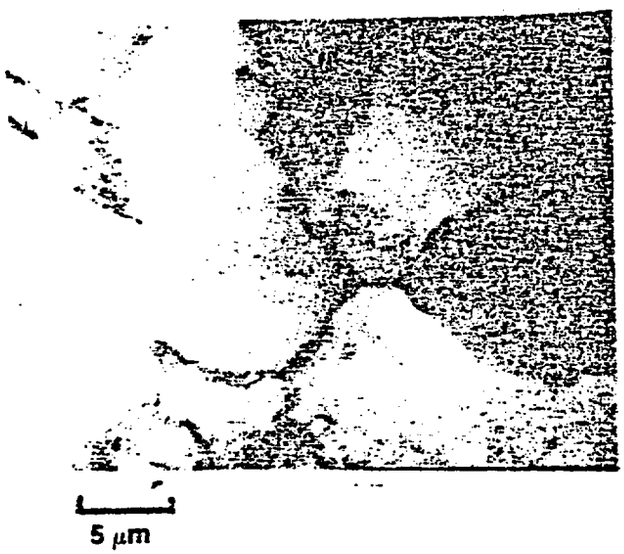


1.0 μm

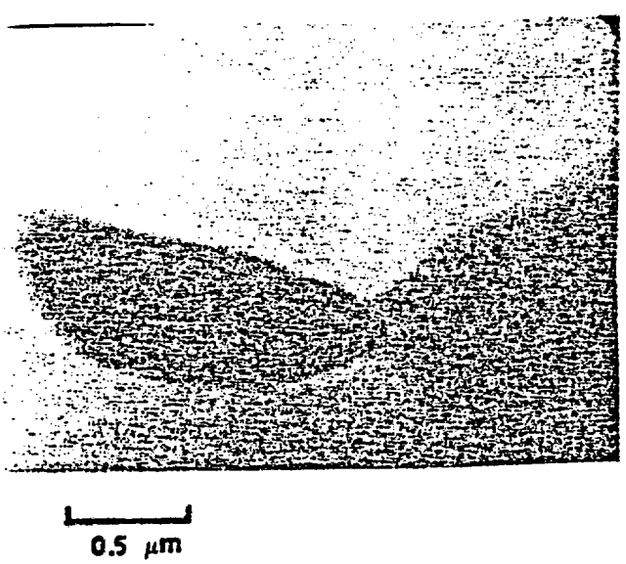
316L Weld

8 hrs @ 800°C
24 hrs @ 750°C

possibly sigma



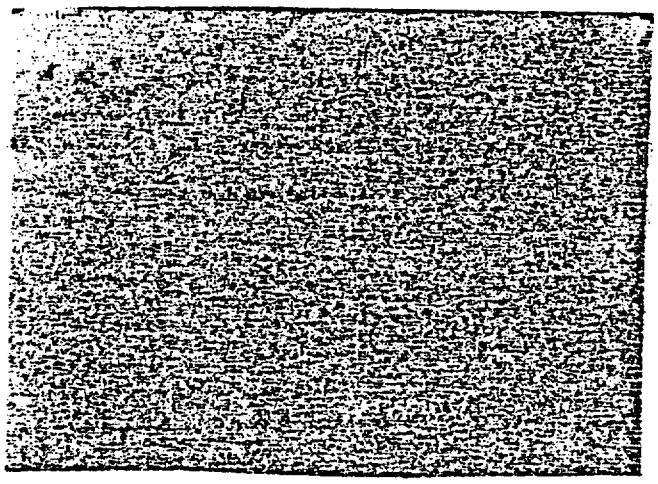
Sigma phase



316L Weld

3 hrs @ 800°C
1 wk @ 750°C

$M_{23}C_6$

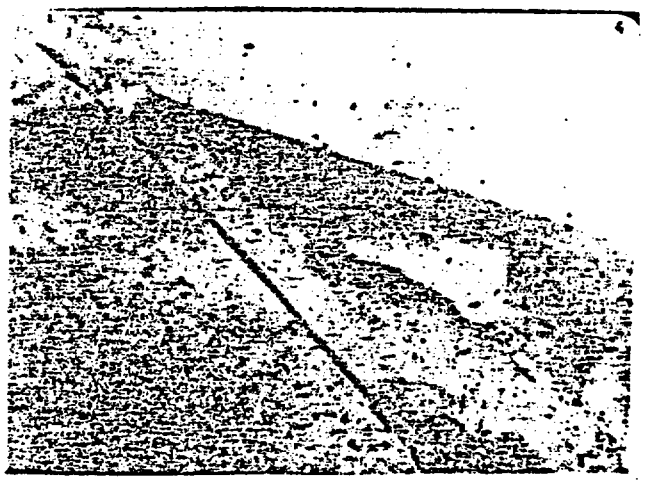


0.5 μm

$M_{23}C_6$ along GB

Intragranular ppts.

maybe Mo_2C

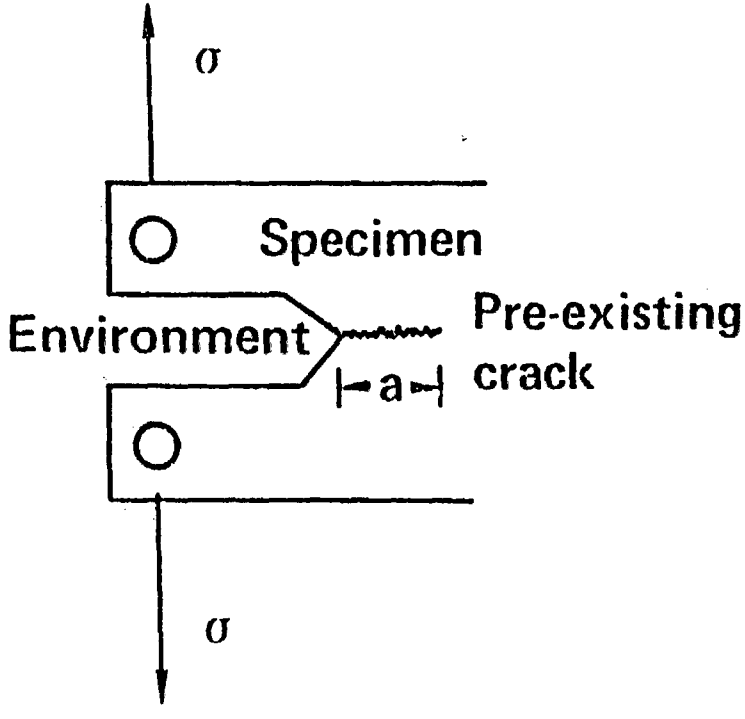


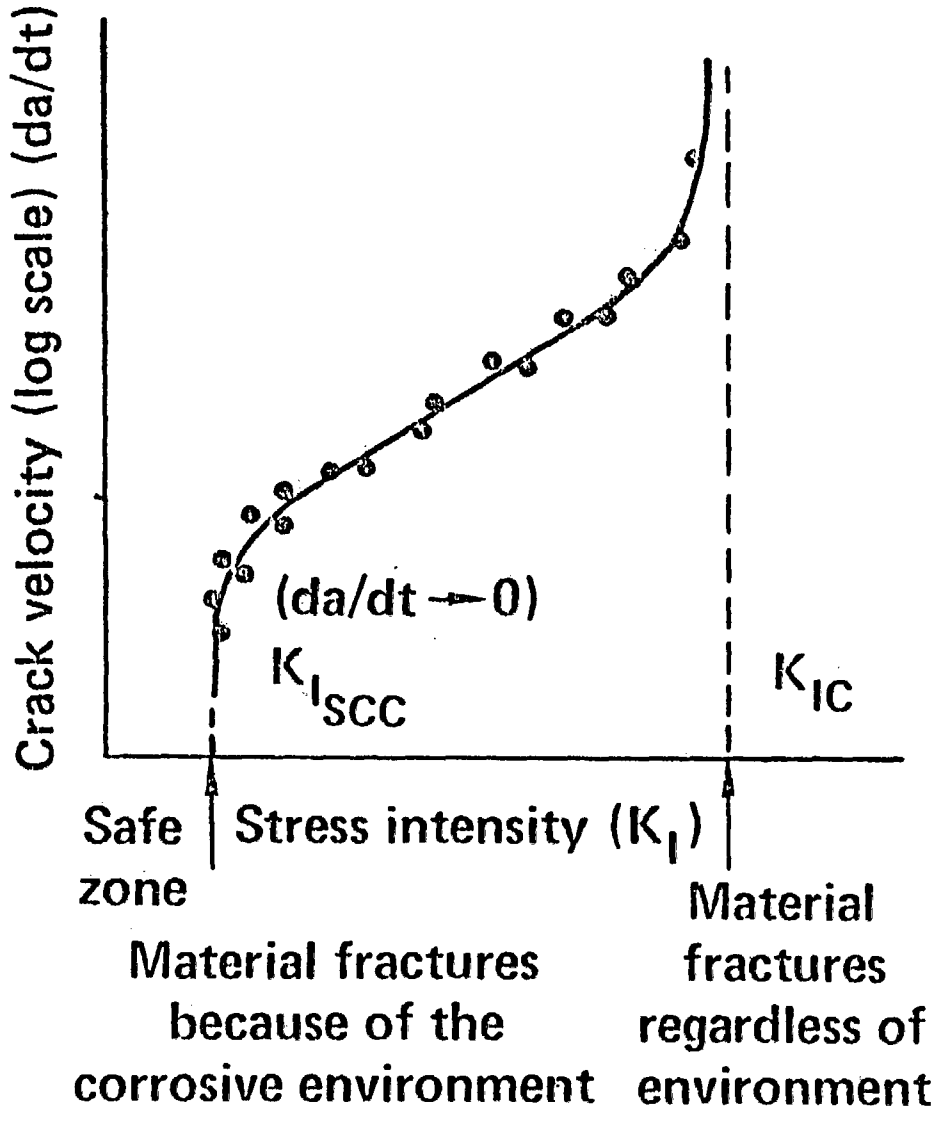
5 μm

Future Work

* Irradiated Slow Strain Rate Tests
* Slow crack growth studies, da/dt
* Initiation studies, K_{1SCC}

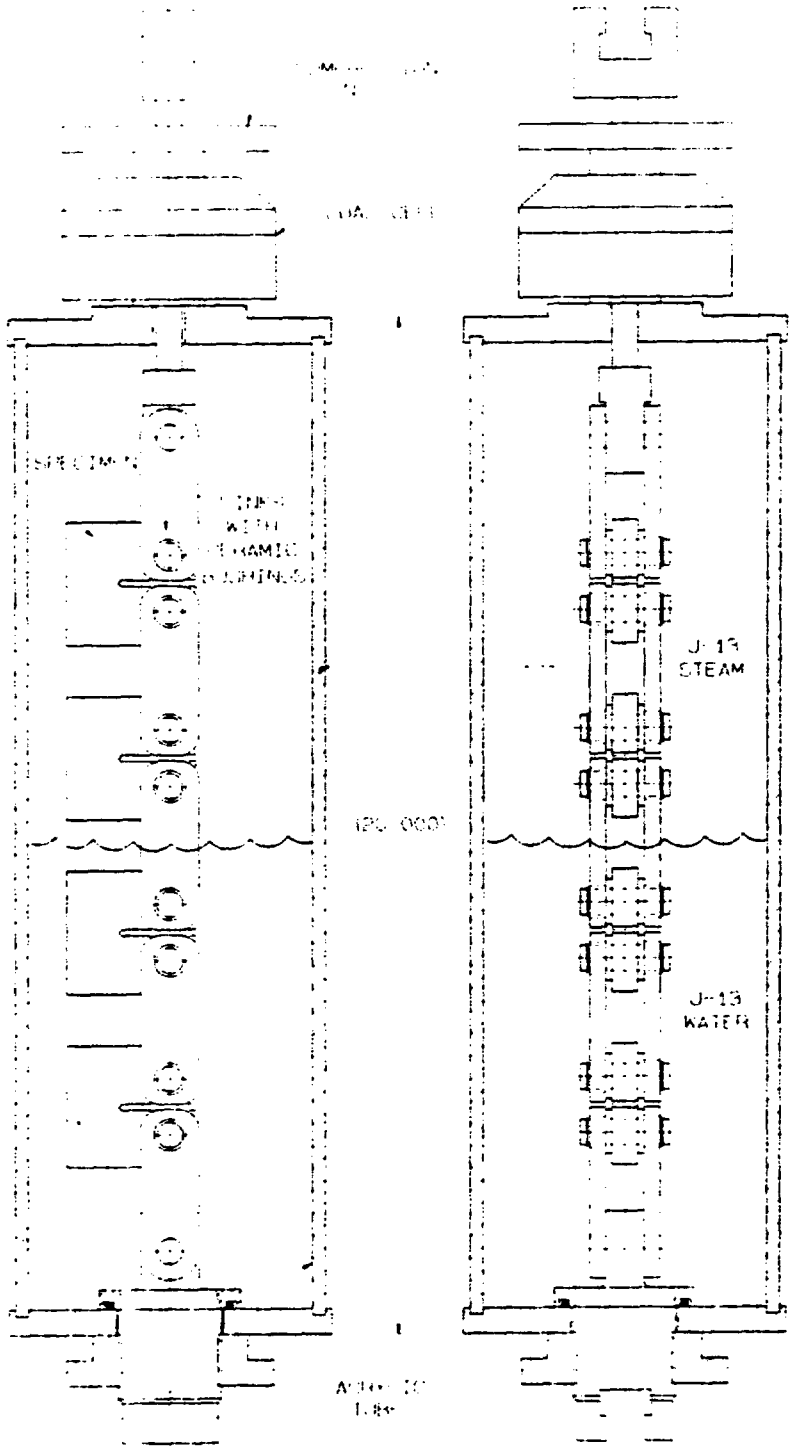
Use fracture mechanics test methods to predict stress corrosion crack propagation rate





Stress intensity = K_I

$K_I = \sigma\sqrt{\pi a}\, f$ (geometry)



SLOW CRACK GROWTH
TEST FIXTURE

Composition of AISI 316L Stainless Steel

(Exp 845)

C	0.022
Mn	1.58
P	0.029
S	0.010
Si	0.47
Cr	17.39
Ni	10.68
Cu	0.27
Mo	2.06
Co	0.20
N	0.065

All mat'l is unwelded.

DeLong equivalents: Cr eq = 20.08

Ni eq = 14.02

Ferrite Number = 4

IMPORTANT MILESTONES IN METAL BARRIERS SUB-TASK

FY 85	REPORT ON FEASIBILITY OF COPPER/COPPER ALLOYS FOR WP CONTAINERS IN TUFF
FY 86	DECISION ON WHETHER TO PURSUE ADDITIONAL WORK ON COPPER
FY 87	RECOMMEND CANDIDATE(S) FOR ADVANCED DESIGN WP CONTAINERS

METAL BARRIERS - SUMMARY OF TEST RESULTS 26 JUNE 1985

STAINLESS STEELS :

- RESULTS TO DATE INDICATE MATERIALS BEHAVE AS EXPECTED
- GENERAL CORROSION RATES PREDICT CONTAINMENT FOR WELL OVER 1000 YRS. FOR VARIETY OF GRADES IN WATER AND STEAM ENVIRONMENTS 50-150 °C
- CORROSION RATES NOT ENHANCED BY GAMMA RADIATION (LIMITED TEST RESULTS)
- HIGH-CARBON HIGHLY-SENSITIZED AISI 304 DOES STRESS CORROSION CRACK (SCC) IN IRRADIATED AND NON-IRRADIATED ENVIRONMENTS; THUS FAR, L-GRADES DO NOT SCC.
- VERY PROLONGED TIMES AT ELEVATED TEMPERATURES (600-800°C) ARE NEEDED TO SENSITIZE L-GRADES; EVEN THEN, ONLY PARTIAL DEGREE OF SENSITIZATION IS OBTAINED.
- SIMILARLY, POTENTIALLY DAMAGING BRITTLE PHASES DO NOT READILY TRANSFORM FROM AUSTENITE

SUMMARY (CONTINUED)

S.S. (CONT'D)

- HOWEVER, PROJECTION OF LOW-TEMPERATURE SENSITIZATION (LTS) BEHAVIOR INDICATES 304L MAY BE MARGINALLY CLOSE TO SENSITIZING IN CONTAINMENT PERIOD; "316 FAMILY" OF S.S. MAY OFFER CONSIDERABLE RESISTANCE TO LTS.
- AS EXPECTED, 316 GRADES OFFER INCREASED RESISTANCE TO LOCALIZED ATTACK. 316 LN DOES NOT PIT IN IRRADIATED 100-X J-13 WATER
- "CLEANER" PREMIUM GRADES OF AISI 316LN OFFER HIGH RESISTANCE TO CREVICE AND PITTING ATTACK.

COPPER:

- VERY LIMITED NUMBER OF RESULTS AVAILABLE
- GENERAL CORROSION RATES IN NON-IRRADIATED J-13 WATER ARE HIGHER THAN THOSE FOR S.S. (EXPECTED RESULT), BUT EXTRAPOLATION OF THESE INDICATES 1000-YR CONTAINMENT
- AL BRONZE AND CUPRONICKEL MORE RESISTANT
- NOT YET RESOLVED: LOCALIZED CORROSION, CORROSION IN γ-RADIATION

Lawrence Livermore National Laboratory

WM DOCKET CONTROL CENTER

'85 AUG 12 P3:24

August 7, 1985
WP: 116-85/6179N

KING

WM Record File 102.2
WM Project 11
Docket No.
PDR —
LPDR —
Distribution:
STABLEIN
LINEHAN
23

N. King Stablein
U.S. Nuclear Regulatory Commission
NTS Project Section
Division of Waste Management
Repository Project Section
Washington, DC 20555

Dear King:

As discussed with Tom Jungling today, enclosed is a copy of John Bates' preprint for WM'85. Hard copies of the slides John used at the Livermore meeting are not available; however, essentially all of the information that he discussed is included in this paper.

Yours truly,

Lynden B. Ballou
Waste Package Task Leader
Nuclear Waste Management

LBB/bb

Enclosure

cc: V. Witherill w/enc.
T. Jungling wo/enc.

~~8508300017~~
28 pp.

Preprint - WM'85 paper

NNWSI WASTE FORM TEST METHOD FOR UNSATURATED DISPOSAL CONDITIONS

John K. Bates and Thomas J. Gerding
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

ABSTRACT

A test method has been developed to measure the release of radionuclides from the waste package under simulated NNWSI repository conditions, and to provide information concerning materials interactions that may occur in the repository. Data are presented from Unsaturated testing of simulated Savannah River Laboratory 165 glass completed through 26 weeks. The relationship between these results and those from parametric and analog testing are described. The data indicate that the waste form test is capable of producing consistent, reproducible results that will be useful in evaluating the role of the waste package in the long-term performance of the repository.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations Project (NNWSI) is investigating the volcanic tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository. One of the topics to be addressed during this investigation is the performance of the waste package components in the repository at the termination of the containment period, i.e., following the 300-1000 year period during which containment of high level waste within the waste package will be substantially complete.[1]

The containment period is followed by the isolation period during which the potential for canister breach and subsequent groundwater/waste form contact is significant. Radionuclide release from the waste package would then be possible, although in accord with Nuclear Regulatory Commission regulations[1] the total release rate must be less than one part in 10^5 per year of the total repository inventory of a particular radionuclide after the 1000 year period.

To measure this radionuclide release, a test method is required that incorporates the interactions between the waste package components and the groundwater under realistic repository conditions. Release results obtained in this fashion could then be used as source term data in modeling the long-term behavior of the repository. NNWSI is developing such materials interaction tests and using them to produce waste form release data.

The first test is a rock cup, total submersion test[2] while the second test, termed Unsaturated Test, is a more realistic simulation of conditions expected in the unsaturated zone in tuff. This report summarizes the Unsaturated Waste Form Test procedure. It also describes parametric and analog tests that provide support data, and then discusses the relationship between the data from the three types of tests.

NNWSI UNSATURATED TEST

Purpose and Description

The purpose of the NNWSI Unsaturated Test is to obtain data on the release of waste components from the waste package in the NNWSI repository environment as it is expected to be after the currently envisioned 300/1000 year containment period has elapsed. Specifically, the test will provide information to be used by the NNWSI project in licensing the NNWSI repository site. The test procedure will (1) provide data that describe the release of radionuclides from a specifically designed glass/container assemblage under strictly controlled test conditions, and (2) provide information concerning synergistic effects that may occur between waste package components. Inherent in this goal is that a specific and reasonable description of the waste package and repository at this time period is available, so that aging effects can be incorporated into the test procedure.

The utility of the data depends on the selection and restriction of the repository conditions and on the materials interactions that are incorporated into the test. The rationale used for selecting test conditions and variables was to address those materials interactions that may exist in a repository during the isolation period. The materials consist of the waste form and the canister overpack. No packing material is included because it is not part of the reference waste package.[2] The interactions are promoted by contact between water and air and the waste package components. The test provides for several interactions to occur and allows the experimenter to assess the importance of each. During actual repository disposal, each waste package may not be subjected to all possible materials interactions. The experimental design simulates interactions, but does not attempt to model the current waste package conceptual design. A complete description of the development of the test and of its uses and limitations is presented elsewhere.[3]

Apparatus

The test apparatus is shown diagramatically in Fig. 1. The components are the test vessel, which provides for collection and containment of liquid and support of the waste package; the waste package

Fig. 1. Test apparatus used for NNWSI Unsaturated testing. Groundwater is introduced through tubing (not shown) that enters the vessel through the feedthrough fitting.

assemblage, which consists of the waste form and metallic components representing the canister; the tuff cup, which acts to collect the solution that drips directly from the waste package assemblage and which interacts with vapor; the tuff cup supporting ring, which separates the tuff cup from the test vessel; and a solution feed system to inject test water.

The waste package assemblage is contacted intermittently by dripping repository water. The nature and degree of radionuclide release from the assemblage is determined by collection and analysis of the water that has contacted the package and by surface analysis of the assemblage components. Materials interactions are noted, and secondary alteration products, which influence the nuclide release from the assemblage, are identified.

The test schedule incorporates batch and continuous testing. In the batch mode, tests are terminated at selected 13 week time intervals. The test apparatus is disassembled, and analyses of both the solution and components are performed. In the continuous mode the waste package assemblage (including liquid associated with the assemblage) is transferred to a new test vessel, and the test is continued. Analyses can be done on the solution in the old vessel. Using the continuous testing matrix, replication of solution analysis can be achieved, investigation of the test components is possible at the termination points, yet the test can continue for an unspecified number of test periods or until information most useful to repository evaluation is obtained. A detailed description of the apparatus and test procedure is provided by Bates.[3]

INTERIM UNSATURATED TEST RESULTS

A series of tests using the Unsaturated procedure are in progress. These tests are being done at 90°C with SRL 165 frit borosilicate glass that is doped with uranium, cesium, and strontium. The glass composition is given in Table I. These tests should provide an indication of the degree of reaction expected and the type of interactions that are important, but since no transuranic elements have been incorporated, this series of tests cannot provide data on the behavior of these important radionuclides. The tests have been completed through the 26 week period using the batch testing mode and through five 6.5 week sampling periods using the continuous testing mode.

It is useful to assess the test results based on a) general observations as to what types of interactions occur, 2) what trends can be established from solution analyses and what release can be attributed to the waste form, and 3) the degree of degradation of waste package components as determined by surface analytical techniques.

General Observations

1. A priori it can be judged that the extent of the water/glass contact will greatly affect the amount of release that occurs. Any aspect of the test design that influences this contact is, therefore, a critical test parameter. The appearance of the test components at both the termination and sampling points provides an indication as to how and where interactions occur. When the vessel is opened, the top surface of the test assembly is usually covered by a thin layer of water which evaporates within 30 seconds of opening the test vessel. The sides of the glass are watermarked and there is a considerable amount of standing water around the bottom of the assembly. From these observations, the method of contact between the water and the waste form can be ascertained. After initial contact with the test assembly, the water spreads rapidly over the top surface and down the sides of the glass. Little standing water remains on the top surface because flow is promoted by the tight fit that exists between the perforated 304 L stainless steel (ss) metal section and the glass (Fig. 1). However, at the

TABLE I

Composition of SRL 165 Glass Used in the Unsaturated Test

Component	wt. %
SiO_2	53.3
Fe_2O_3	12.1
Na_2O	10.1
B_2O_3	6.7
Li_2O	4.6
Al_2O_3	4.0
MnO_2	2.9
CaO	1.5
NiO	0.9
MgO	0.8
ZrO_2	1.2
U_3O_8	1.2
Cs_2O	0.17
SrO_2	0.15
F	0.06
Cl	0.05
Pb	0.05

Analysis by dissolution.

bottom interface more water collects and some interaction occurs. Thus, to some degree the test incorporates water reaction with the test components via both thin film and standing water interactions. These types of interactions are expected to exist during the isolation period.

2. There is considerable reaction between the glass and the bottom ss section as evidenced by discoloration of the glass and the metal. The same type of reaction was also seen in earlier tests.[4] This reaction is focused mainly, but not exclusively, around the weld-affected area of the metal. A considerable amount of rust colored flakes are present in the solution. A more complete description of the alteration of the glass and metal is presented later.

3. When tuff is present in the tests, standing water is found inside the tuff cup. This is important because it demonstrates that some water is being removed from the waste form/ss assemblage by a dripping process, as opposed to an evaporative process. It is likely that both processes will be operative in the repository. This also offers an opportunity to analyze the interaction between standing water and tuff.

The following sections on solution and solid components analyses expand on these general observations and are presented, not as detailed explanations of the reaction processes, but as overviews to illustrate important aspects of the test.

Solution Analyses

At the termination of a test (13 and 26 weeks), the samples are rinsed with deionized water so that all of the liquid that has contacted the glass/ss assemblage can be analyzed. For the 6.5 week continuous test series only the liquid that is collected in the test vessel is analyzed. Thus, a difference in measured elemental release is expected between the two test types, but the effect of this difference should be minimized in the longer test periods.

Another difference between the test types is that in the terminated 13- and 26-week tests the liquid has contacted the tuff cup, while in the continuous tests no tuff is present. The tuff cup allows the interaction and migration of nuclides with the tuff to be studied, but complicates the interpretation of waste form dissolution data because the tuff, itself, interacts with the liquid and only selected elements can be identified as having been released uniquely from the glass. The total release of important radionuclides can be determined in tests which contain tuff by completely dissolving the rock, if necessary. However, the total radionuclide release can be obtained more easily from the continuous test series, where no tuff is present. One key in analyzing the experiments is to establish the relationship between the two types of tests.

Selected results for both the continuous and terminated tests are shown in Tables II and III. The data in Table II show the amount of each element that was detected in solution, corrected for the contribution due to E-J13 water added during the test. The amount for most elements in solution has increased with time. Exceptions to this are Na and Si in the continuous tests, which are actually being extracted from solution. In no case does the sum of the short continuous tests equal that of the longer term, terminated tests. The ramifications of this, and the interpretation of these results, are discussed later in relation to the analyses of the solid components of the test.

Table III presents the concentration of elements in the solutions that were collected in the tuff cup at the end of the 26-week test period. The water collects in the tuff as it drips from the glass/ss waste assemblage. The amount that remains in the tuff cup depends on the porosity of the tuff. As this is not constant, so the amount of water collected varies between tests. The concentration of elements in solution depends on what is released from the waste assemblage and what interactions occur with the tuff. While this interplay requires more data for a complete interpretation, the elemental concentrations in the solution are very similar, which is indicative that the same reactions and interactions are occurring in each test.

Solid Component Analyses

Those components available for study at the termination of a test include the glass waste form, the top and bottom sections of the perforated ss waste form holder, and the tuff cup. No component analyses can be done on the continous test series until the test has been terminated.

Weight change measurement provide an initial indication as to the degree of reaction that has occurred. These data for the glass waste form and both sections of perforated ss are given in Table IV, together with the normalized weight loss, $(NL)_{wt}$, for the glass. This value was calculated using standard methods[5] and utilized the entire surface area of the glass (~13 cm^2) in the calculation. This was done because, although the degree of reaction associated with each type of surface, e.g., side, top, or bottom, may be different, the entire surface was contacted by water. The consequences of this approach are being studied in ongoing parametric tests.

The weight loss for replicate glass samples is quite consistent with the total weight loss increasing ~72% between 13 and 26 weeks. The weight changes in the perforated ss sections are less constant, with the observed changes being close to the instrument precision, but indicate the top section has a tendency to lose weight while the bottom section gains weight. These observations correspond well to what is observed when the ss sections are examined optically or with the scanning electron microscopy (SEM).

Optically the top section of the ss appears unreacted, but with the SEM (Fig. 2) a general, Si-rich, coverage is observed on that section of the ss that was in contact with the glass.

In isolated areas, additional reactions have occurred resulting in discrete products containing Fe/Si, Na/Si/Ca, and Si. The distribution of these products are random and limited, and to date they have not been identified. The region of the top ss section where there has been no glass contact appears unreacted after 13 weeks, but some Fe/Si products are evident after 26 weeks.

Visual observation reveals that the bottom ss section has reacted. The bulk of the reaction occurs in the weld-affected area where the vertical support rods are attached (Fig. 1). The weld-affected area is not uniform between samples and likely introduces some variance to the results. Reaction in this region results in extensive coverage of iron and

TABLE II

Solution Analyses[a] for the NNWSI Unsaturated Test

Test Type[d]	Element[b,c]							
	B	Ca	Li	Mg	Na	Si	Sr	U
13 week, terminated	3.9	21.5	5.9	4.4	(8.0)	(13.8)	0.4	0.1
13 week, terminated	5.9	30.3	6.2	5.8	27.7	27.0	0.6	0.3
Sum of two 6.5 week continuous	3.3	3.8	10.0	1.2	(31.7)	(27.7)	<0.3	<0.05
26 week, terminated	15.1	35.5	10.9	7.4	46.9	107.1	0.8	1.1
26 week, terminated	15.5	35.7	11.1	7.5	61.6	112.5	0.7	0.7
Sum of four 6.5 week continous	4.4	7.3	16.4	2.1	(60.2)	(50.4)	<0.3	0.1

[a]Solutions were analyzed by ICP except for U which was done by fluorescence.

[b]The results are presented as the total of each element (μg) analyzed in solution.

[c]The results have been corrected for the elemental contribution due to E-J13 water added during the test, ( ) indicates less of an element is in solution than originally added.

[d]Duplicate tests were terminated at 13 and 26 weeks. Duplicate tests were also run in the 6.5-week continuous test series, and an average of two tests is reported.

TABLE III

Concentration of Water Contained in the Tuff Cup

Solution Type	Element (ppm)							
	B	Ca	Li	Mg	Na	Si	Sr	U
E-J13	0.18	4.50	0.06	0.39	46.60	35.30	0.03	0:004
26 week terminated	4.2	9.9	2.3	1.5	50.3	76.2	0.17	0.07
26 week terminated	4.2	8.8	2.3	1.5	50.3	76.6	0.15	0.06

TABLE IV

Component Weight Changes in NNWSI Unsaturated Tests

Test #	Test Description	Weight Change,[a] μgm			$(NL)_{wt.}$ g/m^2
		Top ss	Bottom ss	Glass	Glass
1	13 week terminated	(160)	360	(350)	0.26
2	13 week terminated	40	20	(320)	0.25
3	26 week terminated	(50)	80	(630)	0.47
4	26 week terminated	(20)	30	(530)	0.40

[a](Values) indicate weight loss, estimated precision ±20 μgm.

chromium silicate nodules (Fig. 3). However, SEM examination reveals that some degree of reaction is widespread outside the weld-affected regions. Here, the surface is continuously covered with small Si-rich deposits (Fig. 4), and intermittently covered with other reaction products. The ss that has not contacted the glass is covered by reaction products to a much lesser degree.

Visual observation also reveals that the bottom of the glass is reacted, especially in regions where there is corresponding reaction on the ss. Examples of the type of reaction products observed are shown in Fig. 5, where Si-rich strands are shown covering a region of iron silicate nodules. There is widespread appearance of a uranium-containing phase (Fig. 6). This phase contains Ca, P, U, and Si, as determined by energy dispersive X-ray analysis (EDS), but to date, X-ray diffraction has not yielded a pattern, and the phase is unidentified. Figure 7 shows the surface in a region not affected by any localized reaction. The surface is enriched in Fe, Mg, and Al and depleted in Na and Si. The circular forms are an outgrowth and have the same composition as the surface.

The top surface of the glass generally shows less evidence of localized reaction and alteration product formation than the bottom and has the appearance shown in Fig. 7. The identification of all the reaction products is an important part in understanding the alteration process that will likely control the eventual release of radionuclides. A more complete description of these phases is being prepared.[6]

Discussions

Testing in this matrix has been completed through 26 weeks so only a preliminary interpretation of the results is warranted. However, several important issues can be addressed and other issues that merit close attention can be identified.

Fig. 2. Dual photomicrograph of the alteration that occurs on the top ss section that has contacted the glass. Magnification 1000 and 10,000X.

Fig. 4. General coverage on the bottom ss section that was in contact with the glass. Magnification 5000X.

Fig. 3. Nodules that form on the weld-affected region of the bottom ss section. Magnification 2500, 12,500X.

Fig. 5. A photomicrograph of alteration that occurs on the bottom surface of glass that has been in contact with the weld-affected ss. Magnification 3000X.

The reproducibility of the reaction process as determined from the physical appearance of the test components, the weight loss of the waste form, and the solution analyses of both the terminated and continuous tests is good enough so that credence can be given to the data, and that observed trends may be interpretable. Trends would provide some measure of the extent of reaction with time, so that it can be determined whether the data can be fit into models that will establish the behavior of the repository for long time periods.

Equally important are that 1) the interactions between the test components (glass, ss, water, tuff) appear to affect and control the reactions that occur and 2) that a relationship between what is found in solution and what is observed on the test components can be established. For example, the extent of reaction of the glass can be estimated by the $(NL)_{wt}$. Yet a value obtained in this fashion must be tempered by the possibility that reaction products may form that incorporate components from the ss and the water, and these products could increase the final weight.

It would be useful to identify a marker element that is not incorporated into alteration products and that does not interact with the tuff. One possibility is Li. The amount of Li found in the water in both the continuous and terminated tests correlates well with what would be expected for an element that does not interact. Li levels found in the continous tests are greater than that found in the terminated tests because ~1 mL of water is retained in the tuff and remains unanalyzed. However, for the other elements the evidence is that they may be retained on the glass/ss waste assemblage or come from the tuff. It will be necessary to correlate the results of surface science analysis of the reacted surfaces with the solution results to adequately assess the degree of

Fig. 6. A photomicrograph of a uranium-containing phase surface of glass. Magnification 10000X.

Fig. 7. A photomicrograph of the general surface of reacted glass. Magnification 2000X.

waste form reaction. However, based on these preliminary data the release from the waste assemblages after 26 weeks is 0.43 g/m^2 based on weight loss, 0.56 g/m^2 based on Li release, and 0.08 g/m^2 based on U release.

Parametric Testing

The NNWSI Unsaturated Test requires that a rigid set of controls be placed on the test conditions. Yet, there are many aspects of the test that need to be further studied, including the effect of removing the perforated ss sections, varying the ratios of the top and bottom surface area to that of the sides, or varying the rate and amount of water that contacts the waste form. Changes in these process parameters are being studied in parametric tests.[4]

The first set of parametric tests[4] is investigating the release from a glass waste form only. The goal is to establish a known release from the glass with no contact with perforated ss sections. The test is being done in a Teflon™ vessel, and the waste form is positioned on a Teflon™ stand so that the release of all elements can be monitored. Otherwise, the test parameters are identical to the Unsaturated Test. This test has been completed through 39 weeks, and selected results are given in Table V.

The striking points in these data are that the waste form is gaining weight, likely due to the extraction of Ca, Mg, and Si from the J13 water, and that except for Fe, Na, and Si, the total amount of elemental release is similar in the continuous and terminated tests.

The first point is confirmed by visual examination of the top glass surface which has a white, crusty appearance, and with SEM where large quantities of Ca-, Mg-, and Si-containing deposits are observed. These deposits form because without any ss present the water is able to remain on the top surface longer, and since the Teflon™ vessels do not maintain a leak-tight atmosphere, may be subject to evaporative forces.

These observations help interpret data from the Unsaturated Test where the elemental release in the continuous and terminated tests do not match. It appears that Na, Si, and Fe may be forming phases on the glass that are washed off during the rinsing process. In fact, the remnant of an unstable Na/Si phase has been observed on the glass surface with the SEM. This would suggest that in the Unsaturated Test the variances for the other elements are caused by interaction with the tuff.

ANALOG EXPERIMENT

In order to establish the relationship between the Unsaturated Test and the repository, an analog test is being performed. The analog test attempts to more closely simulate anticipated repository conditions than the Unsaturated Test and is necessary because some of the constraints required in the controlled Unsaturated Test procedure may not exist in a repository. If these test constraints cause a significant deviation between the analog and Unsaturated Test results, then the data obtained by use of the Unsaturated Test may not be a reasonable repository simulation and should be questioned if used in repository modeling.

The analog test[3] utilizes a tuff rock core the shape of a right circular cylinder, 5" in length and 2-1/2" in diameter, as a reaction vessel. Each core is cut diametrically to give two sections. A cavity is machined in the larger section to accommodate a test assembly similar to that used in the Unsaturated test. The dimensions of the cavity are similar to the inside of the Unsaturated test vessel, except that the upper section of tuff, which acts as the vessel lid, had a flat lapped surface.

The test is initiated by placing the waste package in the cavity and placing both sections of J-13 saturated tuff into a Teflon™ sleeve. The mating surfaces of both tuff sections have lapped faces which produce a good seal. The Teflon™ sleeve is placed in a stainless steel holder and end caps secured over the top and bottom of the tuff core. The end caps are tapered so they only contact the tuff along the outside edges. The end caps are connected to inlet and outlet tubing. The Teflon™ containment is sealed by water which

TABLE V

Parametric Test Results

Test Type	Duration (weeks)	Δwt (mgms)	Total Elemental Release (μg)[a]							
			B	Ca	Fe	Li	Mg	Na	Si	U
Terminated[b]	6	0.1	7.2	(8.8)	1.0	9.8	(1.2)	34.3	(11.3)	0.7
	13	0.7	24.0	(24.5)	1.3	23.9	(3.8)	84.5	(26.7)	1.8
	26	1.2	10.1	(49.6)	2.4	20.4	(7.9)	38.9	(28.5)	1.5
	39	1.5	21.5	(73.8)	2.1	27.0	(12.0)	77.0	(44.0)	2.9
Continuous[c]	6	-	8.6	(9.2)	2.0	2.7	(1.3)	(23.7)	(21.8)	0.3
	13	-	13.8	(20.6)	3.8	5.7	(2.7)	(46.9)	(49.2)	0.8
	26	-	22.1	(41.4)	6.6	16.4	(5.7)	(44.1)	(91.1)	1.8
	39	-	27.0	(62.3)	10.0	26.4	(9.3)	(10.0)	(110.8)	2.9

[a]The values have been corrected for the contribution due to J13 water, (value) indicates a net decrease in the amount in solution.

[b]The terminated tests represent the results of one test per sample period.

[c]The continous tests represent the average of values from two tests, except for B which is one test.

pressurizes the Teflon™ jacket to 1600 psi. This provides for flow through the tuff core and not at the Teflon™/tuff interface.

DWPF glass spiked with with ^{133}Ba, ^{137}Cs, and ^{152}Eu was used as the waste form. ^{137}Cs was used to represent highly mobile, easily leached elements, but is not expected to be a significant radionuclide during the isolation period. ^{133}Ba was used to represent the alkaline earth group of elements. Again few of these elements will be of concern during the isolation period. ^{152}Eu was used to represent fission products and actinide elements that are slowly removed from the glass and will be important during the isolation period.

Three tests were initiated, with one being terminated after 13 weeks. Detailed results of this test are presented elsewhere,[3,4] but there was good agreement between both the analog and Unsaturated Test regarding the appearance of the waste assemblage and the extent of reaction. The test components were gamma-counted for long periods of time (10^6 sec) to determine the amount and directionality of radiotracer release. In relationship to the waste form weight loss the releases were: $(NL)_{wt} = 0.1\ g/m^2$, $(NL)_{Cs} = 0.1\ g/m^2$, $(NL)_{Ba} = 0.09\ g/m^2$, and $(NL)_{Eu} = 0.03\ g/m^2$. Most of the ^{133}Ba was associated with the top and bottom ss sections, while ~30% was found on the tuff. 98% of the ^{152}Eu was associated with the ss sections and ~2% with the bottom tuff, while the ^{137}Cs was found mostly associated with the bottom tuff. Very little of any radionuclide was detected in the rinse solution, and no radioactivity was found on the walls or top section of the tuff cavity.

CONCLUSIONS

Preliminary results of tests done using the NNWSI Unsaturated Test method indicate that consistent reproducible results can be achieved. A close relationship between the laboratory environment of the Unsaturated method and a more realistic repository environment, as simulated in the analog tests, is also indicated. Combined with the results from parametric testing, these observations provide confidence that data acquired in longer term Unsaturated testing will establish trends that will be applicable to modeling long-term NNWSI waste package behavior, ~~and~~ Adaptation of the Unsaturated Test method for use with spent fuel is in progress.

REFERENCES

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6. J. K. Bates and T. J. Gerding, "NNWSI Unsaturated Test Results for Simulated DWPF Glass After One Year," ANL report in preparation.

Test Vessel

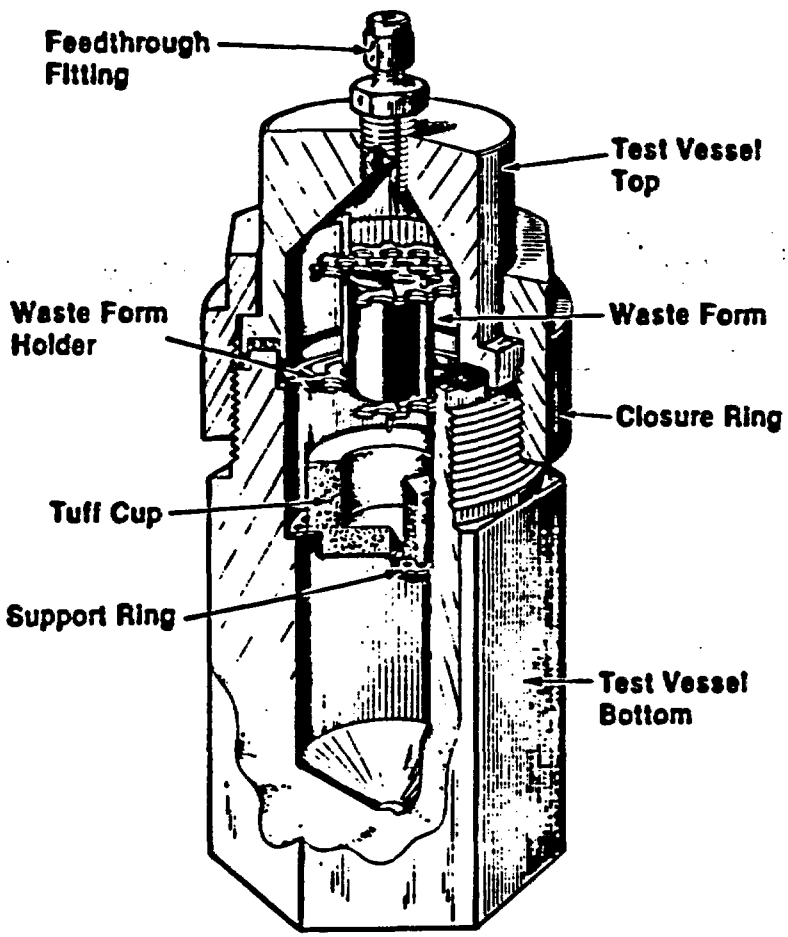


fig 1
83%

fig 2

2/1/15

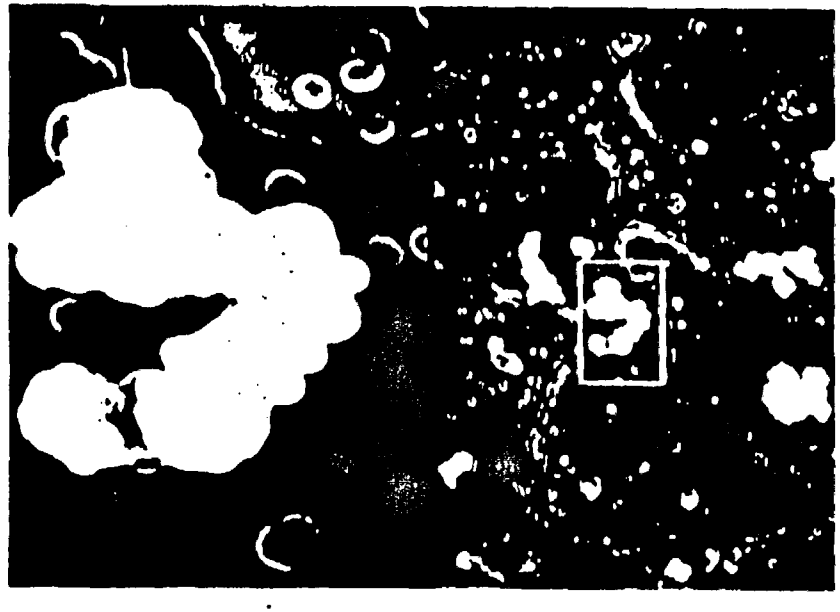


Fig 2

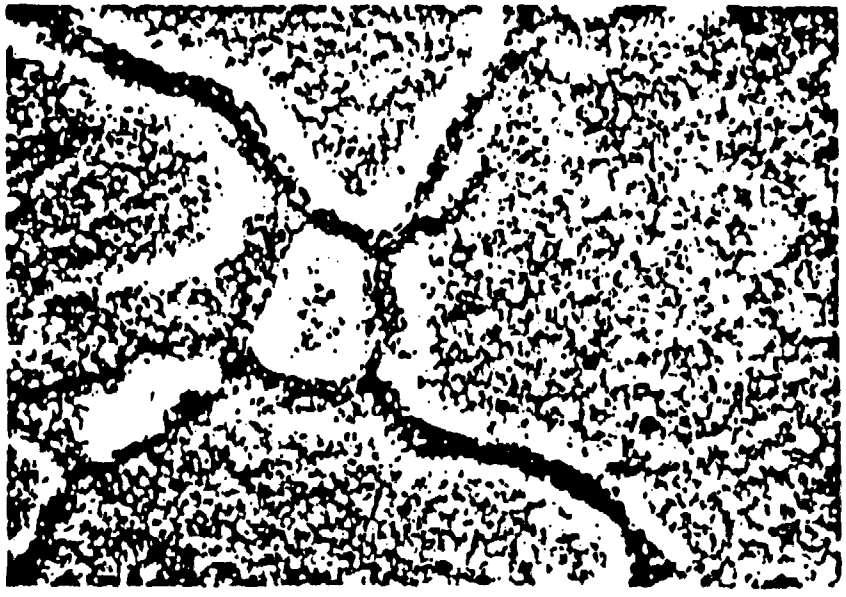


fig 4

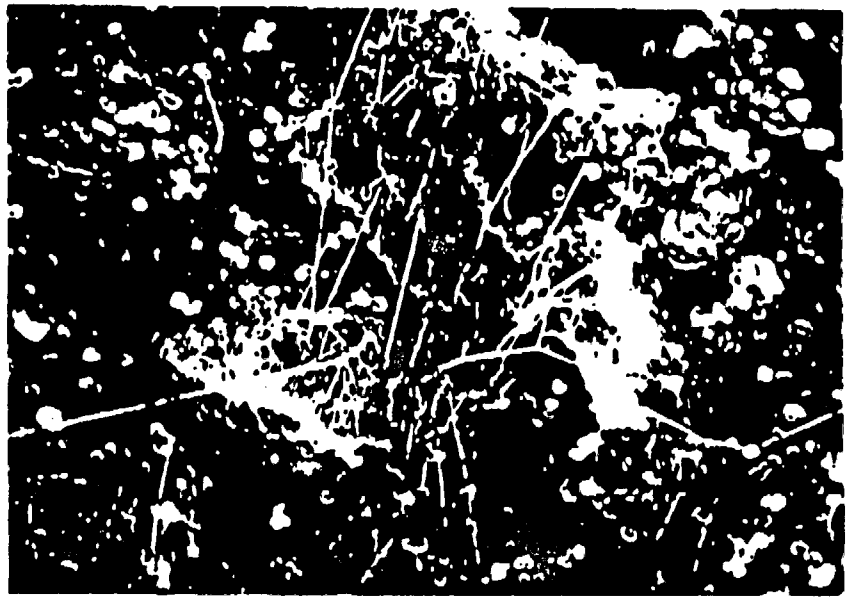
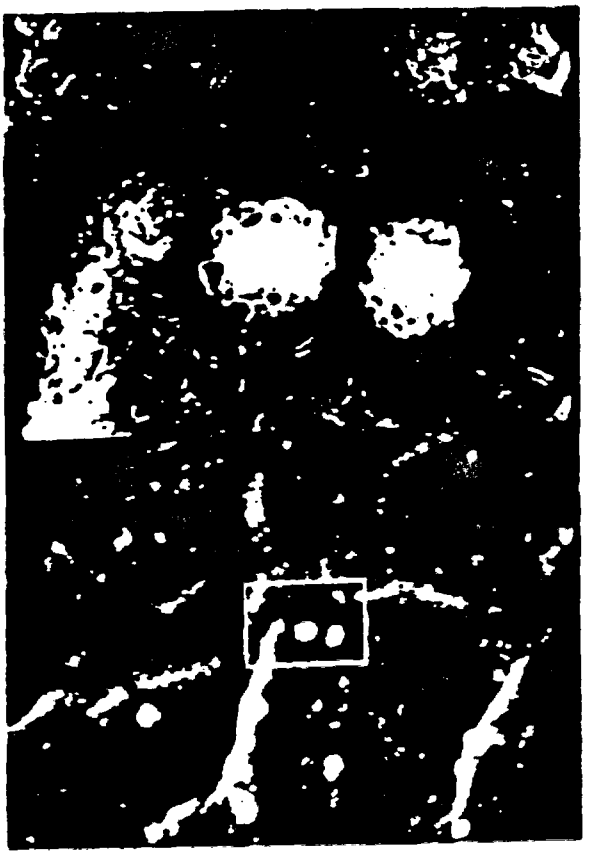


Fig 5

fig6



Enclosure 4

§60.135(b)(1) EXPLOSIVE, PYROPHORIC, AND CHEMICALLY REACTIVE MATERIALS

THE WASTE PACKAGE SHALL NOT CONTAIN EXPLOSIVE OR PYROPHORIC MATERIALS OR CHEMICALLY REACTIVE MATERIALS IN AN AMOUNT THAT COULD COMPROMISE THE ABILITY OF THE UNDERGROUND FACILITY TO CONTRIBUTE TO WASTE ISOLATION OR THE ABILITY OF THE GEOLOGIC REPOSITORY TO SATISFY THE PERFORMANCE OBJECTIVES.

§60.135(b)(2) FREE LIQUIDS

THE WASTE PACKAGE SHALL NOT CONTAIN FREE LIQUIDS IN AN AMOUNT THAT COULD COMPROMISE THE ABILITY OF THE WASTE PACKAGES TO ACHIEVE THE PERFORMANCE OBJECTIVES RELATING TO CONTAINMENT OF HLW (BECAUSE OF CHEMICAL INTERACTIONS OR FORMATION OF PRESSURIZED VAPOR) OR RESULT IN SPILLAGE AND SPREAD OF CONTAMINATION IN THE EVENT OF WASTE PACKAGE PERFORATION DURING THE PERIOD THROUGH PERMANENT CLOSURE.

HOW RELIABLE DOES THE WASTE PACKAGE CONTAINMENT HAVE TO BE?

VUGRAPHS FOR A TALK TO BE PRESENTED BY E.A. WICK AT AN NEA/OECD WORKSHOP IN ALBUQUERQUE, NEW MEXICO, NOVEMBER 13-15, 1984. THE WORKSHOP IS ENTITLED, "SOURCE TERM FOR RADIONUCLIDE MIGRATION FROM HIGH-LEVEL NUCLEAR WASTE OR SPENT NUCLEAR FUEL UNDER REALISTIC REPOSITORY CONDITIONS."

No. 1

NRC's RESPONSIBILITY

UNDER THE ENERGY REORGANIZATION ACT OF 1974, NRC HAS RESPONSIBILITY TO LICENSE DISPOSAL OF HLW BY DOE

THE NUCLEAR WASTE POLICY ACT OF 1982 STATES THAT IT IS FEDERAL RESPONSIBILITY TO PROVIDE FOR HLW AND SPENT FUEL REQUIRING PERMANENT DISPOSAL.

THUS, DOE HAS RESPONSIBILITY FOR DISPOSAL OF HLW AND SPENT FUEL AND NRC HAS RESPONSIBILITY TO LICENSE THE DOE REPOSITORY OR REPOSITORIES.

No. 2

REGULATORY REQUIREMENT FOR CONTAINMENT

10 CFR 60 (TECHNICAL CRITERIA) SPECIFIES (PARAGRAPH 60.113) THAT THE ENGINEERED SYSTEM OF BARRIERS SHALL BE DESIGNED SO THAT, ASSUMING ANTICIPATED PROCESSES AND EVENTS, CONTAINMENT OF THE HLW WILL BE SUBSTANTIALLY COMPLETE DURING THE PERIOD WHEN RADIATION AND THERMAL CONDITIONS IN THE ENGINEERED BARRIER SYSTEM ARE BEING DOMINATED BY FISSION PRODUCT DECAY. (300 TO 1000 YEARS)

No. 3

REGULATORY REQUIREMENT FOR RELEASE AFTER THE CONTAINMENT PERIOD

10 CFR 60 (PARAGRAPH 60.113) ALSO SPECIFIES THAT THE RELEASE RATE OF ANY RADIONUCLIDE FROM THE ENGINEERED BARRIER SYSTEM FOLLOWING THE CONTAINMENT PERIOD SHALL NOT EXCEED ONE PART IN 100,000 PER YEAR OF THE INVENTORY OF THAT RADIONUCLIDE CALCULATED TO BE PRESENT AT 1000 YEARS FOLLOWING PERMANENT CLOSURE, OR SUCH OTHER FRACTION OF THE INVENTORY AS MAY BE APPROVED OR SPECIFIED BY THE COMMISSION.

No. 9

HOW MANY WASTE PACKAGES CAN FAIL?

DEPENDS UPON:

1. ESTIMATED RATE OF RELEASE FROM A FAILED PACKAGE
2. WHEN FAILURE OCCURS

No. 10A

EXAMPLE CALCULATION OF ACCEPTABLE RELEASE

PERMISSIBLE ANNUAL RELEASE =

$$1 \times 10^{-5} \times 1000 \text{ YR INV.(CI)} \times \frac{1000 \text{ YR INV.(CI)}}{\text{CURRENT INV.(CI)}}$$

No. 10B

EXAMPLE CALCULATION OF ACCEPTABLE RELEASE
(CONTINUED)

TOTAL ACTIVITY IN CURIES OF INVENTORY IN ONE BWR SPENT FUEL ROD

10 YRS	300 YRS	1000 YRS
960	11	4.6

THIS EXAMPLE IS ALSO TRUE ON A RELATIVE BASIS OF THE TOTAL INVENTORY OF SPENT FUEL WASTE PACKAGES IN THE REPOSITORY AT 10, 300 AND 1000 YRS.

No. 10C

EXAMPLE CALCULATION OF ACCEPTABLE RELEASE
(CONTINUED)

THEREFORE, THE PERMISSIBLE ANNUAL RELEASE AT 10 YEARS AFTER EMPLACEMENT MAY BE CALCULATED AS A FRACTION OF THE TOTAL RADIONUCLIDE INVENTORY AT THAT TIME.

FOR EXAMPLE,

$$\frac{4.6\ \text{Ci}}{960\ \text{Ci}} \times 1 \times 10^{-5} \times \text{INV. 10 YRS AFTER EMPLACEMENT}$$

$$= 4.8 \times 10^{-8} \text{ OF CURRENT INVENTORY}$$

No. 11A

EXAMPLE CALCULATION OF ACCEPTABLE NUMBER OF WASTE PACKAGE FAILURES

ASSUMPTIONS:

1. No. OF SPENT FUEL WASTE PACKAGES IN THE REPOSITORY = 10,000

2. A FAILED PACKAGE RELEASES 1×10^{-5}/YR OF INV. IN THE PACKAGE

THUS, THE FRACTIONAL RATE OF RADIONUCLIDE RELEASE FROM A FAILED WASTE PACKAGE WOULD BE:

$$1 \times 10^{-5}/\text{YR} \times \frac{\text{NUMBER OF CURIES}}{\text{PACKAGE}} \Big/ \left(\frac{\text{NUMBER OF CURIES}}{\text{PACKAGE}} \times \frac{\text{10,000 PACKAGES}}{\text{INVENTORY}} \right) =$$

$$1 \times 10^{-9}/\text{YR} \times \text{INVENTORY}$$

No. 11B

EXAMPLE CALCULATION OF ACCEPTABLE NUMBER OF WASTE PACKAGE FAILURES (CONTINUED)

THEREFORE, THE NUMBER OF WASTE PACKAGE FAILURES THAT COULD BE TOLERATED 10 YRS AFTER EMPLACEMENT IN A REPOSITORY CONTAINING 10,000 WASTE PACKAGES IS:

$$\frac{\text{ACCEPTABLE RELEASE } (4.8 \times 10^{-8}/\text{YR})}{\text{RELEASE PER PACKAGE } (1 \times 10^{-9}/\text{YR})}$$

$$= 48$$

THEREFORE, 48 PACKAGES COULD FAIL WITH A RELEASE RATE OF 1×10^{-5}/YR PER PACKAGE

No. 12

CONCLUSIONS

NRC HAS NOT DEFINED "SUBSTANTIALLY COMPLETE" CONTAINMENT. SOME OF THE IDEAS BEING CONSIDERED ARE:

A. A RADIONUCLIDE RELEASE RATE THAT DOES NOT EXCEED THE ABSOLUTE QUANTITIES PERMITTED IN THE POST CONTAINMENT PERIOD, I.E., 1×10^{-5}/YR OF THE RADIONUCLIDE INVENTORY OF THE REPOSITORY AT 1000 YEARS.

B. SINCE THE RADIONUCLIDE INVENTORY IS LARGER DURING THE CONTAINMENT PERIOD, THE FRACTIONAL RELEASE OF RADIONUCLIDES AT THE TIME OF CONTAINMENT FAILURE MUST BE CORRESPONDINGLY SMALLER.