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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: INTEGRATED GLASS ALTERATION TESTS

PRESENTER: JOHN K. BATES

PRESENTER'S TITLE AND ORGANIZATION: EXPERIMENTALIST
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS

PRESENTER'S TELEPHONE NUMBER: (708) 972-4385

AUGUST 28-29, 1990

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WHAT DOES A VALIDATED RELEASE MODEL REQUIRE?

- A CONCEPTUAL MODEL BASED UPON A FUNDAMENTAL UNDERSTANDING OF THE GLASS DISSOLUTION MECHANISMS

- DATA TO SUPPORT THE MODEL FROM SIMPLE EXPERIMENTS DESIGNED TO ISOLATE INDIVIDUAL GLASS DISSOLUTION MECHANISMS

- → A DATABASE OF SITE-SPECIFIC AND NATURAL ANALOGUE DATA TO TEST THE MODEL

OVERVIEW

- PURPOSE OF REPOSITORY-RELEVANT WORK
- BACKGROUND AND PERSPECTIVE
- EXAMPLES OF TESTING AND ANALYSIS
  - VAPOR HYDRATION/LEACH
  - STATIC LEACH/SURFACE ANALYTICAL STUDIES
  - DRIP TESTS
- SUMMARY

PURPOSE

SITE-SPECIFIC DEGRADATION TESTS PROVIDE INFORMATION THAT CAN BE USED TO SUPPORT A LICENSE APPLICATION FOR THE REPOSITORY

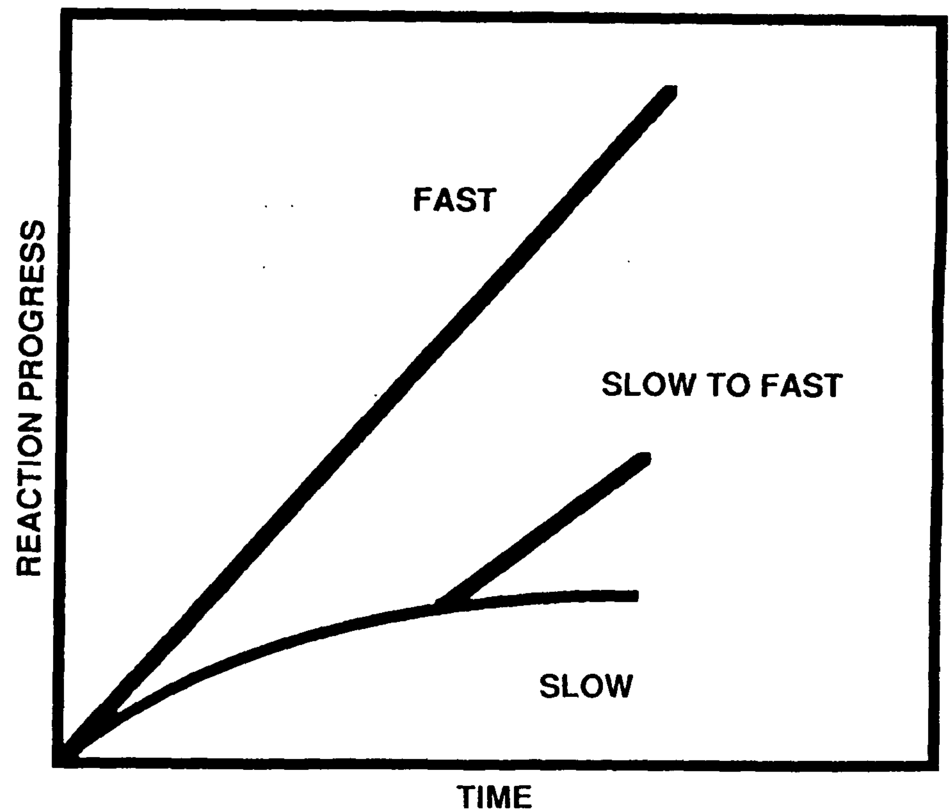
- IDENTIFY SITE-SPECIFIC PROCESSES AND MECHANISMS (DEGRADATION MODES)
- IDENTIFY MATERIALS INTERACTIONS
- MEASURE RADIONUCLIDE DISTRIBUTION AND RELEASE TRENDS
- PROVIDE VALIDATION OF MECHANISTIC MODELS

BACKGROUND

PERFORMANCE ASSESSMENT OF WASTE PACKAGE DESIGN REQUIRES KNOWLEDGE OF BASIC REACTION AND RELEASE PROCESSES

MUST KNOW WHERE ON THE CURVE YOU ARE WHEN EVALUATING WASTE FORM PERFORMANCE AND RADIONUCLIDE RELEASE:

- SITE-RELEVANT TESTS
- RADIONUCLIDE RELEASE
- REACTION MECHANISMS



BACKGROUND

THE VARIABLITY OF CONDITIONS ANTICIPATED FOR THE YUCCA MOUNTAIN SITE OFFERS A CHALLENGE IN DESIGNING AND PERFORMING TESTS TO EVALUATE WASTE FORM PERFORMANCE

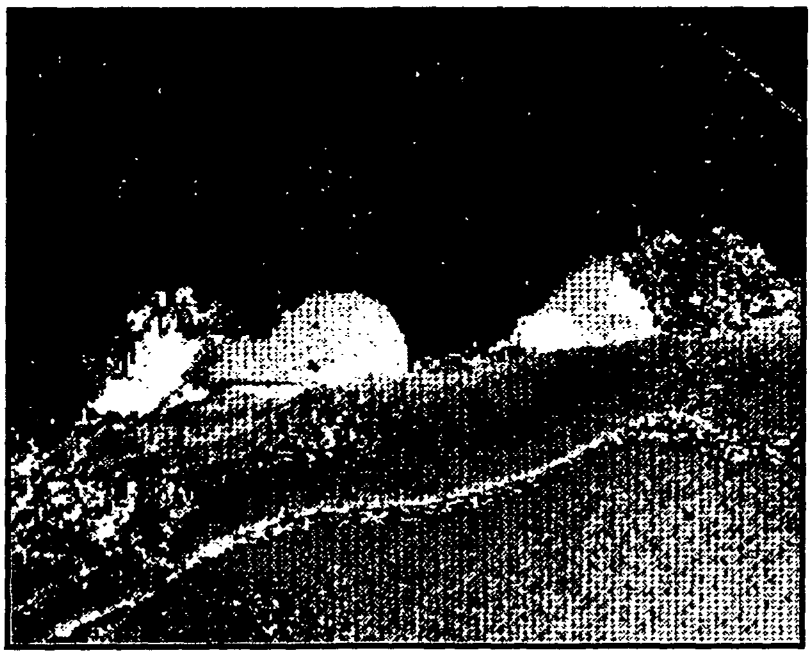
WHAT DOES UNSATURATED MEAN?

- HUMID AIR
- DRIPPING WATER - INTERMITTENT FLOW
- SMALL AMOUNTS OF STANDING WATER

THE SMALL AMOUNT OF WATER HAS A DRAMATIC EFFECT ON GLASS REACTION

BACKGROUND

THE SURFACE OF THE VAPOR PHASE REACTED GLASS IS COVERED WITH SECONDARY PHASES OF UNIQUE STRUCTURE AND COMPOSITION



SECONDARY PHASES

REACTED GLASS

UNDER CERTAIN CIRCUMSTANCES THE FORMATION OF A STABLE PHASE MAY ACTUALLY PROMOTE REACTION

EXAMPLE 1: VAPOR HYDRATION LEACH

AN EXAMPLE OF SITE-RELEVANT TESTING COMBINED WITH RADIONUCLIDE RELEASE IS THE LEACHING OF AGED GLASS

GOAL

- PERFORM SIMPLE TESTS TO COMPARE RADIONUCLIDE RELEASE FROM VAPOR HYDRATED GLASS WITH THAT OF FRESH GLASS

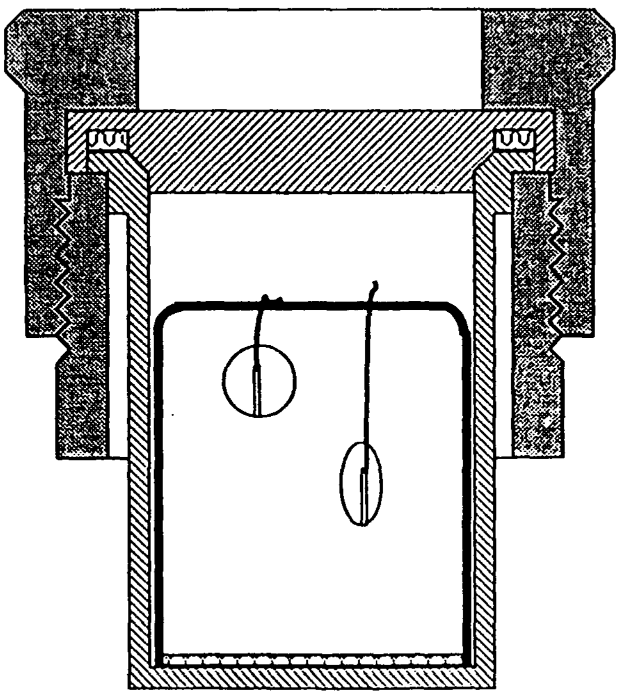
THE PRESENT TESTS ADDRESS

- CONDITIONS FOR STORAGE IN HUMID AIR
- "BOUNDING" CONDITION FOR RELEASE FROM A FLOODED BOREHOLE

EXPERIMENTAL

THE TEST CONSISTS OF TWO PARTS:

- **HYDRATION AGING**
  - SATURATED VAPOR
  - T < 200°C



- **LEACHING**
  - MCC-1 TYPE
  - GROUNDWATER
  - 90° C
  - SURFACE AREA TO VOLUME RATIO (SA/V) OF ~10 m^{-1}
  - 28 DAYS

EXAMPLE 1: VAPOR HYDRATION LEACH

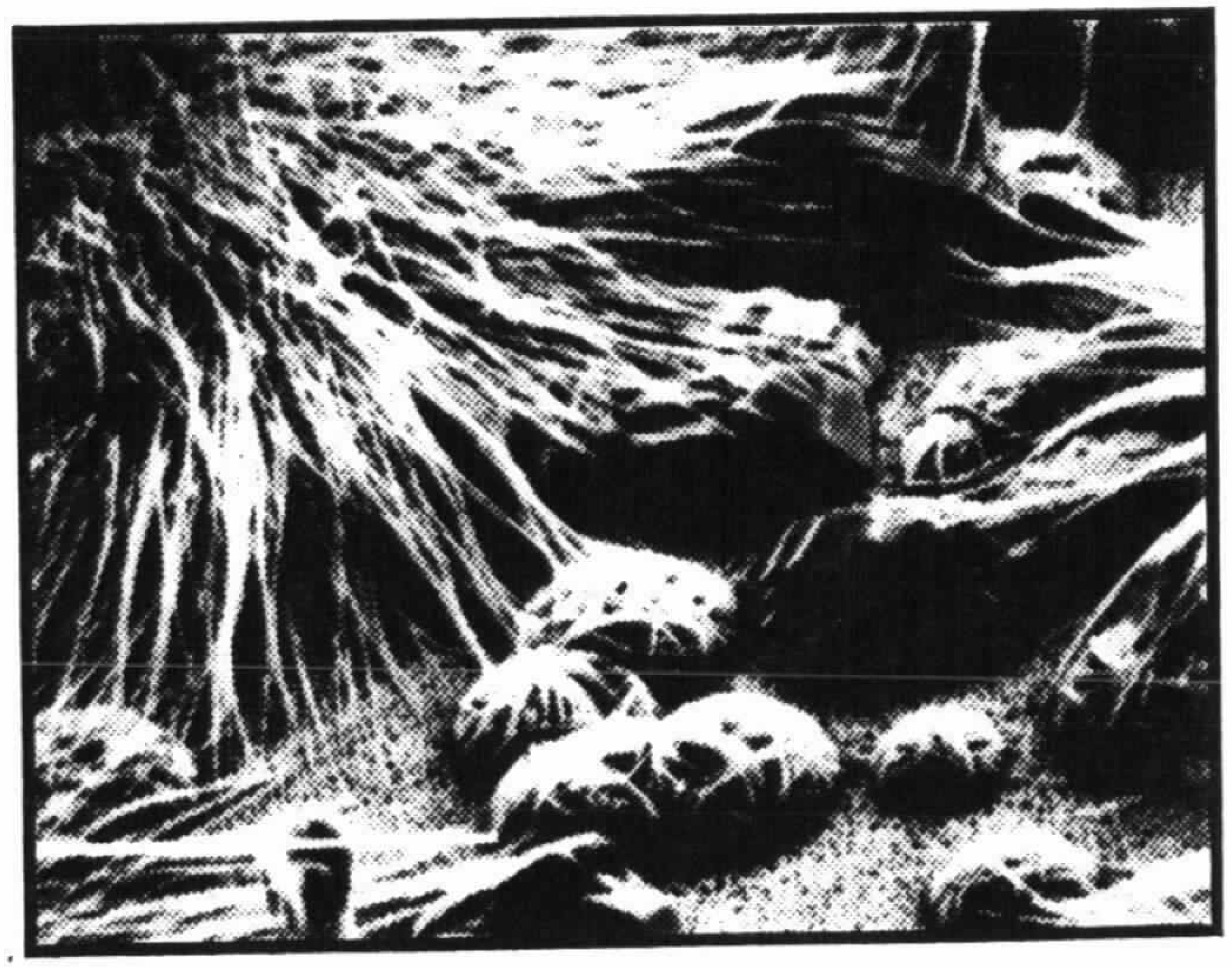
(CONTINUED)

IN THE REPOSITORY, THE HYDRATION AGING PROCESS MAY TAKE PLACE OVER HUNDREDS TO THOUSANDS OF YEARS. HOW DO WE ACCELERATE THE PROCESS IN THE LABORATORY?

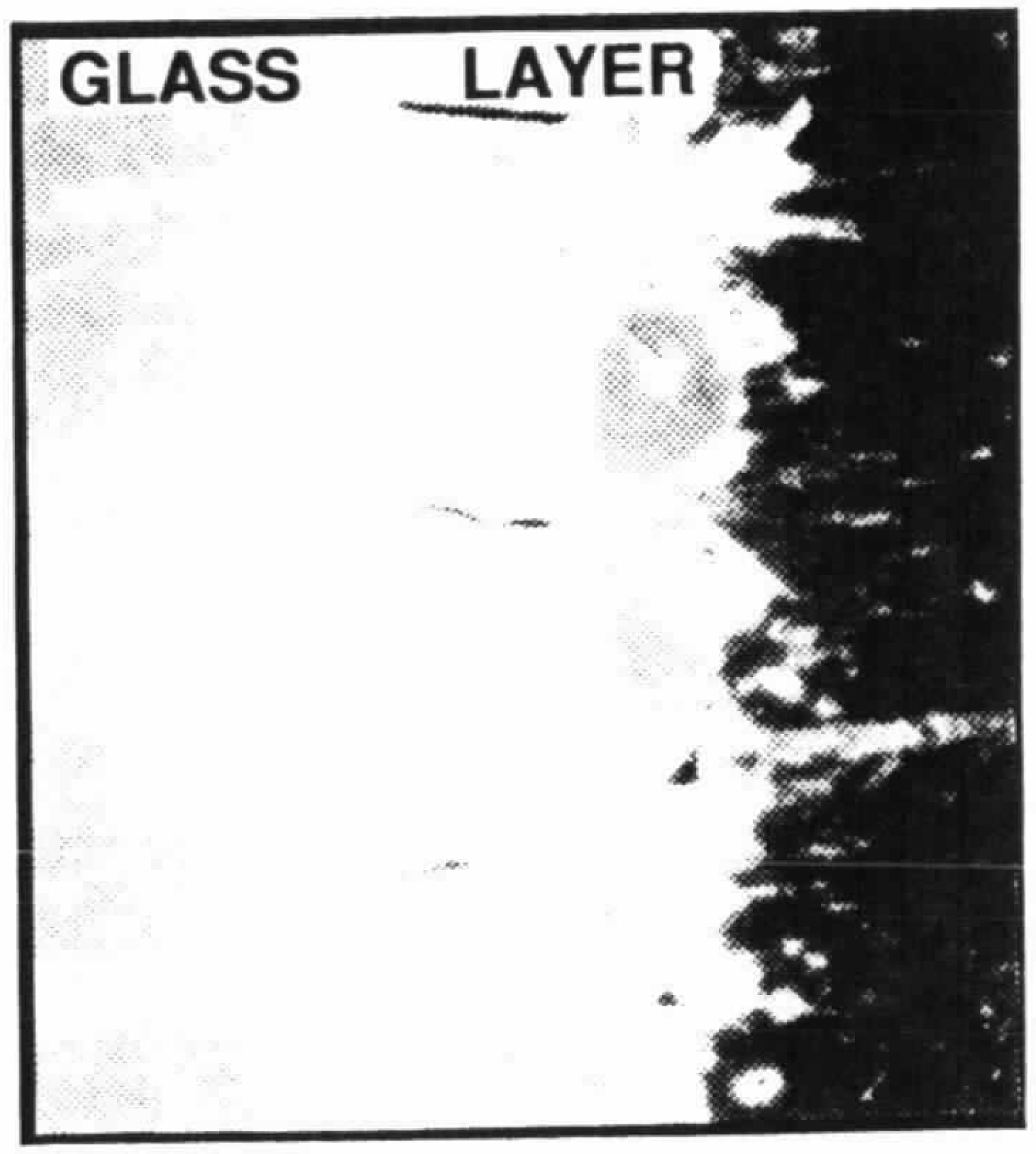
- TEMPERATURE INCREASES RATE
- LARGE SA/V PROMOTES NUCLEATION

HOW DO WE KNOW WHETHER THE ACCELERATION CONDITIONS CHANGE THE MECHANISM OF REACTION ? BY EXAMINING THE

SECONDARY PHASES



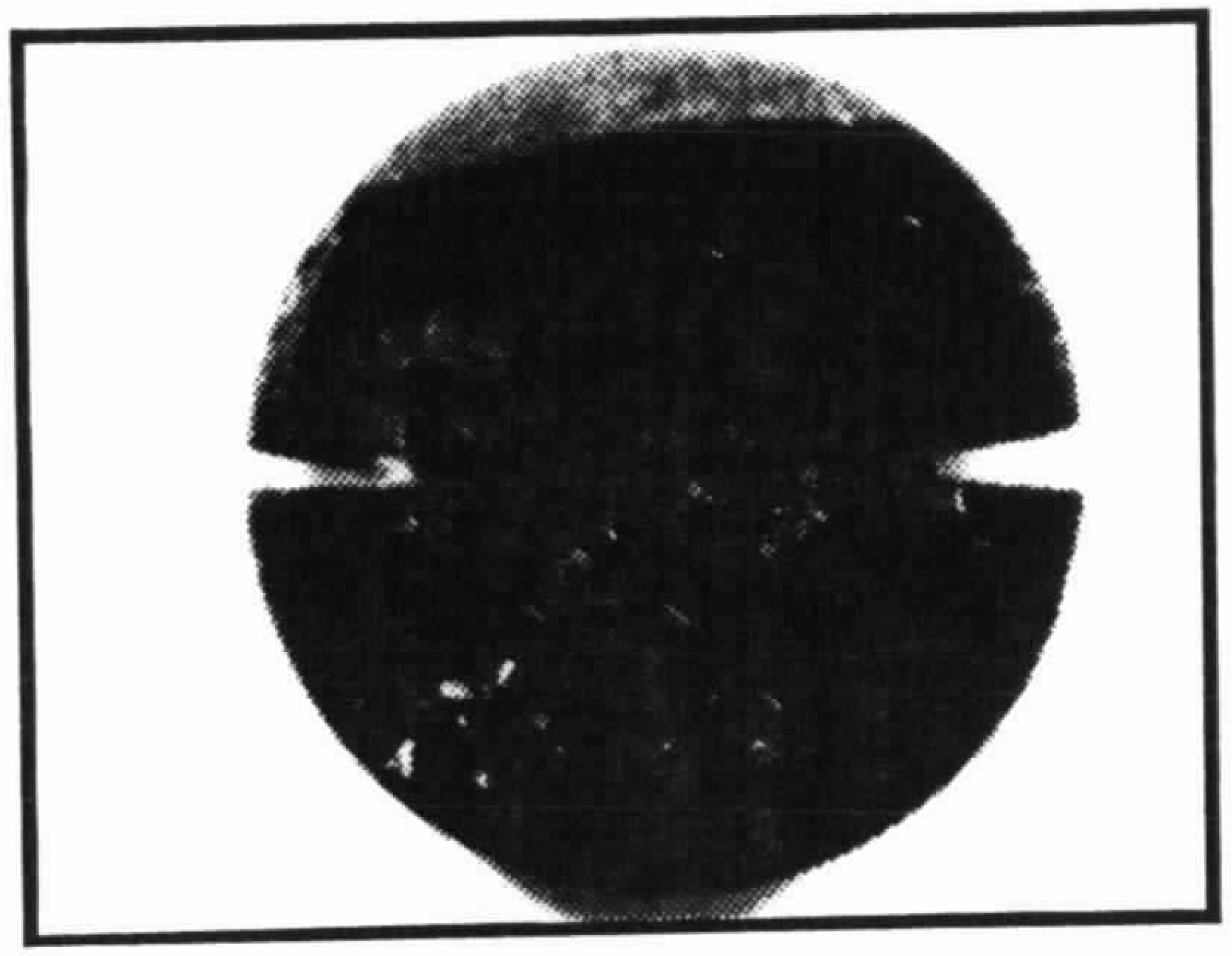
RATE KINETICS



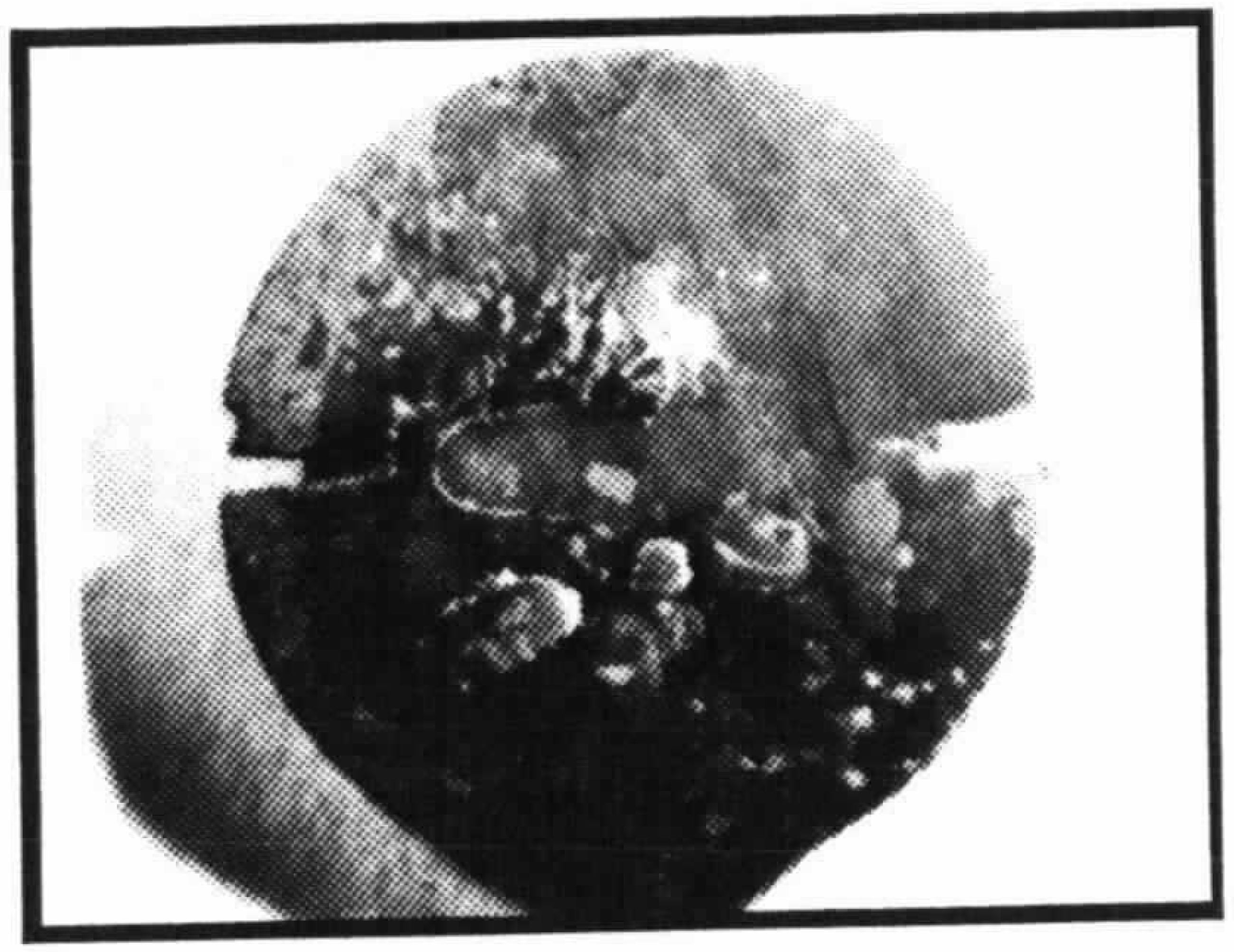
EXAMPLE 1: VAPOR HYDRATION LEACH

(CONTINUED)

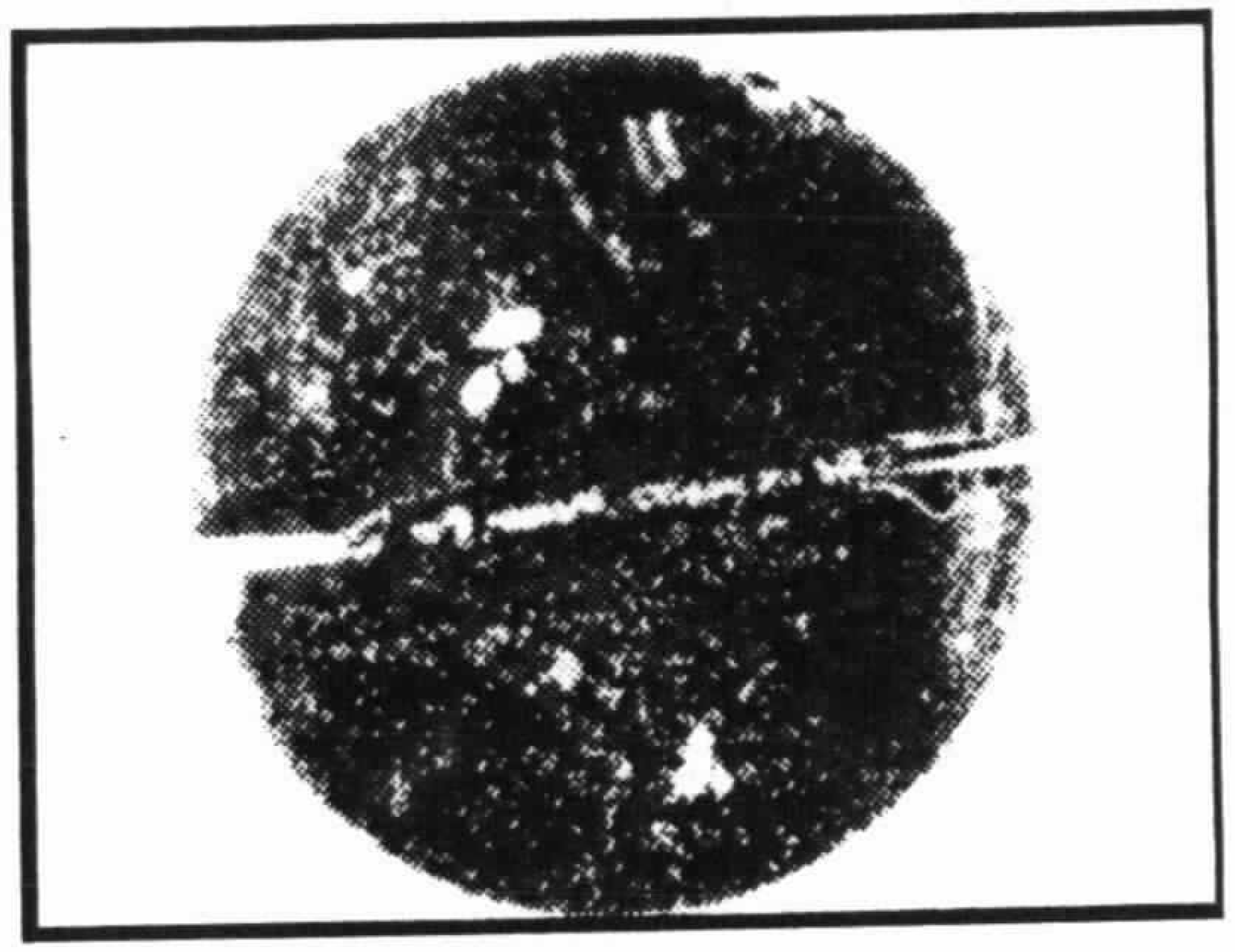
THREE DIFFERENT CONDITIONS OF VAPOR REACTION WERE USED TO AGE THE WASTE GLASSES



90° C



150° C

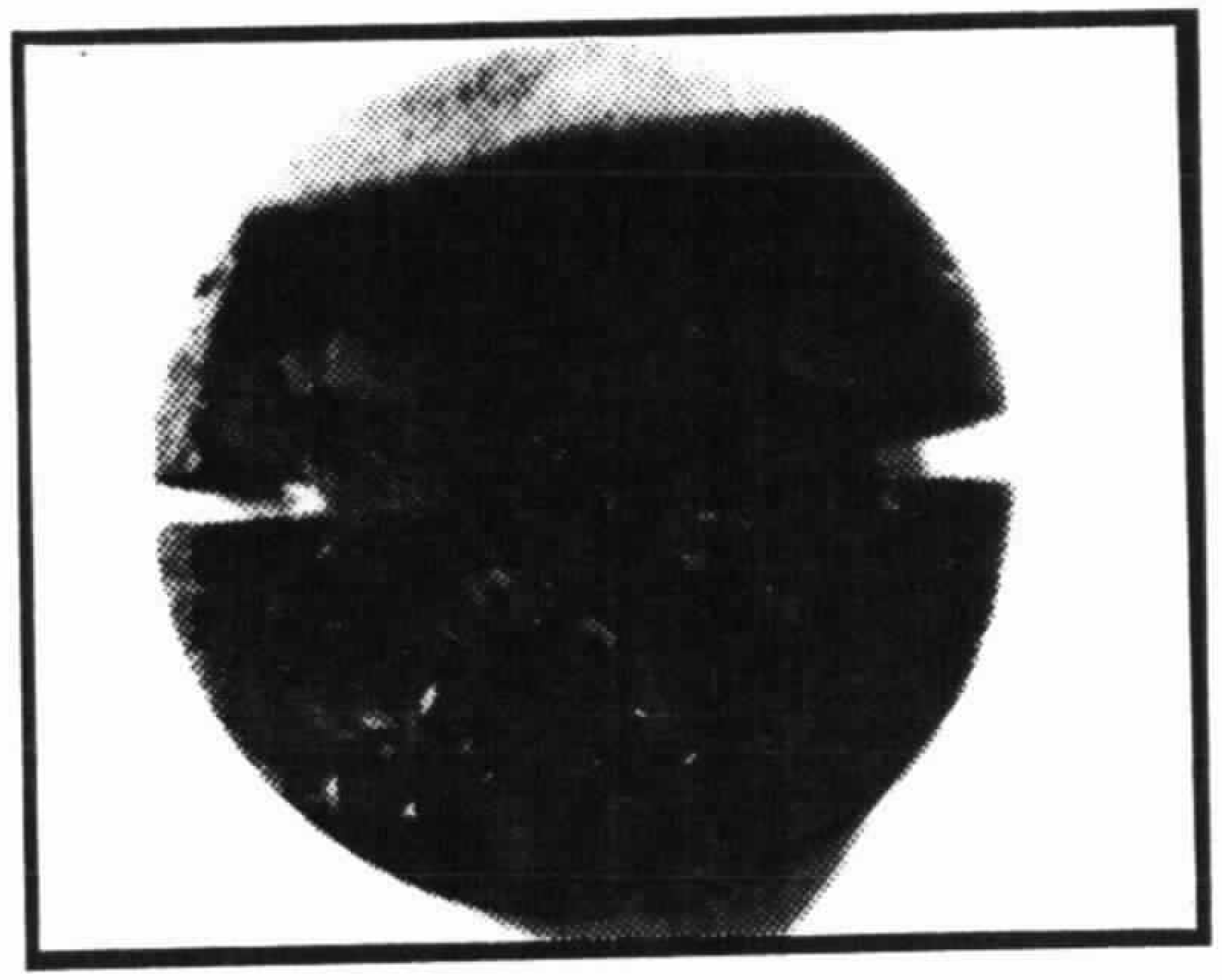


200° C

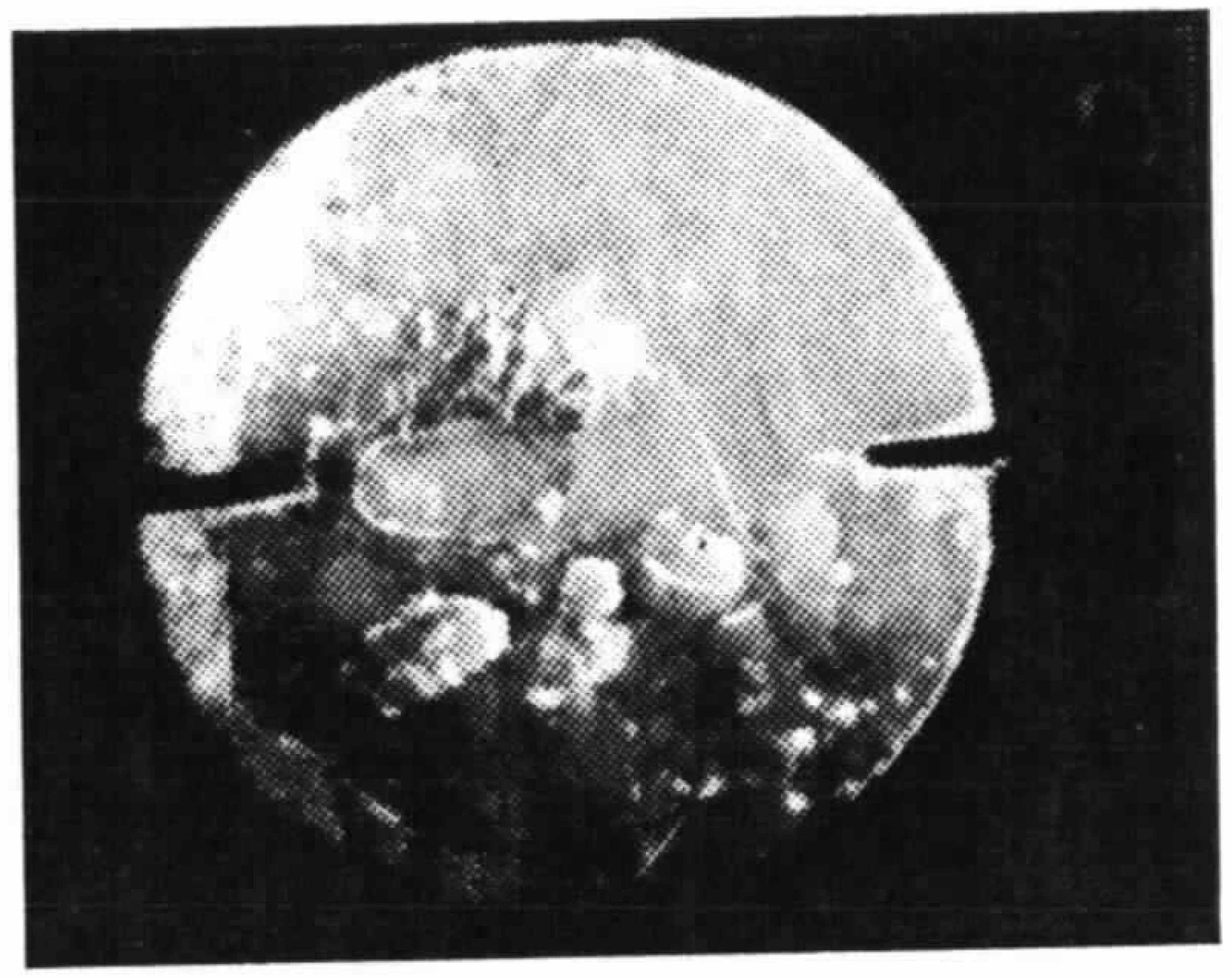
EXAMPLE 1: VAPOR HYDRATION LEACH

(CONTINUED)

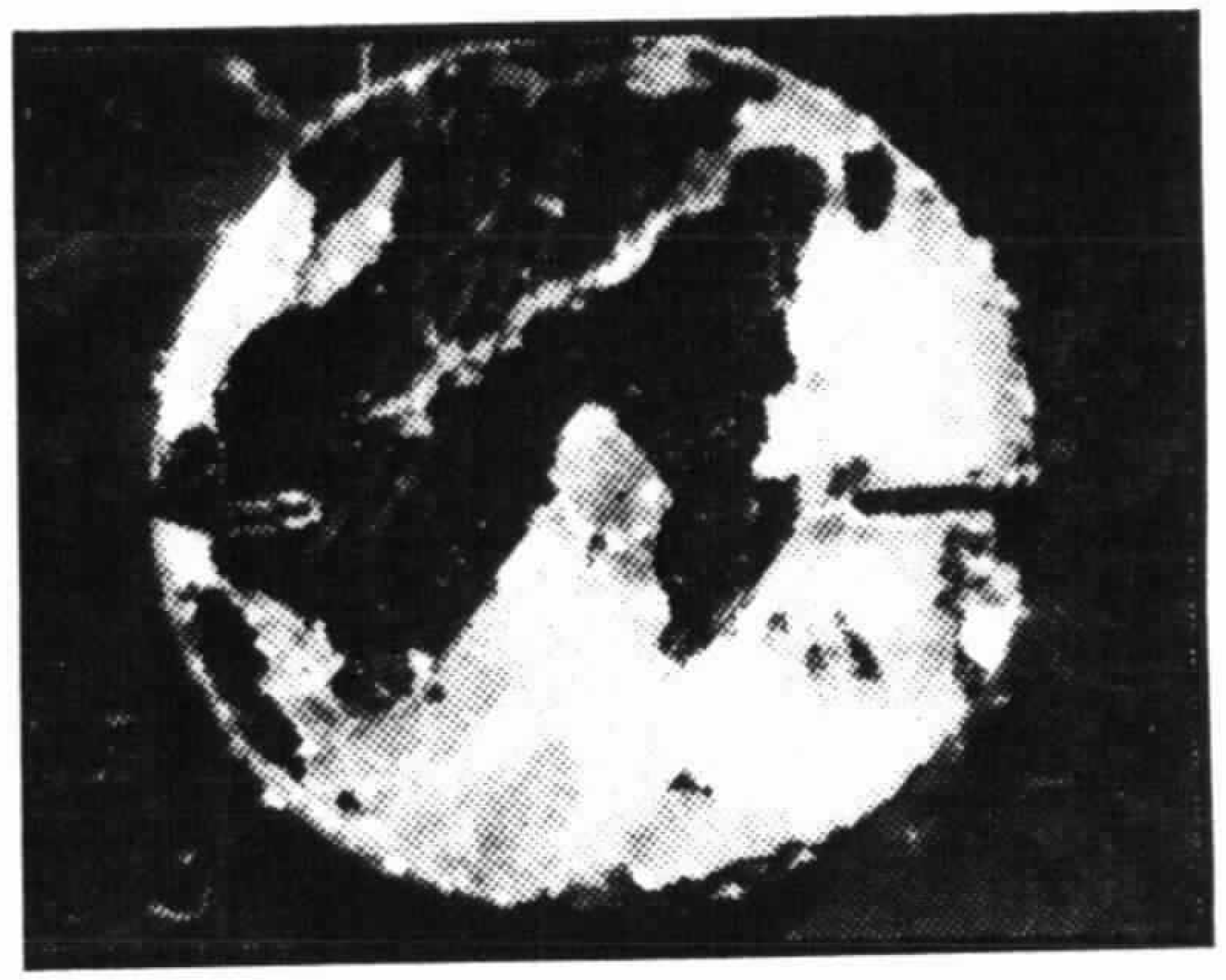
THE GLASSES WERE THEN LEACHED FOR 28 DAYS AT 90° C



LITTLE CHANGE



SLIGHT LAYER CRACKING



LAYER EXFOLIATION Ca-SILICATE DISSOLUTION

EXAMPLE 1: RESULTS/CONCLUSIONS

THE ACTINIDE RELEASE PATTERNS ARE SIGNIFICANT

- Pu AND Am RELEASE FROM THE GLASS IS INCREASED UP TO 2000x DUE TO LAYER SPALLATION FROM HYDRATED GLASS

- MOST OF THE ACTINIDE RELEASE IS NOT SOLUBILITY LIMITED (DISSOLVED IN SOLUTION) BUT IS ASSOCIATED WITH PARTICULATES (SUSPENDED IN SOLUTION)

IF THE LEACH TESTS WERE RUN FOR LONGER TIME, AND THE HYDRATED LAYER SPALLED OFF COMPLETELY, THE COMPARATIVE DIFFERENCES MAY INCREASE BY ANOTHER FACTOR OF 2

EXAMPLE 2: STATIC LEACHING/SURFACE ANALYTICAL STUDIES

AN EXAMPLE OF TESTING TO MEASURE RADIONUCLIDE RELEASE AND TO PROVIDE MECHANISTIC INTERPRETATION IN SUPPORT OF MODEL DEVELOPMENT IS STATIC LEACHING

GOAL

- PERFORM SIMPLE TESTS TO ESTABLISH REACTION PROCESS AND TO MEASURE RADIONUCLIDE DISTRIBUTION

THE PRESENT TESTS ADDRESS

- "BOUNDING" CONDITION FOR AMOUNT OF WATER CONTACT AND TEMPERATURE
- EXPECTED RANGE OF GLASS COMPOSITIONS

EXPERIMENTAL

THE TEST IS A SIMPLE BATCH TEST

- LEACHING
  - MCC-1 TYPE, 90°C, GROUNDWATER, SA/V OF 30 m^{-1}, TIME TO 4 YEARS
  - TWO GLASS COMPOSITIONS (SRL-131 AND SRL-165)

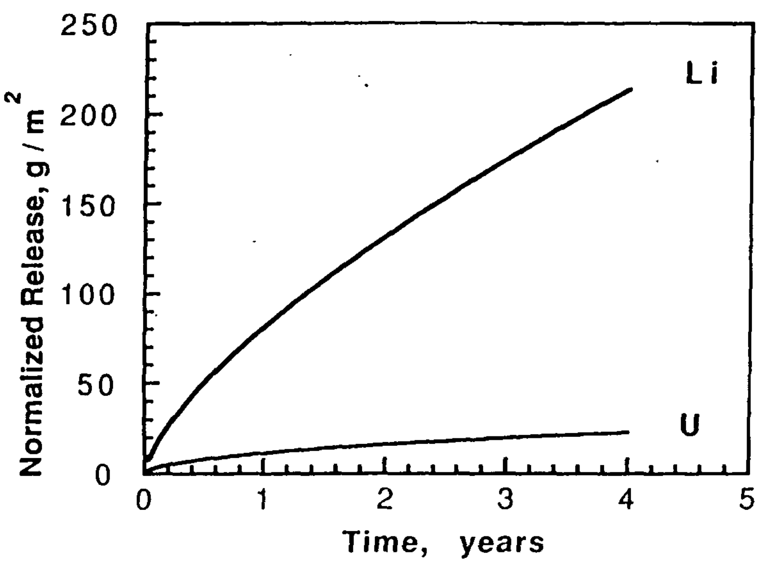
DETAILED ANALYSIS OF THE LAYER IS REQUIRED TO ESTABLISH THE REACTION MECHANISMS AND IDENTIFY REACTION PRODUCTS

- ANALYTICAL ELECTRON MICROSCOPY (AEM)
- SCANNING ELECTRON MICROSCOPY (SEM)
- SECONDARY ION MASS SPECTROSCOPY (SIMS)

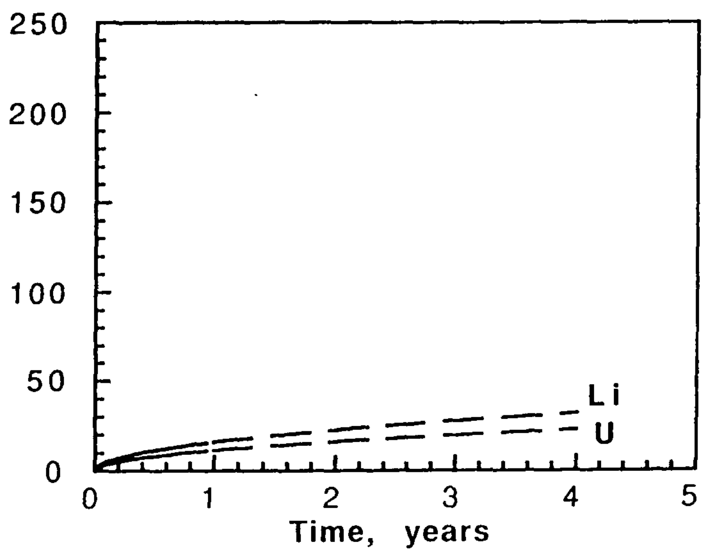
EXAMPLE 2: STATIC LEACHING/SURFACE ANALYTICAL STUDIES

SOLUTION ANALYSES INDICATE THE REACTION OF BOTH GLASSES SLOWS WITH TIME, BUT DOES THAT TELL THE WHOLE STORY?

131 GLASS



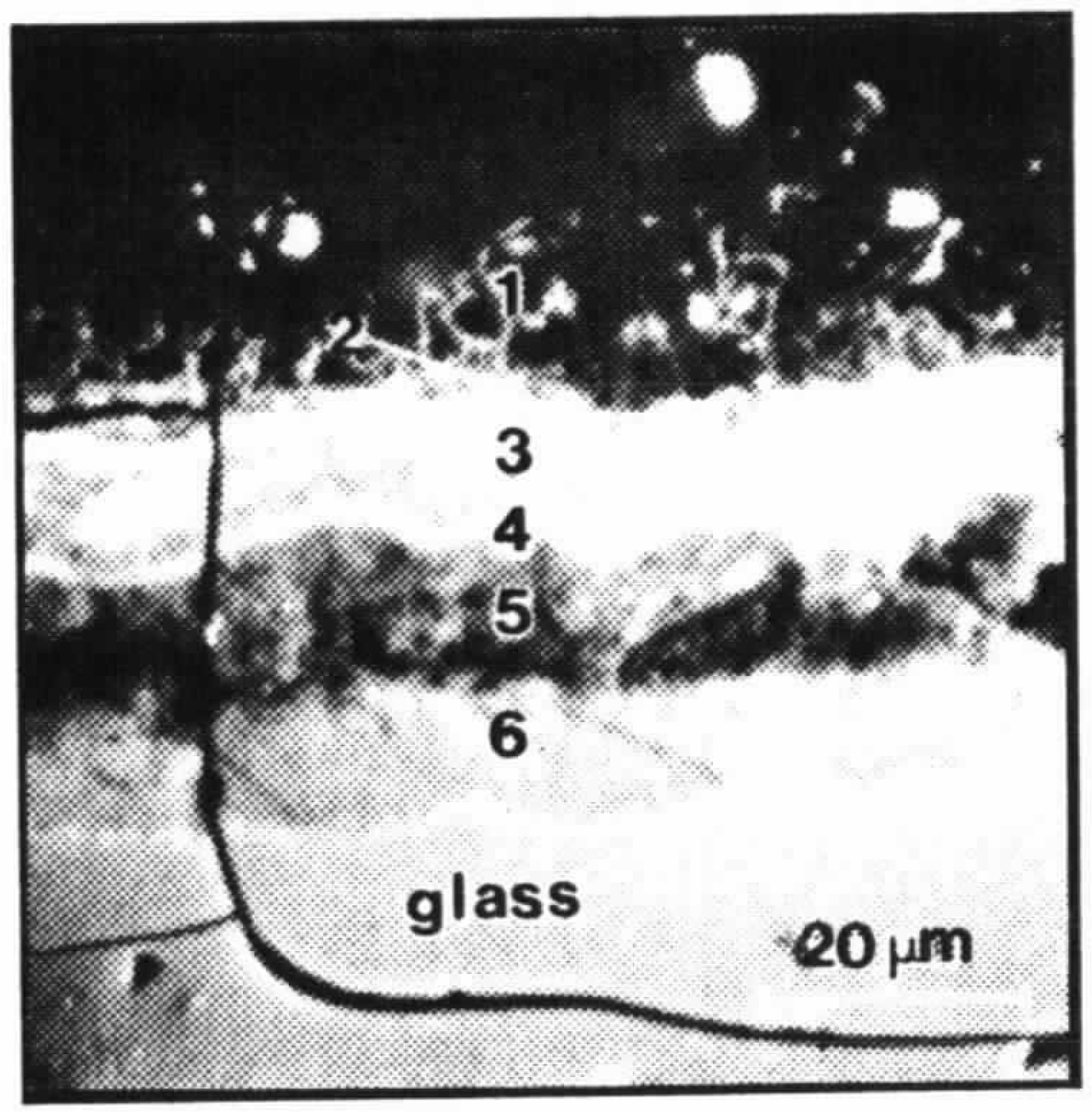
165 GLASS



NOTE: WHILE 131 GLASS REACTION IS FASTER THAN 165 GLASS, U RELEASE IS SIMILAR FOR BOTH GLASSES

131 GLASS

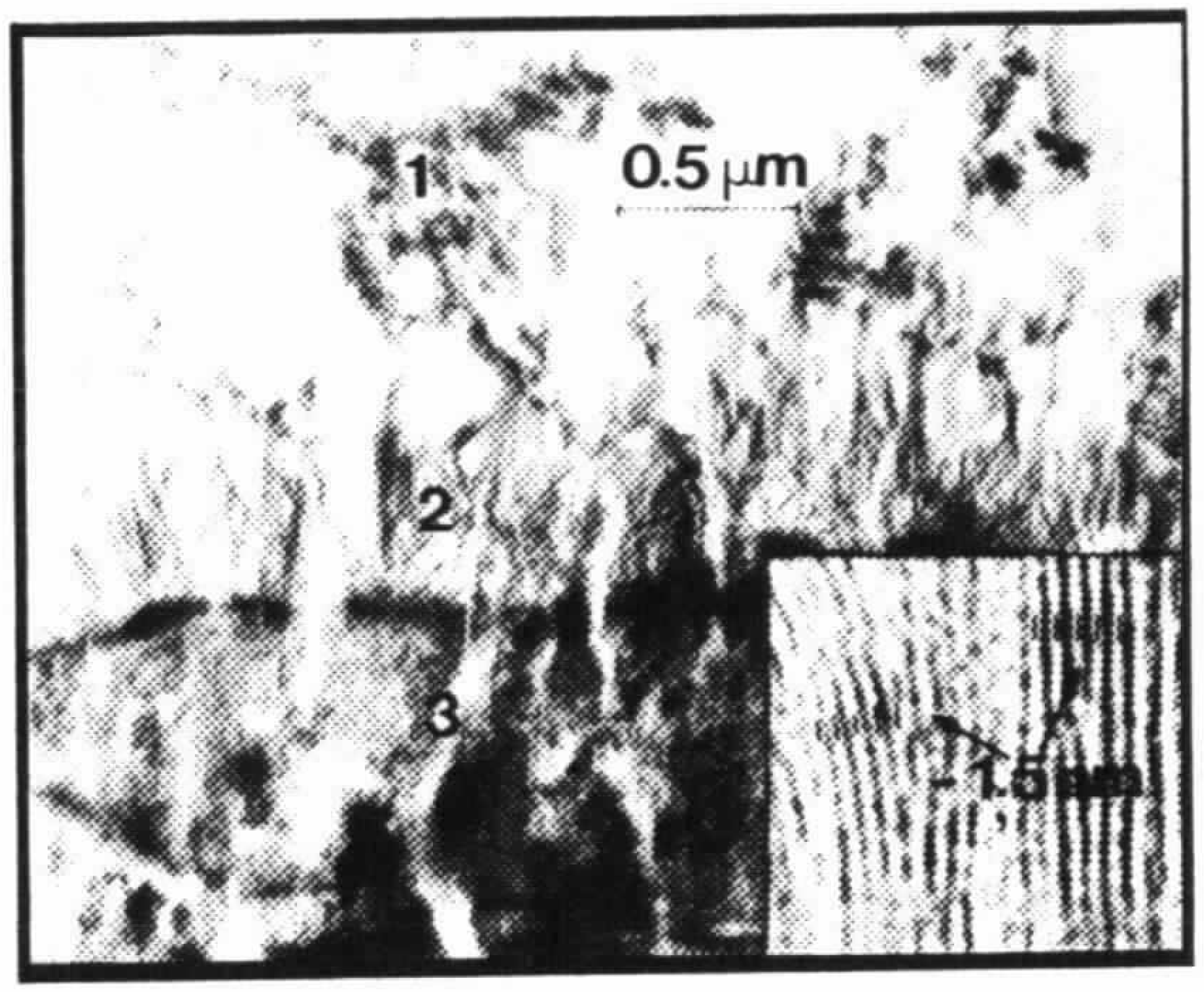
THE STRUCTURE OF THE REACTED GLASS PROVIDES ESSENTIAL INFORMATION TO ELUCIDATE THE MECHANISM OF GLASS REACTION



PRECIPITATION

IN SITU
RESTRUCTURING

REACTION FRONT



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2
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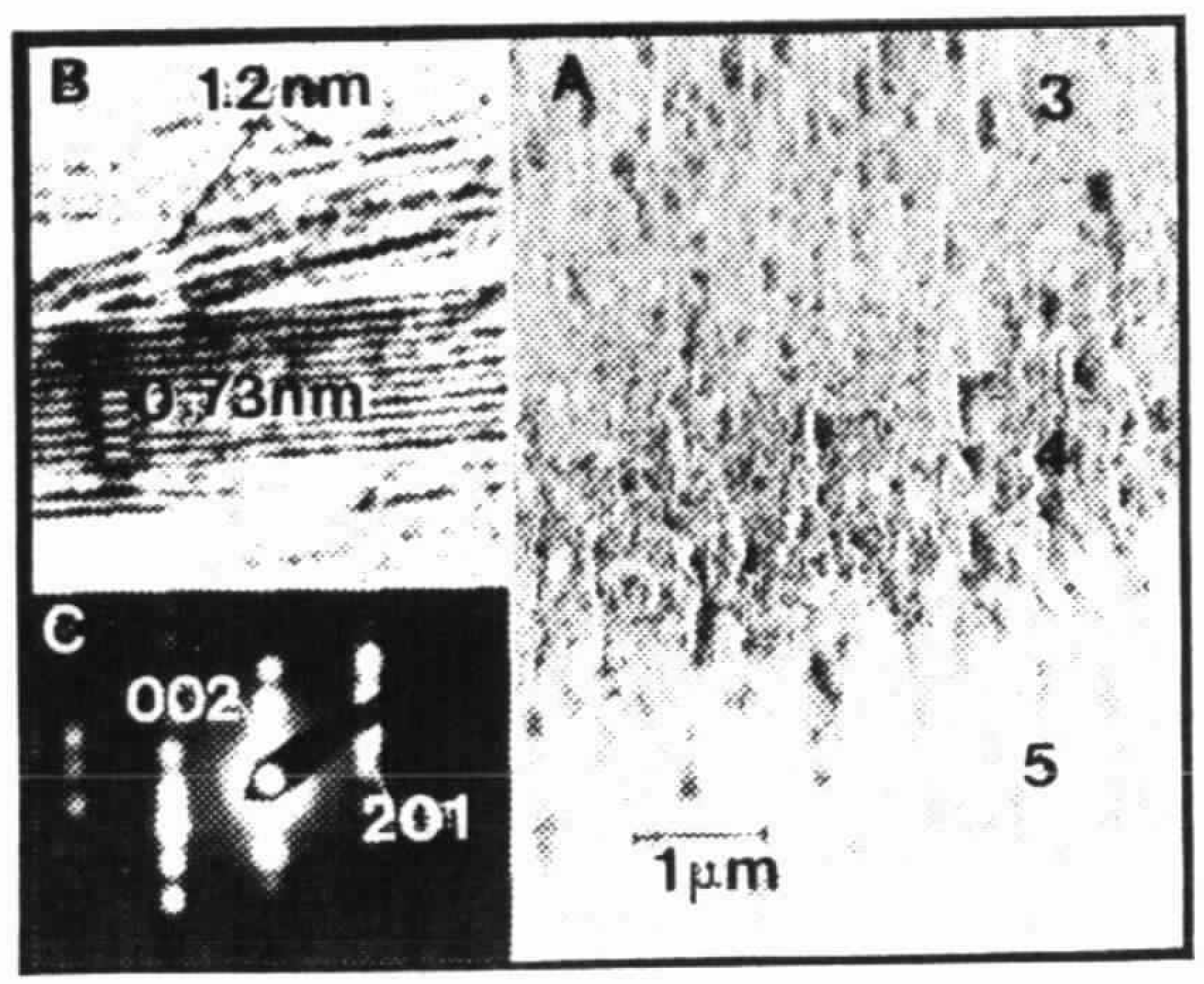

3
4
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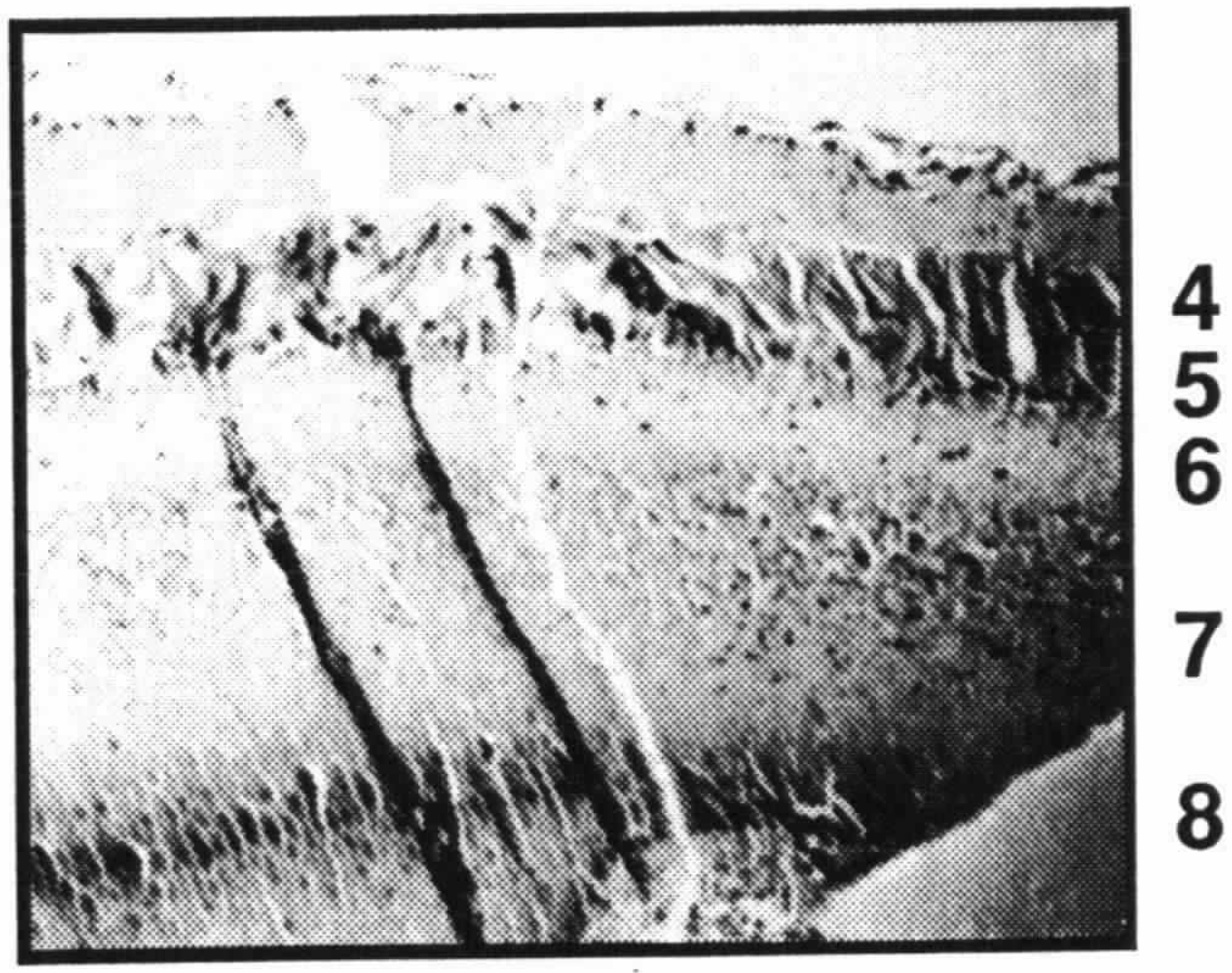
AEM TECHNIQUES INCLUDE:

- LATTICE IMAGING
- MICRO DIFFRACTION
- NANOPROBE COMPOSITION

WHAT HAPPENS TO THE URANIUM IN 131 GLASS?

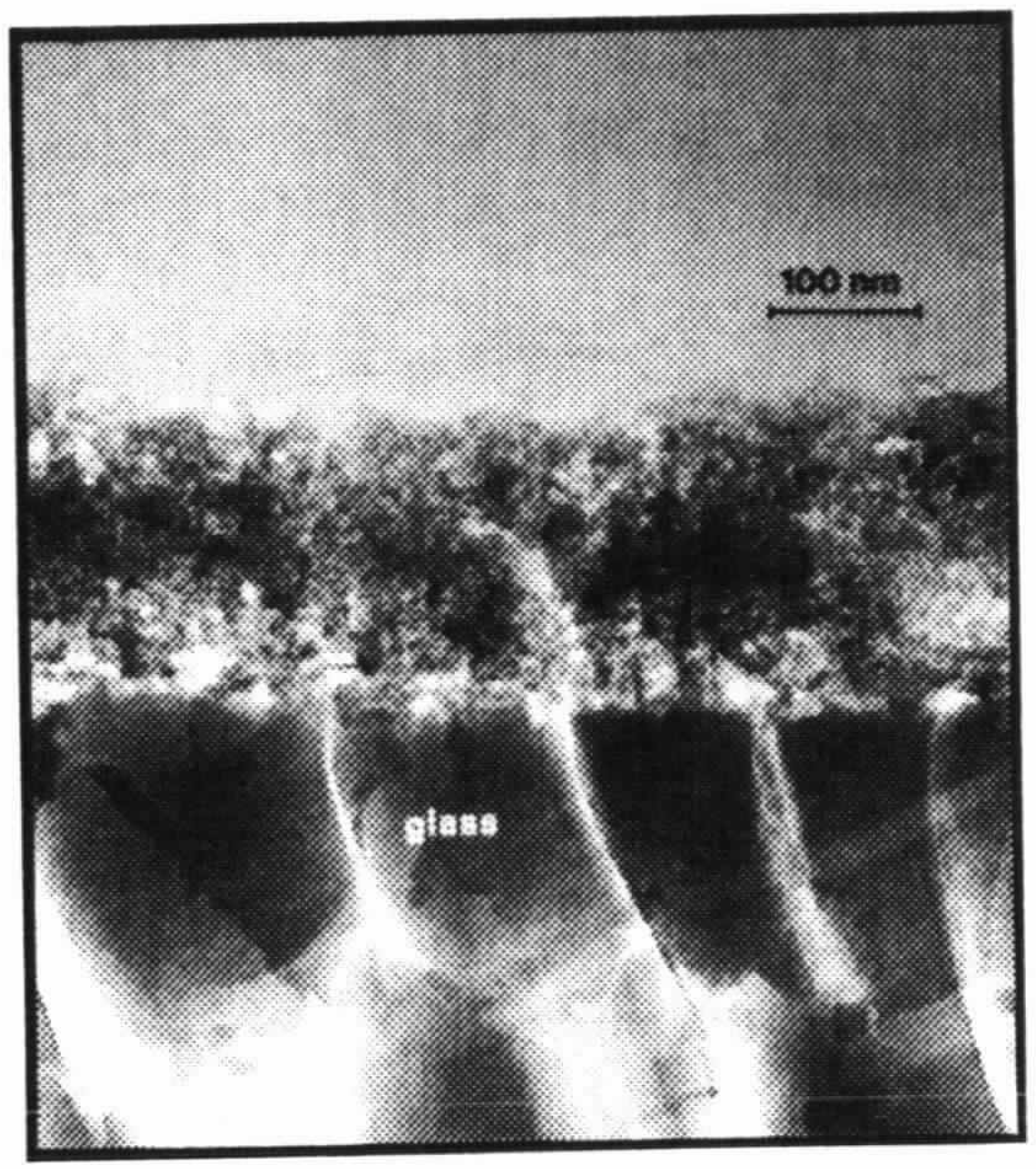


IT IS DISPERSED THROUGHOUT THE LAYERS

IT HAS CRYSTALLIZED AS AGGREGATES OF NANOMETER-SIZED GRAINS, A U-Ti OXYHYDROXIDE

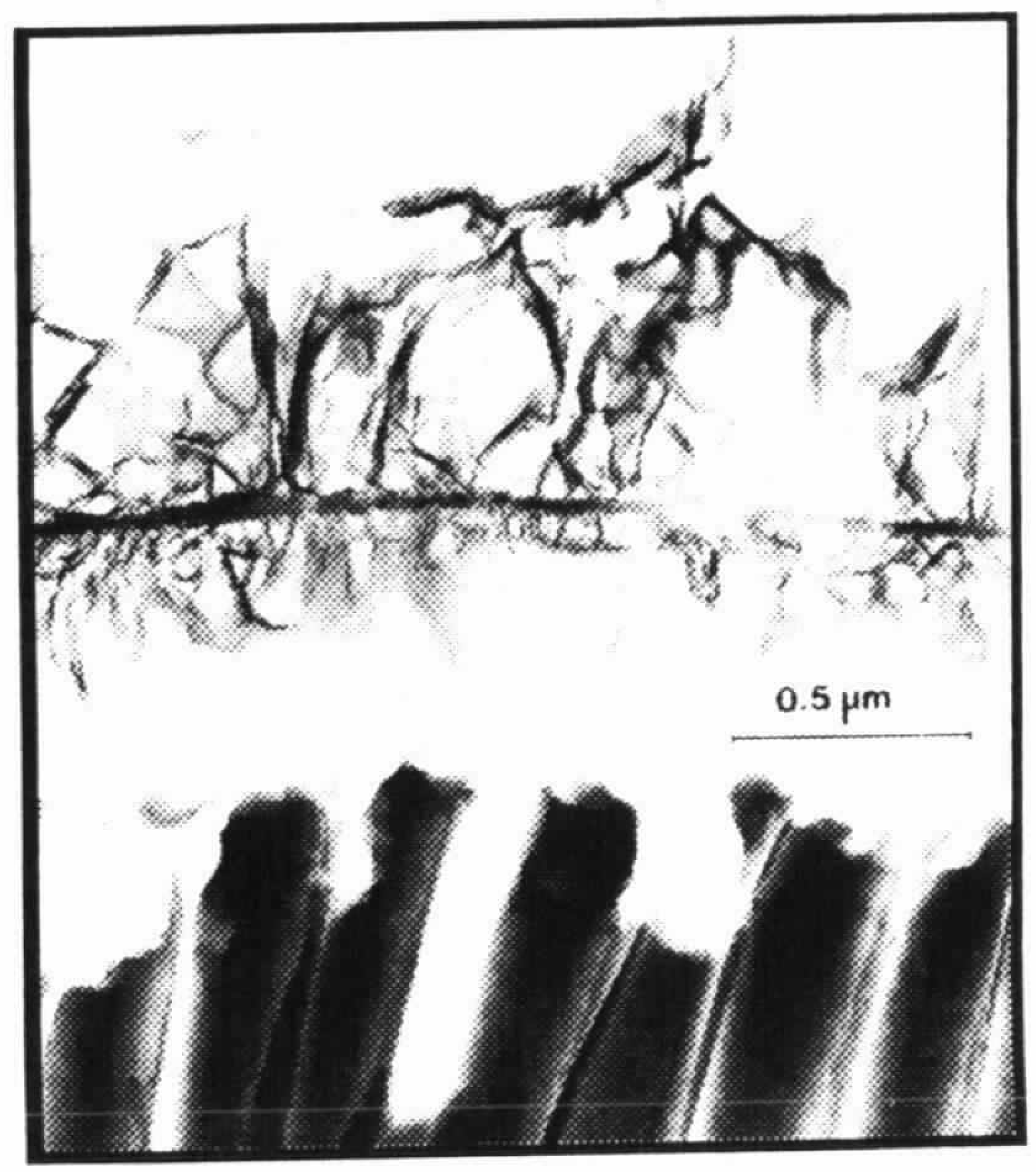
165 GLASS

- TEMPORAL TRENDS IN LAYER GROWTH INDICATE A DIFFERENT ALTERATION LAYER STRUCTURE THAN FOR 131 GLASS
- THE HYDROLYSIS AND <u>IN SITU</u> RESTRUCTURING NOW RESULT IN A LAYER NOT ATTACHED TO THE GLASS SURFACE



56 DAYS

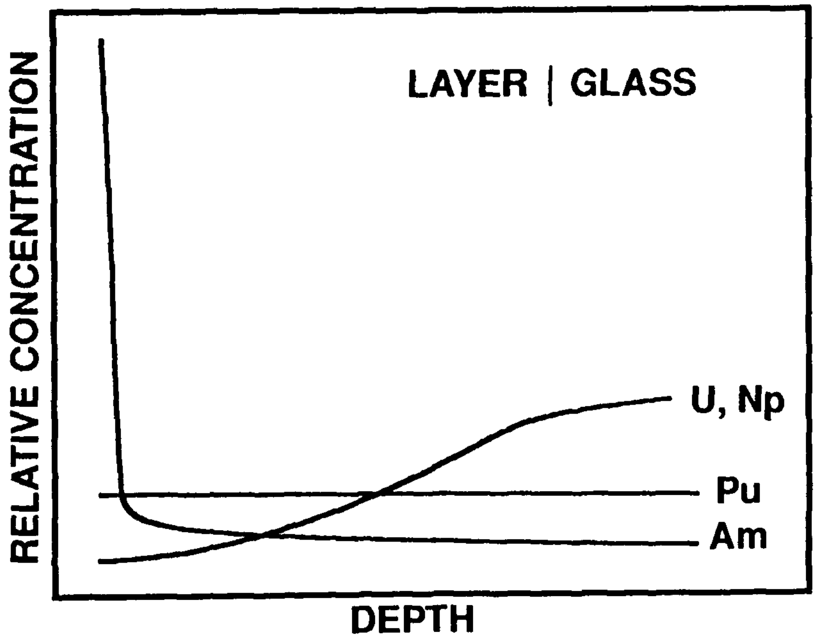
91 DAYS



280 DAYS

WHAT HAPPENS TO U, Np, Am, AND Pu IN 165 GLASS?

SIMS PROFILE



U AND Np ARE LEACHED FROM THE GLASS AND RELEASED TO SOLUTION

Am REPRECIPITATES ON THE OUTER LAYER SURFACE AS ETCHING OCCURS

Pu IS RELEASED TO SOLUTION ONLY VIA ETCHING AND IS STRONGLY SORBED TO THE METAL COMPONENTS OF THE TEST

EXAMPLE 2: RESULTS/CONCLUSIONS

- LAYER STRUCTURE PROVIDES MECHANISTIC INSIGHT AND PHASE IDENTIFICATION TO SUPPORT MODELING
- DISTRIBUTION OF RADIONUCLIDES BETWEEN SOLUTION AND SOLID PHASES CAN BE ACCOUNTED FOR DURING PA
- LONG-TERM TESTS ARE REQUIRED TO INCREASE THE CONFIDENCE LEVEL OF THE RESULTS

EXAMPLE 3: DRIP TESTS

AN EXAMPLE OF SITE-RELEVANT TESTING COMBINED WITH RADIONUCLIDE RELEASE AND MECHANISTIC INTERPRETATION IS THE DRIP TEST

GOAL

- IDENTIFY IMPORTANT MATERIALS INTERACTIONS THAT AFFECT GLASS REACTION AND RADIONUCLIDE RELEASE
- PROVIDE DATA FOR MATURE MODEL VALIDATION

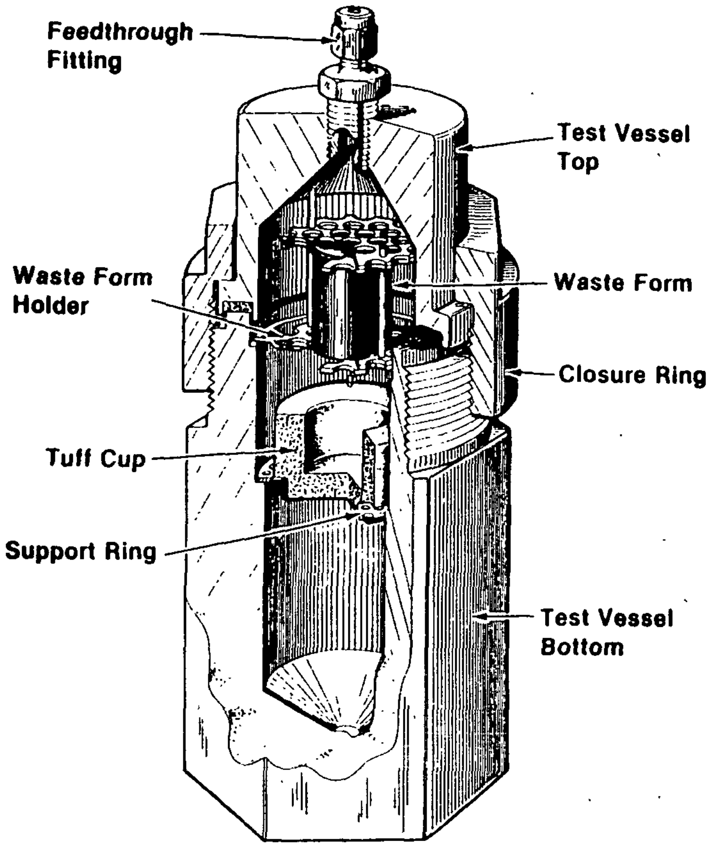
THE DRIP TEST ADDRESSES

- A POTPOURRI OF WATER/GLASS CONTACT MODES
- METAL/GLASS INTERACTIONS

EXPERIMENTAL

DRIP TESTS HAVE BEEN DEVELOPED TO SIMULATE THE CONDITIONS FOR THE REPOSITORY

Test Vessel



EXAMPLE 2: RESULTS/CONCLUSIONS

DRIP TESTS HAVE BEEN CONDUCTED FOR PERIODS NOW SURPASSING FIVE YEARS. A RANGE OF GLASS REACTION RATES HAS BEEN OBSERVED

- FASTEST RELEASE - 20x INCREASE DUE TO SPALLATION OF LAYER
- INTERMEDIATE RELEASE - 2x INCREASE DUE TO SENSITIZATION OF 304L
- SLOWEST RELEASE - 2x DECREASE DUE TO EVAPORATION
- RADIONUCLIDES SORB TO METAL CORROSION PRODUCTS

SUMMARY

SITE-SPECIFIC DEGRADATION TESTS HAVE

- IDENTIFIED PROCESSES AND MECHANISMS THAT OCCUR UNDER REPOSITORY-RELEVANT CONDITIONS - AEM IS PARTICULARLY USEFUL BUT DATA ARE PRELIMINARY

- IDENTIFIED MATERIALS INTERACTIONS - QUANTIFICATION IS REQUIRED

- MONITORED RADIONUCLIDE RELEASE AND DISTRIBUTION, AND DEVELOPED METHODOLOGY TO TRACK RADIONUCLIDES - NEED TO BE APPLIED TO A FULL RANGE OF TESTS

- PROVIDED DATA FOR MODEL VALIDATION - MUST PERFORM LONG-TERM TESTS