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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: SPENT FUEL OXIDATION

PRESENTER: R.E. EINZIGER

PRESENTER'S TITLE AND ORGANIZATION: MANAGER, MATERIALS AND CHEMICALS SYSTEM PERFORMANCE SECTION
BATTELLE, PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

PRESENTER'S TELEPHONE NUMBER: (509) 376-3453

AUGUST 28-29, 1990

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TOPICS

- REVIEW OF SPENT FUEL OXIDATION RESPONSE
- OXIDATION TESTING OF SPENT FUEL (SF)
  - THERMOGRAVIMETRIC ANALYSES (TGA) TESTING
  - DRYBATH TESTING

OXIDATION AND THE TUFF REPOSITORY

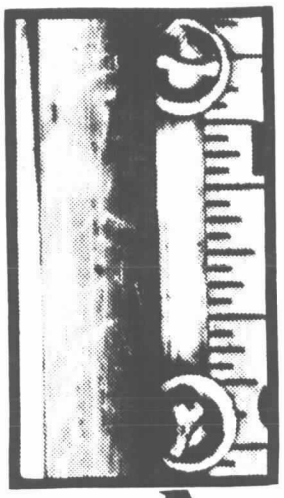
- <0.1% OF RODS WILL ENTER REPOSITORY BREACHED AND BE AVAILABLE FOR OXIDATION WHEN CONTAINER IS COMPROMISED
- CLADDING CORROSION MAY LEAD TO ADDITIONAL BREACHES
- PHASE DIAGRAM INDICATES THAT BELOW 150° C, UO_3 IS THE STABLE OXIDATION STATE
- OXIDATION EFFECTS
  - CHANGE PHASE OF FUEL
  - OPEN ADDITIONAL INTERNAL FUEL SURFACES TO LEACHANT
  - RELEASE TRAPPED FISSION GAS
  - SPLIT CLADDING, CHANGE PATH FOR RADIOISOTOPE RELEASE

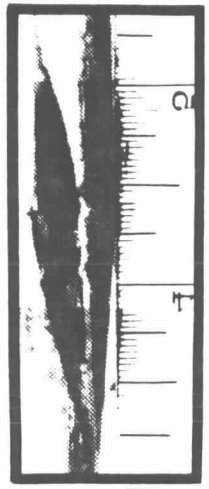
QUESTION?

Δ (O/M) AS A FUNCTION OF TIME

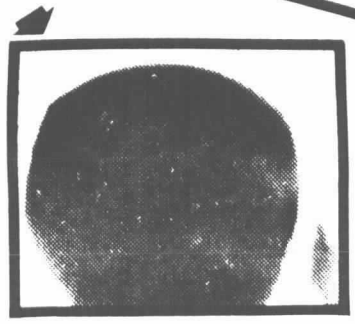
OXIDATION PROGRESSION

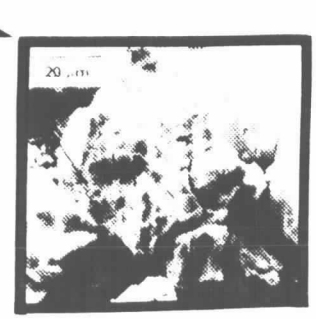
ROD BEHAVIOR





$UO_2 \rightarrow U_4O_9 \rightarrow U_3O_7 \rightarrow U_3O_8 \rightarrow UO_3 \rightarrow UO_3 \bullet 2H_2O$





FRAGMENT BEHAVIOR

BASIS FOR YMP SF OXIDATION TESTING

- OXIDATION BEHAVIOR OF IRRADIATED FUEL COULD NOT BE INFERRED FROM BEHAVIOR OF UNIRRADIATED FUEL
- TEMPERATURE WAS AN IMPORTANT VARIABLE
- OXIDATION RATE WAS LOWERED WITH INCREASING BURNUP
- EFFECT OF MOISTURE UNKNOWN
- LOW-TEMPERATURE OXIDATION DATA WAS NOT AVAILABLE

SF OXIDATION PROGRAM

PURPOSE

- DETERMINE MECHANISMS AND RATES OF OXIDATION
- DETERMINE THE EFFECTS ON OXIDATION RATE DUE TO
  - TEMPERATURE
  - BURNUP
  - MOISTURE
- INPUT DATA TO THE MODELING OF OXIDATION
- PROVIDE OXIDIZED SAMPLES FOR LEACH TESTING

SF OXIDATION PROGRAM

(CONTINUED)

TESTS

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**
  - SINGLE SAMPLES
  - MECHANISTIC
  - SHORT TERM (<3000 hr)
  - CONTINUOUS WEIGHINGS
- **DRYBATH**
  - LONG-TERM (>2 yr)
  - MANY SAMPLES
  - REPEATABILITY
  - MODEL TESTING
  - VERY LOW TEMPERATURES
  - INTERIM WEIGHINGS
- **SAMPLE EXAMINATIONS**
  - CERAMOGRAPHY
  - TRANSMISSION ELECTRON MICROSCOPY (TEM)
  - X-RAY DIFFRACTION (XRD)
  - ION MICROPROBE
  - FISSION GAS ANALYSIS

TGA TEST PARAMETERS

- **FUEL TYPES**
  - PWR, 27 GWD/MTU (TURKEY POINT, ATM-101)
  - BWR, ~32 GWD/MTU (COOPER, ATM-105)
- **TEMPERATURE**
  - 140° to 225° C
- **DEW POINT**
  - 14.5° C (TWO TESTS at -70° C)
- **DURATION**
  - 356 to 2633h
- **FINAL O/M**
  - 2.02 (830h at 140° C)
  - 2.39 (427h at 225° C)

TGA DATA ANALYSIS

ASSUMPTIONS

1. UNIFORM SPHERICAL GRAINS
2. GRAINS OXIDIZE INDEPENDENTLY
3. PLANAR OXIDATION FRONT

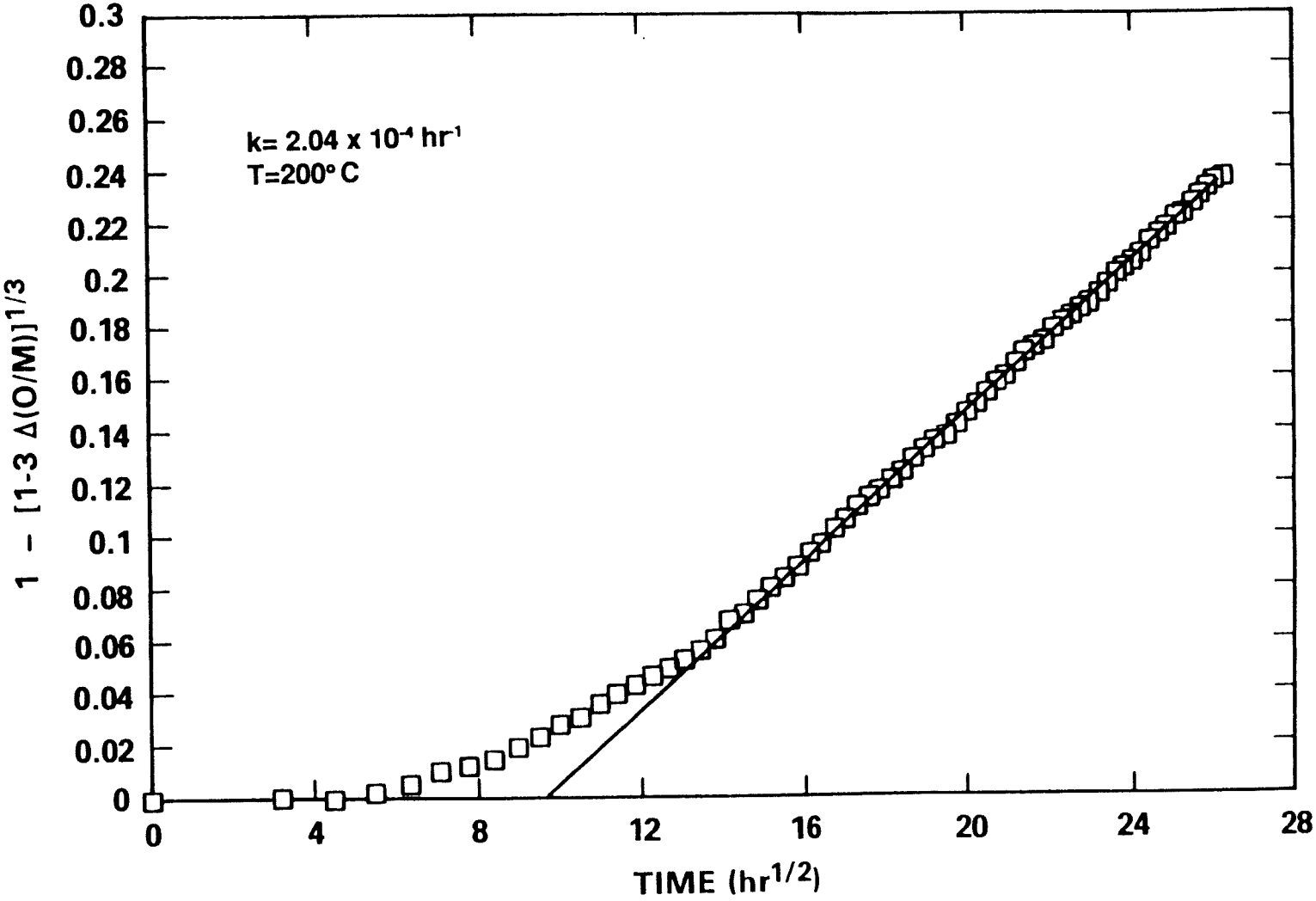
DESCRIPTION

$$1 - [1 - 3\,\Delta(O/M)]^{1/3} = (k't)^{1/2}$$

WHERE

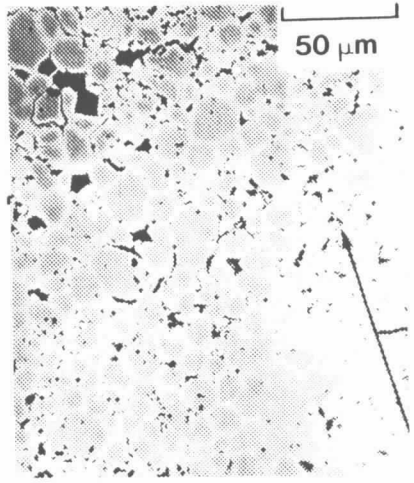
Δ (O/M)	=	CHANGE IN OXYGEN TO METAL RATIO
k'	=	OXIDATION RATE CONSTANT
t	=	OXIDATION TIME

FITTING TGA DATA TO OBTAIN RATE CONSTANT



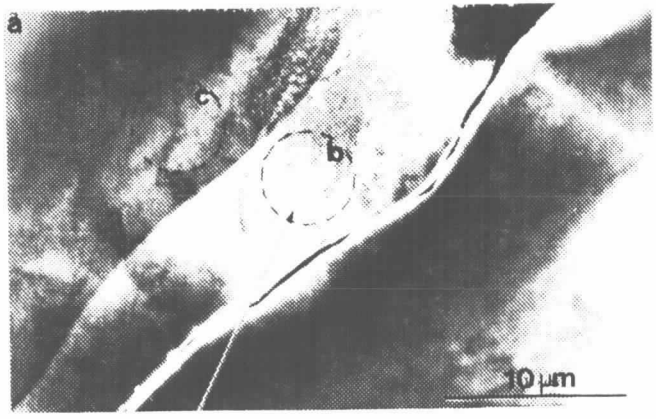
OXIDATION MECHANISM

1. OXIDATION OF THE GRAIN BOUNDARY

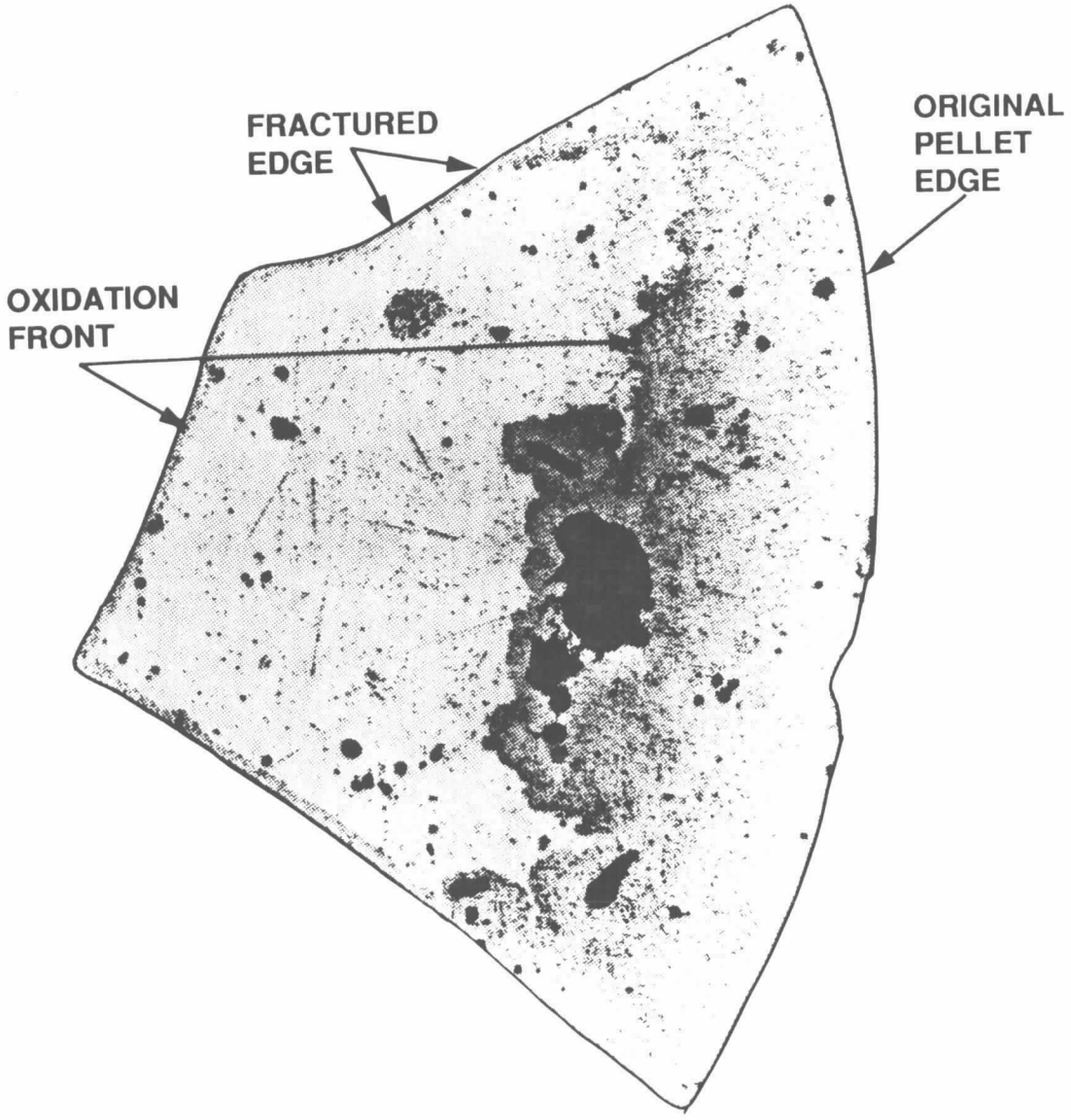


2. RAPID TRANSPORT PATH TO INDIVIDUAL GRAINS

3. OXIDATION FRONT PENETRATES GRAINS



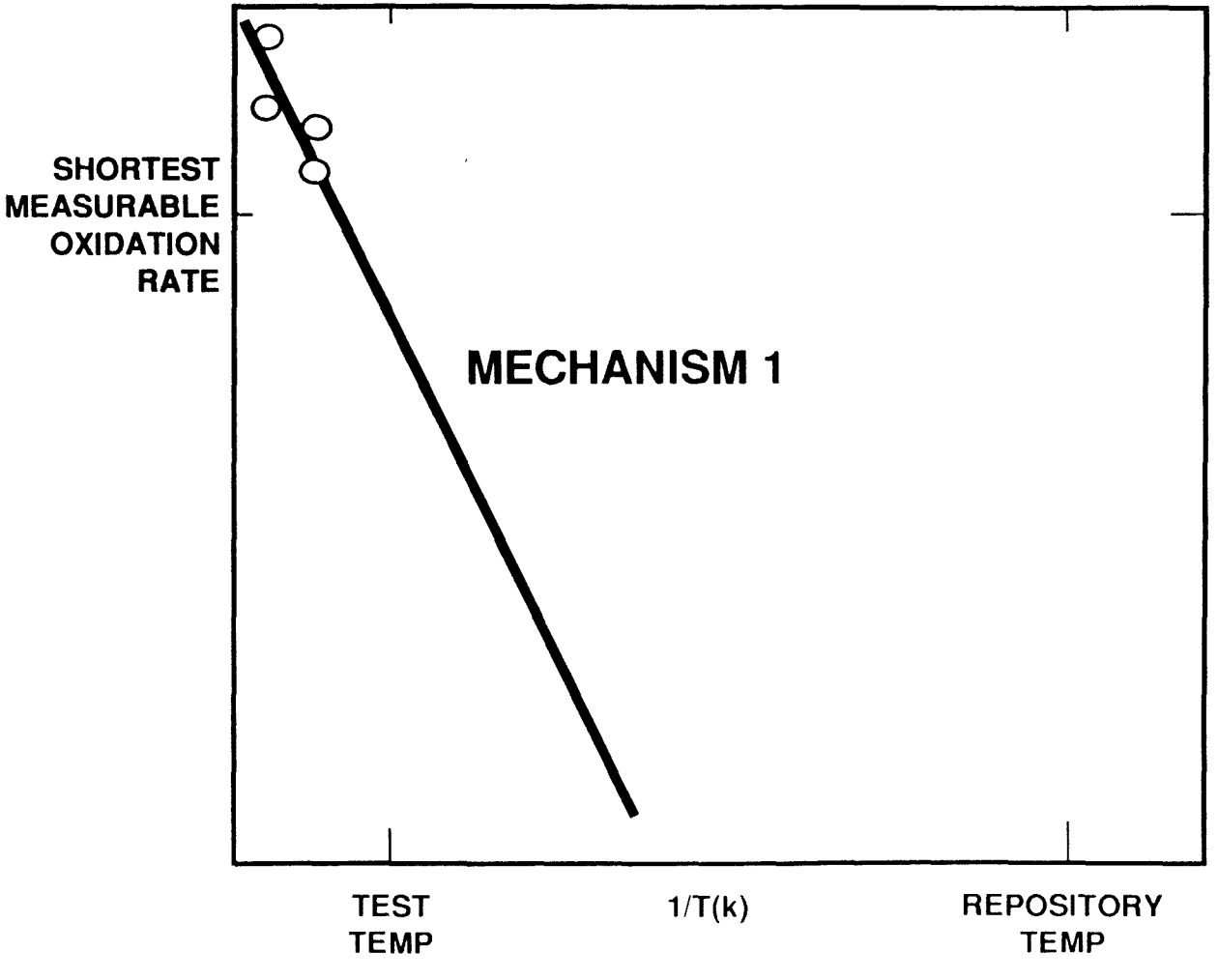
VARIATION OF OXIDATION WITH POSITION IN FRAGMENT



TGA OXIDATION SUMMARY

- SF OXIDATION IS A TWO-STEP PROCESS OCCURRING BY OXYGEN PENETRATION OF THE GRAIN BOUNDARIES FOLLOWED BY OXIDATION OF THE BULK GRAINS
- THE OXIDATION RATE HAS A STRONG ARRHENIUS DEPENDENCE ON TEMPERATURE. THE ACTIVATION ENERGY IS INDEPENDENT OF THE STAGE IN THE OXIDATION PROCESS
- MOISTURE LEVEL HAS VERY LITTLE EFFECT, IF ANY, ON THE OXIDATION RATE
- OXIDATION OCCURS MORE RAPIDLY AT THE PELLET SURFACE
- THE MAJORITY OF THE MECHANISTIC DATA COMES FROM THE MICROSTRUCTURAL EXAMINATION OF THE OXIDIZED FUEL
- CURRENTLY TGA APPARATUS IS IDLE, AND EXAMINATION OF SAMPLES AND ANALYSES OF DATA TO DETERMINE EFFECT OF GRAIN SIZE AND FUEL TYPE ON OXIDATION RATE AND GAS RELEASE HAS BEEN DEFERRED

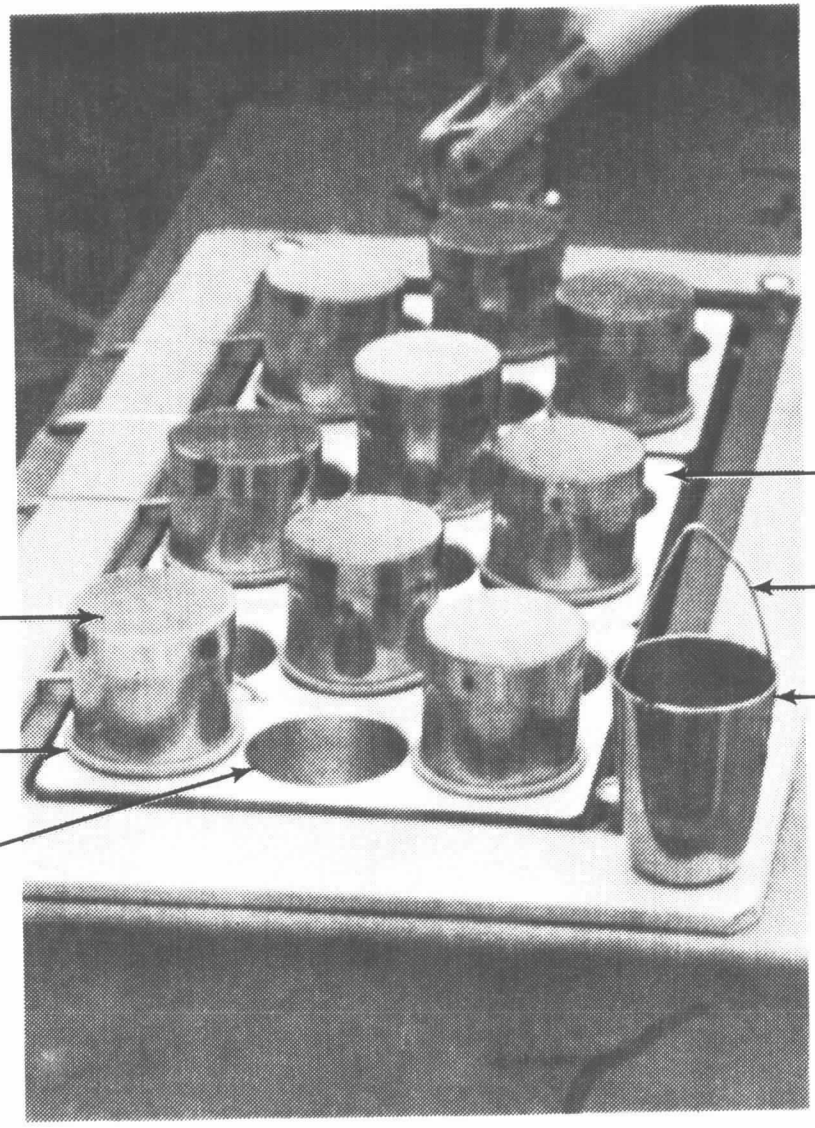
EXTRAPOLATION OF HIGH TEMPERATURE OXIDATION DATA



DRYBATH TEST PARAMETERS

- **FUEL TYPES**
  - TURKEY POINT PWR, 27 GWD/MTU (50 SAMPLES)
  - COOPER BWR, 32 GWD/MTU (30 SAMPLES)
  - CALVERT CLIFFS PWR, 44 GWD/MTU (27 SAMPLES)
  - CALVERT CLIFFS PWR, 46 GWD/MTU - HIGH FISSION GAS RELEASE (27 SAMPLES)
- **TEMPERATURE**
  - 175°, 130°, 110° C
- **DEW POINT**
  - +80°, -55° C
- **CURRENT DURATION**
  - UP to 25,000h
- **CURRENT O/M**
  - $\leq$ 2.38

DRYBATH SAMPLE CRUCIBLES AND COVERS



DRYBATH SF OXIDATION SUMMARY

- TESTS HAVE RUN UP TO 25k HRS WITH Δ (O/M) AS HIGH AS 0.38
- OXIDATION OF SF REPRODUCIBLE TO $\pm$10%
- REASONABLE AGREEMENT BETWEEN RATE CONSTANTS OBTAINED IN SHORT-TERM TGA TESTS AND LONG-TERM DRYBATH TESTS. RATE CONSTANTS HAVE ARRHENIUS BEHAVIOR
- FINER GRAINED BWR FUEL APPEARS TO OXIDIZE FASTER THAN PWR FUEL UNDER ALL TEMPERATURE AND ATMOSPHERIC MOISTURE CONDITIONS STUDIED
- EFFECT OF ATMOSPHERIC MOISTURE ON THE OXIDATION RATE IS STILL UNCERTAIN
- TAILORED FRAGMENT SHAPE SAMPLES OF HIGH BURNUP LOW GAS RELEASE, AND HIGH BURNUP HIGH GAS RELEASE FUEL ARE BEING ADDED TO THE DRYBATHS TO ACCOMODATE THE CURRENT MODELING NEEDS
- CURRENTLY ONLY LONG-TERM DRYBATH OXIDATION IS BEING CONDUCTED; LIMITED SAMPLE EXAMINATION AND DATA ANALYSES ARE BEING DONE