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

NUCLEAR WASTE TECHNICAL REVIEW BOARD FULL BOARD MEETING

SUBJECT: OXIDATION TESTING OF SPENT FUEL

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Oxidation Progression

Why Study Spent Fuel Oxidation?

- Small fraction (< 0.1%) of rods will enter repository breached and be available for oxidation when container is compromised

- Cladding corrosion may lead to additional breaches

- High temperature data indicate that low-density U_3O_8 can form, destroying fuel and cladding

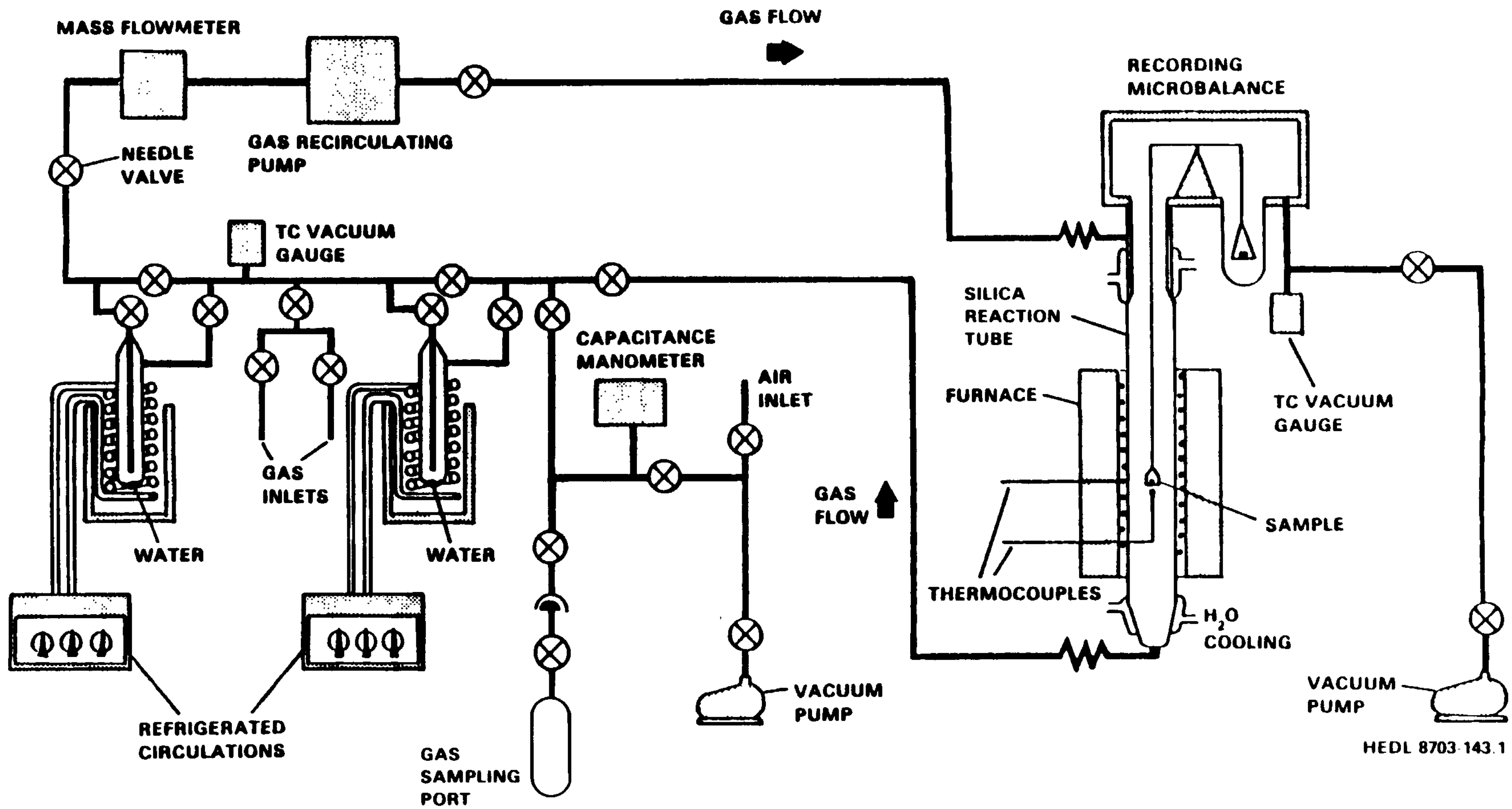
- Four oxidation effects:
  - Change phase of fuel
  - Open additional internal fuel surfaces to leachant
  - Release trapped fission gas
  - Split cladding; change path for radioisotope release

Question?
Δ(O/M) as a function of time, temperature, and atmosphere

Basis for YMP Spent Fuel Oxidation Testing from Early Work

- Temperature was an important variable
- Effect of atmospheric moisture and burnup is uncertain
- Low-temperature oxidation data were not available
- Assumed UO_2 and spent fuel had similar oxidation behavior

TGA Apparatus



TGA Oxidation Summary

- Different oxidation behavior in unirradiated UO_2
- Spent fuel oxidation is a two-step process: oxygen penetration of the grain boundaries followed by oxidation of the bulk grains
- Arrhenius dependence on temperature. The activation energy is consistent with O_2 diffusion into UO_2.
- Moisture level has little effect
- Oxidation more rapid at the pellet surface
- The majority of the mechanistic data comes from the microstructural examination of the oxidized fuel

Oxidation Mechanism

UO_2 Fuel Oxidation in Air (200°C)

Dry-Bath Oxidation Program

- To provide rate data for oxidation model
- Determine long-term oxidation behavior
- Source of fuel for leach testing

Sample Crucibles and Covers

Test Variables

Temperature: 195°, 175°, 130°, 110°C

Dew Points: -55, +80°C

Sample Configuration: As-irradiated fragments
pulverized fuel

Fuels: HB Robinson PWR (ATM-101)
Turkey Point PWR
Cooper BWR (ATM-105)
Calvert Cliffs PWR (ATM-103, -104, -106)

Grain Size Range: 5 to 30 μm

Burnup Range: 25 to 48 GWd/MTU

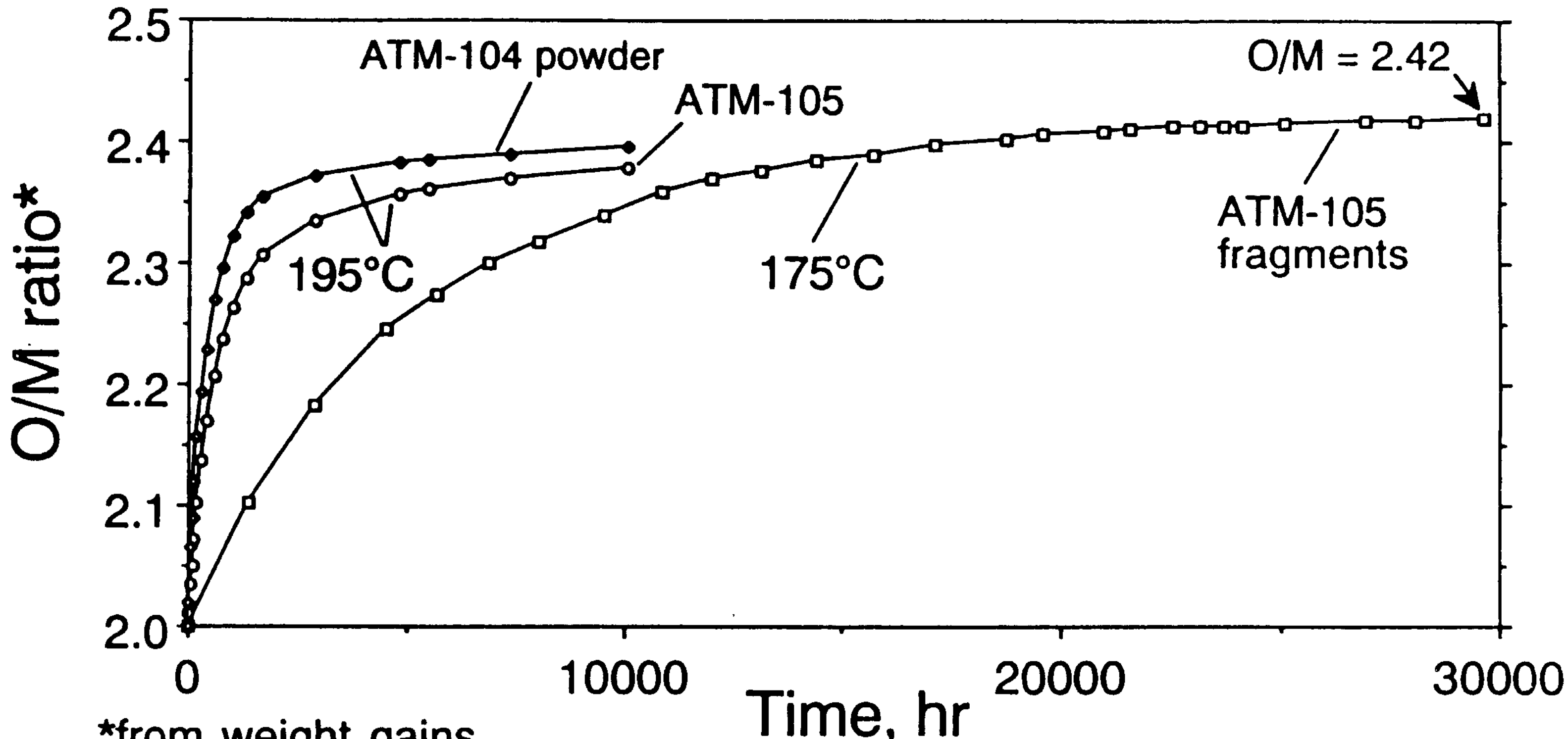
FGR Range: 0.1% to 18%

Current Test Times: Up to 40 kh (5.0 yr)

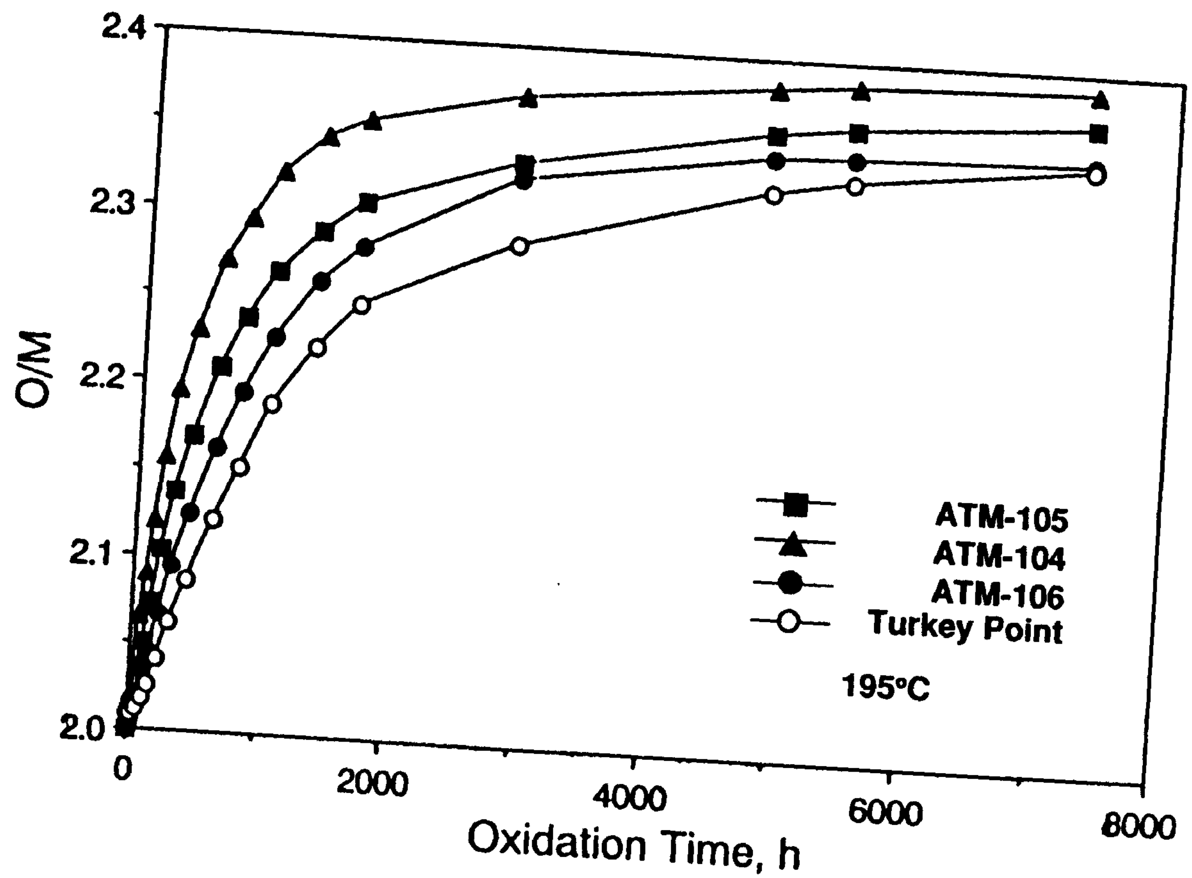
What the Program Shows

- Similar oxidation behavior in all fuels
- Test matrix can be reduced to a manageable size
- Limiting oxidation state for spent fuel in repository is $UO_{2.4}$ (U_4O_9 structure)

Oxidation of LWR Spent Fuel



*from weight gains



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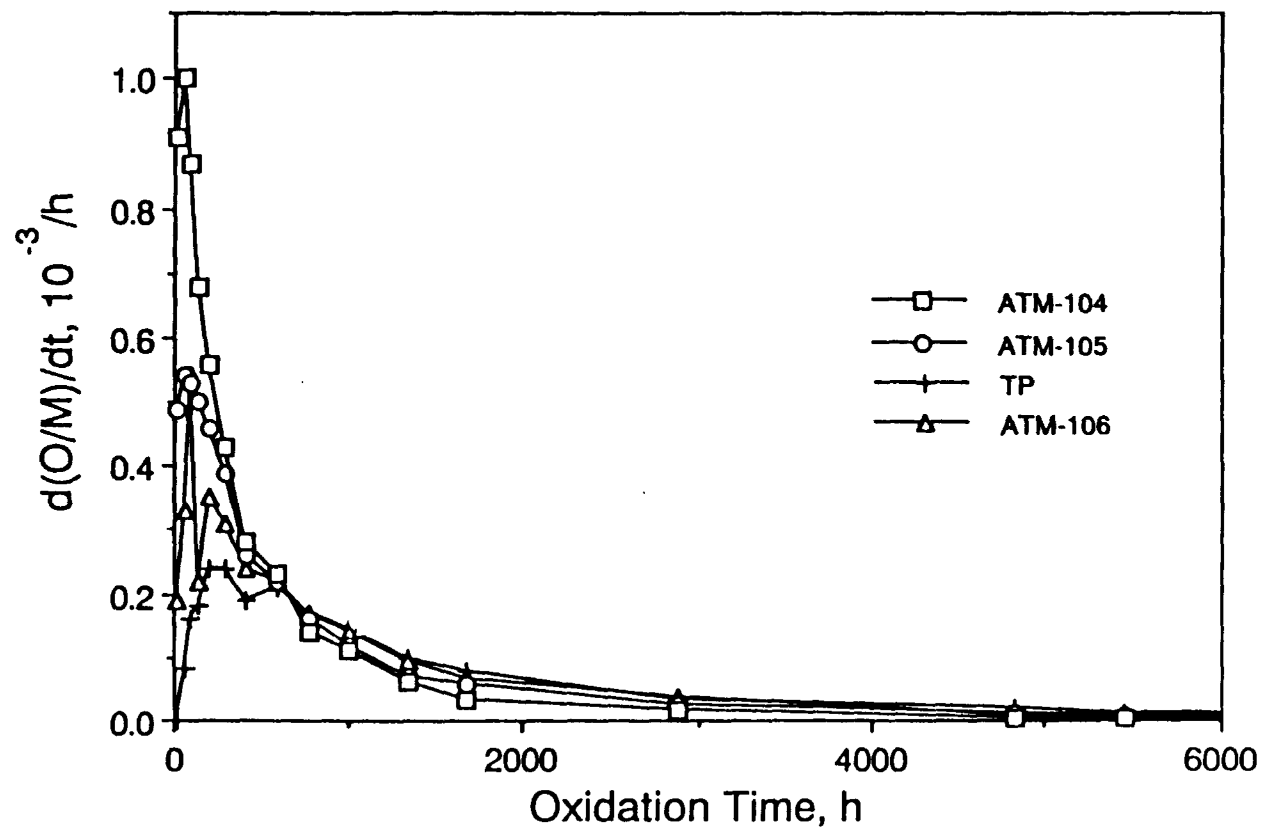
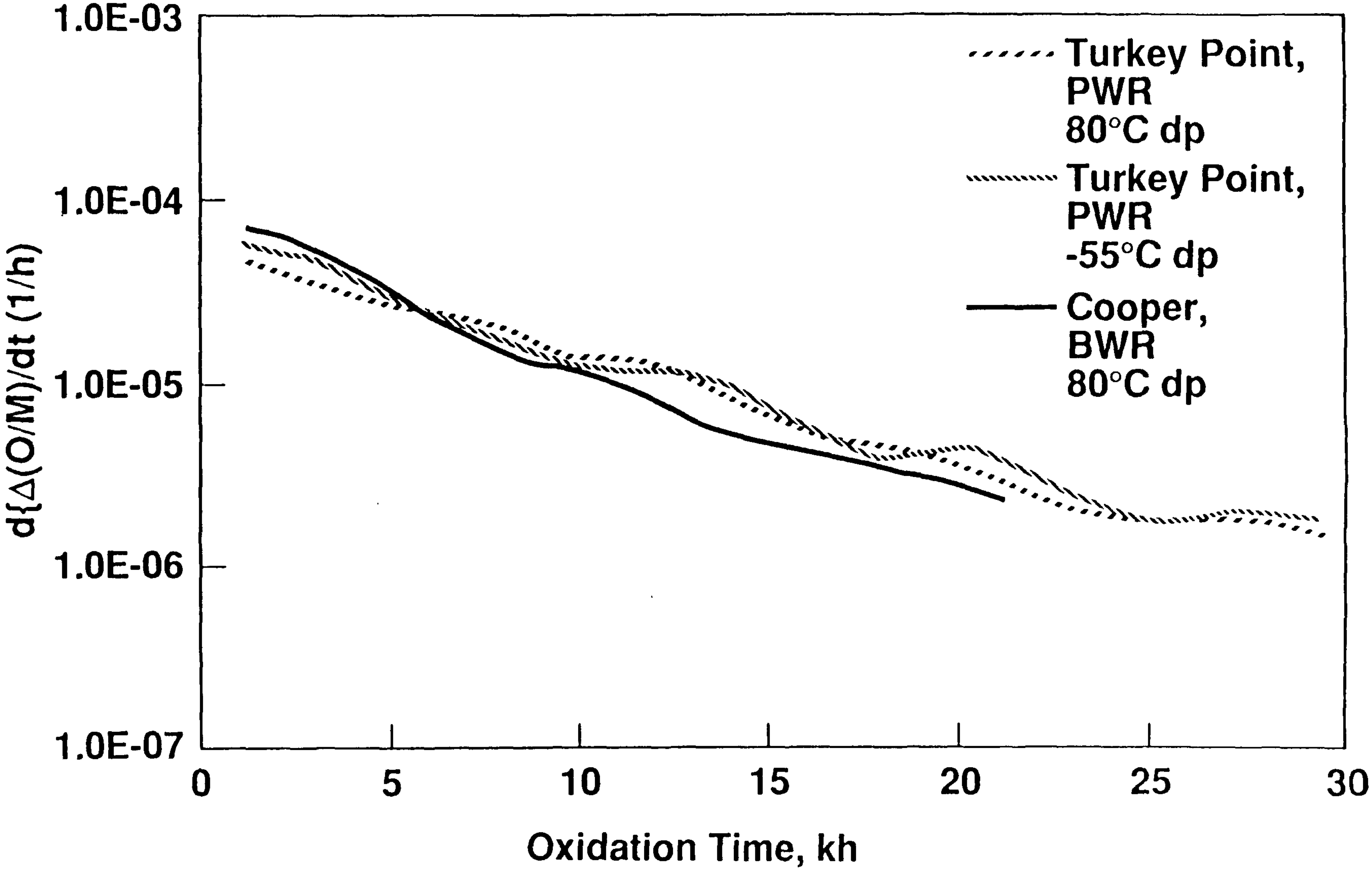


1.0
0.8
0.6
0.4
0.2
0.0
0
2000
4000
6000
d(O/M)/dt, 10 -3 /h
Oxidation Time, h
ATM-104
ATM-105
TP
ATM-106

Change in O/M with Time, 175°C



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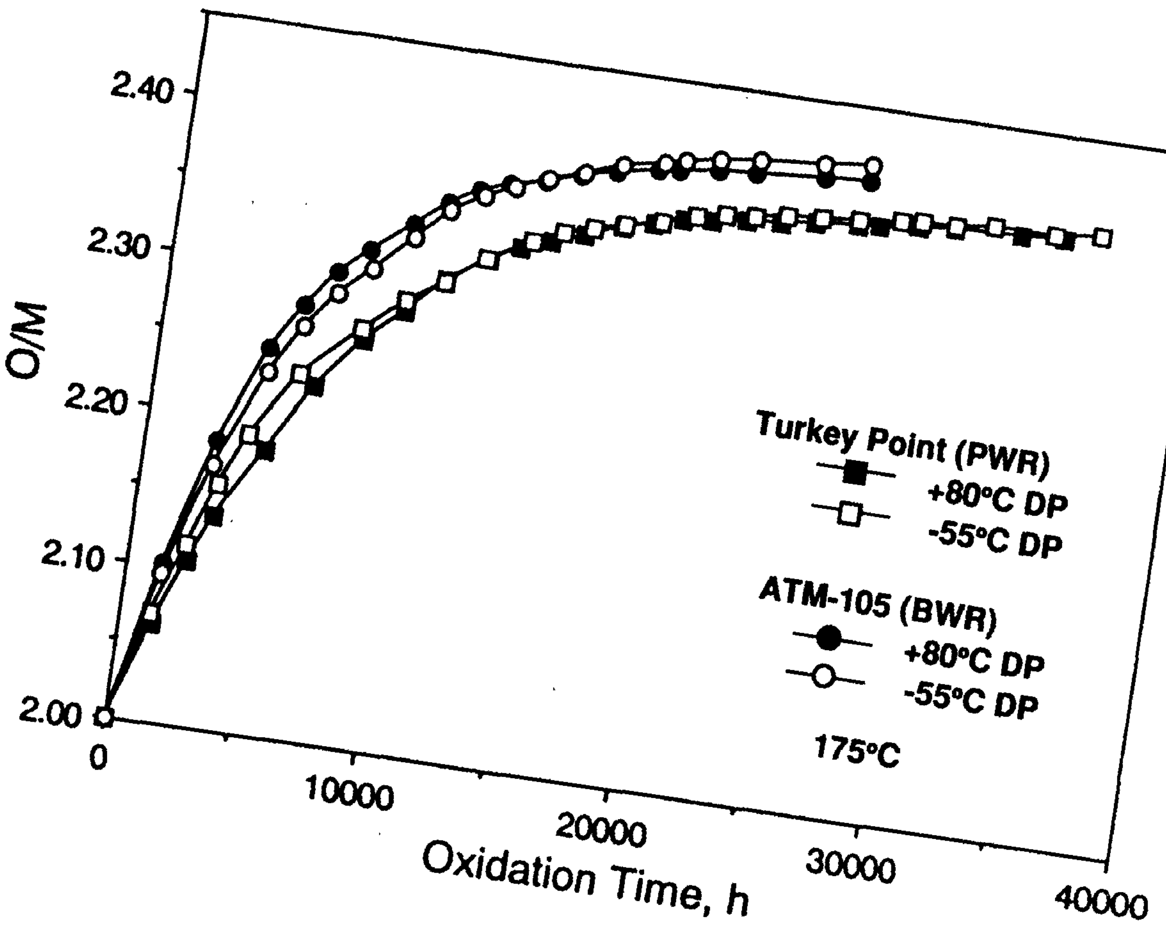

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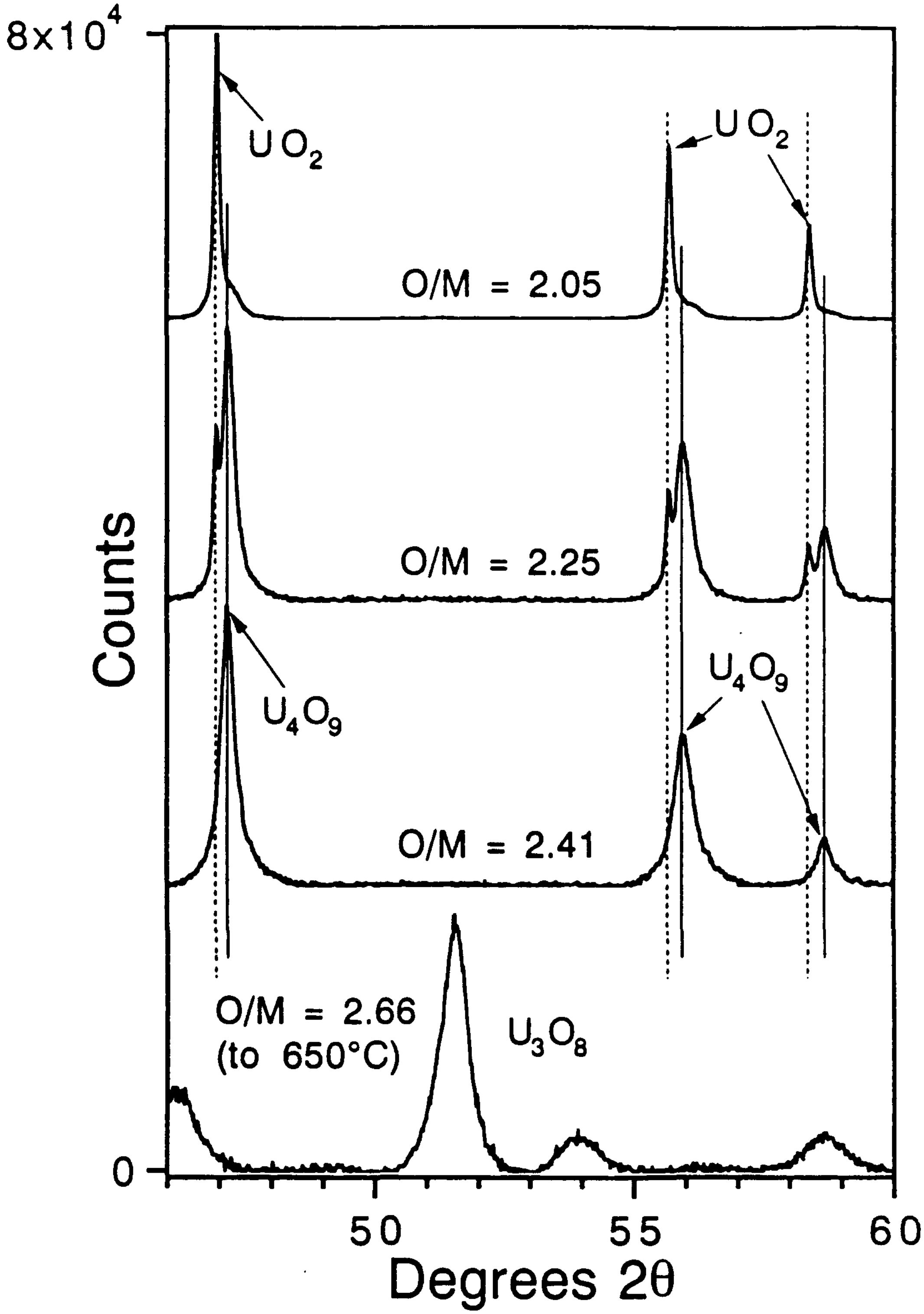
195°C Oxidation of ATM-105 Spent Fuel

ATM - 105 Spent Fuel



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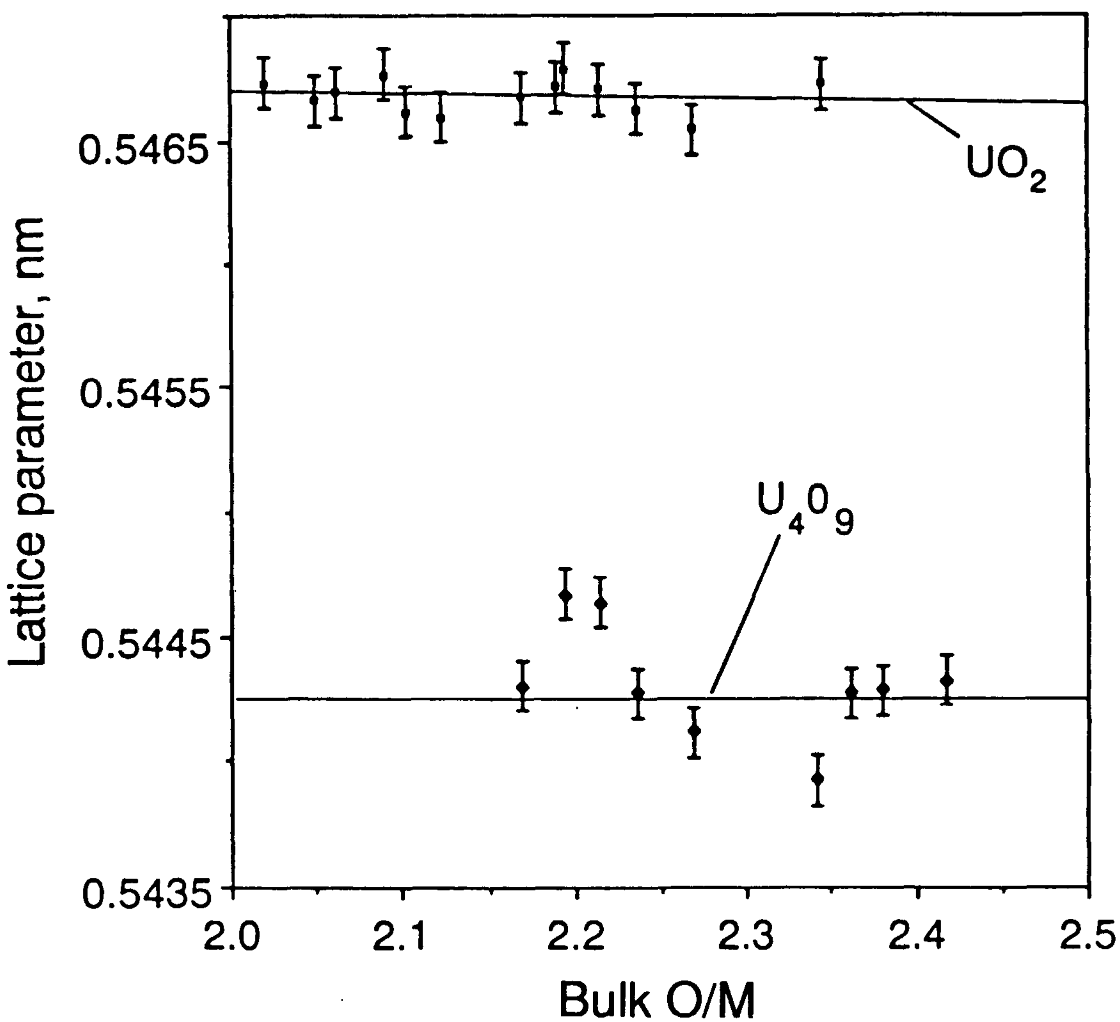
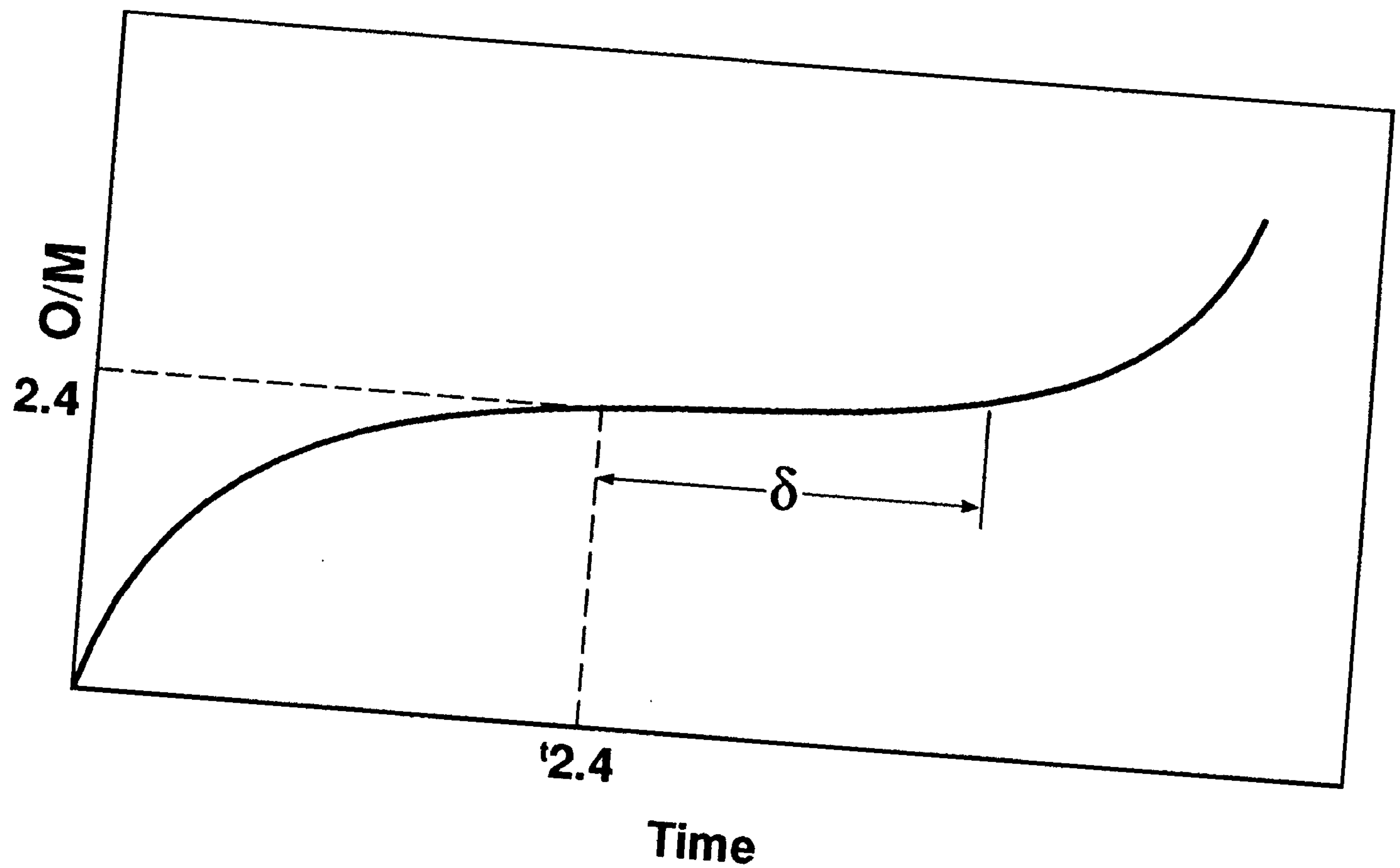


Lattice parameter, nm
0.5465
0.5455
0.5445
0.5435
2.0
2.1
2.2
2.3
2.4
2.5
Bulk O/M
UO2
U4O9

Generalized Spent Fuel Oxidation Curve



SNTRRE20P.125.NWTRB/10-14/16-92

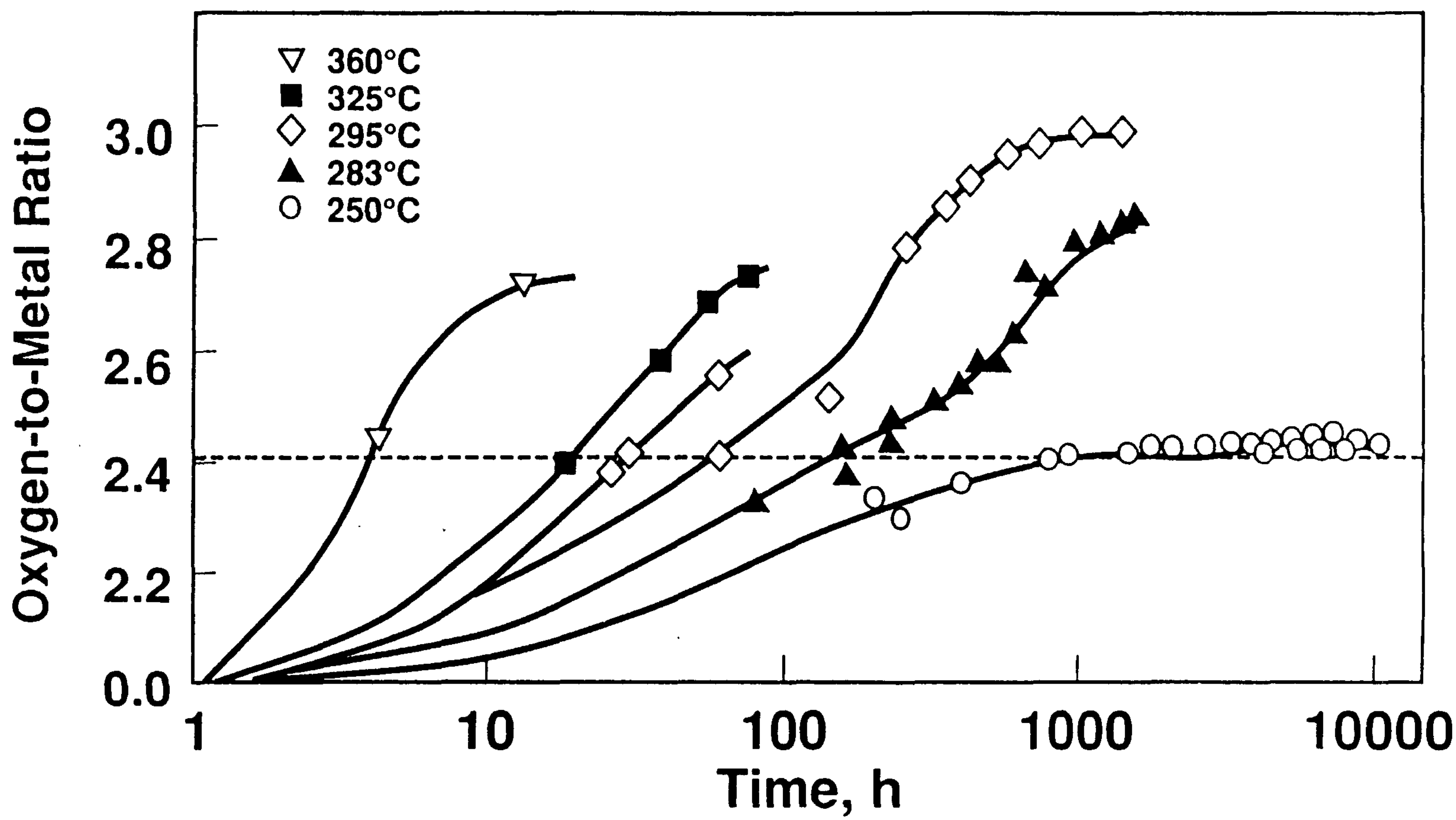
Questions

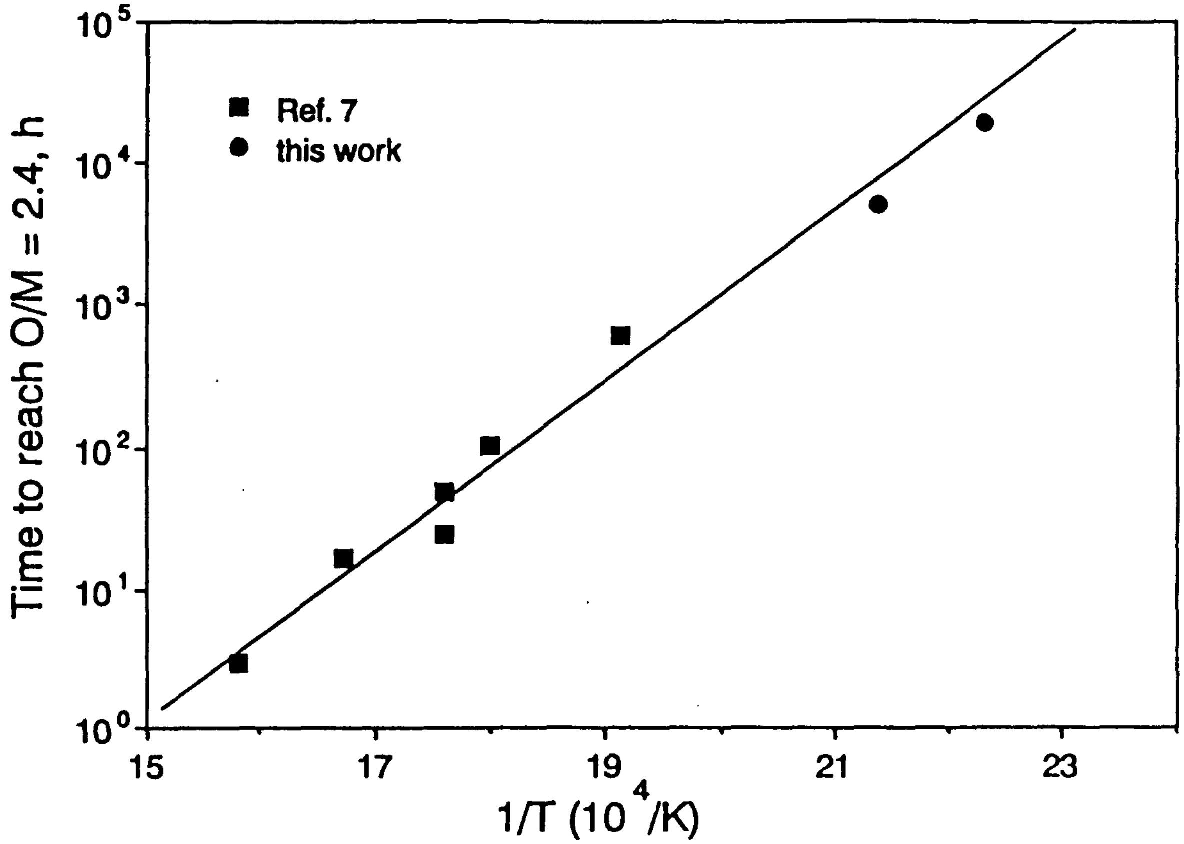
1. How long does it take to reach O/M ~ 2.4 as a function of temperature?

2. Is the radionuclide release from UO_2 and $UO_{2.4}$ spent fuel the same?

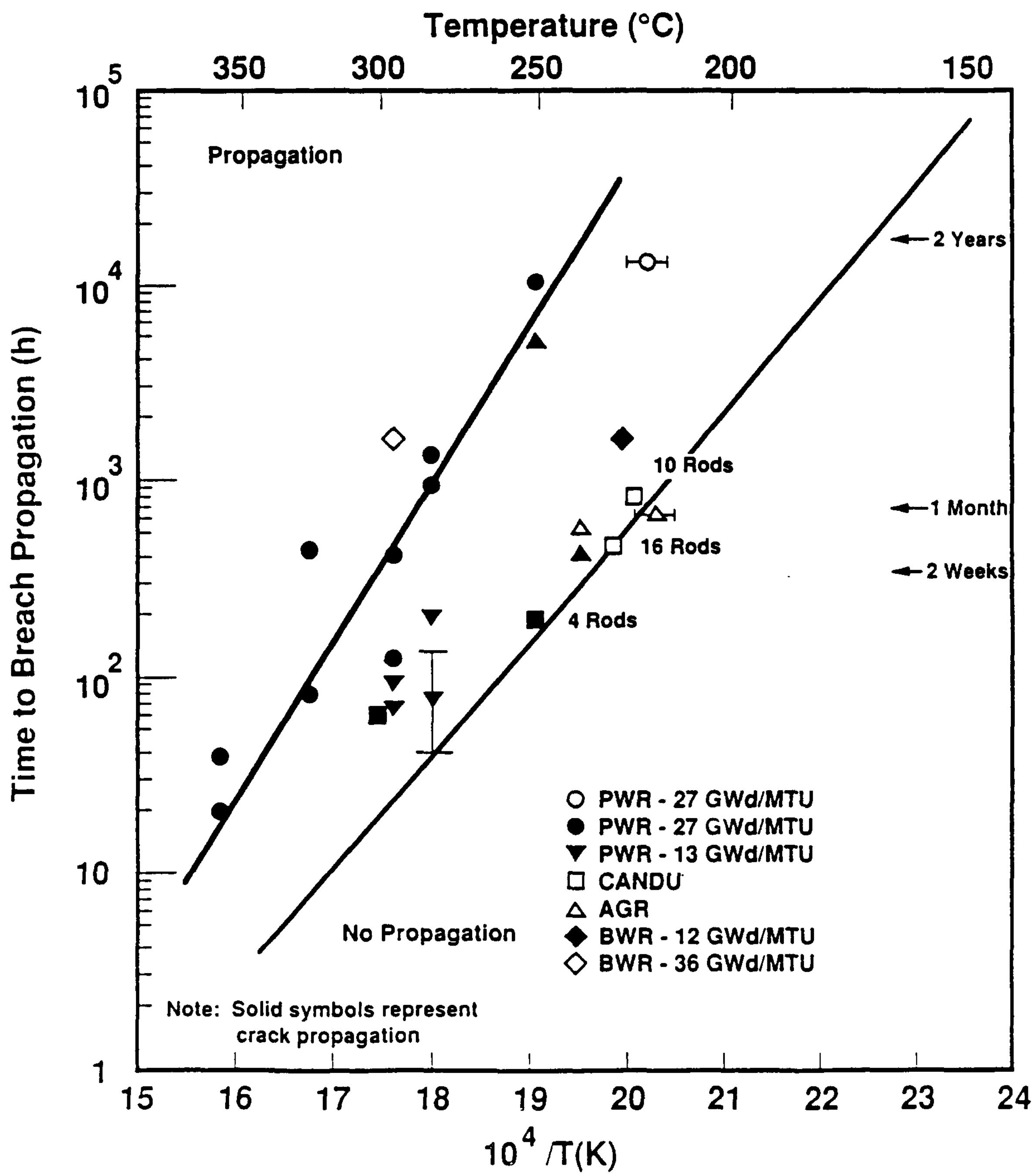
3. Does another phase form; and, if so, when?

Oxidation of Fragments of Turkey Point Fuel




Ref. 7
this work
Time to reach O/M = 2.4, h
10^5
10^4
10^3
10^2
10^1
10^0
15
17
19
21
23
1/T (10^4/K)

Time Required to Propagate Existing Cladding Defects



SNTRRE24P.125.NWTRB/10-14/16-92

Preliminary Conclusions

1. Spent fuel has different oxidation behavior than unirradiated UO_2

2. Fuel variability affects oxidation rate in a transitory manner

3. After transient, all tested fuels show similar oxidation behavior

4. No effect of atmospheric moisture

5. Test temperatures too low for oxidation beyond $UO_{2.4}$

6. Only UO_2 and U_4O_9 phases found at O/M <2.4

7. At 95°C, >2000 years to reach plateau

Information Needs:

1. No tests of high-burnup or Gd-containing fuels

2. Long-term stability of $UO_{2.4}$.
   Thermodynamics to aid modeling?

3. Oxidation kinetics beyond $UO_{2.4}$ (to U_3O_8)

4. Tests on low burnup fuel (12 GWd/MTU) ?

5. Leaching studies from oxidized and
   non-oxidized fuel

Scoping Studies:

1. Gadolinium (Gd) additions may improve fuel oxidation resistance

2. With Gd additions, unirradiated UO_2 has similar oxidation behavior to spent fuel

3. Not all fission products are the same

4. Another oxidation plateau at $UO_{2.66}$