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VOLOXIDATION STUDIES WITH UO_2 REACTOR FUELS

by

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Tritium is an impurity in irradiated fuel formed by both fission and activation. Proposed head-end operations (SLIDE 1) for treatment of spent nuclear fuel include a voloxidation step to remove tritium. In voloxidation (SLIDE 2), UO_2 fuel oxidizes to U_3O_8 above 480°C, and tritium is nearly quantitatively evolved as HTO (water vapor).[1] During oxidation, the fuel expands, disintegrates into a fine powder, and separates from the cladding.

Voloxidation was studied experimentally in small-scale laboratory tests with irradiated UO_2 reactor fuels. The present study (SLIDE 3) developed new data on the effects on the voloxidation reaction of (1) hull length, (2) oxygen concentration, (3) temperature, (4) agitation, (5) fuel density, and (6) fuel type and burnup. The reaction was studied by measuring weight gains, yields of U_3O_8, product densities and particle-size distributions, reaction rates, tritium release, and behavior of other off-gases (^{14}C, ^{85}Kr, and ^{129}I).

Fuels tested (SLIDE 4) were from Robinson, Oconee, Saxton, and Point Beach reactors, with burnups from 200 to 28,000 MWD/MTHM. Twenty-four tests with about 200-g batches of fuel were completed in a stainless steel voloxidizer-dissolver equipped with a rotary agitator and an off-gas analysis system.[2] ^{85}Kr release and oxygen consumption (SLIDE 5) were measured online to monitor the course of the reaction. Each voloxidized batch was dissolved[3] (SLIDE 6) to determine the tritium decontamination factor (DF). In most of the tests, >99.8% of tritium in the fuel was removed by voloxidation; tritium decontamination was not correlated with reaction conditions.

Average reaction rates for voloxidation of Point Beach fuel were determined under a variety of conditions (SLIDE 7).

Effect of Hull Length

The Zircaloy-clad fuels were sheared into pieces either 2.5 or 3.8 cm long. Fuel in cladding and/or as loose fragments was charged to the voloxidizer in each test. The reaction rates were independent of hull length, but were controlled by available UO_2 surface area. For Saxton and Oconee fuels, the reactions were

rapid because the fuel fell out of the hulls in the early stages of the reaction. However, Point Beach fuel did not fall out, but reacted from either end to the center of each hull. Fuels that remain in the hulls after shearing represent the limiting case of maximum difficulty for processing, either with or without voloxidation.

Effect of Oxygen Concentration

Of all the variables tested, oxygen concentration had the largest effect on reaction rates. In each test, oxygen was added as needed to hold reaction conditions constant at either 20, 60, or 100% oxygen. For high-density Point Beach fuel at 490°C, with agitation, the reaction rate (SLIDE 8) varied approximately as the 5/4 power of the oxygen concentration. Power laws were slightly different for other conditions.

Effect of Reaction Temperature

A 100°C increase in reaction temperature increased the reaction rate with high-density Point Beach fuel, but the effect of temperature was much less pronounced than that of oxygen concentration (SLIDE 7). In 20% oxygen, with agitation, the reaction at 590°C was 53% faster than at 490°C. In 100% oxygen, the reaction at 590°C was only 23% faster than at 490°C.

Effect of Agitation

Without agitation, the reaction rate decreased with high-density Point Beach fuel, but the effect was much smaller than that of oxygen concentration (SLIDE 7). In 20% oxygen, at 490°C, the reaction was 24% slower without agitation. In 100% oxygen, the reaction was only 13% slower without agitation.

Effect of Fuel Density

The effect of fuel density was studied by comparing the reaction rates of high-density and low-density Point Beach Fuel (SLIDE 7). The reaction rate of the low-density fuel was somewhat greater: 140% faster in 20% oxygen, with agitation, at 490°C, but only 37% faster in 100% oxygen. Also, more ^{14}C and ^{85}Kr evolved during voloxidation of the low-density fuel. With 50% greater void volume than the high-density fuel, the low-density fuel had greater effective surface area and shorter diffusion paths for off-gases.

Effect of Fuel Type and Burnup

The effects on voloxidation of fuels from different reactors and with different burnups appeared to be minor. Some of the fuels tended to fragment when sheared, while others did not. This had a large effect on the reaction time but not on the reaction rate per unit surface area. Tritium release was nearly quantitative for each of the fuels, when the reaction to U_3O_8 went to completion.

Incomplete Oxidation

In one test, with Oconee fuel (SLIDE 9), oxidation to U_3O_8 was incomplete, and only about 90% of the tritium in the fuel was released. X-ray diffraction measurements showed that the reaction product was U_4O_9. In another test, with high-density Point Beach fuel, U_4O_9 apparently formed as an intermediate but was converted to U_3O_8 by continued heating. No evidence for U_4O_9 formation was found in any of the other tests, and attempts to reproduce the anomalous results were unsuccessful. The occurrence of U_4O_9 appears to be random, and may be related to local variations in the fuel or to other experimental conditions.

Conclusions

The principal conclusions from these studies are given in SLIDE 10. The results contribute to a data base from which large-scale equipment and flowsheets could be designed for head-end operations with UO_2 fuels.

ACKNOWLEDGMENT

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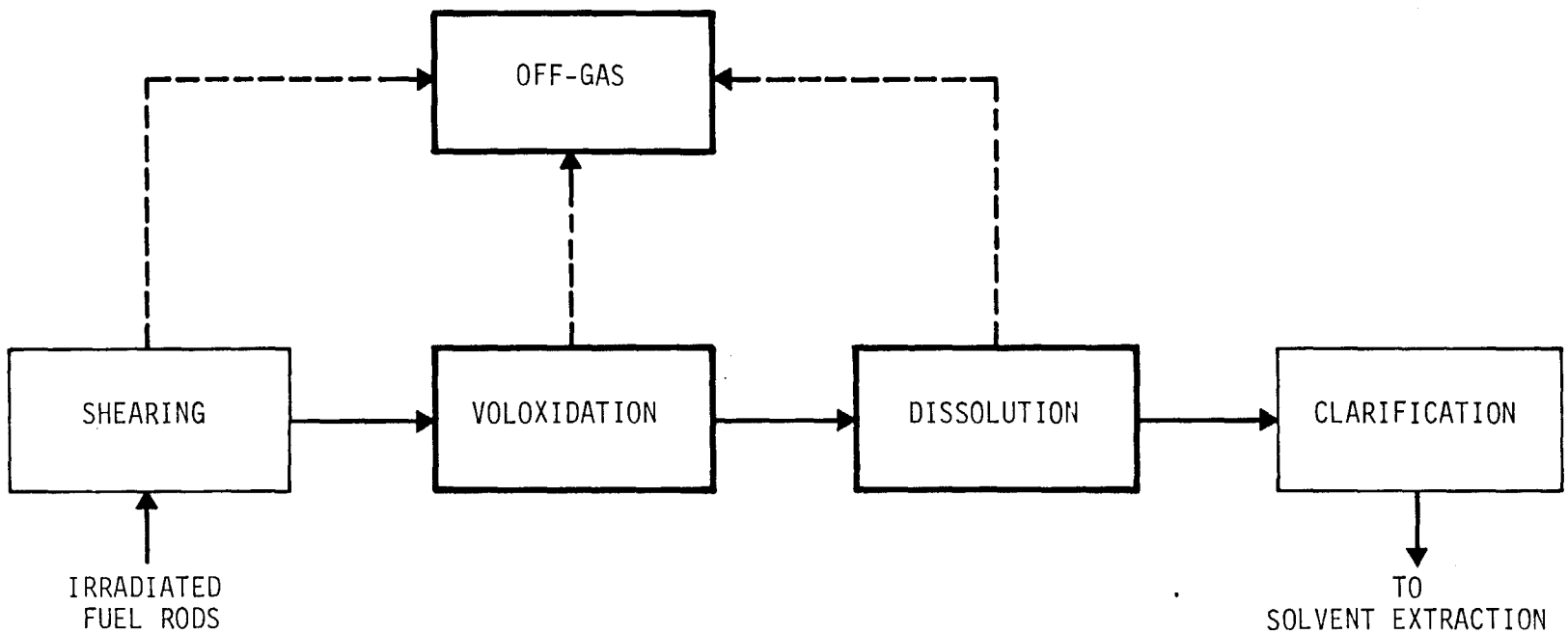
REFERENCES

1. J. H. Goode, Ed. Voloxidation - Removal of Volatile Fission Products from Spent LMFBR Fuels. USAEC Report ORNL-TM-3723 (1973).

2. J. A. Stone and D. R. Johnson. "Measurement of Radioactive Gaseous Effluents from Voloxidation and Dissolution of Spent Nuclear Fuel." Proc. Fifteenth DOE Nuclear Air Cleaning Conf., Boston, August 7-10, 1978. USDOE Report CONF-780819, p. 570, Harvard Air Cleaning Laboratory, Boston, MA (1979).

3. D. R. Johnson and J. A. Stone. "Light Water Reactor Fuel Reprocessing: Dissolution Studies of Voloxidized Fuel." Paper presented at ANS Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, GA, March 19-22, 1978.

HEAD-END PROCESS OPERATIONS



SLIDE 1. Head-End Process Operations

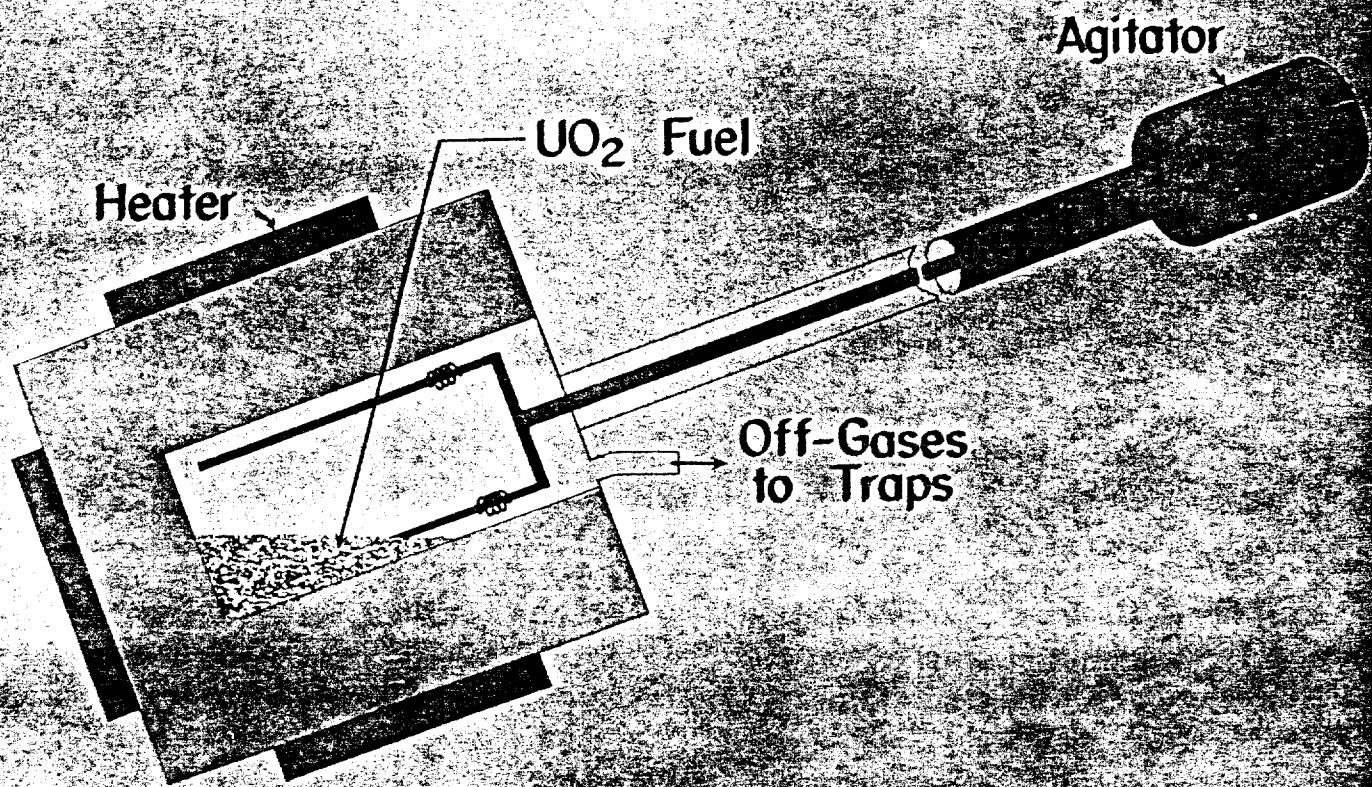
TRITIUM REMOVAL BY VOLOXIDATION

(VOLatile OXIDATION)

$$^{3}H \xrightarrow[490°C]{O_2} {}^{3}H_2O\uparrow$$

$$UO_2 \xrightarrow[490°C]{O_2} U_3O_8$$

Ceramic → Powder



VOLOXIDATION TEST APPARATUS

SLIDE 2. Tritium Removal by Voloxidation

INVESTIGATION OF EFFECTS:

- Hull Length
- Oxygen Concentration
- Temperature
- Agitation
- Fuel Density
- Fuel Type and Burnup

EXPERIMENTAL MEASUREMENTS:

- Powder Properties
- Reaction Rates
- Off-Gas Analyses

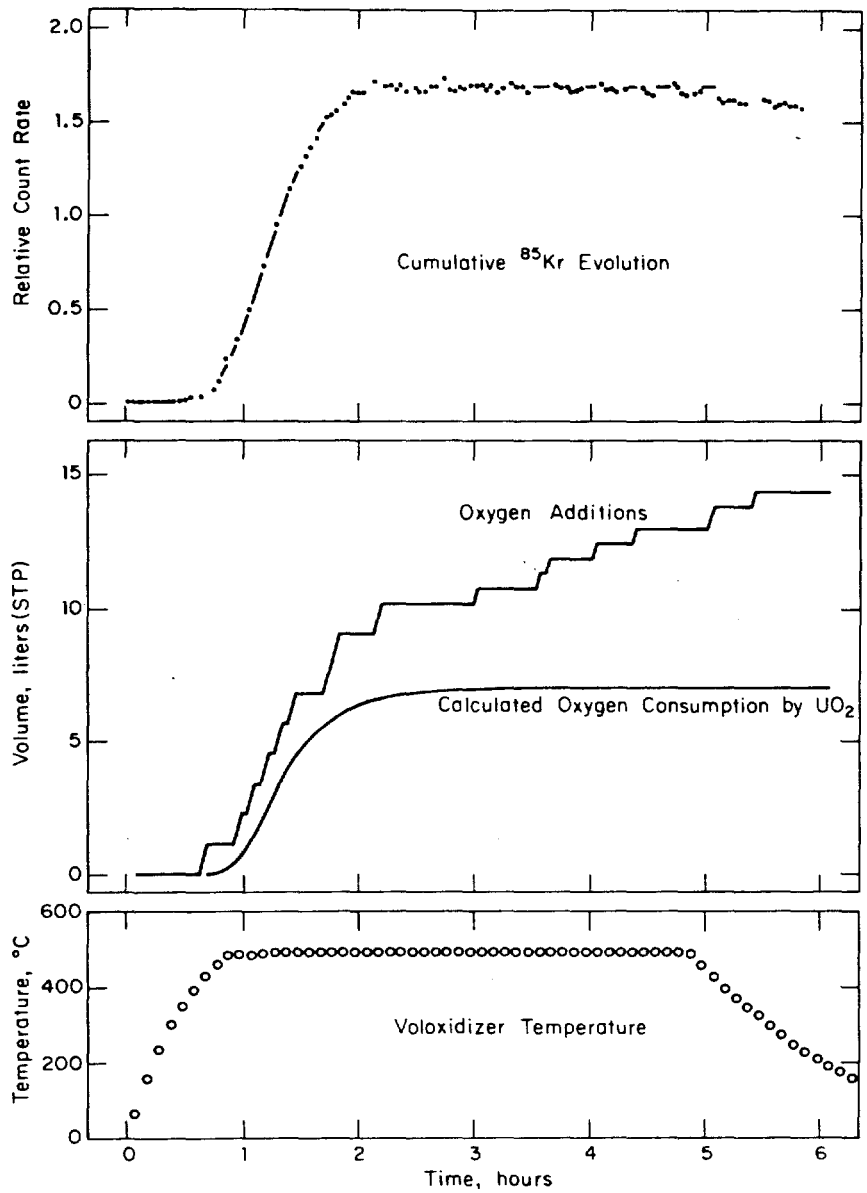
SLIDE 3. Voloxidation Studies

ZIRCALOY-CLAD UO_2 FUEL RODS

Reactor	Burnup, MWD/MTHM
H. B. Robinson-2	∿28,000
Oconee-1	∿11,000
Saxton	∿200 to 8,000
Point Beach	∿25,000 ∿28,000

SLIDE 4. Zircaloy-Clad UO_2 Fuel Rods

TYPICAL VOLOXIDATION BEHAVIOR



SLIDE 5. Typical Voloxidation Behavior

TYPICAL TRITIUM REMOVAL

Fuel	Total ^3H, Ci/MTU	% ^3H from Voloxidation	Tritium DF
Robinson	133	>99.9	33,150
Oconee	16	>99.9	6,560
Saxton	29	99.8	665
Point Beach	154	>99.9	1,140

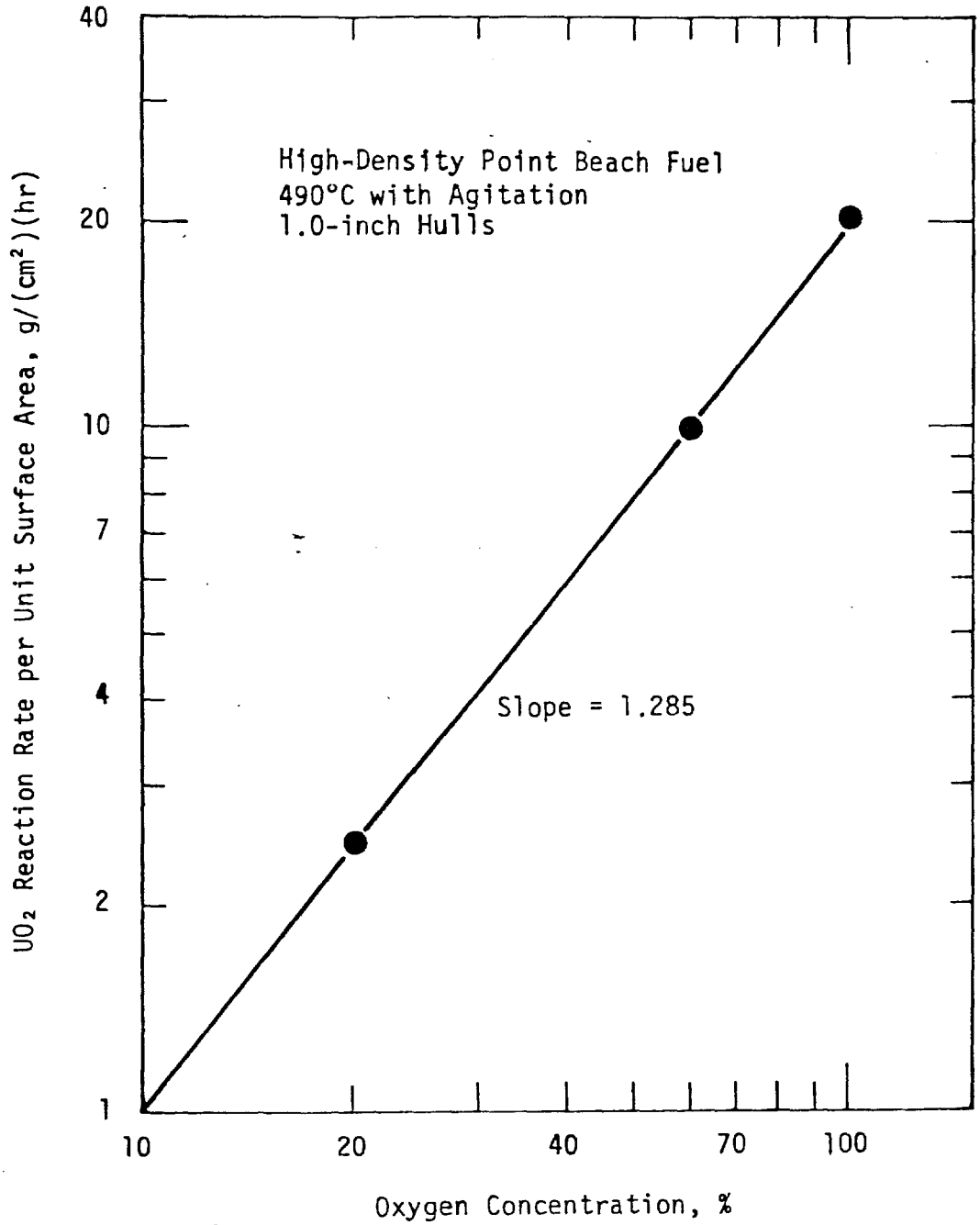
SLIDE 6. Typical Tritium Removal

REACTION RATES FOR VOLOXIDATION OF POINT BEACH FUEL

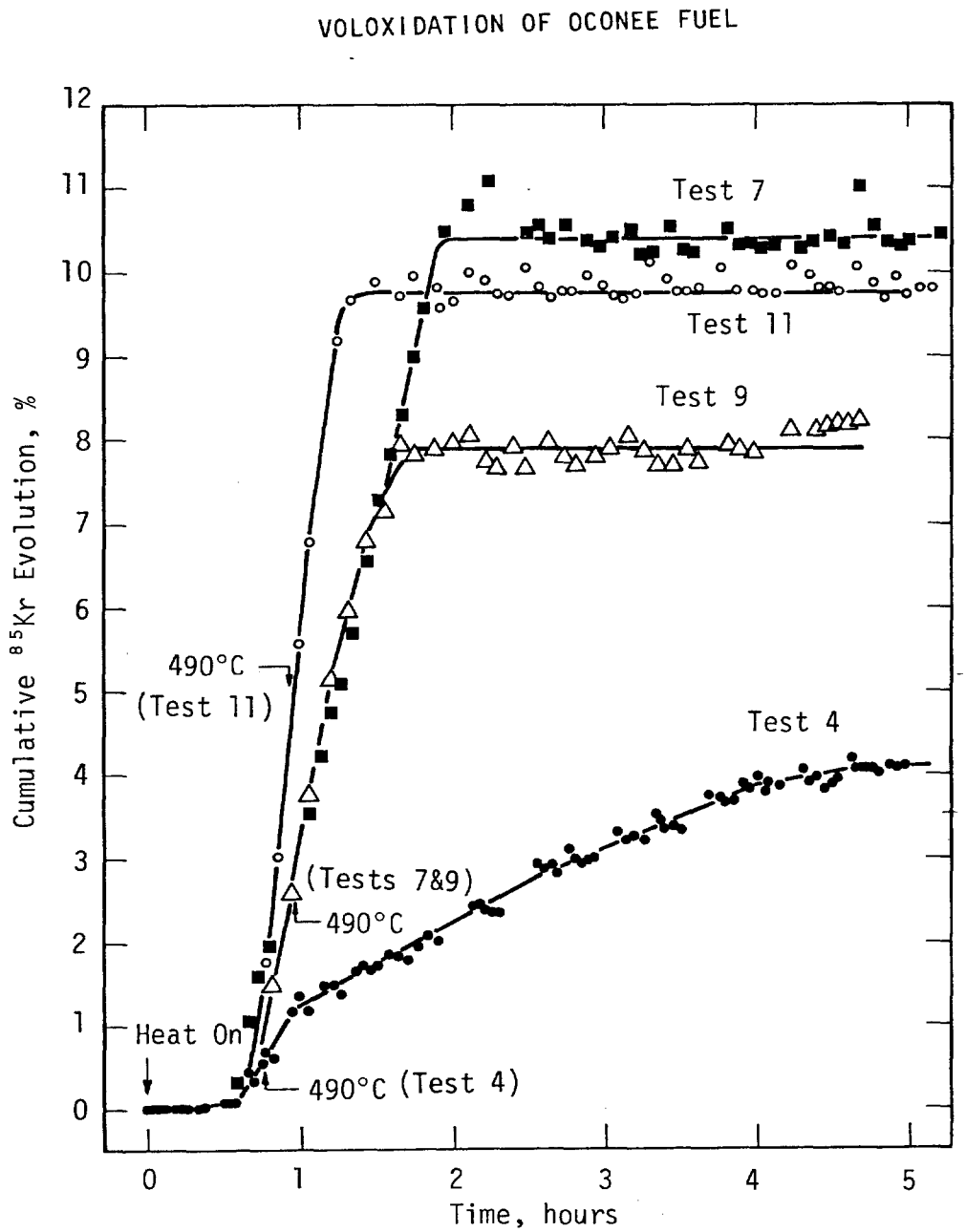
Fuel Density	Agitation	Temp, °C	Oxygen, %	Reaction Rate, g/(cm^2)(hr)
High	Yes	490	20	2.5
			60	9.8
			100	20.1
High	Yes	590	20	3.8
			100	24.7
High	No	490	20	1.9
			100	17.5
Low	Yes	490	20	5.9
			100	27.5

SLIDE 7. Reaction Rates for Voloxidation of Point Beach Fuel

EFFECT OF OXYGEN CONCENTRATION ON UO_2 REACTION RATE



SLIDE 8. Effect of Oxygen on UO_2 Reaction Rate



SLIDE 9. Voloxidation of Oconee Fuel

CONCLUSIONS FROM VOLOXIDATION STUDIES

- Tritium Removal >99.5%
- Reaction Fastest with Pure Oxygen
- Other Factors Less Important
- U_4O_9 Intermediate Formed Rarely
- Reaction Well Behaved with UO_2 Fuels

SLIDE 10. Conclusions from Voloxidation Studies