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INTERIM REPORT

THE METAL-WATER REACTIONS OF IRRADIATED N-REACTOR FUELS AT 1025 TO 1080 °C

D. L. Reid, G. M. Hesson and J. E. Hammond

August 1970

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AEC RESEARCH &
DEVELOPMENT REPORT

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By

D. L. Reid, G. M. Hesson and J. E. Hammond

Reactor Engineering Department
Physics and Engineering Division

For

Doublas United Nuclear, Inc.

August 1970

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INTERIM REPORT
THE METAL-WATER REACTIONS OF IRRADIATED N-REACTOR FUELS AT 1025 TO 1080 °C

D. L. Reid, G. M. Hesson and J. E. Hammond

ABSTRACT

The first experimental data obtained on the metal-water reaction of massive, irradiated, Zircaloy-2 clad uranium tubular fuels at temperatures between cladding rupture and the uranium melting point are reported. Analyses of the data showed that physical changes produced an apparent reaction rate law other than parabolic and the reaction rate constant and translocation of uranium were inversely related to irradiation level for the range investigated. All data correlated to within ±10% with the function $Q = A\ t^{0.72}$ where Q is the volume of hydrogen, t is time after cladding rupture in minutes and A is the rate constant related to the effective surface area. Photographs of the typical physical changes in the fuel are included. An equation was developed for reactor application.

LIST OF FIGURES

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INTERIM REPORT
THE METAL-WATER REACTIONS OF IRRADIATED N-REACTOR FUELS AT 1025 TO 1080 °C

D. L. Reid, G. M. Hesson and J. E. Hammond

INTRODUCTION

Hazards analyses for nuclear reactors require an assessment of the consequences of certain hypothetical accidents, one of which is a loss-of-coolant accident. The analysis requires knowledge of the fission product release from the ruptured fuel, knowledge of the physical behavior of the fuel following the rupture, and knowledge of the rate of the metal-water reaction for the reactor system.

The Fuel Meltdown Study Unit of Battelle-Northwest is involved in an out-of-reactor experimental program for Douglas United Nuclear using massive irradiated fuel elements to provide information bearing on these unknowns for the N-Reactor. The first nine metal-water reaction experiments at temperatures below the uranium melting point have been analyzed. This report presents the tentative conclusions drawn from these data.

SUMMARY AND CONCLUSIONS

Five Outer and four Inner N-Reactor irradiated MK-I fuel elements (601 alloy), each 7.4 in. long, were heated inductively in a steam atmosphere at a temperature somewhat above their rupture point. The hydrogen evolution rate resulting from the metal-water reaction was measured for each of the fuels for periods of time ranging from 11 to 80 min. Tentative conclusions concerning the metal-water reaction rates drawn from these tests are:

1. The hydrogen evolution was found to be correlated to ±10% by the general equation where

$$Q = A\,t^{0.72}$$

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where Q is the total hydrogen evolved in liters, and t is the time in minutes after rupture. The instantaneous rate is, to ±30%, the differential of this, or,

$$\frac{dQ}{dt} = 0.72\ A\ t^{-0.28}$$

where dQ/dt is the instantaneous hydrogen evolution rate in liters per minute.

2. Experimental values for the coefficient, A, ranged from 0.84 to 4.06 for the Outer fuels and from 1.10 to 1.60 for Inner fuels, and were basically a function of the effective metal surface area exposed to the steam atmosphere. For Outer elements near 2300 and 3400 MWd/ton, the total metal-water reaction was inversely related to the exposure level as was the amount of uranium expelled from the cladding.
3. For the tube-in-tube fuel assemblies in the reactor with exposure levels near 2000 MWd/ton and at temperatures near 1075 °C the recommended equation for calculating the hydrogen evolution is

$$Q = 0.136\ t^{0.72}$$

where Q is the total volume of hydrogen evolved in cubic feet per foot of fuel and t is the time after rupture in minutes.

HISTORICAL

Corrosion rates for uranium and Zircaloy-2 in a steam atmosphere have been obtained using small coupons, cubes, or wafers under carefully controlled conditions. Uranium reaction rates under isothermal conditions at temperatures above 500 °C were measured independently by Wilson et al,(1) Lemmon,(2) and

[redacted]

Scott(3) with reasonable agreement. The reaction kinetics were parabolic for temperatures above 500 °C.

The generally accepted rate law for the Zircaloy-2 steam reaction is that given by Baker and Just.(4) This reaction followed the parabolic rate law above about 800 °C.

For the parabolic rate law to apply, two conditions must persist: (1) the surface area remains constant, and (2) the diffusion rate is controlled by an ever increasing thickness of oxide of uniform composition. Experience with massive irradiated Zircaloy-2 clad uranium fuel above 800 °C showed that physical changes would have a marked influence on the oxidation rate and an apparent rate law other than parabolic would be observed at least in the early part of an isothermal test. At fuel temperatures less than rupture, growth due to thermal expansion and internal gas pressure distort the Zircaloy-2 continuously. This then should produce an apparent reaction rate other than parabolic or at least produce a rate constant other than that reported for the small specimens. At temperatures above the cladding rupture, expulsion and translocation of the uranium as well as distortion of the Zircaloy-2 cladding and secondary ruptures should produce an apparent rate higher than parabolic. The observed physical changes indicate that parabolic, linear, and constant reaction rates might occur simultaneously for significant periods of time and be subject to change with time at temperature. It is the summation of all the oxidation reaction rates as a function of time and temperature with typical reactor fuels that requires definition for the total fuel involved in a loss-of-coolant accident.

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EXPERIMENTAL EQUIPMENT AND CONDITIONS

GENERAL

The N-Reactor fuel element assembly consists of an Inner and Outer Zircaloy-2 clad fuel tube. The geometrical differences and cladding thickness preclude similarity in the physical changes of the two fuels subjected to the rapid thermal transients associated with loss of coolant to the reactor. Since early tests showed physical changes might be one of the major controlling factors with respect to fission product release and metal-water reaction rates, tests with both fuels were essential and the furnace systems were sized accordingly. Induction heating with a 10 kHz, 50 kW unit was found to be the best for duplicating fission product decay heating and provided the necessary heating rates. By proper choice of the air gap, coupling was principally to the uranium rather than the cladding at temperatures above 400 °C. Heating rates used followed the calculated temperature transient for centrally located fuel involved in a loss-of-coolant accident.

TEST FUELS

The fuels used in the test were typical reactor grade elements except for the shorter 7.4 in. length. The Inner elements contained about 4 lb of uranium and the Outer elements contained 8 lb. The melting point of the uranium alloy was about 1090 °C. The fuels were irradiated in the reactor tubes assigned for special production test material to obtain relatively accurate exposure levels under typical operating conditions.

FURNACE SYSTEM

For all but the first test reported herein, the fuels were heated inside quartz tubes that approximated either the ID of the process tube for the Outer fuels or the ID of the

[redacted]

Outer fuel for the Inner fuel. This system approximated the radial geometry in the reactor except for a simulant of the Inner fuel during an Outer fuel test. The effect of an infinite fuel column constraint on longitudinal growth during heating was simulated by split Zircaloy-2 tubes butted up against the ends of the Zircaloy-2 boat. The boat positioned the fuel in the center of the horizontal quartz furnace and surrounding heating coil.

The initial high power input required to produce the desired heating rate precluded a uniform axial temperature below the β-γ phase change. This necessitated adjustment in the spacing of the 16 turn induction coil and the programmed power input to produce a uniform temperature between 800 °C and rupture. The temperature difference along the fuel never exceeded 40 °C at any time below 800 °C.

The temperature was measured with a Pt-Pt-13% Rh thermocouple positioned at the longitudinal center of the fuel. The quartz furnace cap had penetrations for air or helium, thermocouple and steam injection. The fission product sampling system was used to strip the gas of fission products before entering the hydrogen measuring equipment. This was a triplicated system for sequential sampling during the tests and downstream of the furnace consisted of a three tubed water cooled condenser with each outlet attached to a condensate flask followed by a vertical condenser, a Maypack sampler, a rough and fine -70 °C cold trap and three -70 °C charcoal traps in series. A fraction of the gas downstream of the last trap was shunted through a thermal conductivity meter to measure the percent hydrogen in the hydrogen-air mixture. For those tests not requiring fission product noble gas analysis, the -70 °C charcoal traps were excluded. Sweep air was introduced into the system at the condensate flasks by establishing a slight vacuum on the entire system. Flow rates and system pressures were measured with standard flow meters and gages.

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GENERAL PROCEDURE

First the entire system was tested for leaks with the steam inlet line plugged off. The desired flow rate was set and the sampling trains checked for identical flows. The vacuum was disconnected and the fuel brought slowly to 400 °C in a stagnant atmosphere. Steam was then introduced at a flow rate of about 5 liters/min, sufficient to preclude a steam limited reaction, and the system allowed to stabilize before starting the temperature transient. Heating rates were programmed to produce rupture of the fuel about 3 min after the start of the heating cycle and a preselected isothermal temperature held for the duration of the test.

RESULTS

DESCRIPTION OF INDIVIDUAL EXPERIMENTS

The general behavior of the fuels in these experiments is for some degree of separation at the clad-uranium bond starting at temperatures ranging from 790 to 1000 °C. The degree of separation was less and its onset at a higher temperature for the fuels with lower exposure levels. Rupture was characterized by a forceful smokey gas expulsion. With fuels of lower exposure levels, the initial gas burst was followed immediately by the expulsion of a mass of foamy plastic uranium through the rupture. Little or no uranium was expelled from the fuels with the highest irradiation level. The behavior of the fuels in each of the experiments was a variation within this general behavior. A summary of the test conditions and rate constants for all the experiments is given in Table 1.

OUTER FUEL ELEMENTS

The first five experiments described are those with Outer fuel elements of the assembly.

[redacted]

TABLE 1. Summary of Test Conditions and Reaction Rate Coefficients

Experiment	Exposure Level, MWd/ton	Rupture Temperature, °C[a]	Isothermal Conditions Temperature, °C	Isothermal Conditions Time, min	Fuel Type	Rate Coefficient A for $t^{0.72}$
SNH-3	3490	1010	1025	35	Outer	1.71
SNH-4	3790	1010	1060	11	Outer	1.0
SNH-6	4120	940	1060	55	Outer	0.84
SNH-10	1900	1035	1080	80	Outer	4.06
SNH-11	1900	1040	1080	65	Outer	1.27
SNH-7	1800	1075	1070	60	Inner	1.60
SNH-8	1800	1060	1070	60	Inner	1.60
SNH-9	2000	1060	1080	65	Inner	1.10
SNH-12	1275	1080	1080	60	Inner	1.10

(a) Time from 400 °C to rupture is about 3 min.

SNH-3

This experiment was unique in two respects. First, the isothermal temperature was 1025 °C rather than the 1060 to 1080 °C used with the other eight. Secondly, no quartz retainer tube was used. The fuel elements used for the rest of the runs were placed in quartz tubes with internal diameters to simulate the radial restraint offered by the process tube to Outer fuels or the Outer fuel piece to the Inner fuels.

Separation at the cladding--uranium diffusion bond started shortly after passing through β-γ phase change temperature (about 830 °C) and a major radial expansion and complete clad-fuel separation occurred prior to rupture at 1010 °C. Postheating examination showed that the inner clad had collapsed and that rupture was by separation of the inner cladding from the end cap. Prerupture cladding expansion precluded the expulsion of uranium from the rupture. Oxidation was

[redacted]

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principally on the Zircaloy surfaces exposed to the flowing steam and from diffusion of steam through the rupture hole to the uranium.

SNH-4

This experiment was identical to SNH-3 except for the use of the quartz radial restraining tube and the isothermal temperature of 1060 °C. Separation of cladding and uranium started at approximately 830 °C. Rupture occurred at 1010 °C. No uranium was forced from the rupture except a very minor amount during a brief temperature excursion to 1075 °C which occurred while the temperature was being leveled at 1060 °C. This test was terminated early when it appeared that further radial expansion would fracture the quartz furnace. This was later found to be an illusion created by the aberrations in the quartz tubing and furnace. Postheating examination revealed that the inner clad had collapsed and the rupture was by separation of the inner clad from the end cap. The outer clad had expanded to completely fill the annular gap between the fuel element and the quartz tube except near the end caps. Oxidation occurred on the inner Zircaloy tube and to a lesser degree by diffusion of steam to the outer Zircaloy surfaces near the end caps.

SNH-6

Experiment SNH-6 was a duplicate of SNH-4 except for the slightly higher irradiation level. The fuel used in this test had two gouges in the weld bead of the end cap, probably incurred during discharge operations. Cladding separation started shortly after passing through the β-γ transformation temperature (790 °C). Rupture occurred at 940 °C by separation of the outer clad from the end cap at the point of the observed weld damage. The low rupture temperature and location of the rupture were apparently caused by the end cap damage. No

[redacted]

uranium was expelled from the cladding. The inner clad had partially collapsed and the outer clad had expanded to fill the annular gap between the fuel and quartz tube for approximately one-half its length. Oxidation was primarily by the flowing steam on the inner cladding surface. Oxidation to a lesser degree occurred by diffusion of steam to the outer clad surface which was not in contact with the quartz tube.

Figure 1 is photographs taken of this fuel after the test. The mottled lighter colored surface seen in the top view is the outer clad surface which was in contact with the quartz tube. The light color is due to dissolution of the autoclaved oxide into the base metal. The tight contact between the clad and the quartz tube prevented steam from reaching this surface to cause further oxidation. The end view of the fuel shows the collapse of the inner cladding.

The rate coefficients of experiments SNH-3, SNH-4, and SNH-6 (Table 1) show that the radial restraint of the quartz tube significantly reduced the metal-water reaction. All subsequent experiments were made using quartz radial restraint tubes to provide a closer simulation to conditions in the reactor.

SNH-10

Experiment SNH-10 was a duplicate of SNH-4 and SNH-6 except its exposure level was a third less and its isothermal temperature 20 °C higher (1080 °C). A few isolated spots of clad-uranium separation were observed at a temperature of 900 °C, but the complete fracture of the bond did not occur as noted with the more highly irradiated material. Rupture occurred at 1035 °C at the juncture of the downstream end cap and cladding. A large amount of plastic uranium foam was forced out through the rupture and nearly filled the longitudinal restraining tube at the end of the fuel. The uranium extrusion occurred to such an extent that a small

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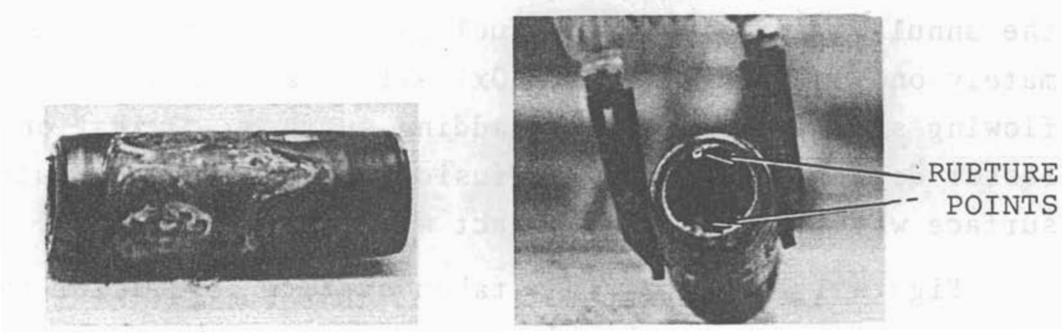


TOP VIEW

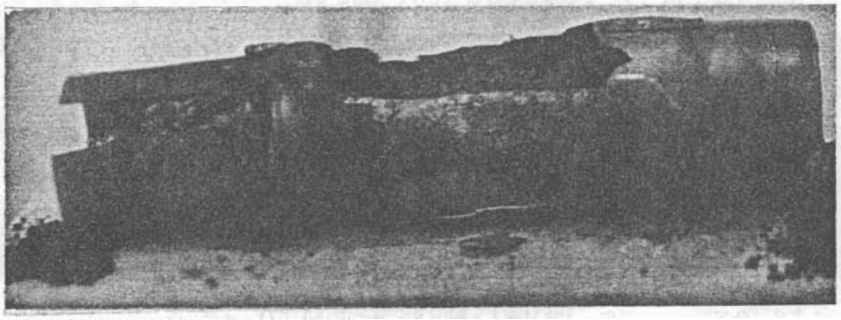
END VIEW

TEST SNH-6

OUTER ELEMENT
TEMP = 1060 C

TIME AT TEMP = 55 MIN

FIGURE 1. Postheating Picture of Fuel Test SNH-6



TOP CLADDING REMOVED TO SHOW INTERIOR

TEST SNH-10

OUTER ELEMENT
TEMP = 1080 C FOR 85 MIN THEN 1200 C FOR 10 MIN

FIGURE 2. Postheating Picture of Fuel Test SNH-10

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amount was forced out over the end of the 14 in. long Zircaloy-2 boat which contained the fuel. The extruded uranium in the end restraining ring provided a relatively large exposed uranium surface area for oxidation--atypical with respect to reactor geometry where adjacent fuel assemblies would severely restrict the effective uranium surface area. No oxidation occurred at the interface of uranium and metal or quartz surfaces.

A picture of the fuel from SNH-10 is shown in Figure 2. This is presented to show the large amount of uranium which was extruded into the end restraining ring and the large surface area it presents for oxidation. This picture is somewhat misleading in two respects. First, there was more uranium at the fuel end than the picture shows--the uranium had oxidized extensively into a loose powdery oxide which fell off during fuel removal. Secondly, the temperature was raised to 1200 °C for several minutes after the metal-water portion of the test was completed to provide some insight into problems which might be encountered in future tests at molten temperatures. Consequently, the uranium remaining in the cladding is not typical of that of fuels whose temperature did not exceed the uranium melting point.

SNH-11

SNH-11 was a duplicate of SNH-10. Spots of cladding separation appeared at 930 °C. Rupture (1040 °C) occurred at the top of the end cap cladding juncture with only a small amount of gas and uranium expelled. Apparently the uranium sealed the original breach, for about 5 sec later a second rupture occurred near a downstream support. An estimated 10 to 15% of the uranium was forced from the second rupture filling the annular space between the fuel and quartz tube for about the lower half. Even though this fuel had a

[redacted]

significant uranium extrusion its hydrogen evolution rate was only a third that of SNH-10. The difference results from extrusion of the uranium into the annular gap between the fuel and quartz tube rather than into the open Zircaloy-2 restraining tube, as in SNH-10. This significantly reduced the effective surface area since oxidation did not occur at the interfaces of uranium and the other materials but only on the rather limited exposed uranium surface and the Zircaloy-2 cladding.

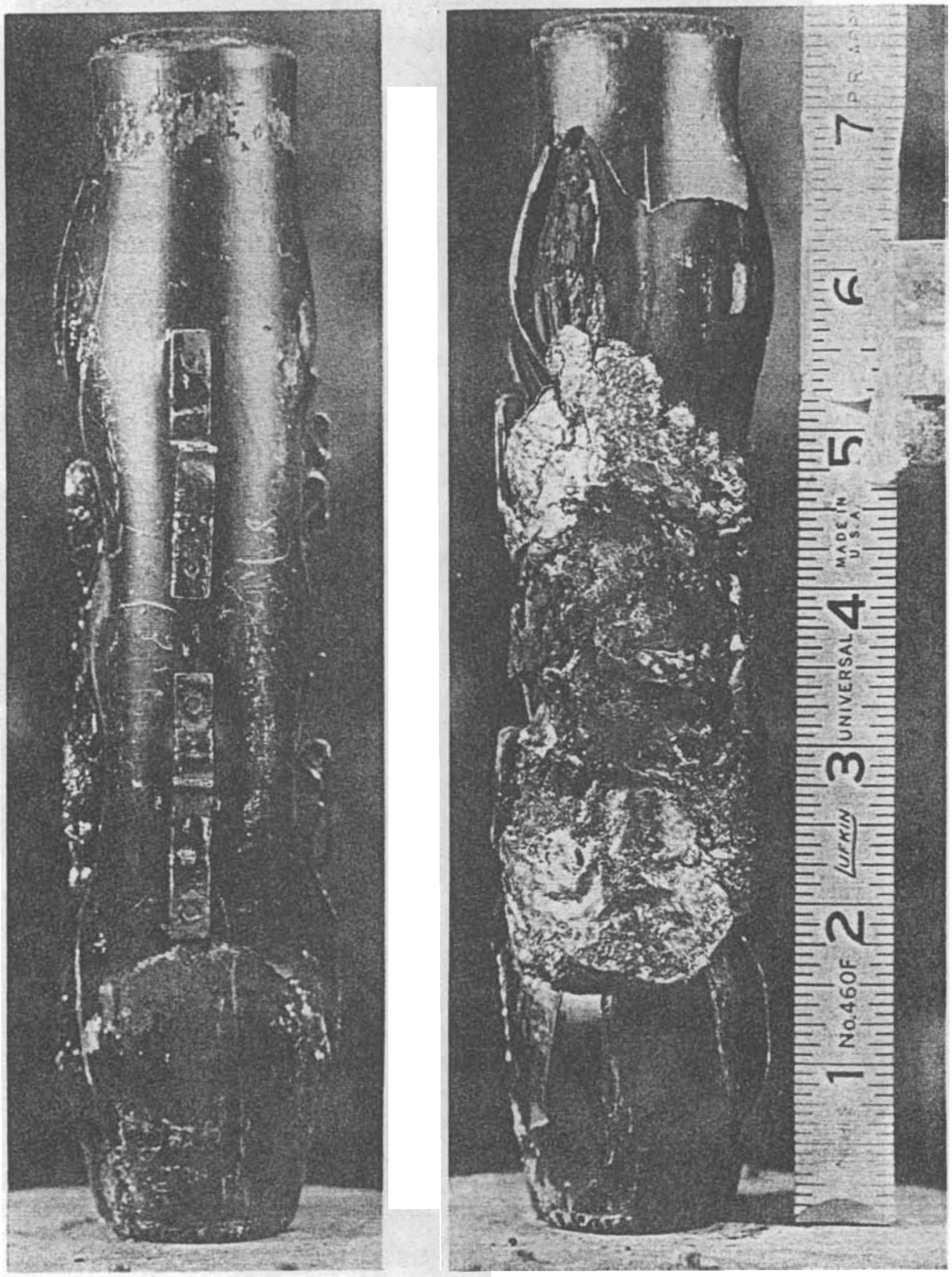
INNER FUEL ELEMENTS

The other four experiments were with Inner fuel elements. Their description is as follows:

SNH-7

The fuel element for Experiment SNH-7 was heated to rupture at 1075 °C following which the temperature was leveled at 1070 °C. Rupture occurred in the outer clad near the longitudinal center of the fuel which is typical of Inner fuel elements when the end caps are restrained. An estimated 15% of the plastic uranium extruded through the rupture and filled the bottom third of the annulus between the fuel and the quartz tube for a length of about 2 1/2 in. Oxidation occurred on the Zircaloy cladding and the exposed surface of the uranium in the annular space between the fuel and tube.

Pictures of the fuel used in SNH-7 are shown in Figures 3 and 4. Figure 3 shows the uranium which was extruded into the lower part of the annular gap between the fuel and quartz tube. The shiny surface of this uranium is indicative of the lack of oxidation at the uranium-quartz interface. The splits in the clad upstream and downstream of the extruded uranium are secondary ruptures that occurred after the initial rupture. These secondary ruptures, prevalent for Inner fuels, apparently



TOP VIEW - ∿0.65X

BOTTOM VIEW - ∿0.65X

TEST SNH-7

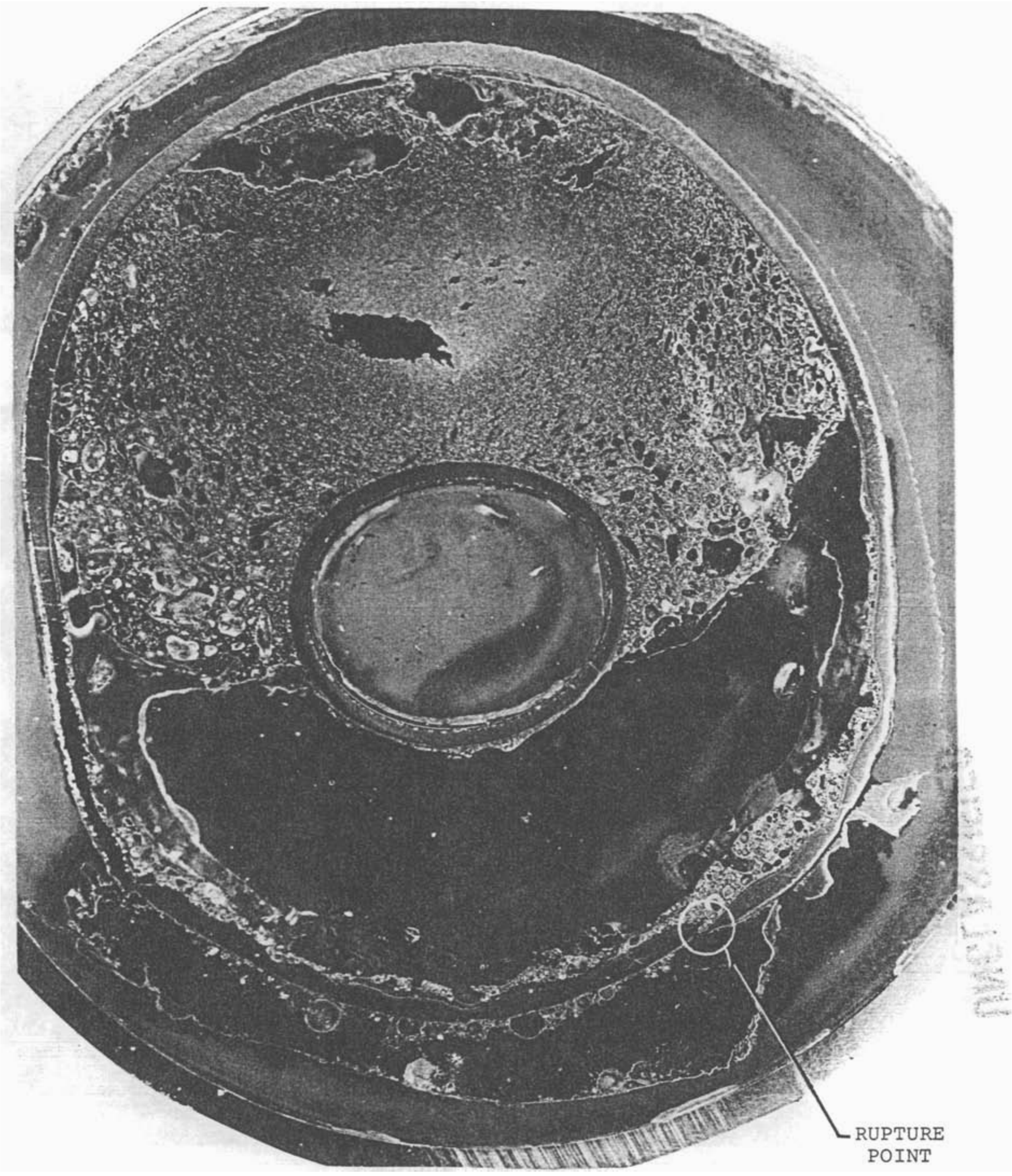
INNER ELEMENT
TEMP = 1070 C

TIME AT TEMP = 60 MIN

FIGURE 3. Postheating Picture of Fuel, Test SNH-7

[redacted]

[redacted]



TEST SNH-7

BOTTOM POSITION

~2.96X

CROSS SECTION SHOWING URANIUM POROSITY,
VOID AND CLADDING RUPTURE

FIGURE 4. Section View of Fuel, SNH-7

[redacted]

resulted from a buildup of internal gas pressure after the original breach was sealed by the expelled uranium. The original rupture is quite small and generally is sealed shortly after decay of the original pressure pulse by the solid uranium packed between the quartz tube and the cladding. The size of the secondary ruptures appears to be inversely related to the amount of uranium expelled. This relationship would be expected if the secondary ruptures were a function of internal gas pressures. Internal uranium oxidation in the neighborhood of these secondary ruptures is not extensive, indicating that turbulent diffusion of steam into the splits was not large, but it was enough to be recognized on the hydrogen trace as an increase in the H_2 concentration. Figure 4 is a cross section of the fuel cut through the rupture point and shows the spongy porous nature of the uranium due to coalescence and expansion of the fission gas.

SNH-8

The fuel element for SNH-8 was heated to rupture at 1060 °C and held at 1080 °C for the duration of the test. Rupture occurred in the outer clad near the longitudinal center of the fuel. The plastic uranium extruded through the rupture was estimated to be 25 to 30% of the total. The extruded uranium filled the lower two-thirds of the annulus between the fuel and tube for a length of about 3 in. (Figure 5). Oxidation occurred only on the free surface of this extruded uranium and on the Zircaloy cladding not covered by uranium.

SNH-9

The fuel element for SNH-9 was heated to rupture at 1065 °C and held at 1080 °C. The uranium extruded through the rupture was 40 to 50% of the total. The uranium completely filled the annulus between the fuel and quartz tube

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SIDE VIEW AS HEATED

TEST SNH-8

INNER ELEMENT
TEMP = 1070 C   TIME AT TEMP = 60 MIN

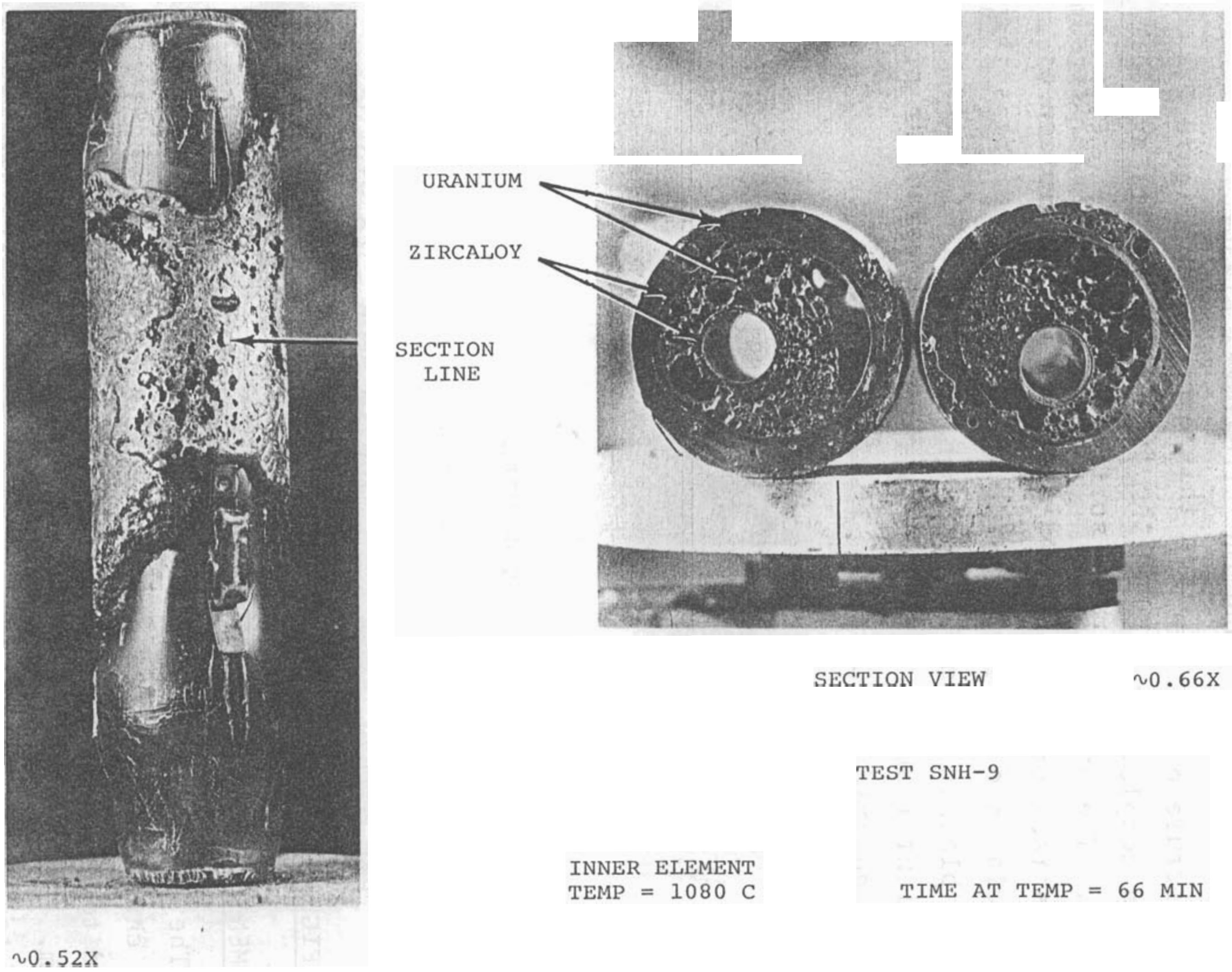
FIGURE 5. Postheating Picture of Fuel, Test SNH-8

and blocked free steam flow through the annulus. The only significant oxidation was on the upstream and downstream ends of the uranium in the annular ring, with less oxidation downstream than upstream, on the surfaces exposed by the secondary cladding ruptures and on the Zircaloy-2 cladding. The pictures (Figure 6) show the complete ring of extruded uranium around the fuel, the secondary ruptures in the outer cladding, the bright unoxidized uranium surface, and the porosity of the uranium created by the expansion of fission gas bubbles.

SNH-12

The fuel for this experiment was heated to rupture at 1080 °C and held at that temperature. Rupture occurred in the outer clad near the center of the fuel. The plastic uranium expelled through the rupture filled the lower half of the annulus between the fuel and the quartz tube for about half the fuel length. In addition, the uranium formed a ring across the top of the fuel 1/4 to 1/2 in. wide--sufficient to block the steam flow through the annulus. Subsequent oxidation

[redacted]



TOP VIEW

SECTION VIEW

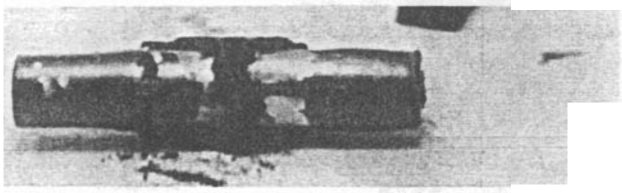
TEST SNH-9

INNER ELEMENT
TEMP = 1080 C

TIME AT TEMP = 66 MIN

FIGURE 6 Postheating Picture of Fuel, Test SNH-9 created two small holes through the ring sometime prior to the end of the test. Oxidation was on the free surface of the uranium in the annulus and the Zircaloy-2 cladding.

A picture of the fuel from this experiment, Figure 7, shows the complete ring around the fuel at about its axial midpoint. The bright Zircaloy surfaces immediately upstream and downstream of the ring are attributed to dissolution of the autoclaved oxide into the base metal. This indicates that the ring blocked steam flow through the annulus and there was insufficient reaction at these locations to re-establish or maintain an oxidized Zircaloy-2 surface.



TOP VIEW

TEST SNH-12

INNER ELEMENT
TEMP = 1070 C   TIME AT TEMP = 60 MIN

FIGURE 7. Postheating Picture of Fuel, Test SNH-12

TREATMENT OF THE DATA

The raw data for the metal-water reaction analysis is a strip chart obtained from a thermal conductivity meter calibrated to give the percentage hydrogen in the exiting gas stream. It can be shown that for the fixed system used in these tests both the total gas flow rate and the flow rate of the hydrogen produced are functions only of the percentage hydrogen in the gas. The experimental system was calibrated to give the hydrogen flow rate as a function of the percentage hydrogen.

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A problem in the treatment of the data was encountered when relating the hydrogen evolution as measured at the thermal conductivity meter with earlier events at the time the hydrogen was generated in the furnace. The peak hydrogen generation should occur immediately after fuel rupture and related expulsion of plastic uranium. The thermal conductivity recordings, however, show a peak hydrogen rate some 2 to 6 min after the rupture rather than the normal three-fourths of a minute travel time in the system. It was established that this additional time delay was caused, principally, by the cold charcoal traps in the sample trains and was a function of the partial pressure of air in the gas stream. Investigations showed that each trap absorbed about 8 liters of air and no hydrogen when cooled to the operating temperature of -70 °C. Following the rupture of the fuel when the hydrogen evolution was highest, the partial pressure of the air in the gas stream would be considerably less than initially. During this period the air in the cold traps would desorb and dilute the hydrogen. Once the initial peak hydrogen passed, the increasing air concentration in the gas stream, associated with the decreasing hydrogen evolution, caused a reabsorption of air onto the cold charcoal thus effecting a concentration of hydrogen downstream of the traps. Somewhat later, the hydrogen evolution rate reached a point where its change with time was small and the air loading on the cold charcoal closely approached equilibrium with the gas stream. Quasi steady-state conditions were then established and the hydrogen concentration leaving the cold charcoal traps closely approximated that entering. The quasi steady-state conditions were reached in about 6 to 8 min after the fuel ruptured.

Theoretically, if the equilibrium air loading characteristics of the cold charcoal and the dynamics of its loading

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and release were known, it should be possible to devise calculational techniques to determine the hydrogen input to the cold traps from knowledge of the hydrogen output from them. Before embarking upon the lengthy program necessary to provide the needed information for calculational techniques, the validity of the simplest assumption concerning hydrogen evolution rates during the first 6 min was investigated. The assumption is that the hydrogen evolution during this period conforms to that at later times, and that relations developed for the later periods could be extrapolated back to zero time to describe the early behavior. To check this, two experiments were made in which cold charcoal traps were not used. In both cases, the data for the first 6 min conformed quite closely to that predicted by back extrapolation of the data from times beyond 6 min. Qualitatively, it can be argued that this agreement should be expected since most of the major rapid physical changes associated with an experiment occurred within a few seconds after rupture. After the first 10 to 15 sec the system remained relatively stable physically for the duration of the run and there was no reason to expect behavior for the first 6 min to differ from that at greater times. Also any significant error produced by the charcoal beds would be in the instantaneous rate function and not in the total hydrogen measured for the test.

The analysis of the data, then, proceeded by use of calibration curves to relate the thermal conductivity meter data into hydrogen flow rate data. Typical hydrogen flow rate data are shown in Figure 8 for two fuels under similar test conditions with and without the -70 °C charcoal traps in the sampling system. A comparison of Run SNH-8 and 12 shows the time delay and suppression effects the charcoal traps have on the initial hydrogen peak. SNH-12 shows the normal time delay from point of reaction to point of measurement--about three-fourths of a minute.

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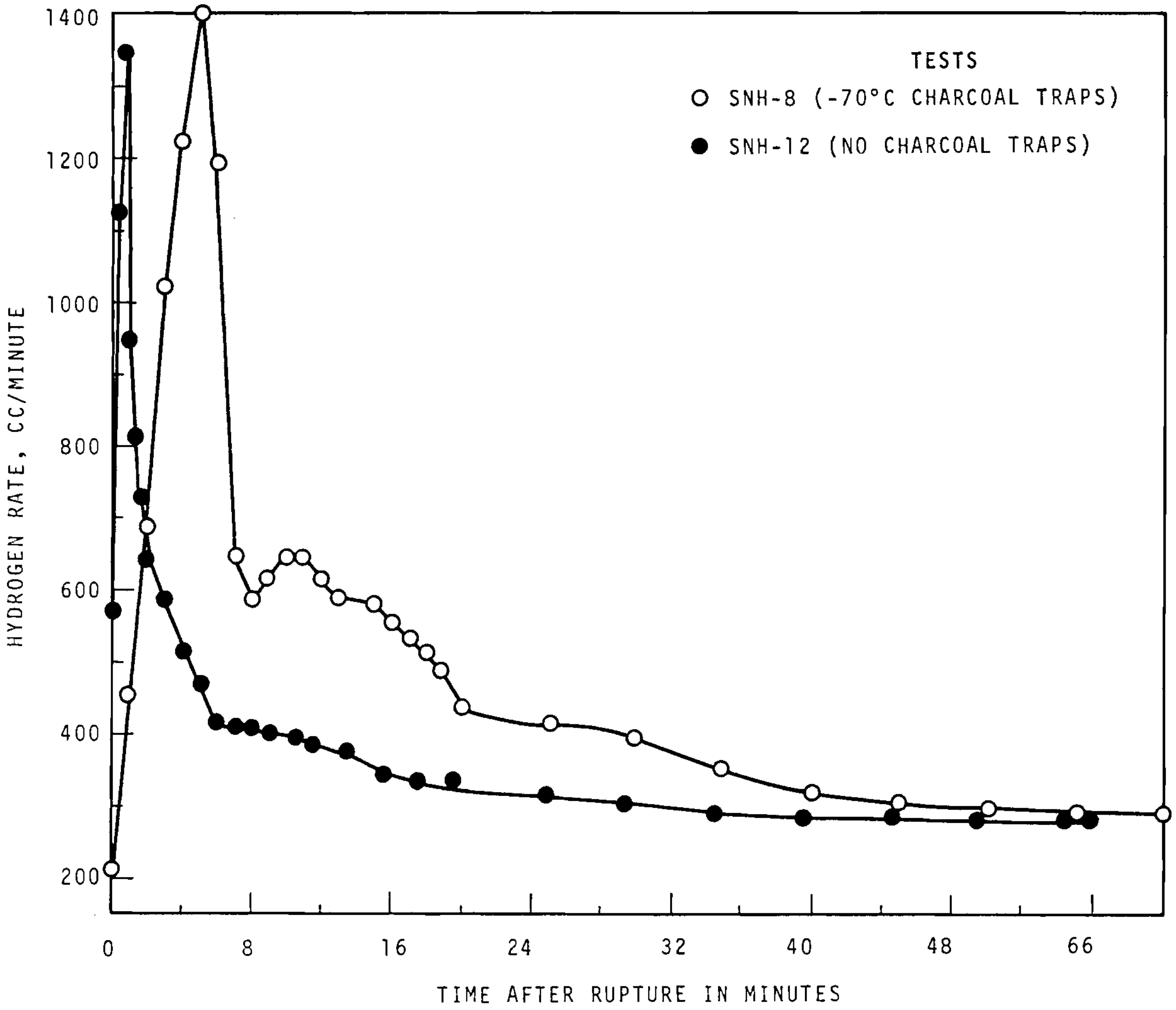

FIGURE 8. Typical Hydrogen Evolution Rate Curves

The next step in the treatment of the data was to perform a numerical integration of the hydrogen rate versus time data to give the total hydrogen evolved as a function of time. Typical curves from this operation are shown in Figure 9.

The first approach to an interpretation of the results as each experiment was completed was to fit equations to the data. In general, a reasonable approximation was obtained by fitting two equations to the data for each run. A plot of the square of the total hydrogen versus time showed that a

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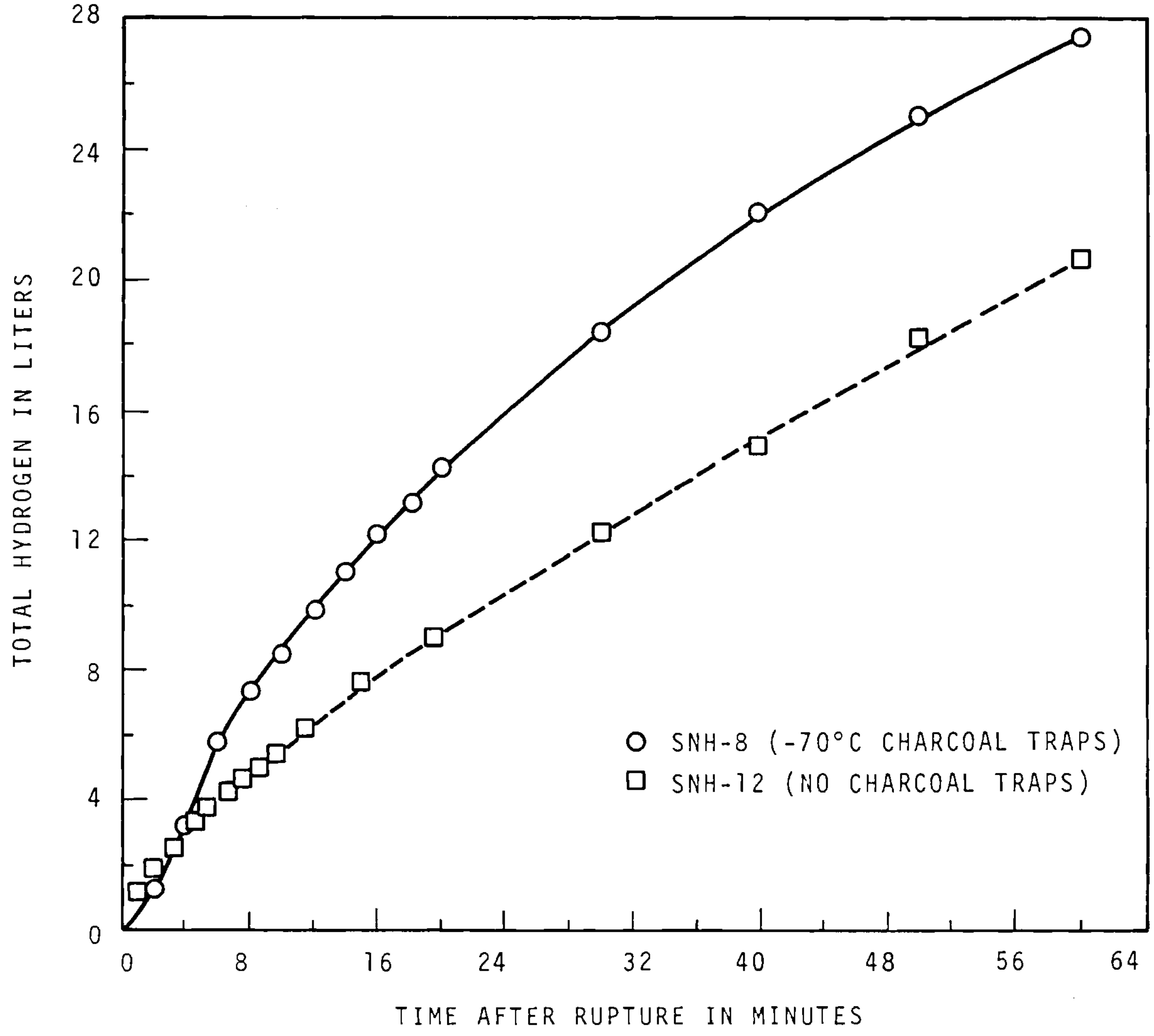

FIGURE 9. Typical Total Hydrogen Evolved Curves, Linear Plot

parabolic equation would approximate the data for the first several minutes and a linear equation for the balance of the experiment. This plot was extrapolated back to zero hydrogen to translocate zero time to obtain a more realistic estimate of the hydrogen generation rate prior to attaining quasi steady-state conditions in the system until all the experiments were completed and a more comprehensive analysis could be conducted. The equations so derived for each of the experiments are summarized in Table 2.

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TABLE 2. Hydrogen Evolution Equations for Individual Runs

Experiment	Equations	Effective Time Periods, min
SNH-3	$Q = 2.35\ t^{1/2}$	0-8
	$Q = 6.65 + 0.59\ (t-8)$	8-35
SNH-4	$Q = 1.66\ t^{1/2}$	0-8
	$Q = 4.70 + 0.253\ (t-8)$	8-11
SNH-6	$Q = 1.45\ t^{1/2}$	0-14
	$Q = 5.42 + 0.230\ (t-14)$	14-55
SNH-7	$Q = 3.13\ t^{1/2}$	0-17
	$Q = 12.9 + 0.422\ (t-17)$	17-60
SNH-8	$Q = 3.18\ t^{1/2}$	0-17
	$Q = 13.1 + 0.348\ (t-17)$	17-60
SNH-9	$Q = 1.64\ t^{1/2}$	0-8
	$Q = 4.65 + 0.310\ (t-8)$	8-66
SNH-10	$Q = 6.44\ t^{1/2}$	0-8
	$Q = 18.2 + 1.038\ (t-8)$	8-80
SNH-11	$Q = 2.34\ t^{1/2}$	0-13.5
	$Q = 8.6 + 0.313\ (t-13.5)$	13.5-65
SNH-12	$Q = 1.69\ t^{1/2}$	0-8
	$Q = 4.8 + 0.309\ (t-8)$	8-60

There is no reason to expect the summation possibly of many different oxidation rates of these experiments to conform to that of a single simple rate law throughout the oxidation period. Rather, an apparent rate law regardless of the function described is more realistic due to the major influencing physical changes that occur during a test. It is obvious from the equations in Table 2, developed as each specific test was completed, that application to an analysis for the total reactor would be laborious and rather speculative at best and might be less accurate than a single apparent rate law. Also the equations from the Outer and Inner fuel tests could not easily be combined to produce a single equation representing the metal-water reaction rate for a fuel assembly.

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The simplest alternate is the assumption of an apparent behavior somewhere between a constant and a parabolic rate. If this assumption is valid, plots of the logarithm of the total hydrogen evolved against the logarithm of the time of oxidation would have slopes between one for a constant rate and one-half for a parabolic rate. Such plots produced single straight lines with slopes between one-half and one that approximated the data for each experiment to within 5%, except for the points at times less than about 6 min for those runs in which the cold charcoal traps were used. Examples of the plots are shown in Figure 10. SNH-8 and SNH-12 were used as examples to provide

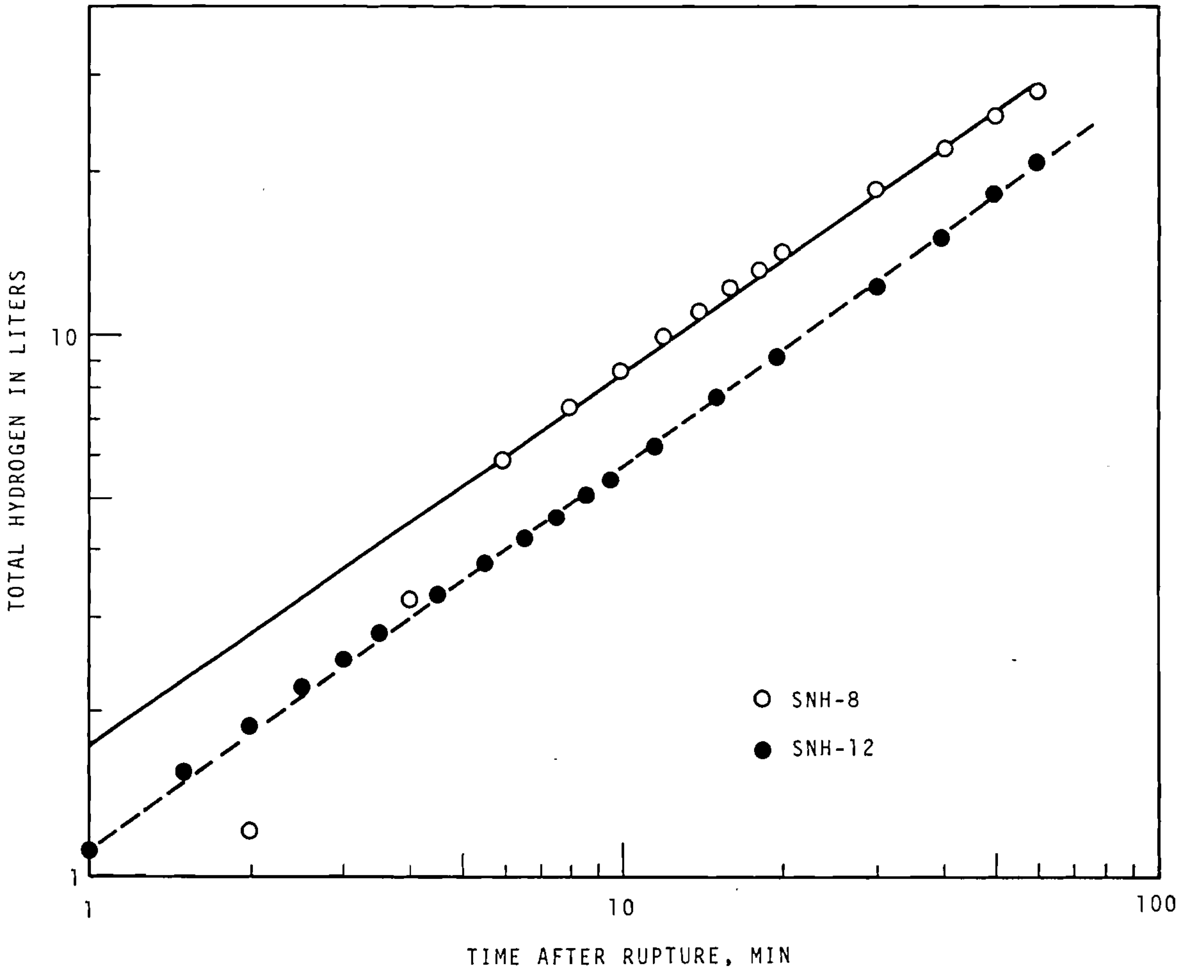

FIGURE 10. Typical Total Hydrogen Evolved Curves, Log-Log Plot

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another comparison of the influence of the cold charcoal traps on the observed hydrogen evolution in the first few minutes of a test. Equations of the form,

$$Q = K\ t^n,$$

where Q is total hydrogen in liters and t is time of oxidation were developed for each plot. The values of the coefficient, K, and the exponent, n, are shown in Table 3. The slopes, exponent n, ranged from 0.59 to 0.82. The average weighed on a time basis was 0.72.

TABLE 3. Constants for the Hydrogen Evolution Equation, $Q = K\ t^n$

Experiment	Coefficient, K	Exponent, n
SNH-3	1.25	0.82
SNH-4	1.37	0.59
SNH-6	0.74	0.75
SNH-7	1.75	0.70
SNH-8	2.06	0.64
SNH-9	0.96	0.74
SNH-10	4.34	0.70
SNH-11	1.52	0.66
SNH-12	1.14	0.71

To further simplify the equations describing the hydrogen evolution, the assumption that the average slope of 0.72 would apply to all cases was investigated. This was done by plotting the total hydrogen evolved against the time of oxidation raised to the 0.72 power. All the data fell within 10% of a straight line for each experiment except for times less than 6 min for those runs in which cold charcoal traps were used. The resulting curves showing the measured slopes for all the experiments are presented in Figures 11 through 13.

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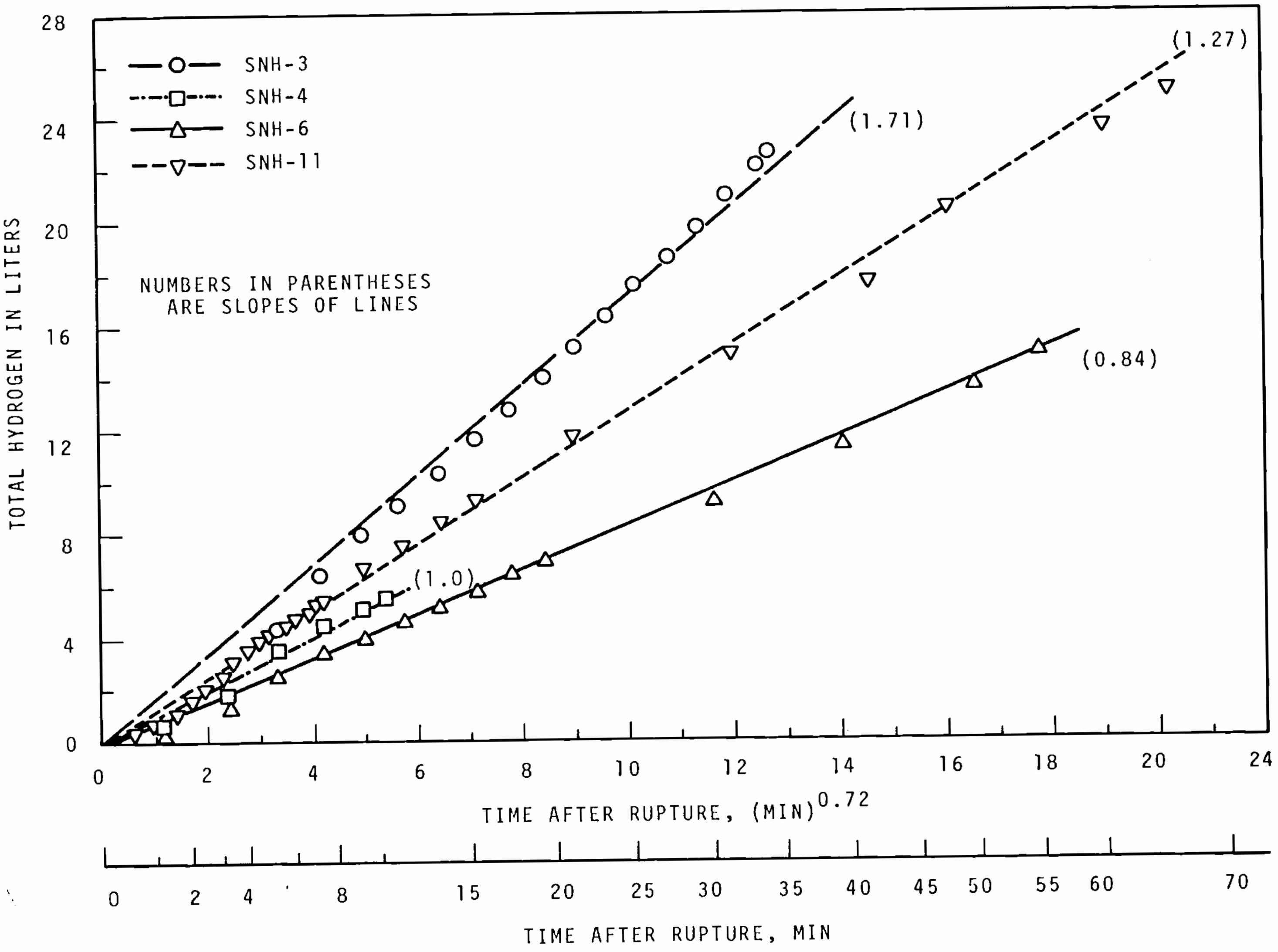

FIGURE 11. Total Hydrogen as a Function of 0.72 Power of Time, Tests 3, 4, 6 and 11

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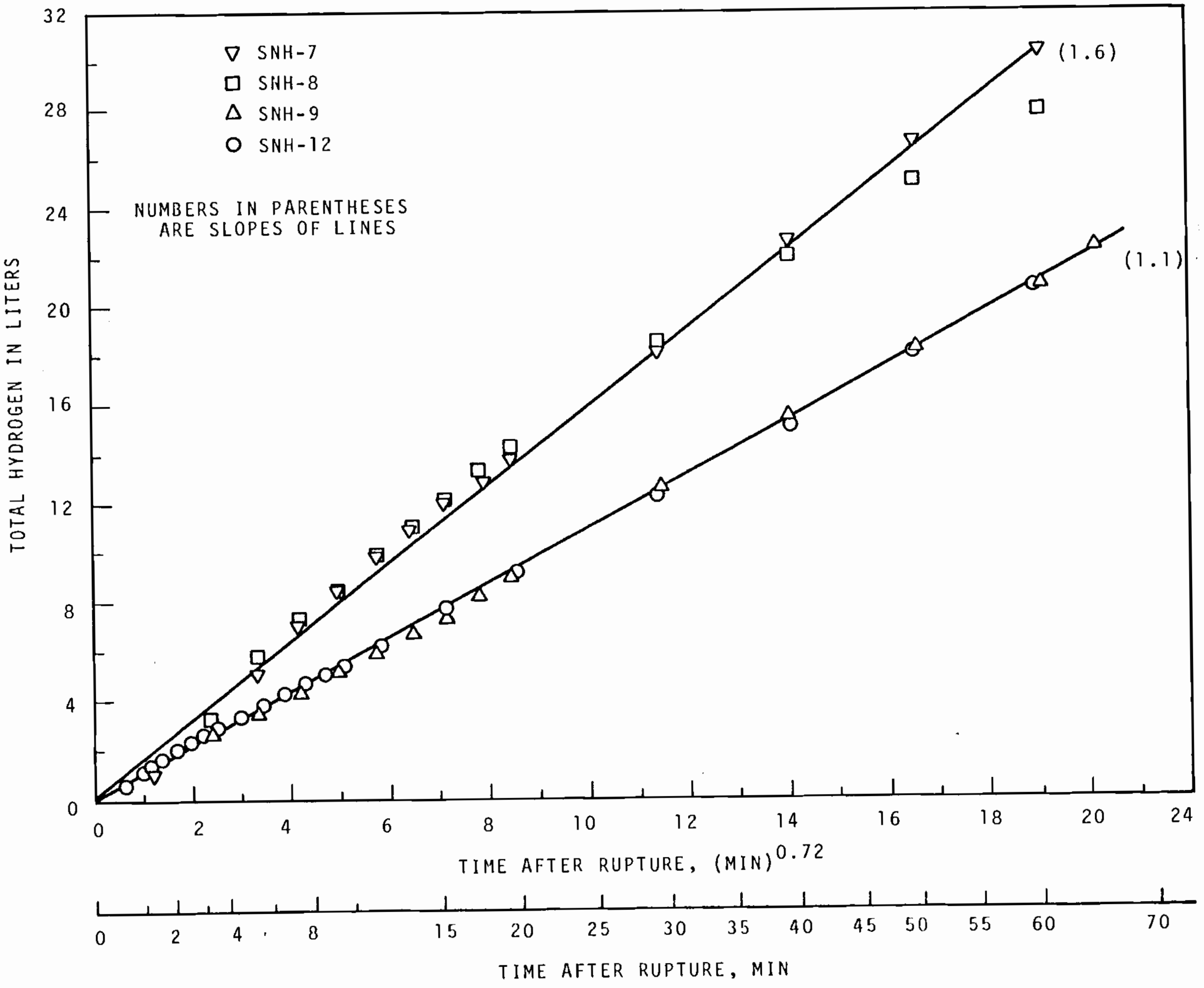

FIGURE 12. Total Hydrogen as a Function of 0.72 Power of Time, Tests SNH-7, 8, 9 and 12

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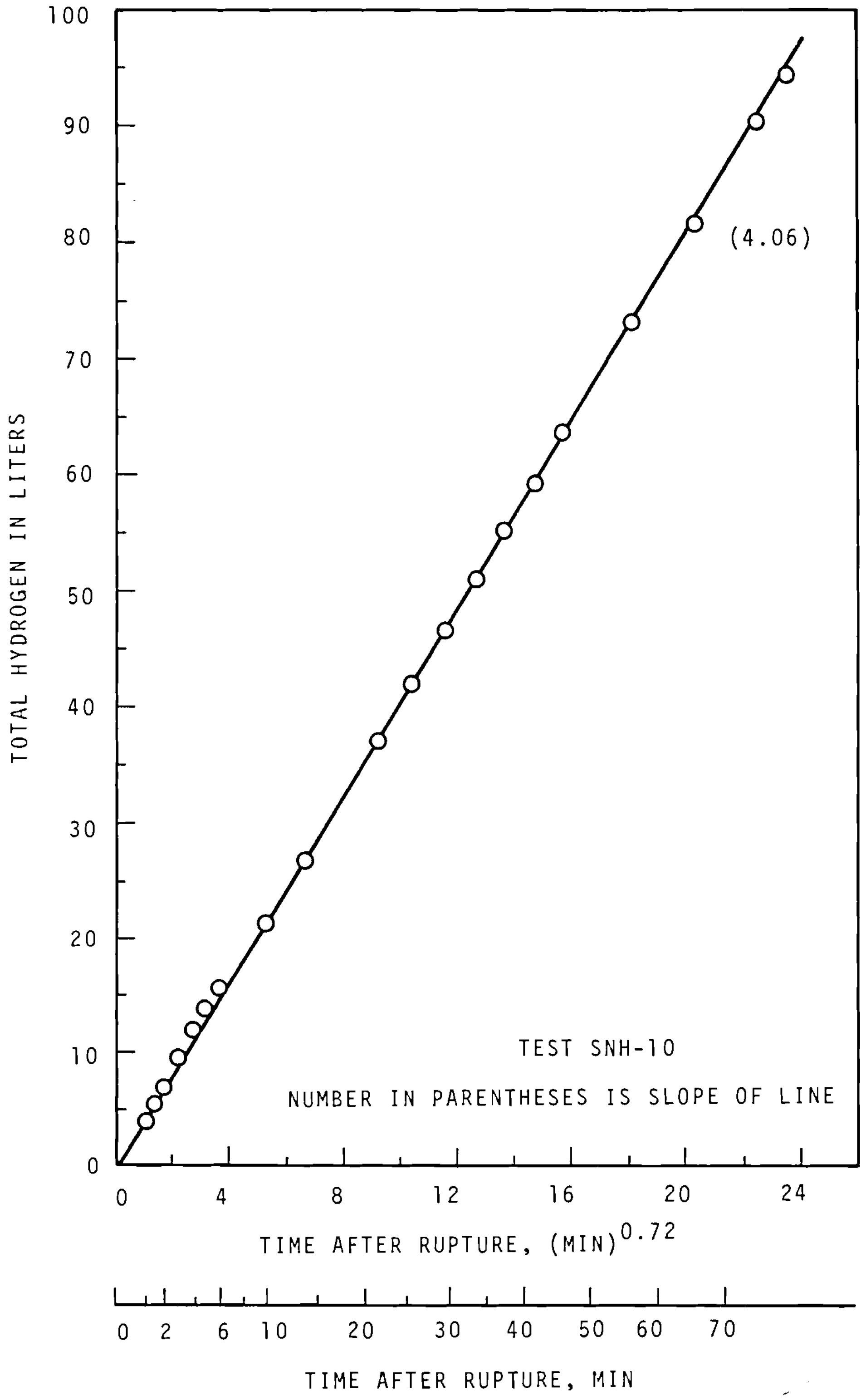

FIGURE 13. Total Hydrogen as a Function of 0.72 Power of Time, Test SNH-10

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Figure 14 is a log-log plot of the lines in Figures 11 through 13. The numbers are the rate constants (A) of Equation (1). Also included is a line representing the equation developed for a fuel assembly (tube-in-tube configuration) as discussed later.

The information from Figures 11 through 13 shows that the metal-water reaction behavior for the fuels in these tests was correlated by the equation

$$Q = A\ t^{0.72} \qquad (1)$$

where Q = total hydrogen evolved in liters
t = time after rupture in minutes
A = proportionality constant determined for each experiment.

The coefficient, A, is a measure of the effective surface area of oxidation for the basic reaction rate at the isothermal temperature. The values for A correlated with the information obtained from postheating examination of the material--the higher the value the greater the effective surface area and oxidation products. The exponent, 0.72, is a measure of the effect of the physical changes on the basic parabolic rate law discussed previously.

It must be emphasized that the above correlation, even though there are qualitative arguments that the form of the equation might be expected, is an emperical approximation which represents an average of two oxidation mechanisms and possibly several rates proceeding more or less simultaneously. Evidence of the averaging embodied in Equation (1) is given by the behavior of the instantaneous hydrogen evolution rate. The instantaneous rate would be the differential of Equation (1) or:

$$\frac{dQ}{dt} = \frac{0.72\ A}{t^{0.28}}. \qquad (2)$$

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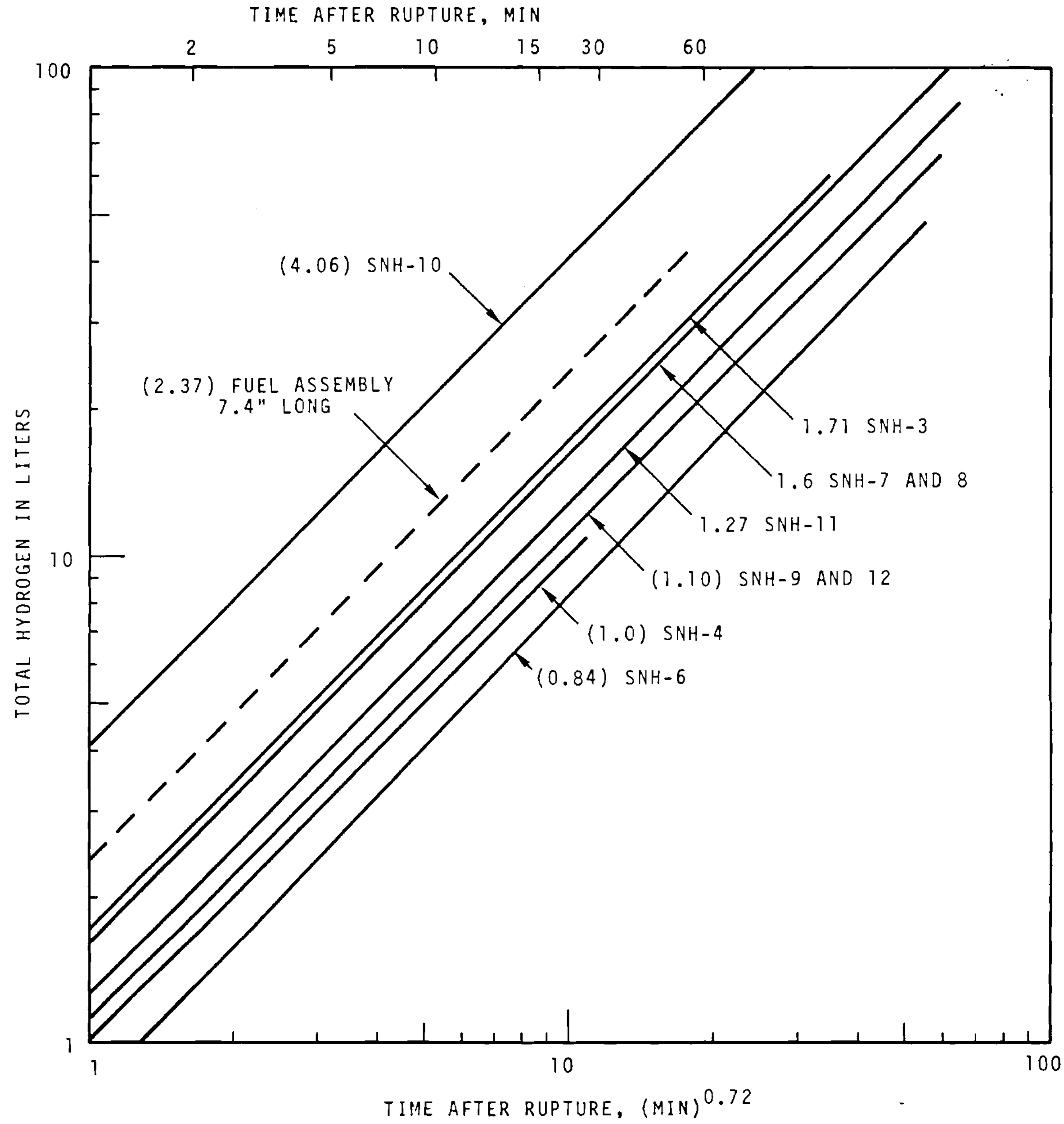

FIGURE 14. Total Hydrogen as a Function of 0.72 Power of Time, Log-Log Plot of all Tests

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Comparisons of the experimental data with values calculated with Equation (2) show agreement to within 30%. While this agreement is reasonable, it is not as good as the 10% found for the total hydrogen generation. The improvement in the accuracy of the correlation when used for the total hydrogen is probably due to the summing operation to obtain the total generation which, in effect, averages the behavior over the total time.

Since Equations (1) and (2) were emperically developed, their use for conditions other than and for times longer than those of these experiments may not be warranted, but if used would produce in general a more conservative estimate of the volume of hydrogen produced than would be shown by empirical data collected for longer time periods.

DISCUSSION

The information in the description of individual experiments and in Table 1 allow some generalizations to be made.

First, the extent of the metal-water reaction rate as measured by hydrogen evolution is reasonably correlated by Equation (1), namely,

$$Q = A\ t^{0.72}.$$

For these experiments, which were mostly done at nearly the same temperature, the rate coefficient, A, is a measure of the effective oxidizing surface area. The information obtained in these experiments is therefore interpreted in terms of an effective area rather than a basic metal-water reaction rate law.

EFFECT OF RADIAL RESTRAINT

An indication of the significance of radial restraint on the metal-water reaction rate is obtained by comparing Test SNH-3 with SNH-4 and 6, which were essentially identical. The major differences in the test conditions were that SNH-3 had a lower isothermal temperature and was the only fuel not heated in a quartz tube simulating the radial geometry of the reactor. The quantitative effect of the lower temperature (1025 °C versus 1060 °C) is not specifically known, but it should produce about a 30% lower reaction rate, all other things being equal. The lower rate coefficients for SNH-4 and 6 (Table 1) compared to SNH-3 was due to the only major observed difference--the reduction of the effective surface area by expansion of the outer cladding to the diameter of the quartz tube. Assuming no oxidation on the outer can wall for SNH-3, an approximation of what occurred for SNH-4 and 6, the effective surface area would be 60% less. This reduces the rate constant from 1.71 to about 0.68 which compares favorably with the 1.1 and 0.84 rate constants for SNH-4 and 6 which were at the higher isothermal temperature and accrued some oxidation on the outer can wall in the region of the end caps. This agreement shows the Zircaloy-2-water reaction as the principal source of hydrogen for these three fuels.

To date, only the Outer fuels in the 3500 to 4100 MWd/ton exposure have exhibited this expansion to the diameter of the process tube prior to rupture. The fuels below 2000 MWd/ton and and those above 5000 MWd/ton rupture before any great expansion of the outer cladding--the first due to a less friable bond and internal pressure, the latter due to a lower rupture temperature through an early collapse of the inner cladding.

EFFECT OF EXPOSURE LEVEL

A comparison of Outer fuel elements from Tests SNH-3, 4, and 6, with 10 and 11 provides information relative to the effect of exposure level on the apparent metal-water reaction rate. The fuel with the highest exposure level (Test 3, 4, and 6) had a much higher degree of clad separation, a lower rupture temperature, and a very much smaller effective uranium surface area than did the lower exposure fuel. Primarily as a consequence of the minimal exposure of uranium to the steam atmosphere, there was less metal-water reaction of the higher exposure fuels.

The absence of uranium extrusion from the more exposed fuels is associated with two conditions--a higher fission gas inventory and a more friable Zircaloy-2 uranium diffusion bond. The result of these two effects is a complete fracture of the clad-uranium bond soon after the temperature passes through the β-γ phase change which frees a significant fraction of the fission gas. The space between the clad and uranium acts as a fission gas reservoir and provides a free path for venting through the rupture without uranium expulsion. For the lower exposed material, bond separation is at isolated spots and does not propagate over the entire fuel length prior to rupture. Thus, more fission gas remains within the cracked uranium structure and upon rupture, the internal pressure is relieved by expulsion of some fraction of the foamy plastic uranium created by expansion of the fission gases. Another possible influencing factor entering into this phenomenon is that the higher exposure material ruptures at a lower temperature where the uranium has lesser plasticity. These conclusions apply to Outer fuel elements only. The two levels investigated are insufficient to fully define the exposure level effect; however, the observed effects suggest that the metal-water reaction for Outer fuels up to 4100 MWd/ton is inversely related to exposure level for temperatures below the uranium melting point. Inner fuel elements at exposures greater than 2000 MWd/ton have not been tested.

Earlier tests designed to determine only the rupture temperature of fuel in the 2000 MWd/ton range showed a direct relationship between rate of heating and extrusion of uranium--the faster the rate the greater the amount of uranium expelled which related indirectly to the equalization of internal gas pressure due to extensive bond fracture. This suggests that to some degree the length of time between the β-γ phase change temperature and rupture of the cladding influences the amount of uranium expelled from the cladding, at least for fuels of equal exposure at temperatures below the uranium melting point. This effect has not been explored in sufficient detail to produce qualitative or quantitative answers, but it might significantly alter the magnitude of the reaction.

RELATIONSHIP OF PHYSICAL CHANGES

Since for massive specimens oxidation and, to some unknown extent, fission product release is primarily a function of the physical changes in the fuel, application of these effects to reactor geometry is important. The quantitative translocation of uranium was established as an inverse function of irradiation level, so a reactor analysis of the physical syndrome must be based on the tube exposure and on a fuel assembly. Since no Inner fuels in the high MWd/ton range have been tested only those fuels in the 2000 MWd/ton range or less can be analyzed without speculation.

Two definite rupture patterns were established--one for the Inner fuel and one for the Outer fuel of the assembly. The Outer fuels ruptured initially at the juncture of the inner can wall and the end cap and Inner fuels near the longitudinal center of their outer cladding. There was one exception to this rupture pattern. Of the twenty Outer fuels ruptured to date, only one produced a secondary rupture that expelled uranium to the annular space between the fuel and the process tube (SNH-11). In this test the oxidation of the effective uranium surface area about equaled that which would have occurred on the Zircaloy-2 surface covered by the uranium and the net effect of the secondary rupture was insignificant. This type of rupture would have a much lower probability of occurring in the reactor since the inner can wall of the Outer fuel would be at a significantly higher temperature than the outer cladding due to radiant heating by the inner element and a lower heat transfer rate.

With both fuels of an assembly rupturing and discharging uranium to their common annulus, the physical changes would be additive. It is obvious from the amount of uranium expelled that the annulus between the Inner and Outer fuel will be plugged both upstream and downstream of the central zone of the reactor. Any circulation, then, would be through the center hole of the Inner fuel and through the annular space between the Outer fuel and process tube. The secondary ruptures observed with the Inner elements would only compound the plugging due to the additional expansion. It is not improbable that uranium might be forced into the Outer-Process Tube Annulus through spaces between the ends of the fuels. However, the seal between fuel assemblies created by axial growth during the temperature transient should be sufficient to prevent forcing an amount of uranium into the annular space that would significantly alter the total metal-water reaction. Thus, after the initial ruptures, the principal source of hydrogen is from the Zircaloy-2-water reaction and to some extent from the exposed uranium upstream and downstream of the plugs. The latter should be a small fraction of the total oxidation since turbulent diffusion of the steam would be required and a steam limited condition would probably prevail.

Although the original pressure pulses from rupturing of the central fuel passed prior to formation of any plugs, some buildup in pressure between the two plugs should occur. However, since the uranium is in the plastic state, it is not inconceivable that the plugs would be pushed outward. Whether or not one plug would be destroyed completely would be dependent on the length of movement required to equalize the pressure across the uranium plug. This to some extent sould be dependent upon the free volume between the plugs and the available free gas, both of which are unknown at the present time. However, one plug should remain, blocking free flow through the annulus.

APPLICATION TO REACTOR USE

The information from these experiments shows that the oxidation mechanism for all cases is about the same and remains about the same for the duration of each experiment. Differences in the metal-water reaction between the experiments depends primarily upon the differences in the effective area available for oxidation. An area factor term was determined from the data of each experiment. There is, however, about a five-fold variation between the minimum and maximum area factor terms. The problem is to select an appropriate average area factor term within this range for reactor use.

Based on the observed additive physical changes for fuels in the 2000 MWd/ton range at temperatures around 1075 °C the applicable hydrogen area coefficient is the sum of the Inner and Outer tests most representative of a plugged Inner-Outer annulus and a free Outer to Process Tube Annulus. Although back diffusion to the downstream end of the uranium plug

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was significant, Test SNH-9 conservatively approximates the plugged Inner-Outer annulus condition. Selecting a test that would typify the expanding outer cladding is more difficult, but comparison of Tests SNH-3 and 11 produced a reasonable estimate. The rate constant of SNH-3 (1.71) adjusted for reactions of the inner cladding becomes about 1.0. The rate coefficient for SNH-11 was 1.27. Since the temperature for SNH-3 was about 50 °C lower than SNH-11, the adjusted rate coefficient of 1 should be low--from Baker and Justs'(4) work by about a factor of 1.34. A correction for the surface area should be applied to normalize for the excessive expansion of SNH-3 cladding beyond the diameter of the process tube. This area difference was calculated to be near 5% and the corrected value for SNH-3 becomes $A = 1 \times 1.34 \times 0.95 = 1.273$--comparable to that obtained for SNH-11. Summing, SNH-9 (1.1) and SNH-3 (1.27) would give an area factor of about 2.37 and the hydrogen generation equation would then be:

$$Q = 3.84\ t^{0.72}\ \text{liters/ft of fuel or}$$

$$Q = 0.136\ t^{0.72}\ \text{ft}^3\text{/ft of fuel}$$

for a fuel assembly of ∿2000 MWd/ton near the uranium melting point. Since these equations were empirically developed, they should be applied only to that portion of the fuel in the reactor that approximates the test conditions with respect to temperature (1060 to 1080 °C) exposure level (∿2300 MWd/ton) and time after loss of coolant (3 to 60 min) and with the assumption that the reaction was not steam limited.

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