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MIT 334-48

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IN - PILE LOOP
IRRADIATION STUDIES
OF
ORGANIC COOLANT MATERIALS

(AEC Research and Development Report
Contract No. AT(38-1) -334)

Progress Report
October 1, 1965 — December 31, 1965

Department of Nuclear Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

MIT-334-48
Reactor Technology
Standard TID 4500

IN-PILE LOOP IRRADIATION STUDIES OF ORGANIC COOLANT MATERIALS

PROGRESS REPORT
OCTOBER 1, 1965 - DECEMBER 31, 1965

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(M.I.T. Project No. DSR 9819)

Work Performed Under Contract No. AT(38-1)-334
with the
Savannah River Operations Office
U. S. ATOMIC ENERGY COMMISSION

Issued: April 1, 1966

(MITNE-75)

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CHAPTER 1

SUMMARY

Transient Run 15 which degraded the terphenyl from the 83% level of Steady-State Run 14 to the level of 61% desired for Steady-State Run 16 was completed this quarter, covering the period October 1 to October 28, 1965. The irradiation temperature for this run was 800°F to minimize the time required to change concentrations between Runs 14 and 16. The start of true steady-state operation in Run 16 was delayed approximately 2 months until December 28, 1965 due to the discovery and repair of several small leaks at the top of the in-pile section and a pump change necessitated by a cracked weld in the cooling jacket of the pump.

The MITR thermal power was increased from 2 to 5 MW this quarter thereby increasing the dose rate in the organic (or decreasing the time required for a low temperature irradiation) by a factor of 2 1/2; the dose rate to the organic averaged over the in-pile section volume is now approximately 0.30 watts/gm in the present irradiation position, Fuel Position 20, and about 0.8 watts/gm in Fuel Position 1 where the irradiations will be carried out following completion of the planned runs in Fuel Position 20.

The analysis of the data from Transient Run 15 is complicated by the occurrence of radiopyrolysis at the irradiation temperature of 800°F as well as the change of reactor power levels which took place during this run; the reactor power level was increased in weekly steps of 1 MW in raising the power from 2 to 5 MW. Using the results of steady-state Run 14 along with the results of Run 15, the radiolysis rate constant, $k_{R,2}$ (second order), and the radiopyrolysis rate constant, k_P, were estimated to be 2.33×10^{-2} and 1.1×10^{-3} hr^{-1} respectively. The value of k_P obtained was approximately 25% lower than previous steady-state runs at 800°F. The value of k_P was approximately three or four times that of unirradiated coolant.

The degradation results from Run 14 were compared and analyzed with those of other investigators in order to investigate the reaction order and the fast neutron effect ratio G_N/G_γ. The value of G_N/G_γ and the reaction rate order which fits the M.I.T. data as well as that of most other investigators appears to be about 4.7 and second order respectively.

Considerable progress has been made in improving the precision and reproducibility of the terphenyl analysis. It is now felt that the terphenyl content of a single sample can be determined to about an accuracy of ±0.5% (one standard deviation). Work is proceeding well on developing gas chromatographic analytical techniques for LIB and HB analysis of the irradiated coolant.

In order to better define the fast neutron spectrum in the organic material, new foil materials are being evaluated for use at M.I.T. to fill in the energy gap from 120 ev (Co^{59} resonance) to 2.9 Mev (Ni threshold) where measurements are not now made. U^{238}, U^{236} and U^{234} have been selected as new threshold detectors with threshold energies of 1.3 Mev, 0.84 Mev and 0.24 Mev, respectively; Na^{23} has been selected as a new resonance detector with a resonance energy of 2.9 kev. In order to increase the accuracy of the calorimetric measurements, particularly the fast neutron dose rate, special low A materials which will have high fast neutron dose rates have been evaluated and LiH selected as a new calorimeter material to supplement those now used.

Irradiated organic samples from Run 14 were analyzed by Atomics International for water content, MST and oxygen content. The values for the Run 14 coolant were found to be similar to those for the PNPF coolant.

CHAPTER 2

PROJECT ACCOMPLISHMENTS THIS QUARTER

Irradiation Run 15 was initiated on October 4, 1965 at a capsule temperature of 800°F and completed on October 28, 1965. The purpose of the run was to degrade the organic in the loop from approximately 83% OMP to approximately 61% OMP in as short a period as practical to reach the OMP concentration desired for Steady-State Irradiation Run 16. On November 1, 1965 the terphenyl concentration reached approximately 61%. At this point coolant recycle was started to begin Steady-State Run 16. However, due to difficulties with loop operation which required maintenance, as discussed below, steady-state operation on Run 16 was not achieved until December 28, 1965. By comparing the results of Steady-State Run 16 with the results obtained previously in Steady-State Run 1C which was completed in August, 1962 at a fast neutron fraction, f_N, of 0.37, an evaluation of the fast neutron effect on radiolysis can be made. Comparison of Run 14 and Run 16 data will be used to evaluate the order of the degradation caused by radiolysis.

During Run 15 the MITR thermal power was raised from a nominal 2 MW to 5 MW in three steps. The power changes were made as follows:

Monday, October 1, 1965	3.0 MW
Monday, October 25, 1965	4.0 MW
Monday, November 1, 1965	5.0 MW

The average radiation dose from neutrons and gammas to the 285 grams of organic in the capsule at 5 MW is approximately 0.300 watts/gm with f_N estimated to be 0.06 ± 0.02.

Foil irradiations were conducted at 2 MW, 3 MW, 4 MW and 5 MW so that an evaluation of the fast neutron dose rate at 5 MW and the linearity of fast neutron dose rate with reactor power could be made. The foil data will be corroborated by calorimetry to be done in May or June, 1966 when the irradiations are completed in Position 20.

On November 13, 1965 a routine inspection of the 1/2" flare fittings, which connect the in-pile assembly to the lines through the biological shield, was carried out. There were no leaks at the fittings; however, very small leaks had developed where a heater and thermocouple had been brazed into the upper stainless steel elbow assembly. The leaks could be characterized as a "weeping" and very little organic was lost; the critical location of the leaks in the M.I.T. reactor required that they be repaired however. The leaks were repaired by drilling the heater and thermocouple out and heliarc welding over the holes. A subsequent inspection on November 26, 1965 revealed additional leaks on the remaining heater and thermocouple on the upper elbow. The leaks were repaired as before and subsequent inspection revealed no further leaks. A spare heater and thermocouple were installed in the central monitor tube of the in-pile assembly so that the planned irradiations in Position 20 can be completed without safety or operation difficulties.

As a result of the above leaks, concerted efforts on improved brazing of In-Pile Section No. 4 were carried out. Substantial delays in completion of the assembly resulted, but they are not expected to delay insertion on In-Pile Section No. 4 in the M.I.T. Fuel Position No. 1 in late June or early July 1966.

On November 25, 1965, it was also necessary to remove the main circulating pump (Chempump) from the loop due to a Dowtherm leak in the pump cooling jacket. The pump itself was still operating quite satisfactorily and had accumulated approximately 10,000-12,000 hours of trouble-free operation. Examination of the rear radial bearings showed negligible wear. The cooling jacket is being repaired and the pump will be used as a spare.

Since the new pump which was put on stream contained unirradiated organic, the OMP concentration for Run 16 was raised to about 64-65%. Approximately 3 1/2 weeks of transient operation were required to lower the concentration to the desired level of 62% terphenyl. Hence, initiation of the steady-state part of Run 16 was delayed until December 28, 1965

CHAPTER 3

PLANNED SCHEDULE OF IRRADIATIONS

In August, 1965 a meeting was held between personnel from M.I.T. and Atomics International to discuss the needs of the HWOCR in light of the in-pile loop capabilities at M.I.T. The proposed experimental schedule is presented in Table 3.1. The salient features of the schedule are:

(1) The first runs in Position 20, Run 14, 16 and XVII, are low temperature runs for the study of pure radiolysis. These runs are expected to provide definitive answers on the reaction order and the fast neutron effect. An understanding of pure radiolysis is considered a prerequisite to interpretation of high temperature irradiation results.

(2) Following these low temperature runs, a set of high temperature runs (XX through XXVIIb) will be made to complete the characterization of the degradation rates over the temperature range of 700°F to 800°F and terphenyl concentration range of 51% OMP to 90% OMP. The temperature range covers expected conditions for HWOCR. Although present HWOCR designs call for high terphenyl concentrations (>85%), the loop will operate in a wider range to allow better optimization studies of power costs and to better define the effects of the concentration of degradation products on radiopyrolysis. The last run in Position 20 is a high temperature run (XVIIIb) at 800°F at the low f_N to evaluate the effect, if any, of the fast neutron fraction on radiopyrolysis. The results of Run XVIIIb will be compared with similar runs at higher fast neutron fractions. Following this run, the irradiation position will be moved to Fuel Position 1 and the eight steady-state (SS) runs scheduled in Position 1 will be compared with the eight other high temperature runs already completed to provide a complete map of degradation rates at temperatures of 700°F, 750°F, 780°F and 800°F and at terphenyl concentrations varying from 51% to 90%.

Table 3.1

Schedule of Steady-State and Transient Irradiations in M.I.T. Organic Loop

Run No.	In-Pile Temp., ^{o}F	Terphenyl wt. %	Reactor Power, MW	f_N	Run Duration
14	572	SS 84	2	0.06 ± 0.02	completed 9/30/65
15	800	tr to 62	2-5		completed 10/28/65
16a	572	quasi SS 62	5		completed 12/29/65
16b	572	SS 62	5		12/29 - early March 1966
XVII	572	SS 90	5		1 month
XVIIIa	800	tr to 51	5		1 month
XVIIIb	800	SS 51	5		1 month

Calorimetry in Reactor Positions 20 and 1 - June, 1966

Start irradiations in Position 1 in late June or early July, 1966.

XIX	700	tr to 84	5	0.40	1/2 month
XX	700	SS 84	5	0.40	1 month
XXI	750	SS 84	5	0.40	1 month
XXIIa	750	tr to 54	5	0.40	1/2 month
XXIIb	750	SS 54	5	0.40	1 month
XXIII	800	SS 84	5	0.40	1 month
XXIV	700	SS 90	5	0.40	1 month
XXV	750	SS 90	5	0.40	1 month
XXVI	800	SS 90	5	0.40	1 month
XXVIIa	800	tr to 51	5	0.40	1/2 month
XXVIIb	800	SS 51	5	0.40	1 month

Calorimetry in Reactor Position 1 in May or June, 1967

Notes: Roman numerals are used to denote planned runs. As soon as a run is started the Roman numeral is changed to an Arabic numeral.

CHAPTER 4

PRELIMINARY EVALUATION OF IRRADIATION RESULTS

An average value of the radiopyrolysis rate constant was computed from the results of Transient Run 15 at 800°F. The results are discussed in Section 4.1. The preliminary degradation results obtained from Steady-State Run 14 were compared in terms of second order kinetics and G_N/G_γ with the results from 21 separate experiments both at M.I.T. and at other laboratories. Section 4.2 discusses these results.

4.1 Transient Run 15

According to the model of radiopyrolysis proposed by Terrien and Mason (1) and Euratom (2), and substantiated further by later reports (3, 4), radiopyrolysis is assumed to occur independently from radiolysis and can be added linearly to the radiolysis contribution to yield the total degradation observed as indicated in Equation (4.1):

$$G_T = G_R + G_P \tag{4.1}$$

where

G_T = observed total degradation rate, molecules degraded/100 ev absorbed

G_R = radiolytic degradation rate, molecules degraded/100 ev absorbed

G_P = pyrolytic degradation rate for radiolyzed coolant, molecules degraded/100 ev absorbed

G_P is a function of the average radiolytic dose around the entire loop and the pyrolysis rate constant k_P. It can be expressed as:

$$G_P = 11.65 \frac{k_P}{\overline{r}} C^m \tag{4.2}$$

where

k_P = radiopyrolysis rate constant, hr^{-1}

$\overline{r}$ = specific dose rate based on the energy absorbed by all the coolant over the entire time the coolant is at temperature, watts/gm

C = total terphenyl concentration, wt fraction
m = pyrolysis reaction order, generally assumed to be unity
11.65 = conversion factor, molecules degraded/watt-hr/100 ev/gm

In addition, G_P (and therefore k_P) was found to depend on the amount of degraded material in the coolant (1, 3, 4, 5). The radiopyrolysis rate was found to increase at a given irradiation temperature as the amount of degradation products increased or, equivalently, as the terphenyl content decreased. Consequently, transient runs in which the omp concentration changes, either in a loop or in a capsule, can be expected to yield only an average value of the radiopyrolysis rate constant at the temperature and over the terphenyl concentration range studied. Chemical analyses by chromatography are generally not accurate enough to define k_P over small terphenyl concentration changes of 2 or 3%.

Figure 4.1 presents a plot of the total terphenyl concentration in the loop during Transient Run 15 as a function of the irradiation time in hours. It can be seen in Figure 4.1 that the terphenyl concentration follows apparent first order kinetics (i.e. m = 1 in Equation (4.2)). It is interesting to note that the effect of increasing the reactor power (and therefore increasing the dose rate) does not appear to significantly affect the total degradation rate. This would be true if (1) the radiolysis contribution to the total degradation observed was small, (2) that the radiopyrolysis, which is assumed to occur by first order kinetics, was the major contributor to the degradation and (3) the radiopyrolysis contribution is independent of dose rate. Previous data (1, 3, 4, 5) would lead one to expect that in irradiations carried out at 800°F, the first two conditions are satisfied; the third condition, which also appears to be satisfied, is a unique feature of this run.

Consider the following simple derivation of the equations used to obtain a preliminary estimate of the radiopyrolysis rate constant for Run 15. The general degradation rate equation is:

$$\frac{G_T}{11.65} = -\frac{dC}{d\tau} = k_{R,n}C^n + \frac{k_{P,m}C^m}{\bar{r}} \qquad (4.3)$$

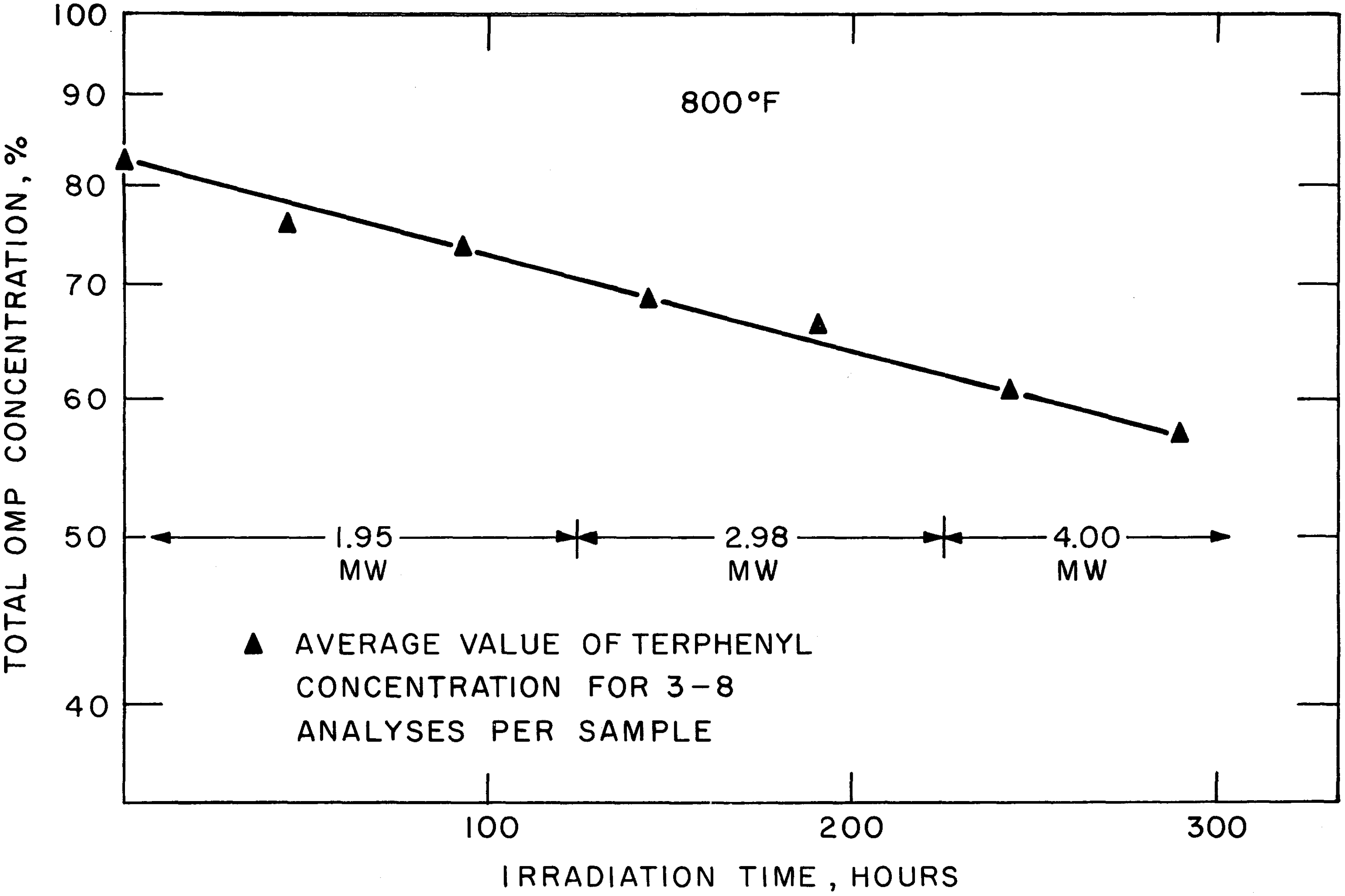

FIGURE 4.1 TOTAL OMP CONCENTRATION VS. TIME FOR RUN 15
800°F

where

$-\frac{dC}{d\tau} = G^T/11.65$ as defined in Equation (4.1)

C = terphenyl concentration, wt. fraction

τ = dose rate, watt-hr/gm

$k_{R,n}$ = radiolysis rate constant for radiolysis kinetics order, n, $(\text{watt-hr/gm})^{-1}$

k_P = radiopyrolysis rate constant for radiopyrolysis kinetics order m and is also defined in Equation (4.2)

$\bar{r}$ is defined for Equation (4.2)

Note that in Equation (4.3)

$$G_R = 11.65\ k_{R,n}C^n \tag{4.4}$$

and

$$G_P = 11.65\ \frac{k_{P,m}C^m}{\bar{r}} \tag{4.5}$$

from Equation (4.1).

If we consider the change in concentration as a function of time as in Figure 4.1, we can rewrite Equation (4.3) as

$$\frac{dC}{dt} = k_{R,n}\bar{r}C^n + k_{P,m}C^m \tag{4.6}$$

after multiplying Equation (4.3) by $\bar{r}$ and using the relation

$$d\tau = \bar{r}dt\ \frac{\text{watt-hr}}{\text{gm}}$$

For n = 2 (second order radiolysis) and m = 1 (first order radiopyrolysis), Equation (4.6) can be rearranged to give:

$$\frac{dC}{C} = \left[(\overline{k_{R,2}\bar{r}C}) + k_P\right] = Kdt \tag{4.7}$$

where

$\overline{k_{R,2}\bar{r}C}$ = pseudo radiolysis rate constant, hr^{-1}

K = overall rate constant, hr^{-1}

From Figure 4.1, K = approximately $1.25 \times 10^{-3}\ \text{hr}^{-1}$ for Run 15. Using the radiolysis data from Steady-State Run 14 and an activation energy, ΔE_R = 1 kcal/mole, the value of $k_{R,2}$ indicates that the radiolysis contribution started at 8% and increased to 12% of total degradation observed during

Run 15. Using the value of $k_{R,2}$ in Equation (4.7) the value of k_P is found by difference:

$$k_P(\text{Run 15}) = \left[K - \overline{k_{R,2}\bar{r}C}\right] \approx 1.1 \text{ x } 10^{-3} \text{ hr}^{-1} \tag{4.8}$$

This value of k_P for Run 15 is approximately 25% lower than the data presented in Figure 3.2 in reference (6). Considering the spread of the data in Figure 3.2, the difference is not too significant. The value of k_P from Run 15 is, however, still 3 or 4 times greater than that of unirradiated coolant (1, 5).

The data from Run 15 could not be used, however, to prove or disprove the existence of any higher radiolysis rates at 800°F than those predicted from low temperature data using an activation energy of ΔE_R = 1 kcal/mole. This was due to the fact that the radiolysis contribution to the overall degradation observed was still too small to appreciably change the total degradation as the dose was increased. Furthermore, the fact that the terphenyl concentration was continually decreasing throughout the transient run caused the relative radiolysis contribution to decrease also, since radiolysis appears to follow second order kinetics.

4.2 Evaluation of G_N/G_γ and Radiolysis Reaction Order - Steady-State Run 14

The preliminary results from Run 14 presented in the last quarterly report (6) have been added to the plot from reference (5) in which $k_{R,2}$ is plotted versus fast neutron fraction at various G_N/G_γ ratios assuming second order radiolysis. This plot shown in Figure 4.2 based on n = 2 (second order kinetics) correlates all the data shown better than n = 0, 1 or 3. The new points from Run 14 are shown at f_N = 0.06. As more data becomes available additional points will be added. G_N/G_γ still appears to equal approximately 4.7 or 4.8 when radiolysis is treated by second order kinetics.

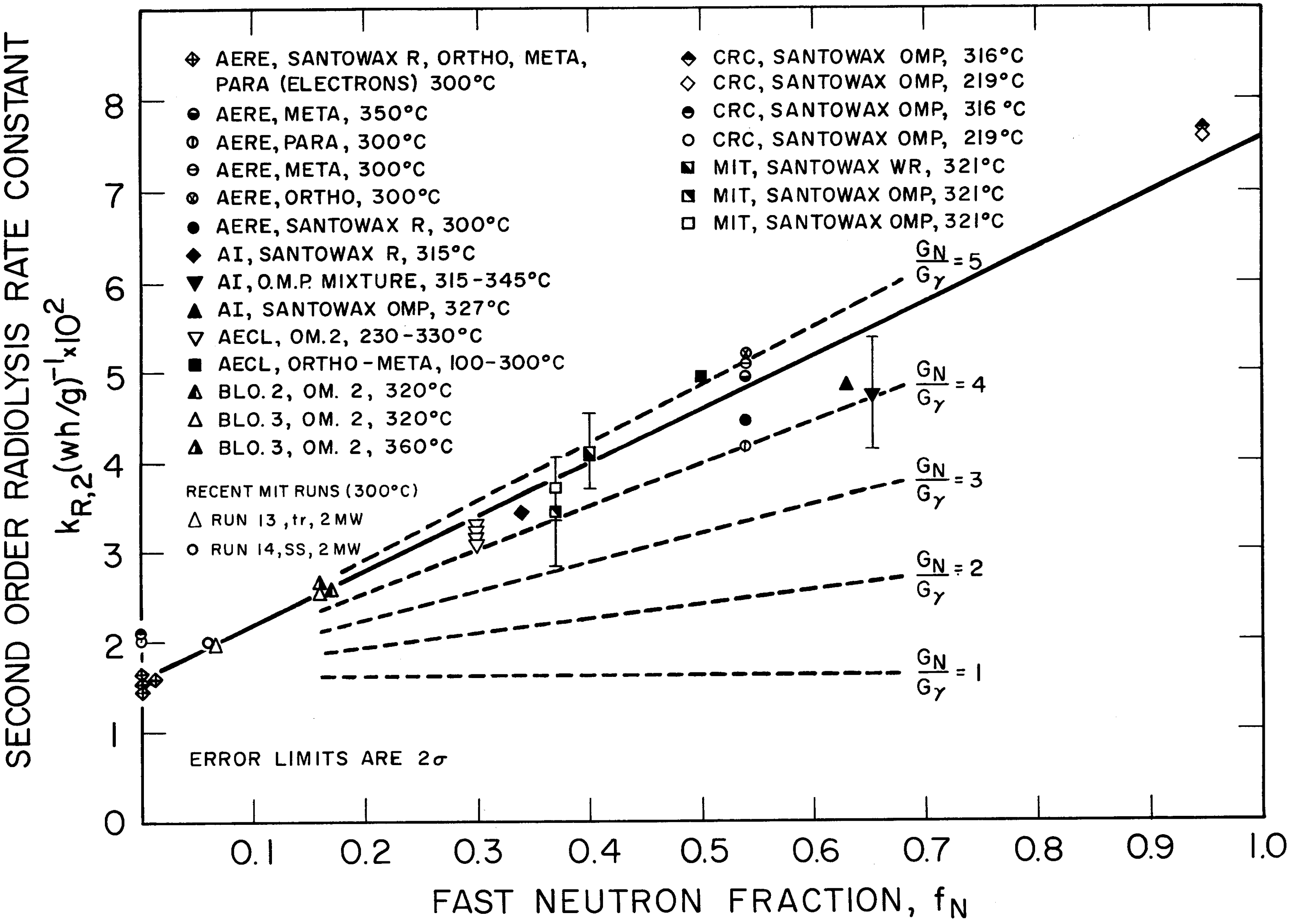

FIGURE 4.2 EFFECT OF FAST NEUTRON FRACTION, f_N, ON THE RADIOLYSIS RATE CONSTANT. SECOND ORDER KINETICS (NORMALIZED TO 320°C BY ΔE_R = 1 kcal/mole)

CHAPTER 5

COOLANT ANALYTICAL TECHNIQUES

Developmental work continued this quarter on improving the precision of the analysis for ortho, meta and para in the irradiated terphenyl by gas chromatography. In addition, gas chromatographic methods are being developed to allow further characterization of the irradiated coolant by analyzing the radiolytic gases, the LIB and the HB. Section 5.1 presents the work and results on gas chromatography.

Samples of Run 14 coolant were analyzed by Atomics International for water, total oxygen, carbonyl-bound oxygen, Membrane Stain Test characteristics and melting point. The results are presented in Section 5.2. Section 5.3 discusses the melting behavior of Santowax WR during Run 16.

5.1 Gas Chromatography

5.1.1 Terphenyl Analysis

The general method of determining the individual terphenyl isomer concentrations in irradiated coolant is well developed. At M.I.T. a Model 1609 F+M flame ionization detector utilizing a 1/4" OD x 6' long column containing 8-10% Apiezon L on 60-80 mesh Chromosorb P(1) firebrick is used. Isothermal column temperatures are between 280-290°C depending on packing density, separation and desired retention times. Over the years it was found that the hand or mechanical integration of the chromatograms and the attendant errors and inaccuracies thereto was limiting the reproducibility of analysis to about 1 or 2%. This was improved somewhat to slightly less than 1% by using an electro-mechanical disc integrator on the chromatograph recorder. However, the interpretation of the chromatograms was still tedious, time consuming and liable to error. A major improvement was noted

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(1) Non-acid wash, manufactured by Johns Manville Co.

in reproducibility and time required for data reduction when an electronic digital integrator[1] with base-line drift correction was purchased to perform the integrations. Reproducibility on total terphenyl content was improved to approximately ±0.5% and the results are available immediately after the sample has run through the chromatograph (about 20 minutes).

5.1.2 LIB Analysis

A temperature programmed separation of the LIB portion of the coolant is being developed. An F+M Model 500 thermal conductivity detector utilizing an 8-10% Apiezon L column (1/4" OD x 8' long) programmed from 50°C to 275°C at a rate of 5.6°C/min is being used. Approximately 40 peaks are detectable by this method. Tentative identification, by retention time, has been made of benzene, cyclohexane, ethylbenzene, triethylbenzene, biphenyl and bibenzyl. With the present method both benzene and cyclohexane elute together so positive identification has not been made. Biphenyl has been positively identified since it can be compared with results obtained with the standard terphenyl analysis described in the previous section.

Table 5.1 is a partial listing of some of the compounds to be used for standards considering ring cleavage and additions. Further acquisitions are planned based on condensation reactions of the organic. The LIB chromatographs have proved useful in qualitatively comparing the coolant composition between runs irradiated at different temperatures. Comparisons made during steady-state runs insure that equilibrium has been attained.

5.1.3 HB Analysis

Development of a high temperature gas chromatographic method for analyzing the HB continued this quarter. A Master's thesis was completed (7) which evaluated various column packings and did preliminary evaluations. The work was continued this quarter.

Forty-five (45) peaks were detected in HB samples using a 10% LiCl (1/8" OD x 8' long) column in conjunction with a

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[1] Infotronics, Inc., Houston, Texas. Model CRS-11HB.

Table 5.1

Tentative Listing of Standards for LIB Analysis

Compound	B.P.	Compound	B.P.
n-Hexane	69.0	Durene	190.0
Benzene	80.1	1,3-Diisopropylbenzene	203
Cyclohexane	81.4	1,2-Diisopropylbenzene	204
Cyclohexene	83	1,4-Diisopropylbenzene	210
n-Heptane	98.4	1,2,4-Triethylbenzene	218
Methylcyclohexane	100.4	1,3,5-Triethylbenzene	218
Toluene	110.6	trans-Bicyclohexyl	217.9
Ethylbenzene	136.2	p-Di-t-Butylbenzene	236
p-Xylene	138.4	Phenylcyclohexane	238
m-Xylene	139.1	cis-Bicyclohexyl	238
o-Xylene	144.4	Biphenyl	255.9
Cumeng	152	Bibenzyl	—
Propylbenzene	159.2	Hexamethylbenzene	265
Mesitylene	164.7	Hexaethylbenzene	298
1,3,5-Trimethylbenzene	164.7	1,1-Dimethylpropylbenzene	—
t-Butylbenzene	169.1	p-Dicyclohexylbenzene	—
1,2,4-Trimethylbenzene	169.5	p-t-Butyltoluene	—
sec-Butylbenzene	173		
Isobutylbenzene	173		
1,2,3-Trimethylbenzene	176		
p-Cymeng	176		
n-Butylcyclohexane	179		
n-Butylbenzene	183.3		

modified Burrell Model K-7 flame ionization detector programmed up to 450°C. LiCl columns have been found to give good separation of the quaterphenyls and several quinquephenyls. For higher molecular species including the quinquephenyls and hexaphenyls a "bottoms" column is used. The "bottoms" are the residues remaining in the pot after distilling HB at 410°C at 5-10 mm of Hg. Life of "the bottoms" column is very short however, and it is difficult to use. As with the LIB chromatograms, the HB chromatograms are used to qualitatively compare coolant composition between and during irradiations. Table 5.2 is a list of the compounds (many in only mg quantities) which M.I.T. has been able to obtain from other investigators. Many of the compounds were prepared by Phillips Petroleum Company in Bartlesville, Oklahoma.

5.1.4 Gas Analysis

In the past the radiolytic gas samples have been submitted to an outside laboratory (Petroleum Analytical Research, Houston, Texas) for mass spectrographic analysis. Due to the expense and time involved in having analyses performed in this way, M.I.T. has been developing a simple gas chromatographic procedure which will analyze for hydrogen, nitrogen, benzene and C_1-C_5 saturated hydrocarbons. These constituents comprise approximately 95% of the radiolytic gas. A short dehydrated silica gel column in series with a 7 1/2' 25% dibutyl phthlate is operated with helium carrier gas and a thermal conductivity detector. The silica gel column is first cooled with solid CO_2 to -72°C and the nitrogen, oxygen and hydrogen are eluted. Then the silica gel column is heated to drive off all the hydrocarbons which are then separated on the dibutyl phthlate column. The dibutyl phthlate column will not separate H_2, N_2 and O_2. Using the procedure as described, preliminary analyses of loop samples give reproducibility of the hydrocarbons to $\pm 2\%$ and the hydrogen and nitrogen to $\pm 5\%$. A gas standard is being prepared so that calibration factors can be determined.

5.2 Analyses of Oxygen, Water and Membrane Stain Tests (MST)

Two sealed sample capsules were removed from the loop at the conclusion of Run 14 and the samples sent to Atomics

Table 5.2

Standards Used at M.I.T. for HB Analysis

Quaterphenyls	Quinquephenyls	Hexaphenyls
o-Quaterphenyl	1,2,3,4-Tetraphenylbenzene	Pentaphenylbenzene
1,2,3-Triphenylbenzene	o,p,o-Quinquephenyl	m,o,m,m-Hexaphenyl
o,m-Quaterphenyl	o,m,m-Quinquephenyl	2,3-Diphenyl-4'-(2-Xenyl)Biphenyl
o,p-Quaterphenyl	2-(3-Xenyl)-5-Phenylbiphenyl	o,p,p,o-Hexaphenyl
1,2,4-Triphenylbenzene	o,m,p-Quinquephenyl	m,o,p,m-Hexaphenyl
m-Quaterphenyl	m-Quinquephenyl	2,4-Diphenyl-3'-(3-Xenyl)Biphenyl
m,p-Quaterphenyl	m,m,p-Quinquephenyl	p,o,p,p-Hexaphenyl
p,p-Quaterphenyl	m,p,m-Quinquephenyl	2,4,3',5'-Tetraphenylbiphenyl
	p,m,p-Quinquephenyl	2,4-Diphenyl-3'-(4-Xenyl)Biphenyl
		m,p,m,m-Hexaphenyl
		m,p,p,m-Hexaphenyl
		3,5-Diphenyl-4'-(3-Xenyl)Biphenyl
		p,m,p,p-Hexaphenyl

International for several analyses. Table 5.3 presents the results of these analyses (8). The differences between the M.I.T. coolant and PNPF are not considered to be significant or unusual.

Table 5.3

Results of AI Analyses on Run 14 Samples

Analysis	M.I.T. Samples	Typical PNPF (a)
MST (e)	$(100 \pm 9) \times 10^{-5}$ A/mg (b)	$(10\text{-}20) \times 10^{-5}$ A/mg
Carbonyl-bound (e) Oxygen	20 ± 3 ppm (c)	(30-50) ppm
Water (f)	213 ppm (c)	50 ppm
Total Oxygen (f)	1295 ± 5 ppm (d)	~1000 ppm

(a) during periods of steady operation

(b) average of four runs

(c) average of two runs

(d) measured by differential calorimetry

(e) M.I.T. Sample No. 14L-15

(f) M.I.T. Sample 14L-16

5.3 Coolant Melting Point

One of the important properties of Santowax WR to be considered if it is to be used as the HWOCR coolant is its melting point or melting range. During a power failure in early November, 1965 (Northeast Blackout) (beginning of Run 16), the loop was without heat for approximately 6 hours. Upon restoration of power it was necessary to heat up the loop to approximately 150-175°F before flow could be restored. The OMP and HB contents were approximately 60% and 29% respectively at that time. Actually, from previous melting point data, the organic should flow at about 150°F. In the loop there are, no doubt, cold portions of the piping on which thermocouples are not installed. From the experience at M.I.T. Santowax WR should pose no insurmountable problem in freezing in the fuel channels, since it should be possible to heat the D_2O to approximately 175°F.

A melting point determination on Run 14 coolant (Sample 14L-15) performed by Atomics International (8) by differential calorimetry indicated a melting range of 117 to 188°F.

CHAPTER 6

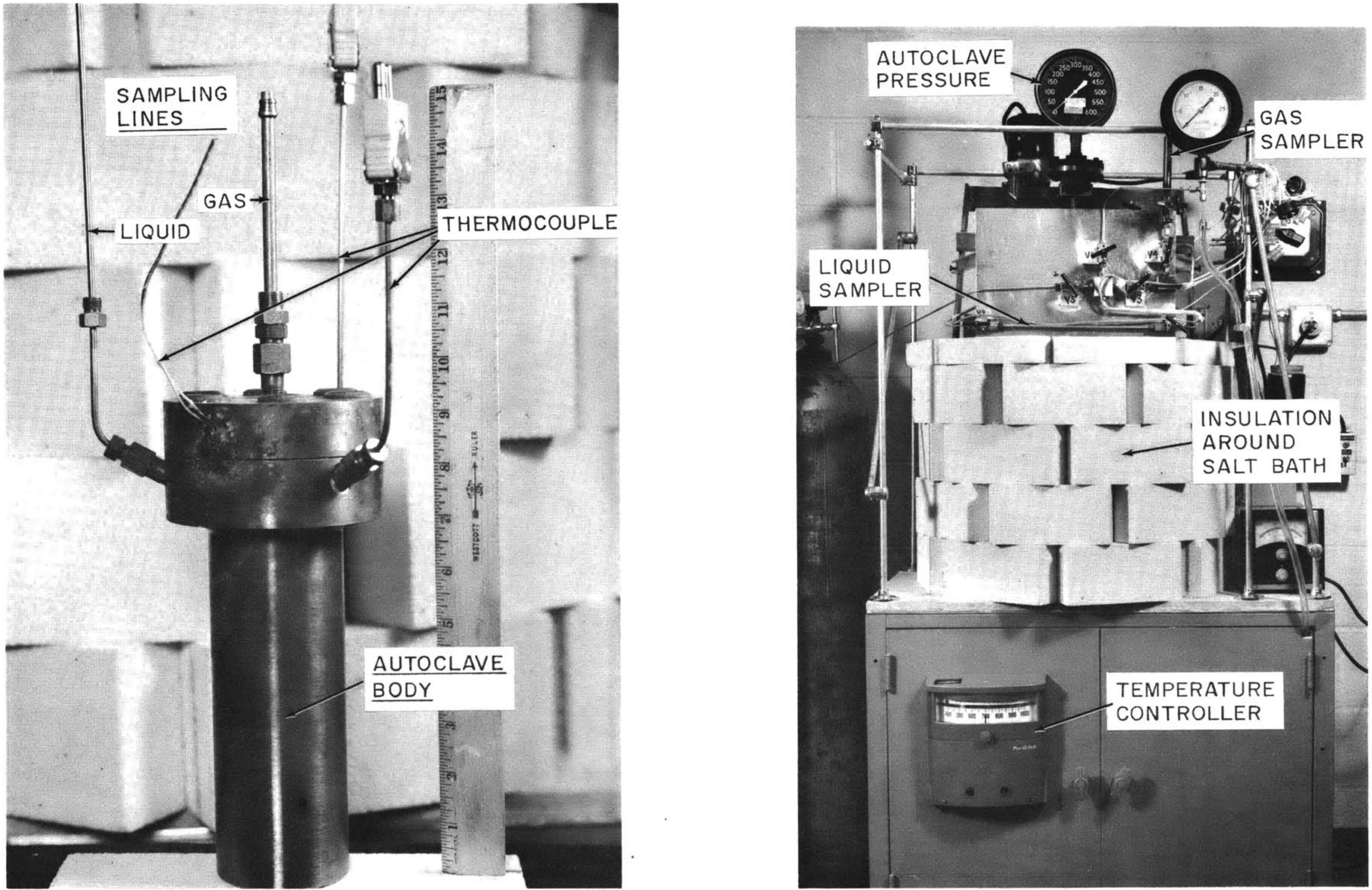
PYROLYSIS EXPERIMENTS

In order to better define the radiopyrolysis rate constants, it is planned to measure the pyrolysis rate of both irradiated and unirradiated Santowax WR in a 300 cc autoclave. Although the pyrolysis rate constants will be derived from transient experiments in the autoclave, samples will be taken often enough to insure that the rate constants obtained will not be averaged over too large a concentration difference.

The results obtained from these pyrolysis experiments carried out in the absence of radiation will be used as a check of the rate constant values obtained from the loop experiments. In the high temperature loop experiments the rate constants are obtained by subtracting the radiolysis contribution from the measured degradation observed. Also, irradiation runs at different temperatures and the same terphenyl content are used in a series of simultaneous equations to determine both radiolysis and pyrolysis. In both cases, the pyrolysis rate constants result from small differences between large numbers and they may therefore be subject to large errors. The pyrolysis experiments are expected to improve this situation.

During this quarter the equipment for the pyrolysis experiments was designed, procured and constructed. Preliminary shakedown testing has been completed and experiments will begin next quarter. Figure 6.1 is a photograph of the experimental apparatus. It is designed to operate at temperatures up to 800°F and 500 psig with a charge of approximately 150 to 200 grams of organic. Provisions have been made to allow gas and liquid samples to be withdrawn from the contents.

In the first experiment unirradiated Santowax WR will be pyrolyzed at 780°F to check the rate constants already published. Then an irradiated sample of SS Run 14, irradiated at 572°F and 83% OMP, will be pyrolyzed at 572°F to insure



300 cc AUTOCLAVE

PYROLYSIS EXPERIMENT

FIGURE 6.1 PHOTOGRAPHS OF PYROLYSIS EXPERIMENT degradation observed in Run 14 was, in fact, substantially all radiolysis.

Plans for future pyrolysis experiments have not yet been completed. However, it is planned to run simultaneous runs with many of the future high temperature irradiations planned in Position 1 (see Table 3.1 on page 6). An experiment to observe if the pyrolysis rate for fresh irradiated coolant decreases as it is pyrolyzed in the absence of radiation is also planned. This effect has been noted in European experiments.

CHAPTER 7
IN-PILE DOSIMETRY AND CALORIMETRY

Development work is underway to improve the determination of the neutron spectrum in which the organic is irradiated by the addition of a resonance detector of higher energy and threshold foils of lower energies than those presently being used. Section 7.1 discusses the progress to date.

In order to improve the precision of the measurements of the gamma and fast neutron dose rate to the organic, several special materials having higher neutron heating rates than the polyethylene or Santowax absorbers have been evaluated. Section 7.2 discusses this work.

7.1 Foil Dosimetry

As mentioned in the last quarterly report (6), additional resonance and threshold detectors have been evaluated for their application to measurements of neutron spectra. At the present time, cobalt, nickel, aluminum and magnesium are regularly used as detectors to define the neutron spectrum. Cobalt serves as both a thermal and resonance detector, while the nickel, aluminum and magnesium serve as threshold detectors. Copper and sulfur have also been used in the past as resonance and threshold detectors respectively. Figure 7.1 taken from the last quarterly (6) presents the latest method of fitting the foil data to a suitable spectrum. The detectors normally used are shown along with four additional detectors which should better define the spectral shape between 120 ev and 2.9 Mev which is not covered with the present materials. The addition of these detectors will aid in defining the slope of the energy spectrum in the epithermal region, that is, determine n, where $\phi(E) = 1/E^n$. The point of joining the $\phi(E) = pE^q$ spectrum in the fission energy range will also be better defined with the addition of these detectors. Na^{24} will be used as a resonance detector with E_R = 2895 ev. U^{234} and

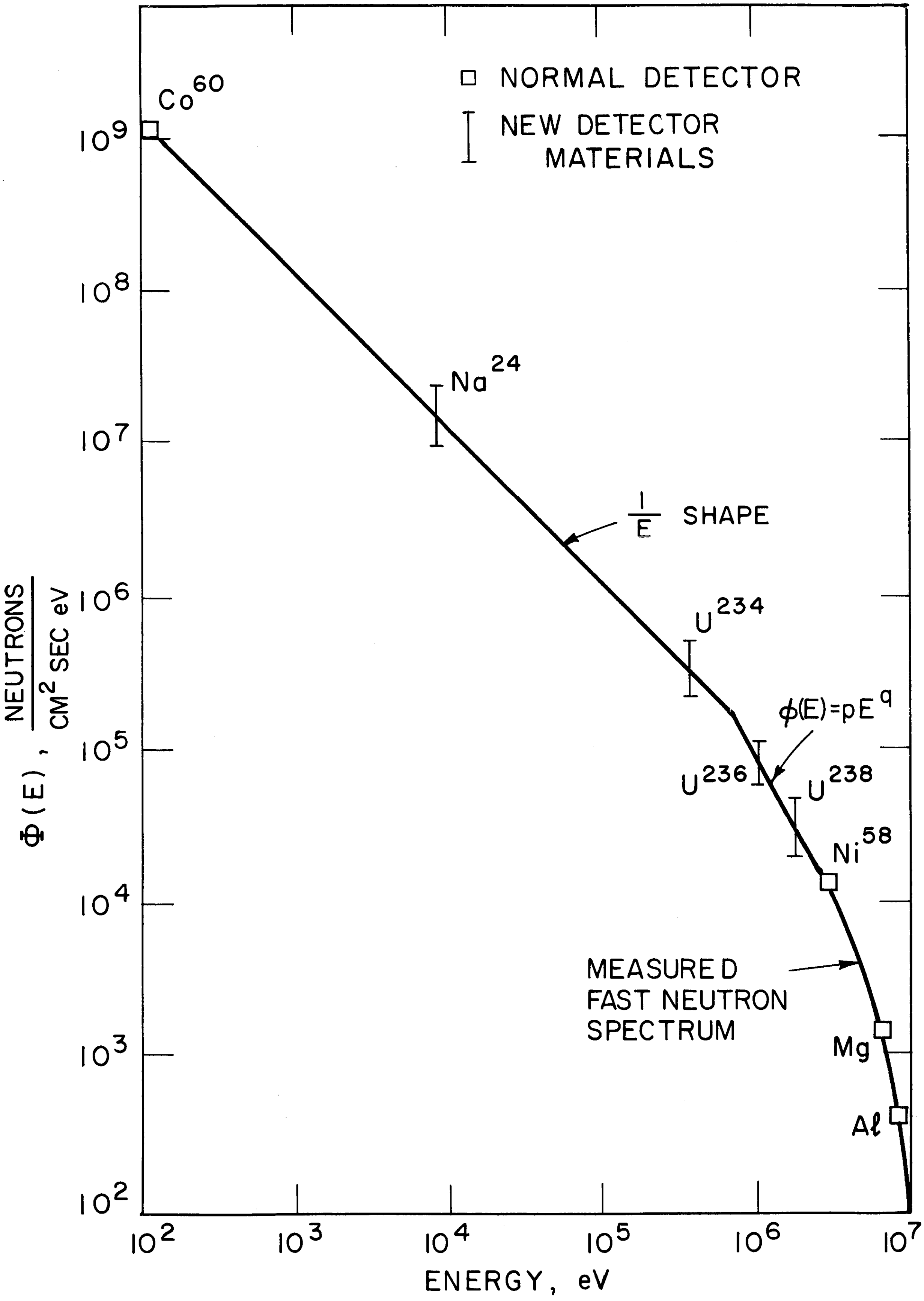


FIG. 7.1 NEUTRON ENERGY SPECTRUM USED FOR FAST NEUTRON DOSE RATE CALCULATIONS FROM FOIL ACTIVATION DATA - RUN 29

U^{238} will be used as fission threshold detectors with E_{th} = 0.24 and 1.3 respectively in a spectral shape similar to the one shown in Figure 7.1.

The U^{234} which is available contains 0.25% U^{235} and will have an approximate 10% U^{235} fission contribution above 0.5 ev (cadmium cutoff). This will be acceptable and the U^{234} has been ordered. The U^{236} which was available had 4.16% U^{235} and has a U^{235} fission contribution which is 8 times greater than the U^{236} fission rate above 0.5 ev. Unless this material can be obtained with U^{235} content less than 50-100 ppm it will not be used. The possibility of obtaining U^{236} of this purity is being investigated. U^{238} is available in high purity (18 ppm U^{235}) at M.I.T. and work is proceeding to devise suitable irradiation capsules, counting and calibration techniques.

Other detectors which were evaluated as fission threshold detectors in the spectrum of Figure 7.1 and found to be unsuitable because of low energy fission contributions were Am^{241} and Np^{237}. Rhodium 103 and Indium 115 were also evaluated as threshold detectors and they seem to have some promise. However, the determination of the absolute count rates would require special counting and calibration techniques. For the time being no further work is planned on these two detectors.

Na^{24} has been irradiated and the counting and calibration techniques are being developed.

7.2 In-Pile Calorimetry

Along with improvements being made in the neutron flux spectrum determinations, an effort is being made to increase the precision of the calorimetric measurements from which we derive the fast neutron and gamma doses directly. Presently, results from polyethylene, polystyrene, carbon and Santowax OMP absorbers are used in the data analysis. Aluminum and beryllium are also used. Aluminum requires corrections due to thermal neutron absorption and corrections due to photoelectric effects and is not regularly used as an absorber except as a check and correlation with previous calorimeter measurements.

Uncertainties in the purity of the beryllium and its specific heat has also limited its use.

Since the MITR has increased its power level to 5 MW the use of polyethylene and polystyrene in regions of high radiation fluxes may be limited due to their low melting points. It would be desirable to have materials to replace the plastic materials which would have a large neutron heating contribution as do the plastics and Santowax, a low thermal neutron absorption probability and low Z so that absorption of γ's by the photoelectric process will be small. Table 7.1 presents the materials mentioned above and some new compounds whose neutron heating (by elastic collisions) and gamma heating (by Compton scattering) has been estimated. Also presented in the last column is the fraction of the total heating due to neutrons. Of the last four listed, only lithium hydride is reasonably stable in air. The others decompose rapidly or have low melting points or decompose at low temperatures. It is planned to fabricate calorimeters from Li^7H to permit fabrication of absorbers which will operate at higher temperatures. Hopefully, two miniature calorimeters, one of carbon and one of Li^7H, will make it possible to make measurements with the in-pile assembly in place.

A computer program is being written so that the effects of thermocouple placement in the absorber, thermocouple heating, thermal contact between the absorber and the thermocouple, sample heating rates and sample and thermocouple specific heats and thermal conductivity can be evaluated in terms of the heating rates expected. Note that in Table 7.1 the value for R_T at 5 MW will result in heating rates in the plastics of between 100 and 200°F/ minute. Serious errors in the rate of temperature rise of the sample could result if the effect of all these parameters is now known.

Table 7.1

Estimated Fast Neutron and Gamma Heating Rates for Selected Calorimetric Materials

(Center of Position 1 10-Plate Element in the MITR at 5 MW)

Material	Fast Neutron Rate R_N, watts/gm	Gamma Rate R_γ, watts/gm	$R_N + R_\gamma =$ R_T, watts/gm	R_N/R_T
Polyethylene	1.225	1.010	2.235	0.551
Polystyrene	0.715	0.955	1.670	0.429
Santowax	0.592	0.939	1.531	0.386
Beryllium	0.222	0.781	1.003	0.285
Carbon	0.120	0.885	1.005	0.120
Aluminum	0.034	0.852	0.886	0.039
Lithium Boron Hydride ($Li^7B^{11}H_4$)	1.583	0.885	2.468	0.641
Beryllium Hydride (BeH_2)	1.615	0.965	2.580	0.601
Lithium Hydride (Li^7H)	1.261	0.885	2.145	0.589
Sodium Boron Hydride ($NaB^{11}H_4$)	0.910	0.885	1.795	0.506

CHAPTER 8

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