IN−PILE LOOP
IRRADIATION STUDIES
OF
ORGANIC COOLANT MATERIALS

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Department of Nuclear Engineering

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IN-PILE LOOP IRRADIATION STUDIES
OF
ORGANIC COOLANT MATERIALS

QUARTERLY PROGRESS REPORT
JULY 1 - SEPTEMBER 30, 1963

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MITNE-21   (IDO 11,104)

MITNE-22   (IDO 11,105)

MITNE-29   (IDO 11,106)

MITNE-39   (IDO 11,107)

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1.0 SUMMARY

Upon completion of the USAEC study on Santowax OMP irradiated at temperatures of 610°F and 750°F on June 30, 1963 (1), in-pile loop studies of organic reactor coolants for the heavy-water moderated, organic-cooled, reactor concept were begun. This work is being conducted under the joint USAEC and Canadian cooperative agreement on heavy water reactor development.

The coolant now being irradiated in the MITR In-Pile Loop is Santowax WR which was produced by the Monsanto Chemical Company in their plant in Anniston, Alabama for this and other studies by AECL. The Santowax WR was produced by benzene extracting a Santowax OMP feed to reduce the para-terphenyl content from approximately 25% to 5%. This extraction produces a coolant feed material which has a melting range of 150°F to 170°F instead of 180°F to 320°F.

A new in-pile assembly was installed in a new ten-plate fuel element (previous irradiations utilized an eight-plate fuel element) and the irradiation of Santowax WR (Monsanto Lot AC-4) began on July 25, 1963.

A comprehensive dosimetry and calorimetry measurement was made in the new fuel element prior to the start of the irradiation. The initial dose rate in the capsule located in the ten-plate element, averaged over the volume of the in-pile capsule, is 0.63 watt/gm. This dose rate represents a 23% increase in the dose over that from the former eight-plate element. The fast neutron contribution to the total dose increased from 37% to 44% in going from the eight- to the ten-plate element.

A semi-batch irradiation was completed in three steps in which the OMP content in the coolant was reduced from 94w/o to 45 w/o, (i.e., from 6 w/o DP to 55 w/o DP) in the period from July 25, 1963 to September 26, 1963. The Santowax WR received from Monsanto was distilled in laboratory glassware prior to charging to the loop so that the composition was essentially unchanged. Activation analyses, performed at the MITR, of the as-received and re-distilled Santowax WR indicated that the gross activity (primarily short lived Mn^{56} and Cl^{37}) was reduced by a factor of three by the distillation in glassware. The chlorine content of the distilled charge material, as determined by

AECL, was found to be 2-3 ppm. Comparison of the gross activation with Eastman White Label para-terphenyl standard indicates that the Santowax WR being irradiated is as impurity-free as any other coolant previously irradiated at M.I.T.

A preliminary $G*(-\phi_3)$ value for the rate of Santowax WR disappearance during the transient period when the DP content increased from 22 w/o to 55 w/o is $G*(-Santowax\ WR) = 0.57 \pm 0.05$ molecules Santowax WR degraded per 100 ev absorbed in Santowax WR. This value is not significantly different from the $G*(-Santowax\ OMP) = 0.53 \pm 0.02$ molecules Santowax OMP degraded/100 ev absorbed in Santowax OMP determined for the steady state Santowax OMP irradiations (see reference (1), Table 4.10). Preliminary values of $G*(-i)$ for each of the terphenyl isomers show the relative stabilities to be para > meta > ortho. The preliminary values of $G*(-i)$ for each of the isomers in the Santowax WR mixture, determined from the transient data, are not statistically different from those obtained for Santowax OMP.

Experimental values of the heat transfer coefficient appear to be approximately the same as those obtained with Santowax OMP under similar conditions. Twenty-five heat transfer data points from the transient period have been analyzed on the computer. The data appears to fit the general recommended correlation in reference (1), equation 6.11, from the Santowax OMP irradiations:

$$Nu = 0.0079(Re)^{0.9}(Pr)^{0.4} \pm 10\% \tag{1}$$

One fouling probe run of approximately 180 hours' duration was completed during the transient run. Visual observation of the tube surface, which operated at $910 \pm 5°F$ indicates that the surface film is very thin. Quantitative evaluation of the deposition rate is in progress.

2.0 RESULTS THIS QUARTER

The major emphasis this quarter has been to install a new fuel element and in-pile assembly, determine dose rates, begin transient irradiation of Santowax WR (Monsanto Lot AC-4) and complete the transient irradiation. Project objectives are being met but, due to a delay in delivery of the Santowax WR, the program is approximately one month behind the original schedule.

Digital computer programs are being used to analyze the data as it becomes available, and hence the results presented herein should be regarded as preliminary since not all of the data have been considered.

2.1 Loop Operation

Due to incomplete filling of the system and a main pump stator failure, it was necessary to add unirradiated Santowax WR on two occasions in the operating period during which the concentration of DP was increased from 6 w/o DP to approximately 55 w/o DP in a semi-batch irradiation. The time between initiation of irradiation and the Santowax WR addition to makeup for incomplete filling of the system is defined as the interim period. The second phase commencing after the interim phase until the pump failure occurred is defined as the Transient 1 period. The third phase commencing after the pump failure until the end of the semi-batch irradiation is defined as the Transient 2 period. Table 2.1 summarizes the various periods of operation during the semi-batch irradiation.

The failure of the Chempump occurred after approximately 12,000 hours of operation. Bearing wear was nil.

2.2 Calorimetry and Dosimetry

Prior to insertion of the in-pile assembly on July 25-29, 1963, a comprehensive calorimetry and dosimetry program was carried out in the new ten-plate fuel element (2MR34) by the methods developed in Chapter 3 of reference (1).

The calculated dose rate distribution in terphenyl as determined

TABLE 2.1

Summary of Semi-Batch Irradiation of
Santowax WR at 750°F

Period	Dates	MWH[a] of Reactor Operation	Range of DP Concentration (w/o)
Interim	7/25/63 - 8/2/63	0 - 276	6 - 19
Transient 1	8/2/63 - 8/15/63	277 - 622	16 - 31
Transient 2	8/15/63 - 9/26/63	623 - 1644	22 - 55

[a]Reactor power approximately 1.95 MW

by calorimetry for fuel element 2MR34, at 2 megawatts of reactor power, is shown versus axial position in Figure 2.1. As a comparison, Figure 2.2 presents the calorimetric results for the eight-plate fuel element, 2MR11. The major increase in the total dose rate can be seen to be the increase in the fast neutron dose rate.

The average dose rate to the coolant in the capsule was obtained by graphically integrating the dose rate over the capsule volume on Figures 2.1 and 2.2. The location of the capsule in relation to the spectra presented is also shown on the figures. Table 2.2 presents the average dose rates obtained by the integrations performed on Figures 2.1 and 2.2 at the normal reactor power of approximately 2 MW. The ratios of fast neutron and gamma dose to total dose are also presented in Table 2.2. The error quoted is an estimate of the accuracy.

Threshold foils were used to obtain the differential neutron spectrum in the capsule as described in Chapter 3 of reference (1). The dose rate to the Santowax WR or terphenyl from fast neutrons was calculated by using the scattering cross sections as a function of energy, the neutron spectrum, and the IBM 7090. The computed dose to Santowax was found to be slightly lower than the calorimetrically determined value but the agreement is within the possible experimental error. Figure 2.3 presents a comparison of the neutron dose computed from threshold foil measurements, utilizing Ni, S, Al, and Mg foils, and calorimetric measurements.

2.3 Coolant Composition

High temperature vapor phase chromatography is being utilized to determine the rate of monomer disappearance.

Samples of coolant from the loop were initially analyzed using an Apiezon L Column and an F and M Model 500 thermal conductivity cell to measure the terphenyl concentrations. Figure 2.4 presents the terphenyl concentrations during the transient periods.

However, an Apiezon L column was not capable of detecting the quaterphenyls which exist in the coolant. Consequently, an analytical procedure utilizing a 10 w/o CsCl column in conjunction with a flame ionization detector was developed which now permits a quantitative analysis for the terphenyls and a semi-quantitative analysis for the
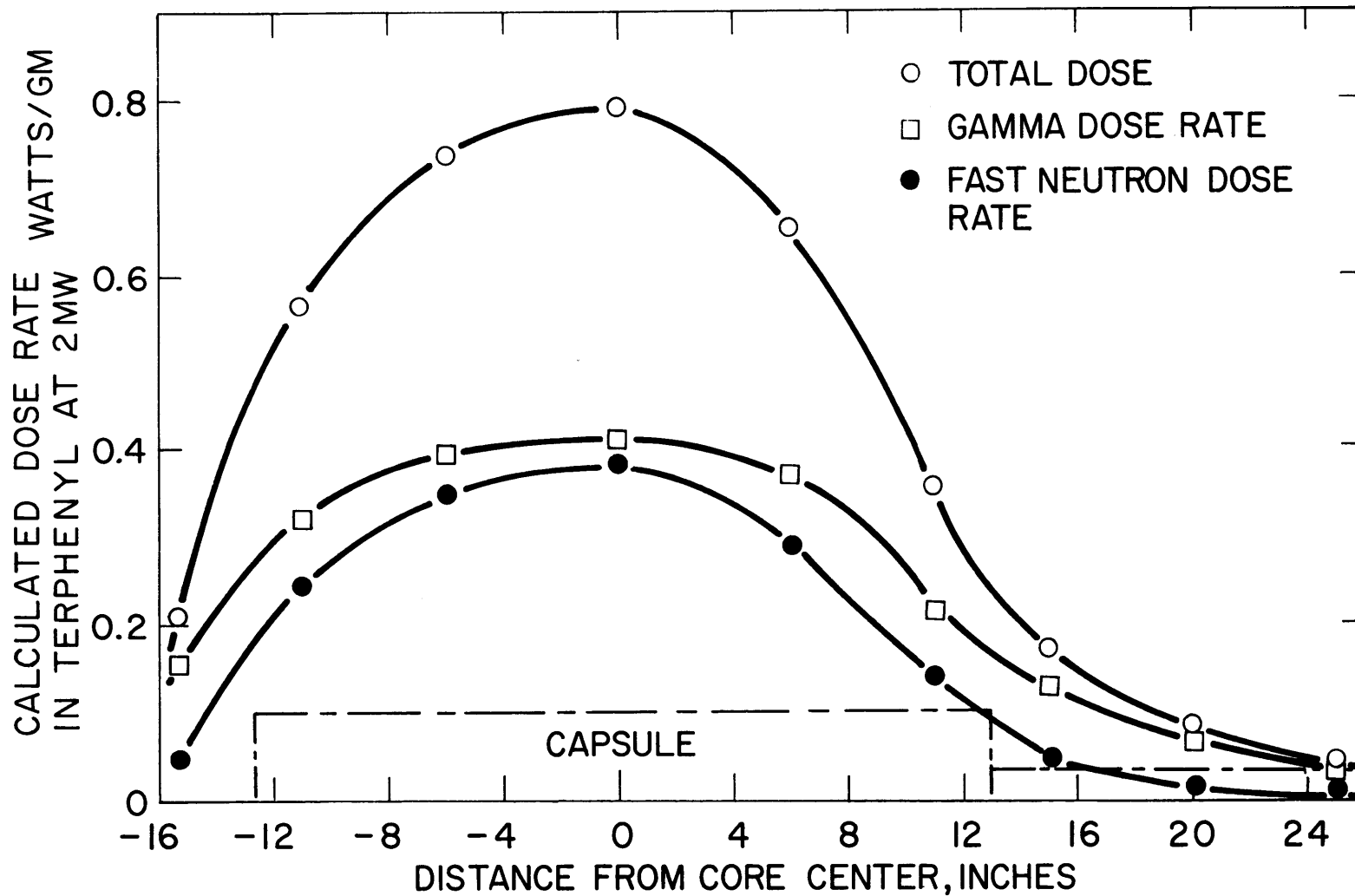
FIGURE 2.1   AXIAL VARIATION OF THE DOSE RATE ALONG FUEL
ELEMENT 2MR 34 (JULY 16 TO 19, 1963)
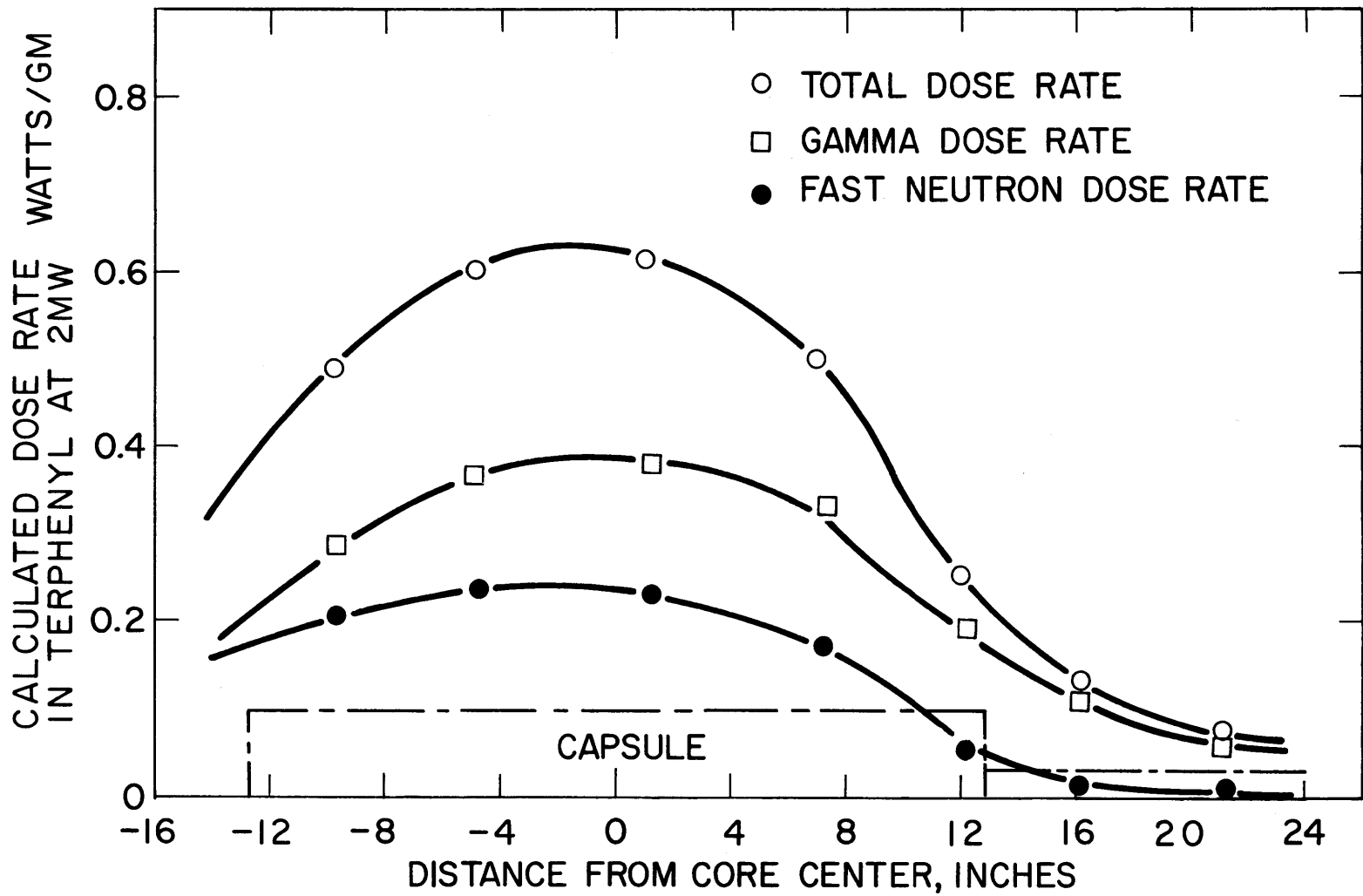
FIGURE 2.2 AXIAL VARIATION OF THE DOSE RATE ALONG FUEL
ELEMENT 2MRII (APRIL 1963)

TABLE 2.2

Comparison of Average Dose Rates in
Terphenyl in 8- and 10-Plate MITR Fuel Elements
(200 cc in-pile capsule)

| Fuel Element | Dose Rates* (watts/gm) | | | Fast Neutron Fraction | Gamma Fraction |
	Fast Neutron Dose	Gamma Dose	Total Dose		
8-plate No. 2MR11	0.194	0.320	0.514	37.8%	62.2%
Std. Error	0.006	0.007	0.009	1%	1%
10-plate No. 2MR34	0.294	0.354	0.648	45.3%	54.6%
Std. Error	0.012	0.011	0.018	1.5%	1.5%

*MITR operating at 2 megawatts

FIGURE 2.3 AXIAL DISTRIBUTION OF NEUTRON DOSE RATE IN FUEL
ELEMENT 2MR 34

FIGURE 2.4 TERPHENYL ISOMER CONCENTRATIONS
DURING THE SEMI-BATCH PERIOD OF THE
IRRADIATION OF SANTOWAX WR AT 750°F

quaterphenyls. The terphenyl concentrations obtained with Apiezon L and CsCl agreed. Table 2.3 presents the analysis of starting coolant and an analysis of a sample near the end of Transient 2. The quaterphenyl content can be seen to increase at higher DP.

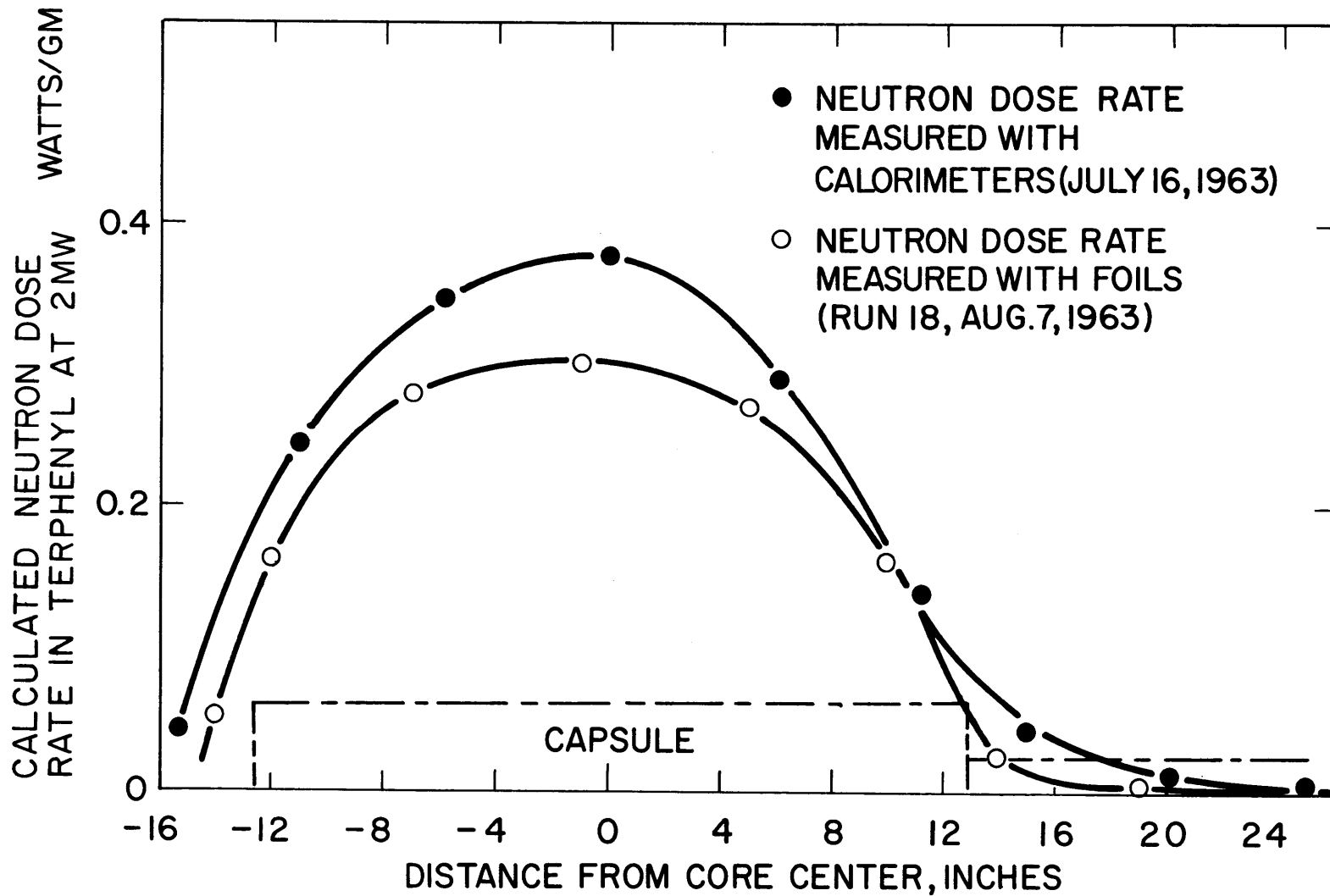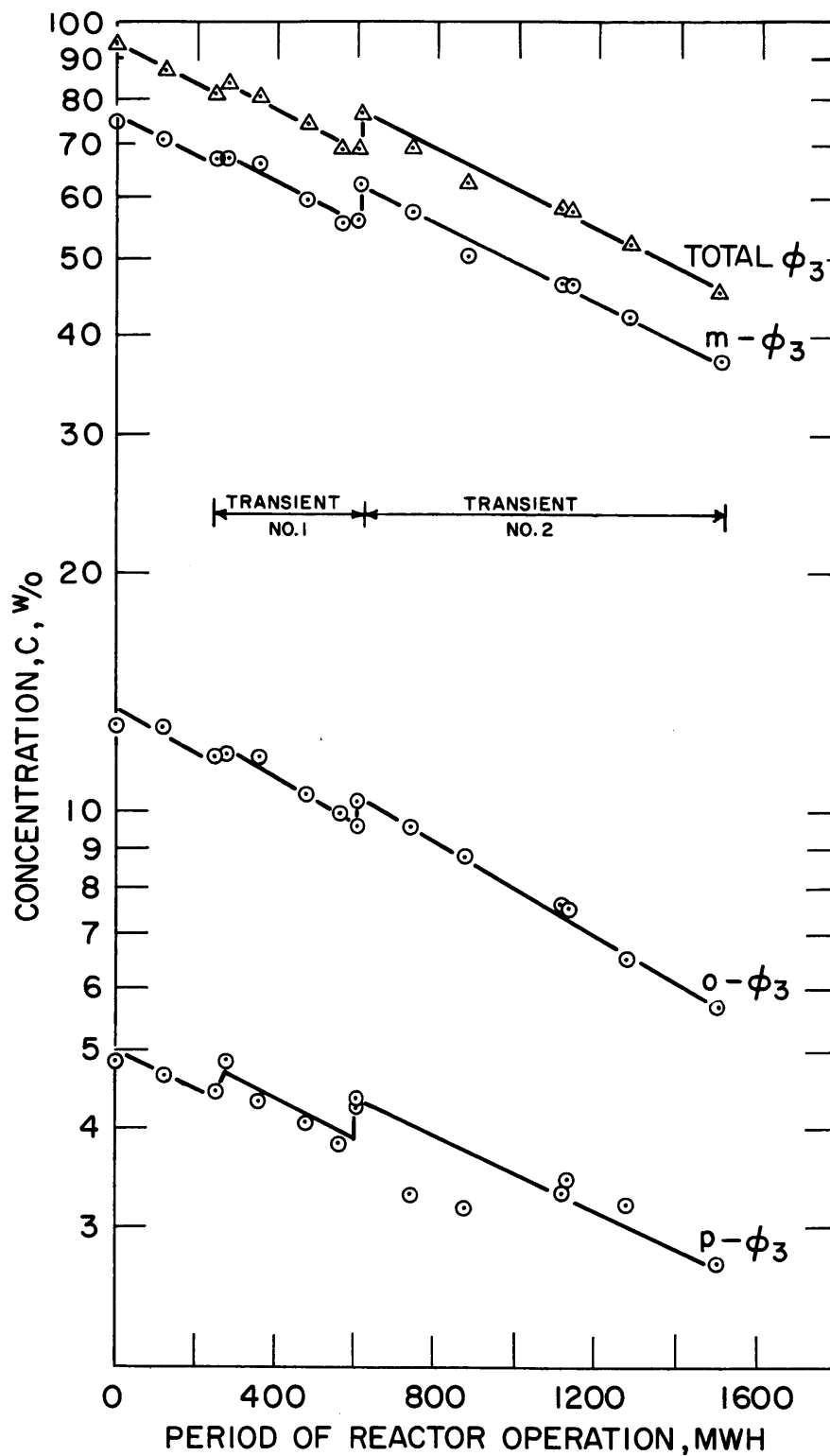Based on the results obtained from the CsCl column, a distillation procedure for the coolant recycle steady-state run, which is scheduled to begin in early October, was developed. All coolant up to and including triphenylene will be recycled back into the loop. This recycle includes about 75% of all the quaterphenyls.

The distillation cutoff occurs between the ortho-para-quaterphenyl and the meta-quaterphenyl. However, approximately half of the m-ϕ_4 and m,p-ϕ_4 is still returned to the loop. The level of material less volatile than the triphenylene and most of the quaterphenyls will be maintained at a level of approximately 30 w/o during the recycle period. This would maintain the HB level (based on the accepted definition of HB being components less volatile than para-terphenyl) at approximately 33 to 34 w/o.

2.4 Degradation Yields

Preliminary analysis of the data obtained for the transient period of the 750°F irradiation of Santowax WR has been completed. Figure 2.4 presented the terphenyl concentrations during the transient period as a function of the period of reactor operation, in MWH. Using the least-squares procedure described in section A2.6 of reference (1), the data were analyzed by first-order kinetics. The results are expressed in terms of the stability criterion $G^*(-i)$, where

$$G^*(-\underline{i}) = G(-i)/C_{\underline{i}} \qquad (2)$$

$$G(-\underline{i}) = \frac{\text{molecules of component } \underline{i} \text{ degraded}}{100 \text{ ev absorbed in the total coolant}} \qquad (3)$$

and $C_{\underline{i}}$ is the weight fraction of component $\underline{i}$ in the coolant. Table 2.4 presents the results and also lists, as a comparison, the $G^*(-\underline{i})$ values obtained during the steady-state-HB period of the 750°F irradiation of Santowax OMP (1).

TABLE 2.3

Coolant Composition at Beginning and End
of 750°F Semi-Batch Irradiation of Santowax WR
(w/o)

	Sample No. 3L-1	Sample No. 3L-17
Exposure Time (MWH)	0	1500
Date	7/25/63	9/21/63
Constituents		
Biphenyl	0	2.3
Terphenyls		
ortho-ϕ_3	14.0	5.7
meta-ϕ_3	74.9	37.5
para-ϕ_3	4.7	2.7
Total OMP	93.6	45.9
DP	6.4	54.1
Quaterphenyls		
1,2,3 Triphenylbenzene	0	0.3
o,m-ϕ_4	0.6	0.6
Triphenylene	0.2	0.8
o,p-ϕ_4	0.2	0.2
m-ϕ_4	0	0.7
m,p-ϕ_4	0	0.9
Total Quaterphenyls	1.0	3.5

TABLE 2.4

Comparison of $G*(-\underline{i})$ Values During the Transient Irradiations of

Santowax WR with Best Values for Santowax OMP at 750°F[a]

$$G*(-\underline{i}) = G(-\underline{i})/C_i$$

Component	Santowax WR		Santowax OMP[b]
	Transient No. 1	Transient No. 2	
ortho-ϕ_3	0.76 ± 0.50[c]	0.73 ± 0.11	0.79 ± 0.07
meta-ϕ_3	0.65 ± 0.39	0.56 ± 0.09	0.52 ± 0.03
para-ϕ_3	0.75 ± 0.49	0.33 ± 0.28	0.45 ± 0.03
Total-ϕ_3	0.65 ± 0.33	0.57 ± 0.09	0.53 ± 0.04

[a]Not corrected for pyrolysis

[b]See Table 4.10 of reference (1)

[c]95% confidence limits

Corrections for pyrolysis occurring in the out-of-pile volume of the loop have not yet been applied. The results for Transient No. 1 are not too reliable as only four data points covering a small concentration range are available on which to calculate the G* values. In addition, the para-terphenyl results are subject to large uncertainties as para-terphenyl constitutes less than 5 w/o of the unirradiated coolant. No significant difference was observed between the degradation yields for the terphenyl isomers in Santowax WR and Santowax OMP. The relative stability of the isomers remains as para > meta > ortho.

The steady-state-distillation operation is scheduled to begin in early October, and more accurate G* values will be available from this portion of the irradiation of Santowax WR, but considering the coolant and the transient results obtained to date, the results obtained during the steady-state operation are expected to be similar to those previously reported for Santowax OMP (1).

2.5 Physical Properties

2.51 Density

Densities of samples of irradiated Santowax WR for the transient period of the 750°F irradiation were measured over the temperature range 400-800°F. The data for each sample were smoothed according to the relation

$$\rho = A + BT \tag{4}$$

where

ρ is the sample density, gm/cc

T   is the sample temperature, gm/cc, °F

A, B   are constants.

The dependence of the smoothed densities on the DP concentration is shown in Figure 2.5. A comparison with the density measurements on Santowax OMP irradiated at 750°F (see Figure 5.4 of reference (1)) shows the density of Santowax WR to have about the same DP concentration dependence. The density of 750°F irradiated Santowax WR at a given DP concentration agreed with that of Santowax OMP irradiated at 750°F to within 1%.
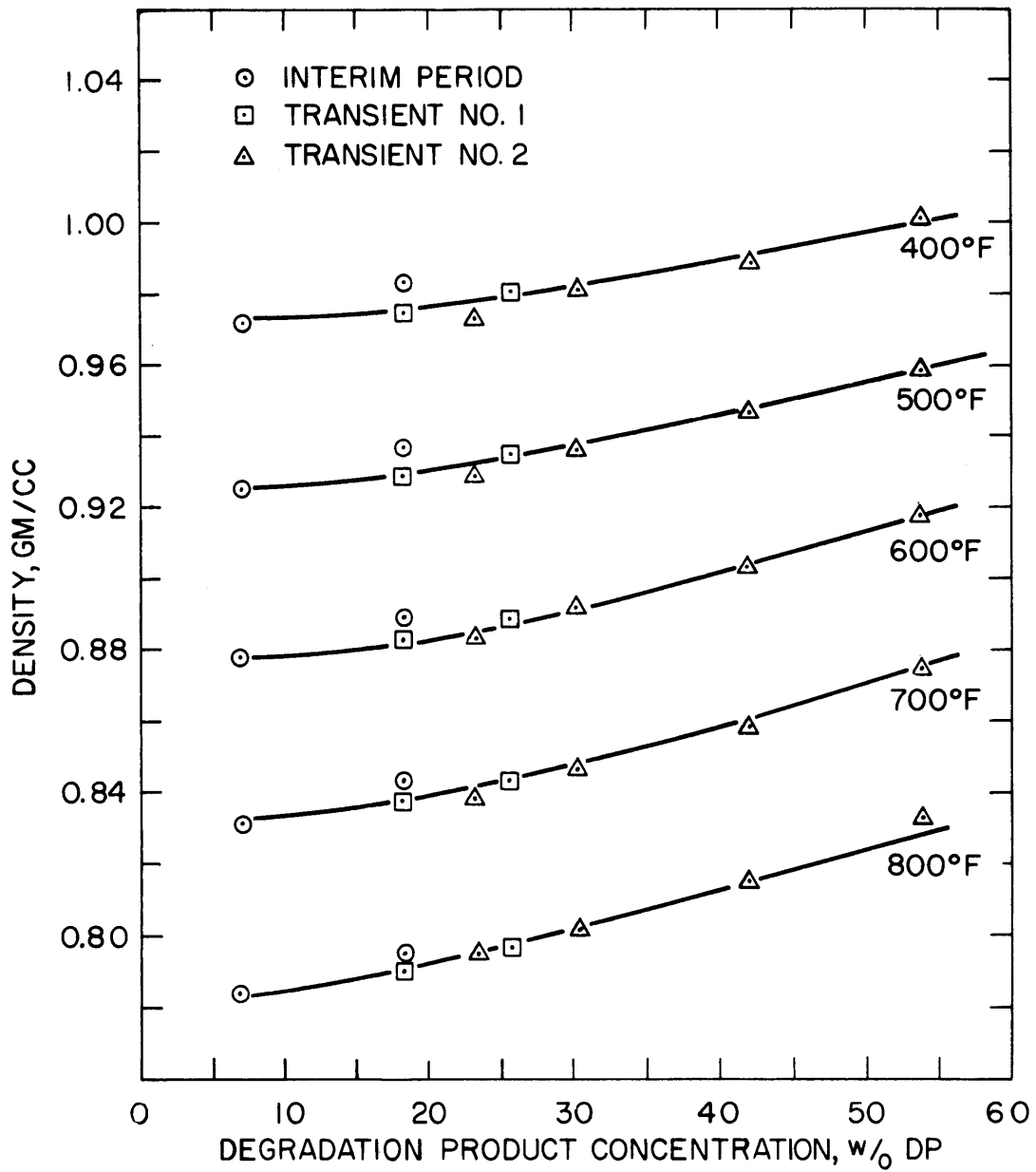
FIGURE 2.5 DENSITY OF SANTOWAX WR COOLANT IRRADIATED
AT 750°F

2.52 Viscosity

Viscosities of samples of irradiated Santowax WR for the transient period of the 750°F irradiation were measured over the range 400-800°F. The data for each sample were smoothed according to the relation

$$\mu = ae^{b/T} \tag{5}$$

where

μ is the sample viscosity, centipoises

T   is the sample temperature, °F

a, b   are constants.

The DP concentration dependence of the smoothed viscosities is shown in Figure 2.6. A comparison with the viscosity measurements on Santowax OMP irradiated at 750°F (see Figure 5.11 of reference (1)) shows the viscosity of Santowax WR to have about the same DP concentration dependence. However, the viscosity of Santowax WR at a given DP concentration appears to be about 10% lower than that of Santowax OMP. Previous work (2) has shown the viscosity of pure p-terphenyl to be greater than that of pure m-terphenyl at temperatures between 500-700°F, so the lower p-terphenyl relative to m-terphenyl content of Santowax WR may be the reason for the lower viscosity of Santowax WR.

2.53 Number Average Molecular Weight

Number average molecular weight measurements have been performed on samples of irradiated Santowax WR coolant from the transient period of the 750°F irradiation. The DP concentration dependence of the data is shown in Figure 2.7. A comparison with the number average molecular weight of Santowax OMP irradiated at 750°F (see Figure 5.21 of reference (1)) shows the increase with increasing DP concentration to be slightly less for Santowax WR. At 54 w/o DP the average molecular weight of Santowax WR was about 300 and that of Santowax OMP irradiated at 750°F about 320.

2.54 Coolant Melting Point

The initial melting and final liquidus points on the Santowax WR starting coolant were 150°F and 170°F, respectively. However, by the time the DP concentration reached approximately 10 w/o, the coolant
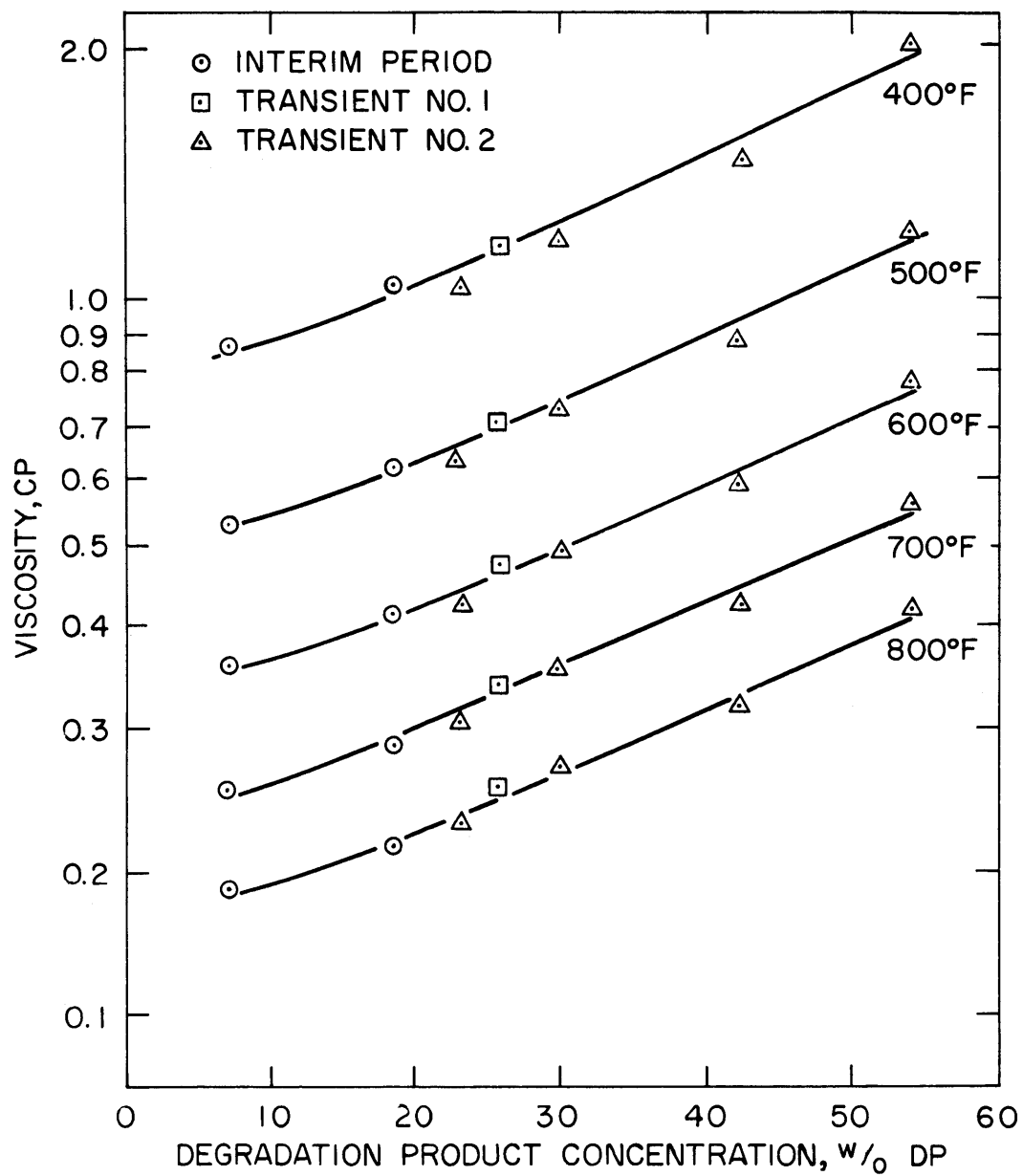
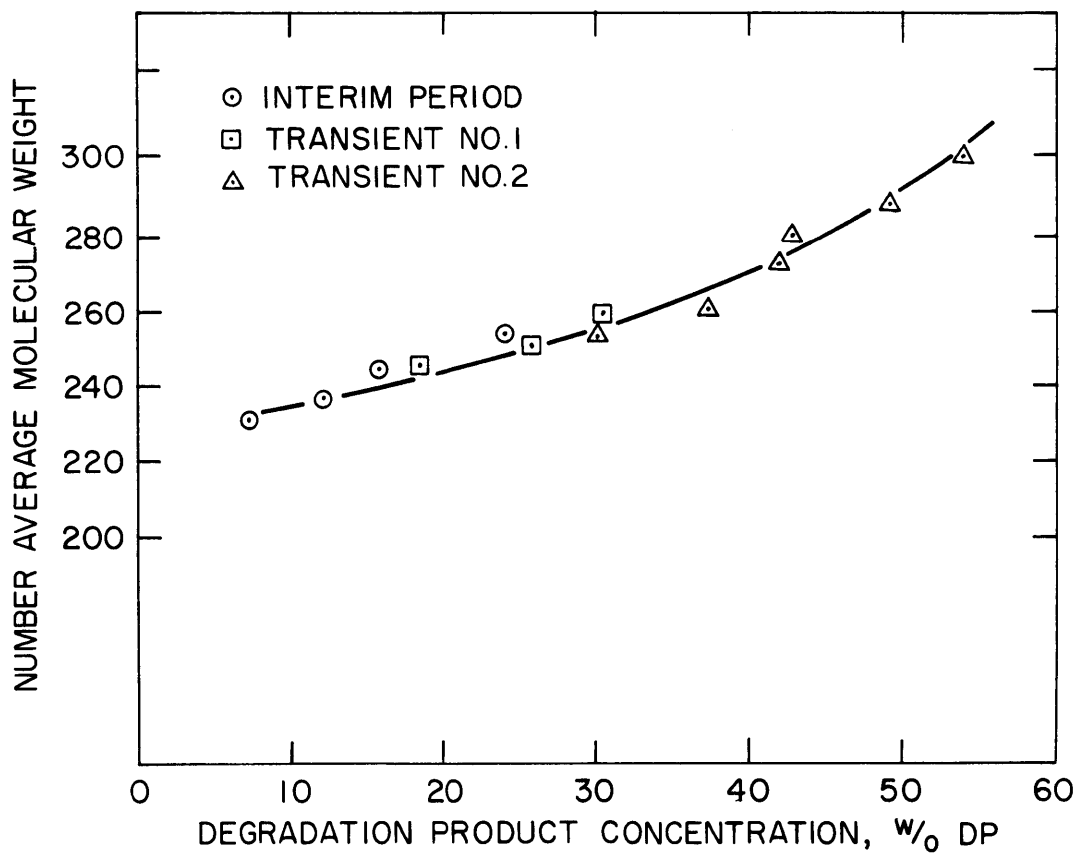FIGURE 2.6 VISCOSITY OF SANTOWAX WR COOLANT IRRADIATED
AT 750°F

FIGURE 2.7 NUMBER AVERAGE MOLECULAR WEIGHT OF SANTOWAX
WR COOLANT IRRADIATED AT 750°F

was a very viscous fluid at room temperature. The coolant appears to
be sub-cooled, since samples that initially were liquid at room tempera-
ture solidified after a period of time varying from several days to
several weeks, the samples at higher DP requiring the longer time for
solidification. It has not been possible to obtain even initial melting
points on the samples even by cooling to sub-zero temperatures.

2.55 Carbon-Hydrogen Content

Measurements of the carbon-hydrogen content of samples of irradi-
ated Santowax WR during the transient period of the 750°F irradiation
showed no trend and an average deviation of about +4% from the value of
15.4 for terphenyls, which is within the experimental uncertainty in the
measurements.

2.56 Ash and Semi-Quantitative Emission Spectroscopy

As with the measurements on Santowax OMP (see Section 5.10 of
reference (1)), no significant amount of ash has been found in the samples
of irradiated Santowax WR which have been analyzed to date. In addition,
concentrations of the principal inorganic constituents, silicon, iron, mag-
nesium, copper, aluminum and nickel, as determined by semi-quantitative
emission spectroscopy, were all found to be less than 10 ppm by weight.

2.57 Thermal Conductivity

Additional thermal conductivity measurements on samples of irradi-
ated Santowax OMP from previous irradiations have been performed at
Grenoble, France (3). These data are presented in Table 2.5. They do
not vary significantly from the previous data for Santowax OMP presented
in Figure 5.17 of reference (1).

2.6 Heat Transfer

The heat transfer data taken during the semi-batch operation of the
Santowax WR run were correlated using the least-squares analysis
described in section A4.4 of reference (1).

To compare the Santowax WR data with the Santowax OMP data, the
Santowax WR data were then correlated with the exponents for the Reynolds
number and the Prandtl number fixed at 0.9 and 0.4, respectively.

TABLE 2.5

Thermal Conductivity of Santowax OMP

$(cal/cm-sec-°C)$

Sample Number	1L116	2L17	2L41
Per Cent DP	60%	50%	41%
Irradiation Temperature	610°F	750°F	750°F
Temperature °F	$k \times 10^4$	$k \times 10^4$	$k \times 10^4$
302	3.4	3.43	3.265
392	3.34	3.34	3.19
482	3.28	3.24	3.12
572	3.22	3.14	3.05
662	3.16	3.04	2.98
752	3.1	2.95	2.90

This correlation is:

$$Nu = 0.0074Re^{0.9}Pr^{0.4} \qquad (6)$$

The best fit for the Santowax OMP data taken at 750°F at M.I.T. from reference (1) was:

$$Nu = 0.0073Re^{0.9}Pr^{0.4} \pm 10\% \qquad (7)$$

It can be seen that the coefficients for both sets of data agree to within 1.5%.

The data is presented in Figure 2.8 where equation (6) has also been plotted. The correlation of $Nu/Pr^{0.4}$ was selected as the ordinate so that the data can be easily compared with the Santowax OMP data as presented in reference (1).

Fouling studies have continued through the irradiation of Santowax WR at 750°F. The location of the AECL Fouling Probe, as described in reference (1) (pp 6.23), was changed to make it more convenient to conduct long fouling tests with the probe. The fouling probe is now located in parallel with the in-pile section and hence runs do not have to be interrupted for liquid sampling operations.

One test section was run at 900°F outside wall temperature for 172 hours. The deposition rate on this sample is currently being measured. It is planned to run another test section at the same wall temperature for approximately 400 hours.

The extended time runs are not continuous as it is necessary to shut down the organic loop for the weekends. A run consists of approximately 100 hours at temperature (900°F) during the week and then during weekends (approximately 68 hours) at 425°F. There is no power to the probe over the weekend; hence the test section is at the loop temperature of 425°F for the weekend.
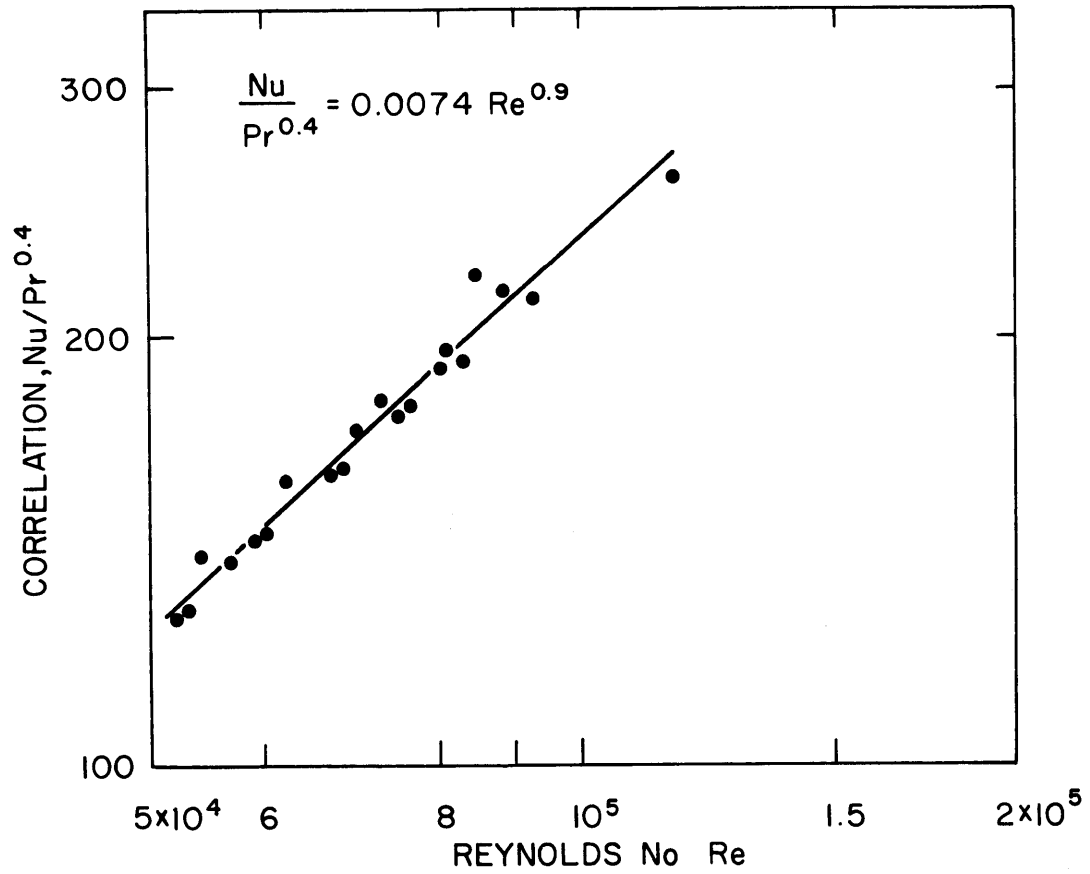
FIGURE 2.8 PRELIMINARY HEAT TRANSFER DATA FOR SANTOWAX
WR IRRADIATED AT 750°F (6 ^{W}/o TO 55 ^{W}/o DP)

3.0 EXPECTED RESULTS NEXT QUARTER

It is planned to begin a steady-state coolant recycle run with irradiated Santowax WR in early October. The recycle rate will be adjusted so that the distillation cutoff will maintain a constant bottoms concentration of approximately 30 w/o in the loop. Section 2.3 of this report describes the distillation cutoff. It is anticipated that the steady-state coolant recycle phase will be completed by early or mid-December, 1963.

Since project termination is on January 31, 1964, no plans have been made for loop operation beyond the steady-state coolant recycle irradiation.

Preparation of the final report will begin next quarter and will take the place of a quarterly if the project termination date remains January 31, 1964.

4.0 REFERENCES

(1) C. D. Sawyer and E. A. Mason, "The Effects of Reactor Irradiation on Santowax OMP at 610°F and 750°F," MITNE-39 (IDO 11107), Department of Nuclear Engineering, M.I.T., Cambridge, Massachusetts, September, 1963.

(2) R. W. Bowring et al., "Measurements of the Viscosity of Santowax R, Para-, Meta-, and Ortho-Terphenyl, Diphenyl, and Dowtherm A," AERE-R3309, Harwell, 1960.

(3) Letter dated 17 October 1963 from S. Elberg of C.E.A. Centre d'Études Nucléaires de Grenoble, France to J. P. Casey of M.I.T.