IRRADIATION LOOP STUDIES

OF

ORGANIC REACTOR COOLANTS

Quarterly Report

July I - September 30, 1961

Department of Nuclear Engineering

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QUARTERLY REPORT
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TABLE OF CONTENTS

FIGURES

TABLES

1.0 Summary

Irradiation of Santowax OMP was initiated in the M.I.T.
Reactor Organic In-Pile Loop on August 9, 1961 and is con-
tinuing. As of September 30, 1961 the total absorbed dose
to an average inventory of 5000 grams of coolant was 79,900
watt-hrs. In this same period of time approximately 35%
of the terphenyls in the coolant had been degraded. The
dose rate (determined by calorimetry) is 52.4 watt-hrs ab-
sorbed/Megawatt-hour of reactor operation for unirradiated
Santowax OMP at 600°F. Thirty three per cent of the absorbed
dose is from fast neutrons and 67% from gamma photons in
this experiment. The G value for the mixture of ortho,
meta, and para terphenyls is estimated to be -0.19 molecules
of o,m,p-terphenyl/100 ev absorbed in the coolant at 30%
DP. The portion of the degradation due to fast neutrons is
estimated to be G_n(-omp) = 0.375 molecules of terphenyls/100
ev absorbed. Both results are in good agreement with OMRE
and Curtiss Wright Reactor results.

The heat transfer coefficients have decreased as the
concentration of degradation products (%DP) increased.
Essentially all of the change in the coefficients can be
accounted for by the increases in the viscosity and density
which have occurred.

Preliminary results of the ash content, carbon-hydrogen
ratios, density, viscosity, and the radiolytic gas composition
are presented, as a function of %DP.

Plots of the measured neutron spectra from fission
energy to thermal energy are presented and work is continuing
on the comparison of this data with calorimetric measurements.

2.0 Operation of In-Pile Loop

On August 9, 1961, irradiation of Santowax OMP* was
begun in the organic in-pile loop at the M.I.T. Reactor.
The reactor operated continuously at 1.8 megawatts until
August 25, following which, the normal reactor operating
schedule was resumed.

Normally, the reactor is operated at full power each
week from about noon on Monday until Friday evening when
the reactor is shut down for the week-end period. Circulation
of the organic liquid in the loop is, however, maintained
7 days per week, 24 hours per day, to provide mixing and to
prevent solidification of the organic material in the event
of in-pile heater failure.

Exposure of the initial charge of Santowax OMP has been
carried out without the addition of fresh Santowax OMP
makeup, and no nitrogen addition has been required to main-
tain system pressure. Liquid samples are withdrawn period-
ically for determination of chemical composition and physical
properties. Gas samples are withdrawn as necessary to
maintain a constant system pressure and are being analyzed
for nitrogen and various hydrocarbons. The rate of gas re-
moval is being correlated to determine the gas generation
rate.

When the reactor is at full power the bulk organic
temperature in the capsule is maintained at $600^{o}F \pm 10^{o}F$ by
use of the external test heater and trace heaters. Loop
pressure varies from 90 psig to 115 psig depending on the
frequency of gas sampling. Maximum flow ($\sim$ 2 gpm) of the
organic is maintained throughout the system except when heat
transfer measurements are being made.

During the weekend periods when the reactor is shut
down so that the rate of energy absorbtion in the coolant

*Registered Trademark Monsanto Chemical Co. It is an
isomeric mixture of terphenyls. Starting composition in
this case 11 w/o ortho, 26 w/o para, and 63 w/o meta, terphenyls

is essentially zero, the loop temperature is lowered to approximately 425°F to minimize any possible pyrolytic effects on the coolant. Maximum flow is maintained through the capsule during this period. In correlating the data obtained from operation of the loop the weekend interruption of irradiation is assumed not to effect the degradation of the organic. Based on this assumption the changes in coolant properties are being plotted as a function of reactor operating time (MWH). The curves are smooth through all periods of reactor shutdown indicating that degradation during reactor shutdown is indeed negligible.

Heat transfer measurements were made using the electric test heater (1) at one week intervals. This corresponds to measurements at every 4 to 5 per cent change in the total concentration of ortho, meta, and para terphenyl in the organic, or each 4 or 5 per cent increase in DP.

As of September 29, 1961, the irradiation of Santowax OMP had proceeded for a total of 1485 megawatt hours of reactor operation. The dose rate to the organic in the in-pile irradiation capsule is 52.4 watt-hr/MWH of reactor operation for unirradiated o, m, and p terphenyls at 600°F with a density of 0.857 gms/cm^3. Of the total dose, 33% of the energy deposited is from fast neutrons. Based on an average density of 0.880 gms/cm^3 for the period to 1485 MWH, the total energy absorbed in the coolant charge of approximately 5000 gms is 79,900 watt-hrs.

Mechanical performance of the loop equipment, i.e., pumps, valves, flowmeters, etc., has been excellent to date. There are no indications of bearing or stator winding difficulties with the canned rotor pump in use. This pump has operated continuously since August 9, 1961.

will be removed, and the distillate and fresh Santowax OMP makeup will be returned to the loop. The frequency of sampling will be regulated to maintain a constant average concentration of high boilers in the coolant. (Note that, consequently, the % DP will probably not be maintained constant).

Heat transfer and the physical and chemical properties of the coolant will be measured during this period. Of special importance will be the expected changes in molecular weight distribution in the less volatile portion of the coolant and the appearance of "intermediate boilers."

4.0 Preliminary Results

This section presents and discusses the results obtained
up to September 30, 1961, during the first irradiation of
Santowax OMP in the M.I.T. facility. Since analyses of the
samples have not been completed and the irradiation is still
continuing, the information contained here is of a preliminary
nature and is subject to change as the experiment continues
and more information becomes available.

A summary report covering all the results obtained will
be prepared when the irradiation is finally completed and all
the analytical results have been correlated.

4.1 Changes in Coolant Composition

Figure 1 presents the results of analyses of samples of
the circulating organic coolant removed from the loop at
various reactor exposure levels. The concentration of the
individual terphenyl isomers in the samples are determined by
gas chromatography (GC); these concentrations are summed to
give the total concentrations of o, m, and p-terphenyls
remaining in the coolant. The difference between 100 and the
total per cent omp concentration in any sample represents the
concentration of degradation products (DP) formed as a result
of the in-pile irradiations. The last set of data points
shown in Figure 1 indicate a decrease of 34.6% in the total
concentration of o, m, and p-terphenyls (34.6% DP) since the
initiation of the experiment at a total average absorbed
dose of 16 watt-hrs per gram of coolant.

The use of fused salt columns is being investigated to
provide separation of the high boiling components of the
coolant. Apiezon "L" columns have been used to detect the
terphenyls in the coolant and small amounts of intermediate
boilers have been detected. The compounds causing these
peaks have not been identified. The biphenyl content of the
coolant has remained constant at 0.5%.
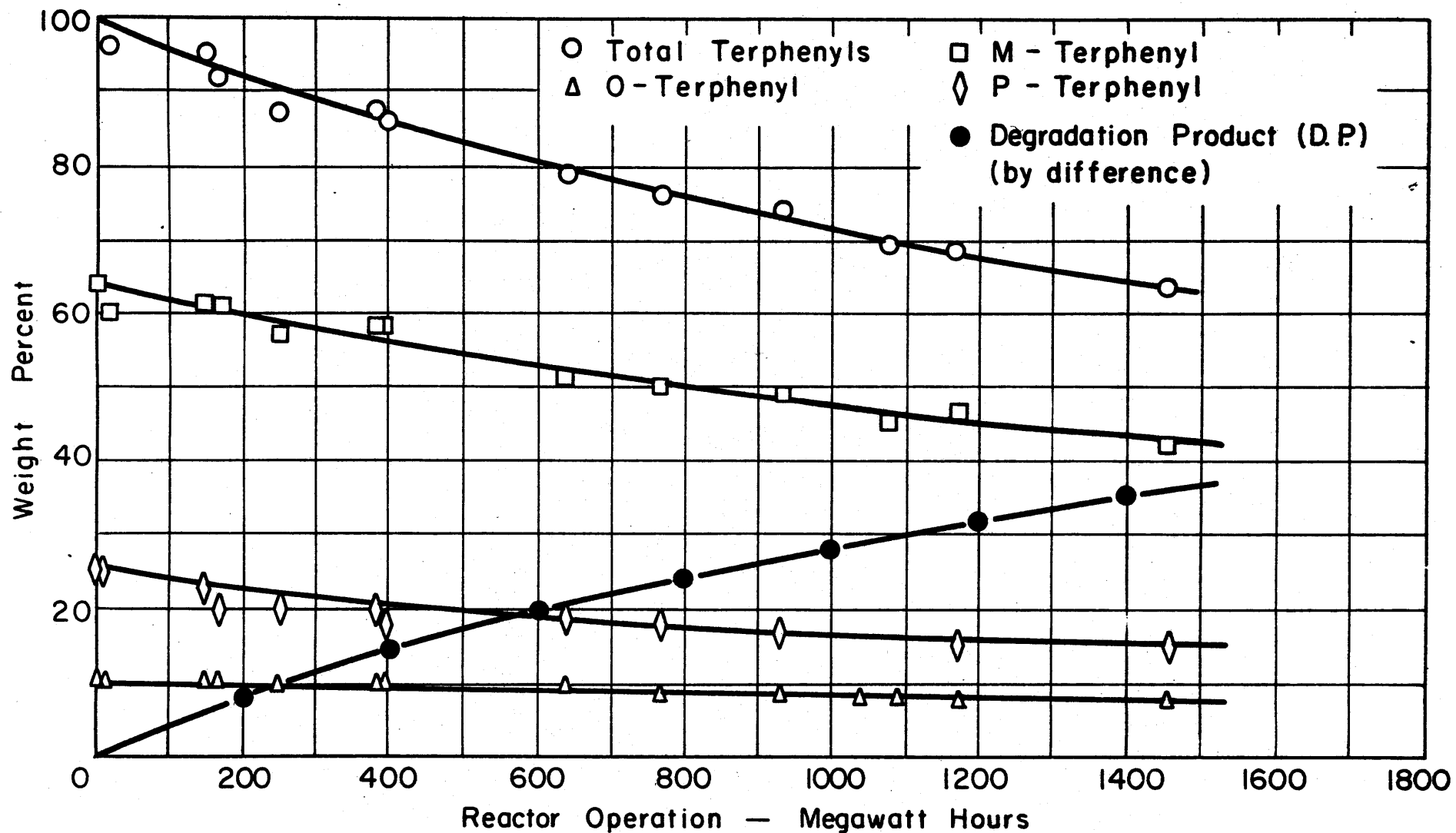
FIG. I CHANGE IN SANTOWAX OMP COMPOSITION — MITR IRRADIATION

4.2 Degradation Rates

Preliminary values for the degradation or decomposition rates for the mixture of ortho, meta, and para terphenyl and the individual isomers have been determined from the slopes presented in Figure 1 and the rate of energy deposition as reported in Section 2.0. The index or G value expressing the yield of terphenyl molecules per 100 electron volts absorbed in the coolant mixture is negative since the terphenyl molecules are being degraded to other molecular species. Figure 2 presents the preliminary values of $G(-omp)$, $G(-o\phi_3)$, $G(-m\phi_3)$, and $G(-p\phi_3)$ as discussed above, where (omp), $(o\phi_3)$, $(m\phi_3)$, and $(p\phi_3)$ represent the mixture and the ortho, meta, and para isomers respectively.

During the next quarter the degradation yields, $G(-)$ values, will be evaluated by statistical methods.

The $G(-omp)$ value presented in Figure 2 at 70% omp (30% DP) terphenyls is 0.19 molecules of terphenyls degraded per 100 ev of energy absorbed in the mixture. This result is approximately 30% greater than the results presented for the OMRE (3) for coolant containing 30% of high boiling components (HB).

The data presented in reference 3 are plotted against the concentration of HB in the coolant and are not directly comparable with the results presented in Figure 2 where the abscissa is the concentration of all degradation products. It has been found by Canadian investigators (4) that % DP (i.e., 100% - % o, m, and para terphenyls) does not correspond to the per cent HB as determined by distillation or sublimation. This is due to the fact that the techniques for determining HB only analyze for those degradation products which have lower volatility than the highest boiling terphenyl in the coolant, in this case para terphenyl. Since there is always a finite amount of degradation products of volatilities lower than those
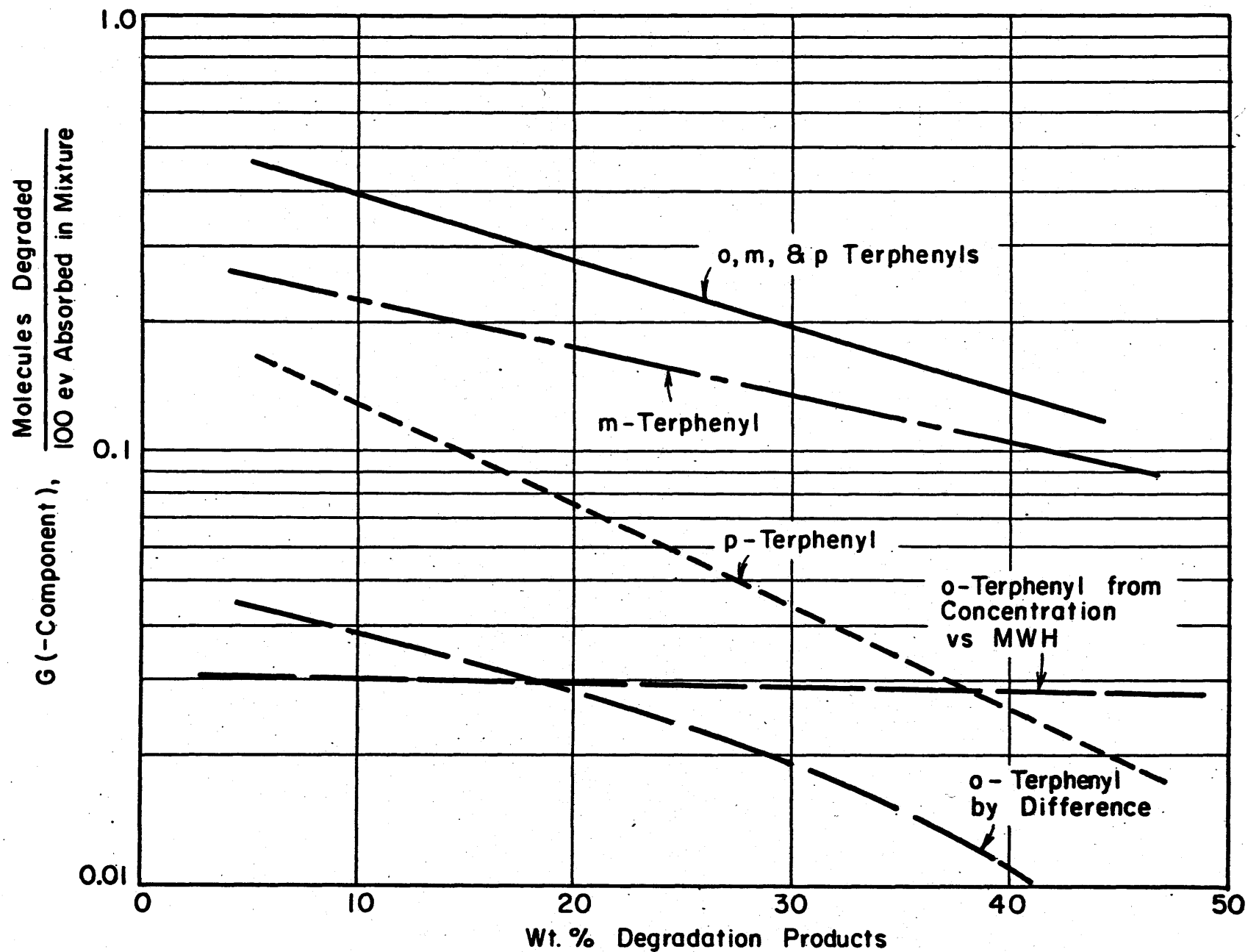
FIG. 2   G (-COMPONENT) IN IRRADIATED SANTOWAX OMP

reported as HB (this is especially important as radiation exposure progresses), the % DP for a given sample is greater than the % HB, and hence, comparison of G values should allow for this. Duplicate HB (by distillation or sublimation) analyses and per cent coolant (by GC) have not yet been completed on the M.I.T. samples. However, if we assume that the M.I.T. samples contain approximately 10% intermediate boilers (4), then 30% DP would correspond to 20% HB in the OMRE results. Using this assumption the G values from the two sources agree.

The degradation coefficient, or G_n value, of the irradiated ortho, meta, and para terphenyl mixture due only to the fast and epithermal neutron scattering can be estimated from the data obtained to date. If the G(-) values for terphenyl molecules caused by the fast neutrons and by gamma photons are assumed to be additive, then the total G value can be written as:

$$f_\gamma G_\gamma(\text{-omp}) + f_n G_n(\text{-omp}) = G(\text{-omp}) \qquad (1)$$

where:

f_γ is the fraction of the total dose absorbed from gamma photons

f_n is the fraction of the total dose absorbed from fast neutrons

$G_\gamma(\text{-omp})$ is the yield of terphenyl molecules per 100 ev of energy absorbed from gamma photons

$G_n(\text{-omp})$ is the yield of terphenyl molecules per 100 ev of energy absorbed from fast neutrons

$G(\text{-omp})$ is the yield of terphenyl molecules per 100 ev absorbed due to both effects and is shown in Figure 2.

For the MITR loop $f_n = 0.33$ and $f_\gamma = 0.67$. Also, $G(-omp)$ equals 0.19 at 30% DP. Using a value of $G_\gamma(-omp) = 0.10$ at 30% DP (20% HB) and 662°F (see discussion in previous paragraphs) from Harwell data reported in Reference (3), the following calculation can be made for $G_n(-omp)$

$$(0.67) \times (0.10) \times 0.33G_n(-omp) = 0.19 \qquad (2)$$

and

$$G_n(-omp) = \frac{(0.19) - (0.67) \times (0.10)}{0.33}$$

$$= 0.37 \frac{\text{molecules terphenyl}}{100 \text{ ev absorber from neutrons}}$$

This value is in good agreement with the value of G_{-n} of 0.385 from the Curtiss Wright Irradiations (5) reported by Atomics International.

4.3 Physical and Chemical Changes

The analytical techniques to be used in determining the changes occurring in the coolant have been described in a previous progress report (6).

4.31 Density and Viscosity

The density and viscosity of the irradiated coolant has been determined in the range from 400°F to 750°F. Values of the density and viscosity are plotted in Figures 3 and 4 respectively.

The density in Figure 3 agrees quite well at 600°F with data published by Monsanto (7), Harwell (8), and previous in-pile work when it is assumed that 20% HB corresponds approximately to 70% o, m, and p as discussed in Section 4.1.

The viscosity in Figure 4 agrees well with the unirradiated data presented in Reference (8) at 400°F. However, the data is approximately 10% lower than that previously presented by Bates (8) at 600°F. In general, the results in Figure 4 are approximately 5-10% lower than those reported by Bley for irradiated Santowax R (9).
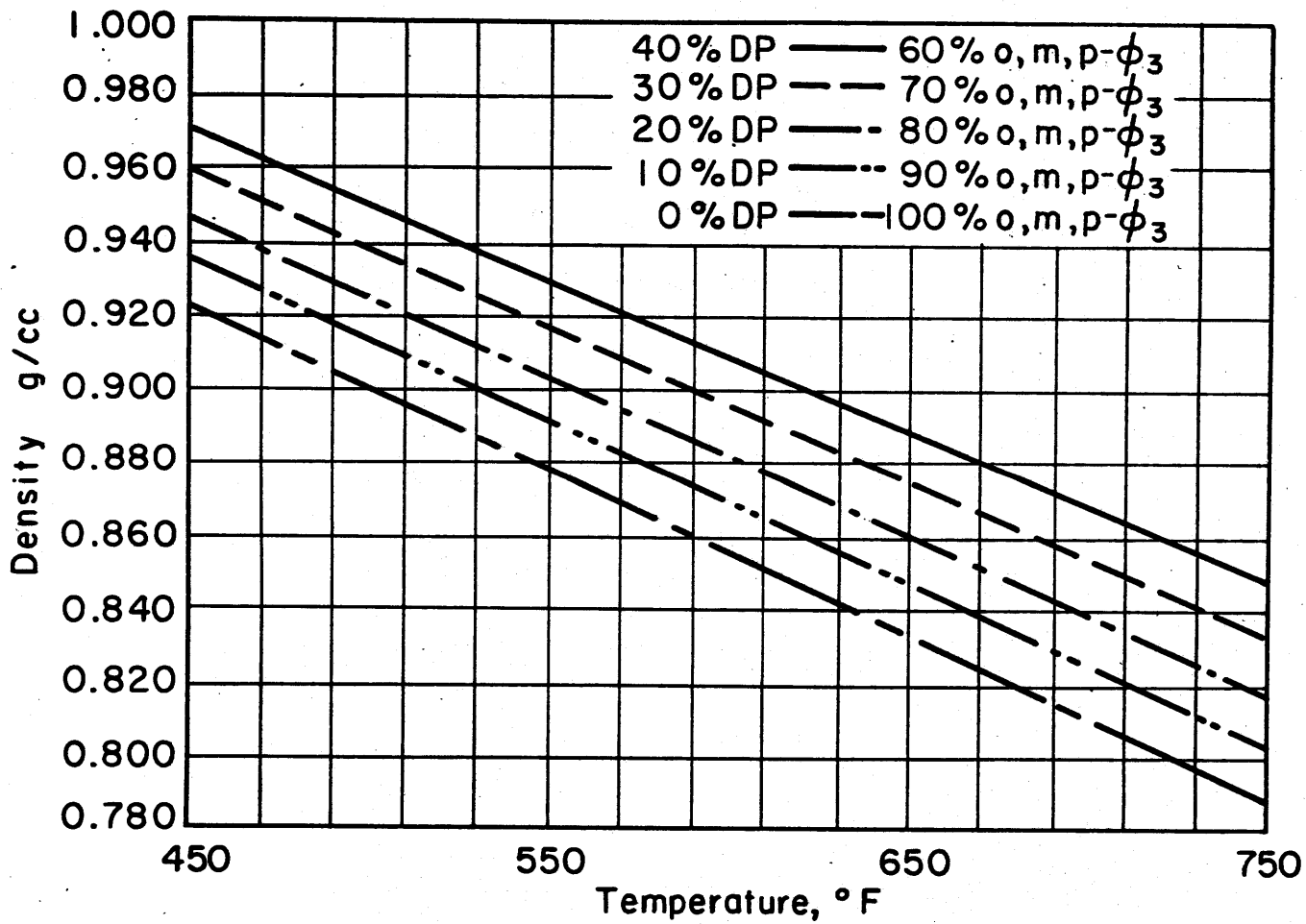
FIG. 3 DENSITY OF IRRADIATED SANTOWAX OMP

Legend (within figure):

40% DP ———— 60% o, m, p-ϕ_3
30% DP —— —— 70% o, m, p-ϕ_3
20% DP ——·—— 80% o, m, p-ϕ_3
10% DP ——··—— 90% o, m, p-ϕ_3
0% DP ———— 100% o, m, p-ϕ_3

Y-axis: Density g/cc
X-axis: Temperature, °F
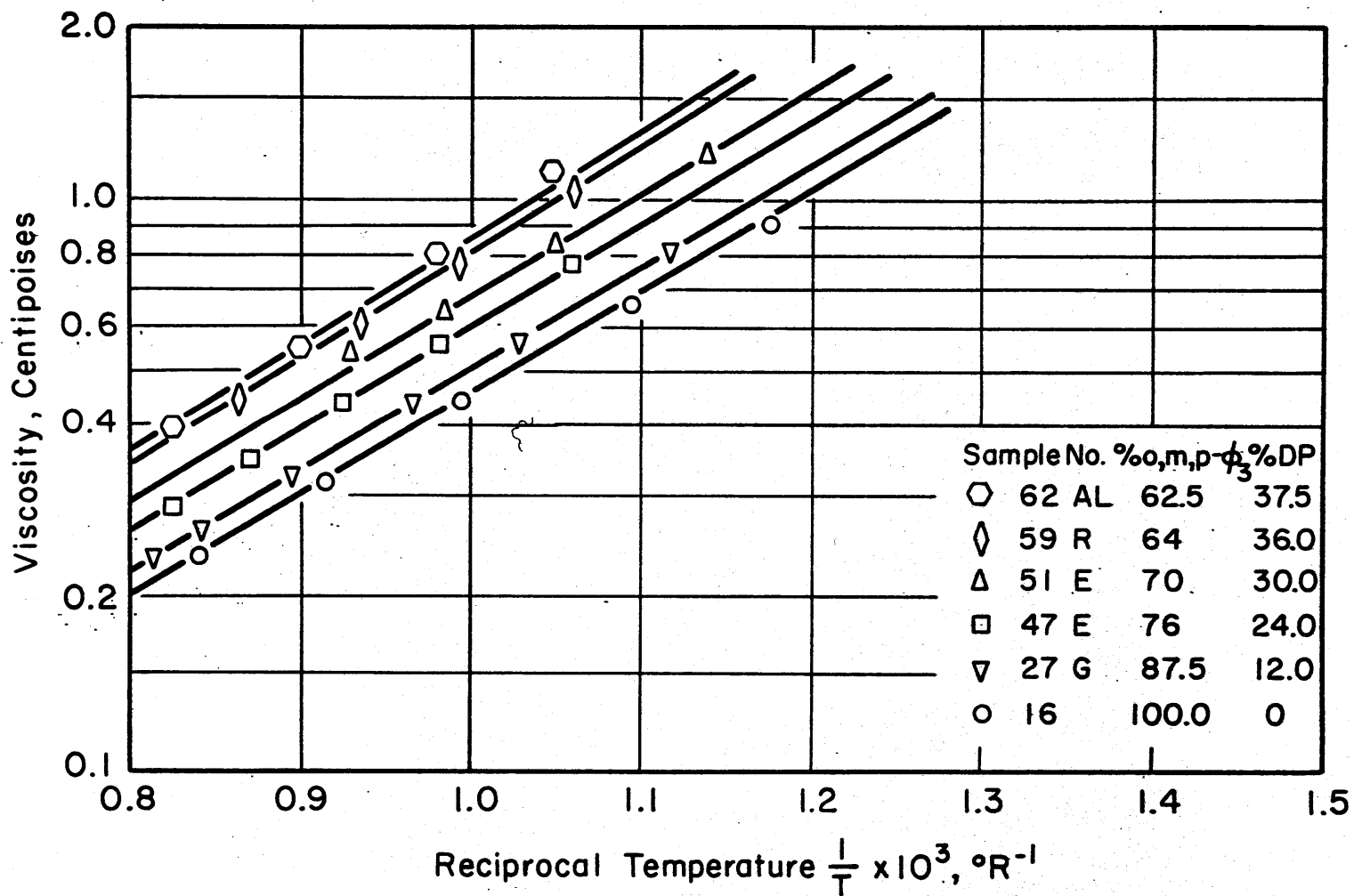
FIG. 4   VISCOSITY OF IRRADIATED SANTOWAX OMP

The figure is a semi-log plot of Viscosity (Centipoises) on the vertical axis (ranging from 0.1 to 2.0) versus Reciprocal Temperature $\frac{1}{T} \times 10^3$, °R⁻¹ on the horizontal axis (ranging from 0.8 to 1.5).

Legend:

Sample No.	%o,m,p-ϕ_3	%DP
⬡ 62 AL	62.5	37.5
◇ 59 R	64	36.0
△ 51 E	70	30.0
□ 47 E	76	24.0
▽ 27 G	87.5	12.0
○ 16	100.0	0

4.32 Average Molecular Weights, Carbon-Hydrogen Ratios, and Melting Points

Determination of the average molecular weights, carbon-hydrogen ratios, and melting points are being made on irradiated samples as the terphenyl content of the coolant decreases. Table 1 presents the data collected to date.

From the average molecular weights presented, it is difficult to draw any conclusions regarding the molecular weight of the degradation products. The values presented were for the total sample since it was not possible to distill the small samples ($\sim$1 gm) to separate the high boilers. Sublimation is a possibility, and it may be used in the future in remeasuring the samples. During the extended period of operation large loop samples will be distilled to separate the "high boilers" as discussed in Section 3.0. The HB obtained from these distillations will be used for molecular weight determinations.

4.33 Emission Spectroscopy and Ash Analysis

It is difficult to make a separate inorganic ash determination on the samples withdrawn from the MITR loop because of limited sample size. The technique being used is to ash approximately 5 grams of sample and then analyze this for inorganic content by emission spectroscopy. The amount of ash resulting from this technique is very sensitive to the ashing procedure and it has been found to vary considerably. In some cases, the weight of ash indicated 0.25% ash in the organic coolant even though the elemental content of the ash detected by emission spectroscopy was found to be very low. This would indicate that ignition was not complete.

Table 2 presents the results of emission spectroscopy on the irradiated material. As can be seen, the detectable elements are only present in ppm concentrations, and they have not shown any consistent trends.

TABLE 1

Molecular Weight, Carbon-Hydrogen Ratio, and Melting Point in Irradiated Santowax OMP

Sample No.	MWH Exposure	w/o Coolant* $(o,m,\&p-\emptyset_3)$	Average** Molecular Weight	Carbon Hydrogen Ratio	Melting Point $^\circ C$*** Initial	Final
16	0	100.0	250	15.42	79	171
18	18	99.0	—	—	—	—
24	171	92.9	238	15.96	75	167
27	249	90.0	—	15.42	62	161
35	386	85.8	260	16.25	—	—
47	770	76.8	263	15.65	—	—
50	935	73.0	278	14.90	—	—
51	1078	70.2	266	16.25	60	150
59	1455	63.9	—	—	59	140

* From smoothed curve of % coolant vs exposure, Fig. 1

** Determined on total sample of coolant plus degradation products

*** Initial liquidus point is when liquid phase first appears. (It is a very difficult point to determine visually.) Final liquidus point is the point when the last crystal disappears. (determined visually)

TABLE 2

<u>Semi-Quantitative Ash Analyses by Emission Spectroscopy</u>
<u>Concentration of Elements Detected[*]-ppm</u>

Sample No.	Ag	Al	Cr	Cu	Fe	Mg	Mn	Mo	Na	Ni	Pb	Si
18	10-31	<4	6-19	<2	13-38	2-6	<2	8-25	1-4	4-13	4	2-6
24	3-8	<6	<6	—	3-8	<3	<1	6-17	—	<3	6	2-7
27	—	<4	—	<4	<4	<4	—	—	2-7	—	—	12-35
35	—	<2	—	—	—	2	—	—	1-3	—	—	3-9
47	—	3-8	—	<1.3	1-2	4-12	—	<1	13-39	<2.6	—	15-154
50	—	1-4	1-4	<2	2-7	7-21	<1	—	6-17	<5	—	28-57
51	—	<2	<2	<2	2-6	<2	—	—	<4	—	—	3-10
59	—	1-3	—	<1	1-3	<1	Trace	<1	—	—	—	2-5

[*] From the ash resulting after ignition at temperatures of 750°C to 1000°C

Higher ignition temperatures are required at lower % coolant and some oxides may be lost

4.34 Activation Analysis

The activity of the irradiated coolant is very low, and
initial attempts to use gamma spectrography for analysis of
the coolant have been unsuccessful. Attempts are being
made to increase the sensitivity of the counting equipment
(since only 1 gm samples are available) in order to deter-
mine if buildup of the impurities is occurring.

4.35 Gas Analysis

Gas samples are withdrawn several times each week to
maintain system pressure. The samples have been analyzed
for nitrogen and various hydrocarbons by mass spectrometry.
Results of gas analyses are presented in Figure 5 plotted
as a function of % DP. The gases are grouped into those
hydrocarbons containing the same number of carbon atoms.
No definite trends or conclusions can be noted from the
analyses completed to date. The buildup of the higher
molecular weight gases is similar to that noted in previous
in-pile irradiations (9).

Future analyses will be compared with gas solubility
measurements during the next quarter. Gamma spectrography
will be employed in an attempt to identify the radioactive
constituents in the gas samples. The radioactivity present
is short-lived.

4.4 Heat Transfer Measurements

Heat transfer measurements are being made at approxi-
mately each 5% increase in % DP. The results of the measure-
ments are presented in Figures 6 and 7.

The rate of change in h versus % DP is increasing as
the per cent DP increases. This is in agreement with the
greater change in the viscosity with a given change in % DP
as shown in Figure 4.

If one assumes that the following equation approxi-
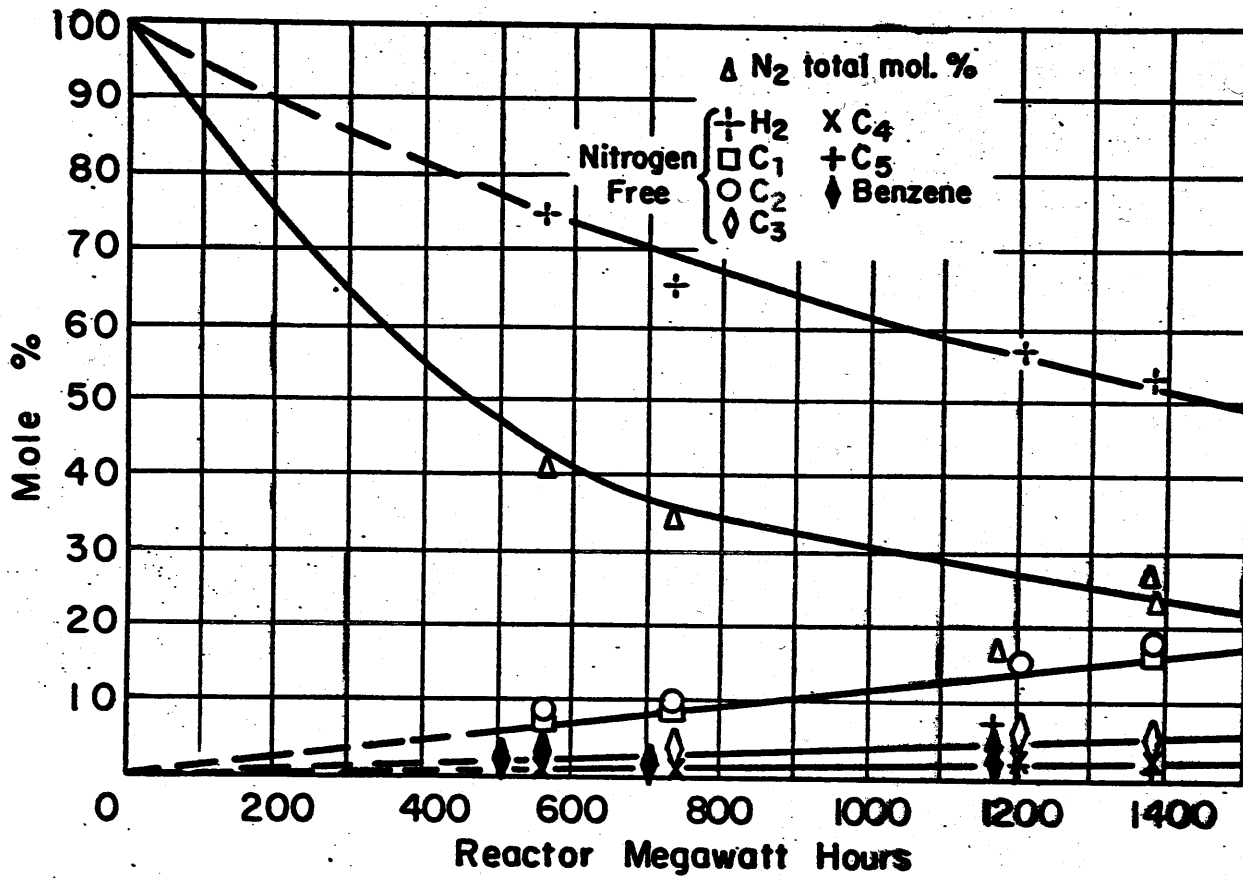mately describes the relationship between the physical

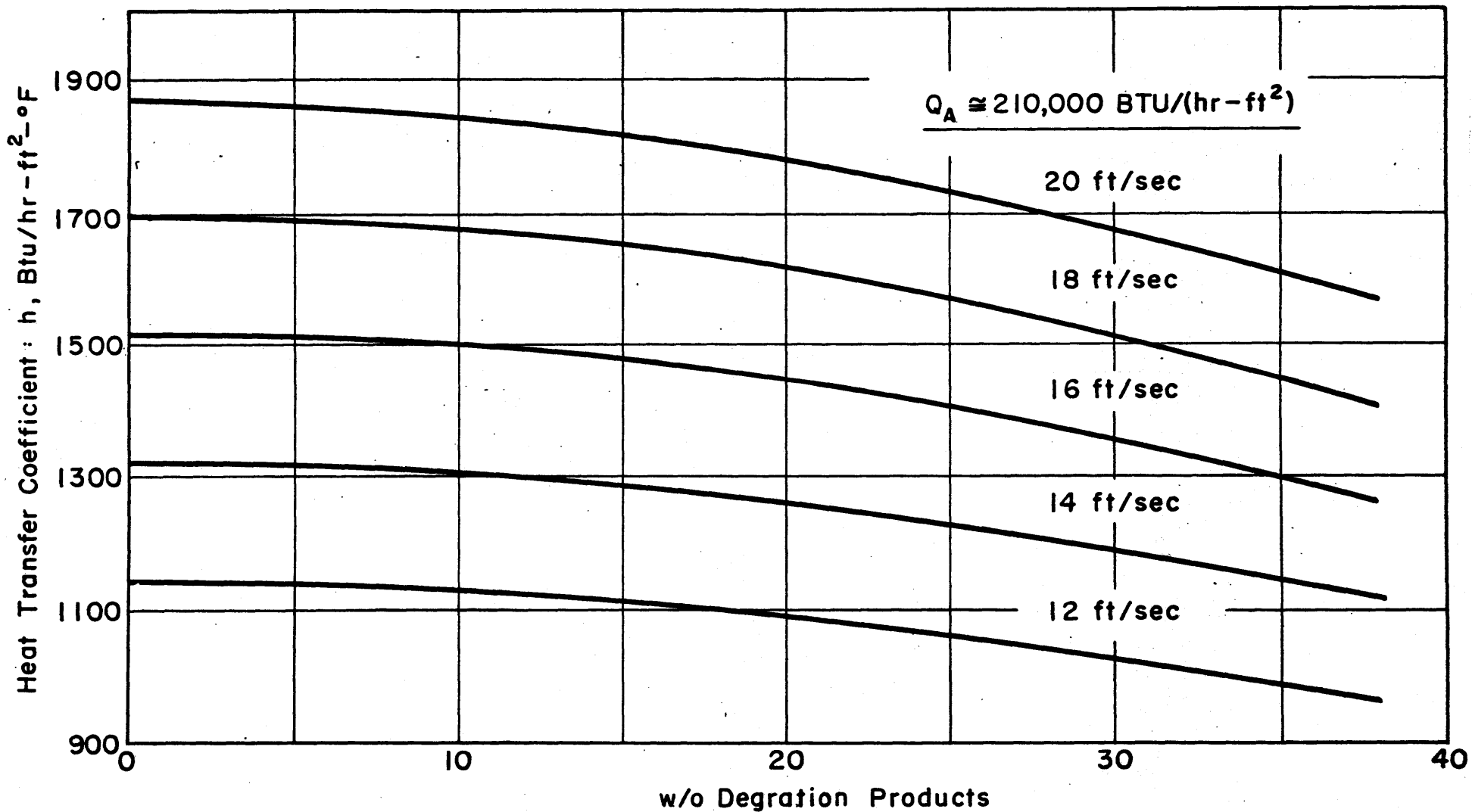FIG. 5 RADIOLYTIC GAS COMPOSITION MITR
ORGANIC LOOP

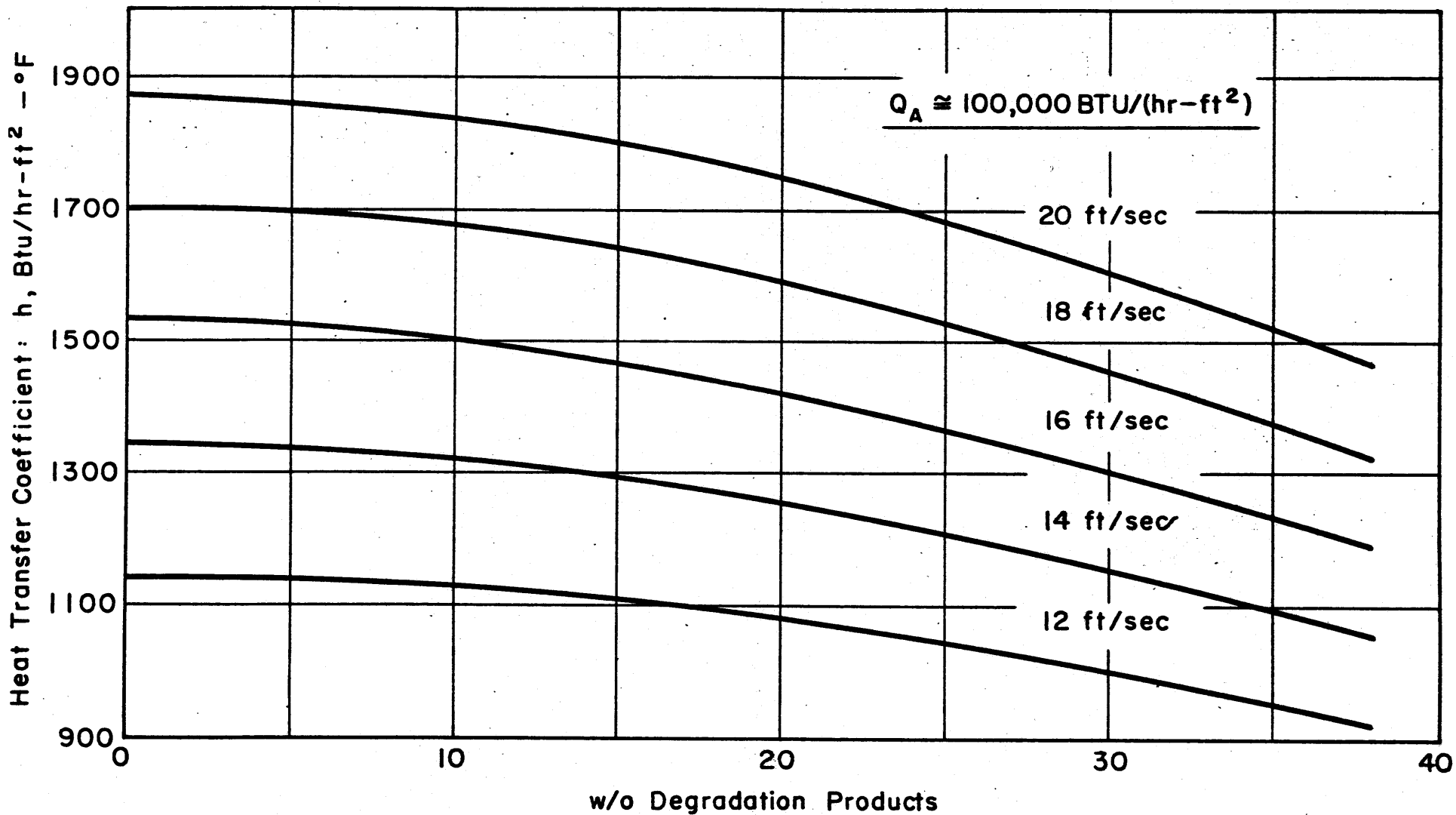FIG. 6 HEAT TRANSFER COEFFICIENT OF IRRADIATED SANTOWAX OMP AT 600°F

FIG. 7 HEAT TRANSFER COEFFICIENT OF IRRADIATED SANTOWAX OMP AT 600°F

properties and the heat transfer coefficient:

$$Nu = K \ Re^{0.8} Pr^{0.4} \qquad \qquad ..(3)$$

and further neglects any changes in the thermal conductivity and the specific heat (for which measurements are not yet available), then the function,

$$h \cdot \frac{\mu^{0.4}}{\rho^{0.8}} \qquad \qquad (4)$$

can be plotted against per cent DP, to determine if the changes in the experimental coefficients of heat transfer are due principally to the changes occurring in the viscosity and density. The data has been analyzed in this fashion and the value of Equation (4) has remained essentially constant ($\pm$3%) as the % DP increased from 0% to 40%.

It has not been possible to detect fouling of the test heater from the data collected. However, the conditions at the test heater wall are relatively mild; maximum wall temperatures during continuous operation when the test heater is being used to maintain the bulk temperature at 600°F is approximately 675°F. Flow through the heater is 20 ft/sec during this time. During heat transfer measurements, the wall temperature reaches as high as 800°F and the velocity is varied between 12 and 20 feet per second.

4.5 Flux Measurements and Calorimetry

Calorimetry measurements were made over a period of one year before insertion of the in-pile assembly. The average dose rate in the in-pile capsule is 52.4 watt-hrs absorbed/Megawatt-hour of reactor operation in unirradiated Santowax OMP and 600°F (ρ = 0.857 g/cc). Of this total dose 33% is due to fast neutron scattering and 67% is due to gamma photon interactions.

In addition, the neutron spectrum was measured just prior to insertion of the in-pile section into the central

fuel element position and again just after reactor startup
by use of monitor wires as described in Reference (6).
Aluminum, magnesium, sulfur, and nickel are being used as
fast flux detectors. Copper and cobalt are being used to
determine the epithermal flux.

Figures 8a and 8b present the neutron spectra measured
at the reactor midplane in the central fuel element as
a function of neutron energy. These measurements were made
(prior to insertion of the in-pile assembly) in a stainless
steel thimble which was designed to produce the same flux
depression as the in-pile assembly. Measurements were then
made in the monitor tube of the in-pile assembly when it
was inserted. As shown in the figures the flux measured
in the monitor tube was slightly greater than the flux
measured in the mock-up assembly at neutron energies below
about 8×10^5 ev and was slightly less at energies above
8×10^5 ev.

Analysis of the results is continuing to compare the
fluxes determined from foil activation with calorimetric
measurements and to evaluate the measured differences in
the fluxes before and after insertion of the in-pile assembly.
There is a large gap in the energy spectrum (from 120 ev
for Cu to 2.9 Mev for S) due to the lack of resonance
detectors in this region. The results of the copper-foil
measurements shown in Figure 8b are not consistent with
the other measurements and are believed to be in error.

The results shown in Figure 8b for the sulfur, magnesium,
and aluminum foils were obtained by assuming a Watt fission
spectrum and integrating the threshold cross sections over
this spectrum. The effect of this assumed spectrum is
being checked.

$\phi(E)$ In Monitor Tube of In-Pile Section

$\phi(E)$ In the Stainless Steel Mock-Up Thimble (Prior to Insertion of In-Pile Section)
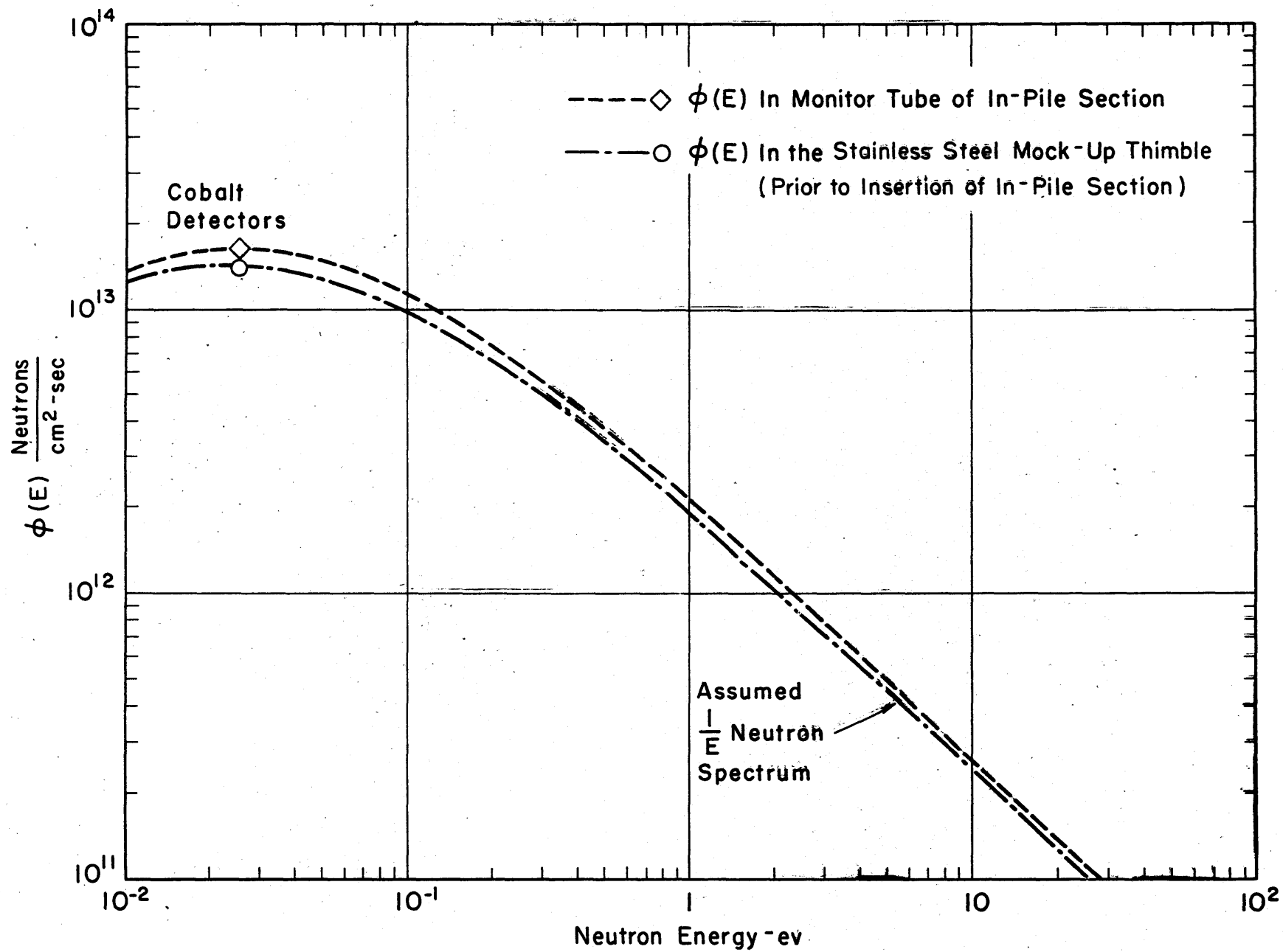
Cobalt Detectors

Assumed $\frac{1}{E}$ Neutron Spectrum

FIG.8a NEUTRON FLUX SPECTRUM MITR ORGANIC LOOP IN THE MITR CENTRAL FUEL POSITION 0.01 ev to 100ev
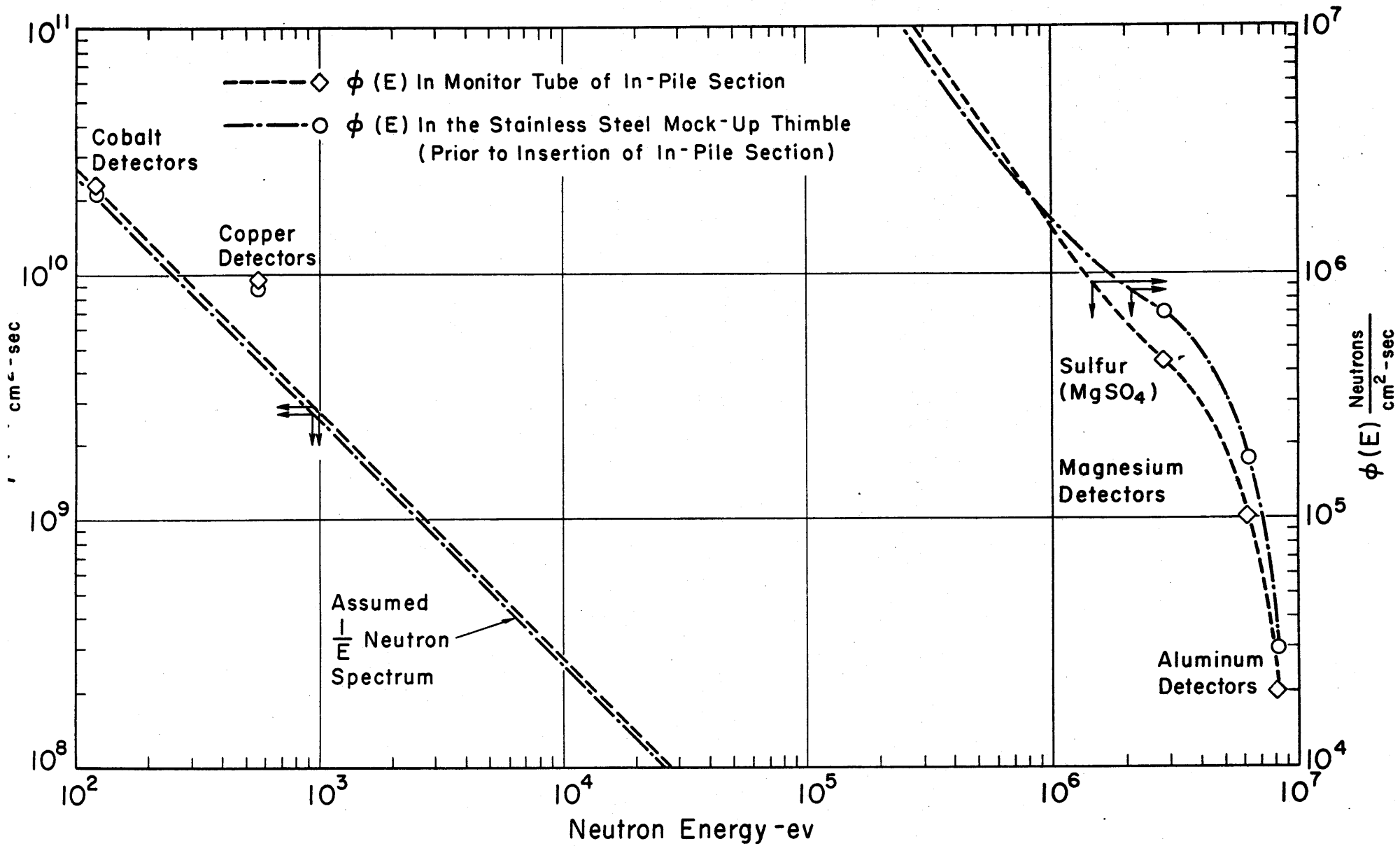
FIG. 8b NEUTRON FLUX SPECTRUM MITR ORANIC LOOP IN THE MITR CENTRAL
FUEL POSITION 100 ev to 10^7 ev

5.0 Reports

Detailed Master's Thesis reports are in preparation on the subjects of calorimetry, neutron dose rates, and heat transfer.

In addition, a Doctoral Thesis covering the MITR in-pile loop program since 1958 to Sept., 1961 is in preparation by D. T. Morgan. This thesis will also report and discuss the work to date on calorimetry, neutron dose rates, and heat transfer; it will be issued as a project report.

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