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Prediction of Yearly Fluid Replenishment Rates for Hydrocarbon Fluids in Thermal Energy Storage Systems

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V. P. Burolla

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115 and Livermore, California 94550 for the United States Department of Energy under Contract DE-AC04-76DP00789.

Printed April 1979

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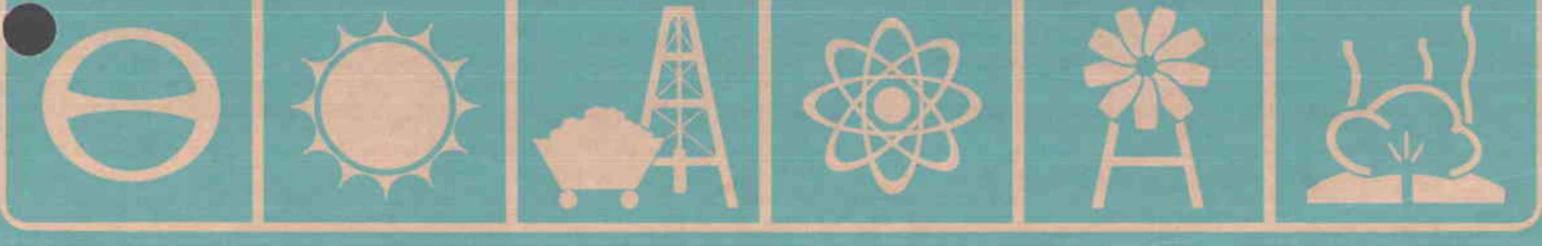

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PREDICTION OF YEARLY FLUID REPLENISHMENT RATES FOR HYDROCARBON FLUIDS IN THERMAL ENERGY STORAGE SYSTEMS

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ABSTRACT

Economic analysis of any thermal energy storage system using hydrocarbon fluids at or near their operating limit hinges on accurate determinations of fluid losses due to thermal and environmental effects. This work presents representative values for these fluid losses in an operating thermal storage system for three different hydrocarbon fluids, Sun 21, Caloria HT43 and Therminol 66.

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Introduction

First generation solar central receiver thermal power systems and many distributed thermal power systems compensate for low or zero insolation periods by storing energy in the form of sensible heat. Studies of such thermal power systems funded by the Department of Energy (DOE) have focused around thermal storage systems utilizing hydrocarbon oils with a normal bulk operating temperature around 316°C. Because the temperature is at or near the operating limit for most fluids of this type, selection of a preferred fluid depends on reliable estimates of yearly fluid replenishment due to thermal degradation. These estimates also depend on the ability to predict the magnitude of any effects on these fluid losses due to the presence in the system of materials other than the fluid itself, and the ability to equate test conditions with a realistic yearly operating scenario.

This report will discuss in detail what fluid replenishment rate can be expected for three different hydrocarbon oils in both single and dual media systems for temperatures as high as 316°C. The porous media in all cases was a mixture of river gravel (essentially granite) and coarse sand (essentially quartz).

The various sections of the report were written to provide the reader with quick access to whatever information he is interested in. If the details of the test are of no particular interest the pertinent results of the testing can be found summarized in one section, while comments on batch-to-batch variations in fluids, test methods, data reduction, and other topics are located in other sections.

Energy Storage Concepts

Several techniques for the storage of thermal energy have been studied. The most obvious way of storing sensible heat is to pump cold fluid from one tank, heat it in a solar collector and return the hot fluid to another tank. To extract the heat the process is simply reversed. This system requires a capital investment for two tanks and has thermal losses associated with two tanks. The first improvement to the system comes by using only one tank which stores the hot fluid above the cold fluid. The hot/cold interface is maintained by virtue of differing fluid densities, that is the hot fluid is lighter and will always rise above the denser cold fluid. The cold fluid is extracted from the bottom of the tank while the hot fluid is pumped into the top during the charging cycle and the hot fluid withdrawn from the top and pumped into the bottom during the discharge cycle. In this way the initial tank investment is halved and tank thermal losses are greatly reduced.

If the working fluid in systems like this is a hydrocarbon oil subject to thermal degradation, the next improvement would be to minimize the fluid inventory by utilizing it more as a heat transfer fluid, yielding its energy to a porous heat sink within the tank. The greater the amount of heat sink material loaded in the tank the less the fluid inventory, the smaller the initial cost of fluid and hopefully the smaller the yearly fluid replenishment rate.

Hence the dual media thermocline storage system. Naturally, the heat sink material must be compatible with the fluid and be relatively inexpensive. It is the fluid compatibility and thermal stability that is the subject of this report.

Test Apparatus

The apparatus was designed to minimize the effort necessary to obtain reproducible and accurate results and yet simulate as closely as possible in a bench scale test, a normal holding condition in a thermal storage system. A cutaway view of the heating bath is shown in Figure 1 while Figures 2 and 3 depict a schematic of the test apparatus used in the first series and the various vessel designs used in all the series. The heat source for the bath was a stirring hot plate connected to a temperature controller. Although the wells in the bath prevented intimate contact between the vessels and the molten salt thereby decreasing thermal conduction, it was considered a necessary safeguard as hot oil from a cracked glass vessel in contact with the strong oxidizing salt would be very inflammatory. Some tests used vessels of an all metal construction but similar in shape to the glass vessels. In the first series of tests the vessel fill tube and thermocouple well extended to a point 5 cm from the bottom of the vessel and as close to the center as possible. In later series, the thermocouple well was lowered to 2.5 cm from the bottom for reasons detailed later in the report. In vessels where the fluid was not to be contacted by any metal or rock, the fill tube and thermocouple well were glass tubes with a glass-metal joint at the end welded to the top plate. The fill tube was connected to a 316 stainless steel valve with a gasket and packing good to 205°C (400°F). The vent tube ultimately connected to a brass check valve set at 2.2 kPa (1/3 psi) cracking pressure. The fill tube was designed to allow the bubbling of

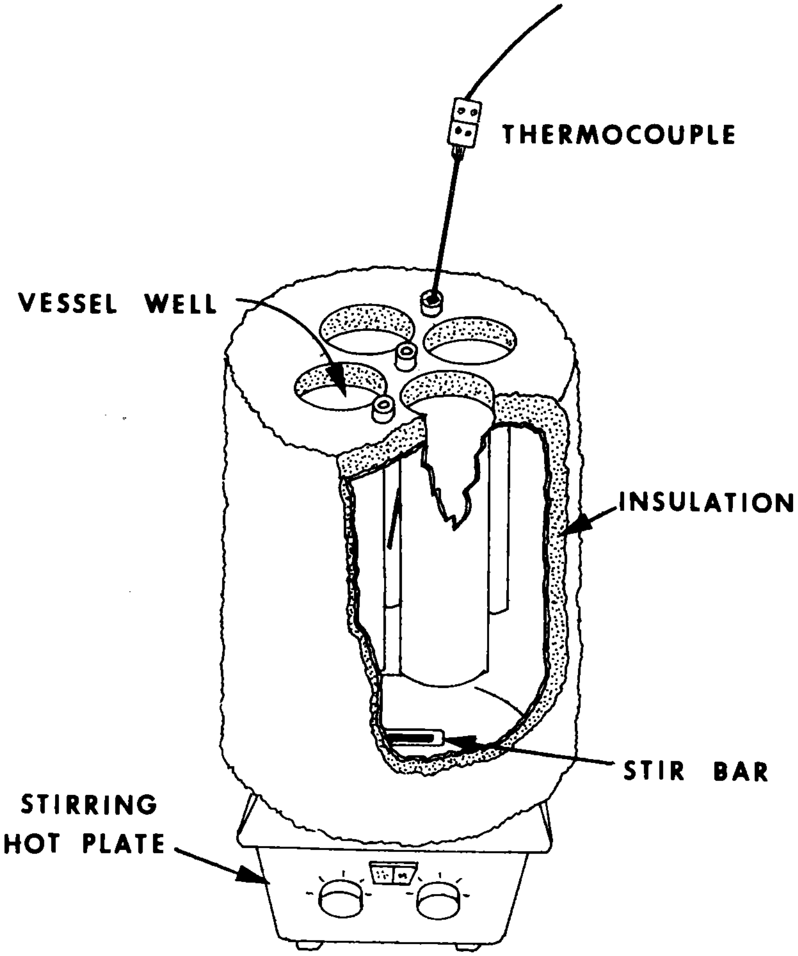

Figure 1. Cutaway view of Heating Bath

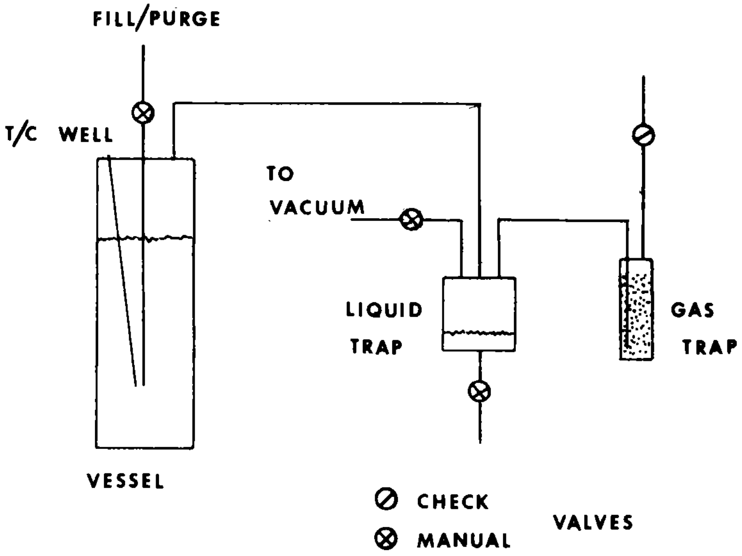

Figure 2. Schematic Diagram of Test Apparatus for Series A Vessels

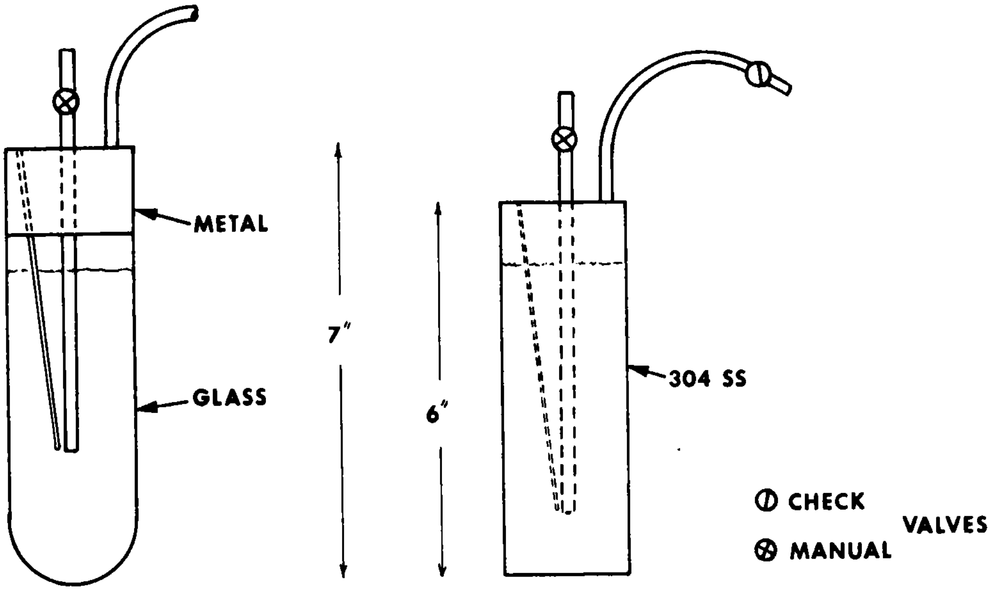

Figure 3. Examples of Vessel Designs Used in the Tests

nitrogen through the oils during startup (to remove water) and to allow the sampling of hot fluid directly if necessary.

Test Description

The intent of the tests was to provide accurate data on the fluid losses to be expected in a thermal storage system consisting of a large metal tank filled with a hydrocarbon fluid,with and without rock and sand, and an inert gas. It was not intended to enable a detailed description of the degradation mechanism(s) of the fluid. To this end the first series of tests (series A) was designed to generate data by measurement of level changes of the fluid and the addition of fluid when necessary to makeup any that was degraded and subsequently lost through the vent. However, the technique proved somewhat awkward and inadequate for accurate determinations at intervals less than 2000 hours. For this reason the first series had only one fluid makeup with no attempt to generate a fluid weight loss curve as a function of time. Even though fluid volume is the critical parameter in a thermal storage system, in all subsequent vessels (series B) fluid losses were measured by weight changes since data from the first series indicated insignificant fluid density changes even after 3000 hours of test.

To assess the compatibility of rock and sand with the fluids tested, some vessels were filled with a rock/sand mixture similar to that found in a typical dual media thermal storage system. That is to say the ratio of rock to sand, the ratio of rock and sand to oil and the size distributions of rock and sand all compared very well with the same parameters used in a large scale systems. However, the ratios were not precisely the same, therefore, appropriate corrections or adjustments to the data were necessitated which prompted additional tests to validate these adjustments.

A summary of all tests reported here is contained in Table I.

Temperature measurements were taken every hour using a Doric digitrend data logger, with an accuracy of ± .1°C over the temperature range of the test.

Data Reduction

Fluid losses from Series A:

As mentioned earlier, the method originally intended for measuring fluid losses (liquid level changes) proved to be more inaccurate than desired. Therefore, the tests were allowed to run at least 2300 hours and fluid levels at that point were compared to the fluid level at 500 hours to obtain a fluid rate loss. The first 500 hours were ignored because of one time fluid losses due to oxygen dissolved in the fluid and oxygen or water physically adsorbed on the surface of the rocks. These are real losses and would most definitely be experienced in a thermal storage system but the emphasis of the study was on yearly fluid replenishment rates. Fluid loss rates are expressed in two units; grams per gram-hour and percent per year, where year implies one year of operation for a thermal storage system.

Fluid losses from Series B:

Since fluid losses in all series B tests were measured by weight, reasonably accurate weight loss vs. time curves were generated. If a particular curve showed an unexpected change, the time-temperature history was checked for any sudden changes and therefore only those portions of the weight loss curves with a constant slope and temperature history were used in the calculations. Weight loss rates for this series are also expressed in two units.

TABLE I

TEST SUMMARY

Vessel #	Fluid		Media		Vessel	T/C[2] Position	Temp (°C)	Duration (Hrs)	Comments
	Type	Quant. (gms)	Type[1]	Quant.	Material				
A1	Caloria HT43	196	----- None -----		Glass	5.0	314.5	2400	
A2	Caloria HT43	111	Rock Sand	200 gms 100 gms	Glass	5.0	309.0	2330	
A3	SUN 21	112	Rock Sand	250 gms 125 gms	Glass	5.0	[316]	500	No useful data
A4	SUN 21	195	----- None -----		Glass	5.0	[316]	500	
A5	Caloria HT43	59	Rock Sand	300 gms 150 gms	Glass	5.0	288.0	2880	
A6	Caloria HT43	172	----- None -----		Glass	5.0	302.5	2880	
A7	Caloria HT43	205	----- None -----		Glass	5.0	302.0	2880	
A8	Caloria HT43	70	Rock Sand	300 gms 150 gms	Glass	5.0	293.0	2880	
B1	Caloria HT43	151	Steel	44 cm^2	Glass	2.5	260[3]	3012	
B2	SUN 21	153	----- None -----		Glass	2.5	260[3]	3012	
B3	SUN 21	152	Steel	44 cm^2	Glass	2.5	260[3]	3012	
B4	SUN 21	150	316 SS	33 cm^2	Glass	2.5	260[3]	3012	
B5	Caloria HT43	153	Steel	44 cm^2	Glass	2.5	282.4	4702	
B6	SUN 21	155	----- None -----		Glass	2.5	285[3]	3522	Leaking
B7	SUN 21	151	----- None -----		Glass	2.5	282.9	4702	
B8	SUN 21	154	Steel	44 cm^2	Glass	2.5	286.4	4702	
B9	Caloria HT43	153	Steel	44 cm^2	Glass	2.5	311.4	3000	
B10	SUN 21	150	----- None -----		Glass	2.5	311.4	3000	
B11	SUN 21	160	Steel	44 cm^2	Glass	2.5	307.1	3000	
B12	SUN 21	155	316 SS	33 cm^2	Glass	2.5	312.7	3000	

TABLE I (continued)

Vessel #	Fluid Type	Fluid Quant. (gms)	Media Type[1]	Media Quant.	Vessel Material	T/C[2] Position	Temp (°C)	Duration (Hrs)	Comments
B25	Therminol 66	151	----- None -----		304 SS	2.5	[316]	3043	
B26	Therminol 66	150	----- None -----		304 SS	2.5	314.6	4220	
B27	Therminol 66	51	Rock Sand	150 75	304 SS	2.5	300.6	4220	
B28	Therminol 66	51	Rock Sand	150 75	304 SS	2.5	[302]	1344	Severe Leaking
B29	Caloria HT43	121	----- None -----		304 SS	2.5	314.7	2777	
B30	Caloria HT43	121	Steel	110 cm^2	304 SS	2.5	312[3]	2777	
B31	Caloria HT43	121	Steel	220 cm^2	304 SS	2.5	315[3]	2777	
B32	Caloria HT43	121	Steel	330 cm^2	304 SS	2.5	311.9	2777	
B34	Caloria HT43	70	Rock Sand	200 100	Glass	2.5	304.7	2736	
B36	Caloria HT43	70	Rock Sand	300 150	Glass	2.5	290.6	2736	

1. Rock is 3/8" nominal river gravel - sand is #6 mesh, both from an area near Barstow, California
2. Distance of thermocouple from bottom of vessel in centimeters
3. Nominal - varied during test

[] Planned test temperature - due to oxygen leaks no useful rate data was obtained and hence no effort was made to calculate actual temperatures

Temperature Calculations:

Once the fluid losses were calculated they had to be related to a temperature representative of the temperature in the vessel during the life of the test. Throughout the entire test series there was a significant difference in the recorded temperature for vessels containing rock and sand and those containing oil only, even though they were immersed in the same heating bath. This prompted the design of a vessel containing ten thermocuples positioned axially and radially to measure any temperature gradients in the rock/sand bed. The #1 thermocouple was positioned precisely where all the A series test vessel thermocouples were, in order to provide a direct comparison to the gradient. Figure 4 is a plot representing the average of two, forty hour runs with temperatures recorded every hour with this vessel. The forty hour runs were more consistent than four hour runs with data taken every five minutes. This was attributed to slow moving currents which would tend to distort the gradient isotherms. Consequently only the data from the forty hour runs were used. Similar runs on the same vessel without the rock/sand bed showed a very slight gradient, however the #1 thermocouple was indicating the calculated average temperature so no temperature adjustments were necessary on test vessels containing only fluid. The temperature data on series A vessels with the rock/sand bed were adjusted upward 5°C as calculated by a weighted averaging technique to account for the non-linear relationship of fluid degradation as a function of temperature. All series B test vessels had relocated thermocouple positions to preclude the need to adjust the recorded temperature (see Table I). Since some series B test vessels were of an all metal construction, another special vessel was used to measure temperature gradients in these vessels. The

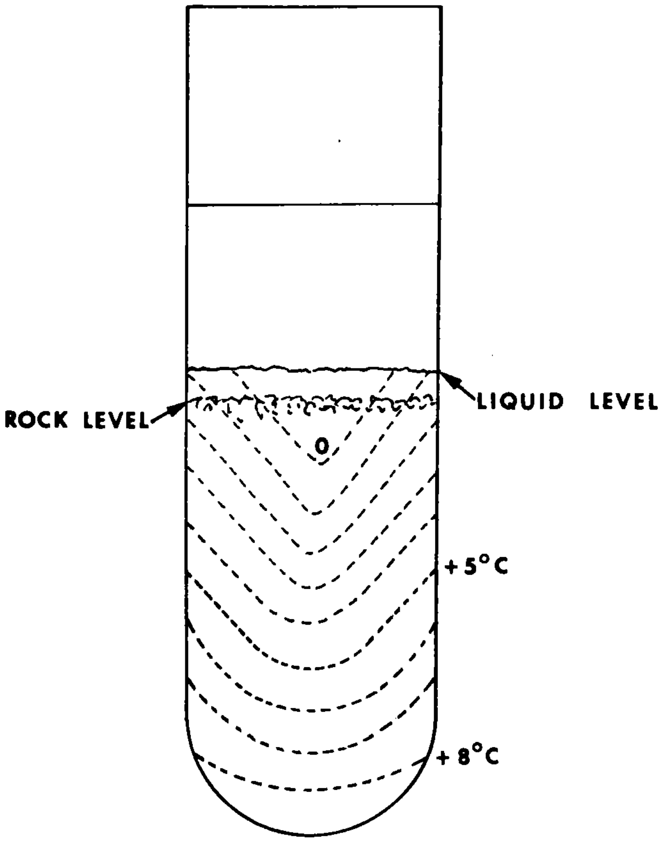

Figure 4. Isothermal Plot of the Temperature Gradient in Vessels Filled With Rock and Sand

results were very similar to the glass vessel gradients, therefore no special adjustments to the recorded temperatures were necessary.

Yearly Fluid Loss Rates:

All the tests described in this report were run at constant temperature to facilitate the experiments and accelerate the degradation. In order to equate the fluid losses observed in the test to those encountered in the cyclic operation of a thermal storage system several assumptions were made. Since there is no standard method of converting this data, in this particular study a typical thermal storage charge-discharge cycle shown in Figure 5 was used. Since a packet of fluid is never at an intermediate temperature for a significant length of time but is at either the low, 218°C, or the high, 302°C temperature, the averaging technique is simply the area under the curve in Figure 5 compared to the area under the dotted line representing the test conditions. This method is easily reduced to a formula which can generate tables of values for various charging, holding and discharging times. Several such tables are contained in Appendix II for reference. For the particular cycle chosen for comparison, 1 day of test time is equivalent to 3 days of cyclic operation. Estimates by others[1] on the number of non-operating days in a year due to inclement weather or repairs, approach 15%. Using approximately this number, and the adjustment from continuous to cyclic use, one can equate 2500 hours of testing to one full year of operation (8760 hours).

Another adjustment made to the data accounted for differences in rock and sand surface area between vessels and between the test and an actual thermal storage system. Very simply stated, if a vessel had 2/3's the surface area of rock and sand as another vessel, the fluid losses due to the presence of rock and sand only were multiplied by 3/2. To do this, the fluid

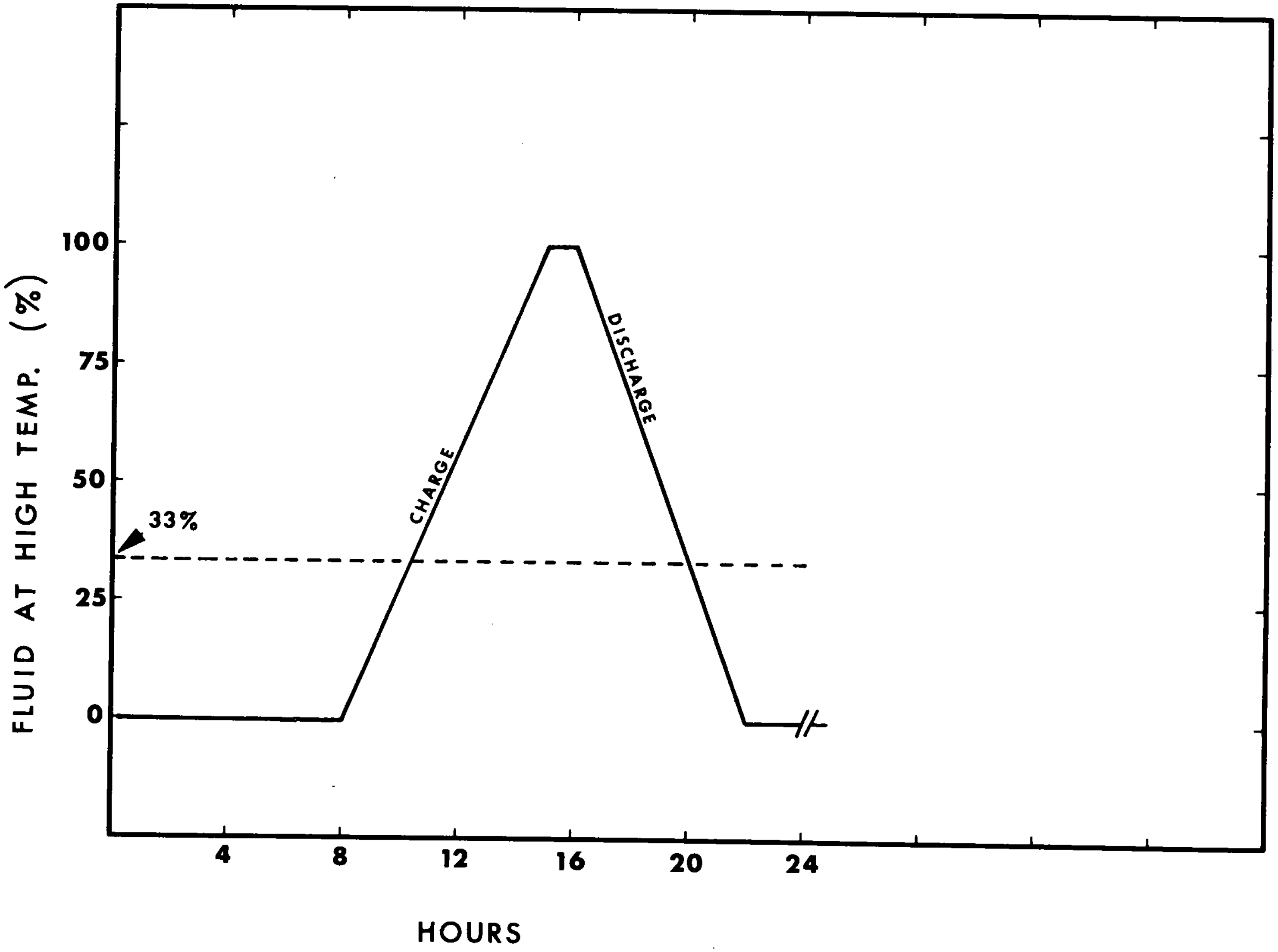

Figure 5. Typical Thermal Energy Storage System, Charge - Discharge Cycle

losses for an oil only vessel were first subtracted from the overall losses on a vessel containing rock and sand, those losses then multiplied by 3/2 and added to the losses for fluid only. This treatment assumes a linear relationship between surface area and fluid losses which was validated in one of the later series of tests.

Results and Discussion

Caloria HT43:

This fluid is a broad mixture of essentially aliphatic compounds with a mean molecular weight of 350 and a considerable amount of chain branching. For the most part it is simply a distillate cut from a petroleum crude oil with some minor refinements one of which is the addition of an anti-oxidant that is not included in some similar fluids mentioned later in the report. Testing of Caloria HT43 began with only 6 vessels in series A designed to evaluate fluid performance at 316°C and 302°C since these were temperatures under study for the Barstow Pilot Plant Thermal Storage System. At the very beginning, fluidized baths were used as the heat source which required the vessels to be suspended. The vessels were of different length which necessitated filling them with different quantities of oil to achieve a similar fluid height for accurate level measurements used in determining fluid losses. The fluid losses for these vessels were adjusted to reflect a loading that would be found in a typical thermal storage unit. For example the normal loading was considered to be a 30:15:8 ratio (by weight) of rock, sand and oil. If a vessel contained more oil than this ratio, the fluid losses were adjusted downward to enable comparison to the proper loading ratio and other test vessels. Figure 6 is a plot of fluid loss rate vs.

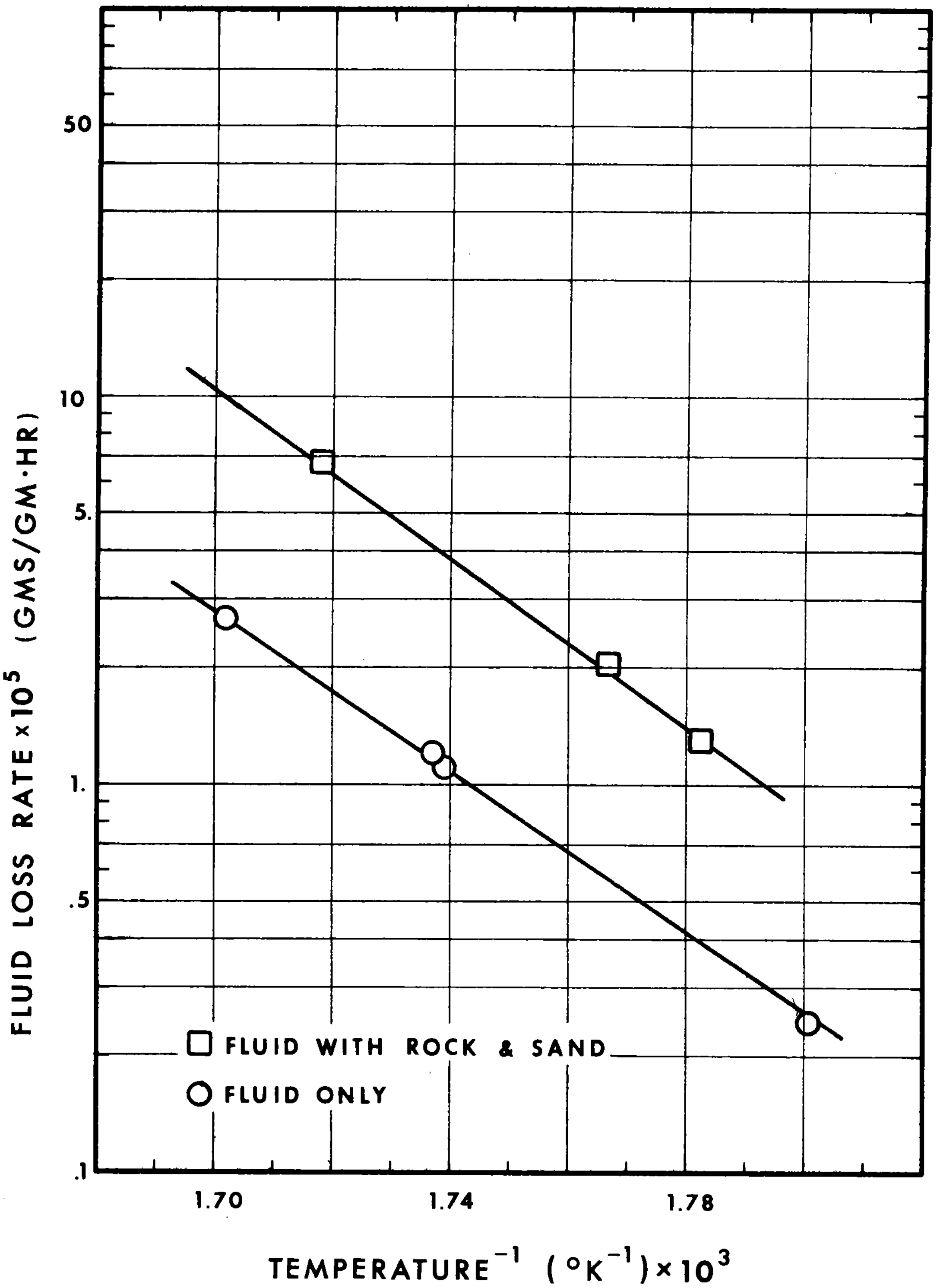

Figure 6. Hourly Fluid Loss Rates as a Function of Temperature for Caloria HT43

temperature for both oil only systems and oil plus rock and sand systems. (The data point for oil only at 1.80 x 10^{-3} °K^{-1} is actually from series B vessel #5). The fluid loss rate is expressed in terms of grams lost per gram of fluid per hr (gms/gm•hr or hr^{-1}) and the temperature is expressed as degrees $Kelvin^{-1}$. The rates shown on the plot apply only if the 30:15:8 ratio is used. These plots can be expressed by two Arrhenius type equations:

$$\ln r = \frac{-E_A}{R}\left(\frac{1}{T}\right) + C_o \qquad (1)$$

For oil only $$\ln r = -2.365 \times 10^4 \left(\frac{1}{T}\right) + 29.73 \qquad (2)$$

For oil + rock and sand $$\ln r = -2.55 \times 10^4 \left(\frac{1}{T}\right) + 34.2 \qquad (3)$$

where r is the fluid loss rate in units of $\frac{\text{grams}}{\text{gram} \cdot \text{hr}}$
and T is temperature in degrees Kelvin

In order to more easily equate fluid losses with temperature, Figure 7 shows the conversion of Figure 6 into yearly losses of a typical thermal storage unit with the abscissa representing the maximum operating temperature in degrees centigrade. These plots assume an equivalent year of 2500 hours and are only accurate over a limited temperature range.

Although the per cent fluid losses for a system with rock and sand are considerably higher than a system without rock and sand, it must be remembered that the inventory of fluid in the fluid only system can be as much as 3 1/2 times as large. Using Figure 7, one can compare fluid losses at 302°C (575°F) and find that a dual media system with a surface area of rock and

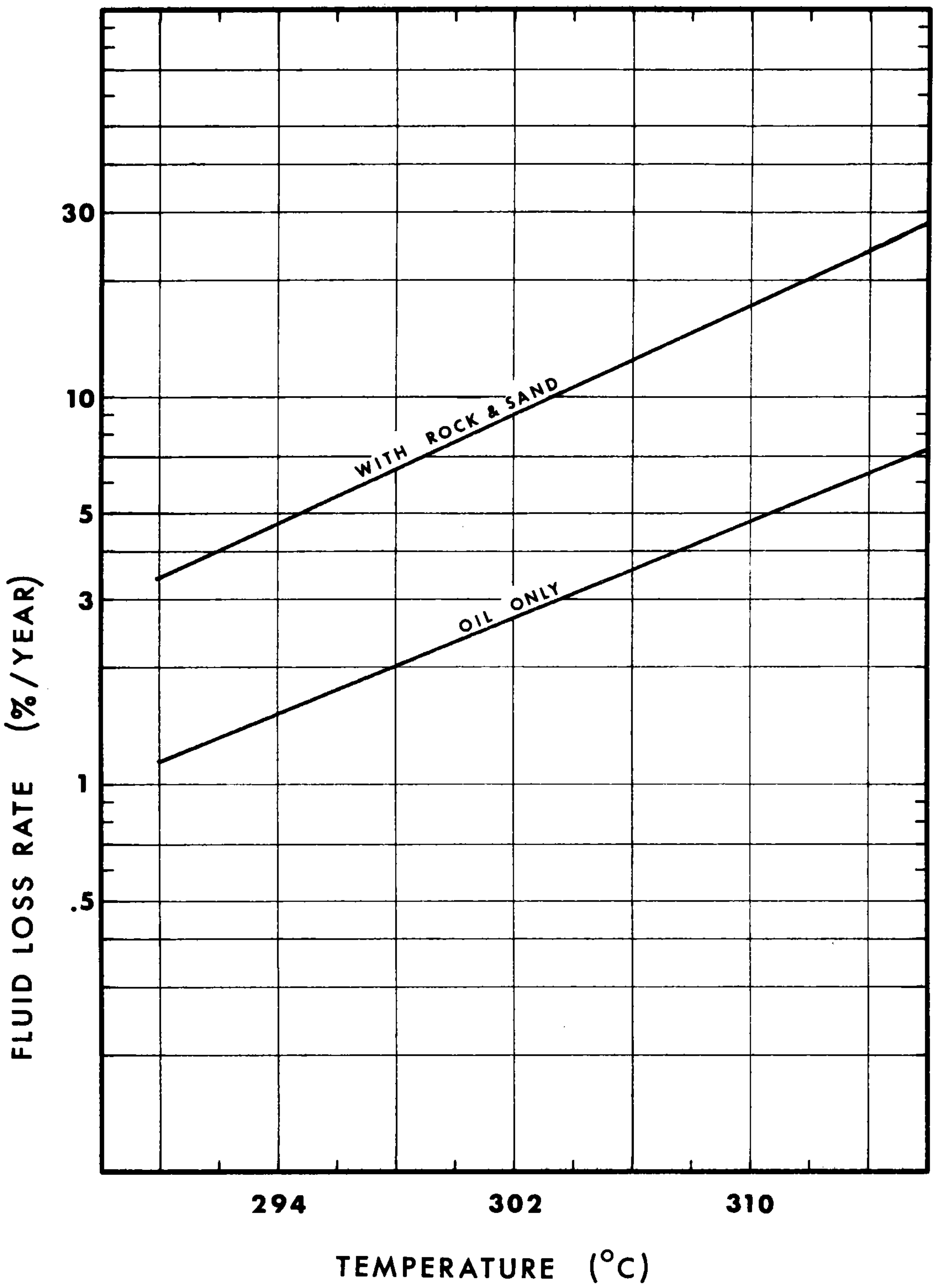

Figure 7. Yearly Fluid Loss Rates as a Function of Temperature for Caloria HT43 in a Typical Operating Thermal Energy Storage System

sand, to fluid volume ratio identical to that in these tests would have to have a void fraction something less than .29 in order to have a lower yearly replenishment rate, in terms of gallons per year, than an oil only system of the same thermal energy storage capacity. A more detailed discussion on the economic benefits/disadvantages of dual media systems will be published at a later date.

Since the precise surface area (of rock and sand) to fluid volume ratio was not duplicated in the tests, adjustments to the data had to be verified by additional tests. The tests consisted of two glass vessels (four were planned, two were broken) with 133 grams of rock and 67 grams of sand in one (B34), and 200 grams of rock and 100 grams of sand in the other (B36). Both vessels contained 70 grams of fluid and were heated to approximately 300°C. Weight losses were recorded approximately every 336 hours and the results are shown in Figure 8. The variations or perturbations in the curve are typical for fluids like Caloria HT43. This necessitated a lengthy test sequence to obtain accurate data for comparison. Normally the first 500 hours of test were excluded due to weight losses that could be caused by oxygen dissolved in the oil or oxygen and water physically adsorbed on the rocks. However, in these tests, thermocouple failure early in the test resulted in no temperature data until 1125 hours. From that time on, both vessels held a very constant time-temperature history, vessel B34 at 304.7°C (standard deviation of .84°C) and vessel B36 at 290.6°C (standard deviation of 1.02°C). Fluid loss rates at 302°C were calculated over the period from 1125 hours to 2735 hours using the sloped lines shown on Figure 8, and using the previously calculated equations for fluid loss as a function of temperature (Equations 2 and 3). Plotting the fluid losses as a function of surface area of rock and sand (proportional to grams of rock and sand), one would expect the curve to intercept the ordinate at a point equivalent to the oil only loss rate.

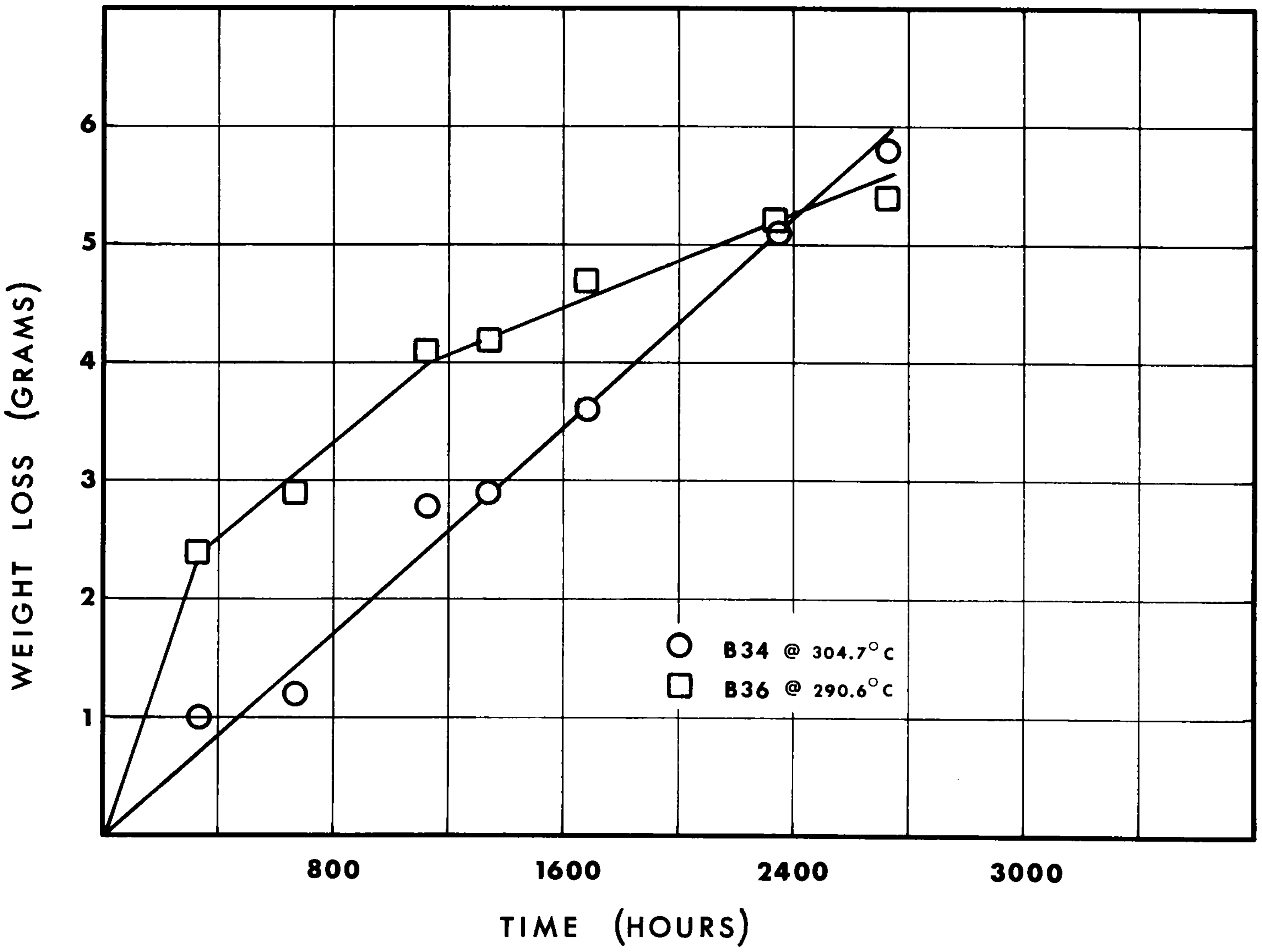

Figure 8. Fluid Weight Loss With Time for Vessels With Caloria HT43 and Different Quantities of Rock and Sand

Figure 9 is such a plot showing actual fluid only losses compared to those predicted by the curve. The error band is fairly large because of only two data points and because of large changes in fluid loss rates with apparently small changes in the slope of the fluid loss vs. time plots (Figure 8). Data agreement was sufficiently accurate to justify a linear relationship between fluid losses and rock and sand surface area, however, there remains an additional test to be conducted to determine if this is due to catalysis by materials contained in the rock or by impeding the flow of reactive radical species to the surface of the fluid. In either case these losses would definitely be present in a dual media thermal storage system employing Caloria HT43 and rock and sand.

A similar analysis was accomplished with 4 vessels of varying metal surface area to determine what effect if any, a large piping system would have on fluid losses. Figure 10 shows weight losses as a function of time for these four vessels. Vessel B29 contained no extra metal while vessels B30, B31, and B32 contained 110 cm^2, 220 cm^2, and 330 cm^2 extra, respectively. Unlike the tests involving rock and sand surface area, the time-temperature history of these vessels was fairly erratic. As a result the fluid loss curves could not be related to a specific temperature over the entire test. Rather, fluid loss rates were calculated by first selecting a constant portion of the time-temperature history and comparing that interval with the fluid loss curves. If both intervals were fairly constant or uniform, a fluid loss rate was calculated only for that portion of the curve and only at that specific temperature. Table II lists the intervals used in evaluating the fluid loss rates.

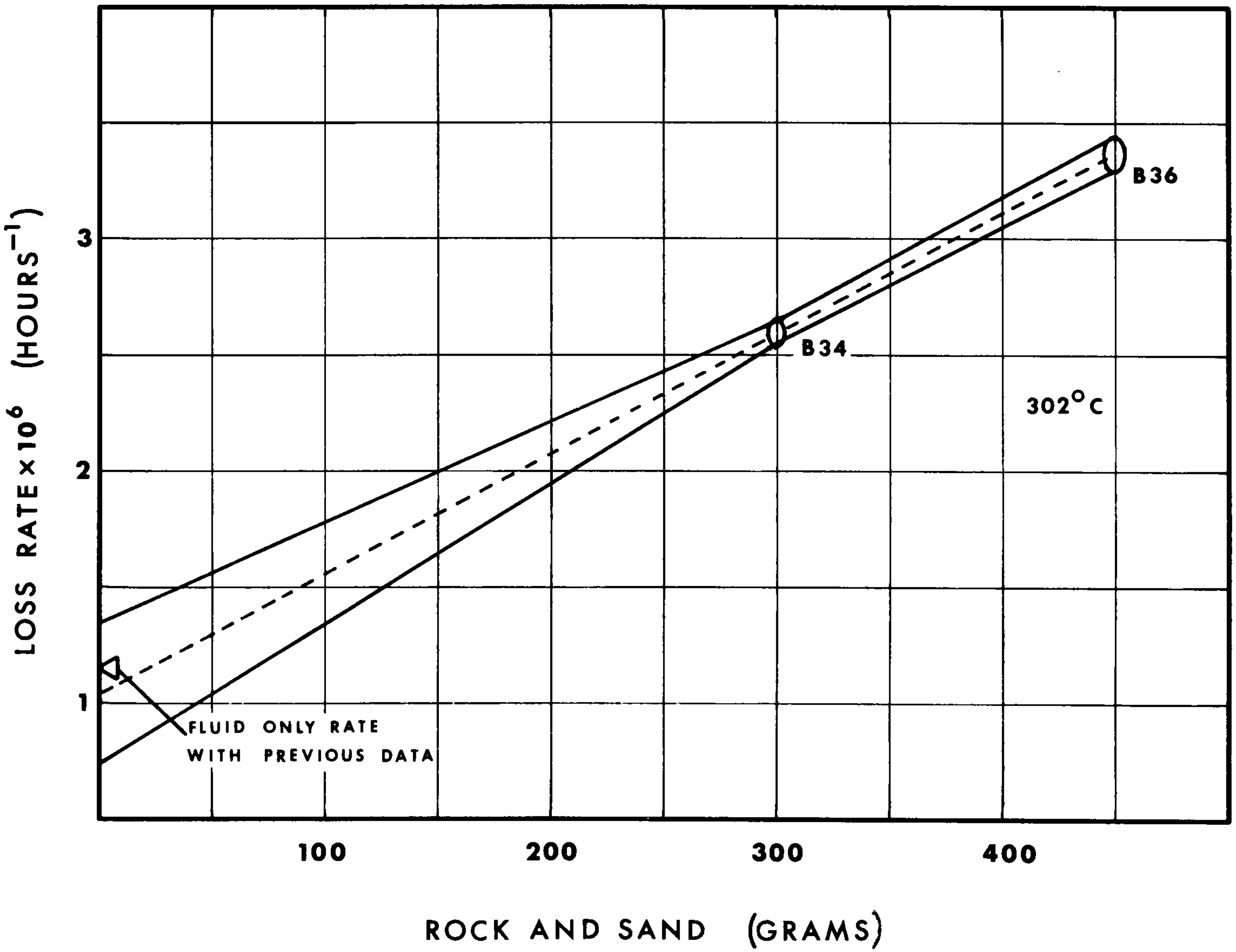

Figure 9. Fluid Loss Rate for Caloria HT43 as a Function of Rock and Sand Surface Area (Expressed in Grams)

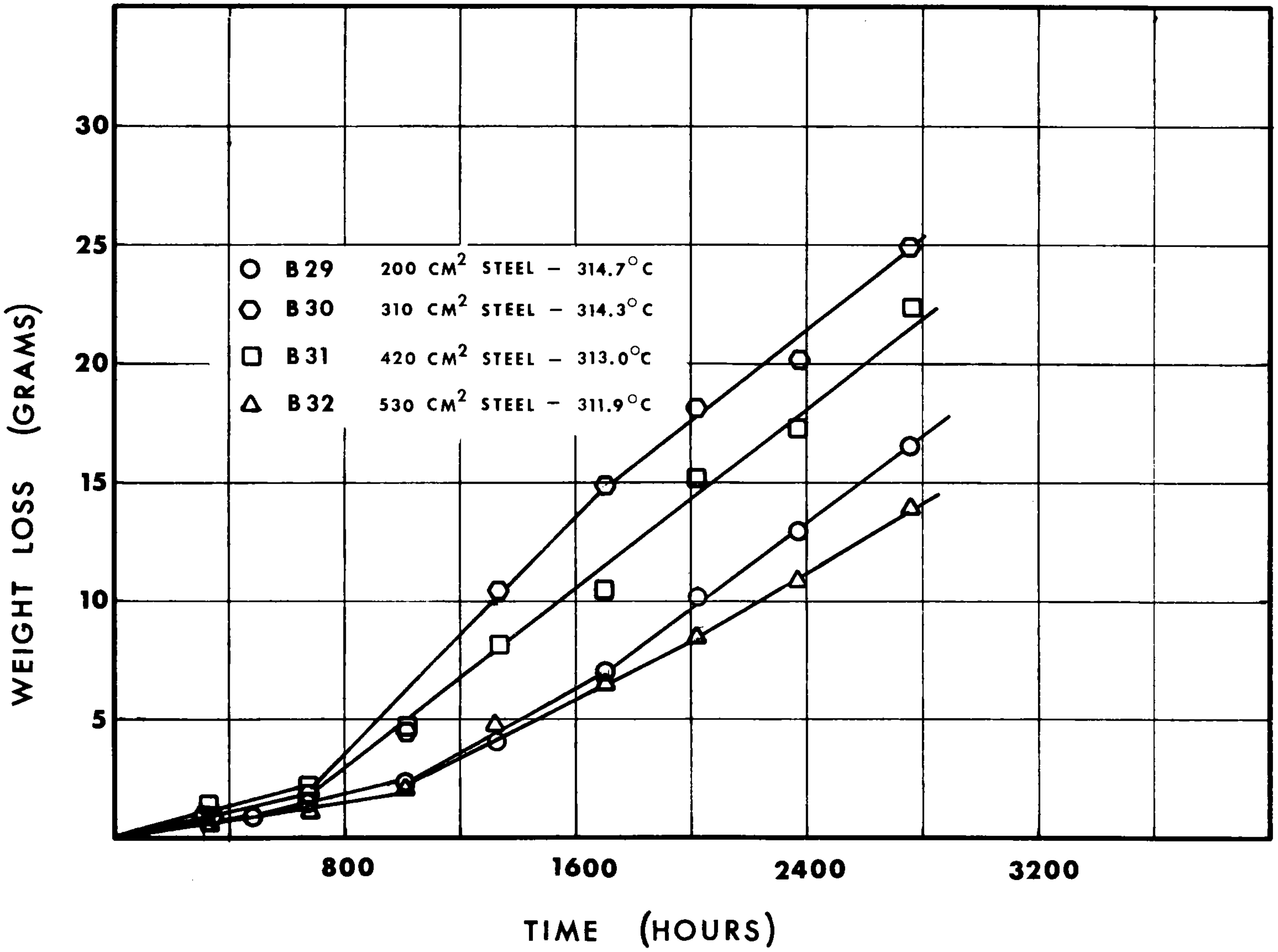

Figure 10. Fluid Weight Loss With Time for Vessels Containing Caloria HT43 and Different Quantities of Metal Surface Area

TABLE II

INTERVALS USED IN CALCULATING FLUID LOSS RATES FOR CALORIA HT43 IN CONTACT WITH METAL

Vessel #	Interval (hrs.)		Temperature (°C)	
	From	To	Average	Standard Deviation
B29	2033	2777	314.7	1.6
B30	1385	1721	314.3	1.8
B31	900	2400	313.0	1.3
B32	2009	2777	311.9	2.5

Attempts at determining the metal surface area contribution by adjustment of these data to a common temperature proved fruitless. No meaningful plots could be constructed. On the likelihood that the metal could have a much greater effect than previously thought, no temperature adjustment was made on the data. A plot of fluid losses versus metal surface area at several temperatures is shown in Figure 11. The lines drawn from the data points to the ordinate, intersect at the oil only fluid loss rate for that particular temperature. The slopes of these lines represent the fluid losses due to metallic surface area expressed as grams per square centimeter per hour ($\text{gms/cm}^2\cdot\text{hr}$). If there is a linear relationship between fluid loss rate and metal surface area, an Arrhenius plot of the slopes from Figure 11 should yield a straight line such as that shown in Figure 12. The implication of this is a very strong relationship between metal surface area effects and temperature. Reducing this to an equation gives:

$$\ln r = -1.7177 \times 10^5 \left(\frac{1}{T}\right) + 281.85 \qquad (4)$$

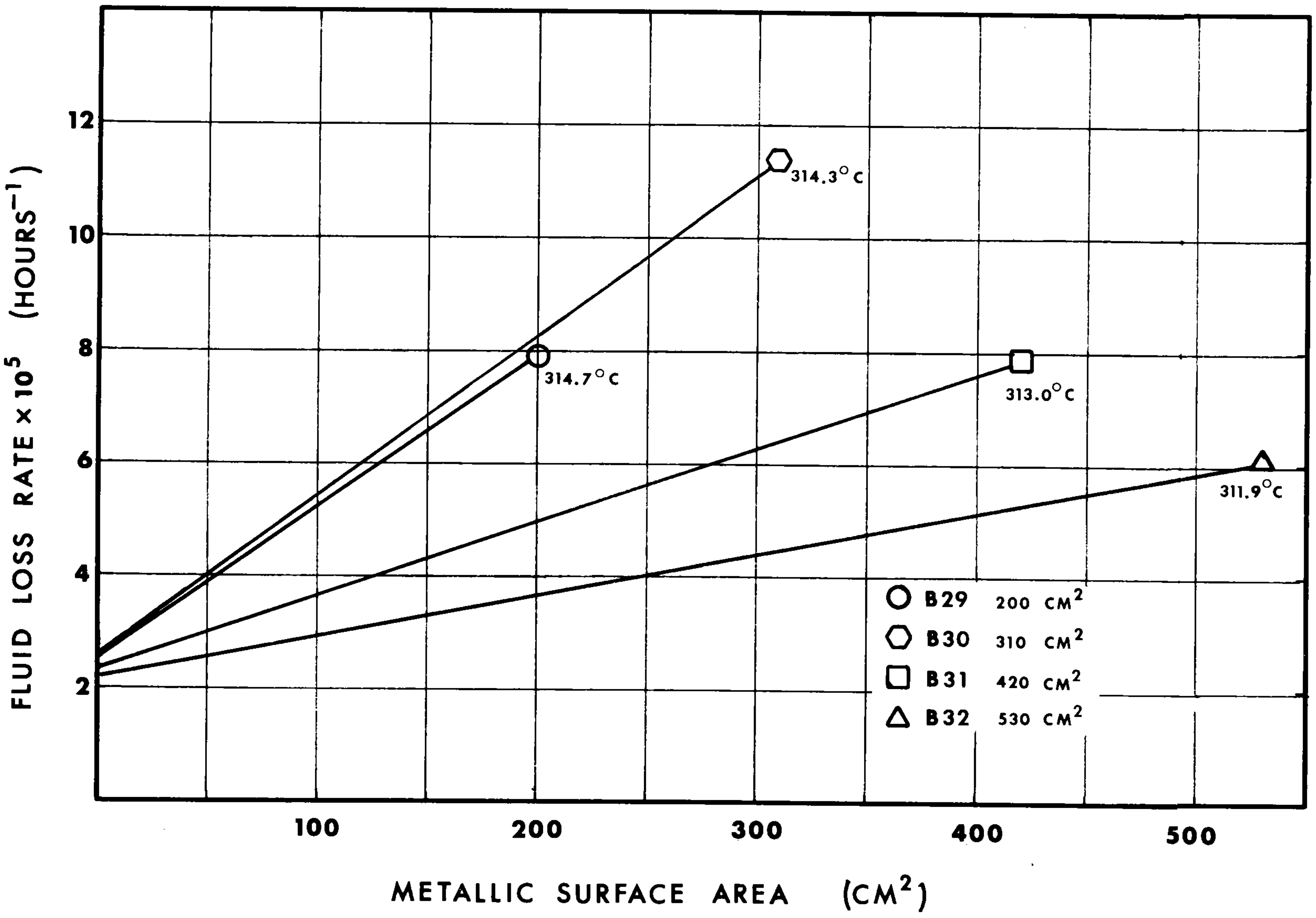

Figure 11. Fluid Loss Rates for Caloria HT43 as a Function of Metal Surface Area

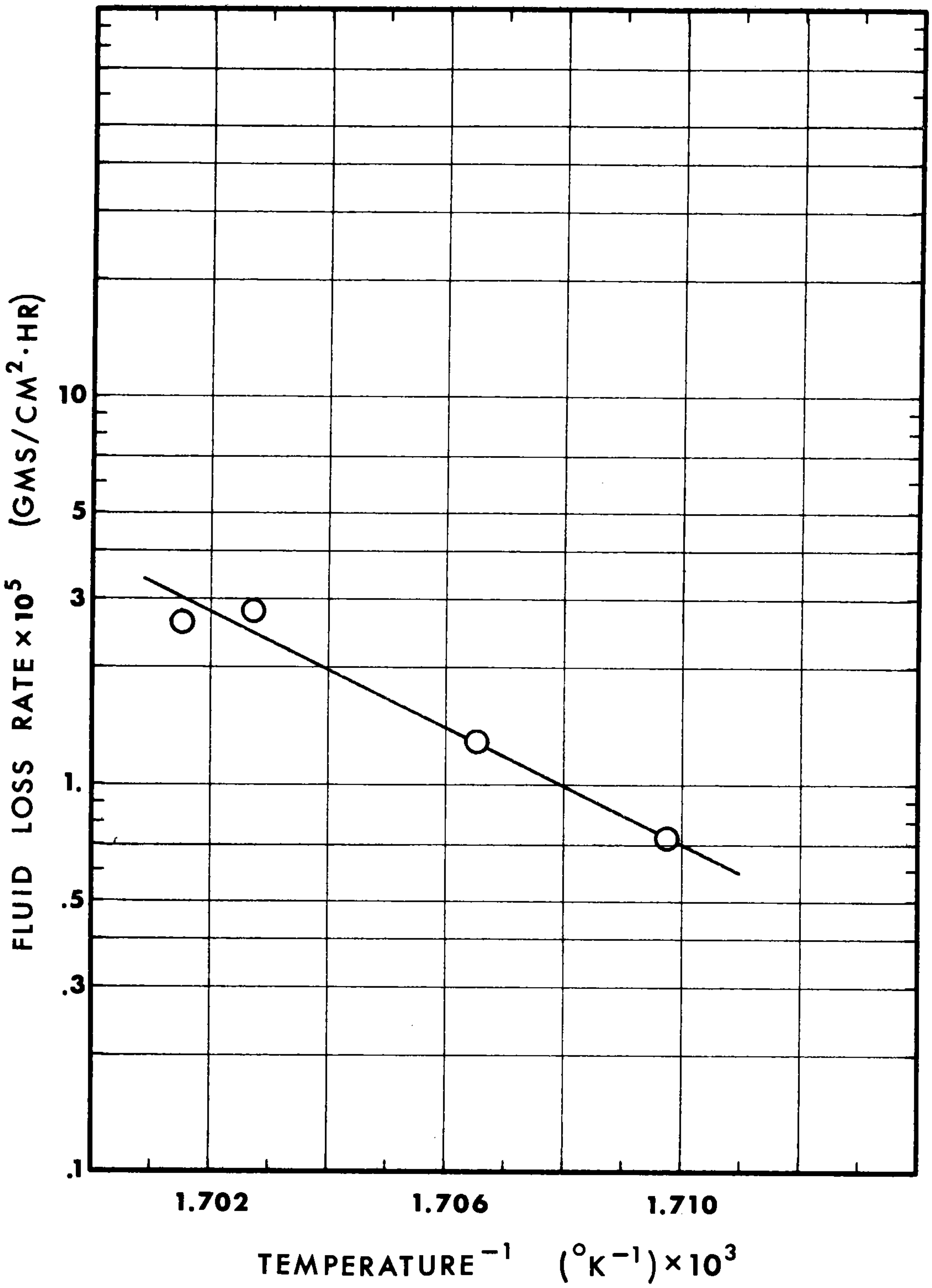

Figure 12. Fluid Loss Rates Due to Metal Surface Area for Caloria HT43 as a Function of Temperature

where r is the fluid loss rate in terms of grams/cm^2•hr

and T is the temperature in degrees Kelvin

At 302°C the loss of fluid in an operating thermal storage system due to metal surface area effects would be approximately 1.2 grams/m^2•yr. However at 316°C these same losses would be greater than 1400 grams/m^2•yr.

Sun 21 fluid:

This product is essentially the same in composition and manufacture as Caloria HT43 except that there is no anti-oxidant added to the base oil. These particular tests were run in support of a solar total energy project at Fort Hood, Texas, however, the data generated is applicable to central receiver thermal storage systems. That system design did not include dual media storage and the maximum bulk temperature of the fluid was designed to be 288°C. Only tests of straight fluid and fluid in contact with an appropriate surface area of metal were begun at 260°C, 288°C and 316°C. In all, nine vessels containing Sun 21 were started and for direct comparison purposes three vessels with Caloria HT43 were also included in this series.

After 3012 hours of testing, no measurable weight loss could be detected in any of the vessels operating at 260°C (B1 through B4) and hence those vessel tests were terminated early. At 288°C, the fluid losses were extremely low except for vessel B6 which demonstrated the catastrophic effect that small quantities of water or oxygen can have on fluid losses (see Figure 13).

The other vessels exhibited such low losses that it was difficult to obtain smooth fluid loss curves, but the error of the reading was ± .1 gram which makes this difficulty understandable. Using only those portions of the fluid loss curves that had relatively uniform losses and temperature

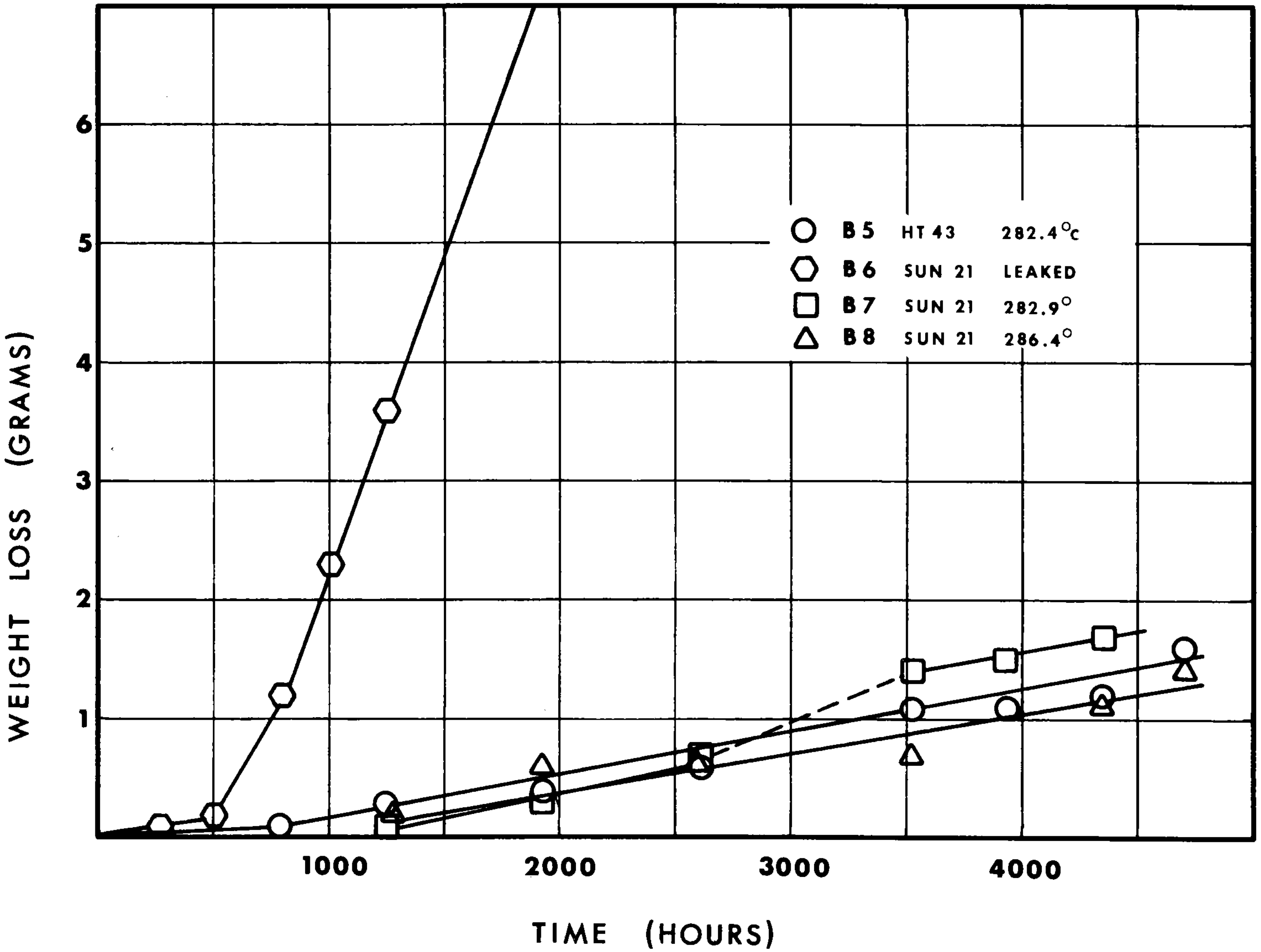

Figure 13. Fluid Weight Loss With Time for Vessels With SUN 21 or Caloria HT43 at 288°C (Approximately)

history, fluid loss rates were calculated (see Table III). These losses agree fairly well with previously calculated losses for Caloria HT43 (see Figure 14).

TABLE III

INTERVALS USED IN CALCULATING FLUID LOSS RATES FOR SUN 21 OIL AND CALORIA HT43

Vessel #	Interval (hrs.) From	Interval (hrs.) To	Temperature (°C) Average	Temperature (°C) Standard Deviation
B5	1263	4671	282.4	1.6
B7	3519	4287	282.9	.84
B8	1400	4600	286.4	1.3
B9	800	3000	311.4	1.5
B10	1900	3000	311.4	2.1
B11	500	1200	307.1	1.6
B12	1900	3000	312.7	.66

The weight loss vs. time plots (Fig. 15) for vessels B9 through B12 were fairly uniform, however, fluid loss rate calculations resulted in unexplainably high rates as compared to Caloria HT43 at those temperatures. One difference in these tests was the presence of metal fill tubes and thermocouple wells in contact with the fluid in all vessels and some amount of additional metal in three of the four vessels. At 260°C and 288°C this additional metal would have very little effect but at the higher temperatures, the presence of the metal could raise fluid losses quite dramatically. Using the previously calculated equations for determining fluid losses due to metal surface areas, one can adjust the experimental values downward somewhat but not enough to coincide with fluid only losses for Caloria HT43 determined earlier. Perhaps

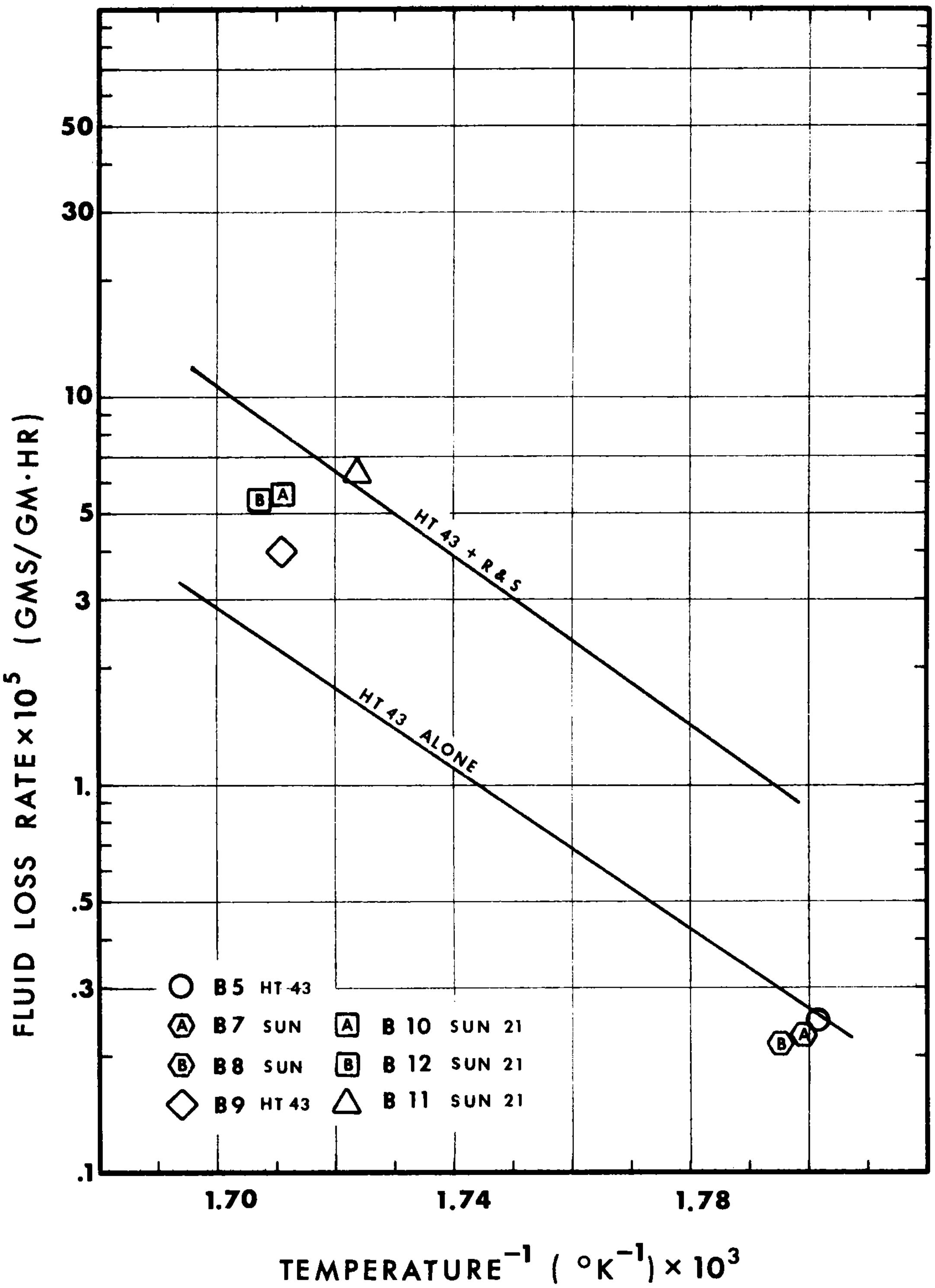

Figure 14. Comparison of Fluid Loss Rates as a Function of Temperature for Caloria HT43 and SUN 21

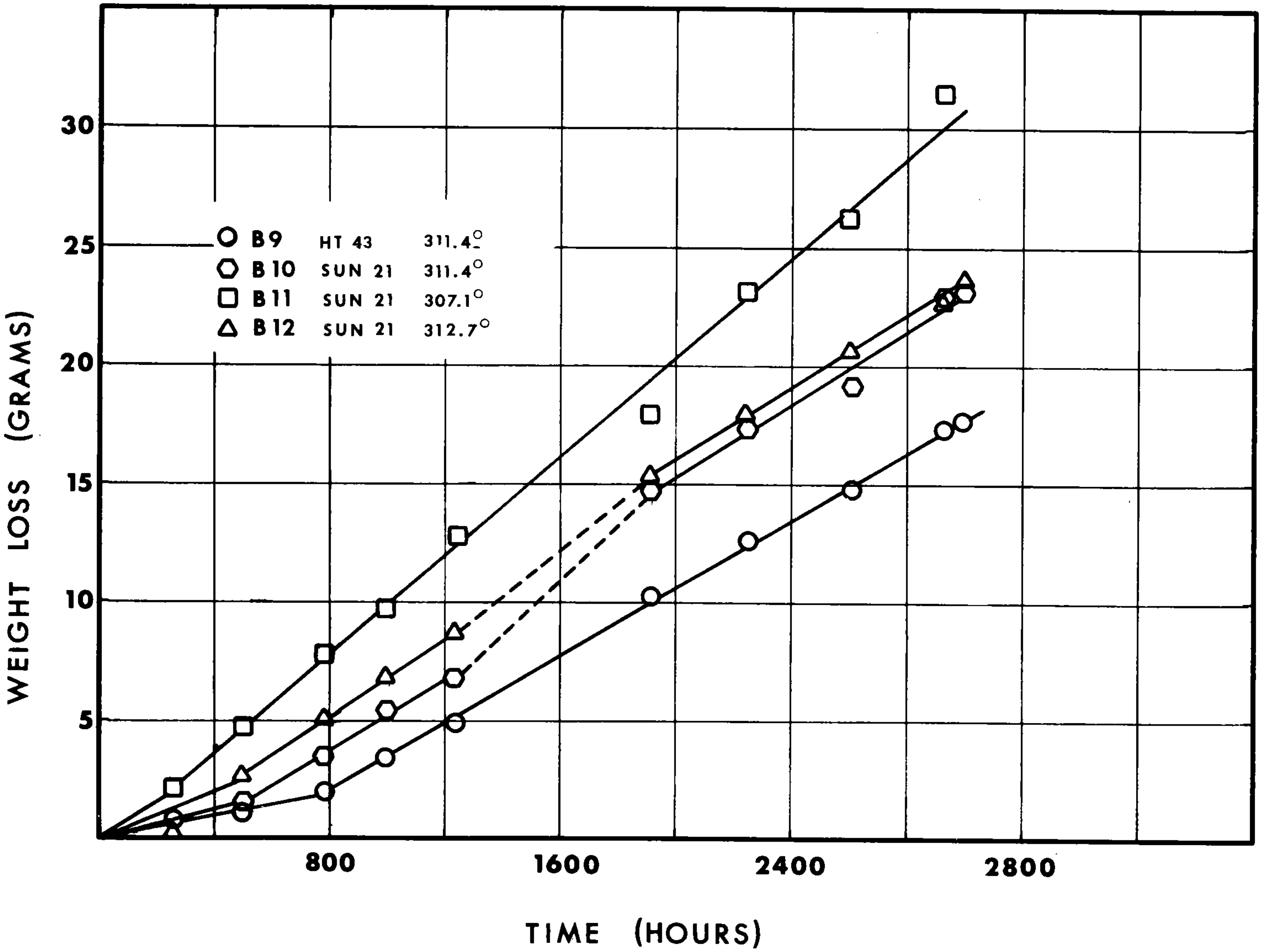

Figure 15. Fluid Weight Loss With Time for Vessels With SUN 21 or Caloria HT43 at 316°C (Approximately)

the position of the metal in the vessel caused it to obtain higher temperatures than the surrounding fluid. If so the magnitude of its effect could be much greater thereby providing better agreement with the oil only loss rates reported earlier. The other explanations would be that vessel B9 (with Caloria HT43) was not representative (leaking, etc.) and vessels B10, B11, and B12 had high losses because of a lack of anti-oxidant as contained in Caloria HT43 or that the surface area of metal effect is more sensitive than originally predicted. All Sun 21 testing is summarized on Figure 14 in comparison to Caloria HT43.

Therminol 66:

Therminol 66 is a hydrocarbon fluid composed chiefly of terphenyls and thereby capable of operating at temperatures as high as 340°C. However, it is approximately seven times as expensive as Caloria HT43 or Sun 21 on a volumetric heat content basis and would have to show markedly lower fluid losses to be economically competitive with Caloria HT43 or Sun 21.

The tests were very similar to those for Caloria HT43, including tests with pure fluid and fluid with rock and sand. Because Therminol 66 is a synthetic product and much more homogeneous in composition, the fluid loss rates were much more uniform. Figure 16 is a plot of fluid losses as a function of time, for only two temperatures. The initial fluid losses were due to oxygen and water, dissolved in the fluid and physically adsorbed on the surface of the rocks. This loss can be reduced drastically by slowly heating the bed while bubbling dry nitrogen through it. The sensitivity of this fluid to oxidation was demonstrated by the fluid losses for vessel B25 which had a pinhole leak in the thermocouple well. The leak tended to plug as the fluid formed a residue around the hole, and as a result a plot of

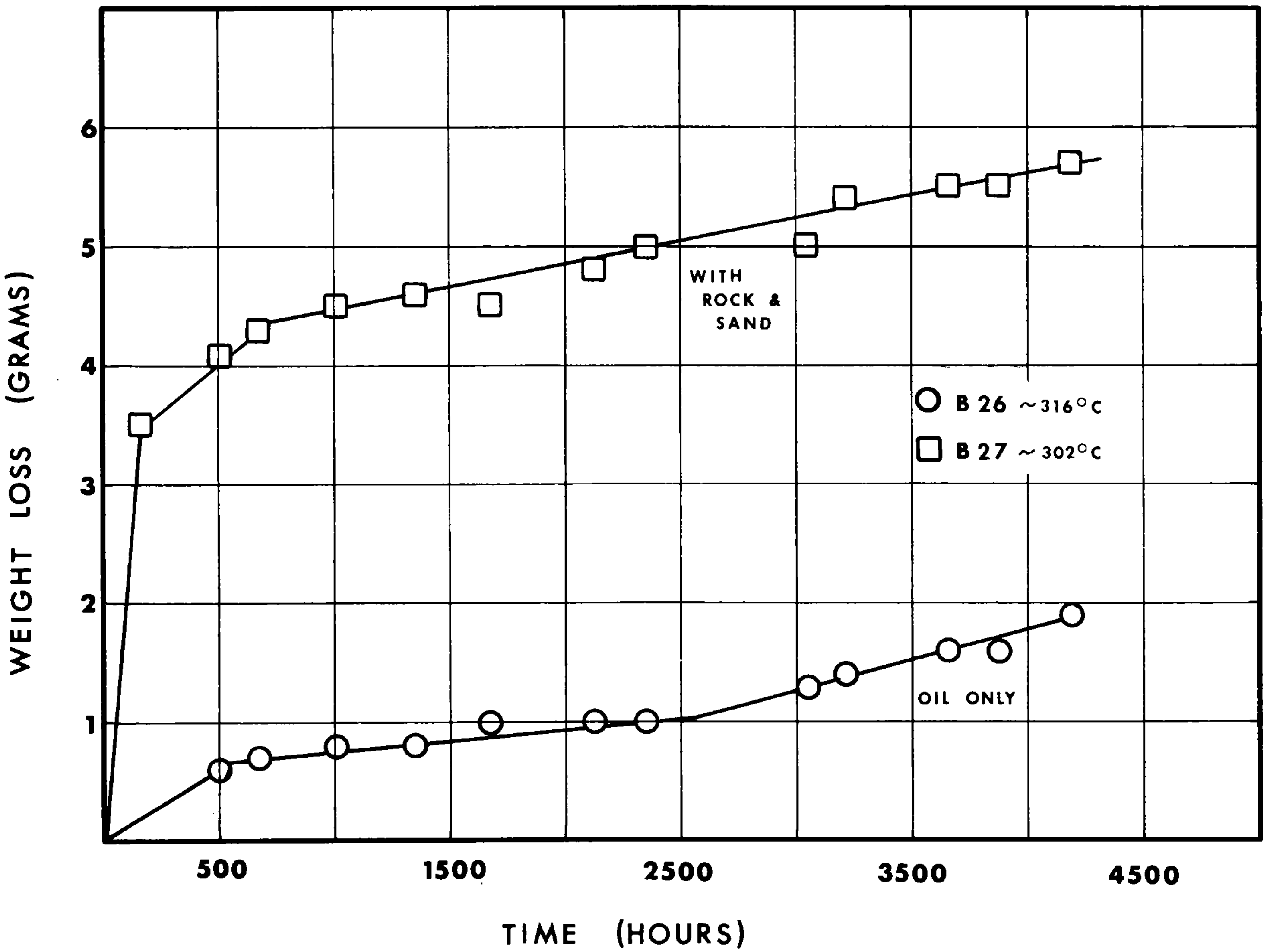

Figure 16. Fluid Weight Loss With Time for Vessels with Therminol 66

fluid loss with time shows several plateaus where the pure fluid behavior is normal and very stable. Unfortunately one of the vessels filled with rock and sand also developed a bad leak and suffered catastrophic losses so that data is available for only one vessel with rock and sand. Table IV shows the intervals used and calculated temperatures for all Therminol 66 vessels completing the test.

TABLE IV

INTERVALS USED IN CALCULATING FLUID LOSS RATES FOR THERMINOL 66

Vessel #	Interval (hrs.) From	To	Temperature (°C) Average	Standard Deviation
B26	200	2535	314.1	.75
B26	2535	3831	315.1	1.45
B27	1719	2367	297.0	2.24
B27	2607	4191	300.6	1.03

Because the fluid loss rate was so low even at 315°C, there can be a fairly large error in calculating the loss rate since the error in the weight measurements was ± .1 gram and at the end of the test, vessel B26 had not even lost 2.0 grams. However, the calculated loss rates for pure Therminol 66 are 3.06×10^{-6} grams/gram•hr at 315.1°C and 1.27×10^{-6} grams/gram•hr at 314.1°C. Averaging these two values using a semi-log plot gives 1.95×10^{-6} grams/gram•hr at 314.6°C. The Therminol 66 vessels were of an all metal construction, unlike the vessels with Caloria HT43 or Sun 21 and therefore may demonstrate Therminol 66's indifference to stainless steel at 316°C.

The calculated loss rates for Therminol 66 in contact with rock and sand were 7.95 x 10^{-6} hr^{-1} at 297.0°C and 9.14 x 10^{-6} hr^{-1} at 300.6°C. Again, averaging gives a value of about 8.55 x 10^{-6} hr^{-1} at 298.8°C. Since no runs were made at other temperatures little can be said about fluid losses as a function of temperature, but one would expect a similarly sloped curve to that of Caloria HT43. Comparing these reults with Caloria HT43 on Figure 17 one can see that Therminol 66 appears to be more adversely affected by the presence of rock and sand than Caloria HT43 but also that fluid losses for an all Therminol system could be as low as 1/20 the fluid loss rate for an all Caloria system.

Overall the choice of a working fluid is determined by economics and although pricing information is subject to fluctuation, the results from these tests would indicate that the use of a more expensive, higher temperature fluid actually lowers yearly fluid replenishment costs somewhat. There may be some advantage to be gained in less frequent replenishment but there are disadvantages to consider in higher initial costs to fill the system.

Variations in Fluid Property

Two of the three fluids under test (Caloria HT43 and Sun 21) are distillate cuts from petroleum crude oils and represent a broad spectrum of compounds. As sources of crude oil are not always the same and as the distillation process is not a true equilibrium process, the fluid can be expected to change somewhat from batch-to-batch. Many physical properties or characterizations were considered but eventually a comparison was made with simulated distillation curves of 4 different batch lots of Caloria HT43. Three of the six samples tested were from one lot but separate drums. The results of this procedure (ASTM D-2887-73) are indicated in Figure 18. The shaded area is

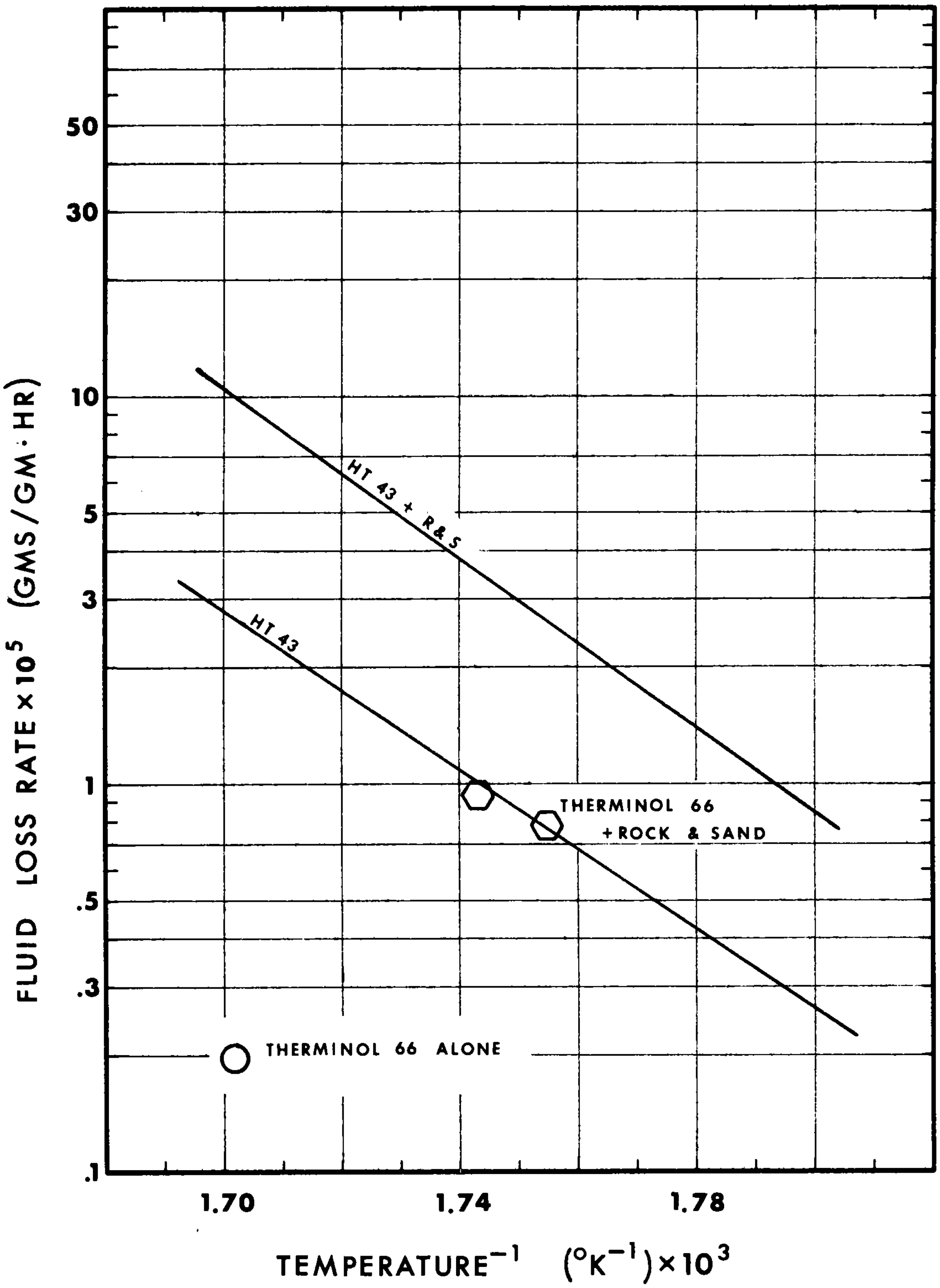

Figure 17. Comparison of Fluid Loss Rates as a Function of Temperature for Caloria HT43 and Therminol 66

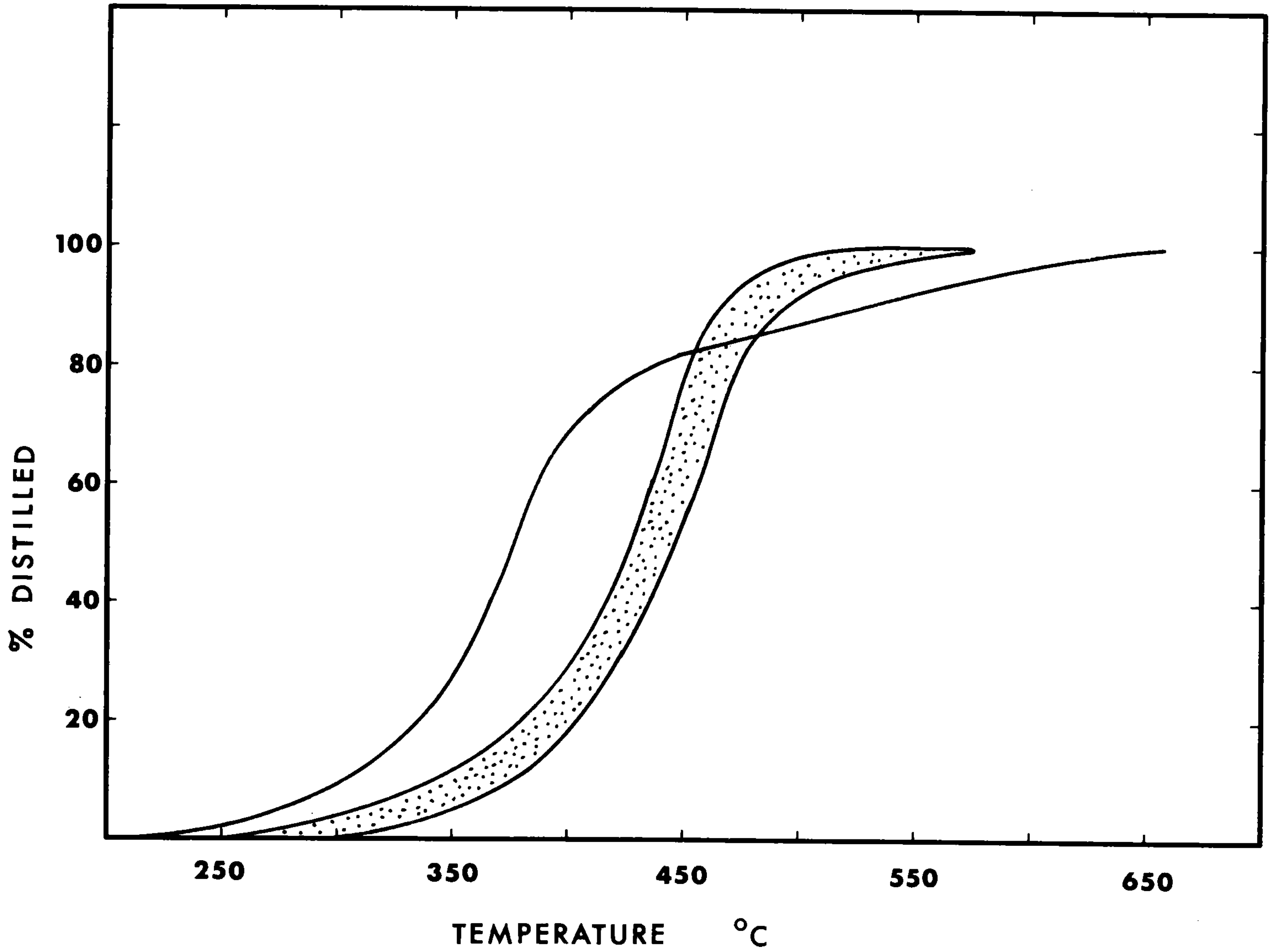

Figure 18. Variations in GC Distillation Curves for Several Lots of Caloria HT43

the maximum spread in the data except for the one curve that is markedly different from all the rest. This is believed to be atypical of batch-to-batch variations but it may be an indication of the possible magnitude of a one time variation in a particular batch of fluid. What effects these variations will have on fluid replenishment rates can not even be speculated at this point, but the information is included here as an aid to designers of thermal storage systems. There is work presently underway at Martin Marietta Corporation, Denver, that may provide a definitive relationship between distillation curves and fluid replenishment rates.

Future Work

Other fluids:

Therminol 66 is part of a family of fluids generically different from Caloria HT43 or Sun 21. Therminol 55 is a less expensive fluid similar to Therminol 66 that has potentially better stability than either Caloria HT43 or Sun 21 and which may prove more economical. Tests are planned for this fluid in contact with rock and sand at 302°C.

A relatively new fluid which is essentially a saturated poly-alphaolefin will be tested both as a straight fluid and in conjunction with rock and sand at 302°C. It is marketed by Ethyl Corporation and designated as ESH-6. Its projected cost is about 3 to 4 times that of Caloria but its synthetic manufacture may provide a stabilizing effect on fluid degradation to offset the price difference.

Fluid Additives:

Because of high fluid losses during the first few hundred hours of operation, the addition of a relatively large quantity of anti-oxidants may reduce initial fluid losses and hence initial costs. The tests are best accomplished with vessels containing rock and sand as they have the highest initial losses. Hopefully tests will be accomplished on both Therminol 66 and Sun 21.

Conclusions:

- Test data show no apparent advantages of a dual media storage system using Caloria HT43 and a mixture of rock and sand over a Caloria only system when just considering yearly fluid replenishment rates (equations 2 and 3).
- Operation of dual media (with rock and sand) storage system at 316°C using Caloria HT43, would cause fluid losses in excess of 25% per year.
- Sun 21 appears to be somewhat less stable than Caloria HT43, which may be due to the lack of an anti-oxidant in the fluid.
- At temperatures greater than 302°C, any common ferrous metal in contact with either Sun 21 or Caloria HT43 may contribute significantly to the overall fluid loss rate (equation 4).
- There is a linear relationship between fluid loss rate and rock and sand surface area for Caloria HT43. Whether or not this is due to surface catalysis or impeding the flow of catalytic products to the top of the tank is unanswerable at this time.
- Therminol 66 appears to be much less susceptible at 316°C to fluid losses due to metal surface area than Caloria HT43. However, it is apparently much more susceptible than Caloria to rock and sand surface area effects.

- The presence of water and/or oxygen physically adsorbed on the surface of rock and sand particles will result in significant one time fluid losses in any system using them with Caloria HT43, Sun 21 or Therminol 66.

Recommendations:

Because of numerous problems encountered in testing the fluids, the following recommendations are made regarding test vessel design and test procedures.

- Where possible all glass vessels should be used to determine fluid degradation due to thermal effects only.
- The heating bath should surround as much of the vessel as possible to preclude temperature gradients in the vessel.
- Thermocouples should be inserted in all test vessels regardless of construction to insure accurate temperature measurements.
- Vessels should be purged with dry, oxygen free, nitrogen while the vessels contents are above 150°C. Flow should be sufficient to remove water vapor condensing as a cloud in the ullage space of the vessel.
- All data should be presented in two formats-grams of fluid lost/gram fluid•hr and percent/year based on an equivalent year of 2500 hours or some other time if so stated.

References

1. Central Receiver Solar Thermal Power System Preliminary Design Report, Vol IV, McDonnell Douglas Astronautics Co., May 1977.

TYPICAL PHYSICAL DATA AND INFORMATION AVAILABLE ON THE THREE FLUIDS TESTED

Caloria HT43

Manufacturer: Exxon Corp.

Description: Paraffinic base stock with a high temperature oxidation inhibitor

Properties*:	Density at 15°C, gms/cc	0.8587
	Color, ASTM	L1.0
	Viscosity, cSt at 40°C	29.6
	cSt at 100°C	5.4
	SSU at 100°F	153

Viscosity index	115
Flash point, COC, °C	204
Pour point, °C	-9
Phenol, mass %	0.002
Saturates, mass % (ASTM D 2007)	91.0
Specific Heat @ 550°F, BTU/lb °F	.65
Thermal Conductivity @ 550°F, BTU/lb ft °F	.0492

*From manufacturer's literature dated 3-1-77

Sun 21

Manufacturer: Sun Oil Co.

Description: Paraffinic base stock without an oxidation inhibitor

Properties** :

Density at 15°C, gms/cc	0.88
Viscosity SSU at 100°F	200
Flash point, °C	226
Fire point, °C	254
Pour point, °C	-18
Specific heat @ 550°F, BTU/lb °F	.732
Thermal conductivity @ 550°F, BTU/lb ft °F	.0652

**From manufacturer supplied data

Therminol 66

Manufacturer: Monsanto Industrial Chemicals Co.

Description: Modified Terphenyl

Properties***:	Density at 15.5°C, gms/cc	1.004
	Viscosity @ 100°F, cSt	30
	Flash point, °C	178
	Fire point, °C	194
	Pour point, °C	-28
	Specific heat @ 550°F, BTU/lb °F	.605
	Thermal conductivity @ 550°F, BTU/lb ft °F	.0562

***From manufacturer's literature dated 10/76

FACTORS USED IN CONVERTING TEST HOURS TO EQUIVALENT OPERATING TIME

$$\text{EQUIVALENT OPERATING TIME} = \frac{\text{TEST LENGTH}}{\text{CONVERSION FACTOR}}$$

HOLD TIME (HRS)	DISCHARGE TIME (HRS)	CHARGE TIME (HRS)						
		2	3	4	5	6	7	8
	1	.0625	.0834	.1042	.1250	.1459	.1667	.1875
	2	.0834	.1042	.1250	.1459	.1667	.1875	.2084
	3	.1042	.1250	.1459	.1667	.1875	.2084	.2292
	4	.1250	.1459	.1667	.1875	.2084	.2292	.2500
0	5	.1459	.1667	.1875	.2084	.2292	.2500	.2708
	6	.1667	.1875	.2084	.2292	.2500	.2708	.2917
	7	.1875	.2084	.2292	.2500	.2708	.2917	.3125
	8	.2084	.2292	.2500	.2708	.2917	.3125	.3333
	1	.1042	.1250	.1459	.1667	.1875	.2084	.2292
	2	.1250	.1459	.1667	.1875	.2084	.2292	.2500
	3	.1459	.1667	.1875	.2084	.2292	.2500	.2708
	4	.1667	.1875	.2084	.2292	.2500	.2708	.2917
1	5	.1875	.2084	.2292	.2500	.2708	.2917	.3125
	6	.2084	.2292	.2500	.2708	.2917	.3125	.3333
	7	.2292	.2500	.2708	.2917	.3125	.3333	.3542
	8	.2500	.2708	.2917	.3125	.3333	.3542	.3750
	1	.1459	.1667	.1875	.2084	.2292	.2500	.2709
	2	.1667	.1875	.2084	.2292	.2500	.2709	.2917
	3	.1875	.2084	.2292	.2500	.2709	.2917	.3125

FACTORS USED IN CONVERTING TEST HOURS TO EQUIVALENT OPERATING TIME (cont'd)

HOLD TIME (HRS)	DISCHARGE TIME (HRS)	CHARGE TIME (HRS)						
		2	3	4	5	6	7	8
2	4	.2084	.2292	.2500	.2709	.2917	.3125	.3333
	5	.2292	.2500	.2709	.2917	.3125	.3333	.3542
	6	.2500	.2709	.2917	.3125	.3333	.3542	.3750
	7	.2709	.2917	.3125	.3333	.3542	.3750	.3958
	8	.2917	.3125	.3333	.3542	.3750	.3958	.4167
3	1	.1875	.2084	.2292	.2500	.2709	.2917	.3125
	2	.2084	.2292	.2500	.2709	.2917	.3125	.3333
	3	.2292	.2500	.2709	.2917	.3125	.3333	.3542
	4	.2500	.2709	.2917	.3125	.3333	.3542	.3750
	5	.2709	.2917	.3125	.3333	.3542	.3750	.3958
	6	.2917	.3125	.3333	.3542	.3750	.3958	.4167
	7	.3125	.3333	.3542	.3750	.3958	.4167	.4375
	8	.3333	.3542	.3750	.3958	.4167	.4375	.4583

Equation used to Calculate Conversion Factors

$$\text{Conversion Factor} = \frac{C + H + D}{24}$$

where C = 1/2 Charge Time (HR)

H = Hold Time

D = 1/2 Discharge Time (GR)

Assuming Constant Charge and Discharge Rates

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