

APPENDIX B

ACUREX FINAL REPORT FR-81-87/EE

CATALYTIC COMBUSTION OF HYDROGEN IN THE PRESENCE OF METHYL IODIDE

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SECTION 1

INTRODUCTION

The accident at TMI-2 demonstrated that hydrogen generation rates greater than originally considered in nuclear power station designs can occur. As a result, concerns over the impact of increased hydrogen generation rates on nuclear station safety have been raised. To address the issue of increased hydrogen generation, Acurex conceptualized a hydrogen mitigation system utilizing a monolithic substrate catalyst to burn lean hydrogen mixtures in a controlled manner. Since monolithic catalysts have not been evaluated as hydrogen combustors, American Electric Power, Duke Power, and TVA jointly funded a program to evaluate the operating characteristics of a catalytic combustor using various hydrogen mixtures. This report presents the results of this program.

Monolithic substrate catalysts, as opposed to packed bed catalysts, can operate at very high mass throughputs and combustion efficiencies with low pressure drop. This high throughput capability, coupled with very broad flammability limits, makes monolithic catalysts attractive candidates for H_2 combustors. Noble metal catalytic combustors can operate at temperatures up to 2300°F without loss of structural integrity or catalyst activity.

Although catalytic H_2 combustion and poison deactivation have been studied by Southern Nuclear Engineering (References 1, 2) for pellet bed configurations, monolithic reactors have not been evaluated as H_2 combustors for the gaseous input conditions of low temperature (ambient to 200°F), high water concentrations, and the possible presence of CH_3I poison. This study presents the performance characteristics of monolithic catalytic combustors using catalysts provided by UOP, Inc. and Acurex Corporation. Catalyst operation was investigated during two test series:

- Catalyst performance
- Catalyst deactivation by CH_3I

Catalyst performance tests investigated minimum lightoff temperature, mass throughput capability, and combustion efficiency over a broad range of H_2 compositions and at high water concentrations. Catalyst deactivation by gaseous CH_3I was investigated to determine catalyst life over a broad range of CH_3I concentrations and H_2 compositions. Procedures required to regenerate deactivated catalytic reactors were also evaluated.

SECTION 2

TEST FACILITY

An experimental test facility was designed and fabricated to evaluate hydrogen combustion using monolithic catalysts. In an effort to simulate gas mixtures that could be present during a LOCA, the catalytic combustion chamber was fabricated to homogeneously mix air, H_2 , steam, and gaseous poisons. The system was capable of flowrates from 12 to 40 scfm and gas preheat temperatures from ambient to 1000°F. The high flowrate capacity of the catalytic combustor was designed on the basis of a rapid post-LOCA clean-up. Figure 1 presents a schematic of the test facility including fuel injector, combustion chamber, steam generator, control console, and emissions monitoring instruments. Each of these components is described below.

Fuel Injector/Mixing Nozzle

A gas mixing nozzle was designed to homogeneously mix a multiple component gas stream consisting of air, steam, H_2 , and N_2/CH_3I . The five-way nozzle, pictured in Figure 2, was optimized for flows of 40 to 150 ft/sec (1-inch diameter catalyst) and constructed of black pipe fittings. The main body was ported in four places 90° apart around the periphery and at 45° apart while H_2 and N_2/CH_3I entered through a 1/4-inch stainless steel pipe located at the axial centerline with the tip positioned at the intersection of the air/steam jets.

Combustion Chamber/Catalyst Reactor

The combustion chamber, Figure 1, shows the five 1-inch by 1-inch catalyst segments mounted in a castable refractory housing. A guard heater,

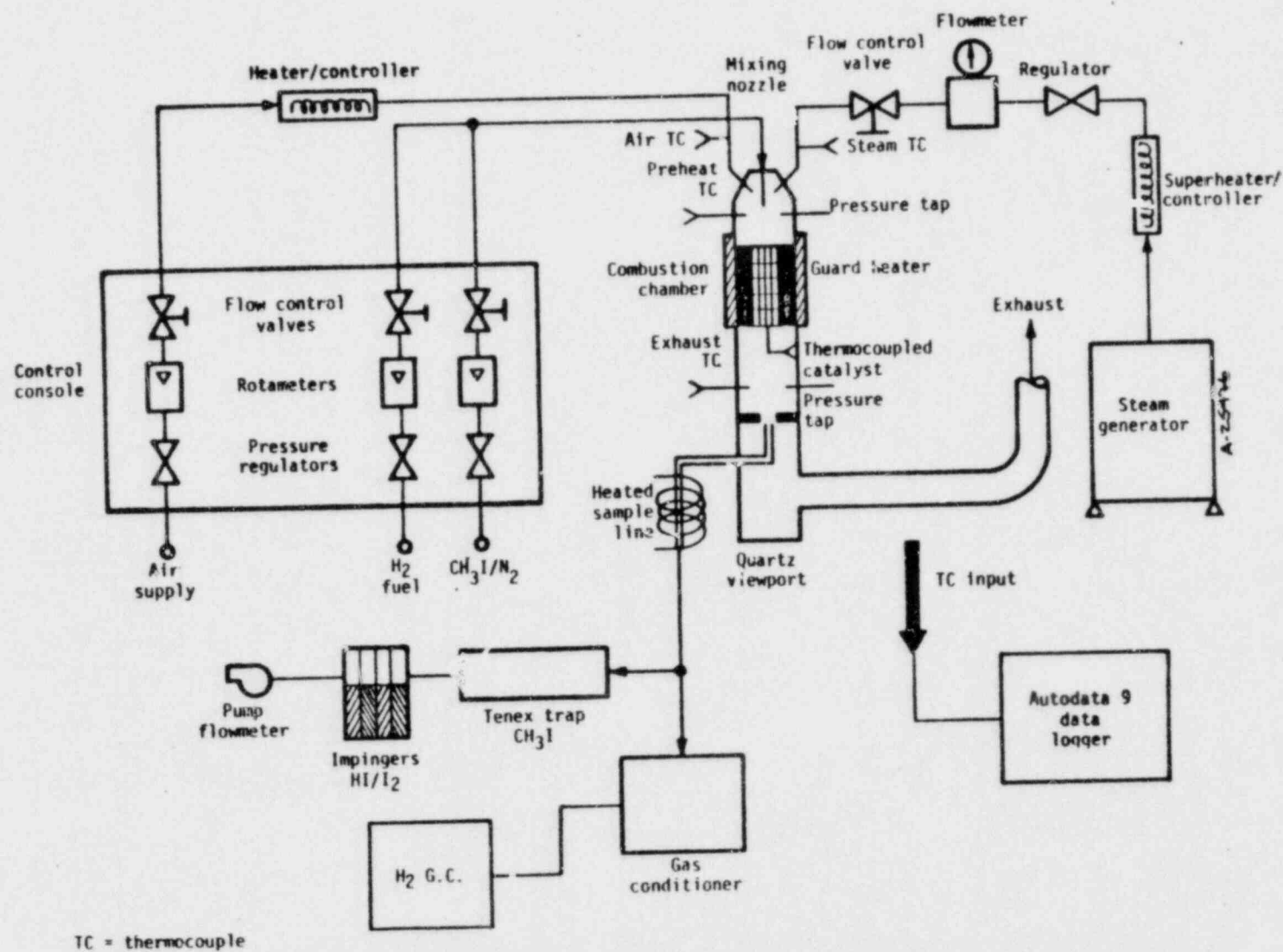


Figure 1. Experimental test facility schematic.

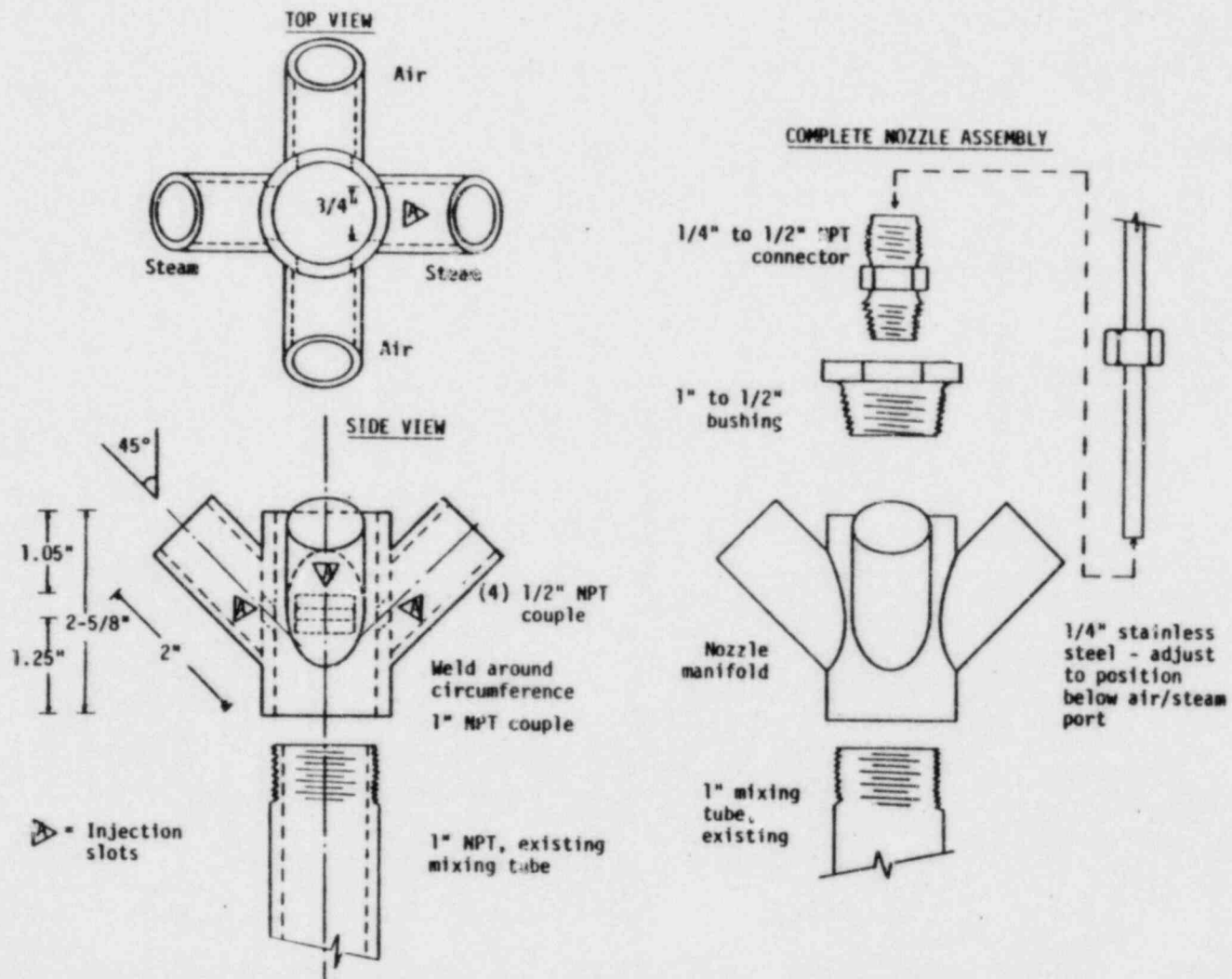


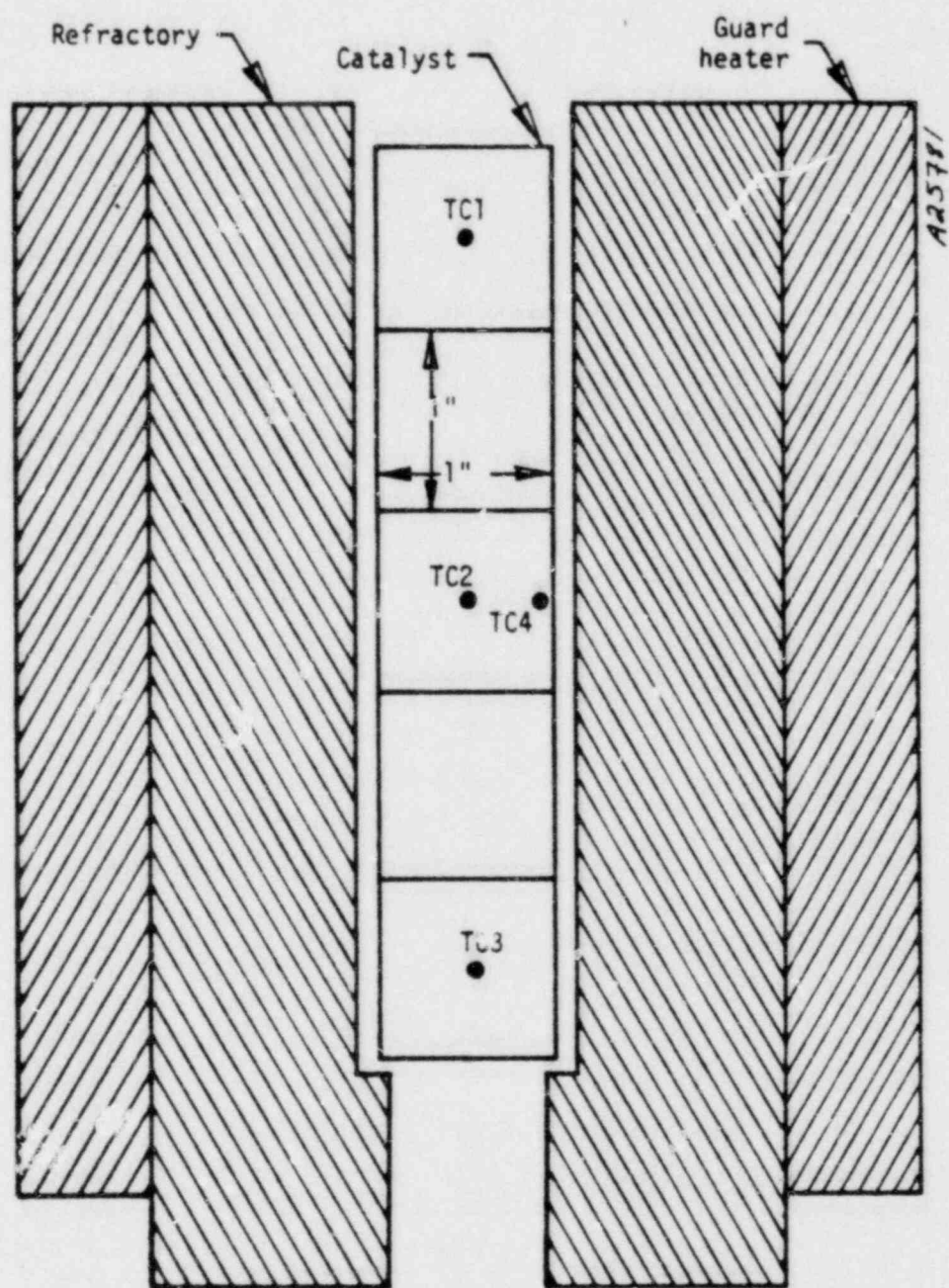
Figure 2. Mixing nozzle/fuel injector.

controlled by a variable voltage source, held the combustion chamber near the adiabatic condition during testing. A 24-inch long, 1-inch diameter mixing zone between the combustion chamber and the gas injector was used to insure complete fuel/air mixing prior to entering the catalyst. Pressure ports located fore and aft of the combustion chamber measured the differential pressure drop across the catalyst reactor.

The first catalyst screened, and subsequently used for all tests, was a noble metal, UOP #4103 fine cell monolith. It was initially selected on the basis of known high H_2 activity at low preheat gas temperatures. Due to the catalyst's high H_2 activity, a graded cell monolith configuration was not needed. (Graded cells are used to increase mass throughput for catalysts of relatively low activity or with hydrocarbon fuels.) The reactor assembly consisted of five 1-inch long by 1-inch diameter segments stacked on top of each other as seen in Figure 3.

In addition to high H_2 activity and low preheat temperature operation, facility and operating limitations were considered prior to catalyst selection. An existing combustion facility compatible with the 1-inch x 1-inch UOP reactor was used to minimize facility capital costs and accelerate initial screening tests. This facility was also used for the remaining catalyst poisoning test series. The dominant factor which determined catalyst size was fuel costs. Increasing the diameter of the catalyst from 1 to 2 inches requires a fourfold increase in the H_2 flowrate.

Catalyst temperature was measured by four Type K thermocouples that were potted in ceramic cement and attached directly to the catalyst cell wall. Figure 3 shows the thermocouples positioned at the top, middle, and bottom segments of the reactor centerline. The middle catalyst segment had an extra side-mounted thermocouple to measure the radial temperature profiles. Thermocouples located 3 inches above the catalyst and 3 inches below measured the preheat and exhaust temperatures within the combustion facility. An Acurex Autodata 9 data logger automatically recorded the operating temperatures.



TC = thermocouple

Figure 3. Catalyst reactor assembly with refractory and guard heater.

Steam Generation

A Chromalox CES-24 (72 lb/hr) steam generator was operated in series with Sylvania gas heaters to produce superheated steam. A Jordan Mark 60 pressure regulator regulated the steam to 10 psig and a Chromalox temperature controller maintained the steam at 300°F upon entry to the gas injector. Two pitot tubes, 1/2-inch and 3/4-inch diameter, were used to measure steam flow-rate. These were fabricated at Acurex; off-the-shelf items were not capable of measuring the low mass flowrates encountered during testing. Figure 4 shows a diagram of the 1/2-inch Acurex-built stainless steel pitot tube. The end of each pitot tube (1-1/4-inch stainless steel plugs) was tapered from the existing 1-inch diameter supply steam line to their respective diameters in order to minimize pressure drop and turbulence. Also, to suppress turbulence, an L/d of 15 was maintained between the inlet convergence and the pitot tube probe.

Control Console

Air, H_2 and N_2/CH_3I flowrates were measured and metered at the control console shown in Figure 1. All gaseous flows were measured by Fischer & Porter precalibrated rotameters and subsequently delivered to the mixing nozzle. Both H_2 and N_2/CH_3I gases were introduced to the fuel injector at ambient conditions. The air supply was preheated by Sylvania gas heaters and the temperature was regulated by a Chromalox controller to values dictated by the operating points of the test matrix.

CH_3I Preparation

Conventional low flowrate rotameters were unsatisfactory for measuring CH_3I as a liquid (liquid at room temperature, BP = 110°F) at the low concentrations needed for testing. Even gaseous CH_3I (vaporized) could not be introduced at sufficiently low flowrates with rotameters. However, gas flowrates

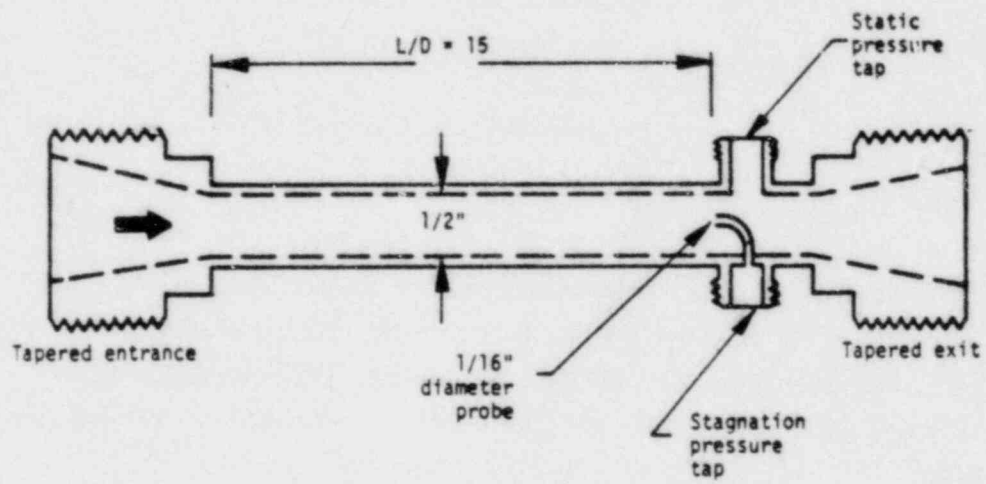


Figure 4. 1/2-inch pitot tube design.

could be raised to measurable levels by diluting the CH_3I with N_2 . Gas cylinders containing 2.4 volume percent CH_3I in N_2 at 150 psig were prepared by AIRCO Gas Products Company. At this concentration, the partial pressure of CH_3I is well below its saturation vapor pressure, thereby insuring that the CH_3I remained gaseous throughout testing. It should be noted that N_2 does not affect catalyst activity or combustion.

Lower CH_3I concentrations were achieved by expending the contents of the original gas cylinder to ambient pressure and refilling it back to 150 psig with N_2 . This dilution, approximately 121 to 1 (when done twice), yielded about 0.02 percent CH_3I by volume in N_2 . Before and after each dilution, the bottle was rolled for about 30 minutes to insure good mixing. To verify the contents of the bottle, samples were periodically analyzed by the Acurex Chemistry Lab.

Emissions Bench

Combustion efficiency and catalyst performance was determined by measuring H_2 emissions. A Carle Model 3500 gas chromatograph measured H_2 in the exhaust that was dried by a TECO GC-1 gas conditioner.

The fate of the CH_3I poison was evaluated by measuring CH_3I , HI , and I_2 emissions. A Tenex trap was used to collect CH_3I samples while an acid/base impinger train absorbed HI and I_2 . HI and I_2 absorbed in the impingers were measured by ion electrodes.

SECTION 3

EXPERIMENTAL RESULTS

3.1 APPROACH

The program goal was to evaluate the performance of noble metal monolithic catalysts with H_2 in the presence of CH_3I . Catalytic combustion can extend the lean flammability limits of H_2 (down to 1 percent H_2) and can initiate combustion passively without external heating. A monolithic configuration was selected on the basis of its high combustion efficiency at high mass throughput and low pressure drop. Interest in conditions that might be expected in a LOCA focused catalyst testing to preheat temperatures between 72°F and 340°F, and steam concentrations from dry to saturated conditions.

Methyl iodide (CH_3I) was chosen as the test poison because it might be present during a LOCA and was shown by other investigators (Reference 2) to have a pronounced effect on catalyst performance.

Initially a 2 x 2 matrix of test conditions was conceived to examine the effect of CH_3I on catalyst performance at two H_2 concentrations (5 and 10 percent) and two steam concentrations (0 and 60 percent). However, initial testing showed rapid catalyst deactivation at CH_3I concentrations of about 20 ppm. As a result, the original test matrix was revised to determine which parameters, H_2 or CH_3I concentrations, were more dominant on catalyst deactivation.

Four separate UGP #4103 fine cell segment catalysts were evaluated at a variety of air, steam, H_2 , and CH_3I flowrates and concentrations. The

total gas preheat temperature was held at ambient conditions during testing and lightoff. As documented by Southern Nuclear Engineering (SNE) (References 1, 2) and substantiated by the results of our testing, increased gas preheat temperatures enhance the performance and lightoff characteristics of noble metal catalysts. Therefore, the catalyst tests conducted at ambient conditions are considered conservative.

Exceptions to these test points were those of high water concentration, where preheat determines the amount of water, as saturated vapor, allowed in the total mixture. For example, 10 percent water by volume under saturated steam conditions corresponds to a gas temperature of about 170°F.

For comparative purposes, an Acurex heavily loaded platinum catalyst was tested under similar conditions to that of UOP's to determine loading effects on life and performance. Due to UOP's proprietary policy, the amount of loading on their catalysts was not known. The Acurex catalyst was heavily loaded with platinum to 6 percent by weight.

The culmination of all tests resulted in the following operating points, listed by their maximum and minimum values:

- H₂ concentrations, 5 to 10 volume percent
- Steam concentrations, 0 to 40 volume percent
- Preheat temperatures, 70°F to 340°F
- CH₃I concentrations, 0.07 to 20 ppm
- Total flowrates, 12.5 to 40 acfm

3.2 RESULTS

3.2.1 Catalyst Performance

Preliminary testing of the noble metal UOP #4103 catalyst demonstrated low temperature lightoff and extremely high mass throughput capability. The

catalyst reactor, as pictured in Figure 3, achieved lightoff at H_2 concentrations as low as 1.5 percent by volume and face velocities (velocity of uncombusted gas stream at catalyst entrance) up to 140 ft/sec. Figure 5 shows the results of these tests.

Packed bed catalysts, though adequate H_2 combustors, have very high pressure drops at high velocities (References 1, 2). A packed bed catalyst would require a much larger volume than the monolithic catalyst to maintain the high mass throughput used in these tests. For reference, a 24-inch diameter monolith reactor operating at 140 ft/sec can consume the contents of an ice condenser containment vessel ($1.25 \times 10^6 \text{ ft}^3$) in less than 1 hour.

As shown in Figure 6, high combustion efficiency is maintained even though H_2 concentrations are well below conventional lean flammability limit operation. Note that combustion efficiency of 100 percent is achieved at H_2 concentrations above 4 percent. Again, comparing the results of SNE's packed bed catalyst tests to the monolithic catalyst tests, we note marked differences in performance. The UOP #4103 catalysts maintain combustion efficiencies of 99 plus percent while packed bed combustion typically operates around 90 percent. The efficiency values quoted for both systems, monoliths and packed beds, are based on the difference between the measured combustion temperature and the adiabatic flame temperature. As an alternative, combustion efficiency can be determined by measuring uncombusted hydrogen in the catalyst exhaust (see Figures 8, A-1, and A-2) using a gas chromatograph. Although calculating efficiency based on emissions can be more accurate than using temperature, the long sampling time of the gas analyzer significantly lengthens the test procedure. To expedite testing, the efficiency data shown in Figure 6 was calculated based on temperature.

3.2.2 Catalyst Deactivation by CH_3I

Deactivation Phenomena

Deactivation of catalyst segments progressed from front to rear of the reactor assembly until combustion terminated. This type of progressive

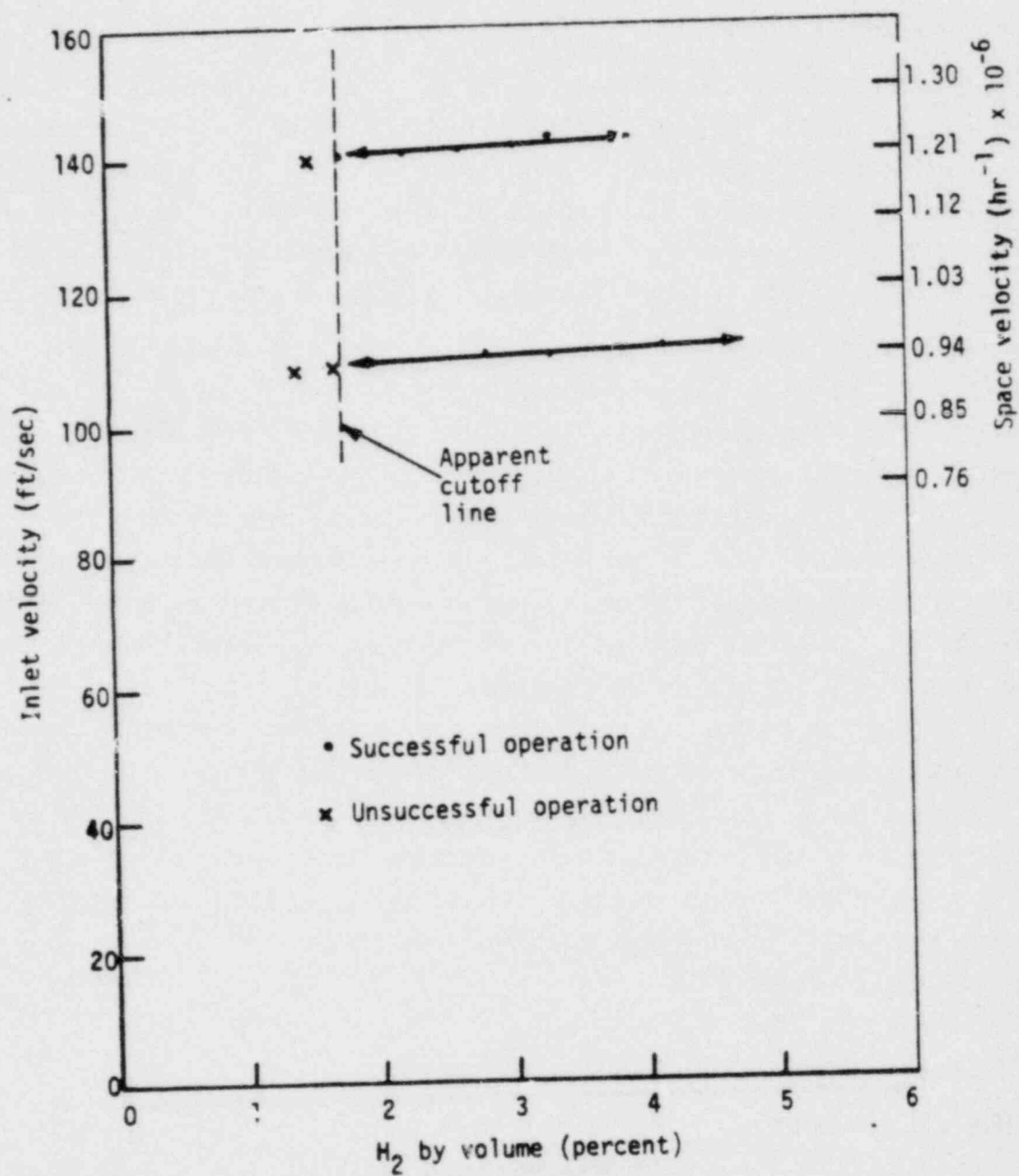


Figure 5. Fuel-lean catalyst activity.

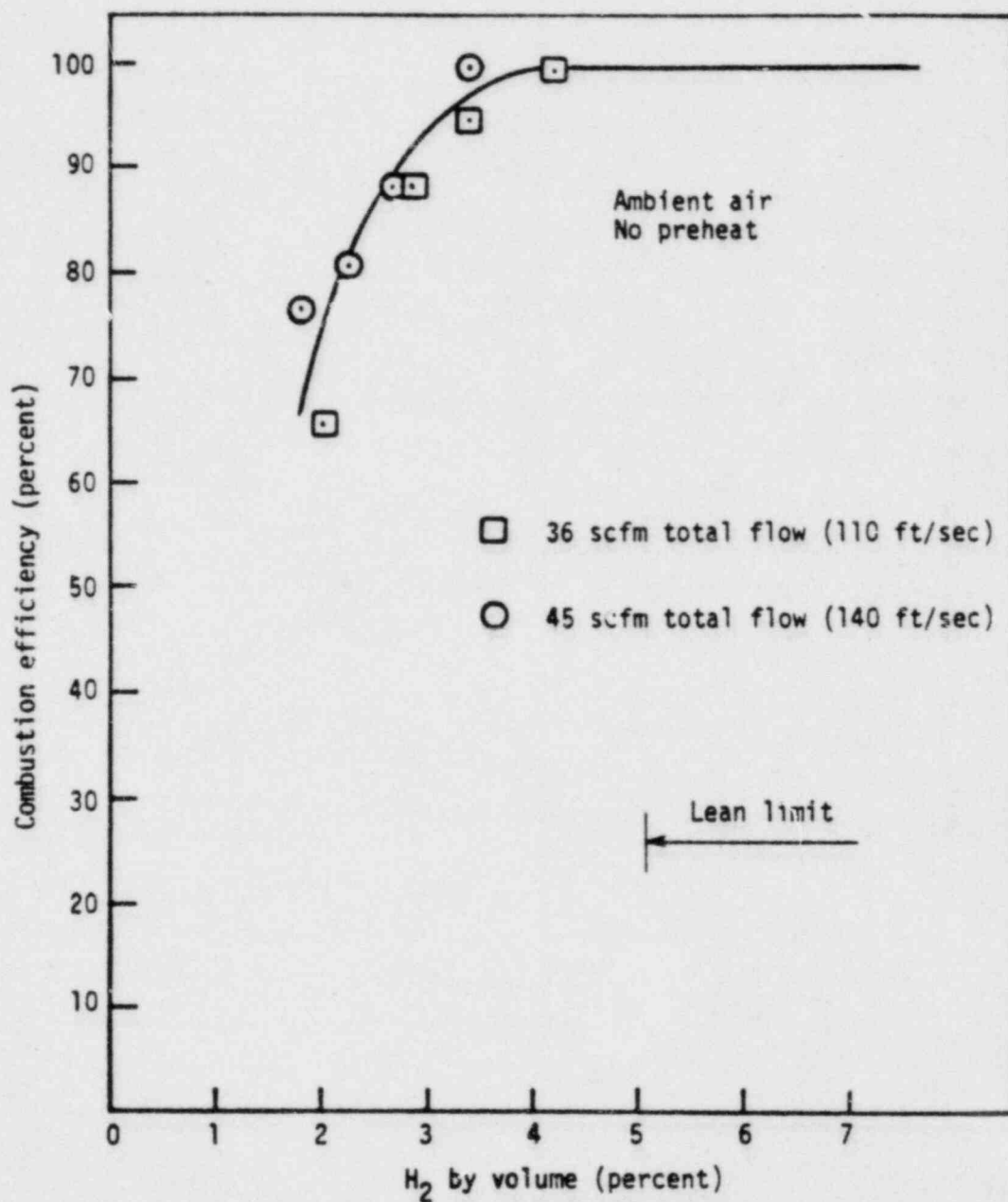


Figure 6. Catalyst combustion efficiency.

deactivation, as opposed to the slow overall decline in catalyst activity reported by SNE, was verified by monitoring the temperature of three of the five catalyst segments which sequentially declined from a temperature greater than the flame temperature to the preheat gas temperature. As the reaction front proceeded, temperature/time relationships such as those pictured in Figure 7 developed. t_1 , t_2 , and t_3 represent arbitrary time intervals at which point the reaction front might be located. Figure 7 is an extrapolation of what was typically seen as the reactor assembly deactivated. This type of temperature/time relationship indicates that the combustion of H_2 with air is essentially complete within a narrow reaction zone and the remainder of the catalyst assembly is heated only by the exhaust gases.

The temperature/time profiles show surface temperatures which exceed values predicted by adiabatic conditions. Due to the substantial difference in hydrogen and oxygen gas diffusivities, surface combustion actually occurs at a richer fuel/air ratio than bulk gas concentrations. This observation is consistent with temperature excursions identified by L. Louis Hegedus (Reference 3).

Figure 8 shows an actual temperature versus time profile for 20 ppm CH_3I (a value 200 times greater than the concentrations recommended by Reg. Guide 1.4), 10 percent H_2 test. As shown, the bulk gas temperature at time zero is at the adiabatic flame temperature (T_{AD}). As time proceeds, segment #1 slowly increases above T_{AD} , then falls off rapidly to the preheat temperature. As the reaction front proceeds down the catalyst, the next segment (#2) slowly raises above T_{AD} and similarly drops to ambient preheat conditions as total deactivation occurs and H_2 combustion is extinguished. These results verify: (1) deactivation of catalysts due to CH_3I injection is progressive, and (2) the complete oxidation of H_2 occurs within a very narrow reaction front. Throughout testing, the deactivation rate for each catalyst segment was consistent for the entire reactor assembly. This information is useful for determining individual catalyst deactivation rates.

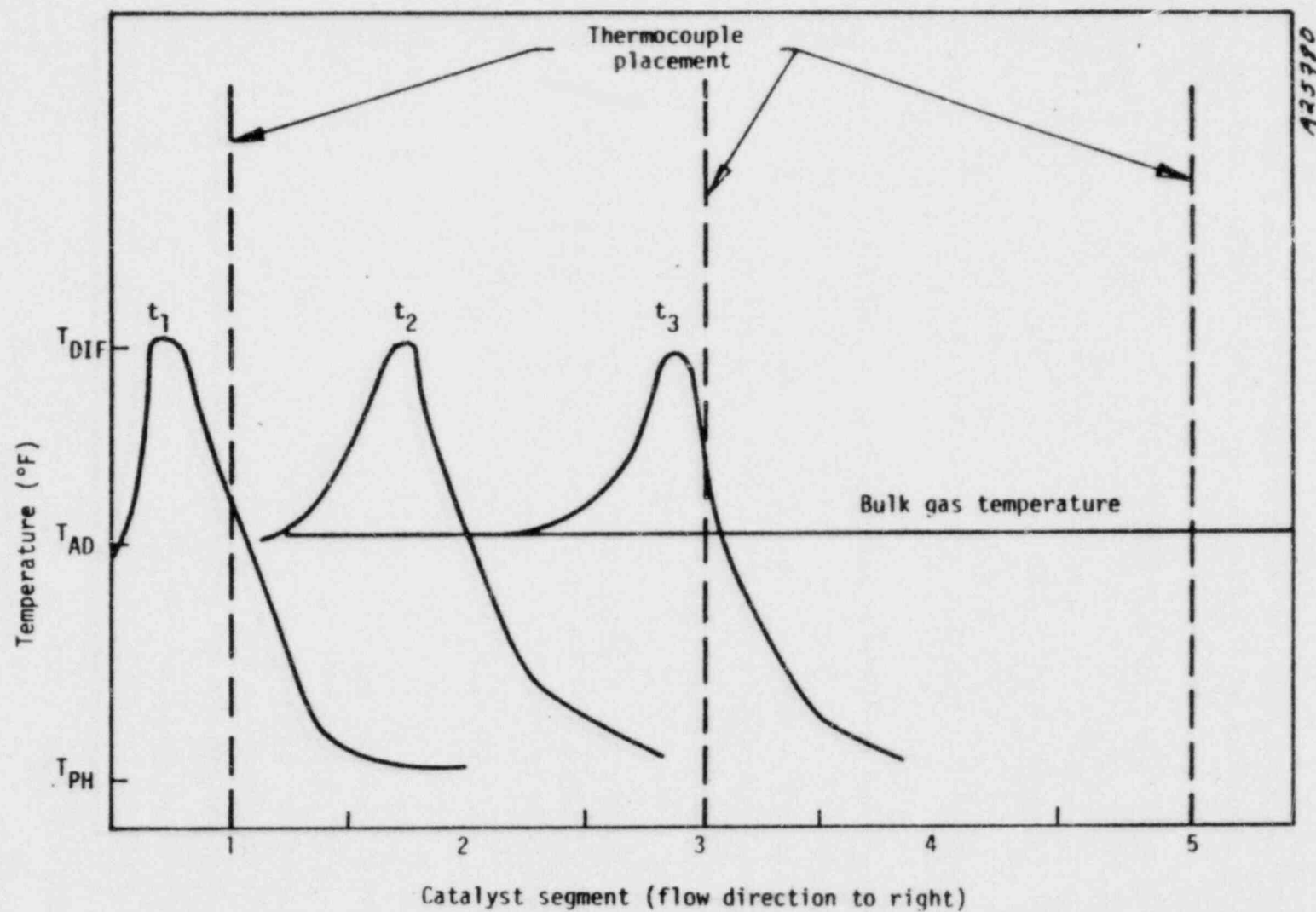


Figure 7. Extrapolated temperature/time relationship during CH_3I deactivation.

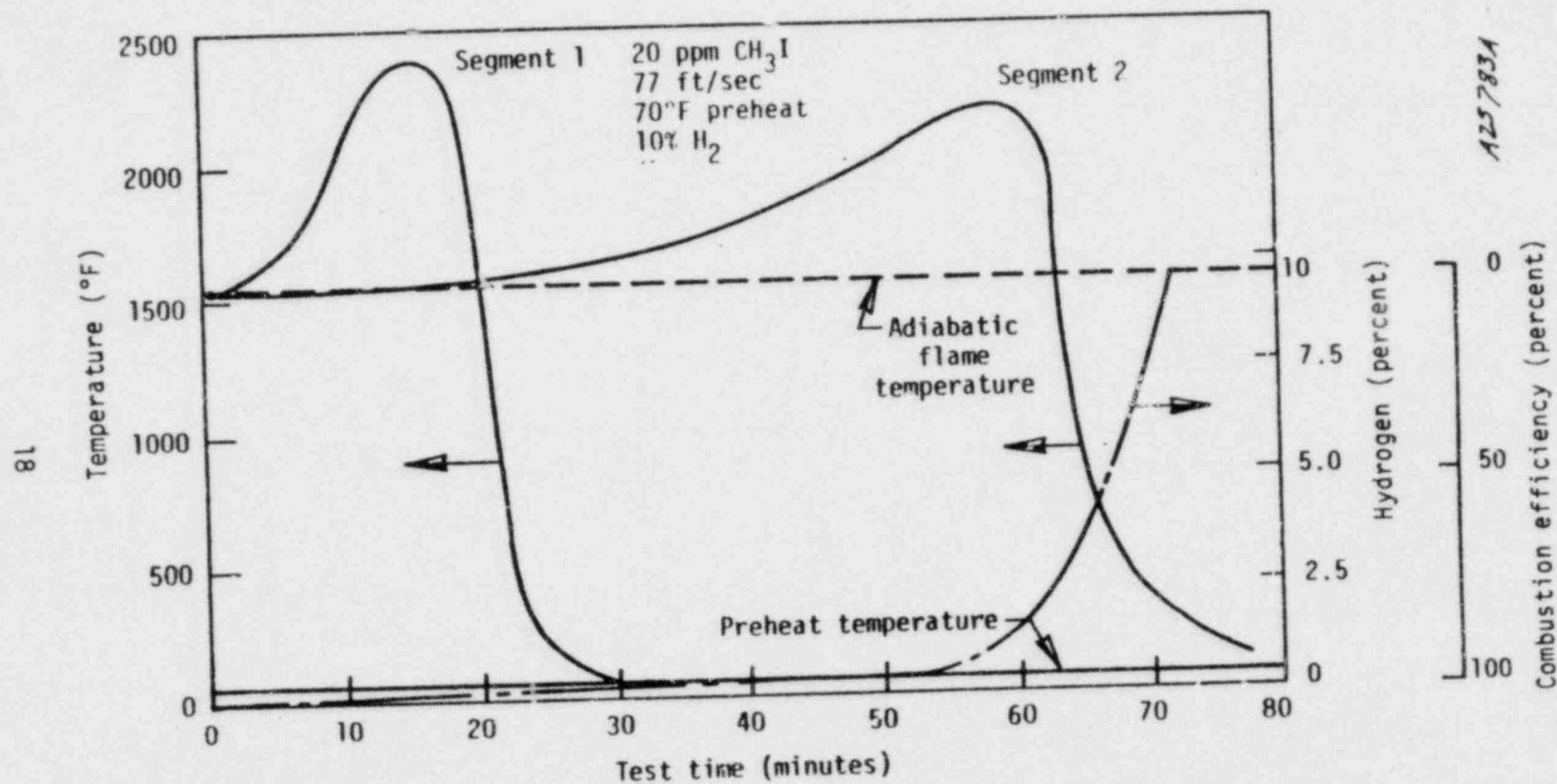


Figure 8. CH_3I deactivation phenomena.

Figure 8 also shows the concentration of H_2 in the exhaust with the corresponding combustion efficiency for the heavily doped CH_3I test. High combustion efficiencies, much greater than 90 percent, were maintained throughout testing until the catalyst was rendered completely inactive. This observation is contrary to other investigators (Reference 1) who report H_2 conversion efficiencies of approximately 90 percent, prior to the introduction of CH_3I , and a steady decrease in efficiency down to 20 percent after poison addition. Note that if no CH_3I is present (indicated by time = 0 on Figure 8), the 99 percent plus efficiency enables monolithic catalysts to be a rapid cleanup device.

An attempt was made to measure HI and I_2 emissions from the catalyst by absorbing each component in an acid/base impinger train and analyzing the resulting solution by ion electrodes. However, at the low CH_3I concentrations encountered during testing, the selected measurement technique was not accurate enough to detect HI or I_2 below 150 ppmv. For future testing, alternate techniques must be devised to measure these species.

Two other tests were conducted measuring H_2 in the exhaust: first, where rapid deactivation occurred, and second, where, although the front segment deactivated, no further catalyst deactivation occurred in the remaining segments. These results are presented in Appendix A.

Test Results

Table 1 shows the tabulated results of all the deactivation tests conducted during this program. Data are grouped generally on the basis of different reactors, 1 through 4, which, coincidentally, corresponds to orders of magnitude changes in CH_3I concentrations. Catalysts 1 through 4 are UOP #4103 reactors, while ACU represents the Acurex heavily loaded platinum reactor. During these tests, H_2 concentrations were varied to investigate its affect on the deactivation phenomena. Percent H_2 , preheat temperature, pressure drop, CH_3I concentration, and segment deactivation time are included in the table. Based on this information, individual segment deactivation

TABLE 1. TEST SUMMARY

| Test Point | H ₂ (%) | Preheat (°F) | CH ₃ I (ppm) | Bed Temperature (°F) | Deactivation Time per Segment* (hrs) | Flowrate (acfm) | Face Velocity (ft/sec) | Pressure Drop (psi) |
|------------|-----------------------|-----------------|----------------------------|-------------------------|---|--------------------|---------------------------|------------------------|
| 1. | 5 | 70 | 9.8 | 750 | 0.02 | 25 | 77 | 1.05 |
| 1.A | 7.6/6.9 | 340 | 9.8/9.7 | 1300 | 0.37 | 37.7 | 117 | 1.72 |
| 1.B | 10 | 70 | 19.6 | 1510 | 0.20 | 25 | 77 | 1.0 |
| 2.A | 5 | 70 | 0.37 | 750 | 0.13 | 25 | 77 | -- |
| 2.B | 8.16 | 70 | 0.8 | 1260 | 2.37 | 25 | 77 | 1.4 |
| 3.A | 5 | 70 | 0.23 | 750 | 0.37 | 25 | 77 | -- |
| 3.B | 8 | 70 | 0.33 | 1250 | 7.0 | 25 | 77 | 1.3 |
| 3.C | 6.5 | 70 | 0.27 | 950 | 1.60 | 25 | 77 | -- |
| 4.A | 8 w/s** | 168 | 0.33 | 950 | 1.22 | 25 | 77 | 1.0 |
| 4.B | 5 | 70 | 0.07 | 750 | 0.67 | 12.5 | 39 | 0.4 |
| 4.C | 6.5 | 70 | 0.07 | 950 | ∞ | 12.5 | 39 | 0.43 |
| 4.D | 6.5 w/s** | 162 | 0.025 | 1050 | ∞ | 25 | 77 | 0.47 |
| ACU | 5 | 70 | 0.09 | 750 | 0.01 | 25 | 77 | -- |

*Segment = 1-inch length of monolith

**w/s - with steam

rates were calculated as a function of H_2 and CH_3I concentrations. Appendix B contains the temperature/time relationship curves that were used to generate Table 1.

Inspection of Table 1 reveals that an individual segment deactivation time of 7 hours occurred at 8 percent H_2 and 0.33 ppm CH_3I (test point 3.B). Under virtually the same H_2 concentrations but over twice the CH_3I concentration (test point 2.B), Table 1 shows a segment life of only 2.4 hours. Similarly, comparing test point 3.B to 3.C we can see that a slight reduction in H_2 (to 6.5 percent) but identical CH_3I concentration reduces segment life from 7.0 to 1.6 hours. These results indicate that CH_3I deactivation is strongly affected by both CH_3I and H_2 concentrations. Tests were conducted at ambient preheat and 25 acfm (77 ft/sec).

Limited high preheat testing was conducted because increased temperatures tend to reduce deactivation rates. This decrease in deactivation with increased temperature was seen in our regeneration procedure (explained in the following section) and also by SNE.

Steam addition was examined for two separate cases: 162°F and 168°F preheat temperatures. Both points were at saturation conditions, corresponding to approximately 40 percent steam by volume.

Surface area and dispersion measurements were performed pre- and post-test on the UOP catalysts. Due to similarities in the data, only catalysts 1, 2, and 3 were completely evaluated. Test results are shown in Table 2. In all cases, there was a significant reduction in both active surface area and dispersion. As discussed earlier, catalyst surface temperatures as high as 2400°F were encountered -- 900°F higher than values predicted based on adiabatic conditions. At these temperatures, noble metal agglomeration can occur as indicated by low dispersion values. These results agree with the UOP surface analysis using a scanning electron microscope (SEM) which found significant metal agglomeration on catalyst rear segments, but only limited

TABLE 2. SURFACE AREA AND DISPERSION RESULTS

| Catalyst No. | Weight (gm) | Pre-Test | | Post-Test | | Hours Tested |
|--------------|-------------|-----------------------------------|---------------------|-----------------------------------|---------------------|--------------|
| | | Surface Area (m ² /gm) | Dispersion (μmol/g) | Surface Area (m ² /gm) | Dispersion (μmol/g) | |
| 1 | 38.53 | 21.75 | 11.59 | 0.11 | 0 | 5 |
| 2 | 38.18 | 20.38 | 12.93 | 4.37 | 0.42 | 10 |
| 3 | 39.45 | 19.07 | 10.35 | 7.00 | 0 | 18 |

agglomeration on front segments. The high steam content of the bulk gas downstream of the main reaction zone will expedite the agglomeration process, and thus increased agglomeration at the rear units is expected. UOP also analyzed the catalyst surface for iodide using an EDX microprobe. Iodide was not found in any location at the instrument's detectable limits (0.5 weight percent).

During testing, pressure drop in the reactor never exceeded 1.5 psi for gas flows of 25 scfm (77 ft/sec). Values listed in Table 1 are the averaged pressure drops seen during testing. These results agree with calculated pressure drop. Catalyst pressure drop data as a function of test time during deactivation for two experiments can be seen in Figures 9 and 10. As shown, pressure drop was a maximum prior to CH_3I addition (at stable combustion) and slowly decreased as deactivation of catalyst segments proceeded through the reactor. This is easily explained by fluid mechanics. When the reaction front is at the beginning of the reactor assembly, hot exhaust gases at correspondingly high velocities must traverse the remaining four segments before exiting. Since pressure drop is proportional to length, combustor pressure drop decreases as the reaction zone (high velocity gases) proceeds down the length of the reactor. Therefore, pressure drop is a function of total reactor length and the position of the reaction front during the deactivation phenomena.

Figures 11 and 12 show the results of eight tests conducted at 25 scfm (97 ft/sec) and 70°F preheat. Figure 11 shows individual segment (1 inch x 1 inch) life in hours versus nominal surface temperature at constant CH_3I concentration holding H_2 concentration constant. Here again, catalyst life was normalized to a 1-inch long segment. As shown, the number of test points was limited. Consequently, lines drawn through data taken at 10 and 20 ppm CH_3I assume trends similar to results obtained at 0.28 and 0.60 ppm CH_3I . For these tests (70°F preheat and no steam), H_2 concentration can be directly

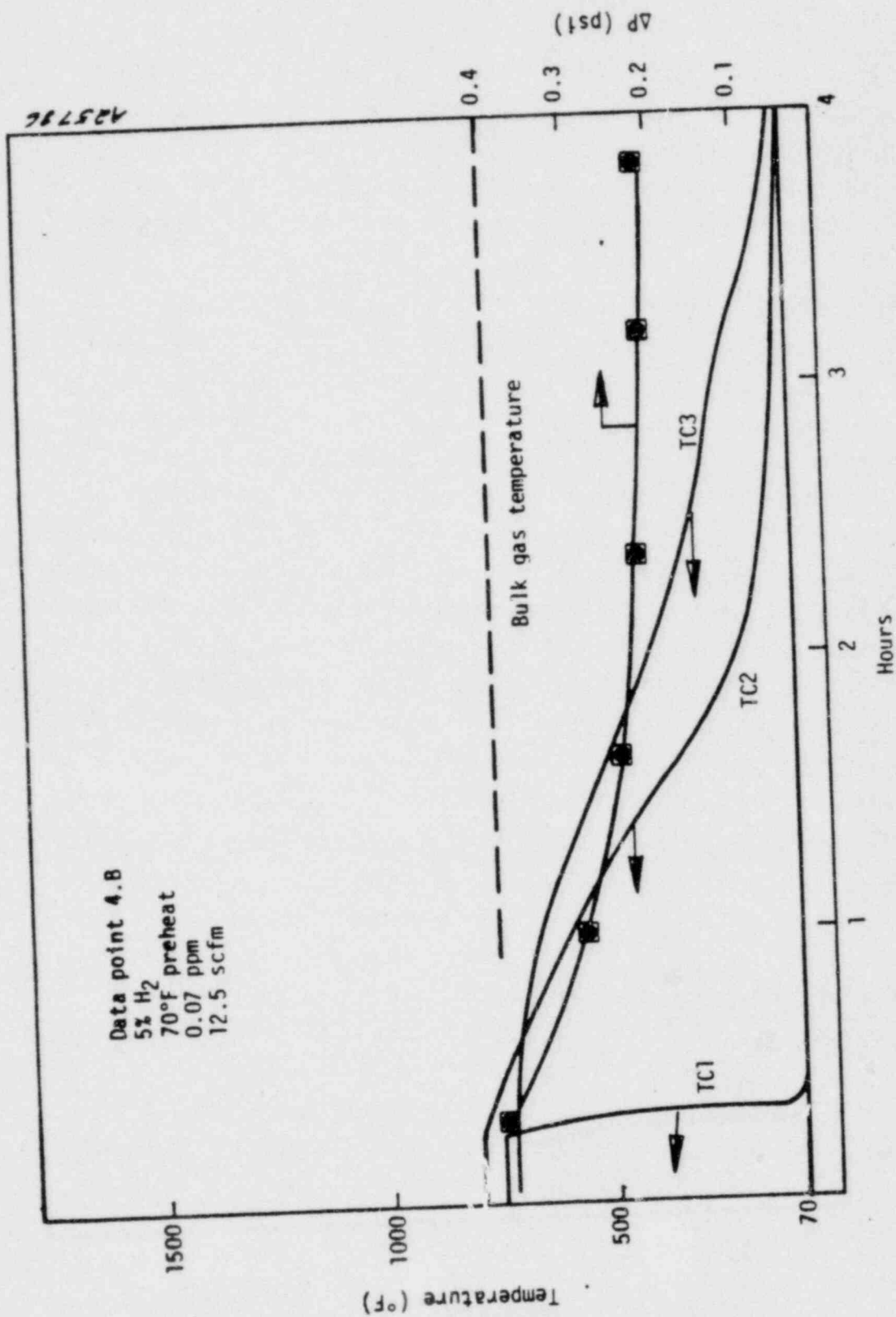


Figure 9. Catalyst pressure drop.

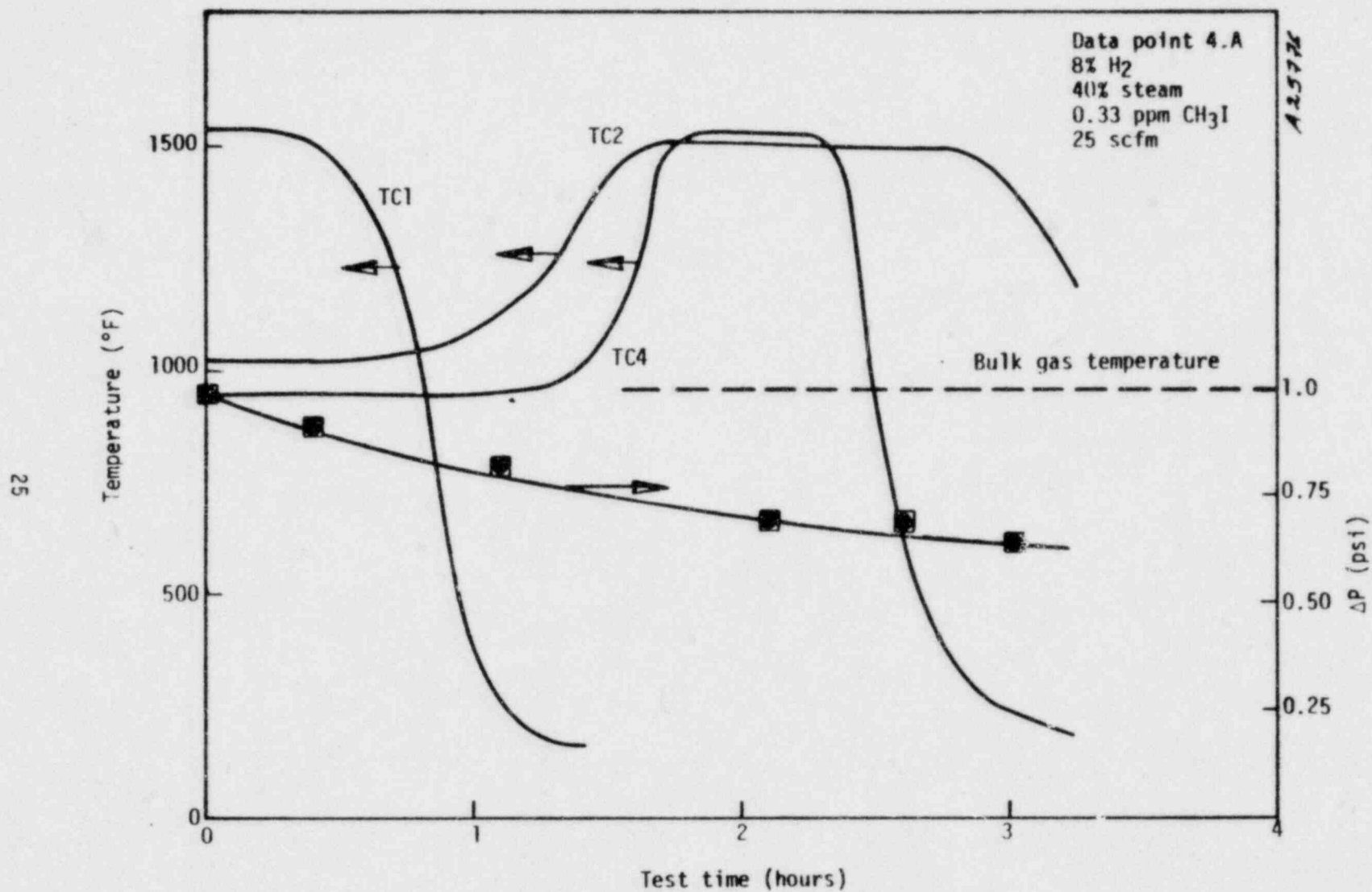


Figure 10. Catalyst pressure drop.

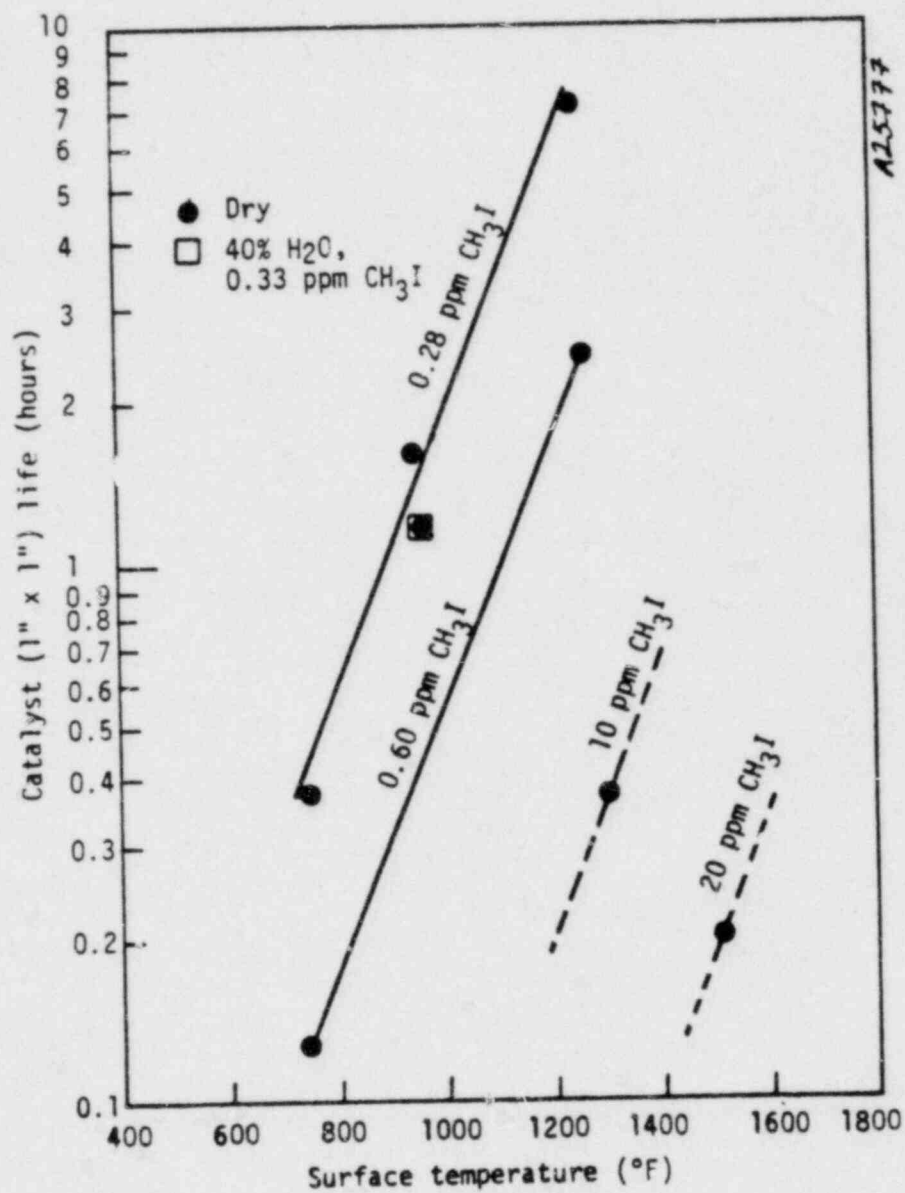


Figure 11. Catalyst life versus surface temperature.

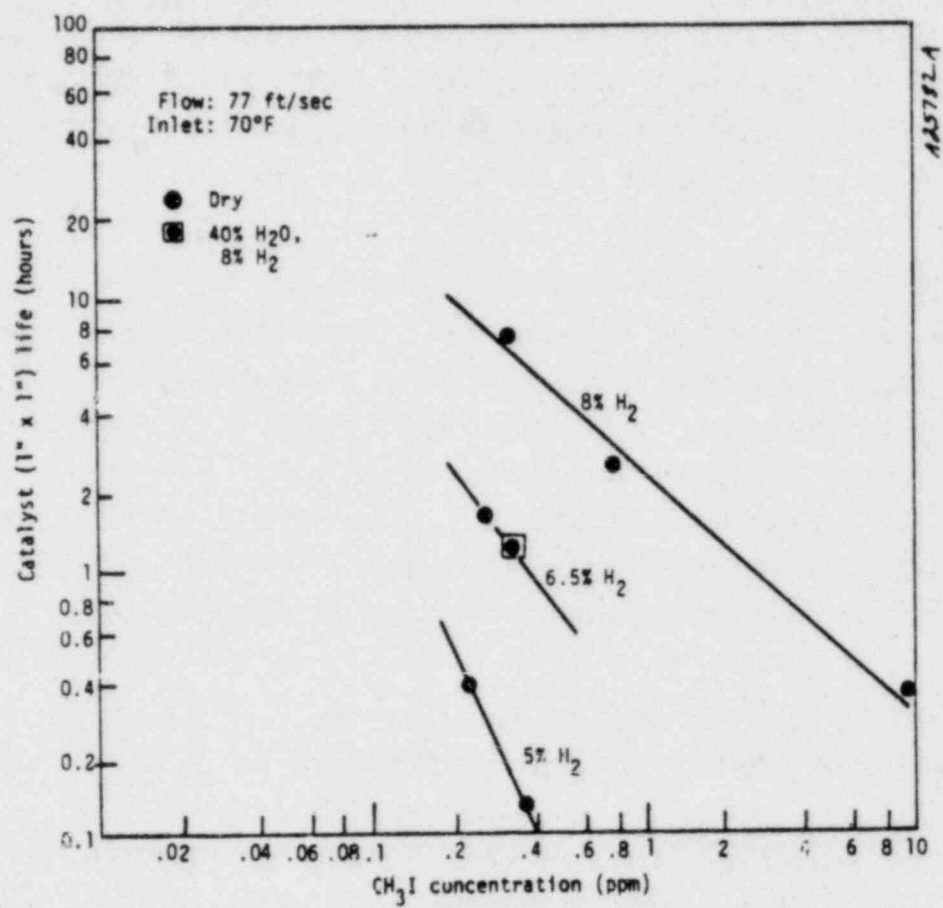


Figure 12. Catalyst life versus CH₃I concentration.

related to reactor temperature. These two figures indicate catalyst life is an exponential function of both H_2 concentration and CH_3I concentration. Thus, longer catalyst life is noted as H_2 concentration is increased and/or CH_3I concentration is reduced. Limited data indicate that if the concentration of CH_3I is very low there may be a threshold limit where no loss of activity occurs in the combustor. This apparent threshold is about 0.1 ppm CH_3I . Extrapolation of the data in Figures 11 and 12 can be used to predict catalyst life.

During steam operation, prior to CH_3I addition, there was an expected drop in the nominal bulk gas temperature. This drop was expected and Appendix C verifies this by comparing dry to saturated adiabatic flame temperatures for various preheat temperatures and H_2 concentrations. The drop in catalyst temperature has the same affect on individual catalyst life as would the introduction of an inert gas or operating at a lower H_2 concentration. Figures 11 and 12 show that the steam point (boxed) agrees with ambient preheat test points indicating catalyst surface temperature is the dominant variable in catalyst life and not the presence of H_2O , per se. This point was operated at 168°F preheat and 25 acfm.

To determine the influence of residence time (space velocity) on deactivation rates, three low velocity test points (4.B and 4.C) were conducted at 12.5 scfm (39 ft/sec). It was found that lower flowrates generally inhibit catalyst life at low H_2 concentration (5 percent), while enhancing life at higher H_2 values (6.5 percent). Specific conclusions regarding the affect of low flowrate on deactivation cannot be drawn due to insufficient data.

The Acurex catalyst (ACU), though heavily loaded with platinum (6 percent by weight), had poor dispersion due to agglomeration of platinum on the substrate. This resulted in poor catalytic activity during steady state combustion and rapid deactivation with CH_3I addition. Table 1 verifies these results.

Catalyst Regeneration After CH₃I Deactivation

Catalysts, deactivated after exposure to CH₃I, could be restored to complete activity (regenerated) and used for further testing. Here regeneration refers to the process of restoring a partially or totally deactivated reactor segment to its original combustion characteristics (i.e., combustion efficiency) achieved prior to CH₃I exposure. The reversibility of the process indicates that CH₃I deactivation does not cause permanent loss of catalyst activity.

To qualitatively describe a typical regeneration process, the following three scenarios were observed. First, catalyst segments with low CH₃I exposure time and segment temperature (downstream reactor segments which were the last to deactivate) were easily restored to full activity by simply stopping the CH₃I flow. Second, segments of longer exposure times (middle of catalyst assembly) required only increased H₂ concentration of typically 6 to 7 percent before restoring activity. Third, front segments exposed to CH₃I for several hours required H₂ concentration greater than 10 percent and air preheat about 300°F before regeneration occurred.

The severity of conditions (elevated temperature and H₂ concentration) required for regeneration reflects the degree of catalyst deactivation. Deactivation can be caused by two phenomena: (1) actual loss of active catalyst sites due to vaporization or agglomeration at high temperature, and (2) adsorption or chemical reaction of poison species with active sites. The former mechanism is irreversible and can occur at high temperature in the absence of a poison, while the latter is generally reversible, permitting catalyst regeneration.

The maximum recommended operating temperature of the UOP #4103 catalyst is 1800°F. As discussed earlier, catalyst surface temperature of the reaction front exceeds the expected adiabatic bulk gas temperature due to the high diffusivity of hydrogen relative to oxygen. In several cases, segments of

the catalyst reactor experienced temperatures exceeding 1800°F and a corresponding loss of catalyst activity was noted by difficulty in achieving catalyst lightoff. However, the severity of deactivation depended significantly on the duration of catalyst exposure to CH_3I at low temperatures. Front segments, which extinguished first, were exposed to CH_3I for a longer period than the remainder of the reactor assembly which continued to operate. As expected, regeneration of the front segments required higher preheat temperature and H_2 concentration. In addition, reactors exposed to CH_3I for long periods of time were more difficult to regenerate than those which deactivated rapidly at high concentrations of CH_3I . This implies that CH_3I exposure time, not concentration, is more influential on the regeneration process.

Cyclic deactivation and regeneration was performed on several of the catalysts tested with no apparent change in performance. Regeneration, typically conducted at 300°F and about 7 percent H_2 , will restore catalyst assemblies to their original pretest combustion efficiency. Regeneration typically required 2 to 10 minutes, depending on the extent of deactivation of each reactor segment. Though regeneration data are somewhat limited, combustion efficiencies can be reliably restored to greater than 90 percent after CH_3I deactivation.

3.3 SUMMARY

The UOF #4103 catalyst is a proven combustor with excellent possibilities to burn hydrogen during and after a LOCA. It is capable of combusting H_2 below conventional lean flammability limits, down to 1.0 percent, and at very high mass throughputs. Tests were conducted at flowrates from 12.5 to 40 scfm and preheat temperatures from 70°F to 340°F. These conditions correspond to face velocities of 39 to 117 ft/sec.

Catalytic combustion of H_2 occurred within a narrow reaction zone. Due to high catalyst activity, combustion efficiency remains high until deactivation of the total catalyst occurs. Combustion efficiency of the

UOP #4103 catalyst is very high, about 99 percent, compared to conventional packed bed noble metal catalysts which typically operate around 90 percent.

The UOP #4103 catalyst deactivated in the presence of CH_3I at low H_2 concentrations and in a predictable (repeatable) manner. Deactivation proceeded sequentially down the length of the catalyst reactor. Combustion activity was maintained greater than 90 percent until the final catalyst segment totally deactivated.

Deactivation depends exponentially on CH_3I and H_2 concentrations while velocity effects are not fully understood. For example, at 5 percent H_2 concentration, catalyst (1 inch by 1 inch segment) life varied from 8 minutes at 0.37 ppm CH_3I to 40 minutes at 0.07 ppm CH_3I . At a CH_3I concentration of 0.28 ppm, catalyst life varied from 22 minutes at 5 percent H_2 to 7 hours at 8 percent H_2 .

Although experimental data was limited above 6.5 percent H_2 concentration, a threshold limit is indicated at 0.1 ppm CH_3I dopant value where catalyst life appears infinite. Additional testing is required to further define this limit.

Because surface temperature depends linearly on H_2 concentration, catalyst life also varies exponentially with surface temperature. Addition of steam to the H_2 /air mixtures lowers catalyst surface temperature by depressing the adiabatic flame temperature. As a result, steam addition reduced catalyst life. For example, steam addition at 0.31 ppm CH_3I and 8 percent H_2 reduced catalyst life from 7 hours to 1.2 hours. Similar trends were noted for changes in the gas preheat temperature. Elevating the gas preheat temperature lengthened catalyst life by increasing catalyst surface temperature.

REFERENCES

1. "Joint Utility Catalytic Hydrogen Recombiner Development Program," Southern Nuclear Engineering, Final Report, Dunedin, Florida/Bethesda, Maryland, July 1971.
2. Brown, G. M., Turner, S. E., Sawyer, C. T., "Joint Utility Catalytic Hydrogen Recombiner Development Program," BWR & PWR Offgas System and Miscellaneous Recombiner Tests, Southern Nuclear Engineering, Dunedin, Florida/Bethesda, Maryland, December 1971.
3. Hegedus, L. Louis, "Temperature Excursions in Catalytic Monoliths," AIChE Journal, Volume 21, No. 5, September 1975.

APPENDIX A
COMBUSTION EFFICIENCY

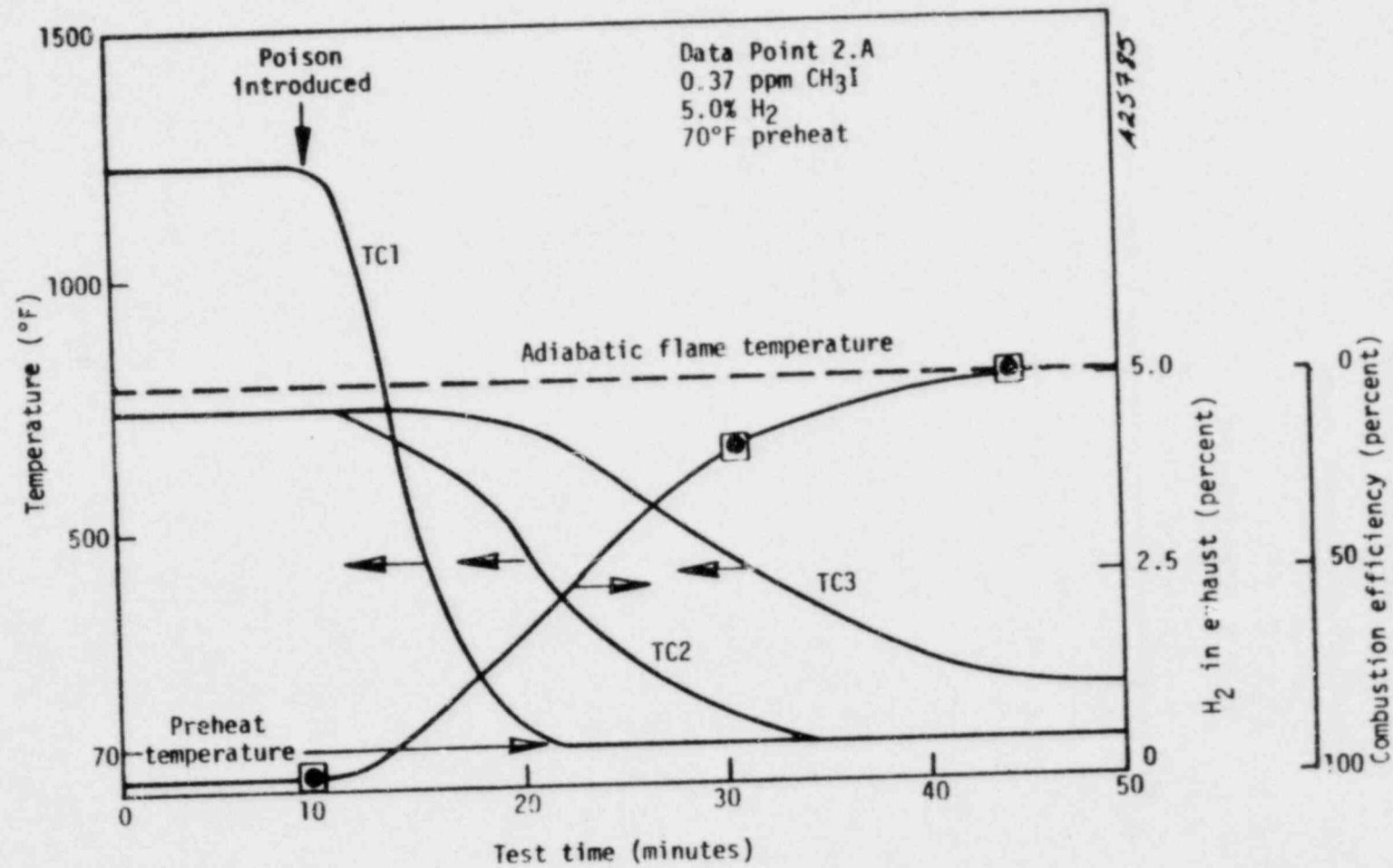


Figure A-1. Combustion efficiency.

35

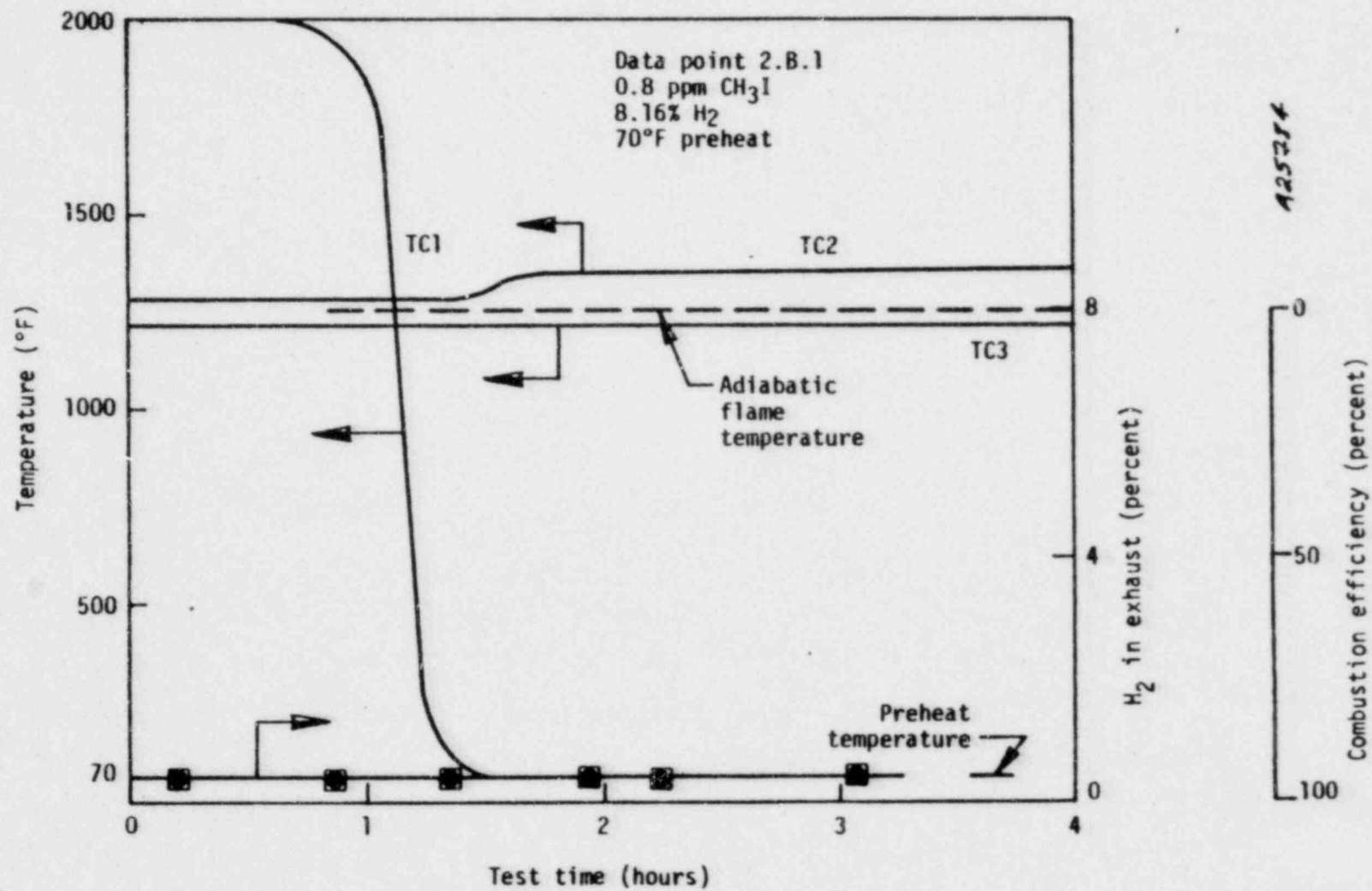


Figure A-2. Combustion efficiency.

APPENDIX B
TIME/TEMPERATURE RELATIONSHIPS

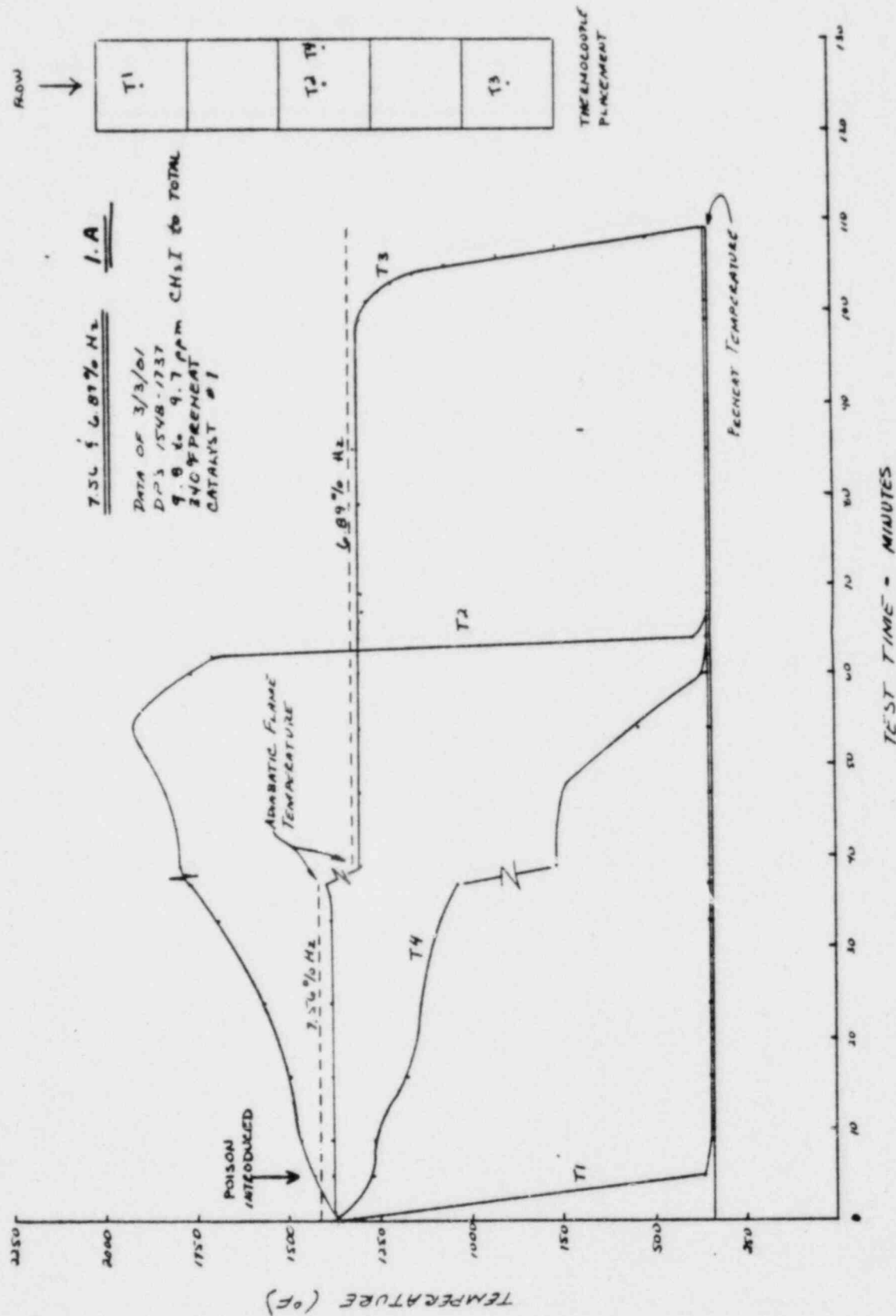


Figure B-1. Time/temperature relationship, test point 1.A.

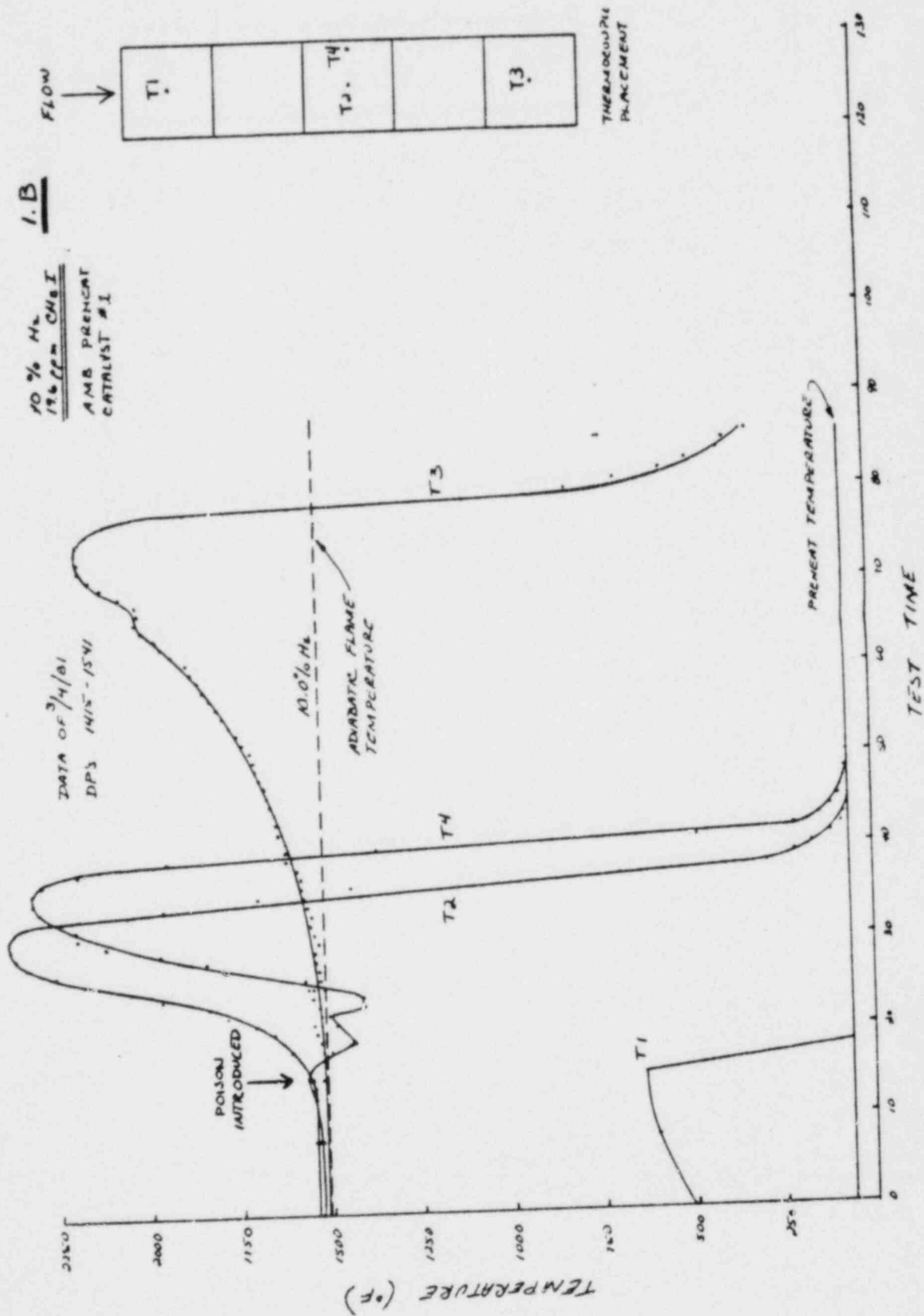


Figure D-2. Time/temperature relationship, test pt. 1.B.

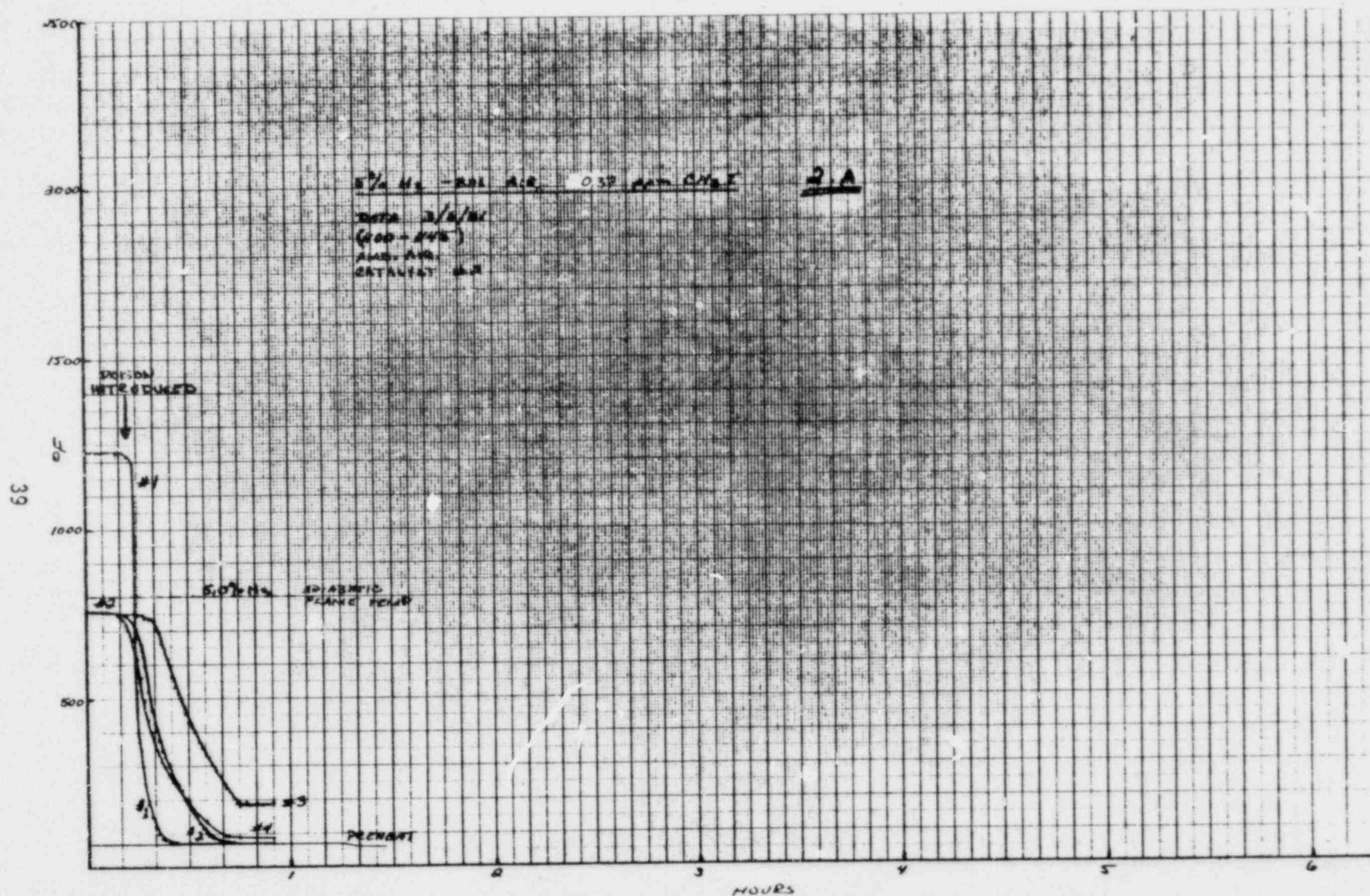


Figure B-3. Time/temperature relationship, test pt. 2.A.

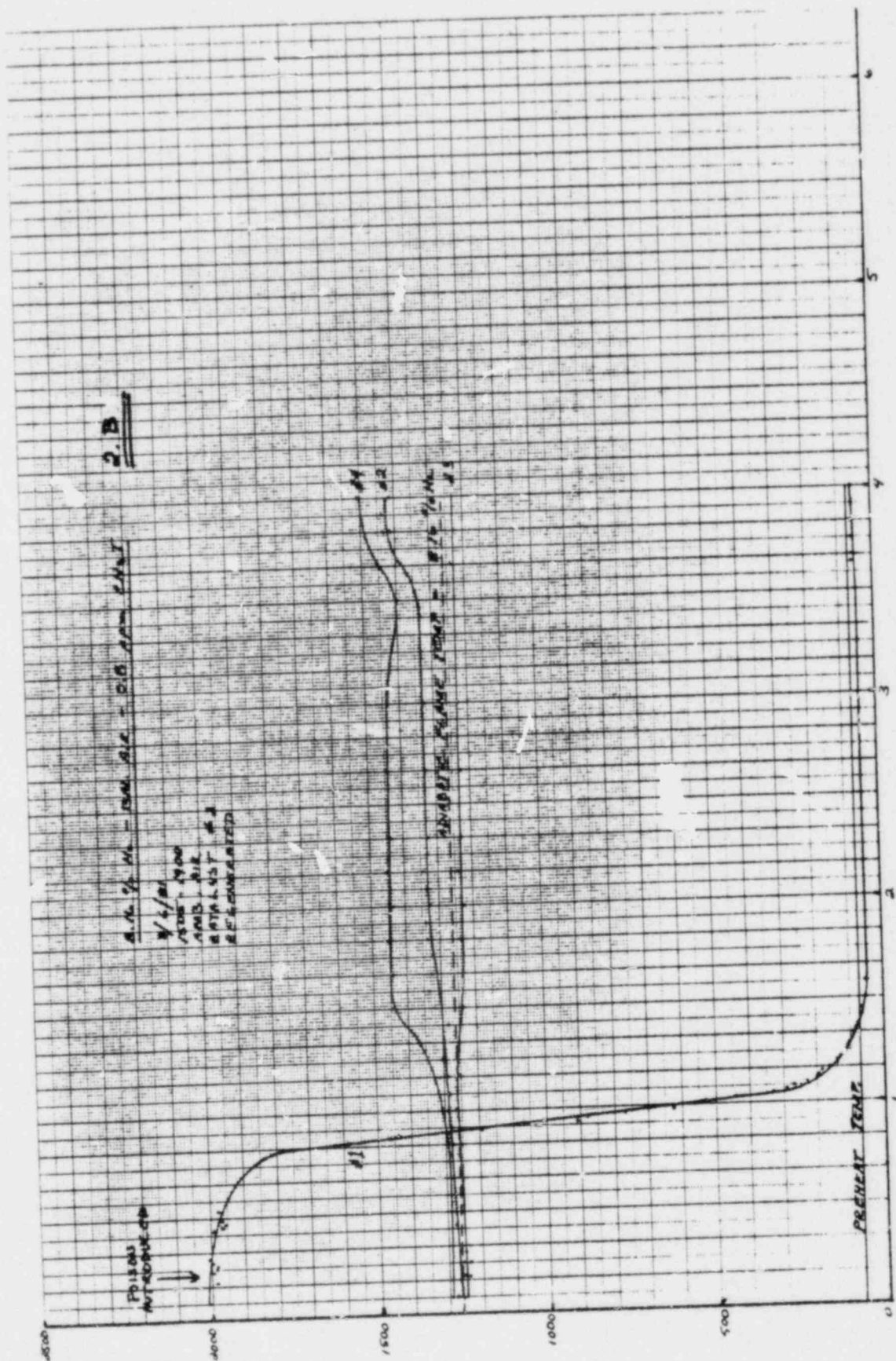


Figure B-4. Time/temperature relationship, test pt. 2.B.

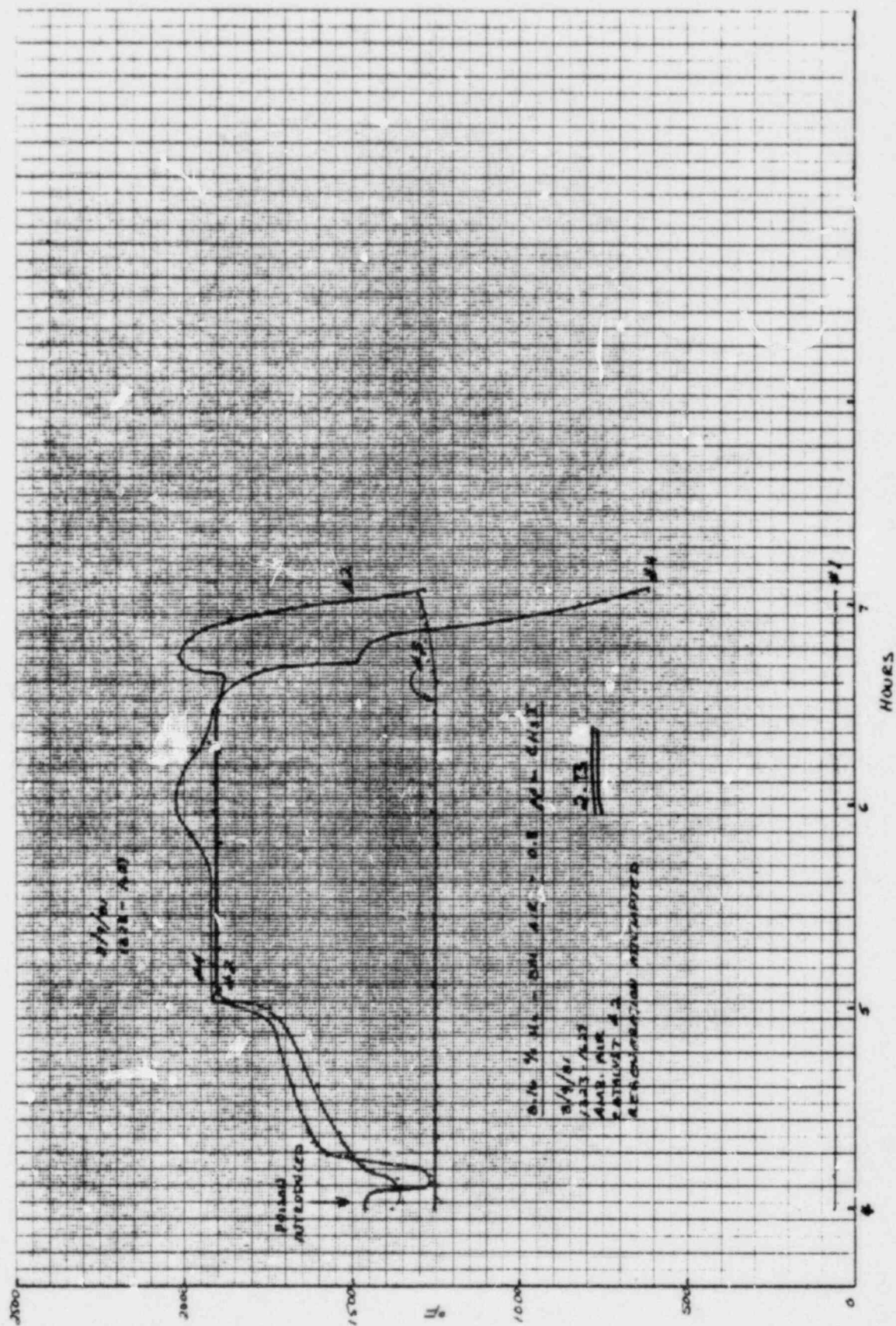


Figure B-5. Time/temperature relationship, test pt. 2.B (continued).

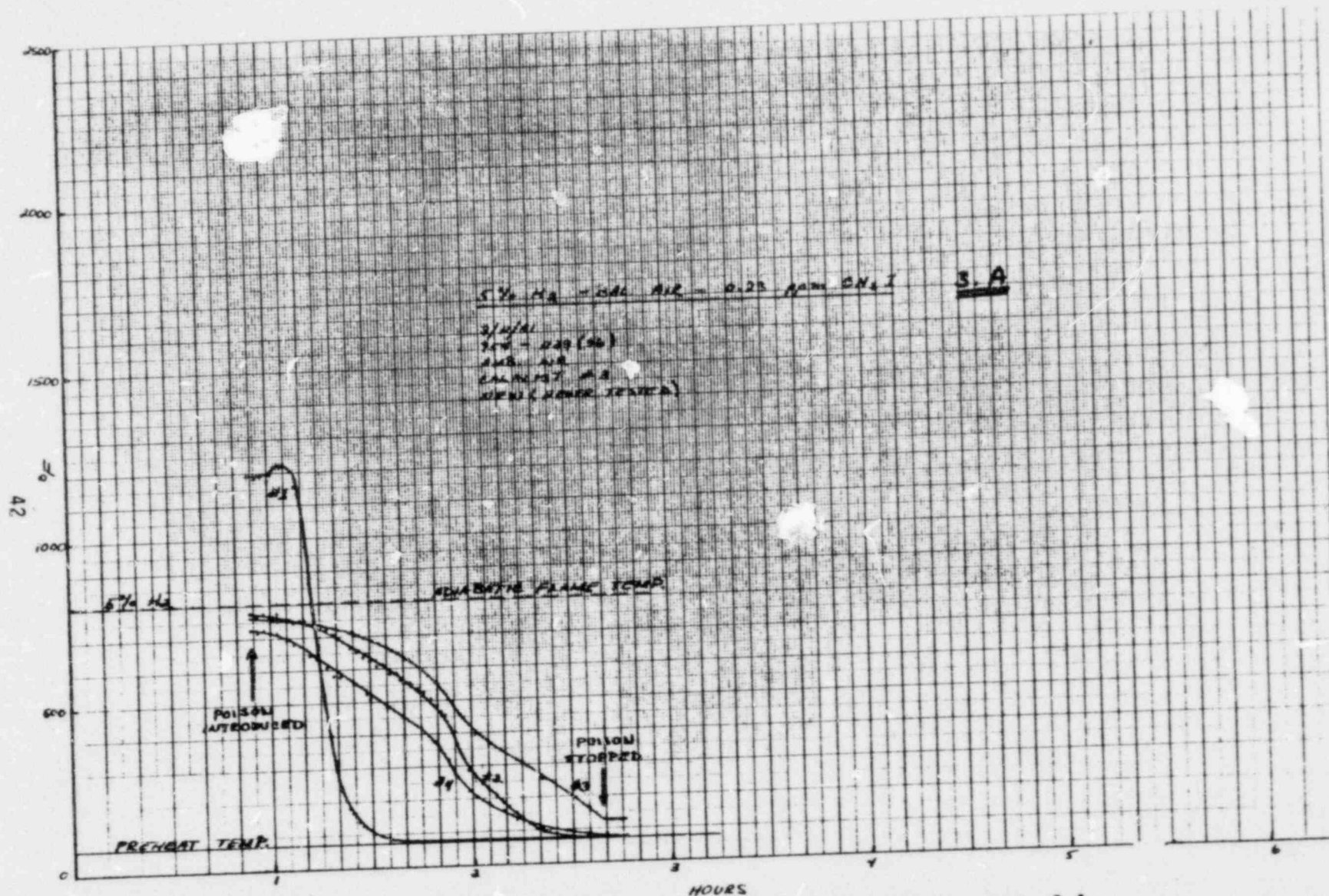


Figure B-6. Time/temperature relationship, test pt. 3.A.

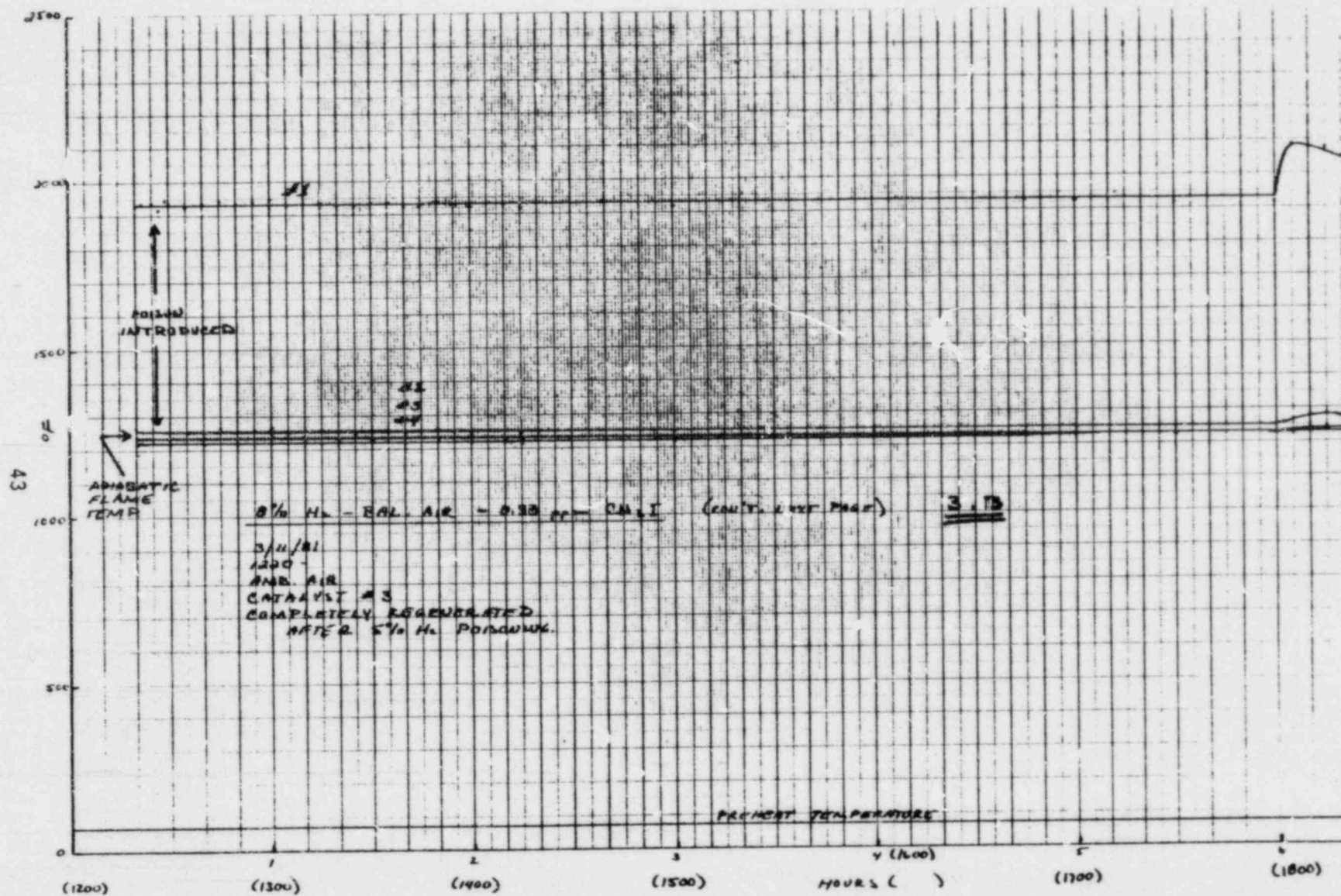
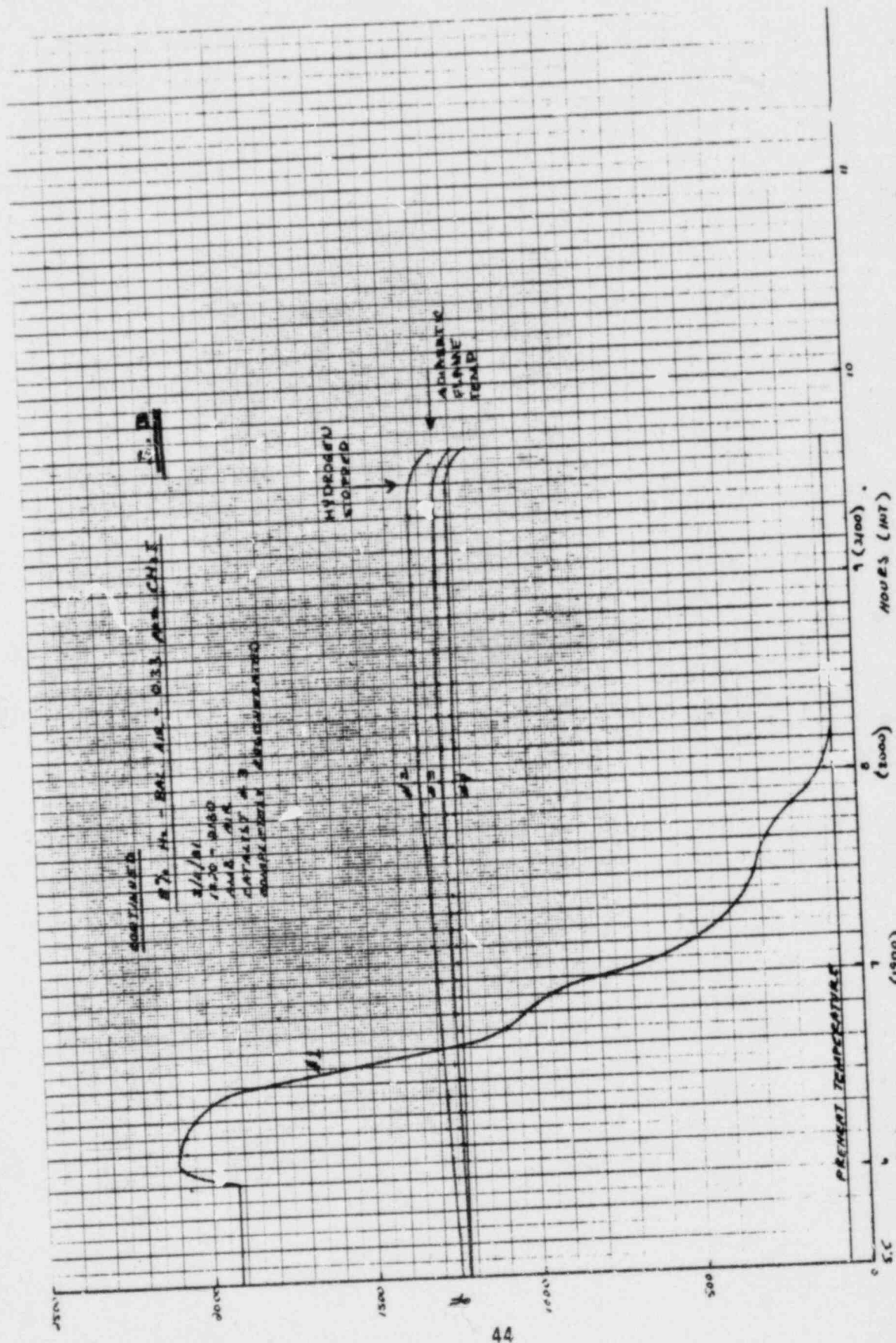


Figure B-7. Time/temperature relationship, test pt. 3.B.



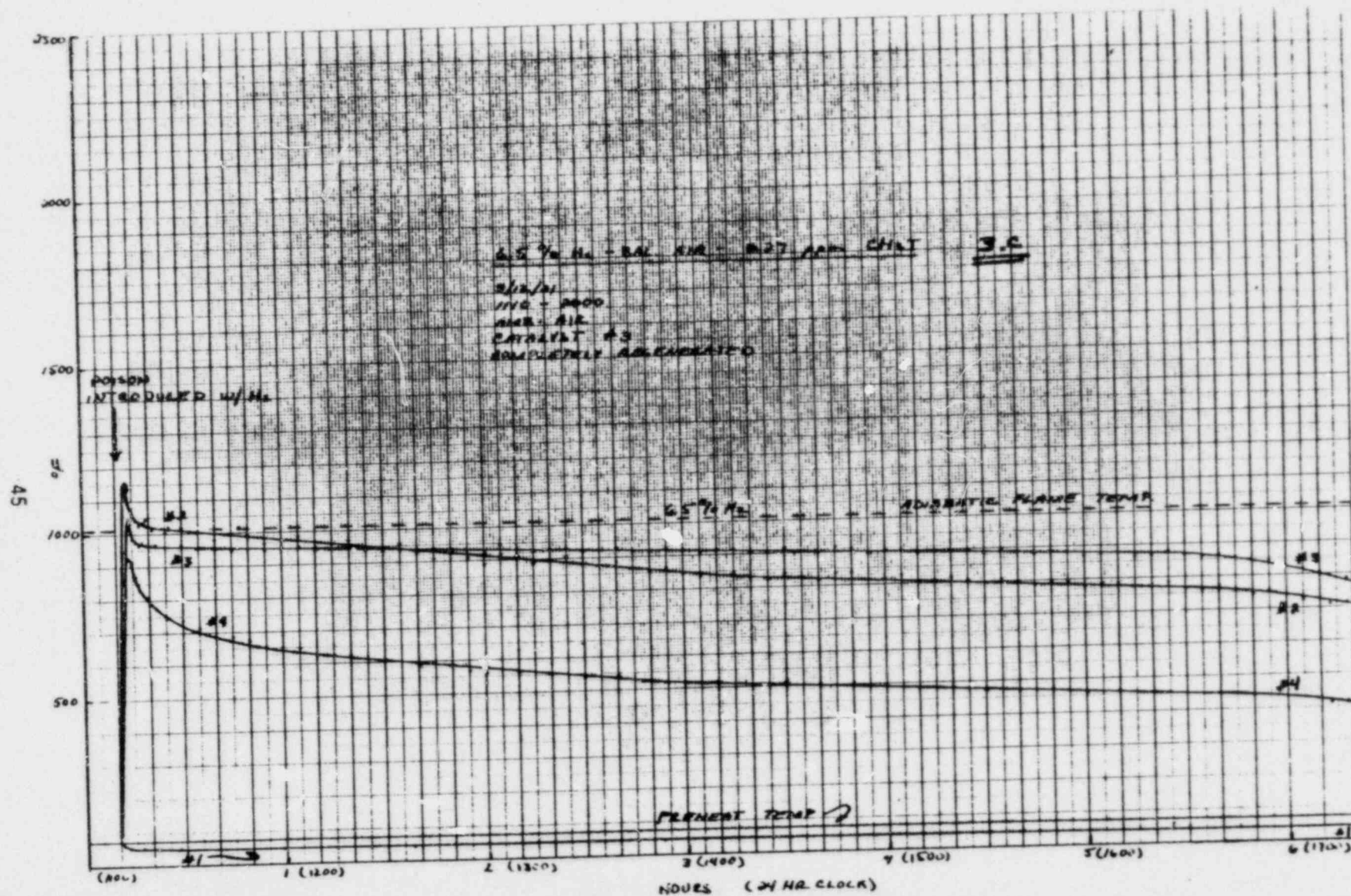


Figure B-9. Time/temperature relationship, test pt. 3.C.

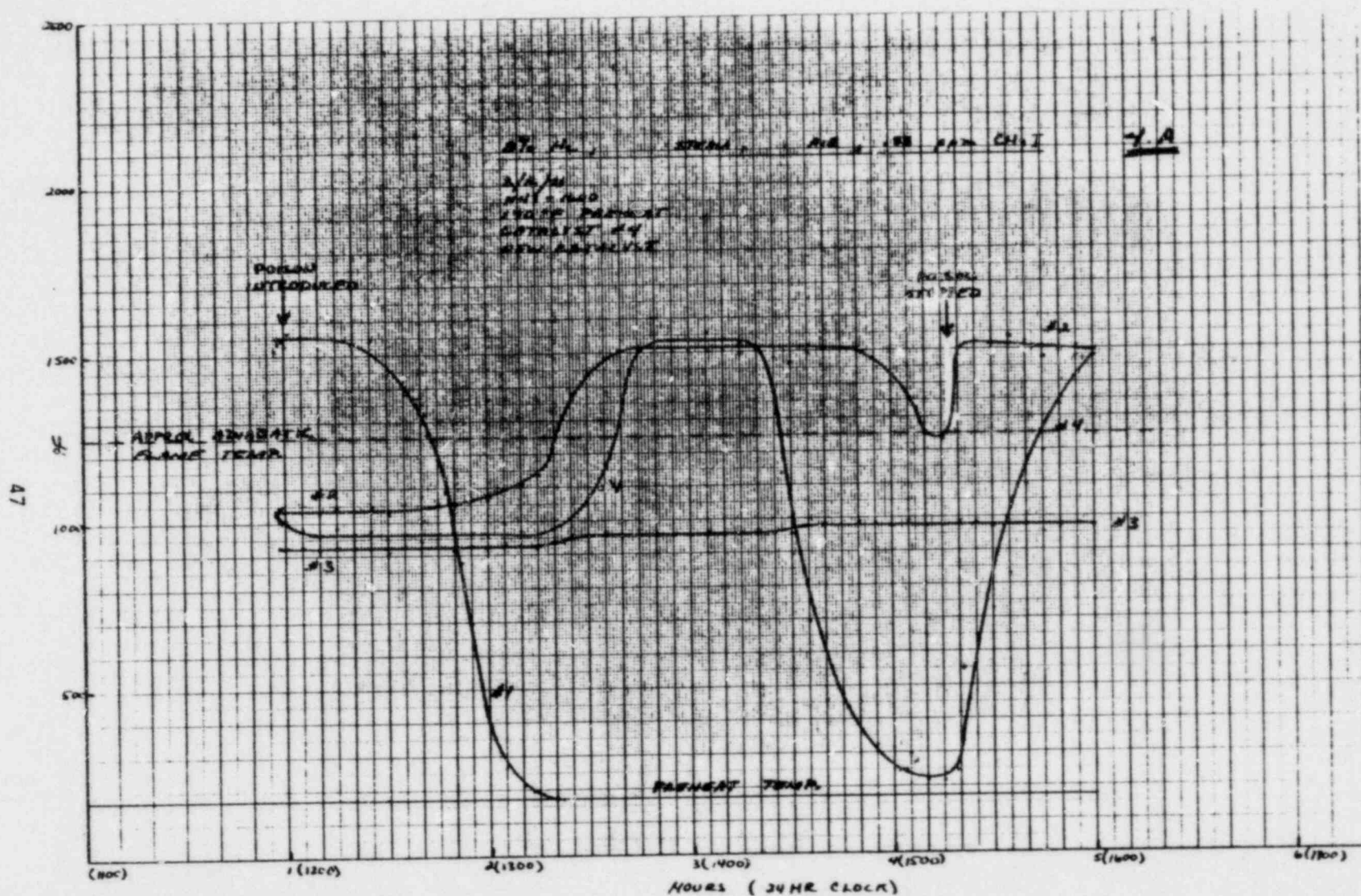


Figure B-11. Time/temperature relationship, test pt. 4.A.

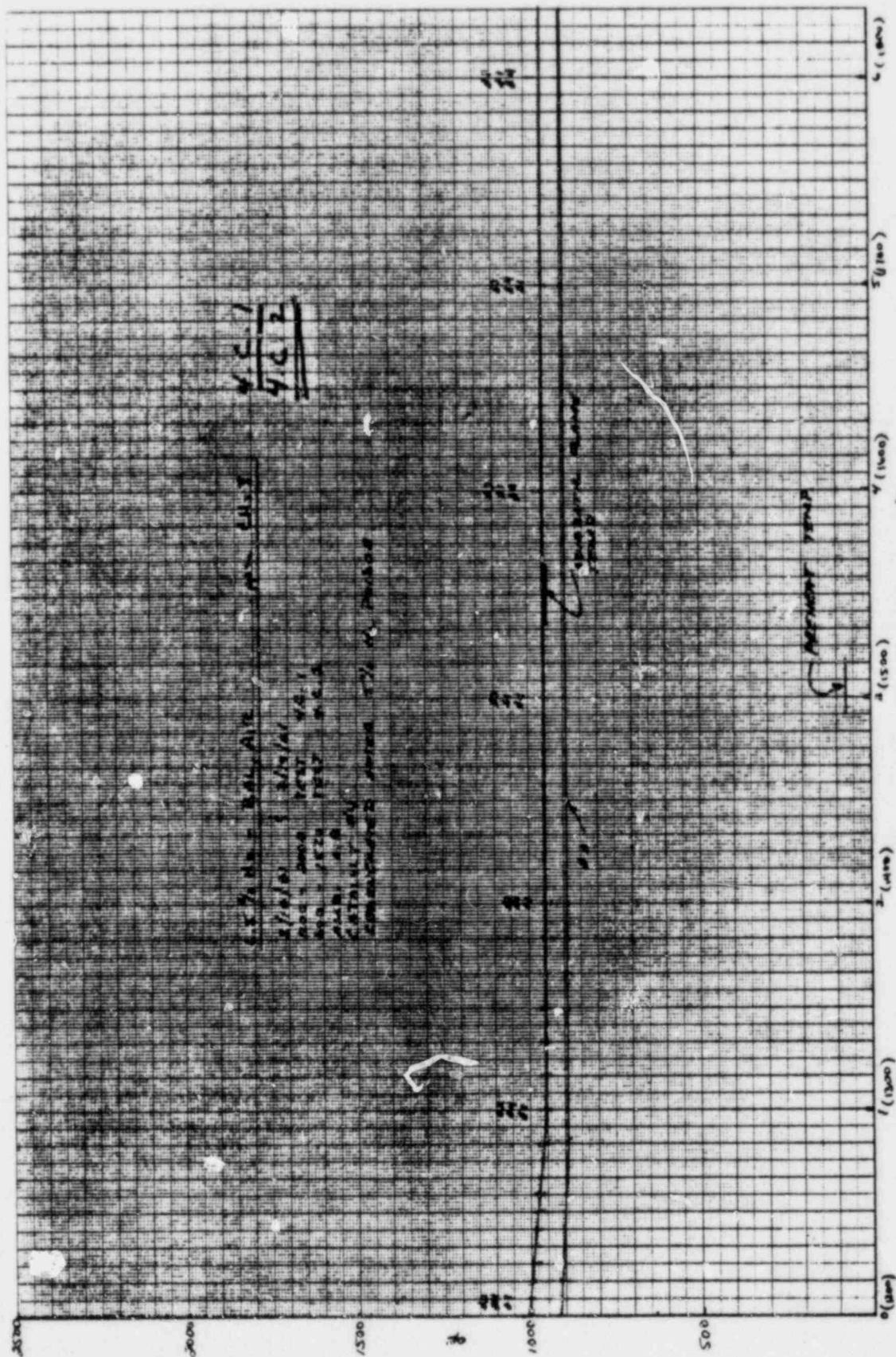


Figure B-13. Time/temperature relationship, test pt. 4.C.

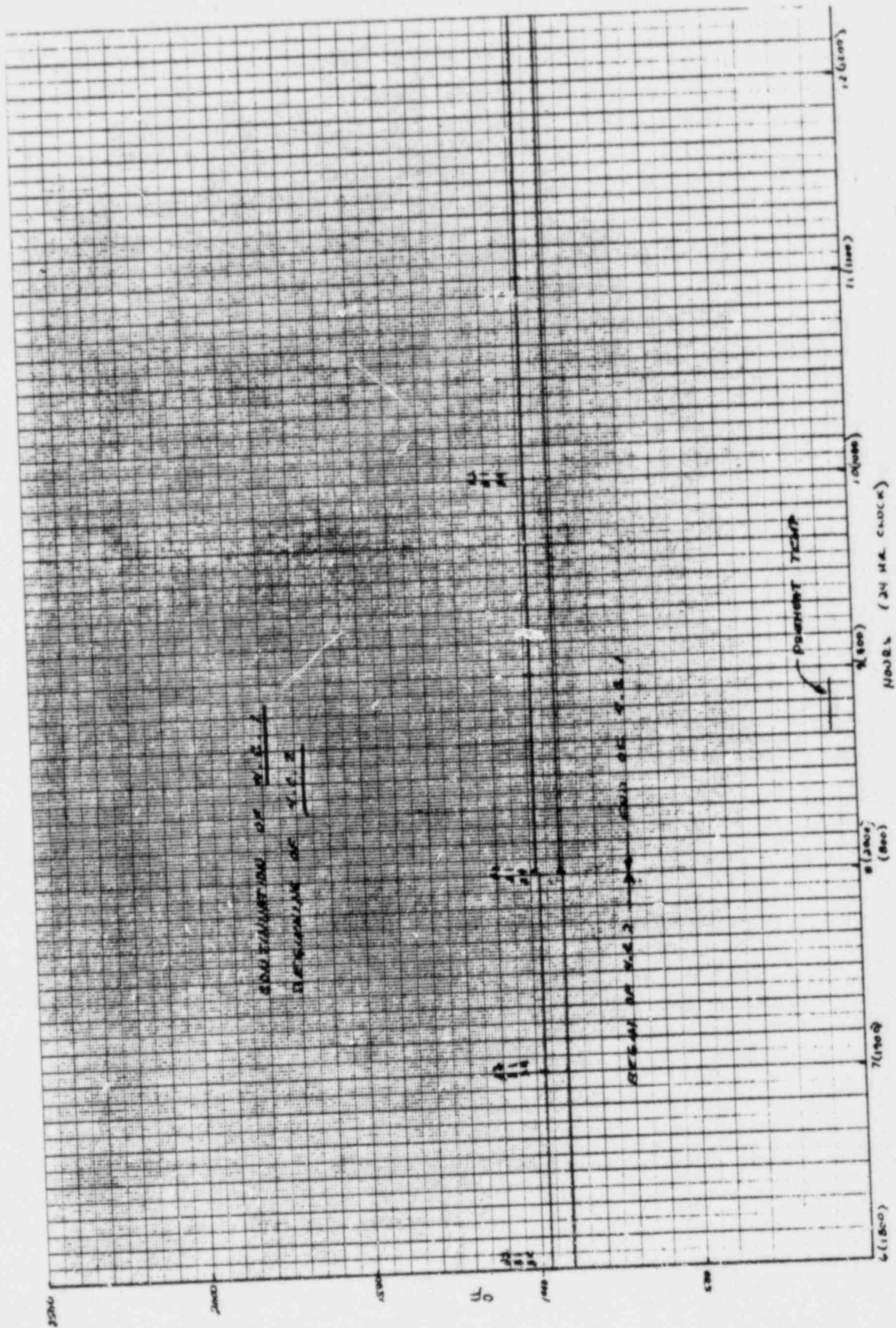


Figure B-14. Time/temperature relationship, test pt. 4.C (continued).

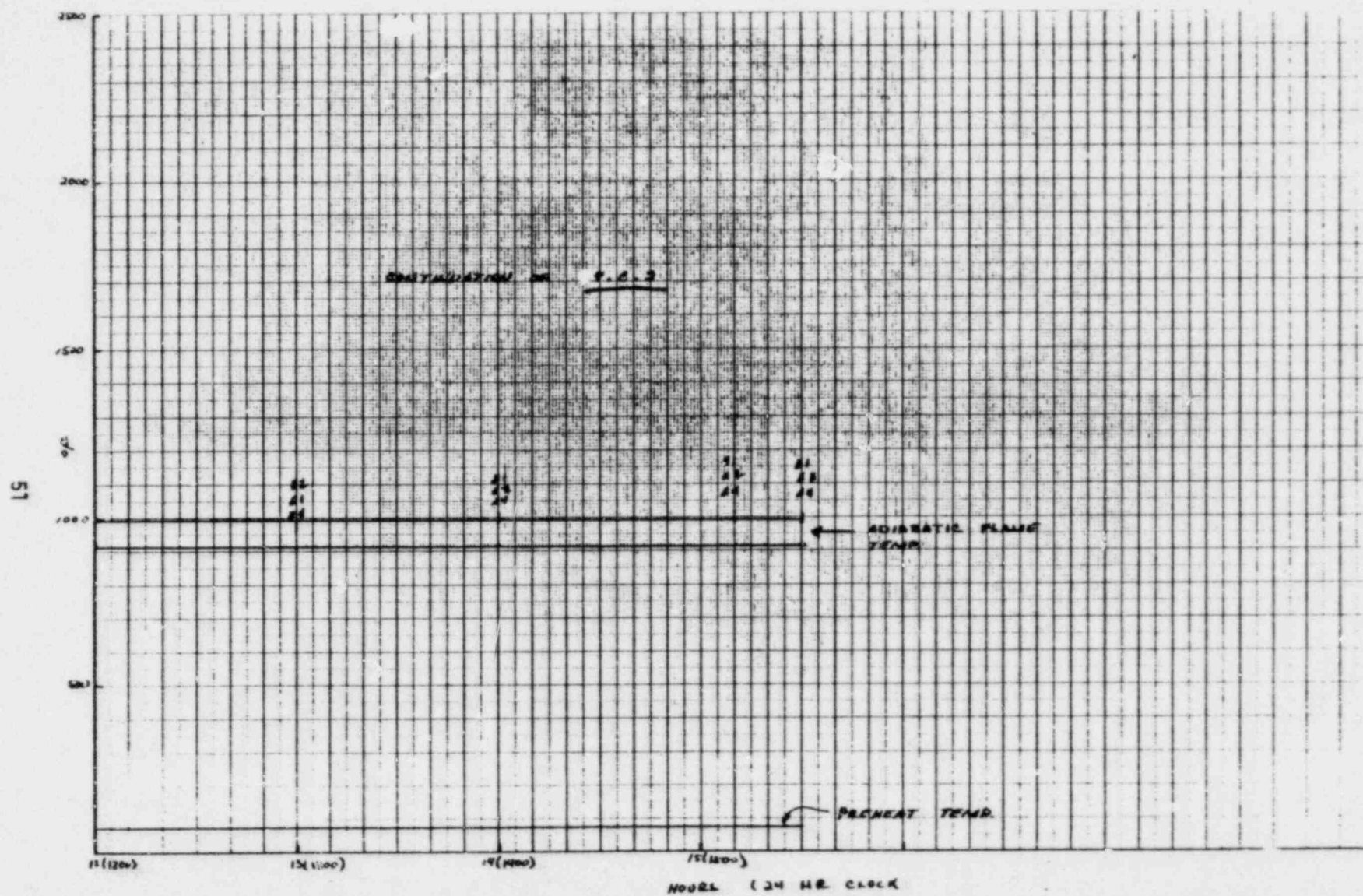


Figure B-15. Time/temperature relationship, test pt. 4.C (continued).

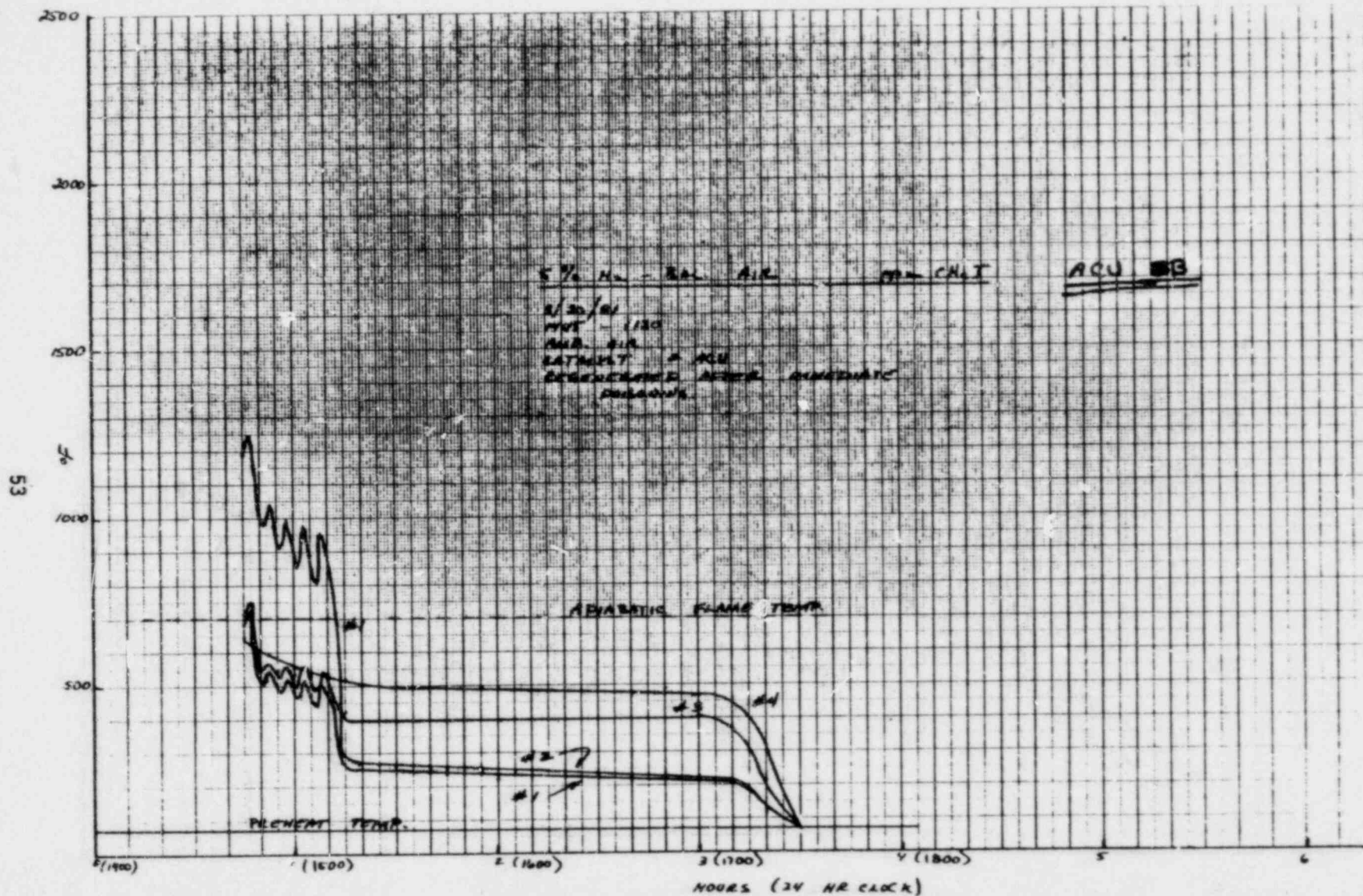


Figure B-17. Time/temperature relationship, test pt. ACU B.

APPENDIX C
ADIABATIC FLAME TEMPERATURE

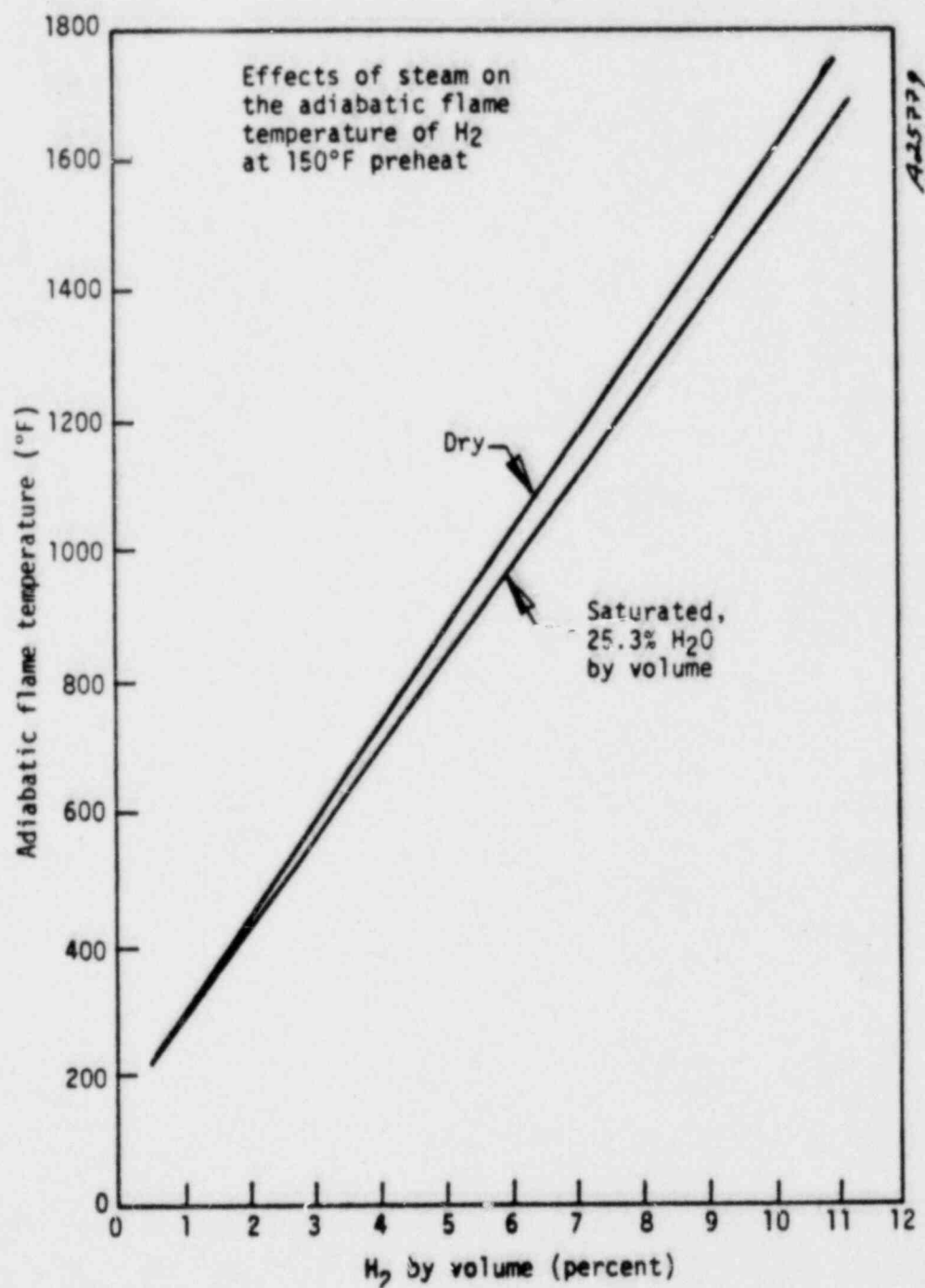


Figure C-1. Adiabatic flame temperature (dry versus 25.3% H_2O saturated).

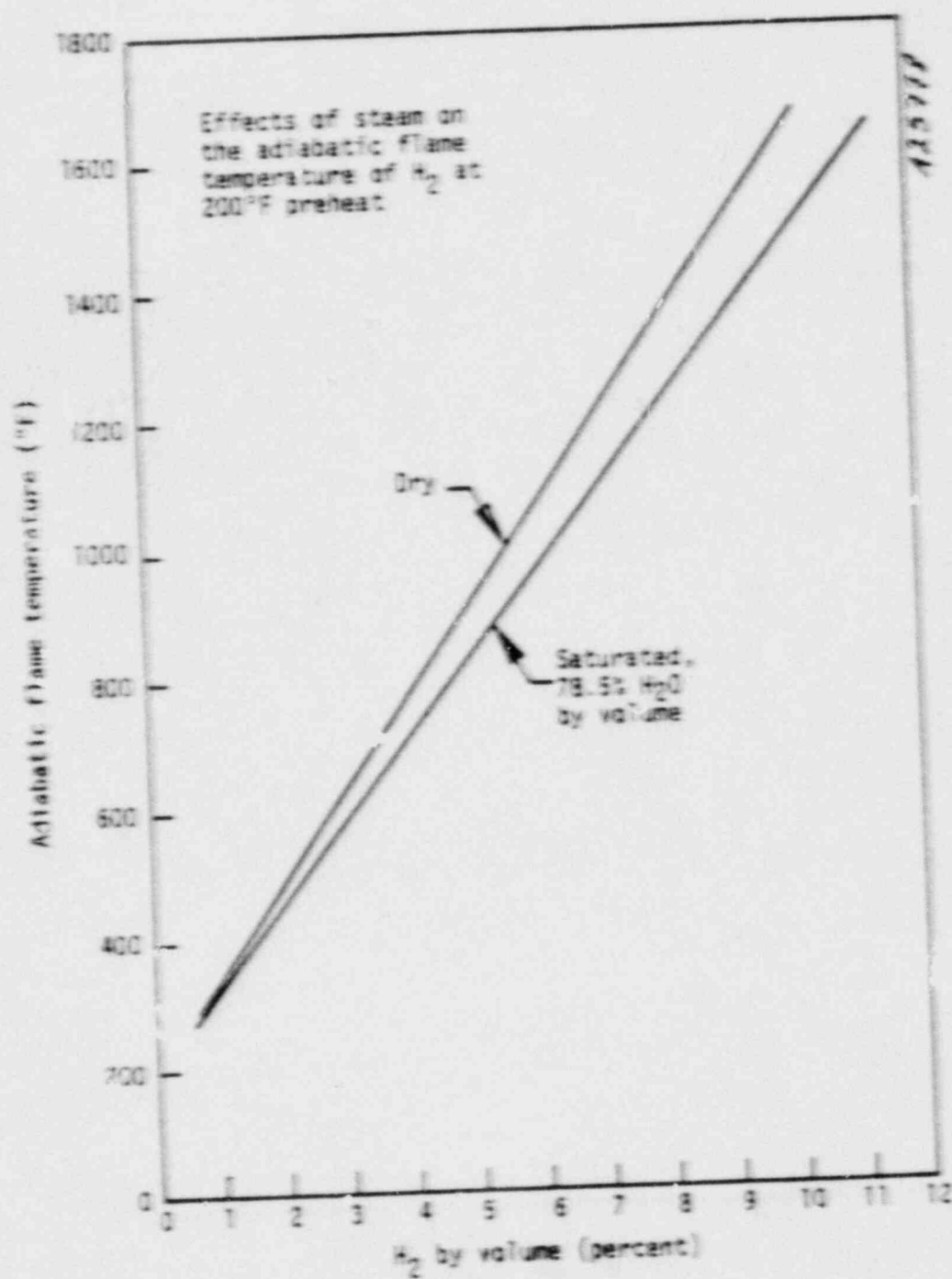


Figure C-2. Adiabatic flame temperature (dry versus 78.5% H_2O saturated).