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HALF-PLANT LOW DICHROMATE EVALUATION AT KW REACTOR
FINAL REPORT -- PRODUCTION TEST-176

A. P. Lerrick

September 30, 1970

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HALF-PLANT LOW DICHROMATE EVALUATION AT KW REACTOR
FINAL REPORT -- PRODUCTION TEST-176

I. INTRODUCTION

Sodium dichromate is added to the Hanford single-pass reactors to control localized corrosion of aluminum-clad fuel elements and aluminum process tubes. The localized corrosion occurs as pitting or as related forms of erosion-corrosion, commonly called groove and ledge corrosion (GLC).

Except for one period of time during 1952, sodium dichromate has been continuously added to the cooling water as a corrosion inhibitor. Severe localized corrosion occurred during the 1952 period when the corrosion inhibitor was not employed. In 1954 an attempt to reduce the dichromate concentration to 0.5 ppm from the 2.0 ± 0.2 ppm (normally 1.8 ppm) which had been satisfactorily employed since reactor startup was terminated due to excessive localized corrosion and fuel ruptures. In the 1954 test, the coolant pH was 7.4. Since 1954, the corrosivity of the coolant to aluminum has been reduced by lowering the pH which has allowed operation at reduced dichromate concentrations. Based on a favorable half-plant test conducted in C Reactor in 1960 employing pH 7.0 coolant, the dichromate concentration was reduced to 1.0 ppm at all single-pass reactors in 1961. The C Reactor test showed that fuel jacket corrosion was substantially increased by reducing the dichromate concentration but that this increase was not severe enough to cause any significant operating problems; therefore, in order to reduce water treatment costs, operation at 1.0 ppm dichromate became standard practice.

With the reduction of coolant pH to the current value of 6.6, several additional tests have been conducted since the 1960 C Reactor test to determine if dichromate concentrations could be further lowered. Data obtained at 0.5 ppm sodium dichromate in the pH 6.6 coolant were contradictory; therefore, additional testing at this dichromate concentration was authorized at KW Reactor (PTA-176).¹ The objectives of the KW Reactor test were:

1. To compare the ability of 0.5 and 1.0 ppm sodium dichromate to inhibit localized corrosion of aluminum fuel element cladding at similar reactor operating conditions.
2. To define the degree of uniform and localized corrosion in 0.5 and 1.0 ppm sodium dichromate as a function of temperature.
3. To define the degree of localized corrosion in 0.5 and 1.0 ppm sodium dichromate as a function of exposure time.

The test was conducted between June 13, 1969 and October 19, 1969. Interim water chemistry specifications for the K Reactors were issued on the basis of a preliminary analysis of the data in November 1969.² The purpose of this document is to report the final results of the test.

II. SUMMARY AND CONCLUSIONS

The primary purpose of this test was to provide a quantitative comparison of fuel element 8001 aluminum alloy cladding corrosion in cooling water containing 0.5 and 1.0 ppm sodium dichromate inhibitor. Secondary purposes were to provide information on cladding corrosion as a function of temperature and as a function of time at both inhibitor concentrations. The primary purpose was well fulfilled: Equations were developed to describe and predict fuel element weight losses at both dichromate concentrations and the effect of dichromate concentration on localized corrosion was clearly established. The corrosion equations show that fuel weight losses can be expected to increase by a factor of 1.45 at a dichromate concentration of 0.5 ppm as compared to exposure to coolant containing 1.0 ppm dichromate. Little effect of dichromate concentration on localized corrosion was observed when fuel cladding temperatures were below 115-120 C but above these temperatures the localized corrosion definitely was more severe in coolant containing 0.5 ppm inhibitor. The localized corrosion (groove corrosion, pitting, erosion corrosion) almost always occurred on the bottoms of the fuel elements, since these surfaces operate at a higher temperature. The bottom rows of fuel element supports rapidly corroded away at the higher temperatures which caused a further increase in local temperatures due to flow imbalances and this in turn accelerated the localized corrosion. Because the higher dichromate concentration reduced the amount of support corrosion, 1.0 ppm dichromate should be employed to control localized corrosion whenever cladding temperatures are expected to be above 120 C for long periods of time. These tests indicated that the corrosion occurring at exposures of 66 operating days, and with clad temperatures of 120 C or above, would not seriously limit fuel integrity at 0.5 ppm inhibitor but that for exposures of 105 operating days extensive pitting corrosion would be expected. However, it was found that even operation at 1.0 ppm dichromate at the longer exposure periods and higher cladding temperatures would reduce but would not completely eliminate localized corrosion.

Based on these data, it is recommended that the sodium dichromate concentration should be controlled as follows:

1. A dichromate concentration of 0.5 ppm should be employed for all operations which result in a maximum fuel element surface temperature below 120 C in the highest powered tube in the reactor, regardless of the exposure time; or, for operation in which fuel cladding temperatures are above 120 C but exposure periods are less than 70 operating days.
2. A dichromate concentration of 1.0 ppm should be employed for all operations which result in over ten fuel columns with fuel cladding surface temperatures exceeding 120 C and exposure periods exceeding 70 operating days.

It is well known that a decrease in pH will reduce aluminum cladding corrosion, and while not investigated during the test, if the severe exposure conditions are expected, it would seem prudent to decrease the pH (6.7 was employed in this test) as well as to operate with higher dichromate concentrations.

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III. EXPERIMENTAL CONDITIONS

A. Water Chemistry

Normal reactor cooling water (alum-coagulated, filtered Columbia River water) from the KW Reactor water treatment plant was used during this test. The sodium dichromate concentration was the only water chemistry variable which was maintained at different levels on the two halves of the reactor during the test. The far (east) side of the KW Reactor was cooled with water containing 0.5 ppm sodium dichromate and the near side (control side) of the reactor was cooled with water containing 1.0 ppm sodium dichromate. Maximum, minimum, and average concentrations are shown in Table I. The average dichromate concentrations very closely approached the nominal specified concentration.

The pH was measured routinely on both sides of the reactor and as may be seen in Table II the average values for the entire test period were 6.69 on each side.

Residual chloride was held at 0.2 ppm on both sides of the reactor during the first month of the test to reduce the Mn-56 radioactivity in the effluent coolant. The residual was reduced to 0.05 ppm on July 17, 1969, where it remained for the balance of the test.

The alum concentration was maintained on both sides of the reactor at about 18 ppm during most of the test using the bauxite generators. During one three-day period in August, 15 ppm of commercial liquid alum was fed as the flocculating agent. Resultant Zeta potentials ranged from 0 to -10 but tended to be near the negative side of the range for most of the test period.

B. Fuel Loadings

A total of 54 columns of fuel elements clad in 8001-F aluminum alloy and fabricated by the standard AlSi process were employed in this test. One-half the fuel was exposed on the test side (0.5 ppm dichromate) and one-half on the control side (1.0 ppm dichromate) of the reactor. Both KSE (enriched to 0.95 percent) and KSN (natural uranium) fuel models with 50-mil thick arch supports were tested.

The number and type of fuel elements in each column were selected so that nominal outlet temperatures of 95, 105, and 115 C could be obtained. The columns with a nominal 95 C outlet consisted of 46 pieces of KSE fuel; the columns with a nominal 105 C outlet consisted of 38 pieces of KSN fuel; and the columns with a nominal 115 C outlet consisted of 51 pieces of KSE fuel. All columns had the normal 16-inch expendable and 5 dummies in the downstream spacer pattern. Nine columns of each loading were exposed on each side of the reactor.

TABLE I. SODIUM DICHROMATE CONCENTRATION, ppm

<u>TEST PERIOD</u>	<u>NEAR SIDE (CONTROL)</u>			<u>FAR SIDE (TEST)</u>		
	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>
June 18 to June 30, 1970	1.02	0.95	0.985	0.50	0.50	0.50
July 1 to July 31, 1970	1.01	0.96	0.995	0.51	0.50	0.50
August 1 to August 31, 1970	1.00	0.98	0.995	0.55	0.52	0.505
September 1 to September 30, 1970	1.00	0.98	0.995	0.50	0.50	0.50
October 1 to October 18, 1970	1.00	0.95	0.995	0.50	0.50	0.50

TABLE II. COOLANT pH

<u>TEST PERIOD</u>	<u>NEAR SIDE (CONTROL)</u>			<u>FAR SIDE (TEST)</u>		
	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>
June 18 to June 30, 1970	6.70	6.66	6.685	6.96	6.66	6.699
July 1 to July 31, 1970	6.73	6.67	6.688	6.74	6.66	6.685
August 1 to August 31, 1970	6.73	6.66	6.695	6.72	6.67	6.695
September 1 to September 30, 1970	6.70	6.65	6.681	6.70	6.65	6.679
October 1 to October 18, 1970	6.70	6.66	6.680	6.70	6.66	6.680

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It was originally intended that three columns of each type be discharged at three separate outages but, because of temperature problems induced by changes in fuel loadings in the remainder of the reactor, three columns of each type were discharged at the end of the first exposure period and all remaining test columns were discharged at the end of the second exposure period.

All fuel columns were charged into smoothbore Zircaloy-2 process tubes.

C. Temperature Data

Inlet and outlet coolant temperature data were measured daily on all tubes during the initial month of testing and then every other day thereafter. Inlet temperatures were 15.9 C at the start of the test, reached a peak of 19.4 C late in August, and decreased to 14.9 C at the end of the test. Complete inlet temperature data are given in Table III.

Outlet temperatures for each individual tube varied several degrees centigrade during any given operating period. Figure 1 gives the daily outlet temperatures for a typical group of fuel columns - those operating at nominally 115 C in coolant containing 0.5 ppm sodium dichromate. Similar plots were made for the other five groups of fuel columns. At the end of the second operating period solid aluminum dummies were inserted into the downstream dummy pattern to increase the temperatures of nine selected fuel columns which were operating at temperatures slightly lower than others in their group. Time-weighted maximum temperatures were calculated from these daily temperature curves for each operating period and are shown in Figure 2. Using the type of data shown in Figure 2, fuel columns which had been operating at similar conditions on both sides of the reactor were selected for discharge for the first discharge. As may be seen in Figure 2, the fuel columns operated at very similar temperature conditions on both sides of the reactor during the first four operating periods. During the fifth and sixth operating periods, a large divergence in outlet temperatures occurred on the columns operating at the lower temperatures and it was decided at that time to discharge all remaining fuel columns while the operating data were still comparable.

D. Fuel Exposures

The minimum and maximum exposure for each grouping of fuel columns is given in Table IV. These exposure values are the range of individual tube average exposures as calculated by the PTA computer program from daily operating data. Because corrosion is dependent on the number of days operation at a given temperature rather than on exposure in terms of MWD/T, the actual days of operation are also given in Table IV.

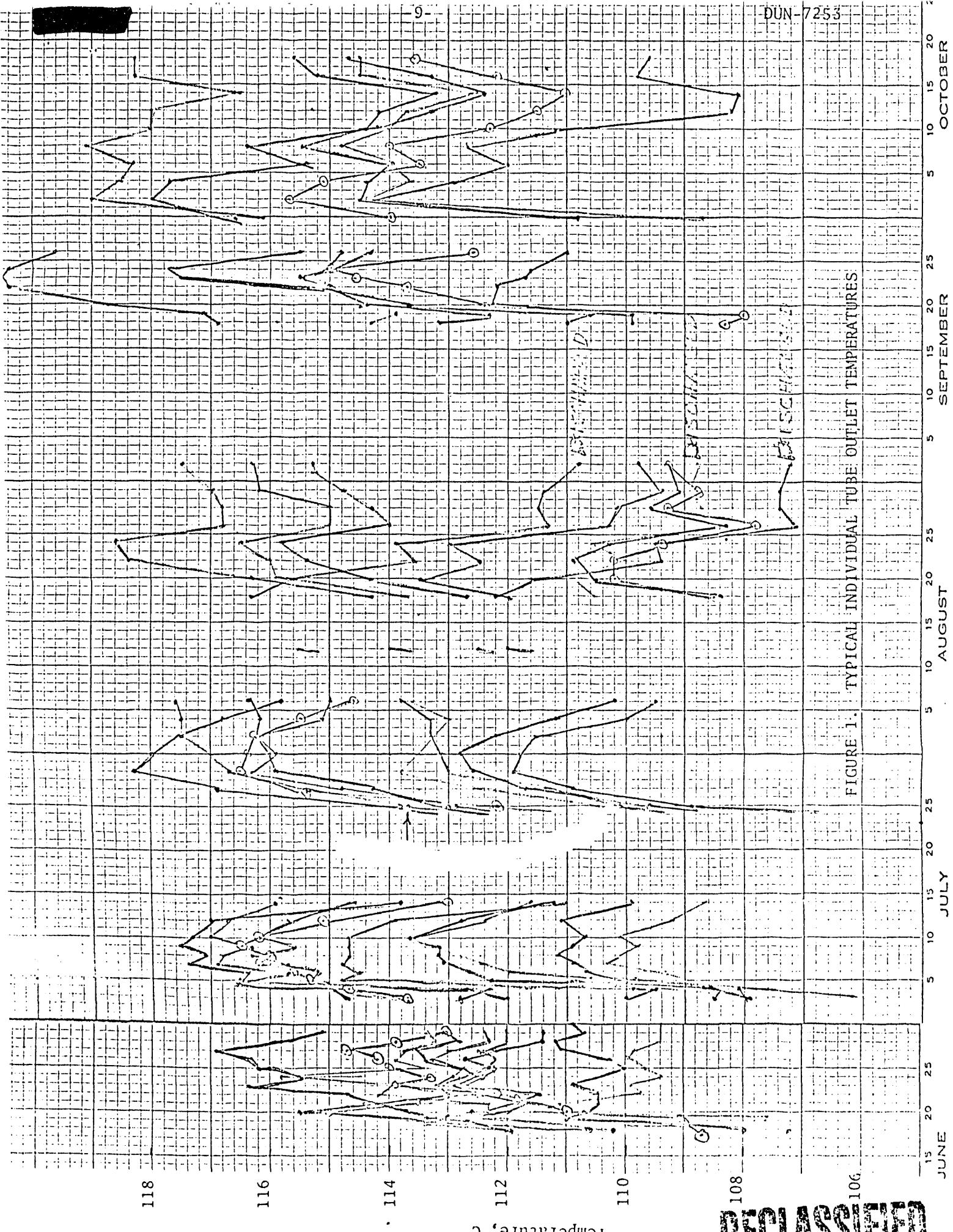
TABLE III. INLET COOLING WATER TEMPERATURE, C

<u>Date</u>	<u>June</u>	<u>July</u>	<u>August</u>	<u>September</u>	<u>October</u>
1					
2		16.4	18.6	18.8	17.0
3		16.4			
4		16.3	18.3		16.2
5		16.4			
6		16.6	18.1		16.2
7		16.6			
8		16.9		18.3	16.3
9		17.1			
10		18.0	18.7	18.8	15.9
11					
12		17.2	18.1	19.0	15.6
13					
14		17.0			15.1
15					
16			18.7		15.0
17					
18				18.2	14.9
19	15.9			18.0	
20	15.9		19.0	18.0	
21	15.8				
22	15.8		19.0		
23	15.8	18.0			
24	15.8		19.4	17.7	
25	15.8	18.5			
26	15.6		18.8	17.7	
27	15.6	18.3			
28	15.4		18.3		
29		18.8			
30			18.2	17.9	
31		18.8			

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Temperature, C

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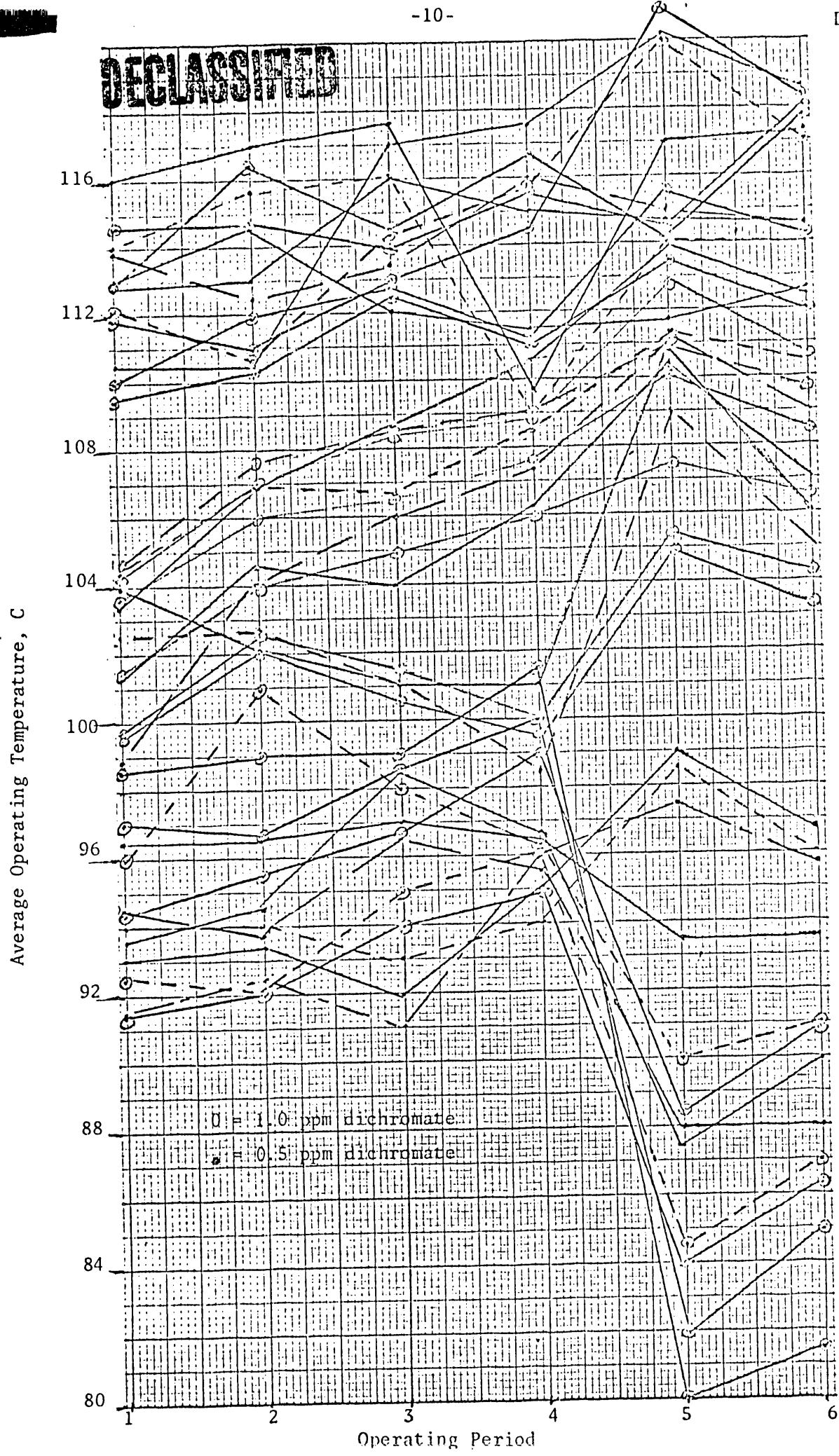


FIGURE 2. AVERAGE OUTLET OPERATING TEMPERATURES

TABLE IV. FUEL EXPOSURES

Goal Temp.	Fuel Type	Fuel Elements per Column	Exposure, *MWD/T	Tube Power, KW
			Min.	Max.
95 C	K5E	46		
	First Discharge		689	827
	Second Discharge		1103	1190
105 C	K5N	38		
	First Discharge		651	717
	Second Discharge		1031	1103
115 C	K5E	51		
	First Discharge		796	822
	Second Discharge		1231	1297

* All fuel was charged June 13, 1969

First discharge was September 3, 1969 (82 calendar days, 66 operating days)

Second discharge was October 19, 1969 (128 calendar days, 105 operating day)

IV. RESULTS

A. Uniform Corrosion

1. Fuel Weight Losses

An excellent correlation of fuel cladding weight loss versus the reciprocal of the absolute value of the surface temperature was obtained in coolant containing both 0.5 and 1.0 ppm sodium dichromate. A summary of the weight loss data is shown graphically in Figure 3 and the data from which Figure 3 is derived are shown in Figures 4, 5, 6, and 7. At any given fuel cladding surface temperature, corrosion increased with time and with a decrease in dichromate concentration. The weight loss data for the K5N fuel in Figures 4-7 were corrected by the area ratio of K5N to K5E fuel so that all data could be plotted on one figure.

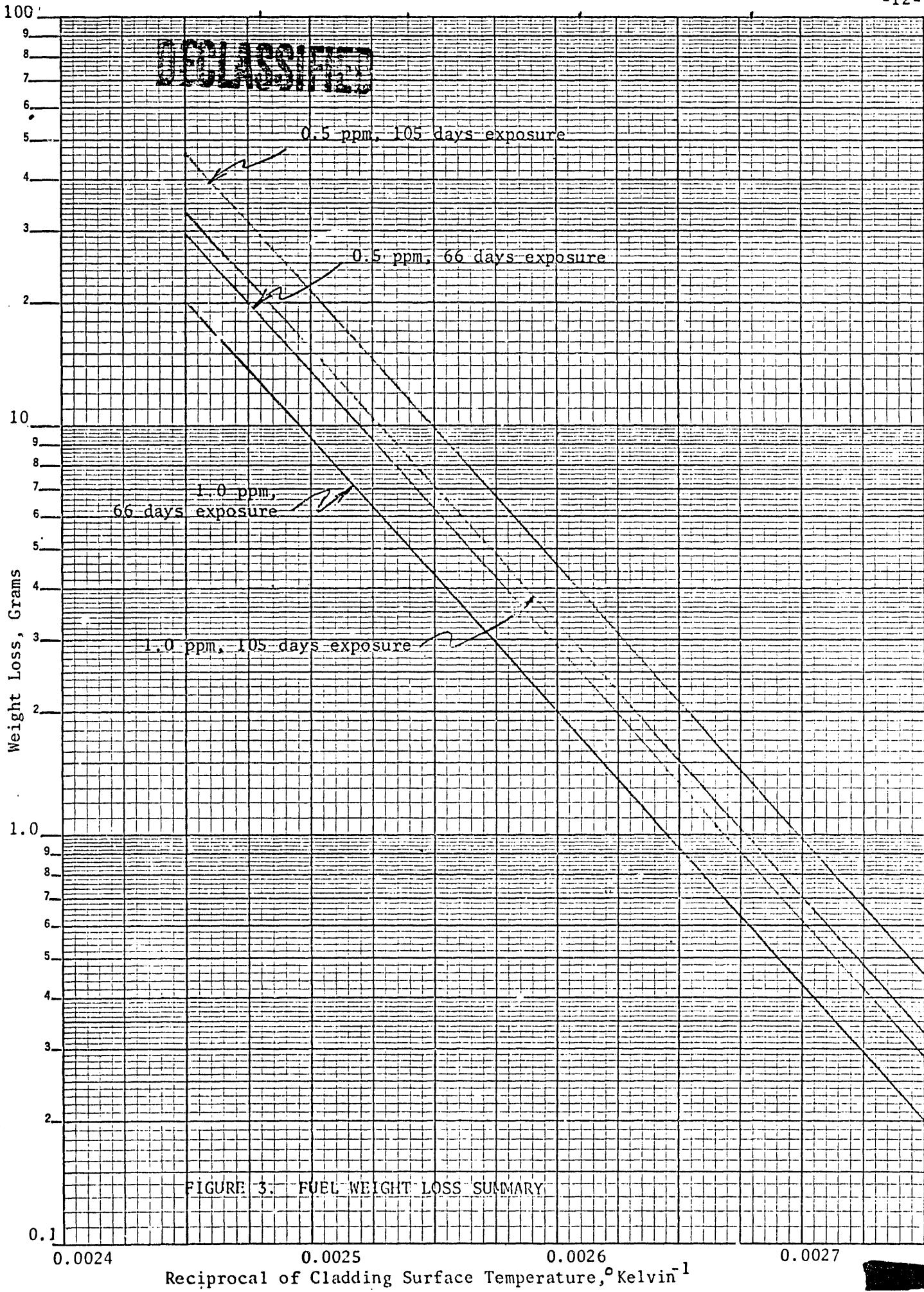
Corrosion rates, which were derived from Figure 3, are shown in Table V. The rate at any given temperature was linear with time.

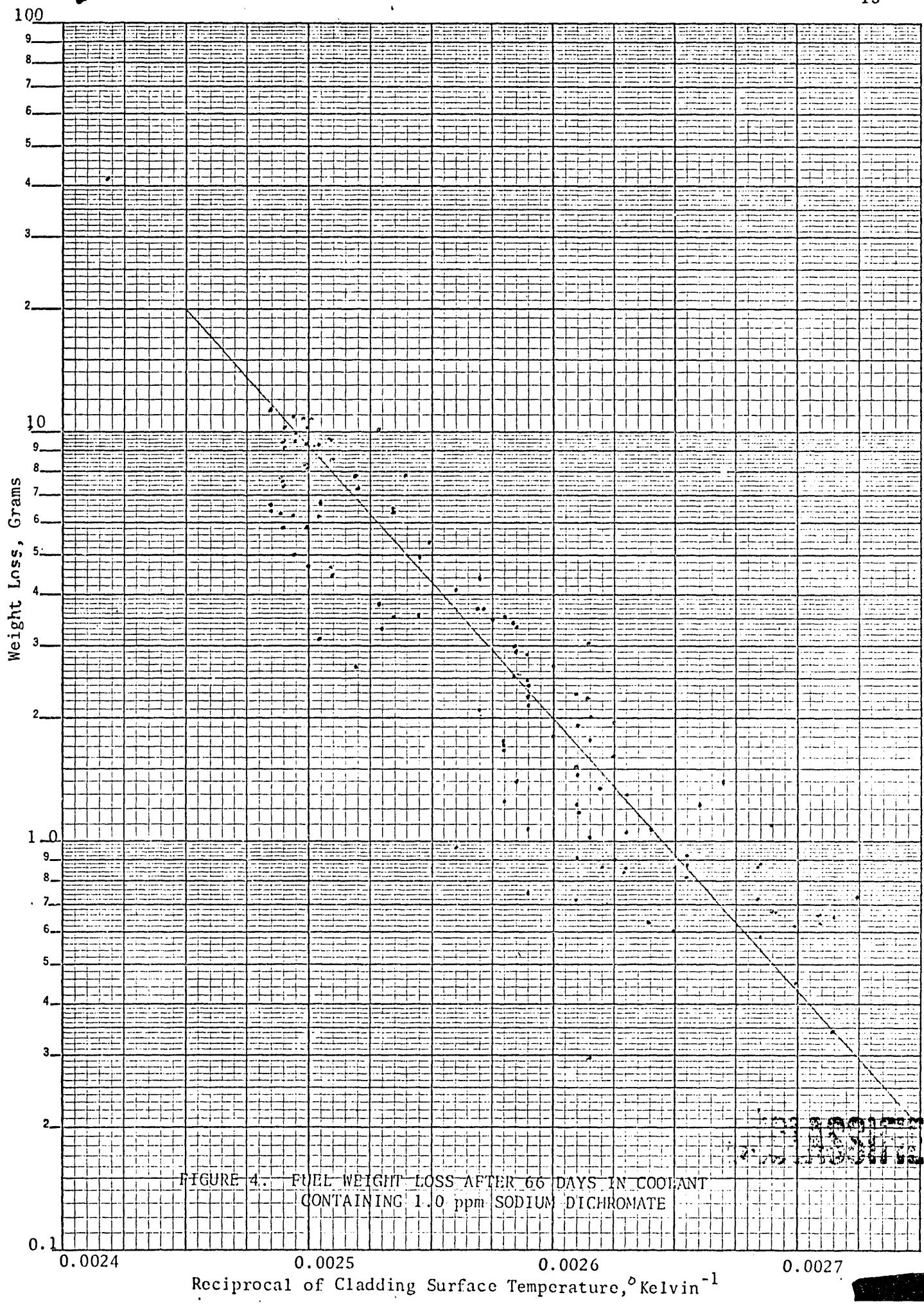
TABLE V. FUEL CLADDING UNIFORM CORROSION
(Mils/Day Penetration*)

Dichromate Concentration, ppm	Temperature, C			
	100	110	120	130
0.5	0.0054	0.016	0.046	0.11
1.0	0.0037	0.011	0.032	0.079

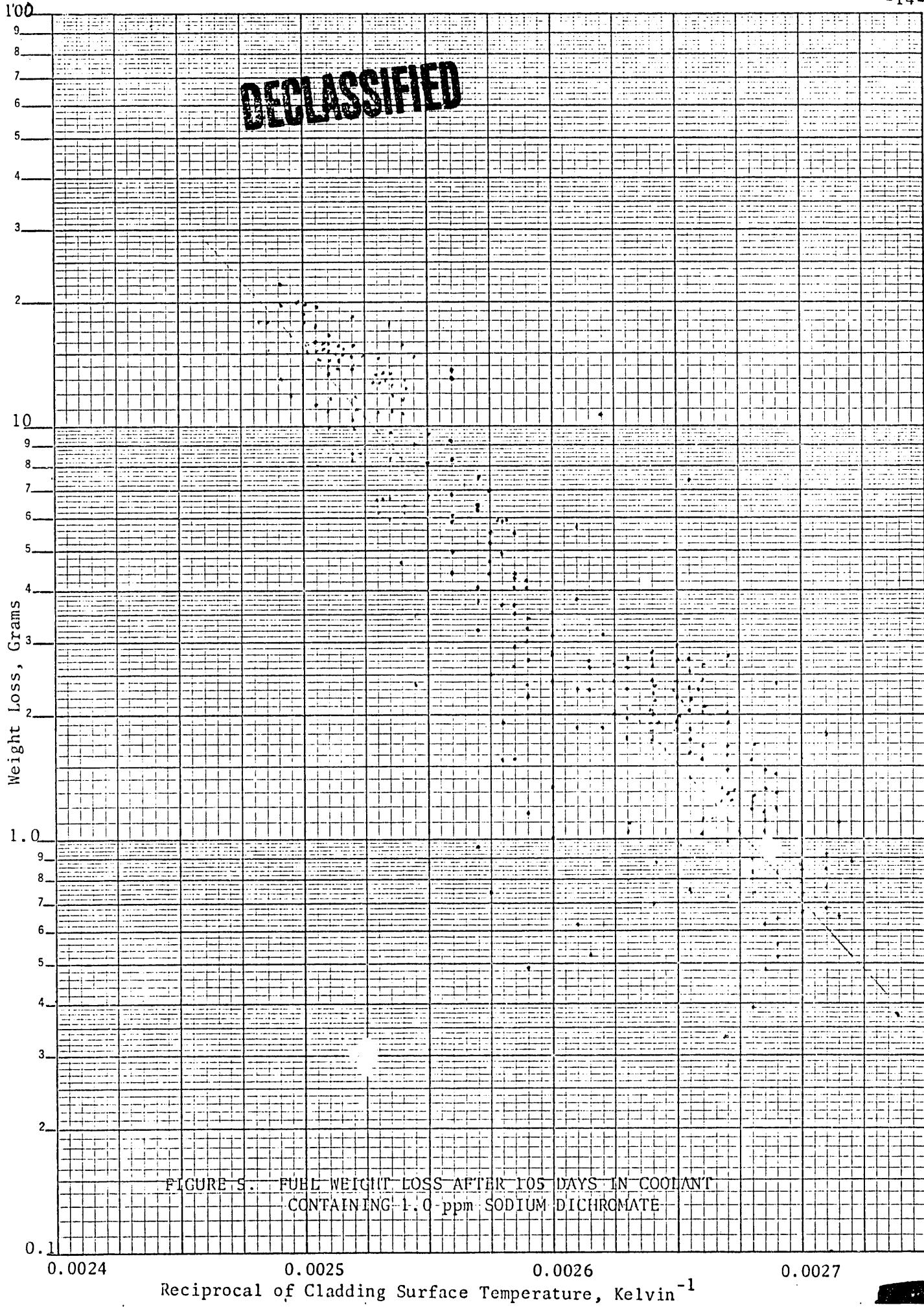
* Calculated from weight loss data in Figure 3. One mil/day penetration is equivalent to 3.30 grams/day weight loss on K5N fuel and 2.37 grams/day on K5E fuel.

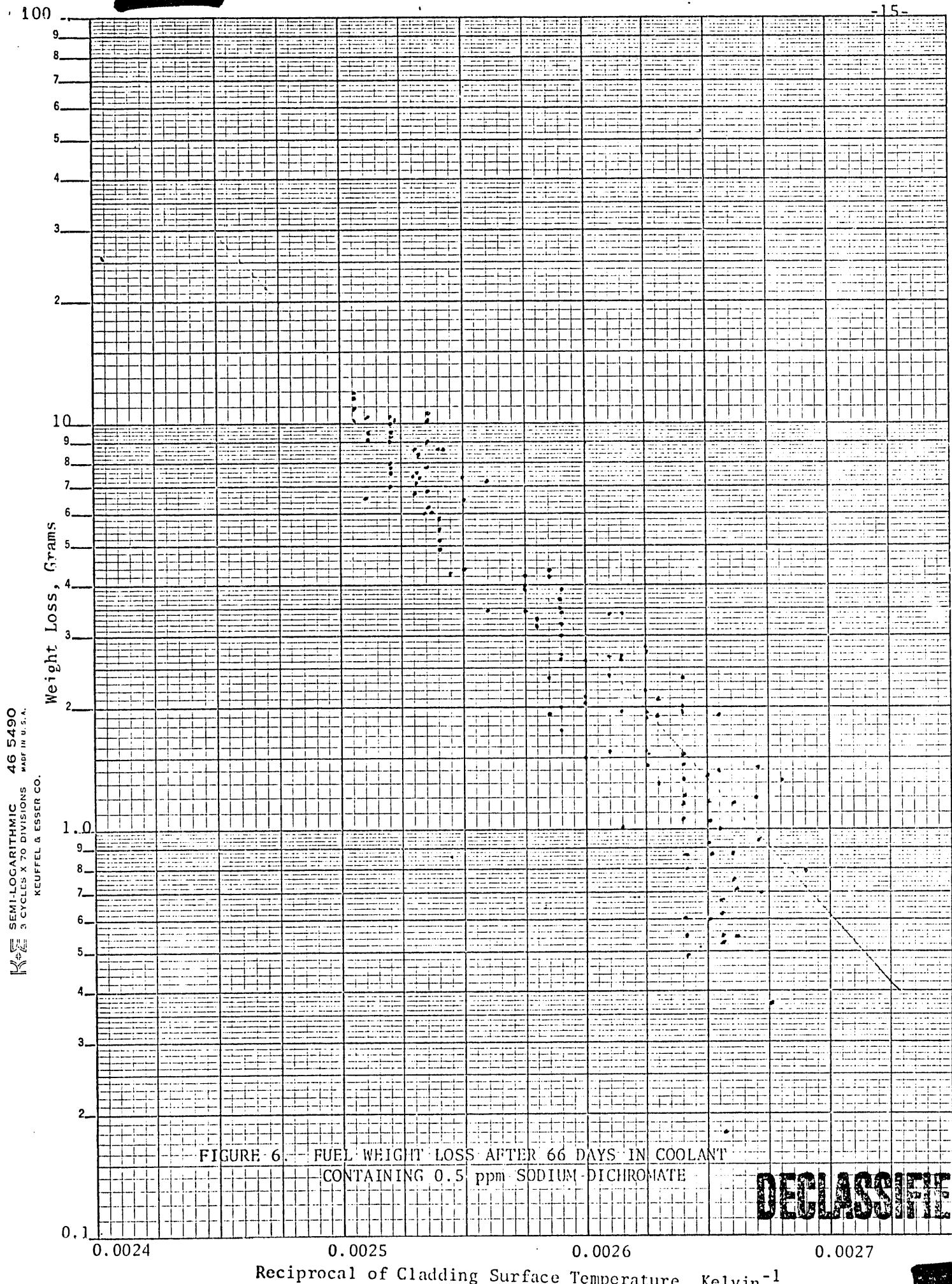
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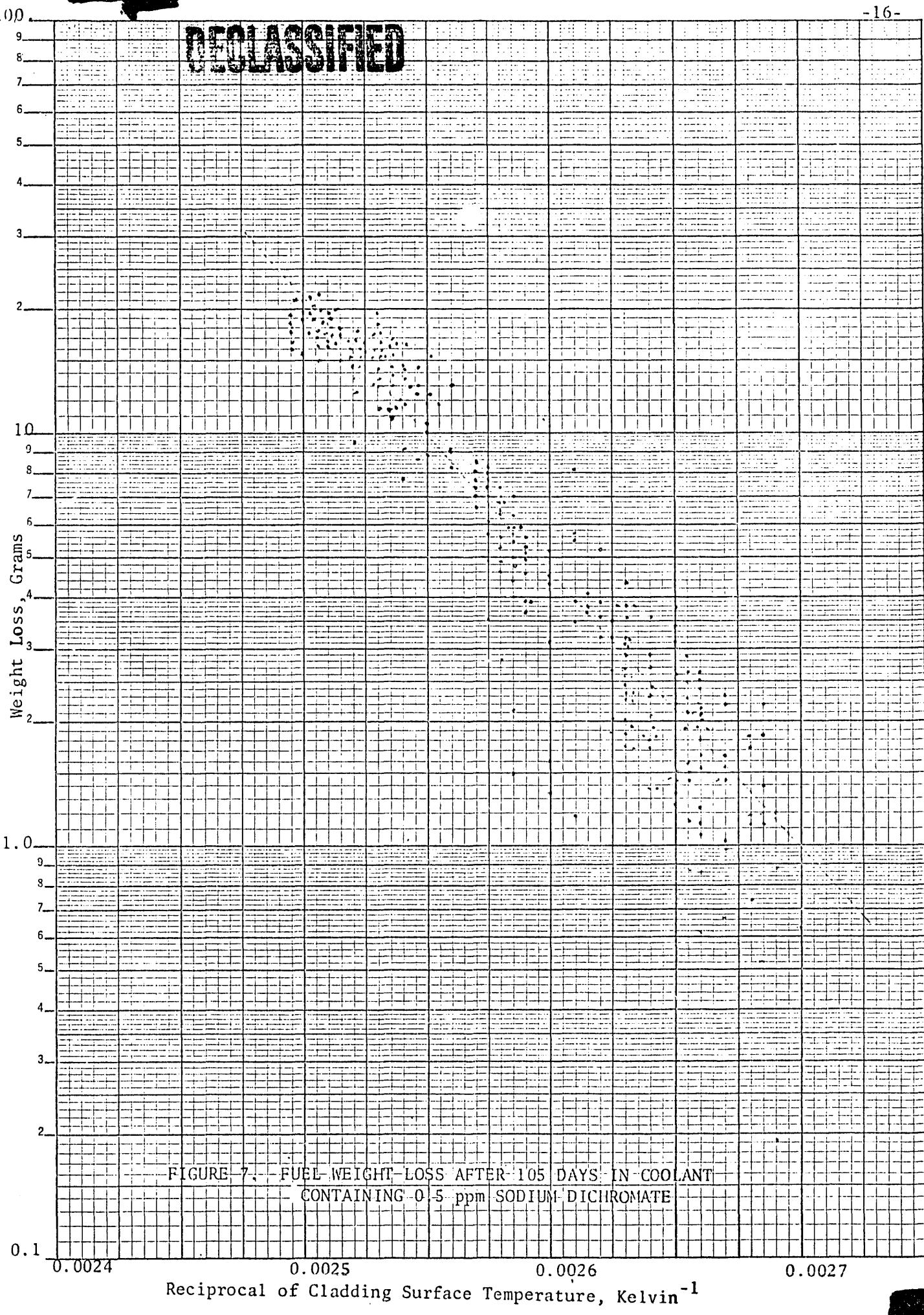




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An increase in fuel cladding temperature by ten degrees Centigrade increased the corrosion by a factor of 2.5 to 3.0 while an increase in fuel cladding temperature of 7.5 C doubled the corrosion rate. A decrease in the dichromate concentration from 1.0 to 0.5 ppm increased the corrosion rate by a factor of 1.45.

2. Mathematical Correlation

The fuel weight loss data were examined to determine if a suitable equation could be found which described the data over the entire range so that predictions of weight loss could be calculated for future tests. As discussed above, a very good fit of the data for each discharge and each sodium dichromate concentration was found by plotting the logarithm of the weight loss versus the reciprocal of the absolute value of the fuel cladding surface temperature (see Figures 4-7). Plots of the weight loss versus time at a given temperature obtained from Figures 4-7 indicated that the kinetics of the corrosion process were zero order; i.e., of the type described by the equation
$$-\frac{dW}{dt} = kW^0$$
, where W is

the weight loss, t is the time and k is the reaction rate constant. Integration of the equation yields an equation of the form $W=kt+C$ showing that the kinetics are linear with time. The C is a constant of integration and for data from this test C was zero.

For many chemical reactions where the rate constant varies with temperature the variation can be represented by an Arrhenius equation of the form $\frac{d\ln k}{dT} = \frac{\Delta E^*}{RT^2}$, where T is the absolute temperature,

R is the gas constant, and ΔE^* is the energy of activation. Integration of this equation yields $\ln k = \frac{-\Delta E^*}{RT} + C_1$ or $k = Z e^{\frac{-\Delta E^*}{RT}}$, where

C_1 and Z are constants. A plot of $\ln k$ versus $1/T$, shown in

Figure 8, yielded excellent straight lines, in agreement with theory. Using a value of R of 1.987 calorie/degree/mole, the activation energy at 0.5 and 1.0 ppm sodium dichromate concentrations were 30,401 and 30,365 calories, respectively, or an average of 30,382 calories. Using the average value of the activation value, the value of Z for 0.5 ppm dichromate is calculated to be 8.315×10^{15} grams/day and for 1.0 ppm to be 5.60×10^{15} grams/day.

Combining the kinetics equation and the activation energy equation yields an equation which can be used to predict fuel cladding weight losses.

For cladding corrosion in coolant containing 0.5 ppm sodium dichromate the equation is:

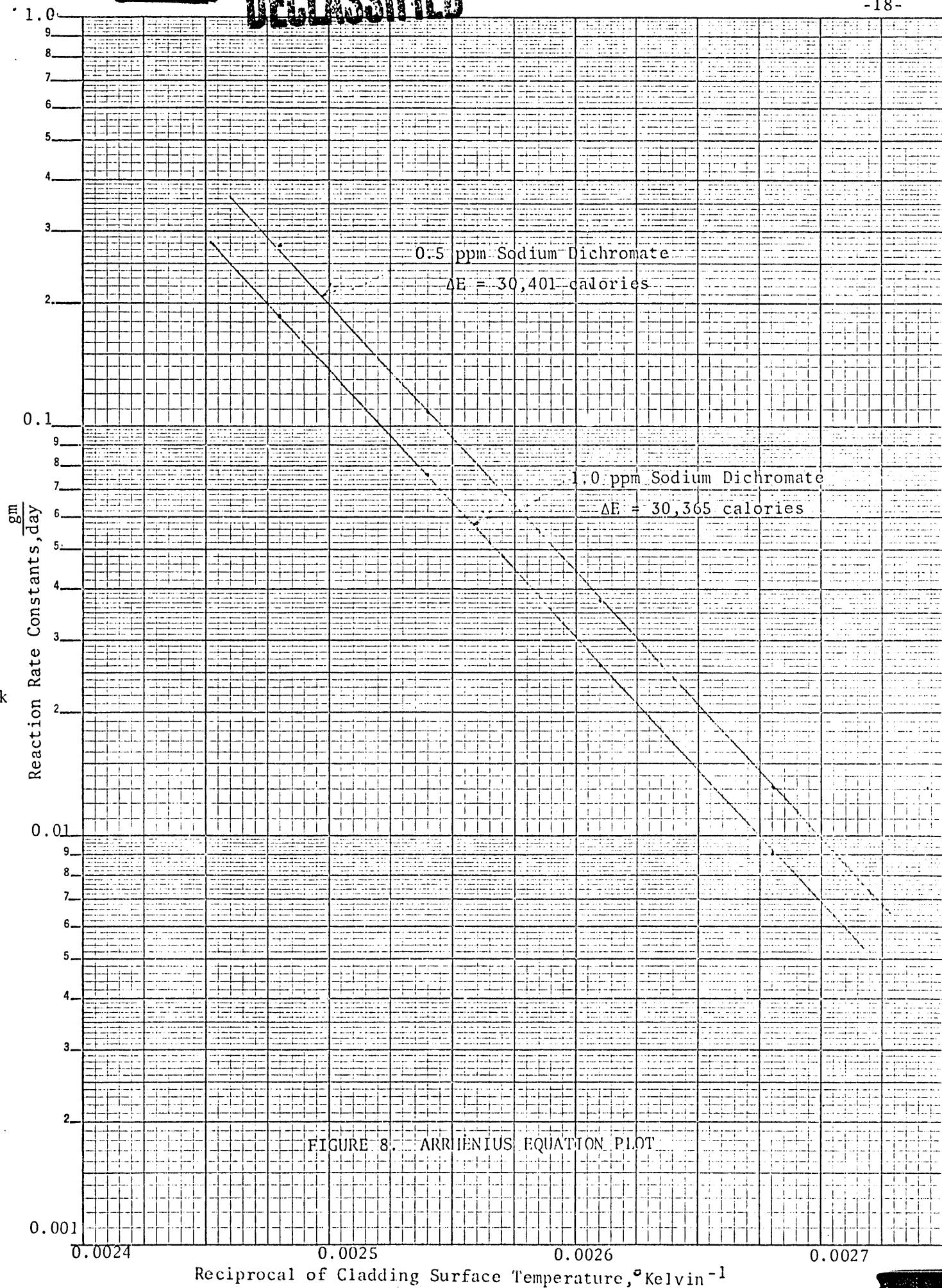
$$W = (8.315 \times 10^{15}) \left(\exp \frac{-30,382}{1.98 T} \right) (t)$$

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where W is weight loss in grams, T is surface temperature in degrees Kelvin and t is time in days.

For cladding in coolant containing 1.0 ppm sodium dichromate the equation is:

$$W = (5.60 \times 10^{15}) \left(\exp \frac{-30,382}{1.98 T} \right) (t)$$

In agreement with the data presented in the previous section, the expected weight loss at a given time and surface temperature with these equations is about 1.45 greater in coolant containing 0.5 ppm sodium dichromate than in coolant containing 1.0 ppm sodium dichromate.

B. Localized Corrosion

1. Severity of Attack

The uniform corrosion data presented above are helpful in predicting fuel cladding life but do not present the true picture of the corrosion processes occurring. The uniform corrosion losses are calculated from the weight losses, which can be measured quite accurately. However, inherent in the calculation is the assumption that the weight losses occur uniformly over the entire fuel element surface. Such is not the case. During a visual inspection of the fuel after exposure in the reactor, it is very evident that much more corrosion occurs on the bottom 90 degrees of the surface than on the remainder of the surface. The selective attack on the bottom of the fuel is because of flow imbalances in the cooling water which allows a higher temperature to occur on the bottom of the fuel. As shown in the section on uniform corrosion, an increase in temperature of 7.5 C is sufficient to double the uniform corrosion rate. The higher temperatures not only increase localized corrosion but also induce localized corrosion. The localized corrosion which occurred during this test was primarily of the form of groove and ledge corrosion, which has been described many times previously, and erosion-corrosion at the upstream ends of the fuel element supports.

An indication of the severity of the localized attack is obtained from a visual inspection of each fuel element. The depth of the localized corrosion, whether it be ledge, groove, pitting, or erosion-corrosion, is categorized at four levels of severity -- no localized attack, some localized attack but less than 10 mils deep, severe localized attack (greater than 10 mils deep), and extremely severe localized attack (AlSi layer visible). Results of the visual inspections are given in Tables VI through XI.

The effect of dichromate concentration at each exposure period and each goal outlet coolant temperature may be determined by comparing the data in Tables VI-XI. Only very slight differences in corrosion severity were observed on fuels operating in low temperature coolant containing 0.5 and 1.0 ppm dichromate. At 95 C goal outlet temperature no

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TABLE VI. NUMBER OF FUEL ELEMENTS WITH LOCALIZED CORROSION OF SEVERITY INDICATED,
EXPOSED 66 DAYS AT 95 C GOAL

Position	0.5 ppm Dichromate			1.0 ppm Dichromate		
	None	<10 Mils	>10 Mils	None	<10 Mils	>10 Mils
AlSi Showing	AlSi Showing	AlSi Showing	AlSi Showing	AlSi Showing	AlSi Showing	AlSi Showing
1*	3	3	3	3	3	3
2	3	3	3	3	3	3
3	3	3	3	3	3	3
4	3	3	3	3	3	3
5	3	3	3	3	3	3
6	3	3	3	3	3	3
7	3	3	3	3	3	3
8	3	3	3	3	3	3
9	3	3	3	3	3	3
10	3	3	3	3	3	3
11	3	3	3	3	3	3
12	3	3	3	3	3	3
13	3	3	3	3	3	3
14	3	3	3	3	3	3
15	3	3	3	3	3	3
16	3	3	3	3	3	3
17	3	3	3	3	3	3
18	3	3	3	3	3	3
19	3	3	3	3	3	3
20	3	3	3	3	3	3
21	3	3	3	3	3	3
22	3	3	3	1	2	2
23	3	3	3	1	3	3
24	2	2	1	1	2	2
25	3	3	3	1	3	3
26	3	3	3	1	3	3
27	1	2	1	1	2	2
28	3	3	2	1	3	3
29	2	1	1	1	3	3
30	2	1	1	1	3	3

* Downstream End.

TABLE VII. NUMBER OF FUEL ELEMENTS WITH LOCALIZED CORROSION OF SEVERITY INDICATED, EXPOSED
105 DAYS AT 95 C GOAL

Position	0.5 ppm Dichromate			1.0 ppm Dichromate		
	<u>None</u>	<u><10 Mils</u>	<u>>10 Mils</u>	<u>None</u>	<u><10 Mils</u>	<u>>10 Mils</u>
1*	6	6	6	6	6	6
2	6	6	6	6	6	6
3	6	6	6	6	6	6
4	6	6	6	6	6	6
5	6	6	6	6	6	6
6	6	6	6	6	6	6
7	6	6	6	6	6	6
8	6	6	6	6	6	6
9	6	6	6	6	6	6
10	6	6	6	6	6	6
11	6	6	6	6	6	6
12	6	6	6	6	6	6
13	6	6	6	6	6	6
14	6	6	6	6	6	6
15	6	6	6	6	6	6
16	6	6	6	6	6	6
17	6	6	6	6	6	6
18	6	6	6	6	6	6
19	6	6	6	6	6	6
20	6	6	6	6	6	6
21	6	6	6	6	6	6
22	6	6	6	6	6	6
23	6	6	6	6	6	6
24	6	6	6	6	6	6
25	6	6	6	6	6	6
26	6	6	6	6	6	6
27	6	6	6	6	6	6
28	6	6	6	6	6	6
29	6	6	6	6	6	6
30	6	6	6	6	6	6

* Downstream End

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TABLE VIII. NUMBER OF FUEL ELEMENTS WITH LOCALIZED CORROSION OF SEVERITY INDICATED, EXPOSED

Position	66 DAYS AT 105 C GOAL			1.0 ppm Dichromate				
	None	<10 Mils	>10 Mils	AISI Showing	None	<10 Mils	>10 Mils	AISI Showing
1*								
2	3	3	3	3	3	3	3	3
3	3	3	3	3	3	3	3	3
4	3	3	3	3	3	3	3	3
5	3	3	3	3	3	3	3	3
6	3	3	3	3	3	3	3	3
7	3	3	3	3	3	3	3	3
8	3	3	3	3	3	3	3	3
9	3	3	3	3	3	3	3	3
10	3	3	3	3	3	3	3	3
11	3	3	3	3	3	3	3	3
12	3	3	3	3	3	3	3	3
13	3	3	3	3	3	3	3	3
14	3	3	3	3	3	3	3	3
15	3	3	3	3	3	3	3	3
16	3	3	3	3	3	3	3	3
17	3	3	3	3	3	3	3	3
18	3	3	3	3	3	3	3	3
19	3	3	3	3	3	3	3	3
20	3							
21	3							
22	1	2						
23	1	2						
24	2	1						
25	2	1						
26	3							
27	3							
28	3							
29	3							
30	3							

* Downstream End

TABLE IX. NUMBER OF FUEL ELEMENTS WITH LOCALIZED CORROSION OF SEVERITY INDICATED, EXPOSED
105 DAYS AT 105 C GOAL

Position	0.5 ppm Dichromate			1.0 ppm Dichromate		
	None	<10 Mils	>10 Mils	None	<10 Mils	>10 Mils
1*	1	5		5	1	
2	2	4		3	3	
3	4	2		4	2	
4	3	3		5	1	
5	4	2		6	6	
6	5	1		6	6	
7	6			6	6	
8	6			6	6	
9	6			6	6	
10	6			6	6	
11	6			6	6	
12	6			6	6	
13	6			6	6	
14	6			6	6	
15	6			6	6	
16	6			6	6	
17	6			6	6	
18	6			6	6	
19	6			6	6	
20	6			6	6	
21	6			6	6	
22	6			5	1	
23	6			4	2	
24	6			1	5	
25	4			6	6	
26	3			6	6	
27	6			6	6	
28	5			6	6	
29	6			6	6	
30	6			6	6	

* Downstream End

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TABLE X. NUMBER OF FUEL ELEMENTS WITH LOCALIZED CORROSION OF SEVERITY INDICATED, EXPOSED
66 DAYS AT 115 C GOAL

Position	0.5 ppm Dichromate			1.0 ppm Dichromate		
	<u>None</u>	<u><10 Mils</u>	<u>>10 Mils</u>	<u>None</u>	<u><10 Mils</u>	<u>>10 Mils</u>
						<u>AISI Showing</u>
1*	1	2	1	1	2	2
2	2	2	1	1	3	3
3	2	2	1	2	2	2
4	1	2	1	1	2	1
5	1	2	1	3	3	3
6	1	2	1	3	3	3
7	2	1	1	3	3	3
8	2	1	1	3	3	3
9	3	1	1	3	3	3
10	2	1	1	3	3	3
11	3	1	1	3	3	3
12	3	1	1	3	3	3
13	3	1	1	3	3	3
14	3	1	1	3	3	3
15	3	1	1	3	3	3
16	3	1	1	3	3	3
17	3	1	1	3	3	3
18	3	1	1	3	3	3
19	3	1	1	3	3	3
20	3	1	1	3	3	3
21	3	1	1	3	3	3
22	3	1	1	3	3	3
23	3	1	1	3	3	3
24	3	1	1	3	3	3
25	3	1	1	3	3	3
26	3	1	1	3	3	3
27	3	1	1	3	3	3
28	3	1	1	3	3	3
29	3	1	1	3	3	3
30	3	1	1	3	3	3

* Downstream End

TABLE XI. NUMBER OF FUEL ELEMENTS WITH LOCALIZED CORROSION OF SEVERITY INDICATED, EXPOSED
105 DAYS AT 115 C GOAL

Position	0.5 ppm Dichromate			1.0 ppm Dichromate		
	None	<10 Mils	>10 Mils	None	<10 Mils	>10 Mils
						AISI Showing
1*						
2	1	1	4	1	2	2
3	1	4	6	2	4	4
4						
5						
6						
7						
8						
9						
10	1	5	6	6	4	4
11		2	4	6	6	6
12		3	3	6	6	6
13		4	2	6	6	6
14		4	2	6	6	6
15		6	6	6	6	6
16		6	6	6	6	6
17		6	6	6	6	6
18		6	6	6	6	6
19		6	6	6	6	6
20		6	6	6	6	6
21		6	6	6	6	6
22		6	6	6	6	6
23		6	6	6	6	6
24		6	6	6	6	6
25		6	6	6	6	6
26		6	6	6	6	6
27		6	6	6	6	6
28		6	6	6	6	6
29		6	6	6	6	6
30		6	6	6	6	6

* Downstream End

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significant differences were observed at either discharge; at the first discharge all fuel elements (except a few at the upstream end where no corrosion occurred) exhibited localized corrosion of a severity less than 10 mils deep. At the first discharge of fuel at 105 C goal outlet temperature, the fuel exposed to coolant containing 1.0 ppm dichromate exhibited slightly less severe corrosion; fuel at this discharge exhibited localized corrosion of a severity less than 10 mils up to the 25th element at 0.5 ppm and up to the 22nd element at 1.0 ppm. At the final discharge, more than twice as many fuel elements (17) exhibited corrosion of a severity greater than 10 mils in 0.5 ppm dichromate than on fuel elements (7) in 1.0 ppm dichromate. Also, the area where no localized corrosion occurred extended slightly further downstream in the fuel columns exposed to 1.0 ppm dichromate than on columns exposed to 0.5 ppm dichromate. At 115 C goal outlet temperature, about twice as many fuel elements (15) exhibited corrosion of a severity greater than 10 mils after 66 days in 0.5 ppm dichromate than on fuel elements in 1.0 ppm dichromate. In addition two fuel elements exhibited corrosion to the AlSi layer in 0.5 ppm dichromate but none were corroded this extensive at 1.0 ppm dichromate. Similar trends were observed after 105 days exposure except that more fuel at each dichromate concentration experienced severe corrosion; eight fuel elements in coolant containing 0.5 ppm dichromate, and four fuel elements in 1.0 ppm dichromate, were corroded to the AlSi layer.

The effect of increased exposure time was to increase the severity of corrosion, particularly at the higher temperatures. At 95 C outlet temperature, many of the upstream fuel elements did not exhibit any localized corrosion after 66 days exposure but all thirty elements in each column exhibited localized corrosion at 105 days exposure. At 105 C, all fuel exhibited localized corrosion less than 10 mils deep after 66 days exposure but after 105 days exposure corrosion severity increased so that many fuels in positions 1 to 6 from the downstream end exhibited corrosion deeper than 10 mils. Similar trends with exposure time occurred on fuels exposed at 115 C outlet temperature; the number of fuel elements exhibiting corrosion of a severity greater than 10 mils more than tripled when the exposure time was increased from 66 to 105 days.

Of the three parameters investigated (dichromate concentration, exposure time, temperature), the variable which had the most influence on severity of localized corrosion was temperature. After 66 days exposure, localized corrosion was less than 10 mils deep on fuel exposed at 95 C and 105 C goal outlet temperature with many of the upstream fuel (above position 20) not exhibiting any local attack. At 115 C goal outlet temperature, all thirty downstream fuel elements examined in each column exhibited localized attack of some form and many of those in the downstream hotter positions exhibited localized corrosion greater than 10 mils. After 105 days exposure, the effect of temperature was even more pronounced. None of the fuel at 95 C goal outlet exhibited localized corrosion deeper

than 10 mils; and 91 elements at 115 C goal outlet exhibited corrosion greater than 10 mils deep or to the AlSi layer.

The effect of temperature on localized corrosion can also be seen by observing the corrosion severity along the length of the fuel column. For example, Table XI shows that corrosion was less than 10 mils deep for the upstream fuel elements, increased to greater than 10 mils deep starting at fuel locations 8 to 13 as the temperatures increased towards the downstream end of the fuel column, and at the area maximum temperature (positions 1-5) severe corrosion to the AlSi layer occurred.

2. Primary Corrosion

The fuel elements were analyzed for type of corrosion attack as well as severity of attack following the in-reactor exposure. Normally, two or more types of corrosion are identified. The more severe type of corrosion, i.e., the type of corrosion considered most detrimental to fuel survival, is classified as primary corrosion and any less severe type of corrosion attack is classified as secondary attack. Uniform corrosion or three types of localized corrosion may be identified. The three localized types of corrosion normally identified are groove, ledge, and pitting corrosion. Groove corrosion is a form of erosion-corrosion which normally occurs on the lateral fuel surfaces. For purposes of brevity, a form of erosion-corrosion which occurs by impingement of cooling water at the upstream ends of the fuel supports is also included in the following discussion in the category of groove corrosion. Groove corrosion, which has been described previously, is a form of localized corrosion characterized by small, smooth-bottomed, oxide-free pits. Many times these pits are connected to form rows of grooves. Ledge corrosion is characterized by a surface where it appears the corrosion has removed broad, shallow layers. Pitting is characterized by small, deep, ragged-edge pits; these pits sometimes overlap one another. Of the three types of localized corrosion normally groove corrosion is the most detrimental and ledge corrosion is the least detrimental. When no form of localized attack is found, the corrosion process is classified as uniform corrosion.

A summary of the types of corrosion found on the fuel elements which was classified as primary corrosion is given in Table XII, and the data from which the summary was derived are given in Tables XIII through XVIII. As may be seen in Table XII, there was very little difference in percentage of each type of primary corrosion between fuels exposed at the two dichromate concentrations. However, the more severe types of corrosion predominated as either exposure time was increased or as outlet temperature (and the corresponding individual fuel cladding temperatures) was increased.

An indication of how the types of localized corrosion was distributed along a fuel column length can be obtained by inspecting the data for each fuel group in Tables XIII-XVIII. At the lower temperatures and

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TABLE XII. NUMBER AND PERCENT OF FUEL WITH PRIMARY ATTACK OF TYPE INDICATED

		Groove		Pitting		Ledge		Uniform	
		0.5 ppm	1.0 ppm						
<u>95 C Goal Outlet Temperature</u>									
1st Discharge	Number	7	6	35	42	4	3	44	39
Percent*	Percent	3.9	3.3	19.4	23.3	2.2	1.7	24.4	21.7
2nd Discharge	Number	70	36	53	68	0	3	57	74
Percent	Percent	19.4	10.0	14.7	18.6	0	0.8	15.8	20.6
<u>105 C Goal Outlet Temperature</u>									
1st Discharge	Number	26	18	25	30	3	3	36	39
Percent	Percent	14.4	10.0	13.9	16.7	1.7	1.7	20.0	21.7
2nd Discharge	Number	42	36	81	81	0	0	57	63
Percent	Percent	11.7	10.0	22.5	22.5	0	0	15.8	17.5
<u>115 C Goal Outlet Temperature</u>									
1st Discharge	Number	47	43	36	31	0	0	7	16
Percent	Percent	26.1	23.9	20.0	17.2	0	0	3.9	8.9
2nd Discharge	Number	128	117	52	56	0	0	0	7
Percent	Percent	35.6	32.5	14.4	15.6	0	0	0	1.9

* Percentage figure is percent of total fuel exposed at 0.5 ppm plus at 1.0 ppm at conditions given.

TABLE XIII. NUMBER OF FUEL WITH PRIMARY ATTACK OF TYPE INDICATED
95 C GOAL, OUTLET, 66 DAYS EXPOSURE

<u>Position</u>	<u>Groove</u>	<u>0.5 ppm</u>	<u>Pitting</u>	<u>Ledge</u>	<u>Uniform</u>	<u>Groove</u>	<u>1.0 ppm</u>	<u>Pitting</u>	<u>Ledge</u>	<u>Uniform</u>
1	1					1		2		
2	1		2			1		2		
3	1		2			2		2		
4	1		1		1			1		
5	1		1		1			2		
6								2		
7	2		1					2		
8			2		1			3		
9			3			1		2		
10	10		3			3		3		
11	11		3			3		3		
12	12		3			3		3		
13	13		3			3		3		
14	14		3			3		3		
15	15		2		2	1		3		
16	16		2		2	1		2		
17	17					3		2		
18	18			1	1					
19	19							2		
20	20							2		
21	21							3		
22	22							3		
23	23							3		
24	24							3		
25	25							3		
26	26							3		
27	27							3		
28	28							3		
29	29							3		
30								3		
	7							6		
								42		
								3		
								39		
								3		
								3		
								3		

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TABLE XIV. NUMBER OF FUEL WITH PRIMARY ATTACK OF TYPE INDICATED

Position	0.5 ppm				1.0 ppm			
	Groove	Pitting	Ledge	Uniform	Groove	Pitting	Ledge	Uniform
1	3	3	1	1	4	1	1	1
2	6	2	3	3	3	3	3	1
3	6	1	4	2	4	2	2	
4	6	5	1	2	5	1	2	
5	6	5	4	1	4	4	2	
6	6	6	3	3	3	3	2	
7	6	6	2	2	2	3	4	
8	6	5	4	1	1	4	4	
9	6	5	1	1	1	3	1	
10	5	4	2	1	1	3	1	
11	5	5	1	1	1	5	5	
12	4	4	2	1	1	5	5	
13	3	3	3	1	5	5	5	
14	1	5	5	1	5	5	5	
15	5	3	3	1	5	6	6	
16	6	6	6	1	5	5	5	
17	6	6	6	1	4	4	2	
18	5	5	4	1	3	3	3	
19	4	4	2	1	3	3	3	
20	3	3	3	1	2	2	4	
21	3	3	3	1	1	1	5	
22	3	3	3	1	1	1	5	
23	1	1	5	1	1	1	6	
24	6	6	6	1	1	5	5	
25	5	5	6	1	1	6	6	
26	6	6	6	1	1	6	6	
27	5	5	6	1	1	6	6	
28	6	6	6	1	1	6	6	
29	6	6	6	1	1	6	6	
30	6	6	6	1	1	6	6	
	70	53	0	0	36	67	3	74

TABLE XV. NUMBER OF FUEL WITH PRIMARY ATTACK OF TYPE INDICATED
105 C GOAL OUTLET, 66 DAYS EXPOSURE

<u>Position</u>	<u>Groove</u>	<u>0.5 ppm</u>	<u>Pitting</u>	<u>Ledge</u>	<u>Uniform</u>	<u>Groove</u>	<u>1.0 ppm</u>	<u>Pitting</u>	<u>Ledge</u>	<u>Uniform</u>
1	3					2	1			
2	3					3				
3	3					3				
4	3					2				
5	3					2				
6	3					2				
7	3					1	2			
8	2					1	1	2		
9	1					1	1	2		
10	1					1	2	3		
11	1					1	1	2		
12						3	3	3		
13						3	3	3		
14						3	3	3		
15						3	2	2		
16						3	2	2		
17						3	2	1	1	
18						1	2	1	2	
19						2	1	1	2	
20						2	1	1	2	
21						3	3	3	3	
22						3	3	3	3	
23						3	3	3	3	
24						3	3	3	3	
25						3	3	3	3	
26						3	3	3	3	
27						3	3	3	3	
28						3	3	3	3	
29						3	3	3	3	
30						3	3	3	3	
	26					25	18	30	36	39

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TABLE XVI. NUMBER OF FUEL WITH PRIMARY ATTACK OF TYPE INDICATED

TABLE XVII. NUMBER OF FUEL WITH PRIMARY ATTACK OF THE TYPE INDICATED
115 C GOAL OUTLET, 66 DAYS EXPOSURE

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TABLE XVII. NUMBER OF FUEL WITH PRIMARY ATTACK OF THE TYPE INDICATED

Position	0.5 ppm			1.0 ppm		
	Groove	Pitting	Ledge	Groove	Pitting	Ledge
1	6			6		
2	6			6		
3	6			6		
4	6			6		
5	6			6		
6	6			6		
7	6			6		
8	6			6		
9	6			6		
10	6			6		
11	6			6		
12	6			6		
13	6			6		
14	6			6		
15	6			6		
16	6			6		
17	6			6		
18	6			6		
19	6			6		
20	4			4		
21	2			4		
22	4			2		
23	1			5		
24	3			3		
25	6			6		
26	6			6		
27	6			6		
28	6			6		
29	6			4		
30	6			4		
	52			0		
	128			0		
	117			56		
				0		
				0		
				7		

times uniform corrosion predominates, at the intermediate temperatures pitting predominates, and at the higher temperatures and exposures groove corrosion predominates. While looking at the temperature effect along a fuel column length, it should be remembered that even though bulk coolant temperature is steadily increasing along the fuel column going toward the outlet, the maximum fuel cladding temperature occurs at elements 4 to 9 from the outlet end.

3. Secondary Corrosion

Secondary corrosion is the type of corrosion present on a fuel element that is not as serious as primary corrosion, but it could lead to future fuel failures. Because the secondary corrosion is not as important as the primary corrosion, only the summary (Table XIX) for the secondary corrosion is presented. The secondary corrosion was predominantly either ledge corrosion or uniform corrosion. Slightly more ledge corrosion occurred at the lower (0.5 ppm) dichromate concentration, at the higher temperatures, and at the longer exposures.

4. Pit Depth Measurements

In addition to the weight loss measurements and the visual inspection of the fuel elements, mechanical measurements of the pit depths were made at specified lines around the circumference at five locations along the length of each fuel element. These measurements were all at the same location on each fuel element and, thus, were not necessarily made at areas of maximum penetration. Indeed, visual observations indicated that maximum depth of corrosion attack usually occurred at the upstream ends of fuel supports where erosion-corrosion had occurred; and, due to size limitations on the measuring device, it was not possible to obtain depth measurements at these areas. Because of these limitations, a statistical analysis of the pit depth data was made to predict maximum pit depth. Graphs of the maximum predicted pit depth versus cladding surface temperature for each of the exposure periods and dichromate concentrations are given in Figures 10-13.

After 66 days exposure, there was little difference between pit depths on fuels exposed to 0.5 ppm and those exposed to 1.0 ppm sodium dichromate; pit depths fell in a wide band averaging about 10 mils deep with a maximum of 20 mils. There was little affect of surface temperature on pit depths.

After 106 days exposure, there also was little difference between pit depths on fuel exposed to coolant containing the two dichromate concentrations at fuel surface temperatures less than 120 C. Below 120 C, the pit depths fell in a wide band averaging about 12 mils deep, exhibited a maximum depth of about 20 mils, and appeared to be independent of temperature. At about 120 C a sharp departure occurred. Measured pit depths immediately became much deeper and maximum depths up to 35 mils deep were calculated (cladding thickness of 45 mils). While more fuel elements exposed to 0.5 ppm dichromate exhibited the severe pitting at temperatures about 120 C than did fuel

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TABLE XIX. NUMBER AND PERCENT OF FUEL WITH SECONDARY ATTACK OF TYPE INDICATED

	Pitting		Ledge		Uniform	
	<u>0.5 ppm</u>	<u>1.0 ppm</u>	<u>0.5 ppm</u>	<u>1.0 ppm</u>	<u>0.5 ppm</u>	<u>1.0 ppm</u>
<u>95 C Goal</u>						
1st Discharge	1	1	13	13	76	76
Number	0.6	0.6	7.2	7.2	42.2	42.2
Percent						
2nd Discharge	0	3	91	52	89	125
Number	0	0.8	25.3	14.4	24.7	34.7
Percent						
<u>105 C Goal</u>						
1st Discharge	1	5	30	18	59	67
Number	0.6	2.8	16.7	10.0	32.8	37.2
Percent						
2nd Discharge	2	1	93	76	85	103
Number	0.6	0.3	25.8	21.1	23.6	28.6
Percent						
<u>115 C Goal</u>						
1st Discharge	1	0	62	53	27	37
Number	0.6	0	34.4	29.4	15.0	20.6
Percent						
2nd Discharge	0	0	165	143	15	37
Number	0	0	45.8	39.7	4.2	10.3
Percent						

FIGURE 10. PIT DEPTHS FOR GLADDING EXPOSED 66 DAYS TO 0.5 ppm SODIUM DICHROMATE

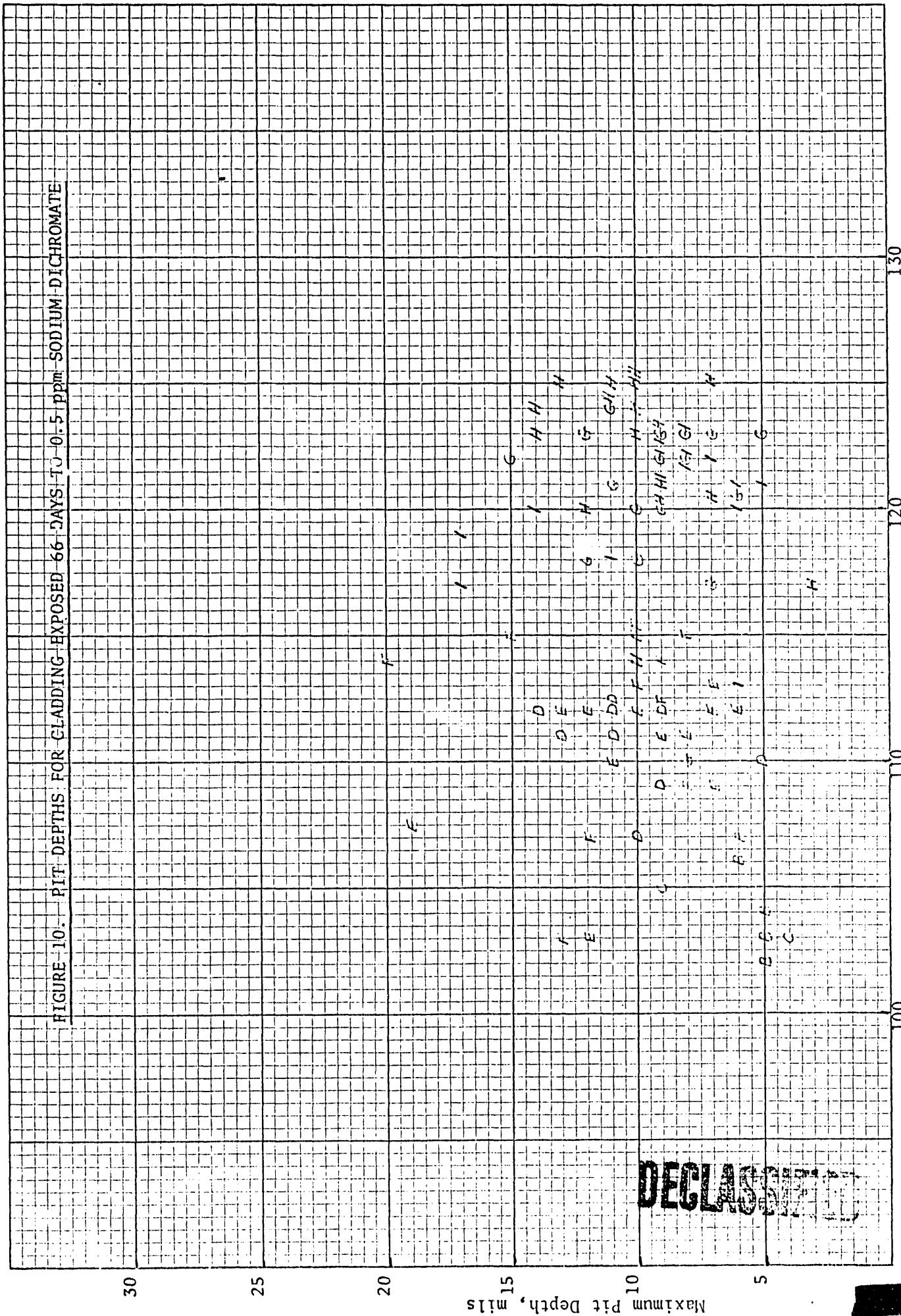
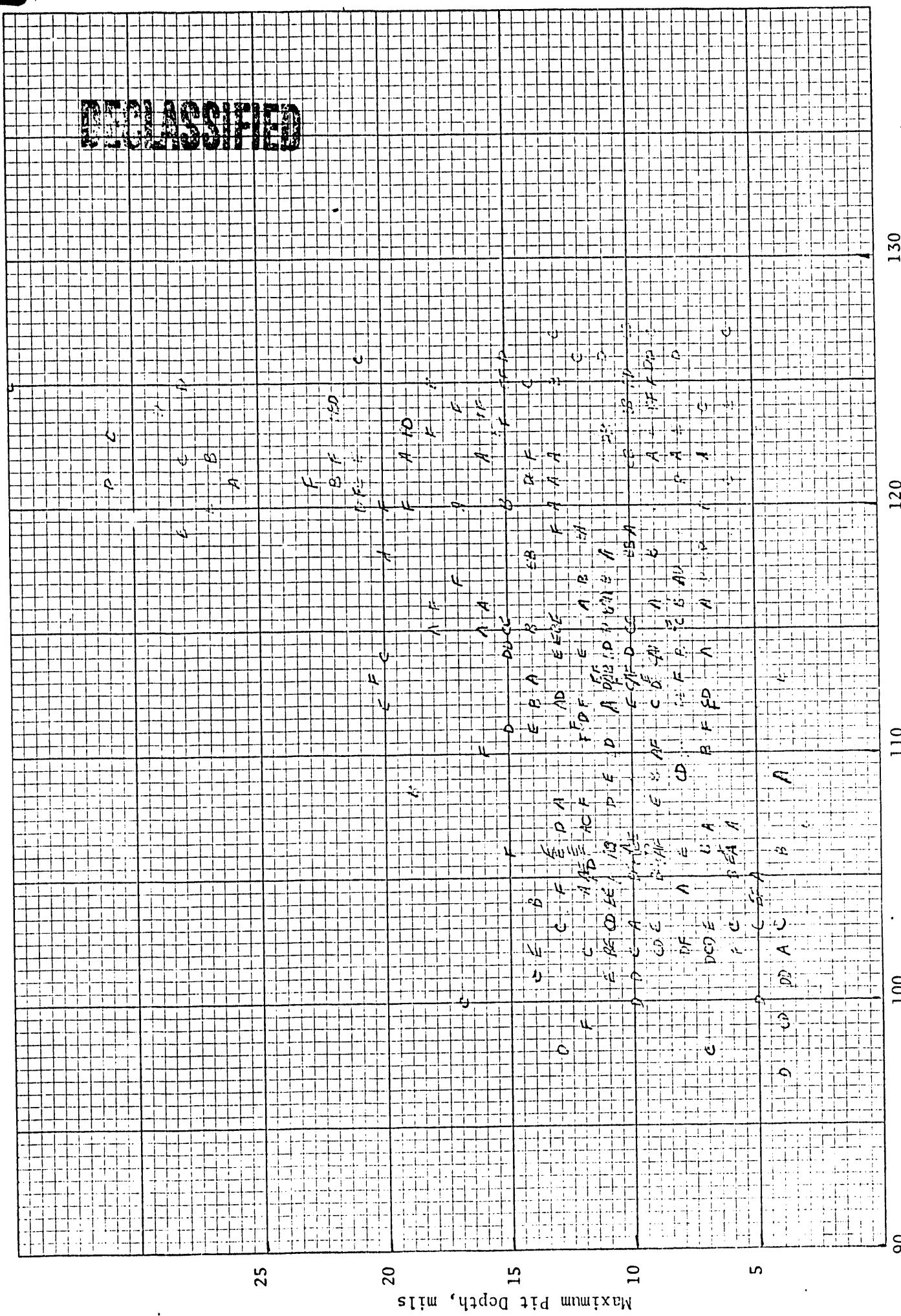


FIGURE 11. PIT DEPTHS FOR CLADDING EXPOSED 105 DAYS TO 0.5 ppm SODIUM DICHRONATE



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FIGURE 12. PIT DEPTHS FOR CLADDING EXPOSED 66 DAYS TO 1.0 ppm SODIUM DICHROMATE

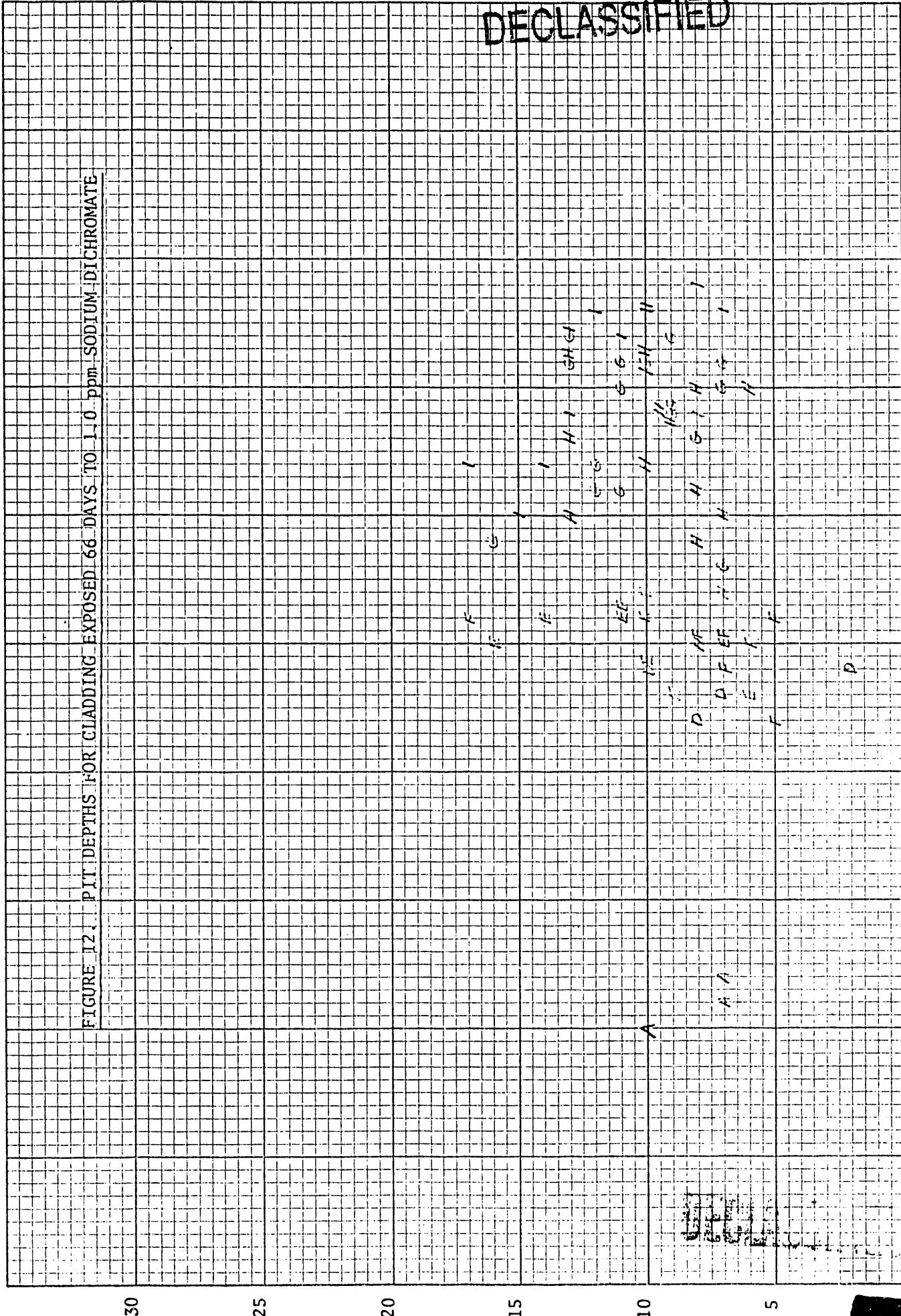
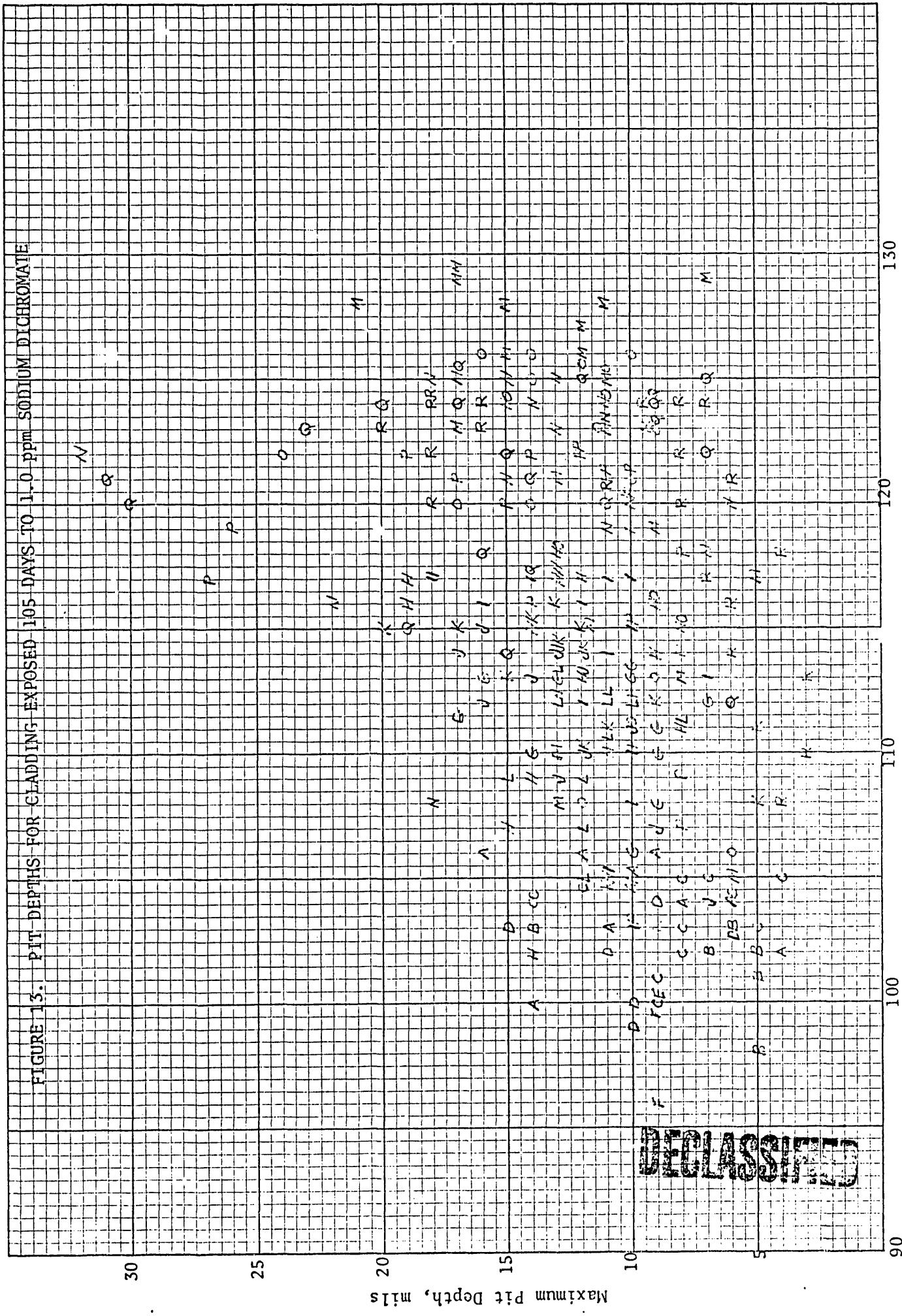


FIGURE 13. DEPTHS FOR CLADDING EXPOSED 105 DAYS.



elements exposed to coolant containing 1.0 ppm dichromate, there were still sufficient fuel elements at 1.0 ppm with deep pits to cause concern about the possibility of fuel ruptures at 1.0 ppm dichromate concentration.

5. Fuel Support Corrosion

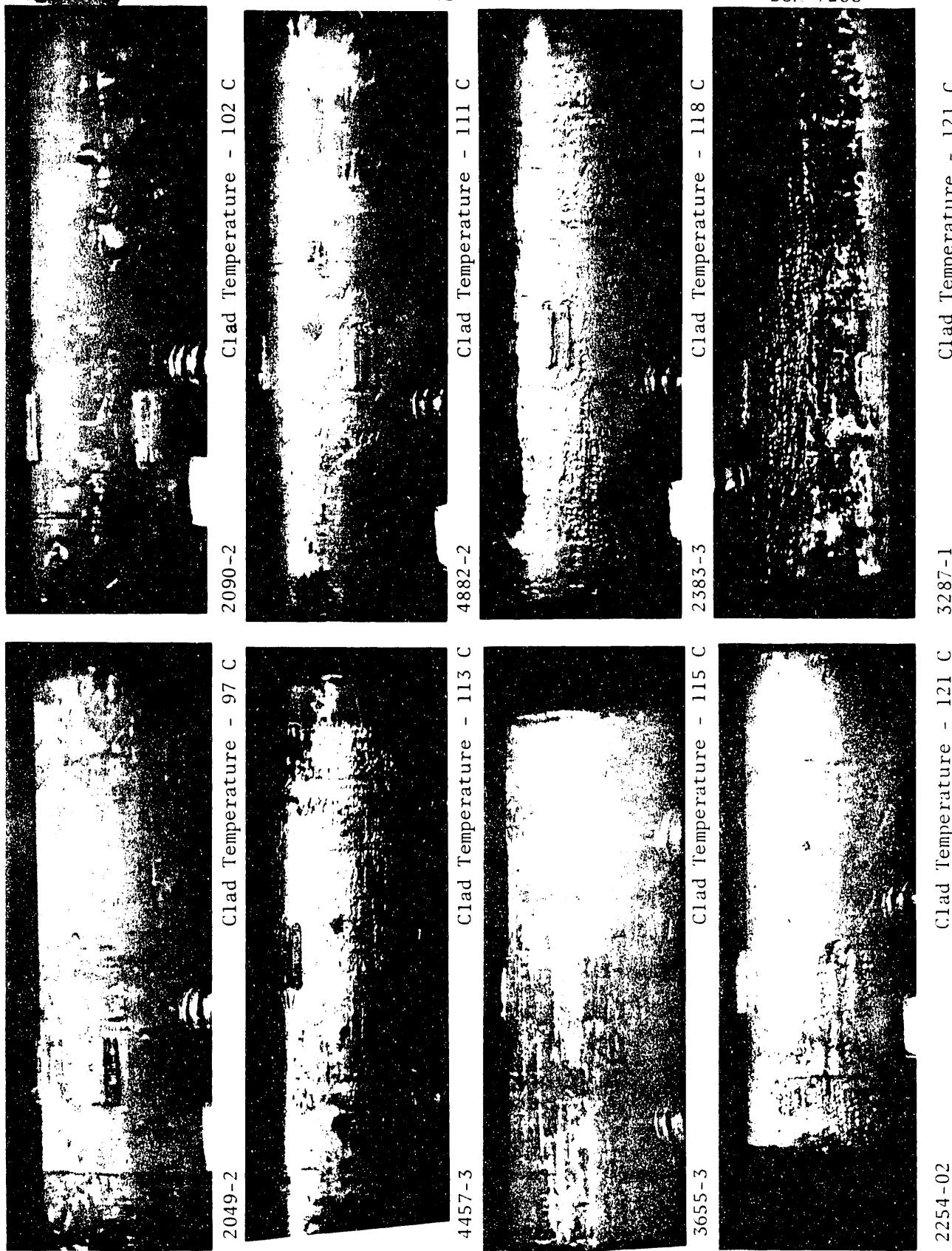
In addition to the regular weight loss, visual and pit depth measurements made in the Fuel Element Examination Facility (presented above), a visual examination to determine the extent of fuel element support corrosion was also conducted on selected fuel columns. The supports were subject to extensive corrosion and because of their protrusion out from the fuel surface, the visual observations on the extent of support degradation could be more quantitatively assessed than on the cladding. Photographs of typical supports on downstream fuel elements exposed 105 days are shown in Figure 14 as a function of dichromate concentration and cladding surface temperature. At cladding temperatures near 100 C (tube outlet temperatures 90-95 C), little corrosion occurred to either the supports or to the cladding on the lateral surfaces at either dichromate concentration. At cladding temperatures near 112 C (tube outlet temperatures 100-105 C), the leading edges of the bottom supports showed some corrosion, erosion-corrosion into the cladding at the upstream ends of the bottom supports was initiating, and ledge corrosion combined with some groove corrosion was starting on the cladding lateral surfaces. Fuel elements appeared similar in coolant containing both dichromate concentrations. At cladding temperatures of 115-118 C (tube outlet temperatures of 105-110 C), the crowns of the bottom rows of supports were completely corroded away, severe erosion-corrosion of the cladding at the upstream ends of the bottom rows of supports was occurring (slightly worse on fuel exposed to 0.5 ppm dichromate), and extensive groove corrosion was occurring on the cladding bottom lateral surfaces. At cladding temperatures near 120 C (tube outlet temperatures of 115 C), the bottom rows of supports were completely corroded away, and severe groove corrosion (in many cases to the AlSi layer) was occurring on the cladding lateral surfaces. Corrosion appeared slightly worse on fuels exposed to 0.5 ppm dichromate. For all cases, very little corrosion occurred on the top rows of supports or on adjacent top cladding.

The support corrosion shown in Figure 14 is somewhat difficult to see; therefore, sketches of the corrosion are given in Figures 15-16 to more clearly illustrate the extent of corrosion which occurred. The sketches represent a plan view of the arch support. Wavy lines represent the extent the crowns have been corroded away. The small teardrop shaped areas at the upstream ends of the support sketch represent erosion-corrosion penetrating into the cladding and the numbers in parenthesis beside the teardrop areas are an estimate made by the author of the depth of the penetrations. These estimates are probably low; estimates by experienced personnel in the Fuel Element Examination Facility on a few of the elements described in the sketches were much deeper; however, in order to be consistent in all fuel columns, the smaller estimates are presented.

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FIGURE 14. FUEL ELEMENT SUPPORT CORROSION

1.0 ppm 0.5 ppm



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FIGURE 15. FUEL CORROSION AFTER 66 DAYS EXPOSURE

Position From Downstream End	Tube Number	4885-KW	3054-KW	4862-KW	5052-KW
	Dichromate Concentration, ppm	0.5	1.0	1.0	1.0
	Tube Outlet Temp, C	112	114	112	114
	Exposure, MWD/T	794	773	774	768
1	Support Appearance				
	Clad Temperature	118		120	
2	Support Appearance				
	Clad Temperature	120	123	121	124
3	Support Appearance				
	Clad Temperature	121	124	123	
4	Support Appearance				
	Clad Temperature	122	125	124	127
5	Support Appearance				
	Clad Temperature	123	126	126	128
6	Support Appearance				
	Clad Temperature	123	126	126	128
7	Support Appearance				
	Clad Temperature	122	127	126	

FIGURE 16. FUEL SUPPORT CORROSION AFTER 105 DAYS EXPOSURE

Position From Downstream End	Tube Number	1284-KW	3285-KW	3254-KW	5054-KW
	Dichromate Concentration, ppm	0.5	0.5	1.0	1.0
	Tube Outlet Temperature, C	114	116	113	115
	Exposure, MND/T	1281	1249	1263	1267
1	Support Appearance				
1	Clad Temperature	120 GC & EC to AlSi *	122 GC to AlSi	120	123 GC to 20
2	Support Appearance				
2	Clad Temperature	121	123 GC to AlSi	122	125 GC to 20
3	Support Appearance				
3	Clad Temperature	122 EC to AlSi	125 GC to AlSi	123	126
4	Support Appearance				
4	Clad Temperature	123	125	124	127 GC to 40
5	Support Appearance				
5	Clad Temperature	124	126 GC to AlSi	125	128
6	Support Appearance				
6	Clad Temperature	124		126	129
7	Support Appearance				
7	Clad Temperature	125	127	126	129

* GC = Groove Corrosion
EC = Erosion-Corrosion

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The columns selected for illustration in Figures 15-16 were those operating at the higher temperatures; the effect of increased dichromate concentration in reducing support corrosion can be clearly seen.

It is pertinent to note that very few of the support crowns were corroded away after 66 days exposure. After 105 days exposure extensive support corrosion had occurred and in many cases the support welding tabs were barely visible. When this occurs, it allows the fuel element to settle to the bottom of the process tube, causes further increases in local temperatures on the bottom of the fuel element, and causes cladding corrosion to accelerate.

V. DISCUSSION

A. General

The primary purpose of this test was to provide a quantitative comparison of fuel element 8001 aluminum alloy cladding corrosion in cooling water containing 0.5 and 1.0 ppm sodium dichromate inhibitor. Secondary purposes were to provide information on cladding corrosion as a function of temperature and as a function of time at both inhibitor concentrations. The primary purpose was well fulfilled: Equations were developed to describe and predict fuel element weight losses at both dichromate concentrations and the effect of dichromate concentration on localized corrosion was clearly established. The corrosion equations show that fuel weight losses can be expected to increase by a factor of 1.45 at a dichromate concentration of 0.5 ppm as compared to exposure to coolant containing 1.0 ppm dichromate. Little effect of dichromate concentration on localized corrosion was observed when fuel cladding temperatures were below 115-120 C but above these temperatures the localized corrosion definitely was more severe in coolant containing 0.5 ppm inhibitor. The localized corrosion (groove corrosion, pitting, erosion-corrosion) almost always occurred on the bottoms of the fuel elements, since these surfaces operate at a higher temperature. The bottom rows of fuel element supports rapidly corroded away at the higher temperatures which caused a further increase in local temperatures due to flow imbalances and this in turn accelerated the localized corrosion. Because the higher dichromate concentration reduced the amount of support corrosion, 1.0 ppm dichromate should be employed to control localized corrosion whenever cladding temperatures are expected to be above 120 C for long periods of time. These tests indicated that corrosion occurring at exposures of 66 operating days, and with clad temperatures of 120 C or above, would not seriously limit fuel integrity at 0.5 ppm inhibitor but that for exposures of 105 operating days extensive pitting corrosion would be expected. However, it was found that even operation at 1.0 ppm dichromate the longer exposure periods and higher cladding temperatures would reduce but would not completely eliminate localized corrosion. It is well known that a decrease in pH will reduce aluminum cladding corrosion and, while not investigated during the test, if the severe exposure conditions are expected it would seem prudent to decrease the pH (6.7 was employed in this test) as well as to operate with higher dichromate concentrations.

B. Application of Corrosion Prediction Equation to Other Data

The actual proof of any corrosion prediction equation is that it is applicable for data obtained from several different sources. A test of the corrosion prediction equation was made using data obtained from fuel elements exposed in KE Reactor between March 27, 1969 and August 12, 1969. This data had been reported previously³ but was not correlated in the manner utilized for the corrosion prediction equation. The KE Reactor fuel data are shown in Figure 17 along with the predicted corrosion calculated from the equation derived in this report. The KE Reactor fuel elements were exposed a total of 81.5 operating days (134 calendar days) to coolant containing 0.5 ppm sodium dichromate. The two parallel lines bordering the predicted corrosion curve represent the ± 50 percent values of the predicted corrosion; this is the approximate range of data scatter in Figures 4-7 from which the equation was derived. It may be seen that the actual corrosion fell well within the boundaries of the predicted corrosion zone; thus providing the general applicability of the derived equation.

C. Comparison of Corrosion Equation with Previous Equations

The current corrosion equation used to predict fuel cladding corrosion in the MOFDA computer program is of the form

$$CR = a \frac{(Q)}{A} e^{-\beta/T}$$

where CR = corrosion rates, mils/mo

a, β = constants (445 and -7260, respectively)

Q/A = heat flux, BTU/hr/ft²

T = surface temperature, °K

This equation, which has been empirically derived, is applied separately to the outer and inner surfaces using the respective surface temperatures and heat fluxes. Data from this test were fitted to the MOFDA equation to determine if the MOFDA equation provided a better fit than the equa-

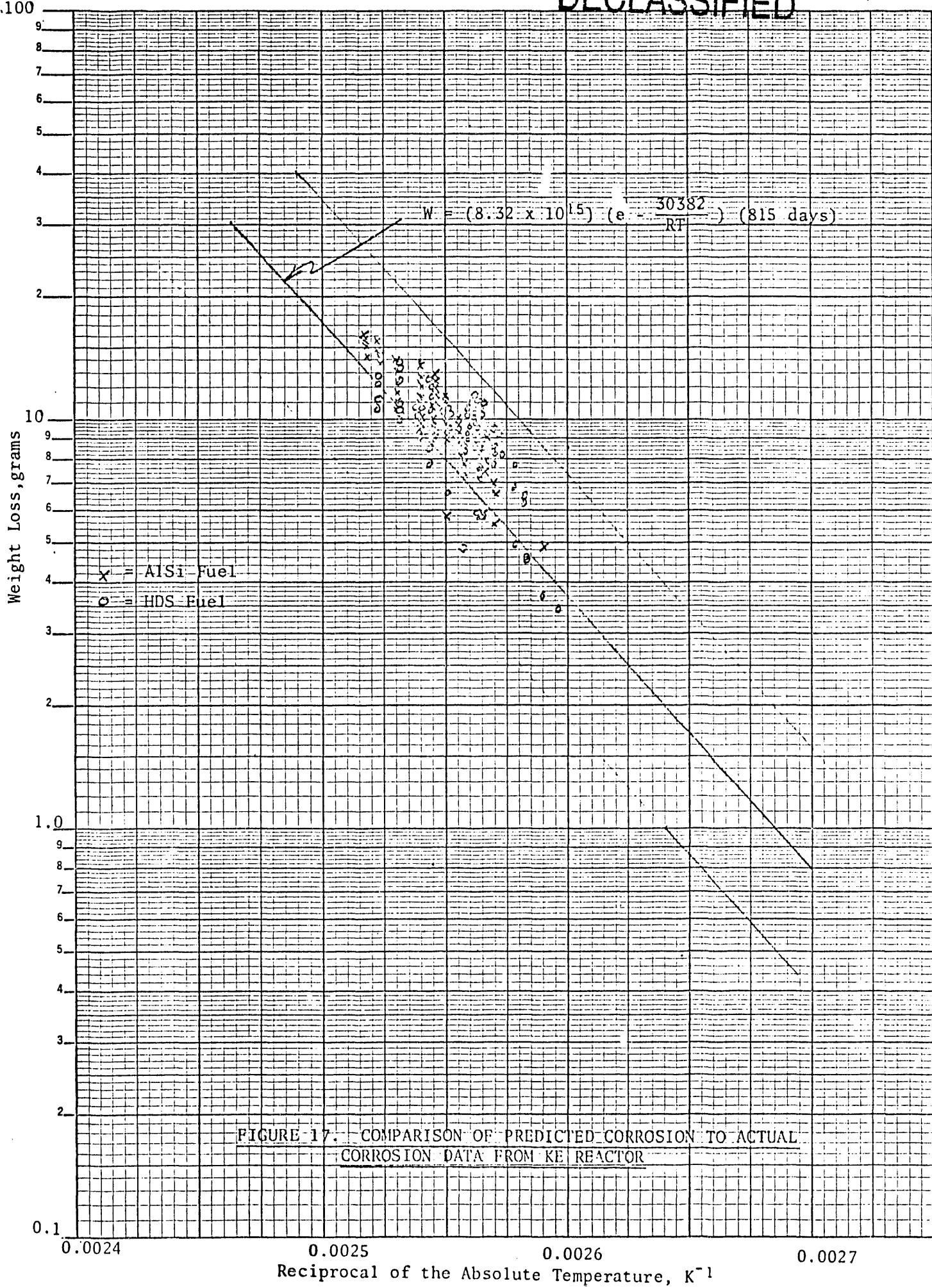
tion derived in this report ($C = A e^{-\frac{\Delta E}{RT}}$); more data scatter was found

with the MOFDA equation than with the present equation indicating that the term involving the heat flux was not an important factor in this test.

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It is interesting to note that the constant β in the MOFDA equation, which was obtained empirically, does not very closely match the value of $\frac{\Delta E}{R}$ in the present equation as derived from kinetic reaction rate constants. The value of β is -7260, while the value of $\frac{\Delta E}{R}$ is -15,350.

There have been many other equations proposed in the past in an attempt to adequately predict in-reactor corrosion rates; however, all have had some shortcomings. The MOFDA equation in current use has shortcomings in that this equation calculates separate corrosion rates for outer and inner fuel surfaces; this complicates fitting actual data to the equation since only a combined weight loss can be measured. This difficulty was experienced in the present equation and for this reason the weight loss data in the present equation have been correlated only with the outer surface temperature. The first attempt at correcting this inconsistency was made by Milier* when he modified the MOFDA equation to the form of $CR = A Pa e^{-\beta/Ta} + a Ph e^{-\beta/Th}$ where a and h represent the annulus and hole, P represents the heat flux, a is the ratio of the annulus and hole surface areas, and the other constants are as before.

A different approach was used by Hahn and Boyd⁵ to correlate measured weight loss data with a corrosion equation. They proposed an equation based on a measured temperature difference which was known to double corrosion rates. This equation was of the form $CR = \frac{2 \left(\frac{T_c - 123}{T_D} \right)}{\exp \frac{T_c - 123}{T_{D_1}}}$ where T_c is the corrosion temperature, T_D is the tempera-

ture increase known to double the corrosion rate, and 123 is an empirically measured corrosion temperature where the corrosion rate is 1 mil/mo. A form of this equation was used to relate inner and outer fuel surface corrosion with measured weight losses. The weight losses of the inner and outer surfaces are expressed by the equations $W = \text{Weight Loss, grams} = (\text{Constant}) (\text{Area}) (\text{Corrosion Rate}) (\text{Time})$

$$W_{(\text{inner})} = W_i = (0.0443) (A_1) (CR_i) (t)$$

$$W_{(\text{outer})} = W_o = (0.0443) (A_o) (CR_o) (t)$$

By combining these equations with the corrosion rate equation a correlation with measured weight loss can be obtained

$$R_o = \frac{W_o}{W_o + W_i} = \frac{A_o CR_o}{A_o CR_o + A_i CR_i}$$

$$= \frac{A_o CR_o}{A_o CR_o + A_o CR_o / 2 \left(\frac{\Delta T}{T_D} \right)}$$

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$$\text{where } CR_o = (CR_i) \quad 2\left(\frac{\Delta T}{T_D}\right) = (CR_i) \left[2\left(\frac{T_{co} - T_{ci}}{T_D}\right) \right]$$

T_{co} = corrosion temperature of the outer surface

T_{ci} = corrosion temperature of the inner surface

Both the Miller equation and the Hahn equation allow the corrosion on the inner and outer surfaces to be expressed in terms of one overall fuel weight loss measurement; however, neither have reduced the large amount of data scatter when actual corrosion data are fitted to the equations. The Hahn equation has one simplification over the Miller equation in that the weight losses are related only to fuel corrosion temperatures and does not include a factor for heat flux.

The fuel corrosion temperature in the Hahn equation is an empirical effective corrosion temperature. Many previous investigators, including Hahn, have noted that the weight losses have not correlated well with the actual fuel surface temperature and have added an incremental temperature to the cladding surface temperature.^{6,7} The value of the incremental temperature in the Hahn equation is 0.2 Twf where Twf is the temperature drop across the water film. This incremental temperature is added to the surface temperature to provide the effective temperature.

Dillon⁶ proposed an effective corrosion temperature based on fuel element power which is of similar form to the Hahn corrosion temperature:

$$Teff = Ts + KP$$

where Teff is the effective corrosion temperature; Ts is the cladding surface temperature; K is a constant equal to 1.7 C/fuel element and P is the power in KW/fuel element. This temperature was derived from the observation that a fuel element in the downstream end of a fuel column corroding at the same rate as a fuel element in the upstream end of the column must be corroding at the same effective corrosion temperature but they are corroding at different cladding surface temperatures and specific power. Thus

$$Teff = T_1 + KP_1 = T_2 + KP_2$$

$$\text{and } K = \frac{T_1 - T_2}{P_2 - P_1} = 1.7 \text{ C/fuel element}$$

An almost identical equation was independently derived by Dickinson,⁷ et al, from in-reactor data obtained in deionized water. The Dickinson effective corrosion temperature is $Teff = Ts + 1.14 \times 10^{-4} Q$, where Q is the heat flux in BTU/hr - ft². The value of the incremental temperature for the Dillon equation and the Dickinson equation when applied to the experimental data from this test were almost identical; however, replacing the surface temperature with an effective corrosion temperature did not improve the corrosion equation fit with the data. The present equation in terms of an effective corrosion temperature takes the form of

$$CR = A \exp \frac{-\Delta E}{R (Ts + KP)}$$

The concept of an effective corrosion temperature, while it did not improve the data fit for the present equation, is founded on a sound experimental and theoretical basis. Numerous isothermal and nonisothermal tests have shown that actual corrosion on heat transfer surfaces is higher than that predicted by the temperature of the oxide-water interface. This can be treated by assuming that either the surface temperature does not control the corrosion but that some higher temperature inside the oxide controls, or that the surface temperature does control corrosion but that in addition the solubility of the protective oxide must be accounted for. Data from several sources,^{7,8,9,12} much too lengthy to discuss here, indicates that oxide solubility is probably the governing factor when an effective corrosion temperature must be employed to obtain good data fit with corrosion prediction equations.

None of the above fuel corrosion equations consider the accelerating effect of radiation on aluminum corrosion in filtered Columbia River water. Radiation was found to accelerate corrosion by a factor of 3 to 5 in filtered Columbia River water on corrosion samples exposed under isothermal conditions but did not accelerate corrosion in deionized water.¹⁰ A radiation factor also was necessary in the Tube 3 Fortran Program for predicting aluminum process tube corrosion rates.¹¹ The process tube corrosion in inches/day had to be multiplied by the factor (0.6 + (0.78) (Relative Radiation Intensity, KW/in²)) before the predicted corrosion would correlate with the measured corrosion. Perhaps this effect of radiation on fuel jacket corrosion in some of the above fuel corrosion prediction equations has been attributed to heat transfer effects, since these values are proportional, and both have been accounted for in the effective temperature factor.

Discussion of the above process tube corrosion prediction equations leads to another important variable not found in the fuel cladding prediction equations. There are considerable temperature imbalances in the water in the annular space between the fuel and the process tube due to cross sectional eccentricity of the fuel setting in the bottom of the tube and, in some cases for ribbed tubes, variations in rib height. These imbalances cause much higher corrosion rates at some circumferential locations on the fuel than on the other locations. This increased corrosion was discussed previously in the results section of this report and on the fuel from this test the increased corrosion occurred on the bottom 90 degrees of the fuel outer surface circumference. The process tube corrosion prediction equations handle this imbalance by introducing an R factor, where R is the ratio of the bulk water temperature to the local water temperature. Typical process tube corrosion equations employing an R factor are the deHalas equation:

$$CR = k e^{-7660/[Ti + R\Delta T]/12}$$

and the Miller equation

$$CR = k_2^{[ti + R\Delta T]/12}$$

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where k is a constant varying from 0.0008 to 0.0019; T_i is the tube inlet temperature; and ΔT is the local tube bulk temperature minus the tube inlet temperature.

From the above discussion, it can be concluded that the equation derived to present the data from this test served a very useful purpose in showing the differences in corrosion between the two sodium dichromate concentrations and that this equation exhibited less scatter over a larger temperature range than other applicable equations. However, even this equation could be improved. Probably the most desirable improvement would be the incorporation of an R factor to account for the localized corrosion which currently occurs on the bottoms of the fuel elements. Thus, the ideal corrosion prediction equation would be of the form $W = ktQPSR$ where W is the fuel weight loss; k is the reaction rate constant equal to a constant dependent on the dichromate concentration times the exponential of the activation energy divided by the gas constant and the absolute temperature ($k = C e^{-\frac{\Delta E}{RT}}$); t is the time in days, Q is a term for corrosion acceleration due to radiation flux; P is a factor to account for corrosion at various pH levels; S is a factor to account for oxide solubility -- this correction is better grounded in fundamental considerations than using a heat flux term and is more meaningful than an effective corrosion temperature -- and R is a factor to adjust for local temperature imbalances around the circumference of the fuel element. The exact form of the equation -- whether with multiplicative terms as shown or with additive terms -- would have to be determined through extensive data correlation.

D. Application of Test Results to Indicate When Dichromate Concentration Should be Changed - Localized Corrosion Aspects

The total corrosion experienced by the fuel elements in this test was found to be dependent on time of exposure, surface temperature, and sodium dichromate concentration. Reducing either of the first two dependent variables or increasing the dichromate concentration all tended to decrease fuel jacket corrosion. Because of the interrelationship between the three dependent variables, all should be factored into any formula to predict fuel corrosion. For example, if surface temperatures are low, either, or both, extremely long times of exposure or low dichromate concentrations could be tolerated without causing excessive corrosion. It is also known that the corrosion is very dependent on pH; however, pH as a variable was not investigated during this test.

In establishing a formula for predicting the corrosion of fuel, the reliability of the values for the dependent variables in the equations must be good. In the PTA-176 test it is felt that the data showing the effects of dichromate concentration is very good and can be used with confidence in a corrosion prediction equation, and that the temperature data, with some reservations discussed below, can also be used with confidence. The exact dependence of corrosion on time of exposure is not felt to be as well established and should be better defined in future tests. The dependence of corrosion on time was assigned a linear relationship in evaluating the test data, but this assignment is subject to debate.

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The reservations expressed above for the temperature data are that an excellent correlation was found between fuel element weight loss and temperature but a well-defined correlation between localized corrosion and temperature was not found. Part of the problem is probably associated with the effect of support corrosion on localized cladding corrosion - when the supports are corroded away accelerated cladding corrosion occurs.

All corrosion prediction equations in the past for the Hanford single-pass reactors have been based on weight loss data, while in actuality the localized corrosion is of more interest in predicting fuel element failures. As an example, the weight losses reported in this document on the fuels experiencing the most severe corrosion were in the neighborhood of 20 grams, or equivalent to about 8.5 mils of wall thickness removed assuming uniform corrosion. In reality, the corrosion was not uniform and occurred primarily on the bottoms of the fuel elements to a depth of 45 mils (AlSi exposed). It is the prediction of the non-uniform corrosion that is difficult since it occurs randomly, and once it occurs, there is no economical method of quantitatively measuring it. (Visual inspections of the fuel to obtain estimates of depth of localized corrosion are still the most economical method of obtaining the measurements, but this type of measurement is not very quantitative. A pit depth measuring device, which was used on the fuels in this test has provided much better information than in the past on depths of localized corrosion, but has not been as useful as desired since selected areas where visual examination indicates the severest corrosion is occurring cannot be easily measured with the pit depth device. Metallography is a very quantitative technique, but it is much too expensive for use on a large number of fuel elements.) The types of localized corrosion found were of the types reported in the past -- groove corrosion, ledge corrosion, and erosion-corrosion around the upstream ends of the fuel supports. Of these types of localized corrosion, the erosion-corrosion and groove corrosion were the most severe.

An inspection of the pit depth data in Figures 10-13, while difficult to interpret because of the high degree of data scatter, shows that the depth of attack, as discussed above, is more dependent on time and temperature and less dependent on dichromate concentration. The effect of surface temperature on pit depth was small when the surface temperature was less than 120 C; pit depths on all fuel between 95 C and 120 C generally lay in a band between 5 and 20 mils penetration. A sharp increase in pit depth occurred when the temperature increased above 120 C. Pit depths on many of the fuel elements with surface temperatures above 120 C ranged from 20 to 35 mils deep. However, even at surface temperatures above 120 C, the majority of the fuel exhibited pit depths less than 20 mils.

Time had little effect on the average measured pit depth up to 120 C but above 120 C the average pit depth increased with time. However, a linear effect of time was found on maximum pit depth; after 66 operating days, the maximum pit depth was 20 mils, and after 105 operating days the maximum measured pit depth was 35 mils.

Dichromate concentration had a much less effect on pit depth than either temperature or time. The effect of dichromate concentration was only noticeable at surface temperatures above 120 C on fuel at the final discharge. While maximum pit depths at these conditions ranged from 20 to 35 mils deep on fuel at both dichromate concentrations, the frequency of pit depths in this range was about twice as great on fuel exposed to coolant with 0.5 ppm dichromate as on fuel exposed to coolant with 1.0 ppm dichromate.

From the above discussion, it can be seen that fuel failures on high exposure fuel at high temperature will most likely occur as a result of localized corrosion and that failures will occur at both dichromate concentrations, but will occur at a higher frequency in coolant containing 0.5 ppm dichromate than in coolant containing 1.0 ppm dichromate. There may be only a few fuel elements in the reactor experiencing localized corrosion sufficiently severe to cause a failure; however, failures of these few elements dictate when the reactor must be shut down. It appears that the best way of reducing fuel failures is to operate with surface temperatures less than 120 C or operate with low exposures. Since neither of these is a suitable method, some reduction in the probability of a cladding failure due to corrosion can be obtained by increasing the dichromate concentration to 1.0 ppm whenever fuel surface temperatures exceed 120 C and exposures of more than 65-75 operating days exposure are planned. This plan assumes that operation during the other less corrosive periods will be with 0.5 ppm dichromate since past experience has shown that dichromate cannot be completely eliminated from the cooling water.

Another method of reducing the probability of a fuel cladding corrosion failure would be to decrease the corrosion rate by decreasing the pH from the current level of 6.6 ± 0.1 to a lower value whenever surface temperatures exceed 120 C. However, pH effects were not investigated during this test and will not be further discussed; interested readers may obtain further information on the effects of pH on corrosion in References 8, 13-15. The important point to make here is that if fuel exposures of 100 days or over are planned, severe localized corrosion penetrating to the AlSi layer can be expected on fuel surfaces operating at surface temperatures greater than 120 C. The corrective action under these circumstances would be to either increase the dichromate concentration to 1.0 ppm, reduce the pH, or both. Thus, some method to identify when the chemistry changes must be made should be available. The best method of determining when the chemistry changes should be made would be to have a computer calculation periodically made on ten to twenty of the fuel columns most likely to be operating with 120 C surface temperatures. Existing computer programs such as the MOFDA program could be used. Simple indicators of when to change chemistry were looked at but none seemed to provide a good indication because there are too many variables associated with surface temperatures. Indicators looked at included bulk outlet temperature, tube outlet temperature, inlet temperature, and tubepower. Fuel surface temperature is dependent on all of these factors (rather than being more dependent on one) in addition to type of fuel, flow rates, flux distribution, and local hot spots. One simple method would be to make chemistry

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changes about the first of May and returning about the first of December, since the hotter surfaces are normally experienced during the summer and fall months. However, this could be wasteful of chemicals by arbitrarily setting the limits at these times; much better control could be obtained by a computer calculation of surface temperatures combined with a knowledgeable factoring of fuel exposure times.

As an indication of the complexity of obtaining a fuel surface temperature, and why a computer run is suggested, a brief outline of the calculations required are given below.

The annular surface temperature T_s of the i th fuel in the column is given by

$$T_{si} = q_i/h_i + T_{mi}$$

where q_i = heat generated per unit area on the annular surface of the i th element.

h_i = convective heat transfer coefficient at annular surface, BTU/hr - ft^2 - $^{\circ}F$

$$h_i = \frac{0.023k (Re)^{0.8} (Pr)^{0.33}}{Da}$$

T_{mi} = bulk water temperature at the midpoint of the fuel element

Re = Reynolds number

Pr = Prandtl number

Da = equivalent diameter

The coefficients in the heat transfer coefficient, h_i , are evaluated at the film temperatures which in turn are a function of surface temperature, thus requiring several iterative calculations to obtain the correct values. In addition the bulk temperature at each given point must be calculated by summing the incremental temperature increases obtained from each fuel element in the column, a calculation requiring knowledge of tube power, total flow, flow and heat splits, and specific power. Since these factors all vary from tube-to-tube, a straightforward relationship of surface temperature with only a single normally measured reactor parameter cannot be made. Thus, a computer calculation is the most efficient method of obtaining the required information.

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