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FINAL REPORT

PART I. THE KINETICS OF DISSOLUTION OF A SPECIAL TYPE AISI-347 STAINLESS STEEL IN SULFURIC ACID

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INTRODUCTION

At the request of the American Cyanamid Company and later the United States Atomic Energy Commission Operations Office in Idaho Falls, Idaho, a study was made of the kinetics of dissolution of a special type of AISI-347 stainless steel. Some of these results were reported in Progress Report 10 of September, 1953. Acid concentration, weight loss, and dissolved ion concentration at a temperature of 50°C were the variables considered in that report. This report considers the same variables at temperatures of 30 and 80°C. The data for 50°C included in this report have been taken directly from the previous report. The general discussion of experimental procedure is the same as found in the previous report. All other work is reported for the first time.

The data presented here are incomplete in several particulars, but experimental work was curtailed by a directive from the Atomic Energy Commission to spend all remaining time on a different phase of the project.

EXPERIMENTAL PROCEDURE

Preparation of the Samples

A special melt of 347 stainless steel in the form of cylinders was supplied by American Cyanamid for the investigations. These cylinders, approximately 0.08 inch in outside diameter and initially about 20 inches long, were cut in lengths of about 5 inches. The samples were then thoroughly degreased in carbon tetrachloride, dried, and weighed. In a preliminary study, a few samples were polished before degreasing and weighing. However, the results from these samples checked closely with those using unpolished specimens. This polishing procedure was therefore omitted. The diameter of the cylinder was measured and then the open ends of the sample were fitted with polyethylene caps in such a manner that the length of sample exposed to the acid would be exactly 5 inches. These caps can be seen in Fig. 1. No attack was found to occur underneath the caps.

Preparation of Sulfuric Acid Solutions

The pure 4, 6, and 8M sulfuric acid solutions were prepared by diluting standard reagent-grade acid with the proper amount of distilled water. The concentrations were checked by measuring the density of the solutions with a Westphal balance. The solutions containing dissolved 347 stainless steel were prepared by dissolving 20, 40, and 60 grams of steel turnings in 1-liter portions of each of these three initial acid concentrations. The steel turnings were obtained from a 1-inch-diameter rod supplied by American Cyanamid and designated as regular type 347 stainless steel.

The addition of steel to the 4 and 6M acid resulted in primarily single-phase deep-blue solutions containing only a small amount of carbon, which settled out on standing. However, in the case of the 8M solution a light-blue precipitate, presumably metallic sulfates, formed after the addition of the steel turnings. It was also necessary to heat the 8M solution for about 4 hours in order to get the steel into solution. The tests were run with this precipitate suspended in the solution.

Suspension of Sample and Conduct of Runs

The cleaned, weighed, and measured cylinder sample was suspended in the center of a large test tube by means of a polyethylene float as shown in Fig. 1. Each tube contained 165 ml of solution and was allowed to come to thermal equilibrium in a constant-temperature water bath before introduction of the sample. The same water bath as that shown in the previous report was used. The duration of the runs varied, but in general the samples were removed when an estimated 10 percent of the metal had dissolved. The samples were then washed, dried, and reweighed, and the diameters remeasured. The rate of dissolution was calculated by dividing the weight loss by the length of the run and the average area exposed to attack.

Observations during the Runs

The samples turned black during the runs. In many cases the black coating, probably carbon, flaked off on washing.

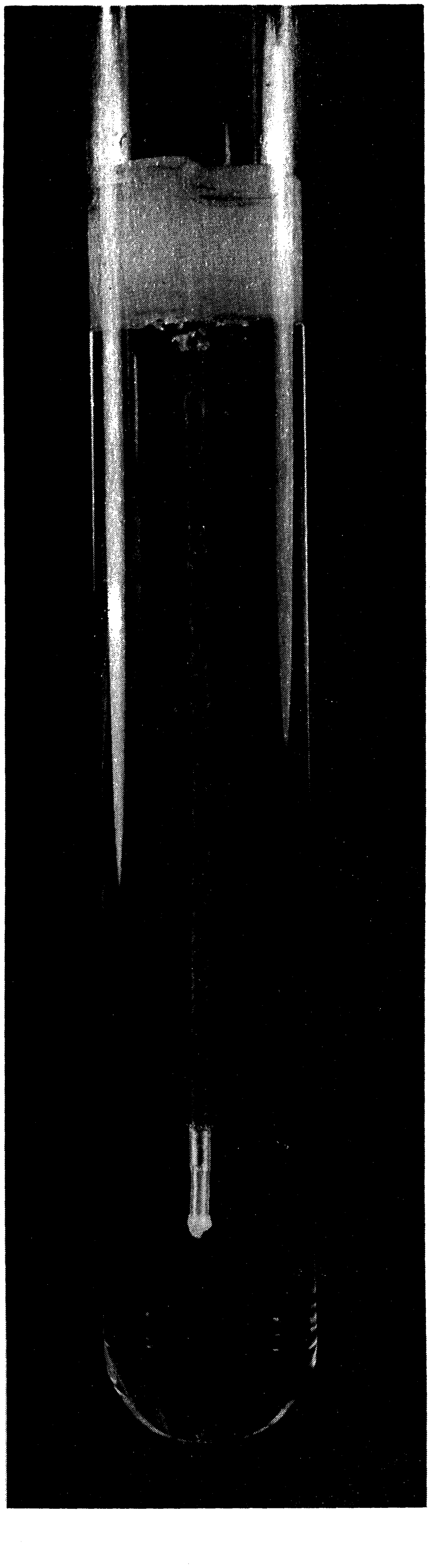


Fig. 1. Stainless Steel Cylinder Dissolving in **Sulfuric Acid.** Distance between Polyethylene Holder at Top and **Polyethylene** Cap at Bottom is Five Inches.

All samples were started using the battery procedure described in part A-5 of the previous report.

Preliminary experiments were performed using samples 3 inches in length, and it was found that the dissolution rate would not check with the dissolution rate determined for the 5-inch samples. Closer comparison of the results showed that the 3-inch runs always gave greater dissolution rates than identical runs using the 5-inch samples. Since the method of preparation and suspension was identical for the two types of samples, this discrepancy must be attributed to vapor blanketing by the hydrogen on the longer-length sample, thus reducing the effective reaction area.

RESULTS

The results of the investigations are presented in both tables and graphs. Graphs of dissolution rate versus molarity of H_2SO_4 at constant temperature and graphs of dissolution rate as a function of temperature at constant acid concentration have been prepared. Cross plotting will yield dissolution rate as a function of other variables. Several seemingly inconsistent results should be mentioned here.

In Fig. 2, showing dissolution rate versus molarity of H_2SO_4 at 30°C, the curve for 0 g/ℓ of dissolved stainless steel could be drawn with no difficulty. At this comparatively low temperature no reaction seemed to be the rule if there was dissolved stainless steel present in the solution. Points at finite rates were determined at 8M20, 6M40, and 6M60 (should be read 8M H_2SO_4 with 20 g/ℓ of dissolved stainless steel), but at all other steel concentrations no reaction or weight loss could be determined even after immersion of the samples for as long as a week. The results are peculiar in that no rate could be found for 6M20 although one was determined for 6M40 and 6M60. Since this is a contradiction of what would be expected, no other curves have been drawn and only the experimental points have been located on the graph. A logical explanation of the inconsistency is lacking; it is possible that the curves go through a maximum near 6M acid, which would account for the low value of the 8M20 dissolution rate in relation to the other observed points.

Figure 3 is the same as Fig. 3 of the September, 1953, report and has been corrected for insertion here. The apparent reversal of reaction rates for the 8M60 and 8M40 was mentioned in the previous report and therefore is only noted here.

Figure 4, showing dissolution rate versus molarity H_2SO_4 at 80°C, follows the fairly well defined pattern. There seems to be more scatter of

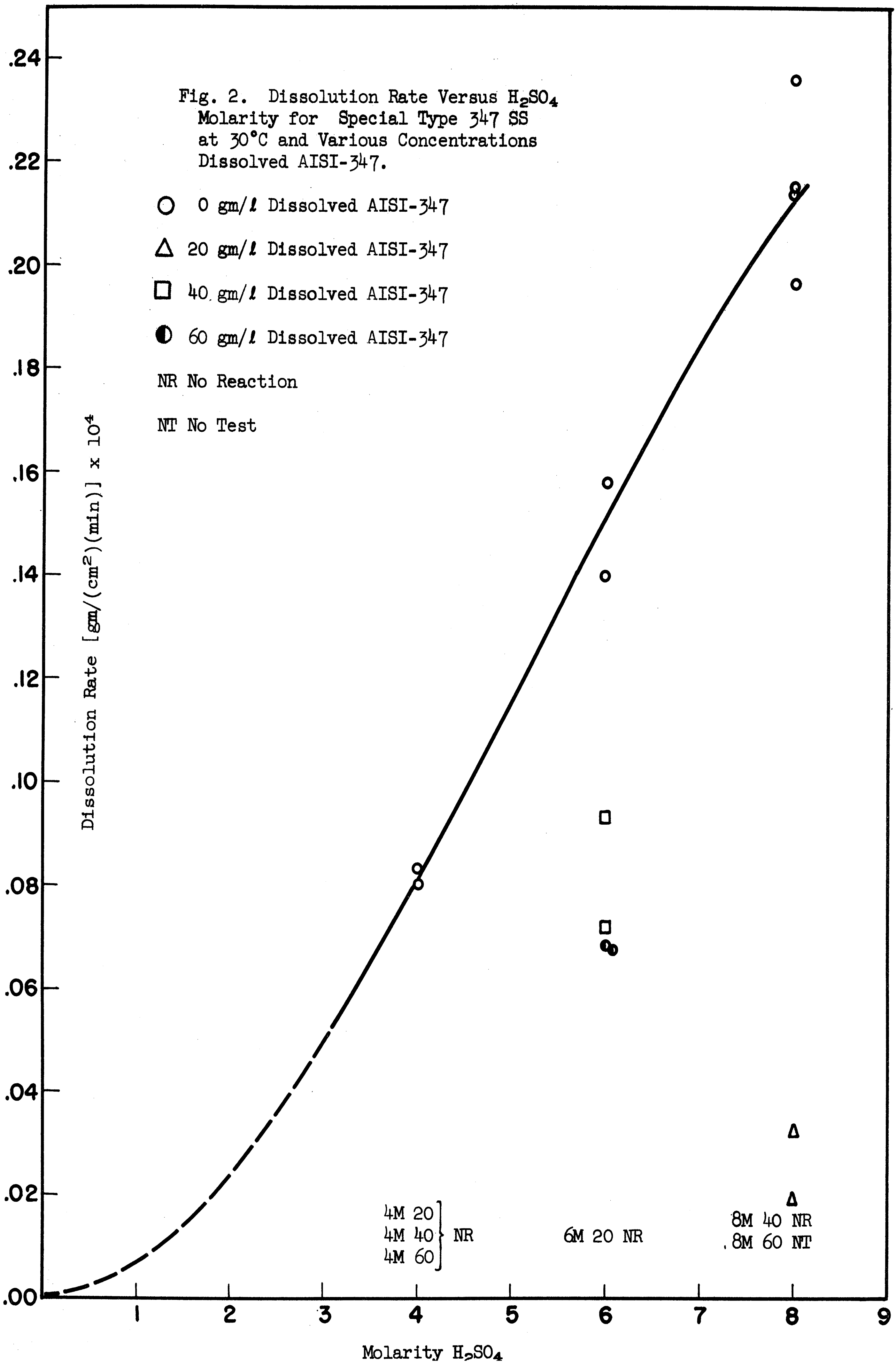


Fig. 2. Dissolution Rate Versus H_2SO_4 Molarity for Special Type 347 SS at 30°C and Various Concentrations Dissolved AISI-347.

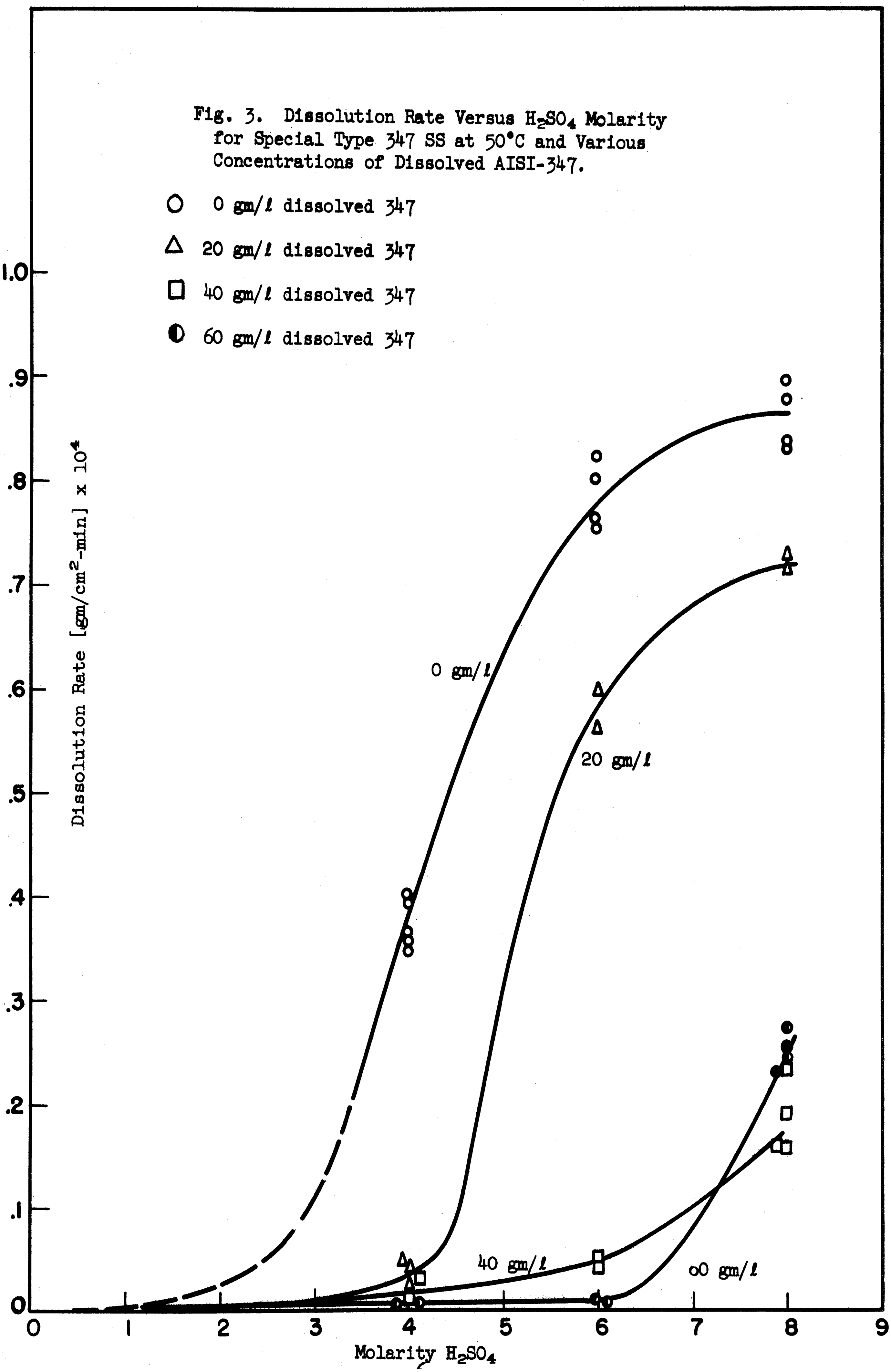


Fig. 3. Dissolution Rate Versus H_2SO_4 Molarity for Special Type 347 SS at 50°C and Various Concentrations of Dissolved AISI-347.

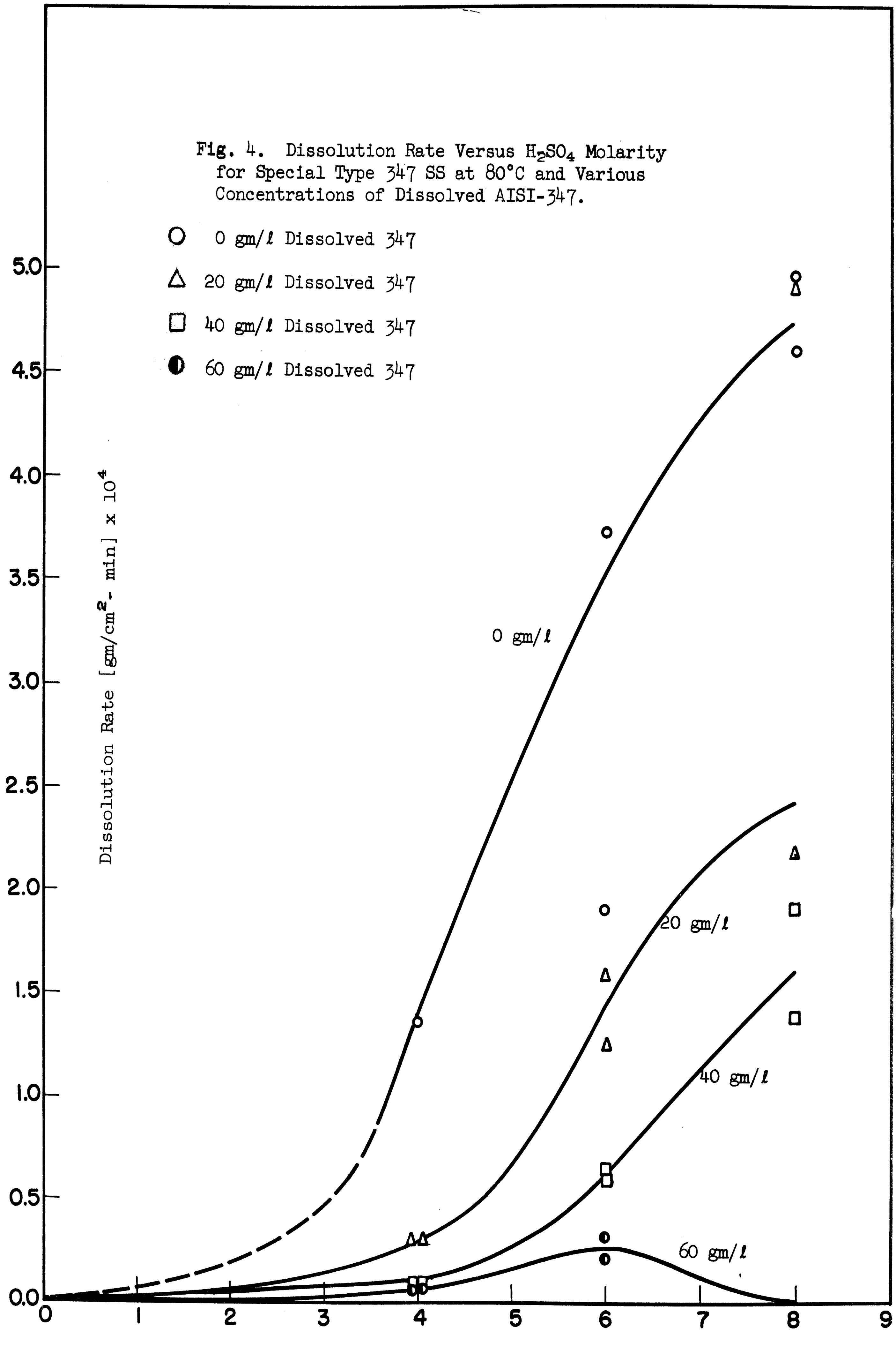


Fig. 4. Dissolution Rate Versus H_2SO_4 Molarity for Special Type 347 SS at 80°C and Various Concentrations of Dissolved AISI-347.

the data but this is normally expected at the higher reaction rates. No reaction was observed to take place with any of four samples run in 8M60 solutions. As mentioned in the Preparation of the Sulfuric Acid Solutions, a large amount of light-blue precipitate, presumably sulfates, was present in the solution. This may have been enough to prevent reaction of the special type 347 stainless steel.

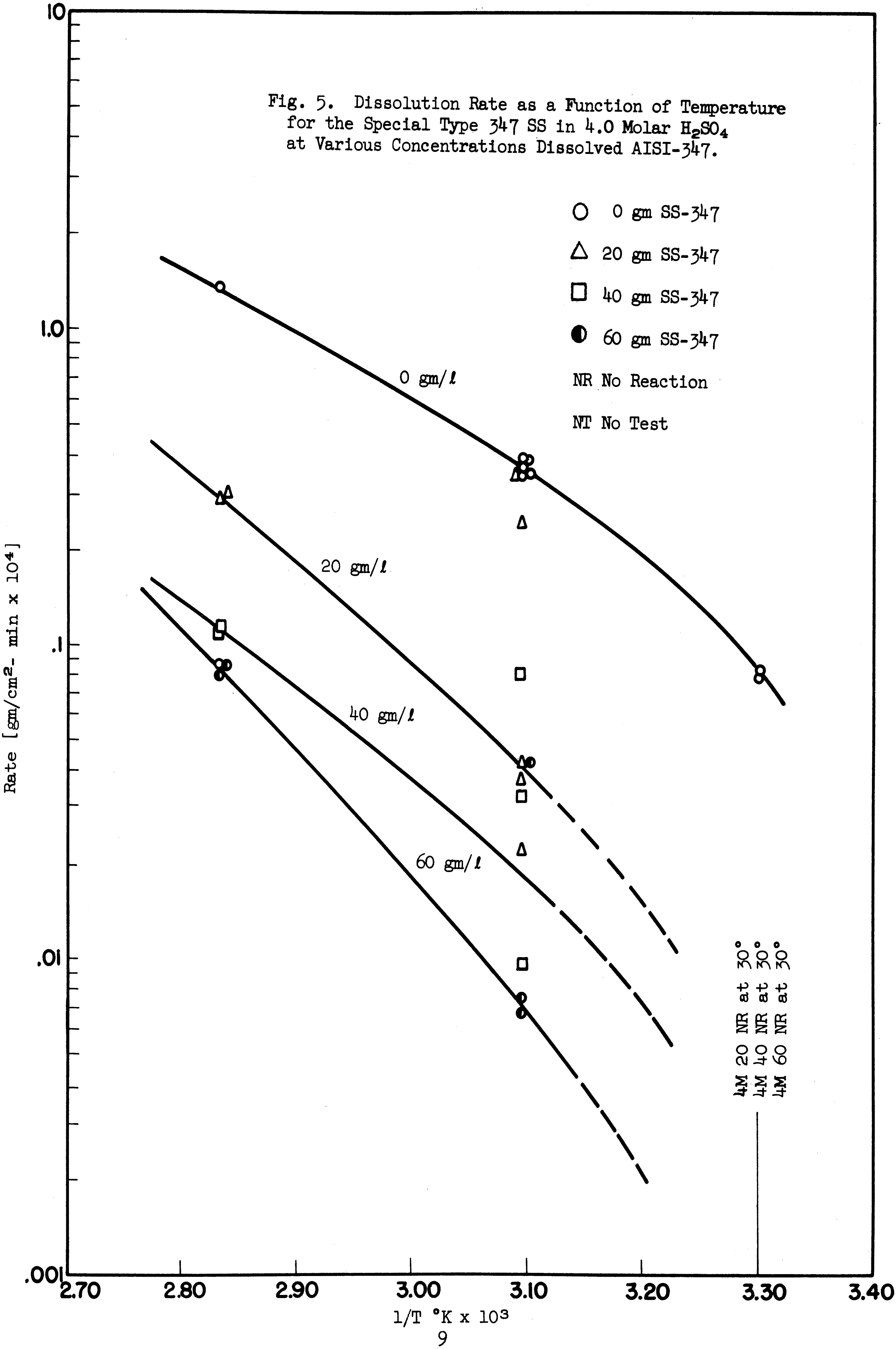
Figures 5 through 7 are plots of dissolution rates as a function of temperature for the special type 347 at constant starting acid molarities with concentration of dissolved stainless steel as the parameter.

Figure 6 shows an unexpected inversion of reaction rate with temperature for the higher concentrations of dissolved steel. Figure 7 is well defined except for the 60 g/ℓ of dissolved steel curves, which have been sketched in as dashed lines since there was no reaction at 8M60 at 80°C and no test at 8M60 at 30°C.

Scattering of the data may have been the result of an inconsistancy in the original samples supplied to Engineering Research Institute. It was noticed and pointed out in personal communications that there seemed to be several different types of coating on the samples. The external appearance varied between samples from shiny to dull gray. All the samples were treated identically with regard to washing, preparation, and starting to eliminate as much of the scatter as possible, but the variance of samples could not be controlled.

Further work had been planned on the apparent inconsistencies of the data, but was discontinued at the time of the directive. Intermediate acid concentrations and temperatures would undoubtedly determine the curves more exactly.

Fig. 5. Dissolution Rate as a Function of Temperature for the Special Type 347 SS in 4.0 Molar H_2SO_4 at Various Concentrations Dissolved AISI-347.



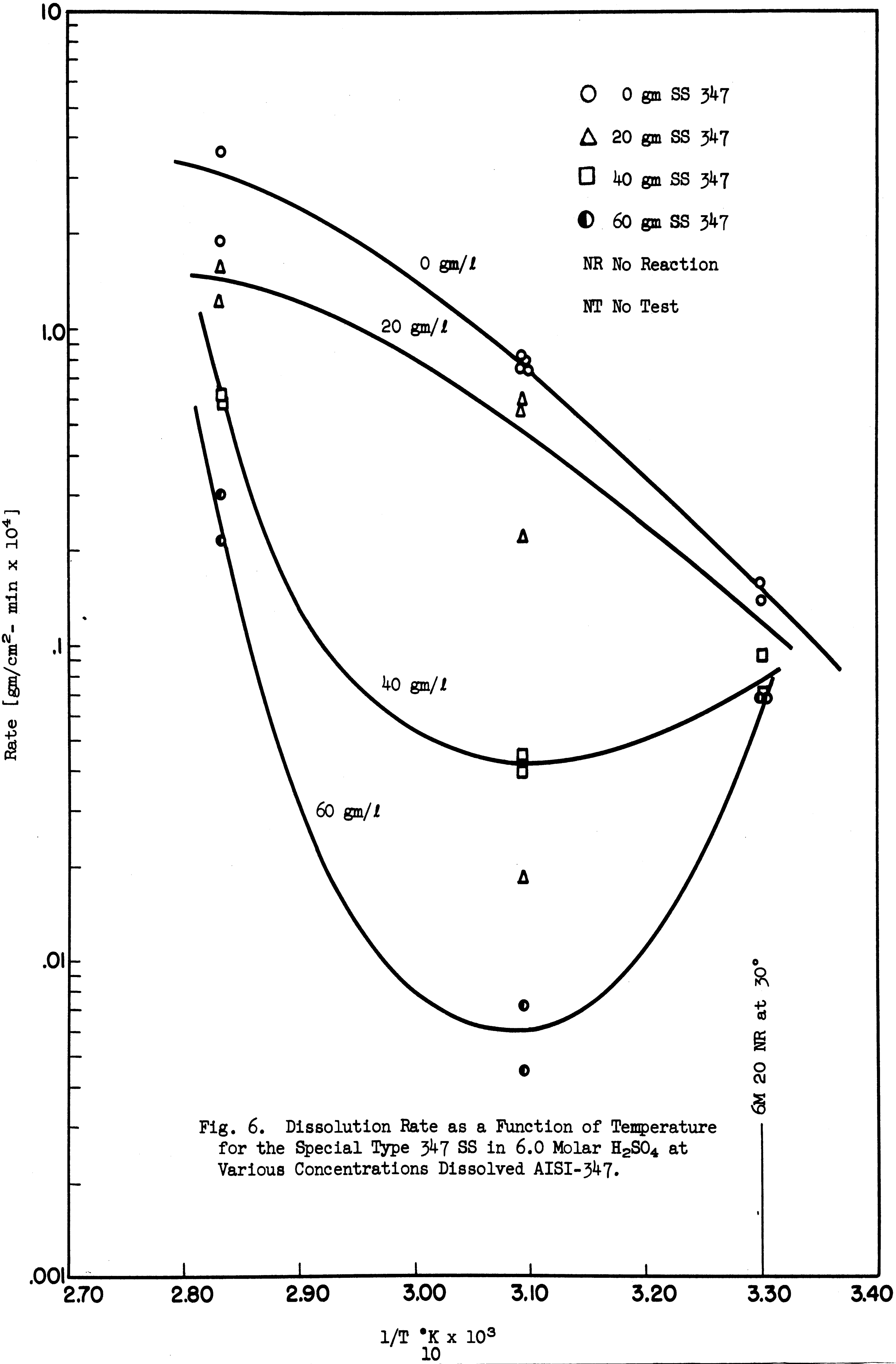


Fig. 6. Dissolution Rate as a Function of Temperature for the Special Type 347 SS in 6.0 Molar H_2SO_4 at Various Concentrations Dissolved AISI-347.

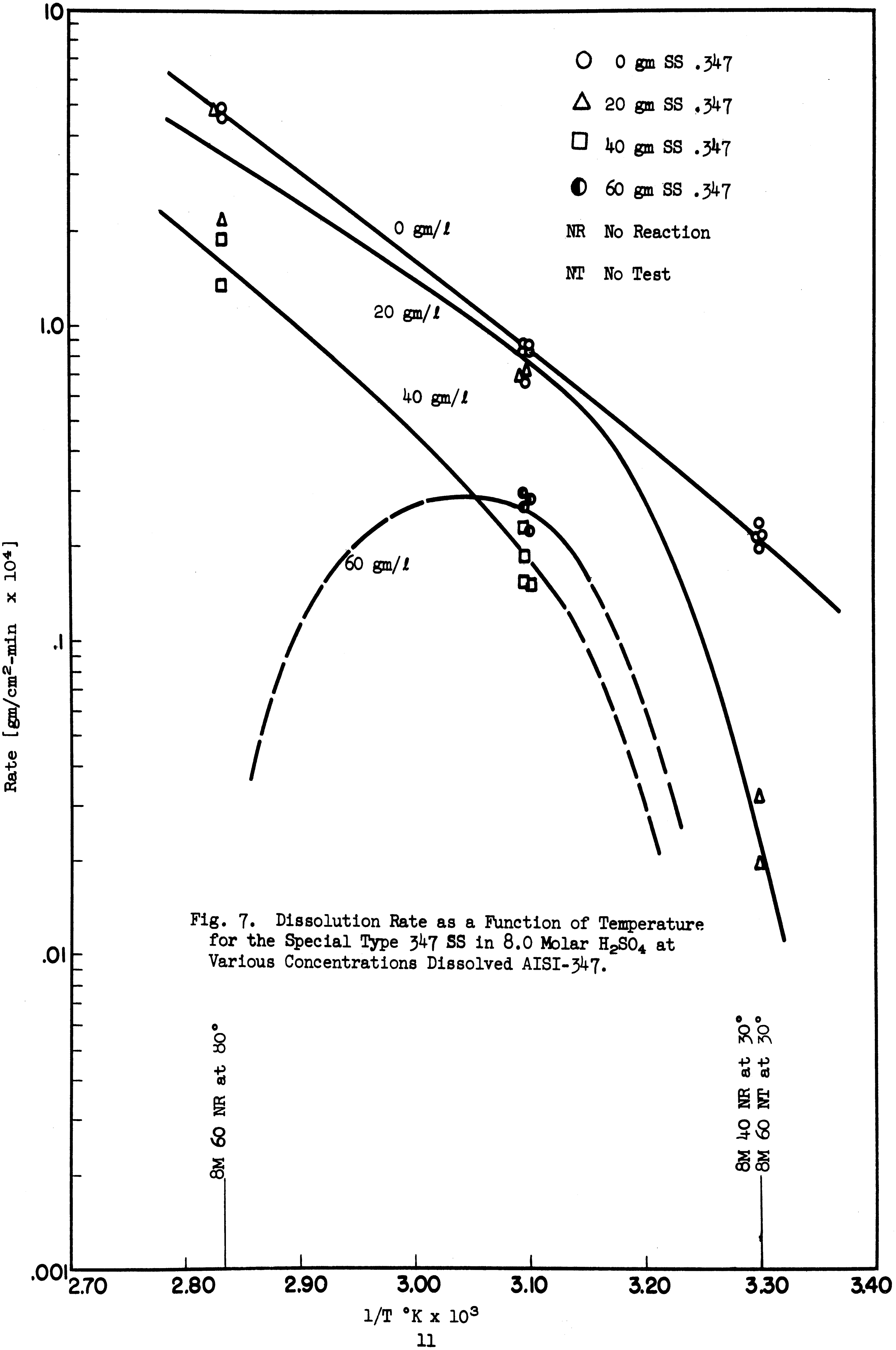


Fig. 7. Dissolution Rate as a Function of Temperature for the Special Type 347 SS in 8.0 Molar H_2SO_4 at Various Concentrations Dissolved AISI-347.

TABLE I

DISSOLUTION RATE OF SPECIAL TYPE 347 STAINLESS STEEL IN VARIOUS CONCENTRATIONS OF SULFURIC ACID AND AISI-347 STAINLESS STEEL AT 30°C

Initial Acid Concentration, moles/liter	Dissolved AISI-347, Stainless Steel grams/liter	Dissolution Rate, $\left[\frac{Gm}{(cm^2)(min)}\right] \times 10^4$
7.97	0	.236
7.97	0	.197
7.97	0	.214
7.97	0	.215
7.97	20	.0190
7.97	20	.0318
7.97	40	No Reaction
7.97	40	No Reaction
5.98	0	.140
5.98	0	.158
5.98	20	No Reaction
5.97	40	.0933
5.97	40	No Reaction
5.97	40	.0717
5.97	60	.0685
5.97	60	.0684
5.97	60	No Reaction
5.97	60	No Reaction
4.06	0	.0801
4.06	0	.0831
4.06	20	4 samp. N.R.
4.06	40	2 samp. N.R.
3.99	40	4 samp. N.R.
4.06	60	2 samp. N.R.
3.99	60	4 samp. N.R.

TABLE II

DISSOLUTION RATE OF SPECIAL TYPE 347 STAINLESS STEEL
IN VARIOUS CONCENTRATIONS OF SULFURIC ACID
AND AISI-347 STAINLESS STEEL AT 50°C

Initial Acid Concentration, moles/liter	Dissolved AISI-347 Stainless Steel grams/liter	Dissolution Rate, $\left[\frac{Gm}{(cm^2)(min)}\right] \times 10^4$
8.04	0	.835
8.04	0	.831
8.04	0	.894
8.04	0	.878
8.04	0	.667
8.04	20	.926
8.04	20	.916
8.04	20	.712
8.04	20	.727
8.04	40	.154
8.04	40	.153
8.04	40	.188
8.04	40	.231
8.04	60	.228
8.04	60	.272
8.04	60	.281
8.04	60	.295
5.97	0	.800
5.97	0	.822
5.97	0	.752
5.97	0	.754
5.97	20	.221
5.97	20	.0818
5.97	20	.558
5.97	20	.596
5.97	40	.0395
5.97	40	.0444
5.97	60	.00448
5.97	60	.00712
3.99	0	.392
3.99	0	.391
3.99	0	.346
3.99	0	.364
3.99	0	.346
3.99	20	.0379
3.99	20	.0432
3.99	20	.0224
3.99	40	.00966
3.99	40	.0334
3.99	40	.0820
3.99	60	.00756
3.99	60	.00678
3.99	60	.0452

TABLE III

DISSOLUTION RATE OF SPECIAL TYPE 347 STAINLESS STEEL
IN VARIOUS CONCENTRATIONS OF SULFURIC ACID
AND AISI-347 STAINLESS STEEL AT 80°C

Initial Acid Concentration, moles/liter	Dissolved AISI-347 Stainless Steel grams/liter	Dissolution Rate, $\left[\frac{Gm}{(cm^2)(min)}\right] \times 10^4$
8.04	0	4.952
8.04	0	4.599
8.04	20	2.176
8.04	20	4.914
8.04	40	N.R.
8.04	40	1.906
8.04	40	1.375
8.04	60	4 samp. N.R.
5.97	0	1.889
5.97	0	3.695
5.97	20	1.224
5.97	20	1.574
5.97	40	.586
5.97	40	.626
5.97	60	.216
5.97	60	.305
3.99	0	N.R.
3.99	0	1.353
3.99	0	.0868 N.G.
3.99	20	.296
3.99	20	.296
3.99	40	.109
3.99	40	.112
3.99	60	.0805
3.99	60	.0868