PICKLING OF STEEL

by

Melvin Kaufman

A Thesis Submitted for Partial

Fulfillment of the Requirements

for the

Degree of Bachelor of Science

in

CHEMICAL ENGINEERING

Approved:

____
In Charge of Investigation

____
Head of Major Department

Virginia Polytechnic Institute

Blacksburg, Virginia

1962

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

I. INTRODUCTION

Pickling is a cheap method for cleaning the surface of a piece of metal with little attack on the metal itself. In the industrial pickling of iron and iron products there are seven solutions most commonly used as pickling baths.

Pickling inhibitors are agents that may be added to an acid pickling bath to diminish the attack of the acid on the metal areas from which the scale has been removed, without appreciably retarding the rate at which the acid removes scale or rust.

The purposes of this investigation are: to determine which pickling bath will remove the most surface oxide in the least amount of time; to determine the effect of the addition of an inhibitor to the pickling bath; to determine the life of the inhibitor; and to determine the frequency factor and energy of activation for the pickling of steel in 18.3 per cent sulfuric acid solution.

II. LITERATURE REVIEW

"Pickling is the term applied to the chemical removal of surface oxides from metal by immersion in an acid solution"[1]. Many different pickling baths with regard to type, strength, and temperature of the acid solution are possible. The bath to be used depends on the material to be pickled, the character of the scale involved, and the surface desired after the pickling.

Pickling Procedures for Various Ferrous Metal Products

When low-carbon steel is pickled for enameling, galvanizing or tinning, special precautions are necessary to insure a surface that is chemically clean as well as free from scale. In pickling low-carbon steel, inhibitors or foaming agents may be used in the bath, but only with careful selection and proper precaution, because some inhibitors leave a thin but very tightly adherent surface film, which clings persistently to the metal even after careful rinsing.

Pickling temperatures are generally between 150 to 160 °F. This range of temperatures produces a better quality finished product than would be gotten at higher temperatures, where time and pickling capacity permit, an acid concentration of five or six per cent is advisable. However, where comparatively low temperatures are employed, it is customary to compensate for decreased thermal activity by raising the acid concentration to about 10 or 15 per cent. Vigorous mechanical agitation of the bath is always advisable. When the solution is allowed to remain stagnant, gas pockets may form, keeping the acid out of contact with the metal and arresting the pickling solution on these localized areas. When the steel is galvanized, these scale-retaining areas remain uncoated. Agitation offers the further advantage of securing uniform acid concentration throughout the bath, assuring a more nearly uniform rate of pickling.

Pickling Solutions

Sulfuric, muriatic, nitric, and hydrofluoric acids, or mixtures of them are generally used[2]. Sulfuric acid is the cheapest pickling acid and the one most commonly employed[1]. Muriatic acid is used for special purposes, such as etching before galvanizing or tinning, and sometimes for pickling stainless steel. Nitric acid is used in the pickling of stainless steel and is occasionally employed to oxidize scaled surfaces in order to facilitate pickling. Hydrofluoric acid is sometimes added to the bath to accelerate pickling, and is used occasionally in pickling castings to remove sand.

Concentration of Acid. The concentration used depends upon the kind and temperature of acid, the type of material being pickled, and the surface desired.

Pickling Inhibitors. Pickling inhibitors are agents that may be added to an acid pickling bath to diminish the attack of the acid on the metal areas from which the scale has been removed, without appreciably retarding the rate at which the acid removes scale or rust; and to diminish the severity of hydrogen embrittlement.

<u>Pickling Temperatures</u>. An increase in temperature greatly increases the activity of the pickling bath. Overpickling is likely to occur at high temperatures. The choice of an inhibitor is an important factor in establishing the limiting temperature, since some inhibitors fail rapidly at high temperatures.

Although a temperature of 170 to 190 °F is sometimes satisfactory when the time cycle is short, pitting may result if the pickling period is prolonged. With many high-carbon and alloy steels, a pickling temperature of 140 to 150 °F has been found satisfactory for efficiency, surface quality, and life of the inhibitor.

<u>Theory and Mechanism of Inhibitors</u>. There are three theories concerning inhibitors. The first theory is that an inhibitor is a negative catalyst selective in action, retarding the reaction of acid on metal but not on scale. In practice, no inhibitor continues its original effectiveness unabated throughout the entire pickling cycle. However, inhibitors lose efficiency so slowly that the loss can hardly be attributed to reactions in which the

inhibitor plays a major part as reagent. The effect seems analogous to the poisoning of a catalyst. The second theory states that inhibitor action seems to be associated with an increase in the hydrogen over voltage at the metal (cathode) surface. A protective coating of hydrogen, maintained on the metal surface, helps to protect the metal from direct contact with the acid, thus diminishing the attack.

The third theory states that a thin layer of inhibitor material is adsorbed or plated out on the surface of the metal. However, if such a layer exists, it is so extremely thin as to escape detection in many instances.

Advantages and Disadvantages of Using an Inhibitor. The advantages gained from using an inhibitor are as follows: reduction in metal loss, saving of pickling acid, prevention or minimizing of scrap losses from overpickling, and a decrease in blistering and in hydrogen embrittlement. The disadvantages incurred in using an inhibitor are: increased pickling time, possibility of residual surface film, which may interfere with subsequent operation, and added cost of the inhibitor.

Pickling Defects

Some of the more common defects brought on by pickling are presented in the following paragraphs.

Blistering. This is a troublesome defect on sheet and strip steel. Blistering is brought about by gaseous inclusions forming gas pockets just beneath the surface of the steel during rolling. Hydrogen generated in the pickling operation, penetrates these pockets and lifts the surface, causing a blister. Properly selected inhibitors may minimize blistering but cannot prevent it.

Hydrogen Embrittlement. Hydrogen embrittlement is a result of the penetration of the steel by nascent hydrogen. Inhibitors are valuable in minimizing this effect.

Overpickling. This error causes porosity of the transverse surfaces and a roughening of the whole surface, accompanied by a discoloration and decrease in size and weight. Overpickling can be avoided by removing the metal from the bath promptly when the pickling has been accomplished. Inhibitors aid in preventing overpickling, but are not a guarantee that it will not occur.

<u>Picklepitting</u>. Electrolytic pitting is the most prevalent and troublesome type. It is characterized by a patchwork of pitted areas irregular in shape. Caused by an electric potential between the scaled areas and the clean steel, electrolytic pitting occurs only where the scale has been removed from small areas before the pickling or at an early stage in the process.

III. EXPERIMENTAL

The following sections contain the purposes of this investigation, the plan of experimentation by which this investigation was carried out, the materials and apparatus used, the method of procedure, data and results, and a sample of the calculations performed.

Purposes of Investigation

The purposes of this investigation are: to determine which pickling bath will remove the most surface oxide in the least amount of time, to determine the effect of the addition of an inhibitor to the pickling bath, to determine the life of the inhibitor, and to determine the frequency factor and energy of activation for the pickling of steel in 18.3 per cent sulfuric acid solution.

Plan of Experimentation

The following paragraphs contain the plan of experimentation by which this investigation was carried out.

Preliminary Investigation. A brief study of the available literature was to be made by the author in order to familiarize himself with the more general principles of the pickling of iron and iron products.

Description of Experimental Work. The experimental work consisted of determining which pickling bath is most efficient, determining the effect of the addition of an inhibitor to a pickling bath, determining the life of the inhibitor, and determining the frequency factor and energy of activation for the pickling of steel in sulfuric acid.

Determination of the Most Efficient Bath. The most efficient pickling solution was to be determined from a plot of loss in weight versus time. The loss in weight, expressed as milligrams per square inch, is the loss in weight of a steel coupon after being immersed in a pickling bath for a three-minute interval. The coupon was to be immersed as many times as was required for the weight loss to become constant. Then the coupon was to be immersed one more time for approximately 30 minutes.

<u>Determination of the Effect of Adding an Inhibitor to the Pickling Bath</u>. The effect of adding an inhibitor to a pickling solution was to be determined from two plots of the loss in weight of the steel coupon versus time. The time of immersions chosen were 1, 2, 4, 8, 16, and 32 minutes. A plot would be made to represent the pickling of the coupon in an uninhibited pickling bath, and a second plot to represent the pickling of the coupon in an inhibited pickling bath.

<u>Determination of the Life of the Inhibitor</u>. From the plot of the pickling of the steel coupon in the uninhibited pickling bath, the time required to remove the surface oxide from the steel coupon may be obtained. Then each of four steel coupons are immersed in a freshly-prepared inhibited pickling bath one at a time for this amount of time. Then a plot of loss in weight versus time for a fifth steel coupon will be made. The length of immersion in the pickling bath will again be 1, 2, 4, 8, 16, and 32

minutes. This procedure will be repeated until the amount of surface oxide removed, and the rate of attack on the metal itself, are approximately the same as obtained using the uninhibited pickling bath. It will be necessary to replenish the amount of acid in the pickling bath so that the acid remains at full strength.

Determination of the Frequency Factor and the Energy of Activation for the Pickling of Steel in 18.3 Per Cent Sulfuric Acid Solution. The frequency factor and the energy of activation for the pickling of steel in 18.3 per cent sulfuric acid solution will be determined using the Arrehenius equation once the rate of attack on the base metal is known.

Materials

Under this heading there will be found the materials used during this investigation.

Acetone. Impure. Supplied by the J. T. Baker Chemical Co., Philadelphia, Pa. Used to dry sample.

Ammonium Hydroxide. C. P., code 1293, lot E501006. Supplied by General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used as a component of the pickling solution.

Citric Acid. Manufactured by J. T. Baker Chemical Co., Philadelphia, Pa. Used as a component of the pickling solution.

Distilled Water. Distilled from Virginia Polytechnic Institute tap water, Blacksburg, Virginia. Used to wash the sample.

Ferric Sulfate. Lot No 13142. Supplied by J. T. Baker Chemical Co., Phillipsburg, N. J. Used as a component of the pickling solution.

Hydrochloric Acid. Assay (HCL) - 37.7 per cent, lot No 6041. Supplied by J. T. Baker Chemical Co., Philadelphia, Pa. Used as a component of the pickling solution.

Phosphoric Acid. Lot No 9127. Supplied by J. T. Baker Chemical Co., Philadelphia, Pa. Used as a component of the pickling solution.

Potassium Nitrate. Lot No 0310, code 2122. Supplied by General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used as a component of the pickling solution.

Rodine 82-A. Lot No 2A 2658. Supplied by Amchem Products, Inc., Ambler, Pa. Used as inhibitor.

Sulfuric Acid. Assay (H_2SO_4) - lot No 90628. Supplied by J. T. Baker Chemical Co., Philadelphia, Pa. Used as a component of the pickling solution.

Apparatus

Under this heading there will be found the apparatus utilized during this investigation.

Basin. Supplied by Blacksburg Hardware Co., Blacksburg, Va. Used to contain water in which pickling solution was heated.

Beaker. Capacity 250 ml, pyrex. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to containing pickling solutions when tests were being run at room temperature.

Beaker. Capacity 800 ml, pyrex. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to hold wash water.

Clamps. Two required. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to hold condenser and flask to ring stand.

Condenser. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to condense vapors from pickling solution when tests were run at elevated temperatures, c.c., temperatures greater than 120 °F.

Flask. Capacity 250 ml. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to hold pickling solution when tests were run at temperatures greater than 120 °F.

Graduated Cylinder. Capacity 50 ml. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to measure volume of acidic components of pickling solutions.

Graduated Cylinder. Capacity 100 ml, pyrex. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to measure volume of distilled water used in pickling solution.

Hot Plate. One hundred and fifteen volts. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to heat water for heating pickling solution.

Power Station. Type 220-C, 115V50 - 6025A Supplied by General Radio Co., Cambridge, Mass. Used to control current to hot plate.

Ring Stand. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used for mounting condenser and flask.

Rubber Tubing. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to supply water to, and remove water from condenser.

Stove Pipe. Per cent carbon 0.095. Supplied by Brown's Hardware, Blacksburg, Va. Used as sample for pickling.

Thermometer. Engraved, 0-300 °F. Supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to measure temperature of pickling solution.

Method of Procedure

The procedure by which this investigation was carried out is presented in the following paragraphs.

Preparation of the Pickling Baths. The pickling baths were prepared according to specified concentrations.

Determination of the Most Efficient Pickling Bath. After preparing the pickling bath according to the specified concentration, and bringing the pickling bath to the desired temperature the steel coupon was immersed for three minutes. The coupon was weighed before immersion. After three minutes the coupon was immersed in distilled water to remove any loose scale which might be clinging to the coupon. The coupon was then dipped in acetone to remove the water, and dried in air. After the coupon was dry it was weighed to determine the loss in weight. This procedure was repeated until the loss in weight became constant. Then the coupon was immersed for approximately 30 minutes, washed, dried, and weighed again. The last step was helpful in determining whether all the surface oxide had been removed, and for measuring the rate of attack on the bare metal. The plots of the loss in weight versus time were made for all the pickling baths used. A straight line beginning at the last point on the curve, and tangent to the curve is drawn until it intersects the vertical (loss in weight) axis. The point of intersection represents the amount of scale removed. The intersection of a straight line drawn from the point of tangency with the horizontal (time) axis represents the time required to remove the surface oxide. By comparison of results the most efficient solution was determined.

Determination of the Effect of Adding an Inhibitor to the Pickling Bath. The pickling bath being studied was 18.5 per cent sulfuric acid solution because the only inhibitor available was Rodine 82-A. This inhibitor is used only for sulfuric acid. This solution was prepared by mixing 22 milliliters of 97 per cent sulfuric acid with 178 milliliters of distilled water. The inhibited pickling bath, containing 0.25 per cent inhibitor, was prepared by mixing 22 milliliters of sulfuric acid, 158 milliliters of distilled water, and 20 milliliters of a solution containing 5 milliliters of the inhibitor, Rodine 82-A, and 200 milliliters of distilled water.

Using the same procedure as in the previous section, a steel coupon was cut in half and immersed in the baths. The times of immersion were 1, 2, 4, 8, 16, and 32 minutes. Using the loss in weight data obtained two curves were plotted, one for the inhibited bath and one for the uninhibited bath. The effect of the inhibitor on the bath can be determined from a comparison of the two curves.

Determination of the Life of the Inhibitor. The pickling bath used to determine the life of the inhibitor was of the same composition as the inhibited bath used in the preceding section.

Four samples were immersed, one at a time, in the bath for that length of time required to remove the scale. The time was determined in the preceding section. The weight of the samples, and the pickling bath were noted before and after immersion of the samples. Then, using a new sample, a test was made on the solution and the loss in weight of the sample versus time curve was drawn. The times of immersion for the last sample are 1, 2, 4, 8, 16, and 32 minutes. This procedure was repeated until the rate of attack on the base metal, the amount of scale removed, and the time required to remove the scale was approximately the same for this pickling bath as for the uninhibited bath.

Maintenance of Constant Acid Concentration. During the determination of the life of the inhibitor it was necessary to keep the concentration of the sulfuric acid at 18.5 per cent.

The acid concentration of the pickling bath, after samples had been immersed for a length of time, was determined using a pH meter and 1.0 N sodium hydroxide solution. Ten milliliters of the pickling bath solution was titrated with one milliliter volumes of sodium hydroxide and the pH read on the pH meter. Each point is plotted on a curve of pH versus volume of sodium hydroxide added. The titration was considered complete when a sharp break in the curve appeared. A straight line drawn from the peak of the curve intersecting the horizontal (volume of sodium hydroxide added) axis represents the amount of sodium hydroxide added. Using this data, the normality, and then the concentration of the acid in the pickling bath, was computed. Then the amount of acid required to return the acid concentration to 18.5 per cent was calculated.

Data and Results

The experimental data and results obtained during this investigation are presented in the form of tables and graphs as indicated in the following paragraphs.

Table I presents the data obtained during the pickling of steel in 18.3 per cent sulfuric acid at 73 °F, 77 °F, 79 °F, 106 °F, 126 °F, 140 °F, and 144 °F. The table indicates the area of each sample pickled, the time of immersion, and the loss in weight of the sample. Figure 1 is the graphical representation of the loss in weight of the sample versus time.

Table II presents the data obtained during the pickling of steel in ferric-sulfate-sulfuric acid solution at 82 °F and 160 °F. This table indicates the area of each sample pickled, the time of immersion, and the loss in weight of the sample. Figure 2 is the graphical representation of the loss in weight of the sample versus time.

Table III presents the data obtained during the pickling of steel in sulfuric acid-hydrochloric acid solution at 80 °F. This table indicates the concentration of the mixed acid pickling bath, the area of the sample, the time of immersion, and the loss in weight of the sample. Figure 3 presents the data in graphical form.

Table IV presents the data obtained during the pickling of steel in a citric acid-ammonia solution at 210 °F. This table indicates the area of the sample, the acid and ammonia concentrations, the area of the sample being pickled, the time of immersion, and the loss in weight of the sample. Figure 4 presents the data in graphical form.

Table V presents the data obtained during the pickling of steel in 18.75 per cent phosphoric acid solution. This table indicates the area of the samples being pickled, the temperature at which these tests were run, the time of immersion, and the loss in weight of the samples. Figure 5 presents the data in graphical form.

Table VI presents the data obtained during the pickling of steel in 20.5 per cent hydrochloric acid solution at 79 °F. This table indicates the area of the sample, the time of immersion, and the loss in weight of the sample. Figure 6 presents the data in graphical form.

Table VII presents the data obtained during the pickling of steel in both inhibited and uninhibited 18.3 per cent sulfuric acid solution at 78 °F. The inhibitor being tested was Rodine 82-A. This table indicates the area of the sample, the acid and inhibitor concentration, the area of the sample, and the loss in weight of the sample. Figure 7 presents the data in graphical form.

Table VIII presents the data obtained during the pickling of steel in spent inhibited 18.3 per cent sulfuric acid solution at 78 °F. This table indicates the acid and inhibitor concentrations, the area of the samples, the time of immersion, the loss in weight of the sample, and the length of utilization of the bath before the sample was immersed in it. Figure 7 presents the data in graphical form.

Table IX presents the data obtained during the utilization of the inhibitor and acid in inhibited sulfuric acid concentration at 78 °F. This table indicates the acid and inhibitor concentrations, the length of utilization, the area of the sample, the loss in weight of the sample, and the loss in weight of the pickling bath.

Table X presents the data used to determine the frequency factor and the energy of activation for the pickling of black stovepipe steel in 18.3 per cent sulfuric acid solution. This table indicates the reciprocal temperature, and the rate of attack on the bare metal. Figure 8 presents this data in graphical form and is used to determine the frequency factor and energy of activation.

Table XI presents the results of the pickling of black stovepipe steel in acid pickling baths. This table indicates the pickling bath used, the temperature at which the tests were run, the amount of scale removed, the time required to remove the scale, and the rate of attack on the base metal.

Table XII presents the results of the pickling of black stovepipe steel in inhibited and uninhibited 18.3 per cent sulfuric acid solution. The table indicates the condition of the pickling bath, the area of the sample, the temperature at which the test was run, the amount of scale removed, the time required to remove the scale, and the rate of attack on the base metal.

The frequency factor was found to be $1.2x10^6$ sec^{-1}, and the energy of activation to be 6000 calories per gram mol.

TABLE I

Pickling of Steel in Sulfuric Acid Solution

Type of Steel: Black Stovepipe
Acid Concentration: 18.3 Per Cent

Test	1	2	3	4	5	6	7
Temperature, °F	73	77	79	106	126	140	144
Area of Sample, sq in.	1.500	1.500	1.500	1.500	1.500	1.125	1.500

Time min	Loss in Weight of Sample mgm/sq in.						
3	3.05	2.55	6.90	5.70	11.75	27.40	17.80
6	5.55	4.20	10.00	11.50	16.20	29.00	19.40
9	6.30	5.55	12.30	16.00	17.20	30.00	20.25
12	7.55	6.60	13.80	17.40	17.80	30.75	21.05
15	8.50	7.95	16.40	17.75	18.25	30.95	21.85
18	--	8.65	17.60	18.50	18.60	31.30	--
20	9.70	--	--	--	--	--	--
21	--	9.45	18.40	--	--	32.35	--
23	11.60	--	--	--	--	--	--
24	--	10.50	18.75	--	--	32.35	--
26	13.65	--	--	--	--	--	--
27	--	11.75	19.05	--	--	33.40	--
29	16.90	--	--	--	--	--	--
30	--	12.65	19.40	--	--	--	--
32	18.10	--	--	--	--	--	--
35	18.90	--	--	--	--	--	--
38	19.60	--	--	--	--	--	--
41	20.25	--	--	--	--	--	--
45	--	--	--	--	--	--	29.80
48	--	--	--	21.30	22.75	--	--
54	--	--	--	--	--	39.90	--
59	--	17.70	--	--	--	--	--
62	--	--	20.25	--	--	--	--
73	21.60	--	--	--	--	--	--
91	--	19.20	--	--	--	--	--

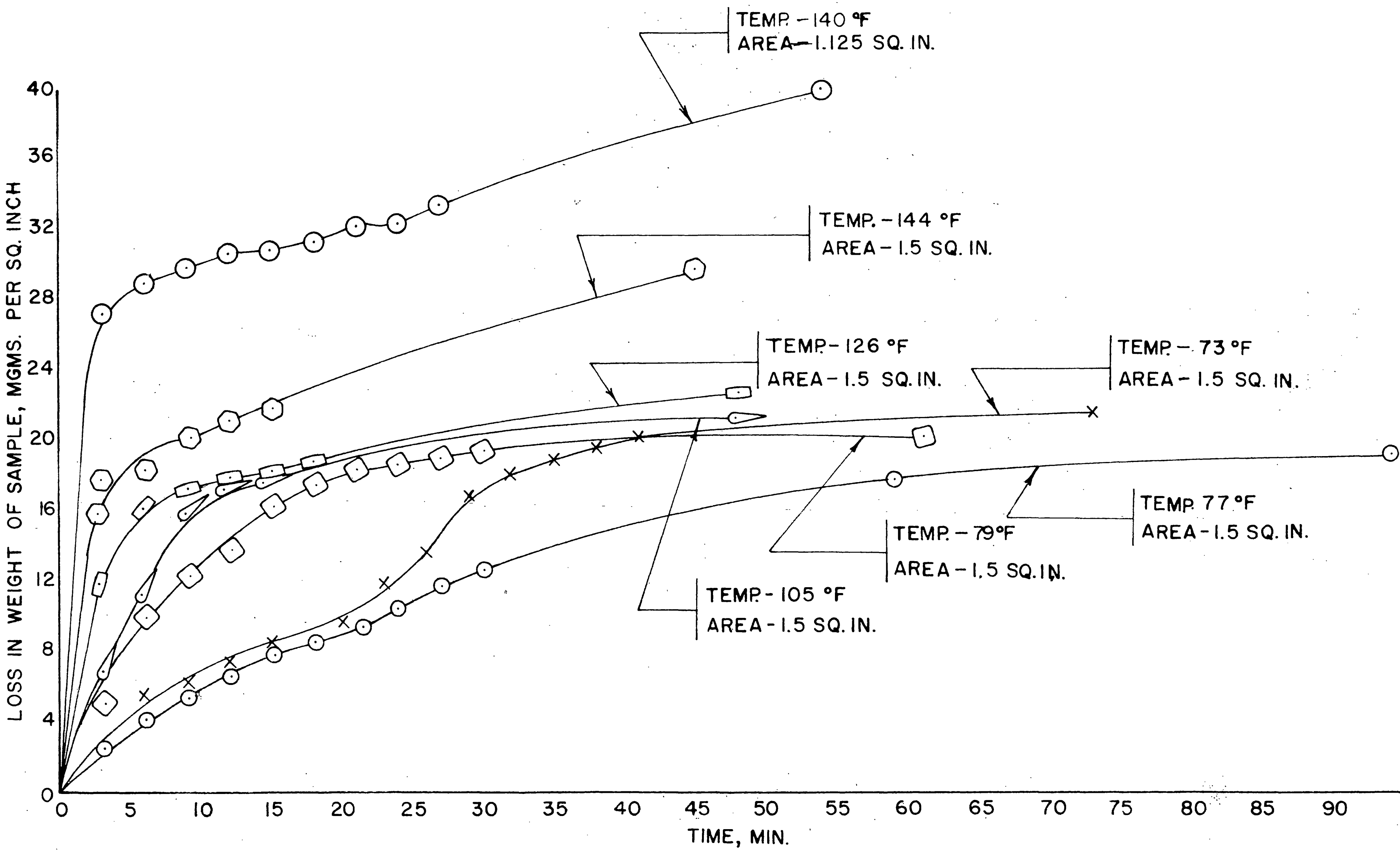

FIGURE I. PICKLING OF STEEL IN 18.3 PER CENT SULFURIC ACID SOLUTION

TABLE II

Pickling of Steel in Ferric Sulfate-Sulfuric Acid Solution

Type of Steel:	Black Stovepipe
Ferric Sulfate Concentration:	6.87 Per Cent
Acid Concentration:	3.98 Per Cent

Test	8	9
Temperature, °F	82	160
Area of Sample, sq in.	2.0	1.75
Time min	Loss in Weight of Sample mgm/sq in.	
3	5.65	22.65
6	9.30	35.55
9	13.75	41.50
12	25.85	55.90
15	29.95	68.75
18	30.30	--
21	33.15	--
24	36.35	--
50	--	177.50
82	70.45	--

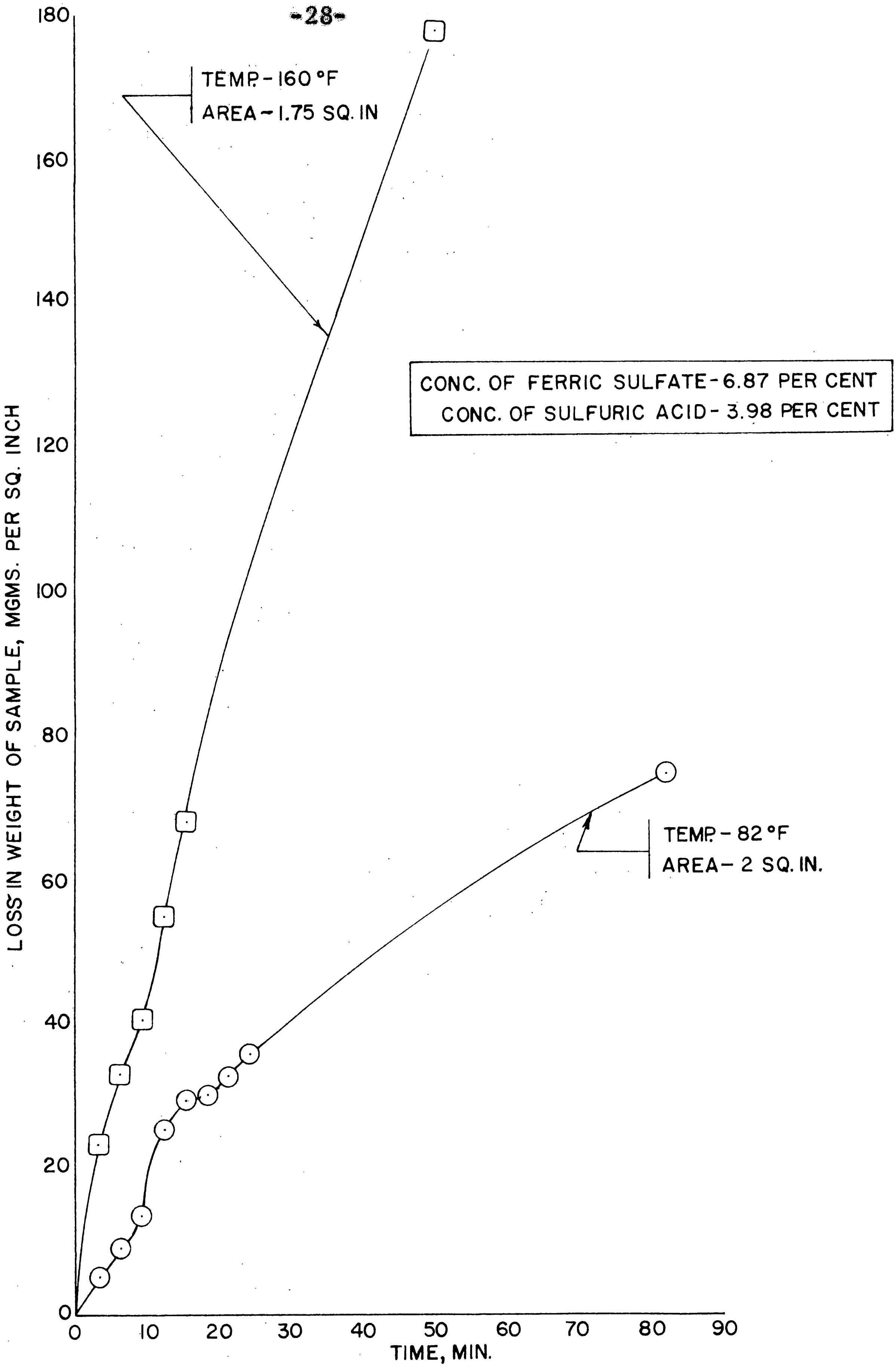

FIGURE 2. PICKLING OF STEEL IN A FERRIC SULFATE-SULFURIC ACID SOLUTION

TABLE III

Pickling of Steel in Sulfuric Acid-Hydrochloric Acid Solution

Type of Steel:	Black Stovepipe
Hydrochloric Acid Concentration:	17.65 Per Cent
Sulfuric Acid Concentration:	3.77 Per Cent
Area of Sample:	1.5 Sq in.
Temperature:	80 °F

Time min	Loss in Weight of Sample mgm/sq in.
3	5.10
6	9.15
9	12.30
12	14.70
15	15.60
18	16.10
21	16.30
24	16.50
64	17.40

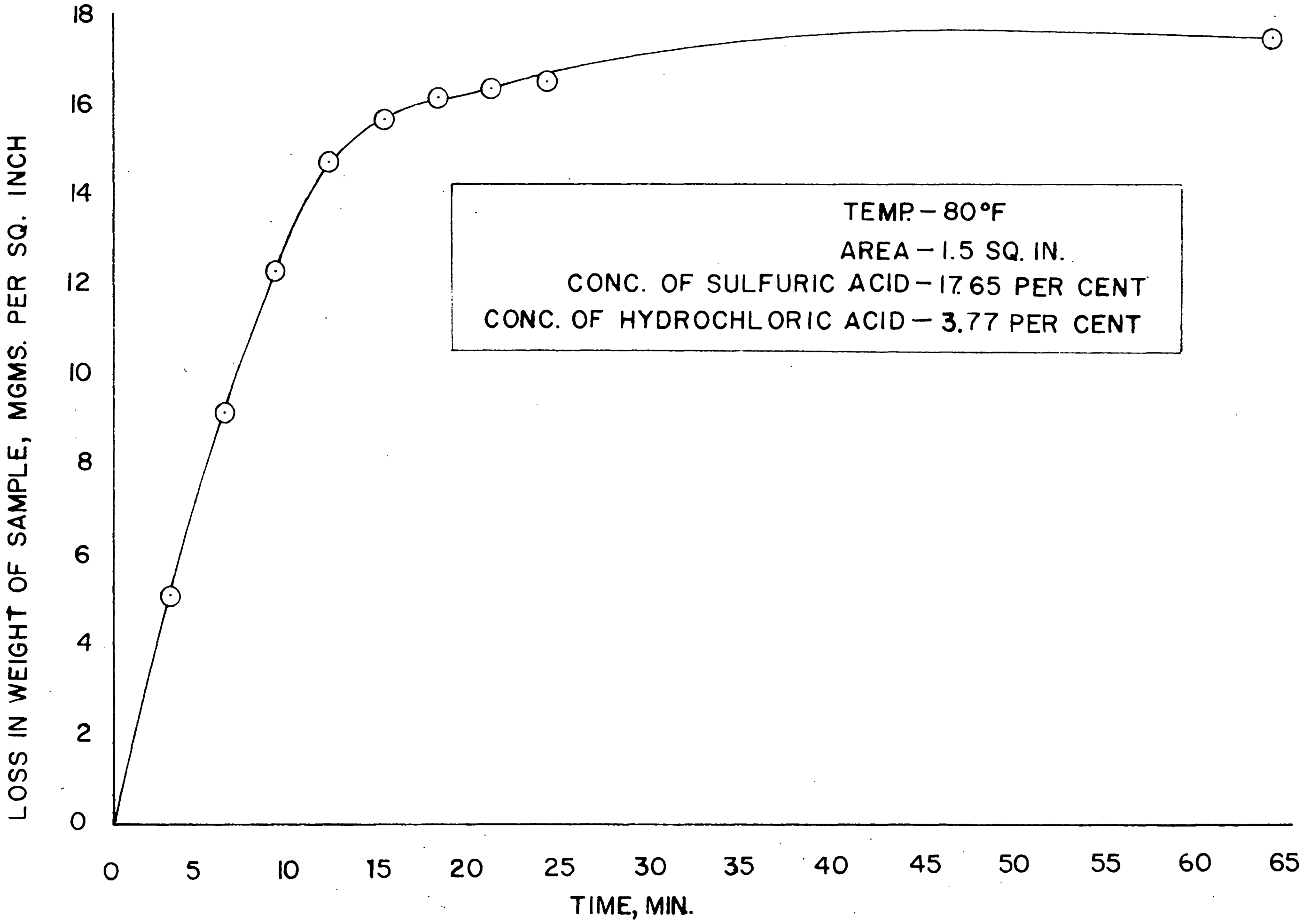

FIGURE 3. PICKLING OF STEEL IN SULFURIC ACID – HYDROCHLORIC ACID SOLUTION

TABLE IV

<u>Pickling of Steel in Citric</u>

<u>Acid-Ammonia Solution</u>

Type of Steel:	Black Stovepipe
Acid Concentration:	8.77 Per Cent
Ammonia Concentration:	2.17 Per Cent
Area of Sample:	1.5 Sq in.
Temperature:	210 °F (boiling)

Time min	Loss in Weight of Sample mgm/sq in.
3	0.215
6	0.240
12	8.300
18	14.550
24	17.400
30	18.200
60	18.350

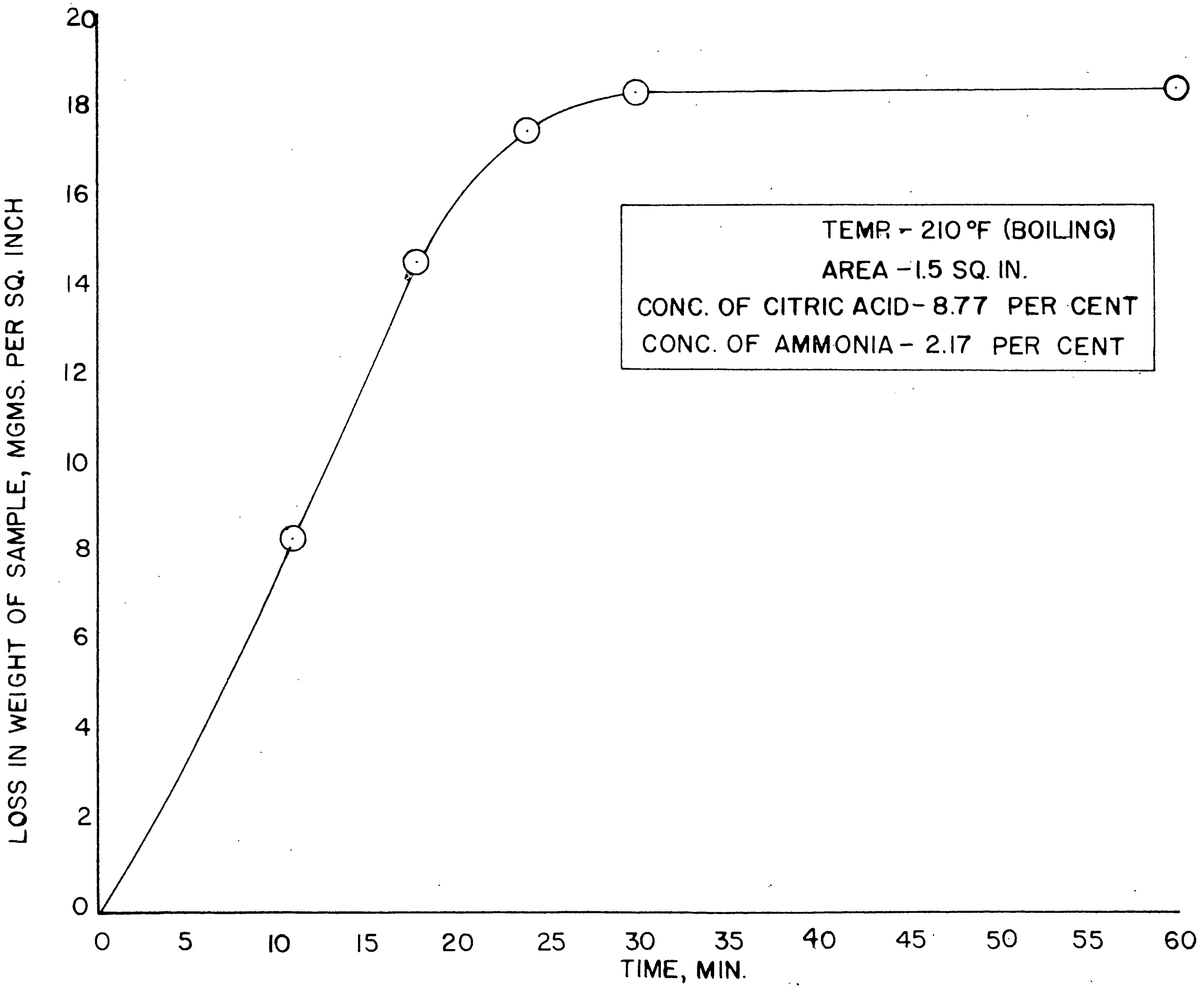

FIGURE 4. PICKLING OF STEEL IN CITRIC ACID-AMMONIA SOLUTION

TABLE V

Pickling of Steel in Phosphoric Acid Solution

Type of Steel:	Black Stovepipe
Acid Concentration:	18.75 Per Cent
Area of Sample:	1.5 Sq in.

Test	12[a]	13
Temperature, °F	165	177
Time	Loss in Weight of Sample	
min	mgm/sq in.	
1	19.05	--
3	20.40	21.65
6	--	22.80
7	21.40	--
9	--	23.60
12	--	25.15
15	23.25	26.65
31	25.00	--
45	--	52.60
63	28.30	--

a Air agitation.

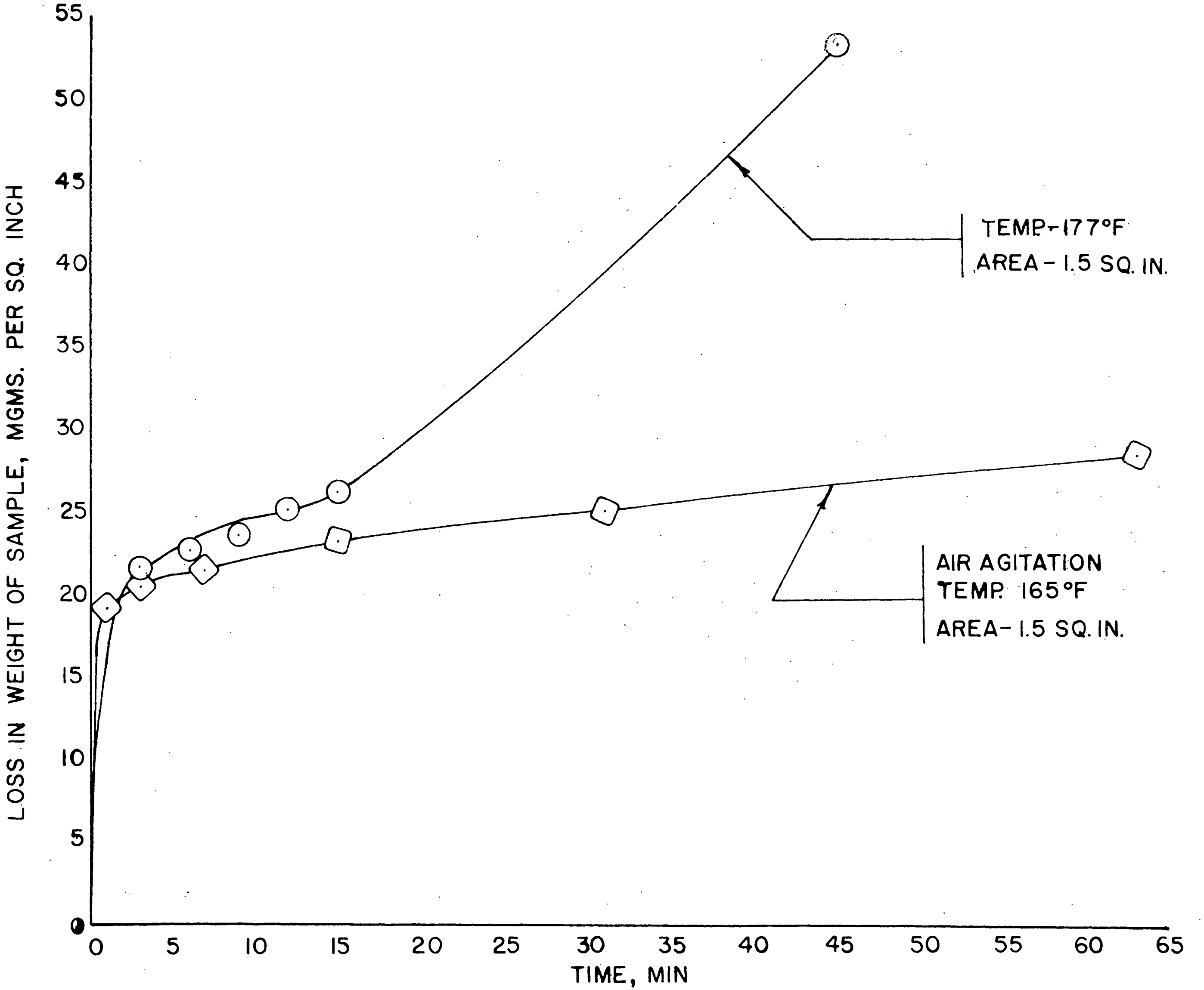

FIGURE 5. PICKLING OF STEEL IN 18.75 PER CENT PHOSPHORIC ACID SOLUTION

TABLE VI

Pickling of Steel in Hydrochloric Acid Solution

Type of Steel:	Black Stovepipe
Acid Concentration:	20.5 Per Cent
Area of Sample:	1.375 Sq in.
Temperature:	79 °F

Time min	Loss in Weight of Sample mgm/sq in.
0	--
3	30.50
6	31.00
9	31.35
12	31.50
15	31.75
18	31.75
51	31.80

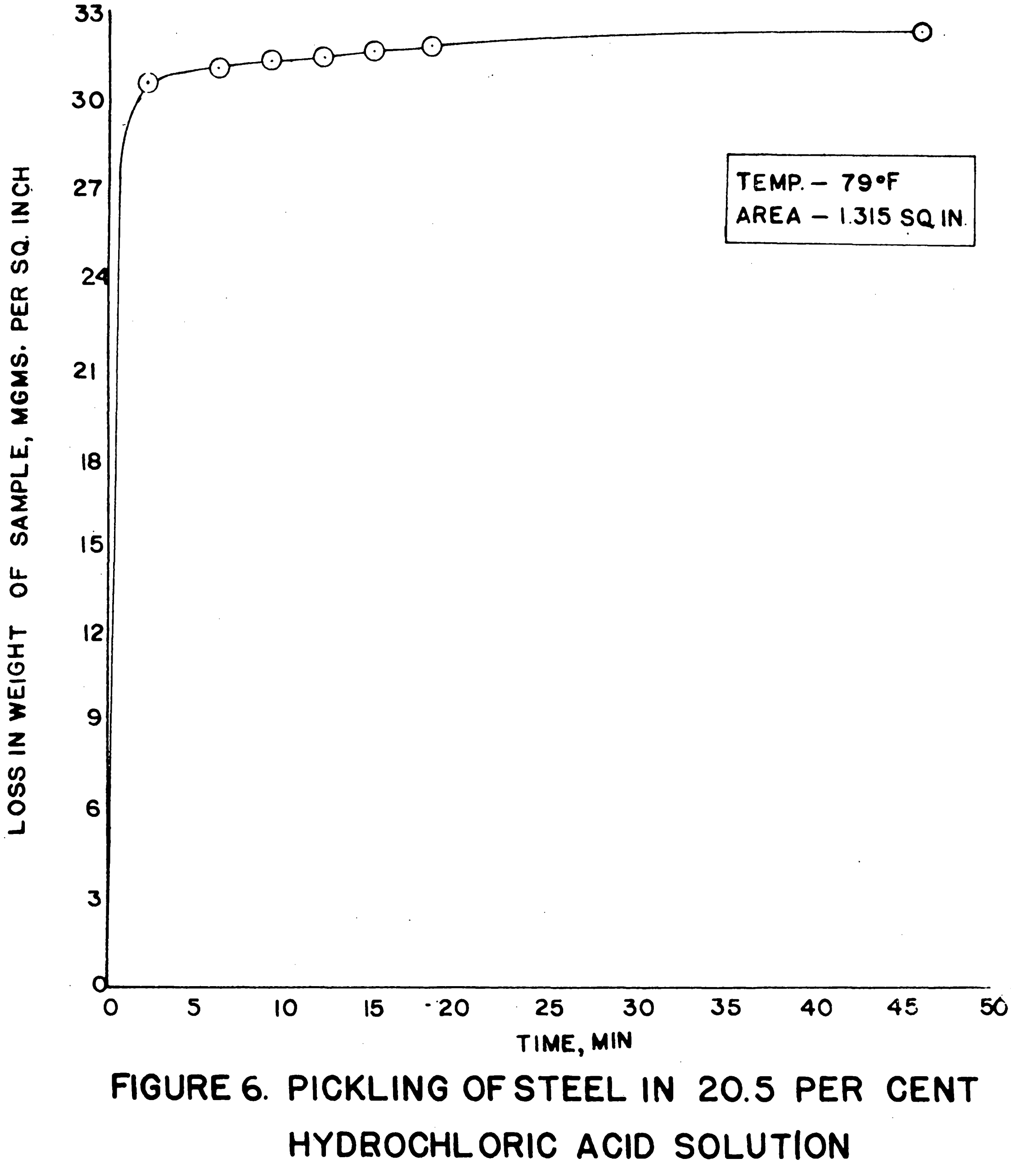

FIGURE 6. PICKLING OF STEEL IN 20.5 PER CENT HYDROCHLORIC ACID SOLUTION

TABLE VII

Determination of the Effect of an Inhibitor on a Sulfuric Acid Pickling Bath

Type of Steel:	Black Stovepipe
Acid Concentration:	18.75 Per Cent
Inhibitor Concentration:	0.25 Per Cent
Area of Sample:	1.5 Sq in.
Temperature:	78 °F

Time min	Loss in Weight of Sample mgm/sq in.	
	Uninhibited	Inhibited
1	3.60	2.35
3	7.60	5.20
7	12.55	10.35
15	17.70	14.40
31	20.00	16.40
63	21.50	16.80

TABLE VIII

Pickling of Steel in Spent Inhibited

Sulfuric Acid Solution

Type of Steel: Black Stovepipe
Temperature: 78 °F
Acid Concentration: 18.5 Per Cent
Inhibitor Concentration: 0.25 Per Cent, by Volume
Area of Sample: 1.5 Sq in.

	Length of Utilization of Pickling Bath		
	112 min	207 min	302 min
Time min	Loss in Weight of Sample mgm/sq in.		
1	1.45	1.00	2.40
3	3.40	1.65	7.35
7	6.80	3.10	12.95
15	12.10	6.10	17.25
31	19.20	11.65	19.40
63	23.25	16.00	20.60
95	25.75	17.20	21.05

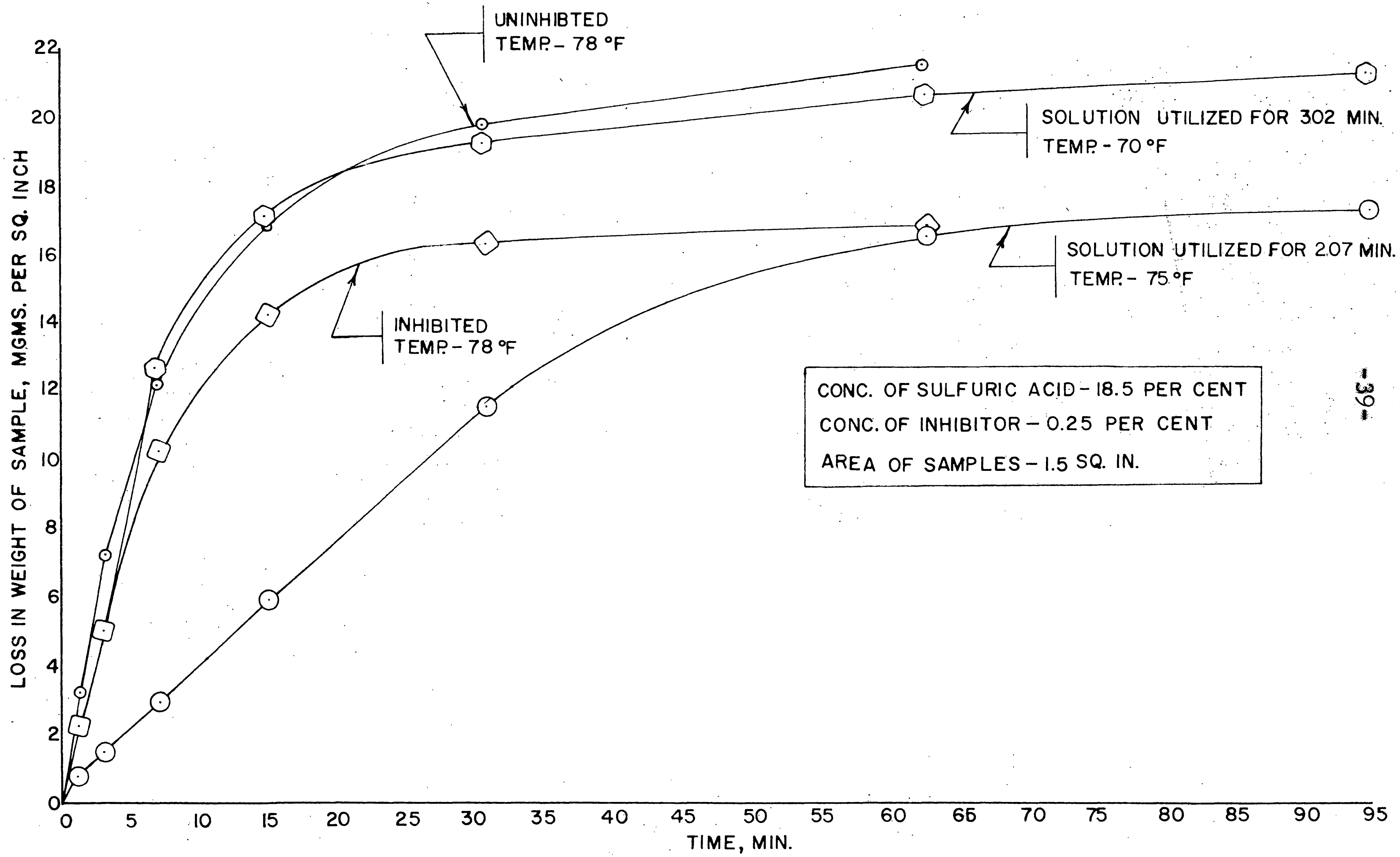

FIGURE 7. PICKLING OF STEEL IN SPENT INHIBITED SULFURIC ACID SOLUTION

TABLE IX

Utilization of Inhibitor and Acid by Pickling Steel in Inhibited Sulfuric Acid Solution

Type of Steel: Black Stovepipe
Temperature: 78 °F
Acid Concentration: 18.5 Per Cent
Inhibitor Concentration: 0.25 Per Cent, by Volume
Initial Weight of Pickling Solution: 219.5518 Grams

Length of Utilization min	Area of Sample sq in.	Loss in Weight of Sample mgm/sq in.	Loss in Weight of Bath gm
28	1.500	8.40	1.9436
28	1.500	10.35	0.3461
28	1.500	8.50	0.2415
28	1.375	16.80	0.2244
95	1.375	25.85	27.2334 [a]
95	1.500	17.20	2.6721
83	1.500	21.05	3.3084

[a] Evaporation loss also included.

TABLE X

Determination of the Frequency Factor and Activation Energy for the Pickling of Black Stovepipe Steel in 18.3 Per Cent Sulfuric Acid Solution

$\frac{1}{T}$ °K	Rate of Attack on Bare Metal mgm/sq in./min
0.00338	0.0903
0.00336	0.0973
0.00335	0.0532
0.00318	0.1870
0.00304	0.2770
0.00299	0.4830
0.00298	0.5300

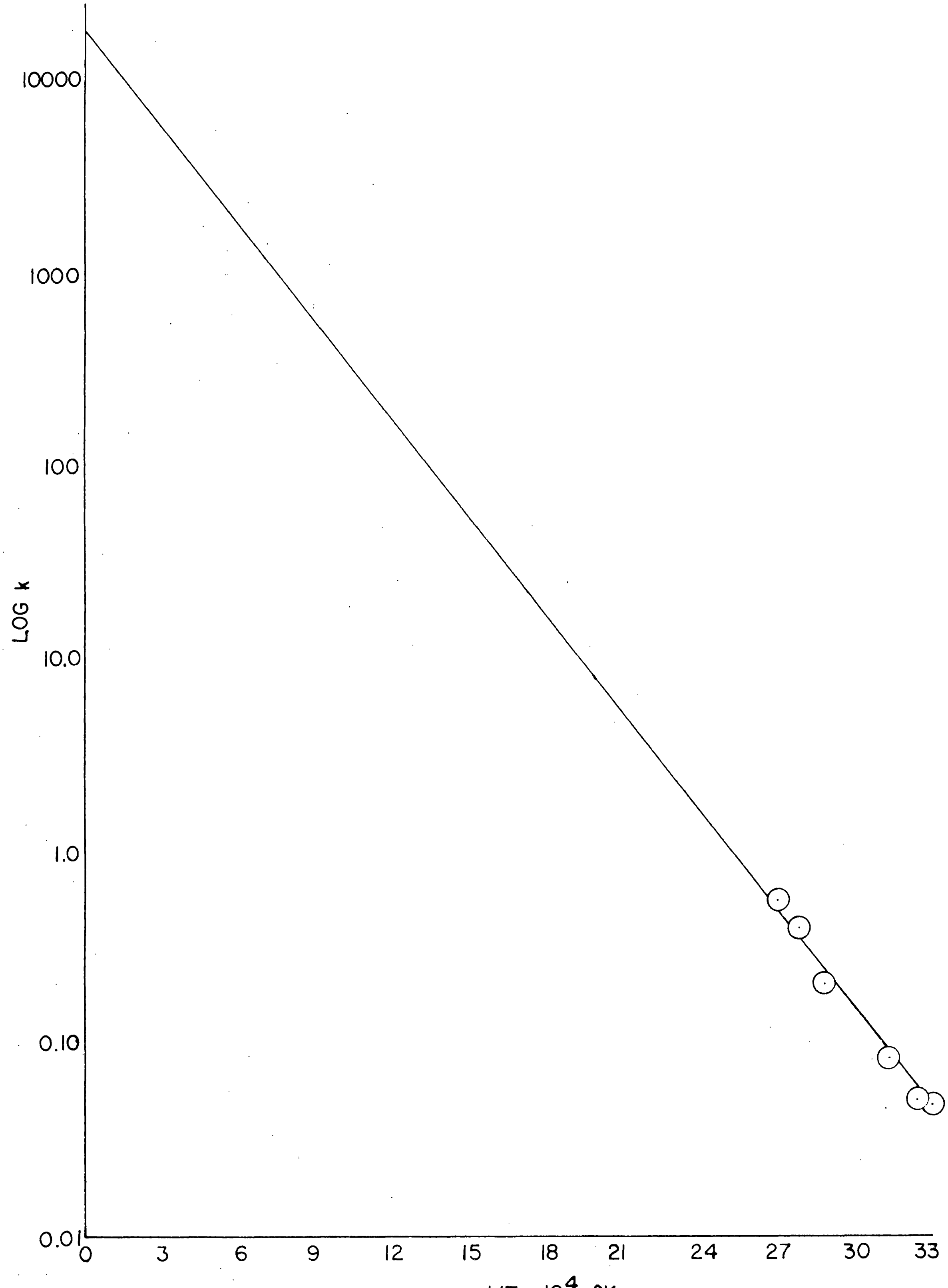

FIGURE 8. DETERMINATION OF THE FREQUENCY FACTOR AND ACTIVATION ENERGY FOR THE PICKLING OF BLACK STOVE-PIPE STEEL IN 18.3 PER CENT SULFURIC ACID SOLUTION

TABLE XI

Results of the Pickling of Black Stovepipe Steel in Acid Pickling Baths

Pickling Bath	Temperature °F	Amount of Scale Removed mgm/sq in.	Time Required to Remove Scale min	Rate of Attack on Bare Metal mgm Fe dissolved sq in./min
18.3 % H_2SO_4	73	18.50	41	0.0482
	77	15.00	61	0.0487
	79	18.60	30	0.0216
	106	16.75	15	0.0935
	126	16.25	15	0.1385
	140	28.10	9	0.2415
	144	17.75	15	0.2650
3.98 % H_2SO_4	82	22.50	24	0.5850
6.87 % $Fe_2(SO_9)_3$	160	27.00	15	3.9050
17.65 % H_2SO_4 3.77 % HCL	80	15.90	24	0.0225
8.77 % Citric Acid 2.17 % NH_3	210 (Boiling)	18.00	30	0.0050
18.75 % H_3PO_4	165[a]	18.50	3	0.3000
	177	20.00	3	1.7100
20.5% HCL	79	31.00	9	0.0105

[a] Air agitation.

TABLE XII

Results of the Pickling of Steel in Inhibited and Uninhibited Sulfuric Acid Solution

Type of Steel: Black Stovepipe
Acid Concentration: 18.3 Per Cent

Condition of the Pickling Bath	Area of Sample	Temperature	Amount of Scale Removed	Time Required to Remove Scale	Rate of Attack on Bare Metal
	sq in.	°F	mgm/sq in.	min	mgm/sq in./min
Uninhibited	1.500	78	18.75	28.0	0.0429
Inhibited	1.500	78	15.55	28.5	0.0143
Inhibited Utilized 112 min	1.375	78	18.75	52.0	0.0724
Inhibited Utilized 207 min	1.500[a]	75	11.50	52.0	0.0615
Inhibited Utilized 302 min	1.500	70	18.75	32.5	0.0230

[a] Acid concentration diminished due to evaporation.

Sample Calculations

The following are the types of calculations performed for this investigation.

1. Loss in Weight of Sample

$$L = \frac{Wo - Wt}{A}$$

where:

L = loss in weight of the sample, mg/sq inch

Wo = weight of the sample before test was begun, gm

Wt = weight of the sample after it has been immersed in the pickling bath for T minutes

A = area of both sides of the square meter.

$$6.1 = \frac{2.9003 - 2.8911}{3.0}$$

2. Calculation of the Initial Concentration of Sulfuric Acid in the Pickling Bath

$$N = \frac{G/E}{V}$$

where:

N = normality of the acidic pickling bath

G = weight of solute, gm

E = equivalent weight of the solute, gm

V = volume of the solute, liters.

$$3.8 = \frac{185/49}{1}$$

3. Calculation of Frequency Factor and Activation Energy

$$k = ae^{-E/RT} \quad \text{or} \quad \log k = \log a - \frac{E}{2.3RT}$$

where:

k = rate of attack on the bare metal, mg/sq in./min

a = frequency factor, $(\text{sec})^{-1}$

E = activation energy, cal/gm mol

R = constant, cal/gm mol/°K

T = absolute temperature, °K.

The intercept of the plot of log $\underline{k}$ vs $\frac{1}{T}$ is the frequency factor, and the slope equals $-\frac{E}{2.3R}$.

IV. DISCUSSION

A discussion of results, those recommendations the author feels might prove useful, and the conditions under which this investigation was carried out are presented in the following paragraphs.

Discussion of Results

In this section are presented those factors which the author feels most directly affected the results.

Condition of the Samples Before Pickling. The author feels that the amount of scale removed from the samples by the pickling baths cannot be properly evaluated because all of the samples were not exposed to the same amount of corrosion. The samples were not cleaned before they were pickled. Thus, the rate of pickling was affected. The effect of the surface film on the sample slowed down the rate only in the initial immersion. Once this film was removed the pickling process proceeded normally. The author feels that the final results were not affected.

<u>Procedure</u>. The procedure devised for this investigation was weak in several areas. Having to dry each sample in air after each immersion caused a great deal of time to be lost. Each time a sample was removed from the pickling bath, some of the bath was lost due to "drag out," or the loss due to the removal of the sample. When tests were run at high temperatures a condenser had to be added to the flask to prevent evaporation losses. The condenser made immersion and removal of the sample from the pickling bath extremely difficult.

<u>Reproducibility of Results</u>. The results of this investigation were extremely difficult to reproduce with any degree of accuracy. The temperatures varied by as much as plus or minus 5.0 °F, and the volumes of the solutions used varied by plus or minus 0.8 milliliters.

<u>Effect of Agitation</u>. Although there was little agitation of the pickling bath during the immersion and removal of the sample from the pickling bath, the rate of pickling was affected by this agitation. If the solution was agitated only slightly for a few

immersions and then greatly agitated, the increase in the rate of pickling was very noticeable.

<u>Effect of the Rodine 82-A Inhibitor</u>. The results of the pickling of the samples in the inhibited sulfuric acid pickling bath were too erratic to lead to any valid conclusions. However, the author does not feel that this inhibitor should be precluded from further use because of this until further tests are made. The only reason for these erratic results, at this point, must lie in the experimental technique because the procedure used in testing this inhibitor did not deviate from the procedure used in the other tests.

<u>Evaluation of Results</u>. Although some of the pickling baths tested removed more scale, and perhaps, had a slower rate of attack on the bare metal, 18.75 per cent phosphoric acid was deemed the most efficient pickling solution because this solution removed the surface oxide in the least time; also, two tests run with this solution produced results which agreed with three milligrams per square inch for the amount of scale removed, and there was no change in the time.

The plots of loss in weight of the sample versus time indicated that the rate of removal of scale decreased as the test proceeded. This was to be expected because most of the scale was removed in the first few immersions. The rate of attack on the bare metal, as the curves show, increased at a constant rate.

When the acid was used up, naturally the amount of scale removed decreased. However, the curves indicate that the rate of attack on the bare metal remained unaffected by the decrease in the amount of free acid.

The erratic action of the inhibitor precludes any discussion of results. The author is unable to account for this erratic behavior.

Recommendations

On the basis of the information obtained from this investigation the following recommendations are made:

1. The effect of temperature on the pickling of steel in 18.75 per cent phosphoric acid solution should be studied by pickling steel in this solution beginning with a room temperature and ending with a temperature of about 175 °F.

2. The effect of air agitation on the pickling of steel in 18.75 per cent phosphoric acid solution at various temperatures should be studied by running two tests at the same temperature; one with air agitation, and one without air agitation.

3. The effect of an inhibitor on the pickling of steel in 18.75 per cent phosphoric acid solution at various temperatures should be studied.

4. All samples should be thoroughly cleaned before any tests are run so that any surface film on the samples will be removed. Therefore, the rate of attack will not be hindered.

5. Constant agitation should be applied to the pickling baths at all times so that the rate of pickling will be more uniform because the

concentration of the pickling bath will be more uniform.

6. A better method of drying the sample should be employed because of the amount of time lost in drying the sample.

Limitations

This investigation was carried out under the following conditions:

1. The steel being pickled was black stovepipe steel containing 0.095 per cent carbon.

2. The pickling solutions used were 18.3 per cent sulfuric acid solution, 3.98 per cent sulfuric acid and 6.87 per cent ferric sulfate solution, 17.65 per cent sulfuric acid and 3.77 per cent hydrochloric acid solution, 8.77 per cent citric acid and 2.17 per cent ammonia solution, 18.75 per cent phosphoric acid solution, and 20.5 per cent hydrochloric acid solution.

3. The temperatures at which the 18.3 per cent sulfuric acid solution was tested were 73, 77, 79, 106, 126, 140, and 144 °F.

4. The temperatures at which the 3.98 per cent sulfuric acid and 6.87 per cent ferric sulfate solution was tested were 82 and 160 °F.

5. The temperature at which the 17.65 per cent sulfuric acid and 3.77 per cent hydrochloric acid solution was tested was 80 °F.

6. The temperature at which the 8.77 per cent citric acid and 2.17 per cent ammonia solution was tested was 210 °F (boiling).

7. The temperature at which the 18.75 per cent phosphoric acid was tested were 165 and 177 °F.

8. The temperature at which the 20.5 per cent hydrochloric acid was tested was 79 °F.

9. The time of each immersion for the samples ranged from one minute to 32 minutes.

10. The total time of immersion for each sample ranged from 48 minutes to 95 minutes.

11. The volume of the pickling media used in the tests to determine the most efficient pickling solution was 250 milliliters.

12. The volume of the pickling media used in the study of the effect of the inhibitor Rodine 82-A was 200 milliliters.

13. The inhibitor studied was Rodine 82-A.

V. CONCLUSIONS

The following paragraphs contain the conclusions drawn from this investigation.

1. The rate of attack on the bare metal increases with increasing temperature, particularly in the pickling of black stovepipe steel in 18.3 per cent sulfuric acid solution where the rate of attack on the bare metal at 75 °F is 0.097 milligrams per square inch per minute, while at 142 °F the rate of attack is 0.51 milligrams per square inch per minute.

2. The time required to remove the surface oxide from the sample decreases with increasing temperature.

3. The 18.75 per cent phosphoric acid solution removed the most surface oxide in the least amount of time at 165 and 177 °F.

4. The effect of Rodine 50 inhibitor on 20.5 per cent hydrochloric acid pickling solution cannot be studied because the rate of attack on the bare metal of uninhibited pickling solution was too small, at 80 °F.

5. The addition of Rodine 82-A inhibitor to a pickling bath containing 18.5 per cent sulfuric acid decreased the rate of attack on the bare metal from 0.0858 milligrams per square inch per minute

to 0.0286, without appreciably affecting the time required to remove this scale, at 78 °F.

6. No valid conclusions can be made concerning the life of the Rodine 82-A inhibitor because of the erratic nature of the results.

VI. SUMMARY

The purposes of this investigation are to determine which pickling solution will remove the greatest amount of scale in the least amount of time, to determine the life of Rodine 82-A inhibitor in a pickling bath containing 18.3 per cent sulfuric acid solution, to determine the effect of the addition of Rodine 82-A inhibitor to the pickling bath containing 18.3 per cent sulfuric acid solution, and to determine the frequency factor and activation energy for the pickling of black stovepipe steel in 18.3 per cent sulfuric acid solution.

The temperatures at which the pickling baths were tested, and the pickling baths used were: 18.3 per cent sulfuric acid solution at 73, 77, 79, 100, 126, 140, and 144 °F; 3.98 per cent sulfuric acid and 6.87 per cent ferric sulfate solution at 82 and 160 °F; 17.65 per cent sulfuric acid and 3.77 per cent hydrochloric acid solution at 80 °F; 8.77 per cent citric acid and 2.17 per cent ammonia solution at 210 °F (boiling), 18.75 per cent phosphoric acid solution at 165 °F (air agitated) and 177 °F; and 20.5 per cent hydrochloric acid solution at 79 °F.

The steel being pickled was black stovepipe steel containing 0.095 per cent carbon. The pickling solution which removed the greatest amount of scale in the least amount of time was determined from plots of the loss in weight of the sample per unit area versus time for each of the tests run. The effect, and life, of Rodine 82-A inhibitor upon a pickling bath containing 18.3 per cent sulfuric acid solution was studied.

The samples were immersed in the pickling baths for one to 32 minutes. The samples were removed from the baths, cleaned, dried, and weighed. This same procedure was utilized in the study of the inhibitor except that the inhibited pickling bath was first utilized before the tests began.

It was found that 18.75 per cent phosphoric acid removed 38.5 milligrams of scale per square inch of sample in three minutes. It was concluded that increased temperature increased the rate of attack on the bare metal, decreased the length of time required to remove the scale from the sample. The addition of Rodine 82-A inhibitor to a pickling bath containing 18.5 per cent sulfuric acid solution decreased the rate of attack on the bare metal without appreciably affecting the amount of scale removed, or the time required to remove this scale. No valid conclusions concerning the life of the Rodine 82-A inhibitor in the 18.5 per cent sulfuric acid pickling bath could be made because of the erratic nature of the results. Due to the slow rate of attack, or 0.0210 milligrams per square inch, on the bare metal in a 20.5 per cent hydrochloric acid pickling bath the effect of the addition of an inhibitor to this bath was not studied. The frequency factor was found to be 1.2×10^{6} sec^{-1}, and the energy of activation to 6000 calories per gram mol.

It is recommended that the effects of temperature, air agitation, and an inhibitor on a pickling bath containing 18.75 per cent phosphoric acid be studied in future investigations.

VII. BIBLIOGRAPHY

1. Hall, Nathan: Pickling and Acid Dipping, Metal Finishing Guide Book - Directory, p. 243. Metals and Plastics Publications, Inc., Westwood, New Jersey, 1961. 29 ed.

2. McCollum, C. H. and D. L. Warwick: The Pickling of Iron and Steel Products, "Metals Handbook" (T. Lyman, Editor), pp. 725-729. Am. Soc. for Metals, Cleveland, Ohio, 1948.

VIII. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. N. F. Murphy, Research Professor, Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia, thesis advisor for the many helpful suggestions given to the author during the course of this investigation.

The author would also like to thank the American Chemical Company, Ambler, Pennsylvania, for the free samples of Rodine.

Special thanks are extended to the author's wife for inspiration during this investigation.

IX. VITA

The vita has been removed from the scanned document