


# Controlling Factors in Unaërated Solutions of Sulfuric Acid

Corrosion rate is directly proportional to oxygen solubility of the acid up to about 25 normality; above 25 normality the oxidizing character of sulfuric acid affects the corrosion rate. The rate of oxygen diffusion through the air-liquid interface controls the corrosion rate except in those cases where the solution surface area is very large in comparison to the metal surface area. Standard corrosion test methods must specify the solution surface area if reproducible results are to be obtained. The maximum corrosion rate for copper in unaërated 0.2 normal solutions of sulfuric acid is approximately 40 mg. per sq. dm. per 24 hours.

These conclusions are based on experimental work performed with copper in sulfuric acid. The same factors should, however, control the corrosion rate for all metals which depend upon oxygen depolarization. A subsequent paper will report on some of the more active metals.

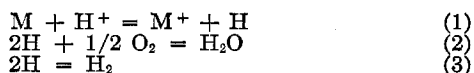
## CORROSION OF COPPER

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 THIS paper reports a study of the controlling variables in the unaërated immersion test for corrosion. The quantitative effect of variations in the concentration of the corroding solution, volume of solution, size of metal specimen, and surface area of liquid is reported for the case of copper in sulfuric acid. This study reveals the probable cause of many of the discrepancies reported in the literature by pointing out the variation in the corrosion rates for different areas of the air-liquid interface, a variable which has been neglected in the standard tests recommended by Calcott, Whetzel, and Whittaker (6) and by Committee B3 of the American Society for Testing Materials (1).

One of the principal difficulties in laboratory corrosion testing is to select methods which will give results analogous to those obtained in actual service. Many different testing methods have been proposed (2, 4, 7, 8, 18); all are open to certain basic objections.

The mechanism of corrosion postulated by Whitney (22) and Walker (19) has been generally accepted as of basic importance. It can be expressed in three general reactions:



The rate of reaction 2 has been shown to be the controlling factor in the corrosion of all but the most active metals. It, in turn, is controlled by either the rate of combination of hydrogen and oxygen or the rate at which the oxygen diffuses to the hydrogen film around the metal. Speller and Kendall (17) and Wilson (23) have shown that the slowest, and therefore the controlling process, is the diffusion of oxygen to the polarizing film of hydrogen. It has generally been considered

(17, 21, 23) that the stationary liquid film around the metal surface has the greatest resistance to the diffusion of the molecular oxygen. Little quantitative data exist on the dependence of the corrosion rate on the diffusion through the air-liquid interface. Speller (16), however, states that the conclusions of Friend (11) have been confirmed for the case of iron by experiments at Massachusetts Institute of Technology.

Since the rate of corrosion of most metals is proportional to the oxygen concentration (9, 12, 14, 15), the unaërated immersion test, which as usually made does not control the oxygen content of the solution, is open to criticism. Further, the difficulties encountered in obtaining check results (3) on unaërated tests have led some investigators (10) to consider such data as qualitative only. Unfortunately, much of the data in the literature was obtained by unaërated tests.

The experimental discrepancies in the unaërated test led to a consideration of the variability of the oxygen content. This variation must be due either to a variation in the amount of oxygen which enters the corroding medium through the air-liquid interface or to a variation in the diffusion from the liquid surface to the metallic surface. Some investigators have controlled the aëration by passing a continuous stream of air through the test solution. This procedure insures a relatively constant amount of oxygen in the solution, but it may not duplicate service conditions any better than does the unaërated test.

### Materials and Methods

The corrosion of copper in dilute sulfuric acid was chosen for this investigation because the activity of copper is such that reaction 3 of the corrosion mechanism cannot take place, and because any corrosion (20), except at a very high acid

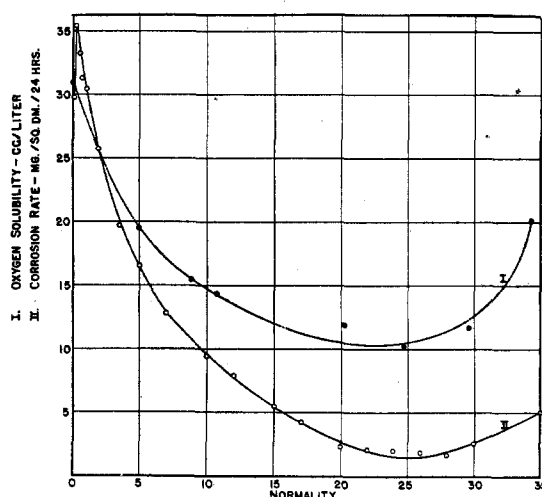


FIGURE 1. INFLUENCE OF ACID CONCENTRATION ON CORROSION OF COPPER

concentration, must be due to reaction 2. The sulfuric acid used was all taken from the same carboy of c. p. grade acid.

Preliminary experiments were made on commercial sheet copper; the final experiments were made on a very high grade of copper obtained from the Revere Copper and Brass Company. This copper was  $\frac{1}{16}$  inch (0.15 cm.) thick and was polished on both sides. Since the previous history of the copper was unknown, the specimens were annealed at  $550^{\circ}$  C. out of contact with air. The air was excluded to prevent the formation of an oxide film on the polished surface. Photomicrographs and an x-ray analysis verified the complete absence of mechanical strain in the annealed specimens. A spectrographic analysis of the copper showed minute traces of silver, nickel, tin, iron, magnesium, and lead, but the total amount of the impurities was much less than could be determined by the usual chemical analysis.

The copper test pieces were cut to exact size before they were annealed. Most of the specimens were square, but a few were rectangular. No difference in results was noted for the different shapes.

The specimens were cleaned by washing with water and then dipping in a solution of nitric acid for several seconds. The acid was removed from the specimens by repeated washing with distilled water. The washed specimens were dried with a clean towel and then passed through solutions of alcohol and of ether. The samples were allowed to stand several minutes to come to room temperature before they were weighed and put into the corroding medium.

The test pieces were supported in a horizontal position by means of glass tripods. All results, unless otherwise specified, were obtained with the specimen immersed 2 cm. below the surface of the liquid.

The effect of the surface area of the corroding solution exposed to the atmosphere was determined by keeping all other variables constant. Glass crystallizing dishes approximately 20 cm. in diameter were used to obtain a large ratio of surface area of solution to surface area of metal. The area of the solution exposed to the atmosphere was then decreased by using glass plates which fitted exactly into the crystallizing dishes. Circular holes of varying diameters were cut in the center of the glass plates, and the glass plates were supported in such a manner that they covered the surface of the liquid except where portions had been cut from them. Care was always taken to see that no bubbles of air were trapped under the plates.

All tests were made at room temperature, which was approximately  $21 \pm 2^{\circ}$  C. The duration of each test was from 3 to 7 days.

### Discussion of Results

Any factor which changes the solubility of oxygen in a solution will of necessity change the corrosion rate of copper in that solution. Table I and Figure 1 show the influence of acid concentration on the corrosion of copper.<sup>1</sup> The oxygen

<sup>1</sup> This material was checked by F. A. Rohrman and F. Asselin of this department.

solubility in Figure 1, taken from the data of Bohr (5), is given on the basis of cubic centimeters (at standard temperature and pressure) per liter of solution.

The fact that the minimum point for both curves comes at practically the same acid concentration is in accord with theory and with published results for some of the more active metals and alloys. For solutions more than 25 N, the corrosion rate does not increase as rapidly as the reported oxygen solubility. It was observed that small bubbles of a gas, probably sulfur dioxide, formed on the surface of the copper for this concentration range. This observation, along with the known character of concentrated sulfuric acid, indicates that the corrosion is due essentially to the oxidizing character of the sulfuric acid. No black deposit of cuprous sulfide, as reported by Pickering (13), was observed.

TABLE I. INFLUENCE OF ACID CONCENTRATION ON CORROSION OF COPPER IN UNAERATED SULFURIC ACID SOLUTIONS

H <sub>2</sub> SO <sub>4</sub> Normality	No. of Test Pieces	Av. Corrosion Rate Mg./sq. dm./24 hr.	H <sub>2</sub> SO <sub>4</sub> Normality	No. of Test Pieces	Av. Corrosion Rate Mg./sq. dm./24 hr.
0.01	5	26.4	10.0	5	9.4
0.1	5	29.7	12.0	3	7.9
0.2	5	35.4	15.0	3	5.5
0.5	4	33.2	17.0	4	4.2
0.7	5	31.4	20.0	3	2.3
1.0	5	30.5	22.0	3	2.1
2.0	5	25.4	24.0	3	2.1
3.5	3	19.7	26.0	3	1.9
5.0	5	16.6	28.0	3	1.7
7.0	5	12.8	30.0	3	2.6
			35.0	3	5.0

The data show that the maximum corrosion rate comes in solutions at or near 0.2 N. The depletion of the sulfuric acid during the progress of the experiment probably accounts for the decreased rates in the more dilute solutions. Since 0.2 N solutions give the maximum corrosion rate, this concentration was selected for all other experiments in this investigation.

Standard test methods usually specify 250 cc. of the corrosive liquid for each test. The following table shows that the volume of the solution is not a controlling factor provided the volume is not extremely small:

Volume Cc.	Corrosion Rate Mg./sq. dm./24 hr.	Volume Cc.	Corrosion Rate Mg./sq. dm./24 hr.
150	10.8	1000	26.2
250	24.8	1500	26.0
550	20.8	2000	27.2
750	24.2		

In the tests reported, the surface area of the solution and of the copper was maintained constant. In order to obtain a uniform depth of immersion of 2 cm. in the large containers used, it was found most satisfactory to use 1000 cc. of solution for the test runs.

One of the express purposes of this investigation was to determine the slowest and therefore the controlling factor in the diffusion of molecular oxygen from the atmosphere to the metal surface. Either the rate of diffusion through the air-liquid interface or the rate of diffusion through the body of the solution must control the corrosion rate. Most investigators have assumed the latter rate to be the more important, although Friend (11) and Speller (16) have indirectly stressed the importance of the former. Standard methods of corrosion testing (1, 6, 14) still specify the use of a wide-mouth bottle or flask without any designation as to the area of the solution to be exposed to the air.

Since the rate of diffusion of oxygen through the surface film must be a function of the surface area exposed to the atmosphere, a detailed study was made of the influence of the solution surface area on the corrosion of copper. Table II

summarizing the dependence of the corrosion rate on the liquid surface area. The copper specimens were all from the same sheet of copper and were given exactly the same treatment. Each result shown is the average of two to five independent checks. One thousand cubic centimeters of fresh 0.2 *N* sulfuric acid were used for each determination. The results show definitely the reason why experimental data obtained in different laboratories may not check. Corrosion rates differing by as much as 200 per cent may be obtained by different investigators using identical copper specimens but different solution surface areas.

TABLE II. INFLUENCE OF SURFACE AREA OF CORRODING LIQUID ON CORROSION OF COPPER IN UNAERATED SOLUTIONS OF SULFURIC ACIDS

Soln. Surface Area Sq. cm.	Corrosion of Different Metal Areas							
	8 sq. cm.		50 sq. cm.		73 sq. cm.		98 sq. cm.	
	Loss <sup>a</sup>	Rate <sup>b</sup>	Loss	Rate	Loss	Rate	Loss	Rate
6.4	...	...	8.2	16.4	10.3	14.2	10.1	10.3
20	3.1	38.8	10.0	20.0	12.9	17.8	13.7	13.8
51	3.1	38.8	11.2	22.4	14.7	20.2	15.2	15.5
82	3.2	40.0	11.7	23.4	15.3	21.0	17.4	17.8
116	3.2	40.0	12.4	24.8	17.1	23.5	19.3	19.7
171	3.2	40.0	13.3	26.6	18.3	25.1	22.1	22.6
200	3.3	41.0	13.5	27.0	17.6	24.2	22.5	22.9
231	...	...	14.3	28.6	20.2	27.7	24.1	24.6
328	...	...	19.9	40.0	25.8	35.4	32.5	33.2

<sup>a</sup> Loss = mg. per 24 hours.

<sup>b</sup> Rate = mg. per sq. dm. per 24 hours.

Table II shows that an increase in the solution surface area had a much greater effect on the larger metal specimens. The smallest specimen tested had practically a constant loss in weight for all solution surface areas. This loss indicates that for them the diffusion through the air-liquid interface was no longer the controlling factor. For the larger specimens the solution surface area was the controlling factor up to a point where the corrosion rate was approximately equal to the rate found for the smallest specimen (Figure 2). Each curve shows the relationship between the size of the copper specimen and the corrosion loss for a given solution surface area. The line *OX* is evidently the limiting condition which would be realized for all sizes of specimens if the solution surface area was of sufficient size. Condition *OX* could not be realized experimentally for the largest specimens because of the im-

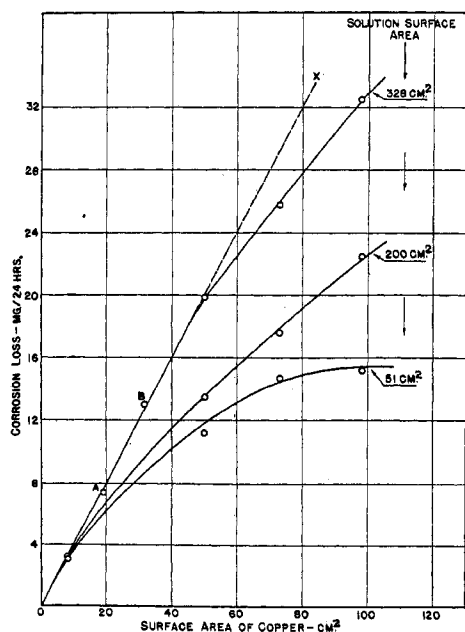


FIGURE 2. INFLUENCE OF SURFACE AREA OF COPPER ON CORROSION FOR DIFFERENT SOLUTION SURFACE AREAS

TABLE III. VARIATION IN SOLUTION SURFACE AREA BY POSITION OF GLASS PLATE

(Area of copper = 50 sq. cm.; area of hole in glass plate = 51 sq. cm.; area of container = 171 sq. cm.)

Case	Condition	Corrosion Rate Mg./sq. dm./24 hr.
1	No glass plate container open	29.7
2	Glass plate below surface of liquid but above specimen	28.1
3	Glass plate covering surface of liquid	20.3

possibility of spreading 1000 cc. of a solution over a larger area and still having the sample immersed 2 cm. below the surface of the liquid. Points *A* and *B* on line *OX* are the results of experimental tests performed in a solution with a surface area of 328 sq. cm.

Line *OX*, toward which the curves are approaching, corresponds to a corrosion rate of 40 mg. per sq. dm. per 24 hours. The data of Table II and the significance of line *OX* in Figure 2 definitely establish the maximum corrosion rate for copper in unaerated 0.2 *N* solutions of sulfuric acid.

Data already presented indicate that the diffusion of oxygen through the air-liquid interface is the controlling factor in corrosion except where the ratio of solution surface area to metal surface area is very large. Table III shows the results of a series of experiments which verify these conclusions. The solution surface area for cases 1 and 2 is the same as the area of the container. In case 2 the glass plate is placed below the liquid surface in a position which will tend to hinder the diffusion through the body of the liquid. The corrosion rate for case 2 is only slightly less than that for case 1, a condition which indicates that the diffusion through the liquid is of such rapidity that it does not control the rate of the corrosion phenomena. The marked decrease in the corrosion rate for case 3 is conclusive evidence that the rate of oxygen diffusion through the air-liquid interface is the controlling factor in the corrosion process for the stated conditions.

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