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CORROSION OF METALS BY AQUEOUS SOLUTIONS OF THE ATMOSPHERIC POLLUTANT SULFUROUS ACID

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It has been found here that the corrosion rate of a metal in an acid such as H_2SO_3, HNO_3, H_2SO_4, or HCl, having a normality between N/1 and N/10,000, is related to the concentration of the acid in accordance with the equation Corrosion rate = a x (Acid Normality)[b] where a and b are constant for each combination of acid and metal and where the temperature is 25°C. Having determined the values of a and b for a considerable number of these acid-metal combinations, it was possible 1—to compare the corrosion rates of the various metals in sulfurous acid with those of the same metals in the well-known nitric, sulfuric, and hydrochloric acids, and 2—to determine the corrosion rates of the metals in sulfurous acid of different normalities.

Sulfur dioxide (SO_2) is a gas that is produced during the combustion of coal and oil, the roasting of sulfide ores, and the operation of certain other industries. When entirely dry, it does not cause any visible change in ordinary low-carbon steel type 1010, a corrosion rate of < 0.1 mil/yr having been obtained in this laboratory (1). Meetham (2) stated that sulfur dioxide "is particularly liable to attack paint, metals, stone work and slates when water is present. When rain water wets the surfaces and interstices of a building, and sulfur dioxide is present in the air, a very dilute solution of sulfur dioxide is formed which becomes more concentrated later as the water begins to evaporate." When sulfur dioxide reacts with water vapor or liquid water, the product is sulfurous acid.

In past years, Hudson and Stanners (3) and Sereda (4), and probably other investigators, performed field corrosion tests on steel in which the metal was exposed to atmospheres containing comparatively small proportions of sulfurous acid. Since the tests were of considerable duration, the sulfurous acid concentrations and the weather conditions varied while they were in progress. While such tests showed definitely that the corrosion rate of the steel increased as the sulfurous acid content of the atmosphere became higher, they could not show the actual corrosion rates of the steel in pure sulfurous acid of different concentrations and at a definite temperature.

More recently, the amount of sulfur dioxide being emitted into the atmosphere, especially in urban and industrial areas, has increased enormously, more than 23 million tons having been emitted in the U.S.A. alone during one recent year (5). Scientists are becoming increasingly aware that accurate information is needed regarding the severity of the metal corrosion due to sulfurous acid. Studies of this kind would have to be performed under carefully controlled conditions in the laboratory.

It was decided that this laboratory would undertake a research program to determine the corrosion rates of the commoner ferrous and nonferrous metals in sulfurous acid solutions of concentrations between N/1 and N/10,000; also that the investigation would include a comparison of these rates with those of the same metals in nitric, sulfuric, and hydrochloric acid solutions of similar concentration. It is believed that the information obtained will be of considerable interest to those who design structures and equipment to be used in environments where sulfurous acid is present.

Certain facts regarding the effect of aqueous sulfurous acid solutions on low-carbon steel already have been published in this laboratory (1); also, a new additive has been found here for effectively combating the corrosion of low-carbon steel in sulfurous acid solutions, and this information has been published (6).

Experimental Materials

The metals whose corrosion rates were determined in this research were as follows:

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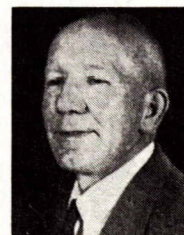
Raymond R. Rogers received his M.A. degree in electrothermics at Toronto University in 1926 and his Ph.D. in electrochemistry at Columbia University in 1933. He continued there as instructor and research supervisor until 1941. Since 1944, he has been in charge of research in metal corrosion and its prevention and in pyrometallurgy at the Canadian Dept. of Energy, Mines and Resources.
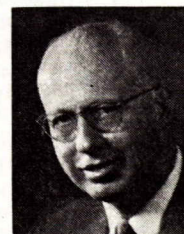
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Table 1. Analysis of steels (%)

| | Type of steel | | | | | | | |
| | Nonstainless | | | | | Stainless | | |
Constituent	1010	1062	1090	4037	4340	304L	316	347
Carbon	0.07	0.64	0.93	0.40	0.38	0.02	0.05	0.07
Manganese	0.33	1.03	0.85	0.76	0.78	0.8	1.8	1.5
Silicon	0.01	0.16	0.30	0.31	0.31	0.8	0.5	0.5
Nickel	0.04	—	—	—	1.71	10.2	13.1	10.9
Molybdenum	—	—	—	0.26	0.21	—	2.5	—
Chromium	—	—	—	—	0.77	18.7	16.7	17.9
Copper	0.13	—	—	—	—	—	—	—
Columbium + tantalum	—	—	—	—	—	—	—	0.8
Phosphorus	<0.011	<0.002	<0.02	<0.02	<0.02	—	—	—
Sulfur	<0.011	<0.009	<0.02	<0.02	<0.01	—	—	—

(a) Nonstainless steel types 1010, 1062, 1090, 4037, 4340, and stainless steel types 304L, 316, 347 (analyses in Table I).

(b) Copper, tin, lead, nickel, zinc, aluminum (all commercially pure).

(c) Cadmium and chromium (electroplated from commercial baths).

The test pieces of most of the metals were approx 5 x 1 x 0.1 cm. Those of steel types 1062, 4037, and 4340 were nails of 0.4 cm diam and approx 7.5 cm length. The dimensions of each test piece were accurately measured for corrosion rate determination.

The hydrochloric, sulfuric, and nitric acids used in these corrosion experiments were of reagent grade, diluted to the desired normalities with distilled water. The sulfurous acid solutions were produced by dissolving sulfur dioxide gas in distilled water. (This gas was obtained from a cylinder of liquid sulfur dioxide manufactured by Matheson of Canada Ltd.) During this research, a sulfurous acid solution was assumed to have the same normality as that of a sulfuric acid solution of the same sulfur content.

In most cases, the normalities of the acids used in the experiments varied between $N/1$ and $N/10,000$. However, in some cases it was necessary to use narrower ranges of normality because of undesirable conditions which developed during the experiments, such as the precipitation of corrosion product on the metal surface or the production of excessive motion in the solution due to gas evolution. Such conditions would have given misleading corrosion rate results.

Experimental Procedures

The following procedure was used in determining the corrosion rate of the metal in each of the experiments performed.

1. The metal test piece was prepared for a corrosion experiment by dry blasting with No. 120 alumina grit at a line air pressure of 48 lb/in.[2] in a Zero Blast-N-Peen machine (manufactured by the Zero Manufacturing Co., Washington, Mo., U.S.A.). It then was thoroughly brushed with a bristle brush to remove loose particles from the surfaces, rinsed with trichlorethylene, dried, weighed, and finally placed in the corroding acid prepared as described in point 2 below.

2. Comparatively concentrated acid (nitric, hydrochloric, or sulfuric) was placed in a 250-ml erlenmeyer flask and diluted with distilled water to produce 200 ml of acid of the desired normality as determined by titration with standard sodium hydroxide solution. (In preparing the sulfurous acid solution, the sulfur dioxide was led into the water through a tube and the final titration was done with a standard iodine solution.) The resulting solution was homogenized with a magnetic stirrer and the temperature was adjusted to 24° ± 2°C (17.5°C in one series). Finally, the metal test piece, prepared as described in point 1 above, was completely immersed in the acid solution, one end resting on the bottom of the flask and the other held at an angle of 45° from the horizontal by a plastic cord. The latter was held in place with a rubber stopper. At the end of 60 min, the corroded test piece

was removed from the acid, rinsed in water, and treated under the influence of a Sonogen Ultrasonic Transducer to remove any adhering solid particles. Finally, it was washed, dried, and reweighed. The loss in weight during the immersion in the acid was converted to corrosion rate in mils per year.

In each experiment, the exposed area of the metal was small compared to the volume of the corroding solution, and the time of immersion was comparatively short. This was done to insure that the acid concentration would be decreased as little as possible, that the concentration of the soluble corrosion products would be kept at a minimum, and that the temperature of the solution would change very little.

The following procedure was used in determining the relationship between the normality of the corroding acid and the corrosion rate of the metal immersed in the acid, in the case of each combination of metal and acid investigated. A series of corrosion experiments was performed with each combination of metal and acid, the acid normality at one end of the series usually being $N/1$ and that at the other end usually being $N/10,000$. After the series had been completed, the logarithm of the acid normality was plotted against the logarithm of the corresponding corrosion rate in the case of each experiment. It was found that the resulting points fell on or close to a straight line whose equation was

$$\log \text{Corrosion Rate (in mils/year)} = (b \times \log \text{Acid Normality}) + \log a$$

where b is the slope of the line and a is the corrosion rate of the metal in $N/1$ acid.

From this equation, it follows that

$$\text{Corrosion rate (in mils/year)} = a \times (\text{Acid Normality})^b = aN^b \quad [1]$$

a and b being constants for that particular combination of metal and acid. The relationship between corrosion rate and acid normality proved to be different in the case of tin in hydrochloric acid. Here, the equation was

$$\text{Corrosion Rate (in mils/year)} = c + d \log N \quad [2]$$

over the range $N/1 \rightarrow N/2100$, c and d being constants. The reason for the difference in the form of these two equations is not apparent.

Each experiment referred to above was performed in triplicate.

Using Eq. [1] above, the corrosion rate of each of the metals affected by sulfurous acid was calculated for the acid concentrations $N/10$, $N/100$, and $N/1000$, constant a being the corrosion rate of the metal in $N/1$ acid, and constant b being the slope of the line having the equation

$$\log \text{Corrosion Rate (in mils/year)} = b \times \log (\text{Acid Normality}) + \log a$$

Experimental Results

Ferrous Metals.—Since iron was the predominant element in each of these metals, there was a similarity

Table II. Values of the constants "a" and "b" for the ferrous metals.
(Normality range for types 1010, 1062, 1090, 4037, and 4340):

$$\frac{N}{1} \to \frac{N}{10,000}$$

Metal / Acid	Type 1010 a	Type 1010 b	Type 1062 a	Type 1062 b	Type 1090 a	Type 1090 b	Type 4037 a	Type 4037 b	Type 4340 a	Type 4340 b	Type 304L Type 316 Type 347
Nitric	55,000	1.227	63,000	1.185	53,000	1.169	64,000	1.207	54,000	1.182	$\frac{N}{2.3} \to \frac{N}{10,000}$
Sulfurous	12,000	0.906	36,000	0.952	15,000	1.084	46,000	0.986	45,000	1.111	No corrosion
Sulfuric	680	0.503	440	0.312	3,300	0.643	850	0.450	9,800	0.778	detected
Hydrochloric	720	0.587	630	0.506	1,620	0.635	660	0.562	4,360	0.578	

in the experimental results obtained, even though there was a considerable variation in the compositions. The values of a and b obtained are presented in Table II.

No detectable corrosion took place in the stainless steels (types 304L, 316, and 347) when the acid normality varied between $N/2.3$ and $N/10,000$, regardless of the kind of acid used.

All of the nonstainless steels (types 1010, 1062, 1090, 4037, and 4340) corroded in all four of the acids, the values of the constants a and b being much greater in the cases of the sulfurous and nitric acids than in the cases of the sulfuric and hydrochloric acids. In addition, the values of a and b were always somewhat lower in the case of the sulfurous acid than in the case of the nitric acid.

No gassing was visible on any of the corroding metal surfaces when they were in contact with sulfurous or nitric acid, regardless of the concentration. On the other hand, gassing occurred on all of the metal surfaces when they were in contact with sulfuric or hydrochloric acid of reasonably high concentration.

It was shown that the value of the constant a decreased appreciably (from 12,000 to 10,000) and that of the constant b increased slightly (from 0.906 to 0.922) when steel type 1010 was corroded in sulfurous acid at 17.5°C instead of 24°C.

Nonferrous Metals.—As anticipated, there was a much greater variation in the values of a and b obtained with the nonferrous metals than with the ferrous ones, as shown in Tables IIIa and IIIb.

No corrosion was detected when sulfurous acid was in contact with copper. The same result was obtained with sulfuric and hydrochloric acids. However, the copper was corroded by nitric acid.

No corrosion was detected when sulfurous, nitric, sulfuric, or hydrochloric acid of normality $N/1.3$ or less was in contact with chromium.

Tin, lead, nickel, cadmium, zinc, and aluminum were corroded by sulfurous and nitric acids, the nickel and aluminum being corroded at a greater rate by the sulfurous acid than by the nitric acid. Sulfuric acid did not corrode the tin, but did corrode lead, nickel, cadmium, zinc, and aluminum. Hydrochloric acid corroded tin, lead, nickel, cadmium, zinc, and aluminum.

As in the case of the ferrous metals, no gassing was observed when corrosion occurred due to the action of sulfurous or nitric acid; however, it was observed when corrosion occurred due to the action of sulfuric or hydrochloric acid when these were of reasonably high concentration.

It was noted that the maximum and minimum values of a and b were much closer in the case of aluminum than in the case of any other metal.

The corrosion rates calculated by Eq. [1], for $N/10$, $N/100$, and $N/1000$ sulfurous acid, are given in Table IV.

Discussion

During the experiments, it was noted that hydrogen gas was evolved when the various steels were corroded by either sulfuric or hydrochloric acid. The reactions could be expressed by the general equations:

$$Fe + 2H^+ + SO_4^= \to Fe^{++} + 2H + SO_4^= \quad [1]$$

$$2H \to H_2 \quad [2]$$
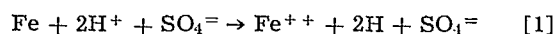
Apparently the atomic hydrogen produced in [1] was converted into comparatively inert molecular hydrogen in [2]. The polarization of the cathodic areas on the steel would be comparatively high under these circumstances.

On the other hand, no gas was evolved when the steels were corroded by sulfurous acid. On the basis of earlier experiments performed by the authors (1), it is suggested that the following reactions occurred:
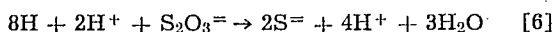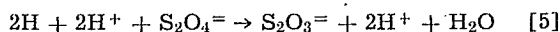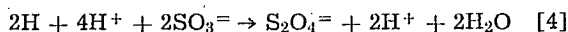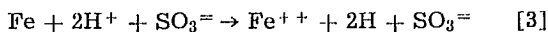
Table III(a). Values of the constants "a" and "b" for the more noble nonferrous metals

Metal / Acid	Copper a	Copper b	Tin a	Tin b	Lead a	Lead b	Nickel a	Nickel b
Nitric	$\frac{N}{1} \to \frac{N}{10,000}$, 560	0.639	$\frac{N}{16} \to \frac{N}{10,000}$, 83,000	1.186	$\frac{N}{1} \to \frac{N}{100}$, 4800	0.803	$\frac{N}{1} \to \frac{N}{10,000}$, 1700	0.472
Sulfurous			$\frac{N}{8} \to \frac{N}{10,000}$, 4050	0.548	$\frac{N}{100} \to \frac{N}{10,000}$, 370	0.295	2230	0.605
Sulfuric	No corrosion detected		$\frac{N}{1} \to \frac{N}{10,000}$ No corrosion detected		Precipitate produced at time of corrosion		180	0.290
Hydrochloric			$\frac{N}{1} \to \frac{N}{2,100}$ c = 86 d = 36.2		$\frac{N}{8} \to \frac{N}{10,000}$, 825	0.288	200	0.340

Table III(b). Values of the constants "a" and "b" for the less noble nonferrous metals

Acid	Cadmium a	Cadmium b	Chromium a	Chromium b	Zinc a	Zinc b	Aluminum a	Aluminum b
Nitric	$\frac{N}{1} \to \frac{N}{10,000}$ 135,000	1.222	$\frac{N}{1.3} \to \frac{N}{10,000}$		$\frac{N}{1} \to \frac{N}{10,000}$ 59,000	1.204	$\frac{N}{1} \to \frac{N}{10,060}$ 1350	0.570
Sulfurous	27,700	1.247	No corrosion detected		14,100	0.967	$\frac{N}{10} \to \frac{N}{10,000}$ 1600	0.630
Sulfuric	2000	0.565			31,400	1.055	$\frac{N}{10} \to \frac{N}{10,000}$ 1800	0.796
Hydrochloric	1400	0.562			20,500	0.877	$\frac{N*}{2.7} \to \frac{N}{10,000}$ 1800	0.605

* $\frac{N}{1} \to \frac{N}{2.7}$ HCl → violent gassing.

$$Fe + 2H^+ + SO_3^= \to Fe^{++} + 2H + SO_3^= \qquad [3]$$

$$2H + 4H^+ + 2SO_3^= \to S_2O_4^= + 2H^+ + 2H_2O \qquad [4]$$

$$2H + 2H^+ + S_2O_4^= \to S_2O_3^= + 2H^+ + H_2O \qquad [5]$$

$$8H + 2H^+ + S_2O_3^= \to 2S^= + 4H^+ + 3H_2O \qquad [6]$$

In other words, when sulfurous acid is used as the initial corroding agent, it soon is joined by smaller amounts of several other acids which have been produced by the atomic hydrogen reduction of some of the sulfurous acid. The presence of these other acids in the sulfurous acid may account at least in part for the comparatively high corrosion rate which was obtained. Doubtless, the polarization of the cathodic area on the steel would be considerably lower under these circumstances than when the steel was corroded by sulfuric acid. It may be added that our experiments have shown that very finely divided iron sulfide is present on type 1010 (low-carbon) steel after it has been in contact with sulfurous acid solution.

It is assumed that a somewhat similar situation existed when nitric acid was used in tests instead of sulfurous acid except that, in this case, nitrogen-containing acids were produced instead of sulfur-containing acids.

Naturally, the results obtained with the nonferrous metals would not be expected to be exactly the same as those obtained with the steels because each metal has certain unique characteristics such as the tendency

Table IV. Corrosion rate of nonstainless steels and nonferrous metals in $\frac{N}{10}$, $\frac{N}{100}$, and $\frac{N}{1000}$ sulfurous acid at 24° ± 2°C

Metal	Corrosion rate in sulfurous acid (mil/yr) $\frac{N}{10}$	$\frac{N}{100}$	$\frac{N}{1000}$
Steel			
Type 1010	1459	181	22
Type 1062	4055	453	51
Type 1090	1227	101	8
Type 4037	4775	493	51
Type 4340	3459	268	21
Tin	1149	325	92
Lead	*	95	48
Nickel	554	138	34
Cadmium	1570	89	5
Zinc	1524	164	18
Aluminum	370	87	20

* Precipitate produced.

of aluminum to form a protective film on its surface. However, it was felt that an experimental method which was adequate for the steels would be satisfactory for the nonferrous metals also.

It is important to note that the success of this research was, to a considerable degree, due to the design of the corrosion test. Since the volume of the corroding solution was great compared to the area of the metal specimen being corroded, the temperature of the solution could not have been greatly affected by the heat of the reaction, and the initial and final concentrations of the corroding solution in each test must have been almost identical. In addition, each test was of comparatively short duration with the result that the total amount of corrosion product in the solution remained small.

During this research, particular attention was paid to the action of sulfurous acid solution on the steels because of the very large tonnage of these materials now in use. Only the most common of the nonferrous metals were dealt with, and no attention was paid to their numerous alloys.

Judging by the values of the constants *a* and *b*, and by the tendency for gas to be produced during the corrosion, the chemistry of the corrosion of the ferrous metals by sulfurous acid resembles that by nitric acid much more than that by sulfuric and hydrochloric acid. This situation also exists to a marked degree in the cases of cadmium and nickel. On the other hand, copper corrodes readily in nitric acid but is not appreciably affected by sulfurous, sulfuric, or hydrochloric acids in the concentration range referred to.

Nickel has a useful resistance to corrosion in many important media. Scarberry, Graver, and Stephens [7] have shown that the resistance of typical nickel alloys to corrosion by chemicals such as hydrochloric, sulfuric, and phosphoric acid and sodium hydroxide increases as the nickel content of the alloys is increased. However, in the same paper they also have shown that the resistance of these same nickel alloys to nitric acid corrosion decreases as the nickel content of the alloys is increased. In view of the comparative similarity between nitric acid corrosion and that of sulfurous acid shown in the present research, it is not surprising that the resistance to $N/10$ and $N/100$ sulfurous acid of the steel type 4340 containing 1.71% nickel was found to be less than that of steel type 1010 which contains almost no nickel. It is interesting to note, however, that when a substantial proportion of chromium is present in nickel-containing alloys (as steel types 304L, 316, and 347) the resulting alloy is free from corrosion by sulfurous acid as well as by

nitric acid. In this way, the useful properties of both nickel and chromium are utilized under these severe conditions.

Aluminum was found to be less corrosive than might have been expected since it is considered to be one of the more active metals. It is probable that, at $N/2.7 \rightarrow N/10,000$, it was covered with an invisible nonmetallic film which gave it considerable protection. Obviously, no such protection existed in the presence of $N/1 \rightarrow N/2.7$ hydrochloric acid because violent gassing occurred under those conditions.

The data presented in Table IV show clearly the great severity of the corrosion which may take place in metal structures which may be in contact with sulfurous acid solution.

Conclusions

The most important conclusions with regard to the sulfurous acid corrosion of the metals investigated may be summarized as follows:

1. The nonstainless steel types 1010, 1062, 1090, 4037, and 4340 are highly susceptible to this kind of corrosion. (While the corrosion rates are lower than those in the case of nitric acid, they are many times greater than those in the case of sulfuric and hydrochloric acids.)

2. The stainless steel types 304L, 316, and 347 are not appreciably susceptible in solutions lower than $N/2.3$.

3. Copper and chromium are not appreciably susceptible in solutions lower than $N/1.3$.

4. Tin corrodes much more rapidly than the other nonferrous metals investigated between $N/100$ and $N/1000$, but comes after cadmium and zinc at $N/10$.

5. Nickel corrodes more rapidly in sulfurous acid than in nitric, sulfuric, or hydrochloric acids.

6. Lead corrodes less rapidly in sulfurous acid than in nitric acid; however, the rates between $N/100$ and $N/1000$ are considerable.

7. Cadmium corrodes much less rapidly in sulfurous acid than in nitric acid, but much more rapidly than in sulfuric and hydrochloric acids.

8. Zinc corrodes comparatively rapidly in $N/10$ or $N/100$ sulfurous acid, but less so than in nitric or sulfuric acids.

9. The corrosion rates for aluminum in the four acids are comparatively low and close together. (However, it corrodes very rapidly in $N/1 \rightarrow N/2.7$ hydrochloric acid.)

It is important to note: 1—that the experiments referred to in this paper have covered a very wide range of acid concentrations (generally from $N/1$ to $N/10,000$), and 2—that the sulfurous acid solutions causing the greatest amount of damage in urban and industrial areas probably are between these normalities.

Obviously, the conditions inside a glass flask in a laboratory corrosion test seldom duplicate those under which the corrosion occurs in the field. Nevertheless, a considerable amount of new information regarding the corrosion properties of aqueous solutions of the important air pollutant sulfurous acid has been presented in the present paper.

Any discussion of this paper will appear in a Discussion Section to be published in a forthcoming issue.

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