Dept. Mines & Technical Surveys
MINES BRANCH
JUN 22 1966
LIBRARY
OTTAWA, CANADA.

DEPARTMENT OF
MINES AND TECHNICAL SURVEYS
MINES BRANCH

SULFUROUS ACID CORROSION OF LOW CARBON STEEL AT ORDINARY TEMPERATURES – I. ITS NATURE

W. McLEOD AND R. R. ROGERS
EXTRACTION METALLURGY DIVISION

REPRINTED FROM CORROSION VOL. 22, NO. 5
MAY, 1966

Reprint Series RS 6
Price 25 cents

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA
Daly Building, Corner Mackenzie and Rideau

TORONTO
Mackenzie Building, 36 Adelaide St. East

MONTREAL
Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 25 cents Catalogue No. M38-8/6

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1966

Sulfurous Acid Corrosion of Low Carbon Steel at Ordinary Temperatures - I. Its Nature*

By W. McLEOD* and R. R. ROGERS**

ABSTRACT

Corrosion rate data are presented for low carbon steel in (1) a combination of sulfur dioxide, water vapor and air, and (2) aqueous solutions of sulfurous acid in the absence of air, at ordinary temperature. Information as to the nature of the corrosion products is presented and it is shown that this depends on the place in which the corrosion takes place to an important extent.

INTRODUCTION

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 completely dry it does not cause any visible change in steel, a corrosion rate of <0.1 mil per yr having been obtained in this laboratory. However, when it comes into contact with water, the resulting material is sulfurous acid, which may act either as an oxidizing or a reducing agent and which corrodes steel at ordinary temperatures, sometimes very severely.

In 1953 Hudson and Stanners[1] reported corrosion results obtained when ingot iron and copper steel were exposed to various types of atmospheres at more than 20 locations in Great Britain and elsewhere in the world. They found that, where relative humidity of the atmosphere was above 70 percent, an almost perfect correlation existed between the amount of sulfur dioxide in the atmosphere and the rate of corrosion. Normally, any excessive corrosive effect due to salt in the atmosphere was observed only within a short distance of the surf on the seashore.

A large proportion of the sulfur dioxide in the air is produced by the combustion of fuels. Most of the coal used in Canada contains between 1 and 3 percent sulfur and some of it contains as much as 7 percent; also most of the oil contains between 0.2 and 3 percent sulfur and some of it contains as much as 5 percent. When these fuels are burned, the resulting sulfur dioxide is free to form sulfurous acid with water in the air. When incomplete combustion of the fuel takes place, particles of unburned carbonaceous material may enter the air along with the sulfur dioxide. Such particles increase the rate of sulfurous acid corrosion of steel, at least partly, because they come into contact with the metal and set up electrolytic cells, the carbonaceous material being cathode and the steel anode. In a test described by Vernon[2] the corrosion rates of mild steel in pure air, pure air + 0.01 percent sulfur dioxide and pure air + 0.01 percent of sulfur dioxide + particles of charcoal were compared, the relative humidity being the same in each case (about 99 percent). The corrosion rate in the pure air + sulfur dioxide was about 20 times as great as that in the pure air and the rate in the pure air + sulfur dioxide + charcoal was about 60 times as great as that in the pure air.

Barton and Beranek[3] have suggested that reactions involving the production of FeS, $FeSO_4$, FeS_2O_3, S, $Fe_2(SO_4)_3$ and, eventually, a lepidocrocite type of iron oxide (γ-FeO.OH), take place when steel is corroded by atmospheres polluted with sulfur dioxide.

Tanner[4] reported the presence of a white crystalline material in pits underneath compact layers of rust on steel specimens from a number of different locations. He found this material to consist of $FeSO_4.4H_2O$ alone, and the crystalline material immediately above it to be a goethite type of iron oxide (α-FeO.OH). Lepidocrocite type of oxide was not detected in the near vicinity of the white crystals. Also there was no evidence of thiosulfates or sulfides.

Corrosion of steel by sulfur compounds at high temperatures also is an important phenomenon, which has been dealt with in a fairly recent paper by Rolls.[5] A considerable number of papers on the subject of the sulfur dioxide corrosion of steel have been written, some of them before the more modern techniques such as X-ray diffraction had become available; however, it is believed that references at the end of this paper give a satisfactory picture of the present status of this problem.

---

*Submitted for publication July 6, 1965. A paper presented in part to the Canadian Region of the National Association of Corrosion Engineers in Toronto, January 29, 1964.

*Senior Scientific Officer and **Head, Corrosion Section, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada.

A study of the sulfurous acid corrosion of a cold-rolled low carbon steel at ordinary temperatures has been in progress in this laboratory for several years. The composition of the steel is given in Table 1.

TABLE 1 - Analysis of Low Carbon Steel (%)

Carbon	0.07	Nickel	0.036
Manganese	0.33	Sulfur	0.011
Silicon	0.01	Phosphorus	0.011
Copper	0.13		

In an attempt to get new information about the nature of this type of corrosion and the products resulting from it, a number of metal specimens were exposed to a combination of sulfur dioxide, water vapor and air and others were immersed in solutions of sulfurous acid in water in the absence of air. It is believed that a large proportion of the cases of sulfurous acid corrosion that occur during exposure to the outdoor atmosphere are due to one or other of these two simple types of exposure or to combinations of them. However, no attempt was made to reproduce any of the possible combinations in the present investigation.

Before they were used in the tests, all specimens were thoroughly cleaned by wet blasting with 220 mesh fused alumina grit, scrubbing in liquid trichlorethylene and then in water with a bristle brush, rinsing in water, rapid dipping in 4N hydrochloric acid and rinsing in water. All corrosion experiments were performed at room temperature, which was 70-75 F (21-24 C).

During this research program an attempt was made to find a satisfactory method of combating the corrosion of low carbon steel in aqueous solutions of sulfurous acid. It was found that certain substances, when added to the acid solution, caused formation of a visible film that gave excellent protection to the steel. This part of the research has been described in a second paper.[6]

CORROSION EXPERIMENTS

Experiments in a Combination of Sulfur Dioxide-Water Vapor-Air

In these experiments air from the atmosphere was passed through the following train of equipment:

(1) Flowmeter, (2) glass container of calcium hydroxide to remove carbon dioxide, (3) glass container of calcium chloride to remove moisture, (4) glass flask equipped with sintered glass bubbler and containing sulfurous acid solution, (5) glass cylinder containing the vertically-suspended, clean steel specimen (5 x 1.5 x 0.1 cm) being corroded, (6) wet and dry bulb equipment for relative humidity determinations and (7) gas pump. In this way the steel specimen was exposed to air containing between 0.7 and 2.2 percent of sulfur dioxide (24-hour average approximately 1 percent), which was less than 100 percent saturated with water vapor and contained no liquid water. The rate of gas flow through the apparatus was approximately 40 linear cm/min.

Each steel specimen was cleaned and weighed and then corroded for a length of time varying between 3 and 500 days. Then it was removed from the apparatus, freed of all corrosion product and weighed again. Finally, the corrosion rate was determined. The average corrosion rates of typical specimens are shown in Table 2. It will be noted that, while the rate was comparatively rapid at first, it eventually became quite slow and practically constant.

TABLE 2 - Variation of Corrosion Rate With Time In a Combination of Sulfur Dioxide, Water Vapor and Air

Length of Corrosion Time (days)	Average Corrosion Rate (mils per yr)
3	9.7
50	2.7
100	1.1
200	0.7
500	0.6

Experiments in Aqueous Solutions of Sulfurous Acid in the Absence of Air

Experiments were performed, in each of which a cleaned and weighed specimen of low carbon steel (5 x 1.5 x 0.1 cm) was immersed completely for 3 days in 200 cc of water in which 1.6 g of sulfur dioxide had been dissolved, at a temperature of 77 F. In each case argon was bubbled through the solution to prevent it from being oxidized by the air. At the end of each experiment the specimen was freed of all corrosion product, dried and reweighed. The average of the corrosion rates obtained was 311 mils per yr. When 3.2 g of sulfur dioxide was used in each of the corroding solutions in a similar manner, the average of the corrosion rates was 622 mils per yr. Although in all cases the corrosion rates decreased after the specimens had been immersed for a short time, due probably to the presence of the solid corrosion product, they still were quite high at the completion of the experiments.

In another somewhat similar experiment the acid containing the specimen and the soluble and insoluble corrosion products was allowed to stand in a closed glass container for about 2.5 years. Long before that time the corrosion of the metal had been completed and the insoluble material remaining consisted largely of sulfur with a smaller amount of some amorphous material, probably iron hydroxide.

CORROSION PRODUCTS

The nature of typical solid corrosion products obtained in the abovementioned experiments was determined by X-ray diffraction except when otherwise indicated. The resulting information is contained in Table 3.

TABLE 3 - Identification of Solid Corrosion Products

Layer	Steel vs Air, SO_2 and Water Vapor	Steel Immersed in Water + H_2SO_3	
		After 3 Days	After 2.5 Years
Next to the metal	black layer: Fe_3O_4 (major) α-FeO.OH α-Fe (trace)	black layer (very adherent): FeS[1] (almost entirely)	
Intermediate layers	light brown layer: α-FeO.OH (major) Fe_3O_4 reddish brown layer: α-FeO.OH (predominant)		largely sulfur
Farthest from the metal	white layer (very soft): $FeSO_4.4H_2O$ (only constituent)	brown layer (porous and poorly adherent): mixture of FeS, S, γ-FeO.OH and unidentified amorphous material	

[1] Identified by chemical analysis

When, as may happen in actual practice, the steel was corroded by an aqueous solution of sulfurous acid and the resulting solution evaporated, a water-soluble iron-containing salt was deposited. In each experiment air was blown through the solution as soon as the corrosion had ceased and the resulting solution was evaporated almost to dryness at room temperature. The nature of the iron-containing salt was determined by X-ray diffraction techniques. No appreciable amount of solid material was produced during the aeration and before the evaporation took place.

In the first experiment a limited amount of air was used and the resulting crystals had the formula $FeSO_4.H_2O$. In the second experiment a somewhat larger amount of air was introduced and the resulting solid product consisted of a mixture of dark brown crystals (apparently a ferric compound) and lighter colored crystals of $FeSO_4.H_2O$ and $FeSO_4$. After several days the brown crystals had become much lighter in color and had changed into the following three layers:

(1) underneath - $FeSO_4.4H_2O + FeSO_4.H_2O$

(2) intermediate - $FeSO_4.H_2O$

(3) above - $FeSO_4.H_2O + FeSO_4$

In the third experiment a much larger quantity of air was introduced until tests showed the presence of ferric and ferrous ions in about equal amounts. The crystals produced on evaporation were dark brown but, in a short time, changed largely to $FeSO_4.4H_2O$. These results suggest that the soluble iron compound, produced eventually after the corrosion of steel by sulfurous acid, is ferrous sulfate regardless of the amount of aeration to which the solution has been subjected. The sulfate may be anhydrous or contain one or four molecules of water of crystallization, depending on the condition of the atmosphere to which it is exposed.

The problem of determining the nature and reactions of other water-soluble materials, produced when the steel was corroded in the aqueous sulfurous acid solutions, was much more difficult to solve because of the complexity of the chemistry involved and because these materials diffused away from the metal surface almost as rapidly as they were produced. In fact, attempts to obtain useful samples at these surfaces for analysis were completely unsuccessful. However, satisfactory samples eventually were obtained by the aid of an electrochemical procedure. A specimen of the steel (5 x 1.5 x 0.1 cm) was made anode and a platinum sheet was made cathode in a 150 cc test tube containing sulfurous acid solution produced by dissolving 4 g of sulfur dioxide in a liter of water. The temperature was approximately 80 F (27 C), the anode current density was maintained at the very low value of 1.6 ma/cm^2, and it was possible for very little air to enter the solution during the experiment. The electrolysis was continued for 5 hr. At intervals a 2 cc pipette was placed against the anode surface and a sample of the solution was withdrawn and spot tested under a microscope for sulfide ($S^=$), hyposulfite ($S_2O_4^=$) and thiosulfate ($S_2O_3^=$), which had been found in a preliminary investigation. Later the experiment was repeated using a solution produced by dissolving 16 g of sulfur dioxide in a liter of water. The concentrations of the soluble anode products of these electrolytic corrosion experiments are recorded in Table 4. A convenient arbitrary scale (0 to 7) is used for this purpose, because the results obtained could not be of great accuracy and were useful for comparative purposes only. It will be noted that elemental sulfur appeared at the anode after the electrolysis had continued for 1 to 2 hours. At both concentrations of sulfurous acid some sulfite ($SO_3^=$) remained in the solution at the end of the five-hour experiment.

TABLE 4 - Concentrations of Soluble Products at the Anode Surface During Electrolytic Corrosion Experiments Is Sulfurous Acid Solutions

(Arbitrary Scale 0 to 7)

Electrolysis Duration (hr)	SO_2 Content = 4 g/l			SO_2 Content = 16 g/l		
	Hyposulfite	Sulfide	Thiosulfate	Hyposulfite	Sulfide	Thiosulfate
	Concentration			Concentration		
0	0	0	0	0	0	0
1	1	2	2	5	2.5	2
	←——	———	——→	←——	———	——→
2	1	0.2	4	4	1	4
3	0.2	0.2	4.5	2	0.2	5.5
4	0.2	0.2	5	0.2	0.2	6
5	0.2	0.2	5	0.2	0.2	6.5

←——→ Appearance of elemental sulfur

DISCUSSION AND CONCLUSIONS

The corrosion experiments referred to above were of the following types:

Type 1: In which the corroding agent consisted of a combination of sulfur dioxide, air and water vapor. In this case the products of the corrosion were the oxygen-containing compounds Fe_3O_4, α-FeO.OH and ferrous sulfate. The corrosion rate gradually decreased to a very low value due to the protection afforded by the corrosion product.

Type 2: In which the corroding agent was sulfurous acid solution in the absence of air. Here the insoluble products were ferrous sulfide and elemental sulfur, which contain no oxygen, together with some γ-FeO.OH. The water-soluble materials included ferrous (Fe^{++}), sulfide ($S^=$), hyposulfite ($S_2O_4^=$) and thiosulfate ($S_2O_3^=$) ions.

The corrosion rate decreased somewhat due to the corrosion product, but continued at a relatively high value.

During the Type 2 corrosion experiments, concentrations of hyposulfite and sulfide ions increased with time until elemental sulfur was produced; then they decreased to a low value. On the other hand, the concentration of the thiosulfate ion continued to increase toward a maximum value.

On the basis of the evidence obtained during the research it is suggested that the reactions listed in Table 5 play an important part in the corrosion of low carbon steel in sulfurous acid solutions at ordinary temperature. During this research no evidence was obtained as to the nature of the reactions in which α-FeO.OH and γ-FeO.OH were produced. However, it is of interest to note Schikorr's[7] suggestion that α-FeO.OH is formed by oxidation of a ferrous salt and γ-FeO.OH by the oxidation of metallic iron. It will be recalled that Tanner[4] found α-FeO.OH in contact with ferrous sulfate.

TABLE 5 - Important Reactions

$$\begin{aligned}
O_2 + 2SO_3^{=} &\rightarrow 2SO_4^{=} \\
Fe + 2H^{+} &\rightarrow Fe^{++} + 2H \\
2H + 2H^{+} + 2SO_3^{=} &\rightarrow S_2O_4^{=} + 2H_2O \\
2H + S_2O_4^{=} &\rightarrow S_2O_3^{=} + H_2O \\
8H + S_2O_3^{=} &\rightarrow 2H^{+} + 2S^{=} + 3H_2O \\
8H^{+} + S_2O_4^{=} + 3S^{=} &\rightarrow 5S + 4H_2O \\
Fe^{++} + S^{=} &\rightarrow FeS
\end{aligned}$$

TABLE 6 - Corrosion Products Referred to by Different Investigators

Present Research	Barton and Beranek[3]	Tanner[4]
In air without liquid water		
Fe_3O_4 α-FeO.OH $FeSO_4.4H_2O$	$FeSO_4$	α-FeO.OH $FeSO_4.4H_2O$
In liquid water without air		
FeS S γ-FeO.OH $S_2O_3^{=}$ No Fe^{+++}	FeS S γ-FeO.OH FeS_2O_3	No FeS No γ-FeO.OH No $S_2O_3^{=}$
In liquid water, followed by aeration then crystallization		
slight aeration { $FeSO_4.H_2O$ No $Fe_2(SO_4)_3$		
much greater aeration { $FeSO_4.4H_2O$ No $Fe_2(SO_4)_3$		
	$Fe_2(SO_4)_3$	No $Fe_2(SO_4)_3$

A comparison of the corrosion products obtained during the present investigation with those referred to by Tanner and by Barton and Beranek, is given in Table 6.

It will be noted that there is a great difference between the compounds referred to by Barton and Beranek and those referred to by Tanner. However, it may be pointed out that the two compounds identified by Tanner were found in the corrosion products obtained in the present investigation when the steel was corroded by a combination of sulfur dioxide, water vapor and air in the absence of liquid water. On the other hand, the compounds referred to by Barton and Beranek were, with the exception of the ferric sulfate, found in the products obtained in the present investigation when the corroding agent was an aqueous solution of sulfurous acid containing no appreciable amount of oxygen. These findings emphasize the fact that the nature of an iron corrosion product depends to a considerable extent on the nature of the environment to which the metal is exposed.

ACKNOWLEDGEMENT

The authors express their appreciation to Messrs. S. Kaiman and M. R. Hughson for identifying a number of the corrosion products by X-ray diffraction analysis.

REFERENCES

1. J. C. Hudson and J. F. Stanners. The Effect of Climate and Atmospheric Pollution on Corrosion. Journal of Applied Chemistry. Vol. 3, 86-96 (1953) February 3.
2. W. H. J. Vernon. A Laboratory Study of the Atmospheric Corrosion of Metals. Transactions of the Faraday Society. Vol. 31, 1668-1700 (1935) October 15.
3. K. Barton and E. Beranek. Werkstoffe and Korrosion. Vol. 10, 377-383 (1959).
4. A. G. Tanner. Iron (II) Sulfate in Rust. Chemistry and Industry. 1027-1028 (1964).
5. R. Rolls. The Scaling of Plain Carbon Steels in Atmospheres Containing Sulfur Compounds. Metal Treatment and Drop Forging. Vol. 30, 427-436 (1963) November.
6. W. McLeod and R. R. Rogers. To be published.
7. J. W. Mellor. Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Green. Vol. XIII: Fe (Part 2), 881 (1934).