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AND ITS CONSEQUENCES IN MIXED  
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CIRCUITS**

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# ON THE OXIDIZING EFFECT OF SULFITE AND ITS CONSEQUENCES IN MIXED STEEL AND COPPER HEAT EXCHANGE CIRCUITS.

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## ABSTRACT

Sulfite is regularly used as an oxygen scavenger in closed heating or cooling circuits. However, sulfite can also act as an oxidizer with respect to a number of reactions that have a rather low equilibrium potential.

The thermodynamics and the reversibility and kinetics of the various oxidation and reduction reactions involving sulfur compounds in aqueous solution are reviewed.

The conditions for the oxidizing effect of sulfite are described as well as some of the consequences observed in practice. One consequence is the sulfidation of copper.

There is thus a case where, in mixed closed circuits with de-aerated water and containing copper and steel, copper corrodes while steel remains non-corroded.

Key-words: water treatment, sulfite, oxygen scavenger, carbon steel, copper.

## 1. INTRODUCTION

Corrosion occurred in a number of mixed steel-copper closed circuits treated with sodium sulfite, orthophosphate and sodium hydroxide. The striking point is that copper was corroded and steel was not corroded. Corrosion of copper was uniform, with an abundant formation of copper sulfide.

The aim of this work is to understand and describe the conditions under which such corrosion may occur, and to derive recommendations to prevent this type of corrosion.

## 2. REDUCTION OF OXYGEN BY SULFITE

Sodium sulfite is probably the most widely used oxygen scavenger. At ambient temperature, its reaction with oxygen is slow. Hence, sodium sulfite is often catalyzed (by cobalt aqueous salts such as 0.1%  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ ). Manganese salts, copper<sup>I</sup> ions, hydrogen peroxide and light also catalyze the reduction of oxygen by sulfite.

The reaction between oxygen and sulfite which is generally cited in the literature is:



The end product is sulfate ions. The mechanism of this reaction deserves closer examination.

Indeed, the equilibrium potential of this reaction is

$$E_0 = -0.891 - 0.059 \text{ pH} + 0.030 \log \frac{[\text{SO}_4^{2-}]}{[\text{SO}_3^{2-}]}$$

For example, at  $\text{pH} = 10$  and for equal concentrations of sulfite and sulfate,  $E_0 = -1.48 \text{ V}_{\text{she}}$ .

But, when these values are plotted in E-pH equilibrium diagrams for the S-H<sub>2</sub>O system [1], it is seen that neither sulfite nor sulfate are stable for these pH and potential conditions: [figure 1](#) is drawn for the most stable forms (sulfate and sulfur) [1], and [figure 2](#) is drawn by considering the

various metastable forms including sulfite, and the stable form sulfur [2]. Most of the diagrams referred to in this paper were originally established by Valensi, who studied in depth the equilibria of the various stable and metastable forms of the sulfur system [3]. Updated diagrams for the S-H<sub>2</sub>O system were published more recently for temperature from 25 to 150°C [2]. In these diagrams, the point for pH 10 and E = -1.48 V<sub>she</sub> lies well outside of the stability domain of sulfite or sulfate.

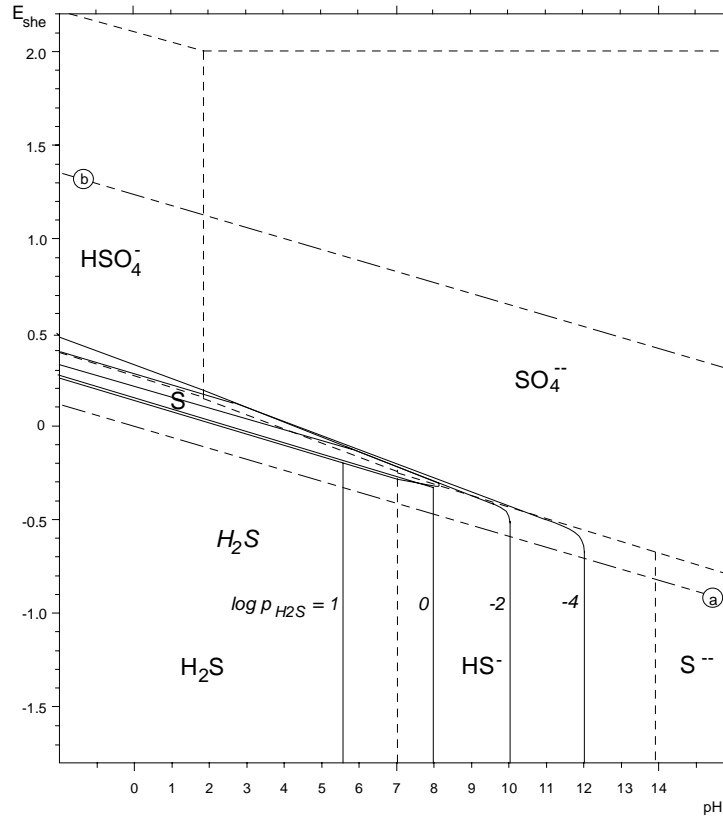


Fig. 1: Potential-pH equilibrium diagram for the system S-H<sub>2</sub>O at 25°C, considering the stable forms sulfide and sulfate [1]

Therefore, the direct oxidation of sulfite to sulfate, with reduction of oxygen, is very unlikely. It is reasonable to consider that this reaction occurs sooner through intermediate steps.

One intermediate step may be the formation of dithionate [4], according to:



The equilibrium potential of this reaction is shown in [figure 3](#) [3], where sulfite, dithionate (S<sub>2</sub>O<sub>6</sub><sup>--</sup>) and hydrosulfite (S<sub>2</sub>O<sub>4</sub><sup>--</sup>) are considered. Indeed, this reaction can occur in a potential range between about 0 and +100 mV<sub>she</sub> in alkaline solutions, i.e. in conditions where oxygen is indeed reduced.

It must be noted that, in reaction (1), sulfite is transformed into sulfate which is completely inactive in terms of oxidation or reduction reactions.

On the contrary, in reaction (2), oxygen is reduced and sulfite is oxidized into dithionate, which itself can be reduced and, thus, can act as an oxidant.

Once formed, and when oxygen is consumed, dithionate can be reduced back to sulfite or can undergo a disproportionation into sulfate and sulfite ions [5-7]. The reduction of dithionate to sulfite can occur on corroding metals. The exact conditions for either the reduction or the disproportionation of dithionate are not known. In the end, sulfate is one of the final products.

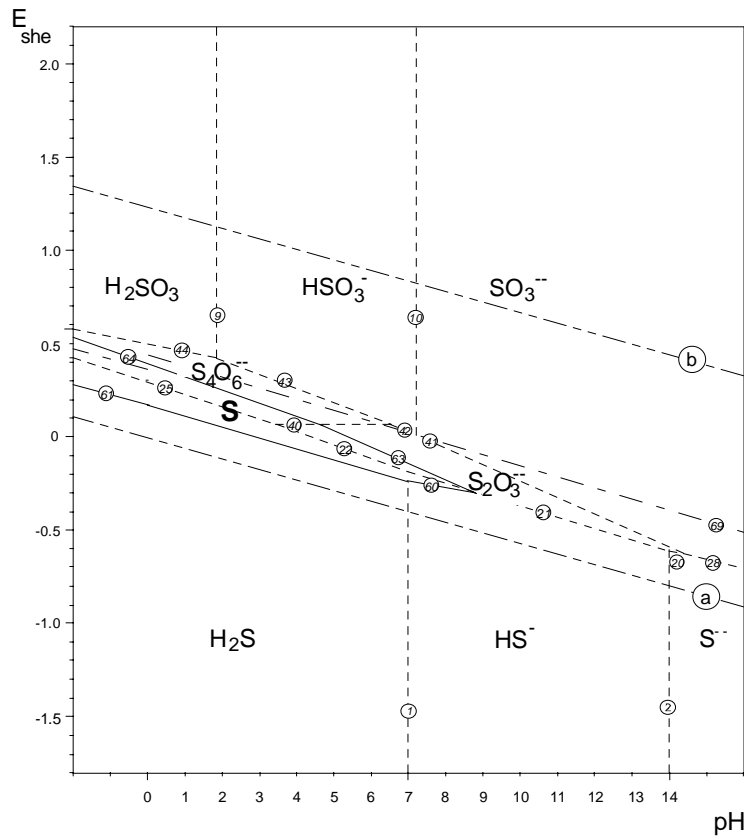


Fig. 2 : Potential-pH equilibrium diagram for the system S-H<sub>2</sub>O at 25°C, considering sulfur, sulfide, thiosulfate and sulfite, for a total dissolved sulfur concentration of 1 g.ion/l [2,3]

Thus, it is likely that the reduction of oxygen by sulfite takes place through the intermediate formation of dithionate, which has some oxidizing effect.

The formation of dithionate is favored in the presence of copper [8]. This information must be related to the corrosion problems that were observed in mixed copper and steel circuits.

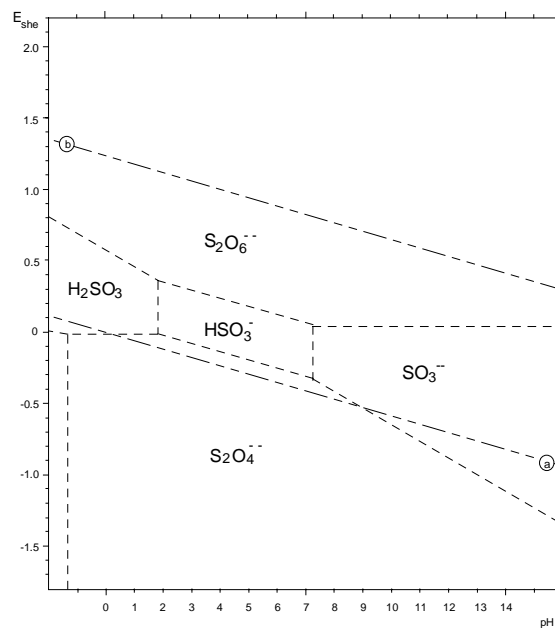


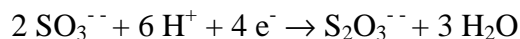
Fig. 3: Potential-pH equilibrium diagram for the system S-H<sub>2</sub>O at 25°C, considering hydrosulfite, sulfite and dithionate, for a total dissolved sulfur concentration of 1 g.ion/l [3]

### 3. SULFITE AS AN OXIDIZER

Sulfite ions  $\text{SO}_3^{2-}$  may in theory be reduced to thiosulfate  $\text{S}_2\text{O}_3^{2-}$  or sulfide  $\text{HS}^-$  in alkaline solutions (pH 9.5 to 10). The potential and pH conditions for this reduction are illustrated in [figure 2](#), between lines 41 or 21, respectively.

Thiosulfate formation has effectively been observed in deaerated industrial circuits containing sulfite. Sulfite was apparently reduced on corroding steel.

The reaction is

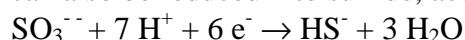


and the equilibrium potential is

$$E_0 = 0.61 - 0.0961 \text{ pH} + 0.016 \log [\text{SO}_3^{2-}]^2 / [\text{S}_2\text{O}_3^{2-}]$$

At pH 10, at 25°C and for concentrations that are reasonable in practice (20 ppm or  $2.5 \cdot 10^{-4}$  M  $\text{SO}_3^{2-}$  and  $2.5 \cdot 10^{-5}$  M  $\text{S}_2\text{O}_3^{2-}$ ),  $E_0 = -0.393 \text{ V}_{\text{she}}$ .

Sulfite can also be reduced into sulfide, according to



for which the equilibrium potential is

$$E_0 = 0.36 - 0.069 \text{ pH} + 0.0107 \log [\text{SO}_3^{2-}] / [\text{HS}^-]$$

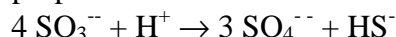
At pH 10, at 25°C and again for concentrations that may be observed in practice (20 ppm or  $2.5 \cdot 10^{-4}$  M  $\text{SO}_3^{2-}$  and  $2.5 \cdot 10^{-5}$  M  $\text{HS}^-$ ),  $E_0 = -0.319 \text{ V}_{\text{she}}$ .

Below these potentials, sulfite can act as an oxidizer. The consequences for steel and copper are discussed in section 6.

### 4. SULFITE DISPROPORTIONATION

Aqueous sulfite solutions are not stable. Disproportionation is observed at ambient temperature with an increase of the pH [9].

The disproportionation reaction for sulfite to sulfate and sulfide is



But this is not the only possible disproportionation reaction: it has been reported that a carefully deaerated alkaline sulfite solution (0.09 M) lost as much as 70% of its initial concentration in one-week time. The formation of thiosulfate was observed [10]. When traces of oxygen are present (when the flasks are not previously purged), disproportionation occurs at approximately the same rate, but dithionate is formed together with thiosulfate.

In industrial and natural waters and in the presence of bacteria, the disproportionation of both sulfite and thiosulfate is possible. The end products are always sulfate and sulfide [10-12].

### 5. SULFITE COMPLEXES WITH COPPER

Several complexes with sulfite and copper<sup>I</sup> exist. One is  $\text{CuSO}_3^-$ . Its free enthalpy of formation  $\mu^\circ$  or  $\Delta G^\circ_f$  is given in [13] as  $-115000 \text{ cal/mole}$ .

A partial E-pH equilibrium diagram for the system Cu-S-H<sub>2</sub>O was calculated at 25°C, considering copper-sulfite and copper-sulfide compounds ([figure 4](#)). The concentration of total dissolved sulfur was chosen as 20 ppm, i.e.  $2.5 \cdot 10^{-4}$  M (which is reasonable in water treatment practice) and for a total dissolved copper concentration (namely  $\text{CuSO}_3^-$ ) of  $10^{-6}$  g.ion/l. The diagram is complete for pH between 7.0 and 13.0. It still must be finalized for lower and higher pH.

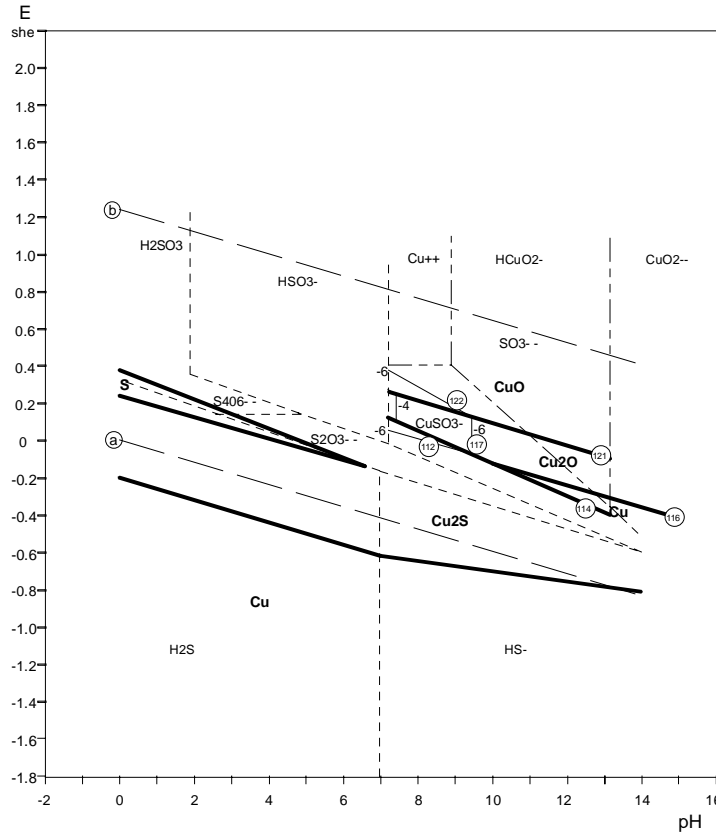
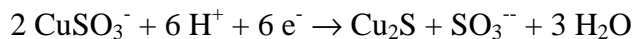


Fig. 4: Potential-pH equilibrium diagram for the system Cu-S-H<sub>2</sub>O at 25°C, considering copper oxides, copper sulfides and the copper<sup>I</sup>-sulfite complex CuSO<sub>3</sub><sup>-</sup>, for a total dissolved sulfur concentration of 2.5 10<sup>-4</sup> M

The interesting point is that the complex CuSO<sub>3</sub><sup>-</sup> appears as a rather oxidizing species. One of the reduction reactions for CuSO<sub>3</sub><sup>-</sup> is



of which the equilibrium potential at 25°C is

$$E_0 = 0.556 - 0.059 \text{ pH} - 0.009 \log [\text{SO}_3^{2-}] + 0.0197 \log [\text{CuSO}_3^-]$$

At pH 10, and for the concentrations indicated above, CuSO<sub>3</sub><sup>-</sup> is reduced into Cu<sub>2</sub>S below

$$E_0 = -0.120 \text{ V}_{\text{she}}$$

This potential is much higher than the equilibrium potentials for the previous reduction reactions of sulfite into thiosulfate or into sulfide. This indicates that the oxidizing effect of sulfite is especially marked in the presence of copper.

Other complexes between sulfite and copper<sup>I</sup> and copper<sup>II</sup> were studied, with respect to the electro-oxidation of sulfite ions in alkaline solutions [8] :

- [Cu<sup>I</sup>SO<sub>3</sub>]<sup>-</sup>, [Cu<sup>I</sup>(SO<sub>3</sub>)<sub>2</sub>]<sup>3-</sup> et [Cu<sup>I</sup>(SO<sub>3</sub>)<sub>3</sub>]<sup>3-</sup>
- Cu<sup>I</sup>(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub><sup>5-</sup>
- Cu<sup>II</sup>SO<sub>3</sub>, [Cu<sup>II</sup>(SO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> et [Cu<sup>II</sup>(SO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup>

It is reasonable to assume that the copper<sup>II</sup> complexes with sulfite are even more oxidant than the copper<sup>I</sup> complexes, but we have no data at this time.

## 6. CONSEQUENCES FOR CORROSION

### Cases observed

Corrosion occurred in a number of mixed steel-copper closed circuits treated with sodium sulfite, orthophosphate and sodium hydroxide. Typical treatments were between 5 and 50 ppm residual  $\text{SO}_3^{2-}$ , 5 to 10 ppm phosphate as  $\text{PO}_4^{3-}$  and pH between 9.5 and 10.5 by NaOH addition. In two cases, the copper tubes from heating-or-cooling batteries were corroded uniformly to the point that leaks occurred, preferentially at bends. The water side of the tubes (interior) was covered with a rather solid but non adherent thick layer of copper sulfide  $\text{Cu}_2\text{S}$ , identified by X-ray diffraction. The rate of corrosion of copper was estimated at 0.15 mm/y.

In another case, copper tubes for thermocouple casing were corroded ([figure 5](#)) with a thick deposit of  $\text{Cu}_2\text{S}$ . Temperature was 105°C and the treatment was  $\text{SO}_3^{2-}$  50 ppm,  $\text{PO}_4^{3-}$  15 ppm and pH 10.3. In these circuits, steel was covered by magnetite and was not corroded.



Fig. 5: Corroded casing for a thermocouple in a circuit treated with phosphate and sulfite, with deposits of  $\text{Cu}_2\text{S}$ .

### Suspected mechanisms

By one of the mechanisms exposed above (reduction of sulfite to thiosulfate or to sulfide, or reduction of  $\text{CuSO}_3^-$ ), sulfite appears to act as an oxidant. It is a weaker oxidant compared to dissolved oxygen, but it is oxidant enough to lead to non-negligible corrosion rates.

The E-pH equilibrium diagram in [figure 6](#) was established for the system Cu-S- $\text{H}_2\text{O}$  at 25°C in 1974, for a total sulfur concentration of 0.1 iong/l [14] and considering sulfate and sulfide, but not thiosulfate or sulfite. It is seen that  $\text{Cu}_2\text{S}$  is stable at potentials below about  $-380 \text{ mV}_{\text{she}}$ , at pH 10. [Figure 4](#) shows a diagram where sulfite, thiosulfate and sulfide are considered. The total dissolved sulfur concentration is  $2.5 \cdot 10^{-4} \text{ M}$  (or 20 ppm  $\text{SO}_3^{2-}$ ).  $\text{CuSO}_3^-$  is an oxidant much stronger than  $\text{SO}_3^{2-}$ . It can be reduced to  $\text{Cu}_2\text{S}$  at potential below  $-120 \text{ mV}_{\text{she}}$  at pH 10 and 25°C. Metallic copper is another possible product of the reduction of  $\text{CuSO}_3^-$ , at slightly higher pH.

When sulfite is present and in the absence of copper ions, iron can corrode with formation of a black film of ferrous sulfide. Significant corrosion rates are indicated in corrosion tables for carbon steel in sulfite solutions [15].

In the presence of copper, iron sulfide was never observed on the steel surface, but only magnetite was found. [Figure 7](#) shows an E-pH equilibrium diagram for the system Fe-S- $\text{H}_2\text{O}$  at 25°C, considering amorphous FeS, mackinawite  $\text{FeS}_{0.943}$ , troilite FeS, pyrrhotite  $\text{FeS}_{1.140}$  and pyrite  $\text{FeS}_2$ , for  $\text{H}_2\text{S}$  partial pressure of 0.01 bar and a total sulfur concentration of  $10^{-3} \text{ M}$  [16].

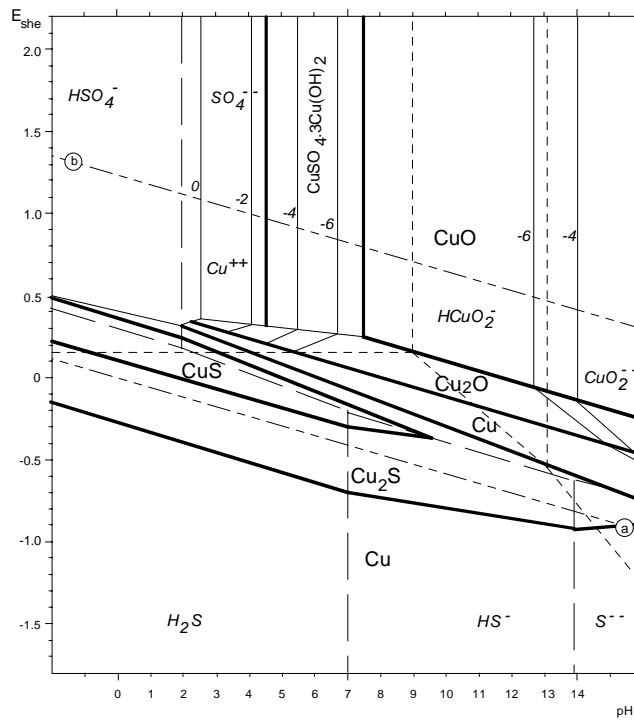


Fig. 6: Potential-pH equilibrium diagram for the system Cu-S-H<sub>2</sub>O at 25°C, considering sulfate and sulfide, but not thiosulfate or sulfite, for a total sulfur concentration of 0.1 iong/l [14]

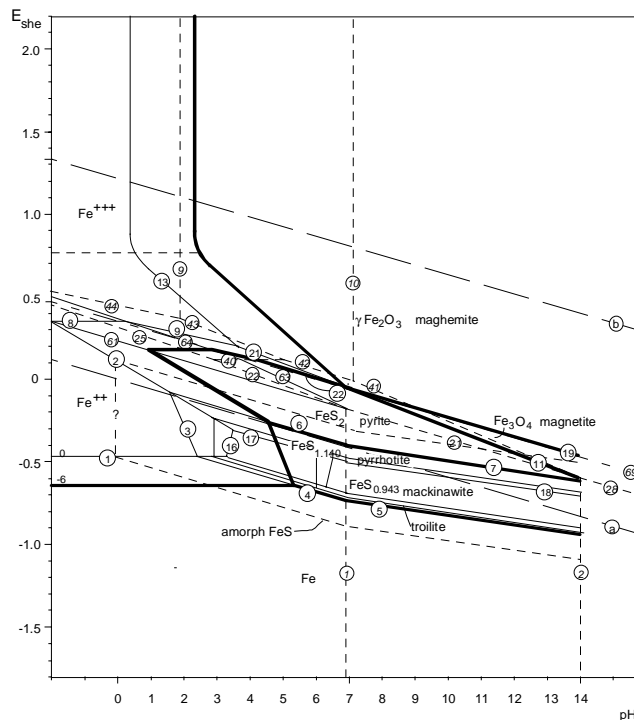


Fig. 7: Potential-pH equilibrium diagram for the system Fe-S-H<sub>2</sub>O at 25°C, considering amorphous FeS, mackinawite FeS<sub>0.943</sub>, troilite FeS, pyrrhotite FeS<sub>1.140</sub> and pyrite FeS<sub>2</sub>, for a total sulfur concentration of 10<sup>-3</sup> M [16]

The potentials mentioned earlier for the reduction of sulfite to thiosulfate or sulfide are -0.392 and -0.319 V<sub>she</sub> respectively, at pH 10 and 25°C. This corresponds to a region where pyrite FeS<sub>2</sub> is stable. But it was also mentioned earlier that the complex CuSO<sub>3</sub><sup>-</sup> formed in the presence of copper

and sulfite is a stronger oxidant. In this case, the reduction potential of  $\text{CuSO}_3^-$  lies in a region where maghemite (or possibly magnetite) is stable.

### Experimental verification

Limited laboratory investigations support the formation of an oxidizing copper-sulfite complex. Figure 8 shows the recording of potential versus time in a deaerated sodium orthophosphate solution at pH 12, with 100 ppm sulfite  $\text{Na}_2\text{SO}_3$ . When sulfite is added, the potential of iron drops to low values. When metallic copper is added, the potentials of copper and of iron increase steadily to surprisingly high values. These values are even higher than what would be expected to be due to the reduction of  $\text{CuSO}_3^-$ . Maybe copper<sup>II</sup>-sulfite complexes are involved. More work is needed to explain these very high potentials in the presence of copper and of sulfite.

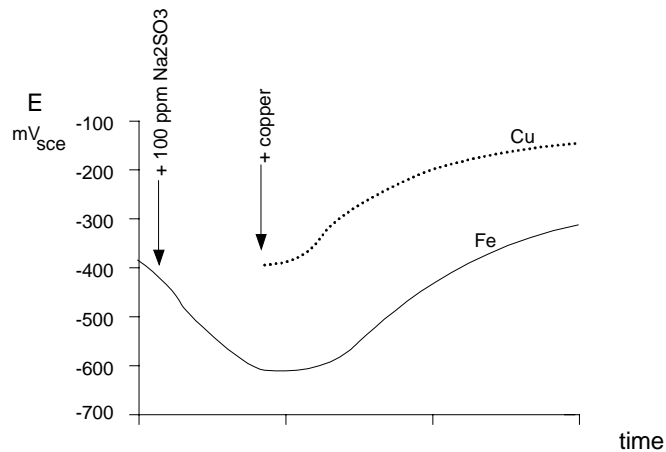


Fig. 8: Electrode potential versus time for iron and copper in deaerated  $\text{Na}_3\text{PO}_4$  at pH 12 with addition of 100 ppm sulfite  $\text{Na}_2\text{SO}_3$  and of copper

### Influence of bacteria

Cwalina et al measured the corrosion rates of steel in sulfate, thiosulfate and sulfite solutions in the presence and in the absence of sulfate reducing bacteria. Without bacteria, the highest corrosion rates are measured in sulfite, compared to sulfate and thiosulfate. This indicates that bacteria are not necessarily involved in the mechanism of corrosion by sulfite. Bacteria can affect these systems: when bacteria are present, the highest corrosion rates are measured in thiosulfate solutions, and the lowest in sulfate solutions, and the corrosion rate of copper is much increased, compared to sterile conditions [17].

## 8. CONCLUSIONS

Serious corrosion problems of copper were observed in mixed copper and steel closed water circuits treated with sulfite, at pH around 10. It is shown that sulfite may act as an oxidizer, either because of the intermediate formation of dithionate in the oxygen reduction process, either because of a direct reduction of sulfite to thiosulfate or sulfide.

The oxidizing effect of sulfite is further enhanced in the presence of copper, apparently due to the formation of a cuprous-sulfite complex  $\text{CuSO}_3^-$  that can be reduced to  $\text{Cu}_2\text{S}$  in alkaline solutions. Indeed,  $\text{Cu}_2\text{S}$  is observed in large amount on copper, in the corrosion cases which are reported. It is suspected that cupric-sulfite complexes can also form, under certain conditions and that these may be even more detrimental.

Because of the possible oxidizing effect of sulfite, a permanent residual concentration of sulfite seems to be detrimental for iron or carbon steel and should be avoided. It is also dangerous for copper.

The corrosion cases observed in practice and the mechanisms that were identified from the literature, from the equilibrium conditions and from some experimental verifications suggest that water treatments based on sulfite should be considered with reserves and great care. In our opinion, excesses of sulfite should be banned, especially in circuits containing copper. We much prefer to avoid completely the use of sulfite and to manage the corrosion protection of closed circuits by combating all ingress of oxygen by physical methods, process control and maintenance and by using a water chemistry that is able to protect steel and copper even in the presence of small amounts of oxygen.

Such alternate water chemistries, based primarily on orthophosphates have been used with success and are still under development for optimization.

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