

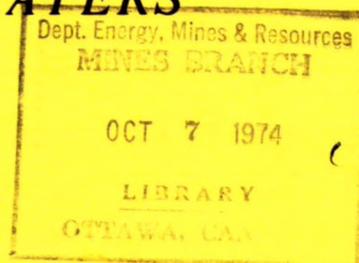
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DEPARTMENT OF  
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OTTAWA

*INHIBITORS FOR THE PREVENTION OF MILD  
STEEL CORROSION IN SYNTHETIC  
ACID MINE WATERS*

by



D.V. Subrahmanyam and G.R. Hoey

EXTRACTION METALLURGY DIVISION

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INHIBITORS FOR THE PREVENTION OF MILD STEEL CORROSION IN  
SYNTHETIC ACID MINE WATERS

by

D.V. Subrahmanyam\* and G.R. Hoey\*\*

ABSTRACT

The efficiency of organic inhibitors as evaluated from 24-hr weight loss of mild steel panels in pH 2.5 solutions containing ferric, cupric and sulphate ions has the following sequence: n-butylamine, urea, guanyl urea sulphate < benzotriazole, hexadecyl pyridinium chloride < thiourea < potassium oxalate. The inhibitor efficiency in the presence of potassium oxalate was 93 per cent. With the other inhibitors, the efficiencies were in the range from below zero to 77 per cent.

Solution analyses after 24-hr corrosion tests showed that ferric and cupric ions were not reduced in oxalate solutions, whereas these ions were partially or totally reduced in solutions containing other inhibitors. Corrosion potentials were shifted to less negative values in oxalate solutions corresponding to the formation of a layer responsible for inhibition. X-ray analysis of the corrosion product layer detected the presence of  $\beta\text{-FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

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Direction des mines  
Rapport de recherche R-274

LES INHABITEURS POUR EMPÊCHER LA CORROSION  
D'ACIER DOUX DANS DES EAUX  
MINIÈRES, ACIDES ET SYNTHÉTIQUES

par

D.V. Sybrahmanyam\* et G.R. Hoey\*\*

RÉSUMÉ

Les auteurs ont trouvé que l'efficacité des inhibiteurs organiques évaluée après une perte de poids de 24 heures des panneaux d'acier doux dans des solutions pH 2.5 contenant des ions ferriques, cupriques et de sulfate avaient la séquence suivante: la n-butylamine, l'urée, le sulfate de guanyle urée <le benzotriazole, le chlorure d'hexadecyle pyridinium, >la thiourée <l'oxalate de potassium. L'efficacité de l'inhibiteur en présence de l'oxalate de potassium était de 93%. Avec les autres inhibiteurs, les efficacités se situaient de sous zéro à 77%.

Les analyses de solutions après des essais de corrosion de 24 heures ont montré que les ions ferriques et cupriques n'ont pas été réduits dans des solutions d'oxalate, alors que ces ions ont été réduits en partie ou totalement dans des solutions contenant d'autres inhibiteurs. Les potentiels de corrosion ont été changés à des valeurs moins négatives dans des solutions d'oxalate qui correspondaient à la formation d'une couche responsable pour l'inhibition. Les auteurs au moyen de l'analyse par rayon X de la couche de produit de corrosion ont pu détecter la présence de  $\beta\text{-FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

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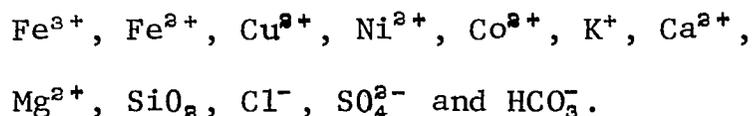
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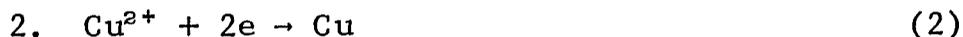
## INTRODUCTION

Mild steel is an important structural material in mining equipment, and can undergo rapid and catastrophic corrosion failures while it is in contact with polluted mine waters. During a corrosion survey of sulphide ore mines, Hoey and Dingley<sup>(1)</sup> sampled mine waters at different locations and had the samples analyzed for various species. The pH of these waters was between 2.5 and 8.0 and they contained the following species:



To find a method to prevent the corrosion of mild steel it was necessary to synthesize the mine waters in the laboratory and to identify the aggressive species. In a previous study<sup>(2)</sup>, the corrosion rates of mild steel immersed in synthetic acid mine waters (pH 2.5) containing  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{SO}_3^{2-}$  ions in various combinations were measured by weight loss and Tafel extrapolation methods. Synthetic waters containing  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  were found to be the most aggressive due to the rapid reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  to  $\text{Cu}$  at the mild steel surface. These were the two key reduction reactions in addition to the  $\text{O}_2$  and  $\text{H}^+$  reduction steps. The partial reduction and oxidation processes contributing to the overall corrosion of mild steel in this medium are given below:



I. Reduction Reactions:II. Oxidation Reaction:

Since the effects of the other ions were negligible, corrosion inhibitors were evaluated in pH 2.5 solutions containing ferric, cupric and sulphate ions. The following organic inhibitors containing nitrogen were chosen from the existing literature:

- 1) n-Butylamine, 2) Urea, 3) Thiourea, 4) Guanyl urea sulphate
- 5) Hexadecyl pyridinium chloride and 6) Benzotriazole.

In addition to these inhibitors, potassium oxalate, which is known to form an oxalate conversion coating on iron surfaces, was tried. It is hoped that this conversion coating might have a protective value

## EXPERIMENTAL

1. Surface Preparation: Mild steel panels (AISI Type 1010) used in the present study had the following composition: C 0.07, Mn 0.33, Cu 0.13, Ni 0.036, S 0.011, P 0.011 and Si 0.01 %. The surface of the panels was prepared by degreasing in boiling acetone, ultrasonically cleaning and vapour degreasing in

trichloroethylene, and pickling in 10 % (by volume) hydrochloric acid for one minute.

2. Corrosion Rates and Potentials: The usual experimental arrangement for corrosion rate and corrosion potential measurements is shown in Fig. 1. The corrosion rates with and without inhibitors were calculated from the weight loss of panels (2 cm x 2 cm x 0.1 cm) exposed for 24 hr. The solution prepared from deionized water had the following composition:

Soln. pH - 2.5; Initial  $\text{Fe}^{3+}$  -  $1.25 \times 10^{-2}$  M and  
initial  $\text{Cu}^{2+}$  -  $1.0 \times 10^{-3}$  M.

The solution pH was adjusted after adding the constituents (also true in the case of solutions containing inhibitors). The solutions (2.2 l) were stirred in all cases.

After the 24 hr experiment, the solutions were analyzed for iron and copper. Iron was determined colorimetrically by using the 0 - phenanthroline method and copper was determined by atomic absorption spectroscopy.

The corrosion potentials were measured with a Wenking voltmeter (PPT 70) using a saturated calomel electrode and agar-agar saturated KCl bridge arrangement. A Hewlett-Packard (7100B) recorder was used to record the potentials with time. All the potentials in this report are referred to the calomel scale.

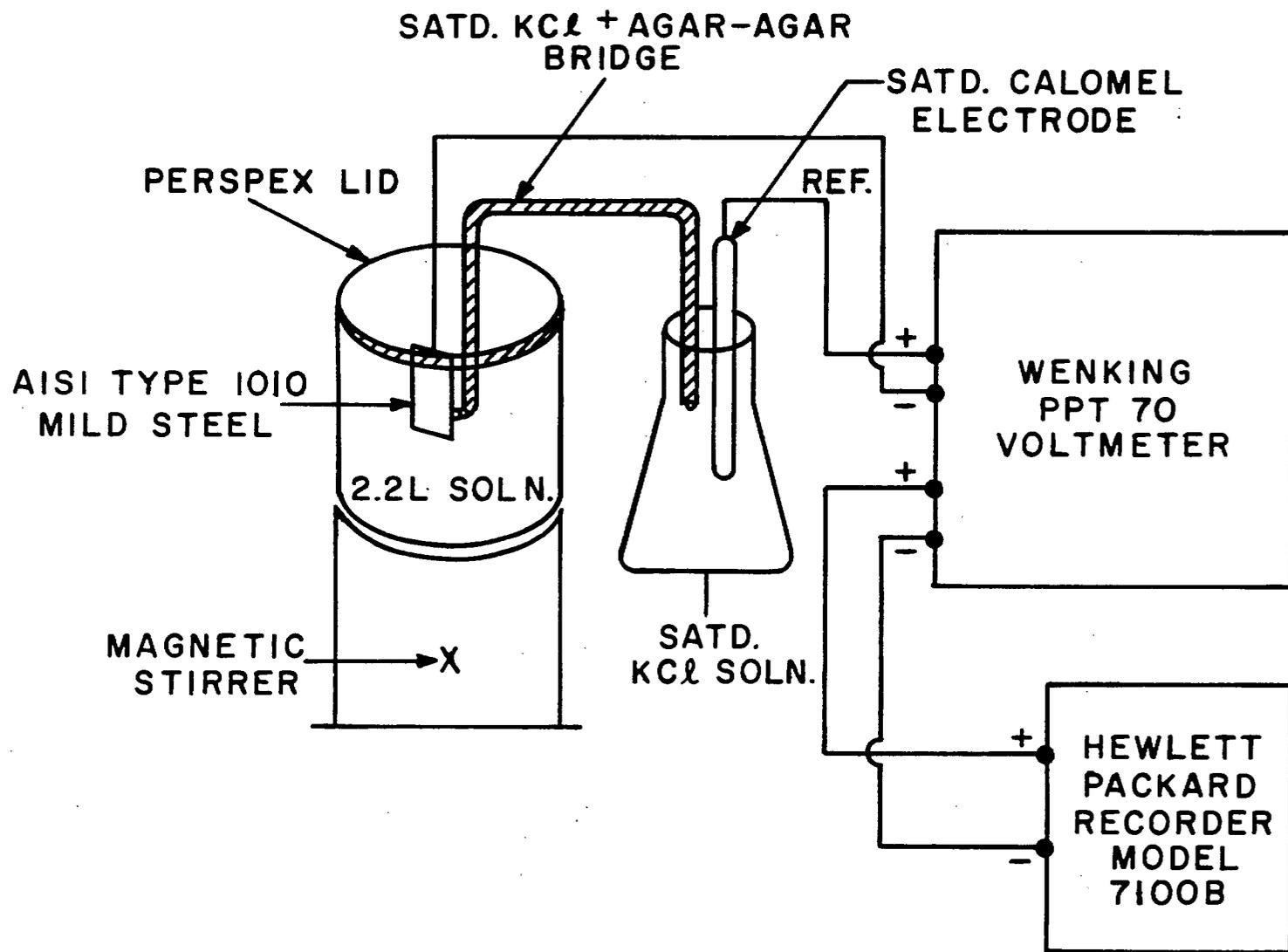


FIG.1. EXPERIMENTAL ARRANGEMENT FOR WEIGHT LOSS AND CORROSION POTENTIAL MEASUREMENTS.

## EXPERIMENTAL RESULTS

1. Corrosion Rates: The influence of inhibitors on corrosion rates is shown in Table 1. It was intended to choose the inhibitor concentrations arbitrarily at 7.5 g/l (approx). However the concentrations (in g/l) of n-butylamine and benzotriazole used were much lower than the above value because of solubility limitations. Benzotriazole<sup>(3)</sup>, n-butylamine<sup>(4)</sup>, thiourea<sup>(5-7)</sup>, urea<sup>(8)</sup> and hexadecyl pyridinium chloride<sup>(9)</sup> were reported to be quite effective at the  $10^{-2}$  M concentration range or below. The inhibitive characteristics of guanyl urea sulphate and potassium oxalate were not previously reported.

The effectiveness of the inhibitors has the following sequence: n-butylamine, urea and guanyl urea sulphate < benzotriazole and hexadecyl pyridinium chloride + sodium chloride < thiourea < potassium oxalate.

The inhibitor efficiencies were calculated from the following expression:

$$\text{Inhibitor Efficiency} = \left[ \frac{\Delta W \text{ uninhibited} - \Delta W \text{ inhibited}}{\Delta W \text{ uninhibited}} \right] \times 100 \quad (6)$$

where  $\Delta W$  = weight loss in 24 hours.

Performance of the inhibitors except potassium oxalate was poor and the inhibitor efficiencies were less than zero with n-butylamine urea and guanyl urea sulphate. Potassium oxalate, on the other hand, had an inhibitor efficiency of 93 per cent.

TABLE 1  
Effect of inhibitors on the corrosion rates  
of type 1010 mild steel

Solution: pH 2.5 H<sub>2</sub>SO<sub>4</sub>  
 Fe<sup>3+</sup> - 1.25 x 10<sup>-2</sup> M  
 Cu<sup>2+</sup> - 1.00 x 10<sup>-3</sup> M

Room Temperature, Stirred Solutions.

Corrosion Rate Without Inhibitor = 1437 mpy

Inhibitor	Concentration M	Corrosion Rate mpy*	Inhibitor Efficiency %
1. n-butylamine	1.0 x 10 <sup>-2</sup>	2175	< 0
2. n-butylamine + HCl	1.0 x 10 <sup>-2</sup> each	3375	< 0
3. Urea	1.25 x 10 <sup>-1</sup>	2575	< 0
4. Guanyl Urea Sulphate	2.24 x 10 <sup>-2</sup>	1682	< 0
5. Benzotriazole	1.0 x 10 <sup>-2</sup>	860	40
6. Hexadecyl Pyri- dinium Chloride + NaCl	1.0 x 10 <sup>-2</sup> each	914	36
7. Thiourea	1.0 x 10 <sup>-1</sup>	326	77
8. Potassium Oxalate	4.8 x 10 <sup>-2</sup>	106	93

\*mils penetration per year

2. Solution and Corrosion Product Analyses: The analyses of inhibitor-containing solutions in which mild steel panels were immersed for 24-hr periods are shown in Table 2.

TABLE 2

Changes in Fe<sup>3+</sup> and Cu<sup>2+</sup> ion concentrations  
in solutions\*

Solution: pH 2.5 H<sub>2</sub>SO<sub>4</sub>  
Fe<sup>3+</sup> - 1.25 x 10<sup>-3</sup> M  
Cu<sup>2+</sup> - 1.00 x 10<sup>-3</sup> M

Room Temperature, Stirred Solutions.

Inhibitor	Concentration M	Concentration after 24 hr, M	
		[Fe <sup>3+</sup> ]	[Cu <sup>2+</sup> ]
1. Nil	-	7.20 x 10 <sup>-5</sup>	6.30 x 10 <sup>-5</sup>
2. Hexadecyl Pyridinium Chloride + NaCl	1.0 x 10 <sup>-2</sup> each	3.94 x 10 <sup>-3</sup>	5.35 x 10 <sup>-4</sup>
3. Benzotriazole	1.0 x 10 <sup>-2</sup>	7.52 x 10 <sup>-3</sup>	9.60 x 10 <sup>-4</sup>
4. Thiourea**	1.0 x 10 <sup>-1</sup>	-	9.45 x 10 <sup>-4</sup>
5. Potassium Oxalate	4.8 x 10 <sup>-2</sup>	1.24 x 10 <sup>-2</sup>	1.01 x 10 <sup>-3</sup>

\*Steel panels were exposed in the solutions for 24 hr.

\*\*The ferric ions were reduced before the mild steel was immersed in solution.

The observations are as follows:

- 1) In the inhibitor-free solutions, the ferric and cupric ions were almost completely reduced.
- 2) In solutions where there was a partial protection of mild steel by hexadecyl pyridinium chloride + sodium chloride, and benzotriazole, the reduction of ferric and cupric ions was incomplete.

- 3) In the presence of thiourea, where there was 77 % inhibition, the ferric ions were selectively and completely reduced. The ferric ion reduction took place even before the mild steel samples were immersed in the solution.
- 4) The addition of potassium oxalate stopped the reduction of ferric and cupric ions completely.

The corrosion products on mild steel were ferrous sulfide (electron microprobe analysis) and  $\beta$ -ferrous oxalate dihydrate (X-ray analysis) in thiourea and potassium oxalate solutions respectively. There was no necessity to analyze the corrosion products obtained with the other inhibitors because of their poor inhibitor efficiencies. In the absence of inhibitors, the corrosion products were hydroxides of iron<sup>(2)</sup> (in solution).

Corrosion Potentials: The initial corrosion potential of mild steel in inhibitor free solutions containing  $1.25 \times 10^{-3}$  M  $\text{Fe}^{3+}$  and  $1.0 \times 10^{-3}$  M  $\text{Cu}^{2+}$  is -532 mV. The potential changed with time as shown in Fig..2. The potential shifted by -48 mV within the first  $10^3$  seconds. In the interval from  $10^3$  to  $10^4$  seconds, the potential shifted again towards less negative value with a peak at -544 mV at  $7 \times 10^3$  sec. (approximately 2 hr). From then on, the potential decreased and reached a value of -600 mV at the end of  $2 \times 10^4$  (approximately 6 hr). The corrosion rate in this solution was 1437 mpy. The curves are similar in shape but the potential is changed to more negative values with n-butylamine,

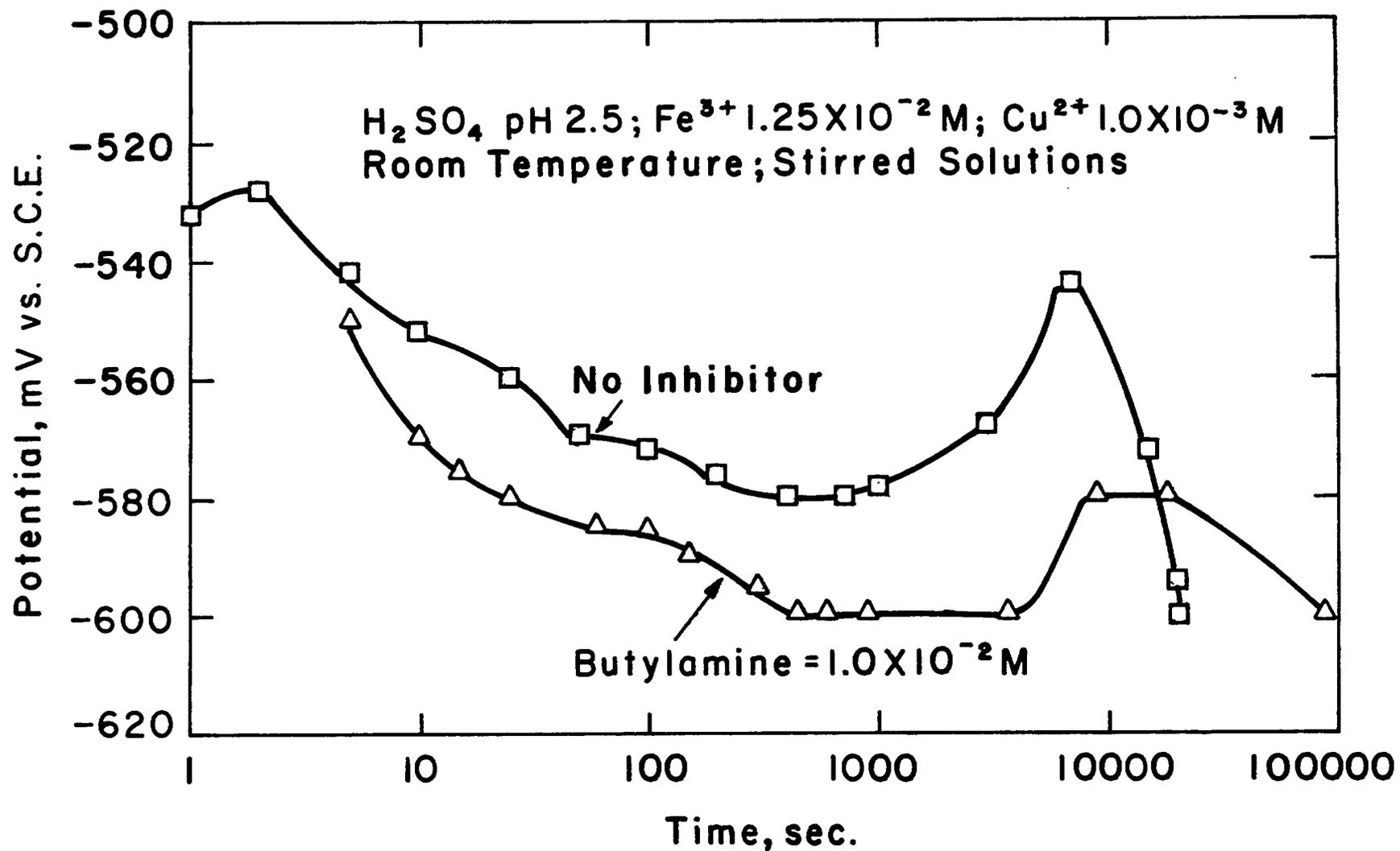


FIG. 2. Influence of Butylamine on Potential-Time Curves.



which implies acceleration in corrosion rate. The hydrochloride of n-butylamine, urea and guanyl urea sulphate produced similar changes in the potential as a function of time. The following features are evident from Fig. 3.

- 1) The initial corrosion potential in presence of thiourea and hexadecyl pyridinium chloride +  $\text{Cl}^-$  ion was the same, i.e., -455 mV. This value is approximately 77 mV positive to the corrosion potential exhibited in uninhibited solutions.
- 2) In the presence of thiourea the potential did not change to less negative values with time after  $10^3$  sec.
- 3) Hexadecyl pyridinium chloride + sodium chloride shifted the corrosion potential from -528 mV at  $10^4$  sec. to -360 mV at  $8.6 \times 10^4$  sec.
- 4) In the presence of benzotriazole, the potential was more or less time independent.
- 5) On the other hand, the oxalate ion shifted the corrosion potential from -515 mV to -110 mV within  $2 \times 10^3$  seconds or 35 minutes. This value did not change unless the film was removed by scratching and etching.

#### DISCUSSION

From the results mentioned above, one can see that the changes in corrosion rates were critically related to the ease of reduction of ferric and cupric ions. Thus, when these ions are

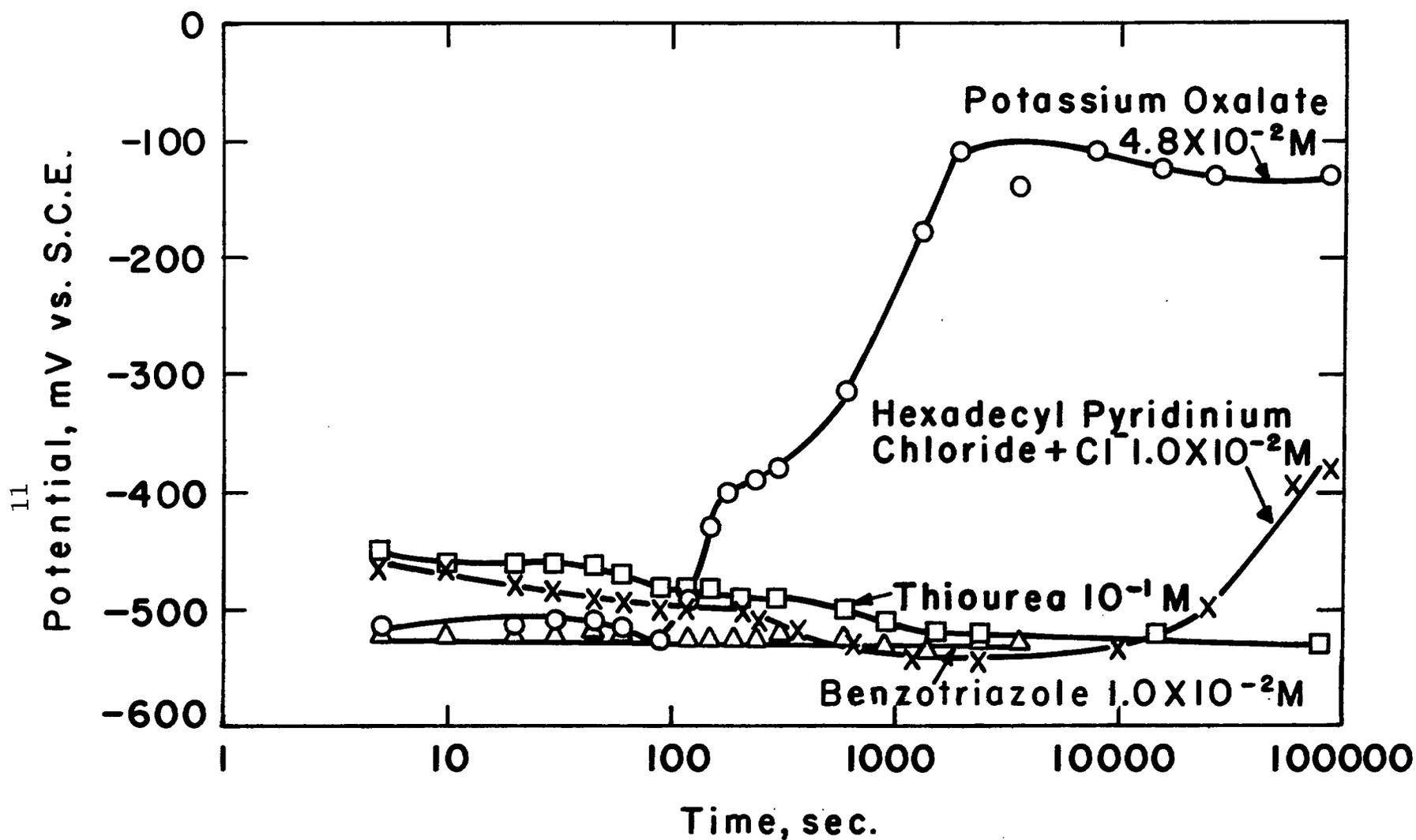
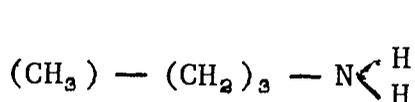


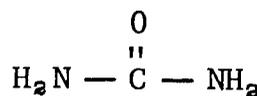
FIG.3. Influence of Benzotriazole, Hexadecyl Pyridinium Chloride, Thiourea and Potassium Oxalate on Potential-Time Curves. Conditions as in FIG.1.

not reduced in solutions containing potassium oxalate, the inhibitor efficiencies were 93 per cent. These features are reflected in the shape of the potential-time curves. A negative shift in the potential means that a reduction reaction is operative, whereas a positive shift means that an oxidation or layer forming reaction is operative. Thus, in solution where there was acceleration by n-butylamine, urea, and guanyl urea sulphate, the shape of the potential-time curve was essentially the same as that without inhibitor, where ferric and cupric ions were completely reduced (negative shift of potential-time curve in figure 2). On the other hand, potentials shifted to less negative values up to -100 mV in oxalate solutions indicating the probable barrier or passive layer formation. In this case the film was identified as  $\beta\text{-FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  by X-ray analysis. Furthermore, the shape of the potential-time curve indicated that ferric and cupric ion reduction is not possible. This trend was confirmed by solution analysis.

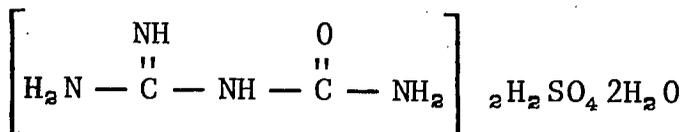
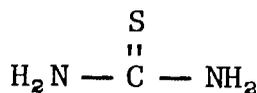
The structures of n-butylamine, urea, guanyl urea sulphate, benzotriazole, hexadecyl pyridinium chloride and thiourea are shown below:



I. n-Butylamine

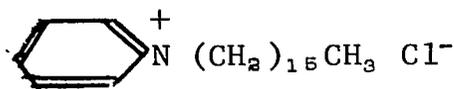
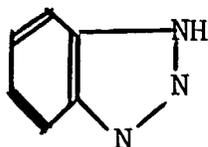


II. Urea



III. Thiourea

IV. Guanyl Urea Sulphate



## V. Benzotriazole

## VI. Hexadecyl pyridinium chloride

These compounds are characterized by their polar functional groups namely  $-NH_2$ ,  $-NH$ ,  $-N$ ,  $C = S$  and  $C = O$ . Numerous studies with organic compounds containing these groups have shown that these compounds are chemisorbed from acid solutions on iron surface. Chemisorption is primary step in inhibition by these compounds. The strength of the adsorption bond is determined by the electron density of the atom, polarizability of the group and surface charge of the metal. In the literature, the effectiveness of atoms in the polar groups with respect to adsorption processes were classified as follows<sup>(10,11)</sup>:

$$S > N > O$$

In the present study also, it is probable that n-butylamine, urea, thiourea, guanyl urea sulphate, benzotriazole and hexadecyl pyridinium chloride are chemisorbed. The observed fact that thiourea gave 77 % protection while urea accelerated the corrosion, (Table 1) fits into the above classification very well. The low efficiency value and the sulphide scale on mild steel which can result in hydrogen embrittlement, limit the use of thiourea as an inhibitor.

The process of chemisorption involves the formation of

a monolayer. This may be true with all the inhibitors used, except potassium oxalate. The monolayers are not dense enough to reduce the corrosion rate by hindering the transport of ferric and cupric ions to the mild steel substrate. The present experience rules out the use of any chemisorbing inhibitor for the prevention of mild steel corrosion in ferric and cupric ion containing solutions.

An alternative approach is to choose an organic compound which is capable of forming multilayers on metal surface as well as complex ions in solution. The oxalate complexes of iron and copper are known<sup>(12)</sup> and in fact,  $\text{Cu}^{2+}$  is reduced to metal from the complex while  $\text{Fe}^{3+}$  is not reduced. This condition seems to be fulfilled by the oxalate ion which forms complex ions with  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  as well as multilayers of  $\beta\text{-FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  on the surface as evidenced by surface analyses, solution analyses and potential-time curves.

#### CONCLUSIONS

1. The inhibitors which are known to form chemisorbed layers, namely urea, guanyl urea sulphate, benzotriazole, butylamine, and hexadecyl pyridinium chlorides are unsatisfactory in the pH 2.5 solution containing  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{SO}_4^{2-}$  ions. The chemisorbed layers are incapable of stopping the  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  reduction reactions at the metal surface.

2. Although thiourea reduced  $\text{Fe}^{3+}$  ions completely before mild steel got into contact, the inhibitor efficiency was only 77 per cent, and it produced a sulfide film responsible for hydrogen embrittlement, thus prohibiting its use.
3. The inhibitor efficiency with potassium oxalate was 93 per cent. Solution analyses showed that ferric and cupric ions were not reduced.
4. The potential-time curves were used to predict whether barrier or passive layers were formed or reduction reactions were operative. Thus, in potassium oxalate solutions the corrosion potentials shifted to less negative values corresponding to the formation of a barrier or passive layer responsible for inhibition. X-ray analysis of the corrosion product layer detected the presence of  $\beta\text{-FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .
5. Inhibitors like potassium oxalate which function by forming multilayers to prevent the reduction of depolarizers (like  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions) are possible choices for the prevention of corrosion of mild steel in acid mine waters.

#### ACKNOWLEDGEMENTS

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