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The Corrosion of Copper Metal in HCl Solutions and the effect of Molybdate and Chromate

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Abstract: Dissolution characteristics of copper in hydrochloric acid medium and the effect of potassium chromate and sodium molybdate on the corrosion process have been studied using potentiodynamic technique, and Electro impedance spectroscopy (EIS). corrosion current density (I_{corr}) were obtained by Tafel extrapolation technique. Charge transfer resistance (R_{ct}) was obtained from the electrochemical impedance spectroscopy (EIS). The corrosion rate was retarded in presence of sodium molybdate mainly because of the adsorption of the inhibitor on the electrode surface and it was found that the optimum concentration of this inhibitor in 1 M HCl was 0.008 M with an protection efficiency 79.17%, while the corrosion rate was accelerated in presence of potassium chromate.

1. Introduction

Copper has wide applications in industry owing to its high electrical and thermal conductivities, mechanical workability, and its relatively noble properties. It is employed extensively for condensers, evaporators and fractionating columns in the chemical industry [1]. Copper is also exclusively used for piping and delivery of water for marine industry. These pipes are frequently employed in a medium where Cl⁻ ions are present [2]. In some particular environmental conditions, attack by pitting sometimes occurs. These problems result from the presence of specific aggressive species such as chloride, sulfate or nitrate. Each of these species alone can produce pitting corrosion in copper but with different levels of aggressiveness. Sulfate ions appear more aggressive than chloride ions and nitrate ions are more aggressive than sulfate ions. [3, 4] Pitting corrosion is recognized as an insidious type of attack that results in many unexpected failures of metallic structures. The pitting corrosion of metals and alloys occurs when passivity breaks down at local points on the surfaces exposed to corrosive environments containing aggressive anions [5-9], at these points, anodic dissolution proceeds while the major part of surface remains passive.

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It is well-known that corrosion products have a negative effect on heat transfer on the copper based heat exchanger, which can be reduced by periodic cleaning in hydrochloric acid pickling solutions. Corrosion inhibitors could effectively eliminates some of the undesirable reaction connected with destructive effects of hydrochloric acid pickling solutions on copper surface and prevents its dissolution.[10-13]

Copper and copper alloys are materials broadly used in drinking distribution systems. In soft waters with slightly acidic pH values, the metal can be actively dissolved releasing important quantities

of Cu^{2+}, which can be harmful for the health of the consumers [14]. Corrosion inhibitors have been used to prevent the dissolution of copper. These inhibitors should be innocuous for human consumption and they should not have a negative impact on the environment.

A compound that is frequently employed for this purpose is sodium orthophosphate [15–20]. The action mechanism of this inhibitor is not clearly understood but it was suggested that it reduces the copper solubility forming a cupric phosphate layer on copper [15,21]. However, there is no exhaustive study that evaluates the composition, thickness and other related characteristics of this layer using in situ techniques. When the electrolyte composition and pH allow the development of a superficial protective layer on the metal, Cu^{2+} release to the medium is minimum. However, this layer can suffer localized rupture or pitting that can lead to pipe perforation [22].

In this work, The effect of different concentrations of HCl (0.5 , 1.0 , 1.5 , 2.0 , 2.5 M), and some inorganic compounds as potassium chromate and sodium molybdate (with 1.0 M HCl as blank) were studied on the corrosion performance of Cu.

2.   Experimental:

The working electrode employed in the present work was made from pure copper rod (99.9 %) axially embedded in an araldite holder to offer a diameter (0.8 cm). Prior to each experiment, the working electrode was polished successively with fine grade emery papers. The polished metal surface was rinsed with ethanol and distilled water before dipping it into the electrolytic cell. A platinum wire was used as the counter electrode. Silver/silver chloride (Ag/AgCl) electrode was used as a reference electrode to which all potentials are referred. For each run, a freshly prepared solution as well as a clean set of electrode was used. Potentiodynamic polarization technique and Electro impedance spectroscopy (EIS) were employed using a potentioscan type apparatus (potetiostat / Gill AC SERIAL No. 948). The experiments of Potentiodynamic polarization technique were carried out by changing the electrode potential automatically from -100 mV to 500 mV at scan rate 10 mV/S till the end of the experiment. The experiments of EIS were carried out using AC signals in the frequency range between 30 KHz and 1 Hz. The All solutions were freshly prepared using distilled water and Analar chemicals which were from Merk.

3.   Results and Discussion

1.Potentiodynamic polarization measurements:

1.1. Effect of different concentrations of HCl:

Fig.(1) illustrates the potentiodynamic E- I curves for Copper in different concentrations 0.5-2.5 M HCl solution at 25° C. These curves were swept from -1 to 0.5 V at scan rate 10 mV/S. The curves imply that on positive going sweep the cathodic current corresponding to Hydrogen evolution reaction decreases gradually and changes its sign at zero potential $E_{i=0}$. The anodic excrusion exhibits active- passive – transition. The active dissolution involves the appearance of two anodic peaks (P_{A1}, P_{A2}) followed by a permanent passive region.

The first anodic peak PA$_1$ located at almost 0.08 V is due to the formation and adsorption of insoluble CuCl$_{ads}$ species on the copper surface, according to the following reactions [23-24]:

$Cu \rightarrow Cu^+ + e^-$ (1)

$Cu^+ + Cl^- \rightarrow CuCl_{ads}$ (2)

The insoluble CuCl$_{ads}$ species will retarded the dissolution process and the current densities will drop down to a minimum current density the density will increase again forming second oxidation peak P$_{A2}$ located at 0.26 V. Formation of P$_{A2}$ due to oxidation of the cuprous chloride complex to cupric chloride according to the following reactions [25].

$CuCl_{ads} + Cl^- \rightarrow CuCl_2^-$ (3)

$CuCl_2^- \rightarrow Cu^{2+} 2Cl^- + e^-$ (4)

Inspection of the curves of figure (1) reveal that the increasing addition of HCl concentration increase the height of the anodic dissolution density of the peak currents I$_{PA1}$ and E$_{corr}$ shifts to more positive values, while the peak current density of I$_{PA2}$ decrease.

A straight line relation was obtained between the logarithm of I$_{PA1}$ and the logarithm of concentration of HCl as shown in Fig. (2).

The equation for the straight line is represented by

Log I$_A$= a +b log C$_{HCl}$ (5)

Where a and b corresponding to its intercept and slope respectively [26].

A plot E$_{corr}$ vs log C$_{HCl}$ is shown in figure (3) where a linear relationship is obtained which follows the equation [27].

$E_{corr} = a - b \log C_{HCl}$ (6)

Where a and b are constants.

Fig. (4) reveals that I$_{pass}$ decrease with increase the HCl concentration due to the increase of thickness of passive layer (CuCl) on copper surface. A linear relationship between concentration of HCl and I$_{pass}$ is obtained in Fig.(4).
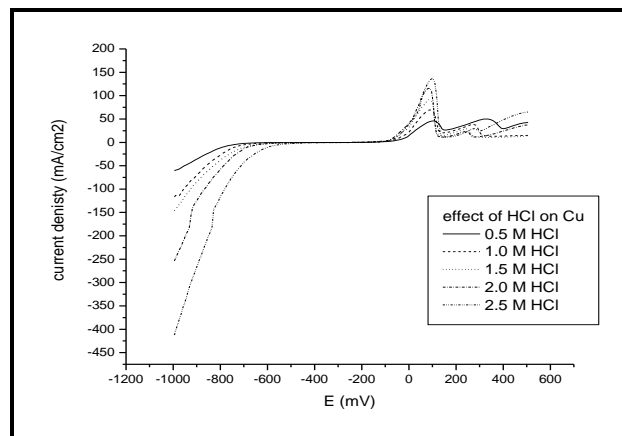

Fig.1 potentiodynamic polarization curves for Copper electrode in different concentrations of HCl with scan rate 10 mV/S at 25˚ C
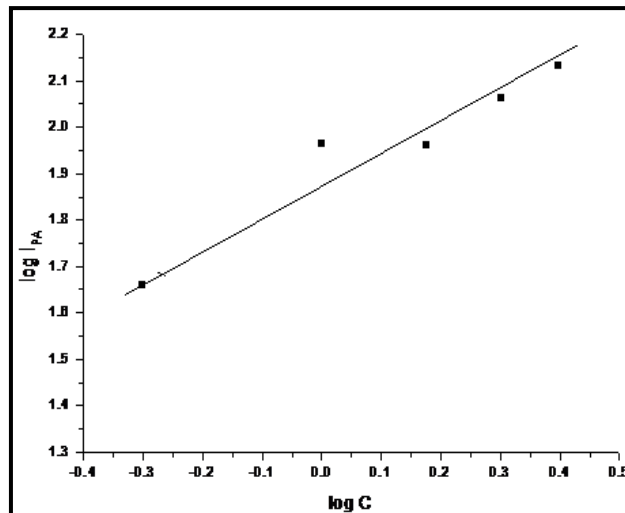
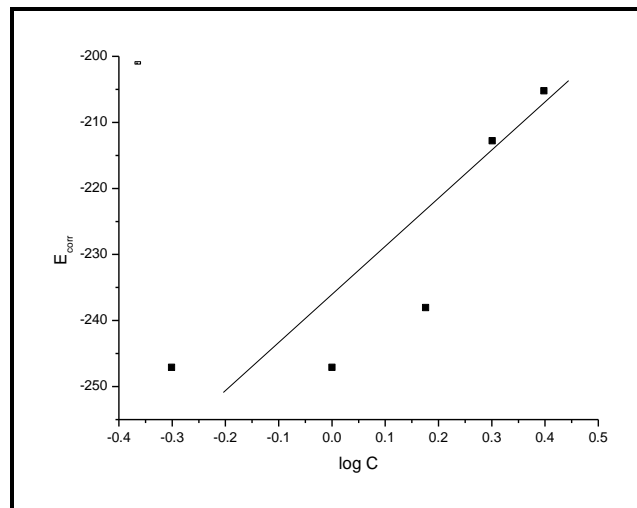**Fig. 2 Relationship between log C vs log I_{PA1}**

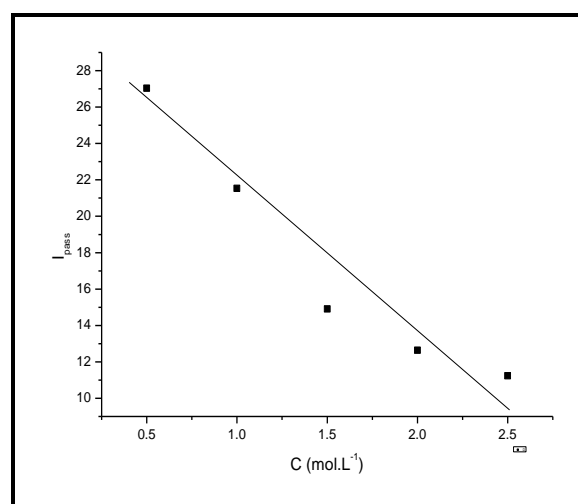**Fig. 3 Relationship between log C of vs E_{corr}**

Fig. 4 Relationship between I_{pass} and different concentrations of HCl

1.2. Effect of inorganic inhibitors on the corrosion characterization of Cu:

Fig. (5) displays the influence of MoO_4^{--} on the potentiodynamic polarization curves of copper in HCl. The MoO_4^{--} ion decreases the height of peak current densities of peak A_1 and shift corresponding peak potential E_{PA1} to more positive potential. The primary inhibitive function

of this anion is believed to be associated with their adsorption on the metal surface and retarding the entry of Copper ions into the solution at the anode [26].

The properties of molybdate solutions change with pH [29-30]. In alkaline solution, molybdate specie is present in the monomer form: MoO_4^{2-}. In neutral or acid solutions, molybdate specie polymerises to form a series of polymolybdates. The size of these polyanions increases with decrease of pH. At about pH 6, the first reaction is the formation of paramolybdate: $Mo_7O_{24}^{6-}$. At lower pH, the octamolybdate is formed: $Mo_8O_{24}^{6-}$ Larger polyanions can be formed with further decrease of pH.

The polymeric ion formation can be symbolised with the reaction [31]:

$$n \, MoO_4^{2-} + 2nH^+ \rightarrow H_{2n} \, (MoO_{4n}) \tag{7}$$

Table (1) shows the values of corrosion current (I_{corr}) and the protection efficiencies (%P) of different concentrations of molybdate.

$C_{MoO4^{--}}$ (mol/L)	I_{corr} (mA/ cm²) $\times 10^{-1}$	P%
0.0	1.841	-
0.002	0.927	49.65
0.004	0.475	73.17
0.006	0.450	75.56
0.008	0.384	79.17
0.01	0.496	73.04

The relationship between I_{PA1} against C_{inh} is given in Fig. (6) Whereby a straight line relation is noted. The inhibitory properties of this anion increase with their concentrations. So MoO_4^{--} function as efficient inhibitor for active dissolution of copper in HCl.

The effect of addition of different concentrations of CrO_4^{--} as Potassium salt on the potentiodynamic response for Copper electrode in 1.0 M HCl solution was examined.

Fig. (7) represents voltammetric response for Copper under the influence of adding increasing concentrations of CrO_4^{--} anion stimulates the active dissolution of Copper and increase the peak current densities I_{PA1}. The stimulating influence of this anion is due to its oxidizing power. The decrease in cathodic polarization of a metal accelerates its active dissolution in an electrolyte containing a concentration of anodic inhibitors insufficient for inhibition [28]. Increase of effectiveness of cathodic process is accompanied by depassivation of the electrode, which leads to arise I_{PA1}.
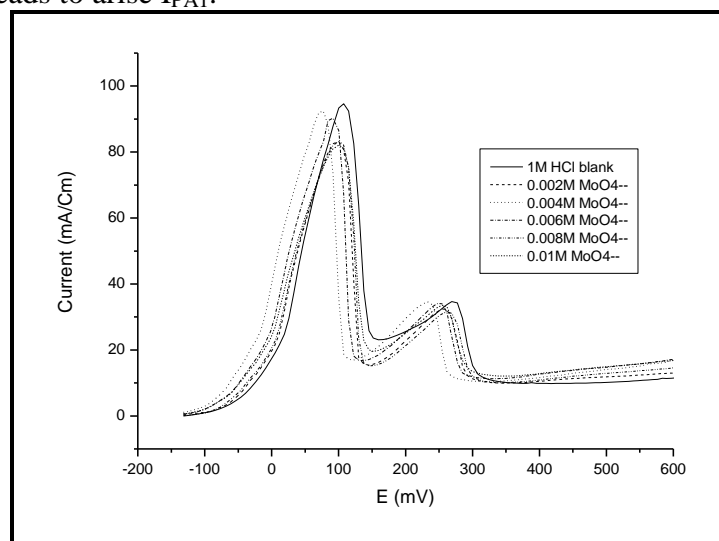

Fig. 5 potentiodynamic polarization curves for Copper electrode in 1.0 M HCl with different concentrations of MoO_4^{--} with scan rate 10 mV/S at 25˚ C
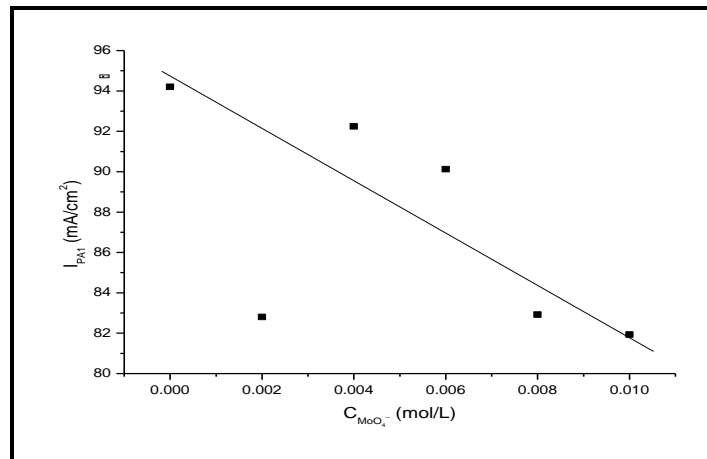
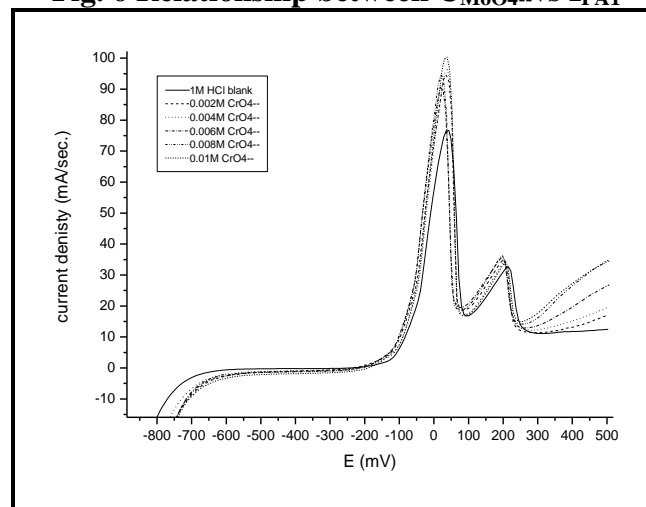**Fig. 6 Relationship between C_{MoO4^-} vs I_{PA1}**

Fig.7 Potentiodynamic polarization curves for Copper electrode in 1.0 M HCl containing different concentrations of chromate with scan rate 10 mV/S at 25° C

2. The electrochemical impedance spectroscopy:

Figs. (8-9) show the Nyquist plots for Copper in 1.0 M HCl solution in the absence and presence of different concentrations of $NaMoO_4$ and K_2CrO_4 at 25° C. The obtained Nyquist impedance diagrams in all cases does not show perfect semicircle, generally attributed to the frequency dispersion as a result of roughness and inhomogenates of the electrode surface[32-34].

The diameter of the semicircle is associated with the polarization resistance and thus the corrosion rate. The larger the semicircle diameter, the lower the corrosion rate. Thus the highest corrosion rate is obtained for the uninhibited solution.

It is clearly seen from Figs. (8-9) that the diameter of the semicircle increases with Na_2MoO4 concentration. On the other hand the diameter of the semicircle decreases in the presence of K_2CrO_4. These results indicate that the presence of Na_2MoO_4 has the inhibition effect on the corrosion of copper in 1.0 M HCl solution, while the addition of K_2CrO_4 leads to accelerate the corrosion of copper in 1.0 M HCl solution.

Figs. (8-9) show EIS diagrams with the provided equivalent circuit where R_s respresents solution resistance, R_{ct} charge transfer resistance, C_{dl} the double layer capacitance for oxide film, CPE the constant phase element and R_{oxide} oxide film resistance.

The electrochemical impedance parameters derived from these investigations are mentioned in table (2).

From the impedance value obtained, the protection efficiency was calculated according to:

$P\% = [R_{ct} - R_{ct(0)}/R_{ct}] \times 100$ (8)

Where R_{ct} and $R_{ct(0)}$ are the charge transfer resistance with and without inhibitor, respectively. The values of protection efficiency P% are listed in table (2).

It is apparent that in presence of $NaMoO_4$ the value of R_{ct} and P% increases where as the value of C_{dl} decreases. Further the increase in $NaMoO_4$ concentration brings about an increase in the P% and R_{ct} values in presence of $NaMoO_4$ is attributed to the formation of a protective film on the copper/ HCl interface.

The decrease in C_{dl} values, which normally results in the dielectric constant and/ or an increase in the double layer thickness, can be attributed to the adsorption of inhibitors onto the metal/ electrolyte interface.

Protection efficiency is observed from table (2) and the optimum concentration for protection was 0.008 M with an efficiency 79.17%.

The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) with a small variation.
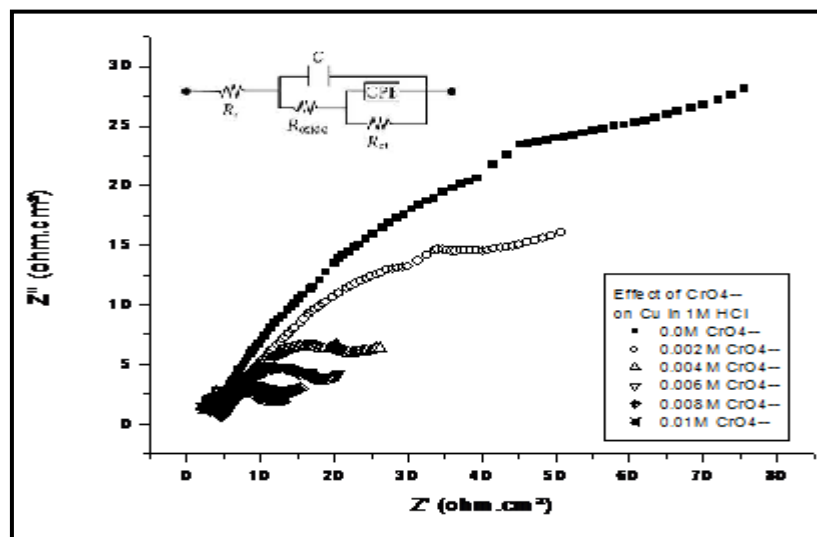

Fig 8. Nyquist plots for copper electrode in 1.0 M HCl, without and with different concentration of K_2CrO_4 at 25°C Inset: the proposed equivalent circuit of the impedance results.
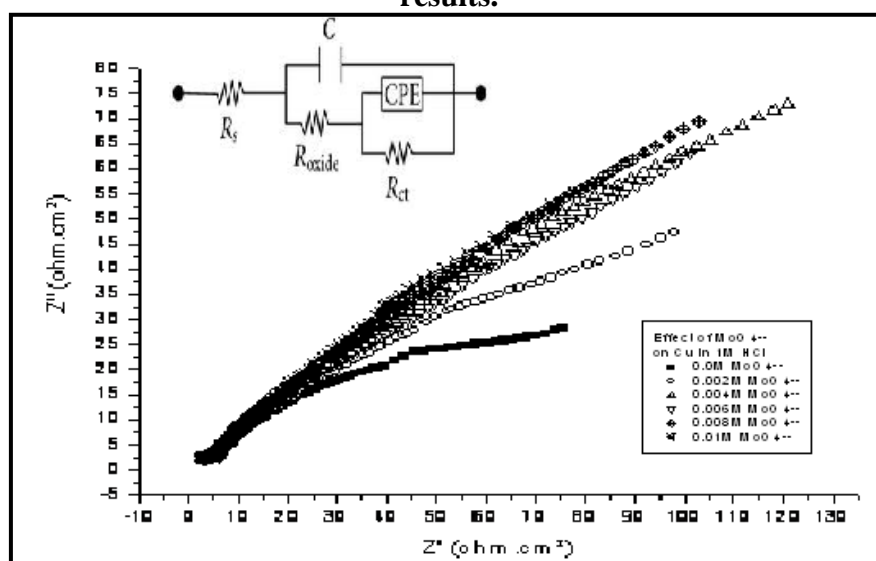

Fig 9. Nyquist plots of copper in 1.0 M HCl, without and with different concentration of Na_2MoO_4 at 25^0C Inset: the proposed equivalent circuit of the impedance results

Table 2: **The electrochemical Parameters and the corresponding protection efficiency of Cu in 1.0 M HCl in the absence and presence of different concentrations of CrO_4^{--} and MoO_4^{--} with scan rate 10 mV/S at 25° C (EIS)**

K_2CrO_4 conc. (M)	R_{ct} (Ohm.cm^2)× 10^2	C_{dl} (µF/cm^2) × 10^{-3}	
0.0	1.417	2.653	
0.002	0.946	3.793	
0.004	0.376	4.046	
0.006	0.293	3.761	
0.008	0.182	5.959	
0.01	0.158	4.673	
Na_2MoO_4 conc.	R_{ct} (Ohm.cm^2)× 10^2	C_{dl} (µF/cm^2) × 10$^-$	P (%)
0.0	1.417	2.653	-
0.002	2.814	2.834	49.64
0.004	5.493	1.759	74.20
0.006	5.797	2.293	75.56
0.008	6.803	1.877	79.17
0.01	5.256	2.518	73.04

Conclusion

The potentiodynamic polarization technique approved that the corrosion rate of copper increases by increasing the concentration of HCl (0.5 M- 2.5 M) with the appearance of 2 anodic peaks at 0.08 V and 0.26 V.

The potentiodynamic polarization technique and EIS approved that different concentrations of MoO_4^{--} inhibits the corrosion of copper in 1 M HCl with an optimum concentration 0.008 M with a protection efficiency 79.17%, while CrO_4^{--} accelerates the corrosion of copper in 1 M HCl due to its oxidizing power.

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