Study of the Role of Ammonium Ions on the Corrosion of Copper in Sulfate Containing Media

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Summary

Corrosion of copper in urban atmosphere is of great interest because several historical monuments made with this metal and its alloys are exposed outdoors in big cities all over the world. When submitted to natural weathering, copper develops a corrosion product layer which composition depends both on the exposure time and on the composition of the atmosphere. Ammonium sulfate is a major constituent of urban atmospheric dust, and, consequently, must play a major role in the formation of copper patinas. In the present work, the role of ammonium ions concentration on the corrosion behavior of copper exposed to a 0.5 M sulfate solution was investigated. The study was carried out through visual observation after immersion tests, ICP-OES analysis, anodic and cathodic polarization curves and electrochemical impedance spectroscopy measurements. Visual analysis of the samples after different immersion periods evidenced that ammonium (NH_4^+) ions hinder the formation of the black tenorite (CuO), whereas ICP-OES analysis of the solutions after the immersion tests showed that corrosion rate increases with NH_4^+ ions concentration and indicated an effective reduction of the corrosion rate by the corrosion product layer. The results of the polarization tests performed after only few hours of immersion confirmed the findings of the ICP-OES analysis regarding the solutions aggressiveness, whereas impedance results evidenced the increasing in the corrosion resistance of the samples with immersion time.

1 Introduction

Copper was one of the first metals shaped by humans. Its importance is evidenced by its wide use in different technological domains. Among them, we highlight its use to build historical monuments. When exposed to natural weathering copper develops a corrosion product layer that goes through a series of change [1]. The composition and appearance of this layer, generally denominated patina, depends both on the exposure time and on the composition of the atmosphere. Many historical monuments are exposed outdoors in urban environments. Therefore, they are constantly exposed to pollution and to weather. Ammonium sulfate is a major constituent of urban atmospheric dust, and, consequently, must play a major role in the formation of copper patinas.

Lobnig *et al.* [2,3] and Odnevall *et al.* [4], studied the corrosion of copper in the presence of submicron ammonium sulfate particles and have clearly demonstrated that they play a major role in the formation of copper patinas. They suggested [2,3] that ammonia originated from the dissociation of NH_4^+ ions stabilizes Cu^+ ions as a complex ($Cu(NH_3)_2^+$) in solution, which can, afterwards, react with water forming a dense cuprite layer. Continuous exposure of these samples to atmospheres with controlled humidity gave rise to the formation of copper sulfates, which precipitated from solu-

tion when the relative humidity was below the critical value. However, these authors did not investigate the effect of ammonium concentration in the corrosion rate of copper.

In the present work, the corrosion of copper samples immersed in 0.5 M sulfate solutions with different concentrations of ammonium ions was investigated. For this purpose, copper samples were immersed in such solutions for different time spans, and the corrosion products were evaluated both by visual examination and by SEM/EDS, furthermore, the composition of the solution was analyzed by ICP-AES. In addition, the electrochemical behavior of the copper samples was studied by polarization curves and EIS experiments after short immersion times.

2 Experimental

Electrolytic copper sheets were used as material. For the immersion experiments rectangular-shaped samples were cut, whereas round-shaped samples were employed in the electrochemical experiments. For all the experiments samples were sequentially ground with #320, #400, # 600 grit silicon carbide emery paper and subsequently thoroughly washed with deionized water, alcohol and acetone and dried in a hot air stream.

Solutions were prepared from analytical grade Na_2SO_4 and $(NH_4)_2SO_4$ and deionized water. For their preparation $(NH_4)_2SO_4$ was initially added to the desired NH_4^+ concentration and, subsequently, Na_2SO_4 was added to adjust the constant sulfate concentration to 0.5 mol L^{-1}. The ammonium concentration in the different solutions was 0.01, 0.05, 0.1, 0.5 and 1.0 mol L^{-1}.

Immersion experiments were performed by vertically plunging two samples of similar surface areas in a beaker with 400 ml of the test solution. Experiments were carried out for 1, 3, 7, 15 and 30 days of immersion. For each immersion time and for each NH_4^+ ions concentration two different samples were used. After the completion of the planned immersion period, the samples were withdrawn from the test electrolyte thoroughly washed with distilled water, dried in a hot air stream and stored for photographic documentation and SEM/EDS analysis. The solution was homogenised and collected for the Inductive Coupled Plasma (ICP-OES) analysis.

An $Hg\text{-}Hg_2SO_4$ (K_2SO_4 saturated) and a large area platinum sheet were used, respectively, as reference and counter-electrode in the electrochemical experiments, which were all performed using a FRA2µ AUTOLAB TYPE III potentiostat equipped with an impedance modulus.

Anodic and cathodic polarization curves were obtained after 3,000 s stabilization at the open circuit potential at a scan rate of 0.2 mV s^{-1}. A different sample was used to acquire each branch of the polarization curve.

Electrochemical impedance spectroscopy (EIS) experiments were performed at the open circuit potential after 3,600 s and 10,800 s of immersion. The perturbation amplitude was 10 mV (rms) and the acquisition rate was 10 points per logarithmic decade. The investigated frequency range was from 100 kHz do 10 mHz.

ICP-OES analyzes were performed using an optical atomic emission spectrometer with inductively coupled plasma Spectro, Arcos. The wavelength for copper determination was 324.754 nm.

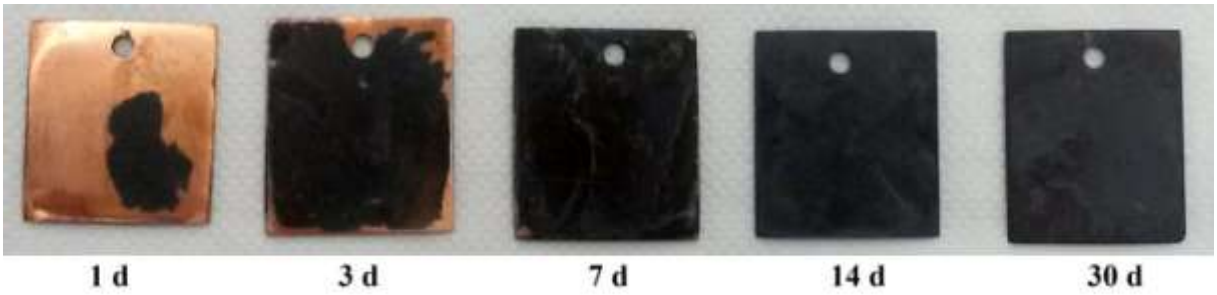
3 Results and Discussion

Figure 1 presents selected digital images of copper samples after different immersion times in the 0.5 mol L^{-1} sulfate solution with different concentrations of HN_4^+ ions. The images reveal that the lower the HN_4^+ ions concentration the sooner a dark patina layer develops on the sample surface. In addition, for longer immersion times, the samples in contact with the solutions with higher ammonium ions concentration (0.1, 0.5 and 1.0 mol L^{-1}) start to develop a green patina over layer, likely associated with the formation of copper sulfates (brochantite). SEM/EDS analysis performed on samples immersed for shorter immersion periods, up to seven days, revealed the development of cubic-octahedral crystals, which densities and sizes increased as the samples surface darkened. EDS analysis of these regions showed high oxygen content, indicating that they must be CuO (tenorite) crystals, which can be formed from the oxidation of Cu_2O (cuprite) by water molecules [5]. The visual analysis of the whole set of tested samples suggests that NH_4^+ ions hinder the formation of tenorite and that the copper sulfate, brochantite, develops from the cuprite layer as suggested by Kratschmer *et al.* [6] and by Fitzgerald et al. [7].

Figure 2 presents the copper concentration in solution, determined from ICP analysis, as a function of immersion time. These values were determined from the exposure of two samples with equivalent areas in the same solution and, therefore, no corrosion rate could be determined. The overall analysis of this Figure shows that for each immersion time the higher the NH_4^+ ions concentration the higher the Cu ions content in solution. Luo *et al.* [8] investigating copper dissolution in ammonium containing slurry suggested that both CuO and Cu_2O could be chemically etched by ammonia molecules (generated from NH_4^+ dissociation) yielding copper ammonia complexes. The results presented in Figures 1 and 2 are in accordance with the findings of these authors [8], as they evidence, respectively, a slower development of the corrosion product layer and higher corrosion rates as the NH_4^+ ions concentration increases.

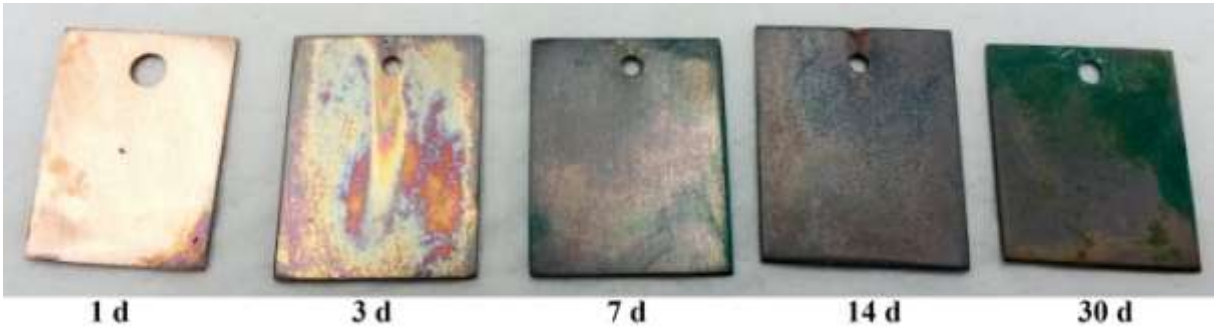
Figure 2 shows that, for all the conditions, at the beginning of the exposure period the concentrations of Cu ions in the solution increase sharply, showing a high dissolution rate, and then stabilizes. The correlation between these results and the visual observation of the samples allows us to conclude that the stabilization period is coincident with the formation of a thick patina layer that effectively blocks the electrode surface drastically diminishing the corrosion rate, this phenomenon takes place after longer immersion times as the NH_4^+ ions concentration increases.

For the samples immersed in the solutions with higher NH_4^+ ions concentration (0.1, 0.5 and 1.0 mol L^{-1}), an inflection point with a maximum can be observed in the concentration profile of Cu ions presented in Figure 2. This maximum is displaced to longer immersion periods as the NH_4^+ ions concentration increases. On the surface of these particular samples the black corrosion product layer hardly developed and the growth of a green patina over layer, likely brochantite, could be visually observed after different immersion times, which was longer the higher the NH_4^+ ions concentration. These two points allow us to hypothesize that NH_4^+ ions hinder the formation of the black tenorite (CuO) layer and that the diminution of Cu ions concentration in solution could be associated with the precipitation of brochantite.



(a)

(b)



(c)

Figure 1: Digital images of copper samples after different immersion times in 0.5 mol L^{-1} sulfate solution with different concentrations of NH_4^+ ions: (a) 0 mol L^{-1}; (b) 0.1 mol L^{-1} (c) 0.5 mol L^{-1}. The numbers in the legend correspond to the immersion days.

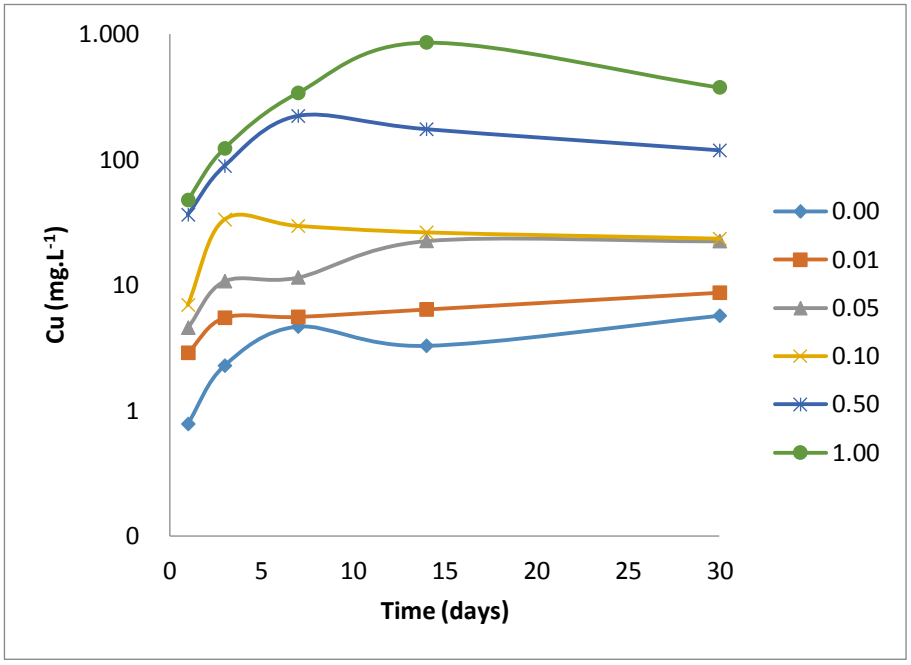


Figure 2: Copper ions concentration in solution with immersion time.

Figure 3 and 4 present, respectively, the anodic and the cathodic polarization curves for copper samples after 3,000 s immersion in the 0.5 mol L^{-1} sulfate solution with different amounts of NH_4^+ ions. The anodic branches, Figure 3, are characterized by a logarithmic increase of the current with potential, indicating that copper oxidation is an activation-controlled process, irrespectively to the presence of NH_4^+ ions in the electrolyte. In accordance with the ICP measurements, the corrosion current densities (i_{corr}) in the NH_4^+ containing solution were higher than in the absence of these ions, and the diagrams indicate a slight increase of i_{corr} with increasing ammonium concentration. On the other hand, the cathodic branches, Figure 4, present a clear diffusion-controlled plateau which current density increases with NH_4^+ ions concentration. The current in the plateau increases with NH_4^+ concentration indicating a contribution of the Cu^{2+} reduction to the overall cathodic current.

The Nyquist and Bode phase angle plots acquired after 3,600 and 10,800 s immersion of the copper samples in the sulfate solutions containing the different amounts of NH_4^+ ions are presented in Figures 5 and 6, respectively, as a reference diagrams acquired in the solution without NH_4^+ ions were added in both figures. The comparison of the two figures shows, for all the investigated conditions, that impedance increases with immersion time and the high frequency phase angle widens and becomes slightly more capacitive pointing towards an increase in the corrosion resistance of the samples. Even though performed after very short immersion times these results are in accordance with those found in the immersion tests, which took one month to be accomplished. Nyquist diagrams are flattened and in some of them a low frequency diffusion-controlled feature is evident. The diagrams acquired in the absence of NH_4^+ ions exhibit different features when compared with the others indicating a different corrosion mechanism for copper in the absence of NH_4^+ ions.

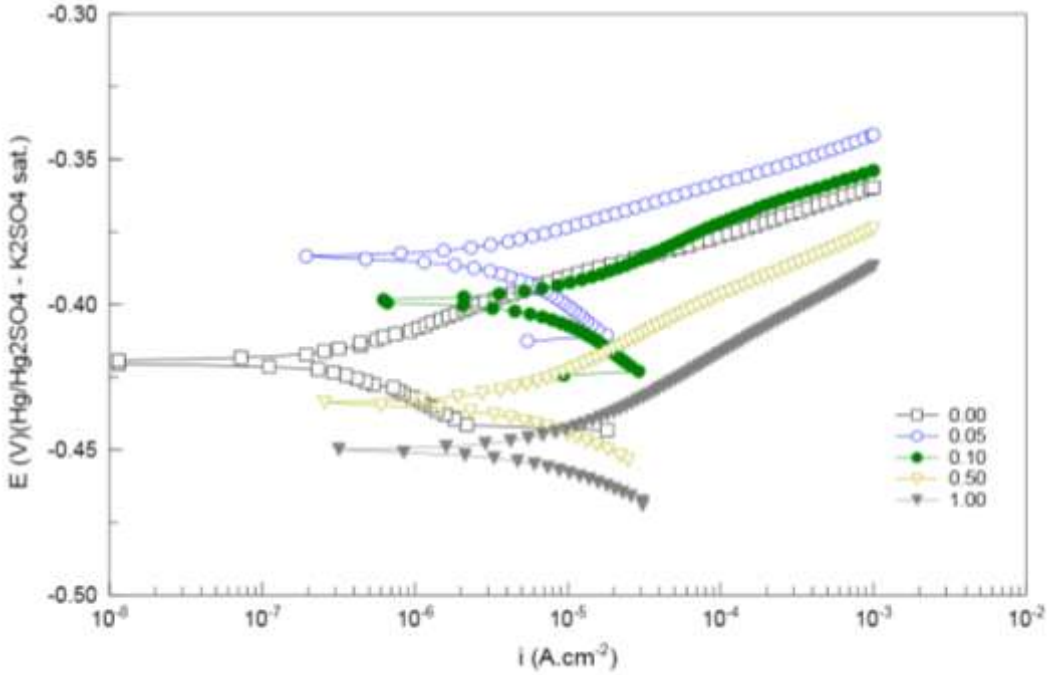


Figure 3: Anodic polarization curves for copper samples in 0.5 mol L^{-1} sulfate solution with different amounts of ammonium ions.

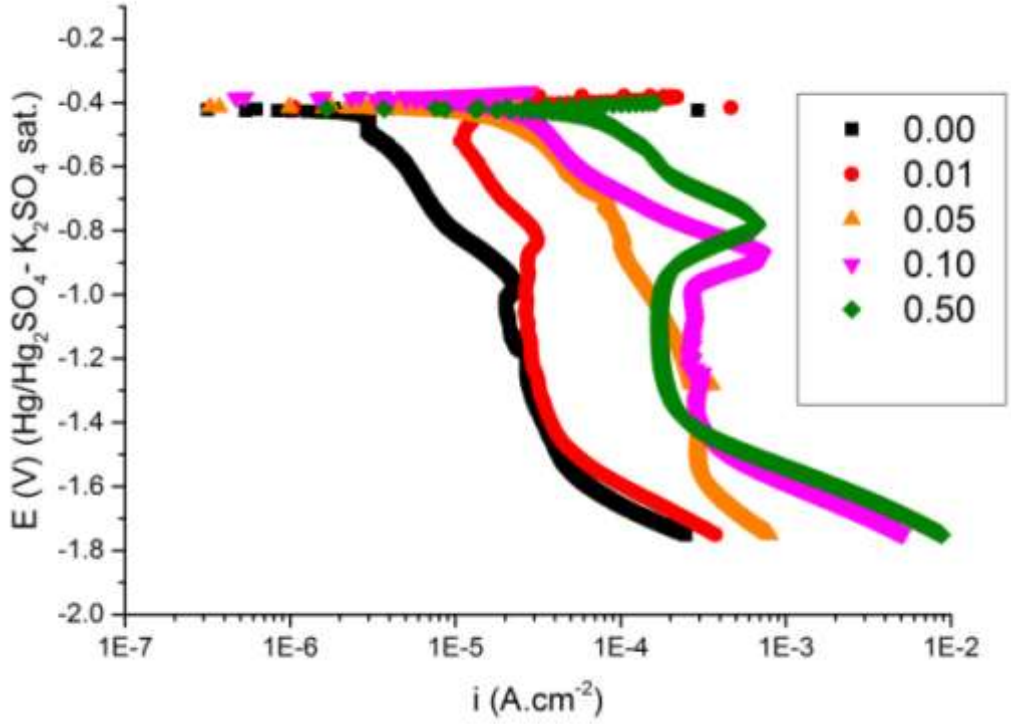
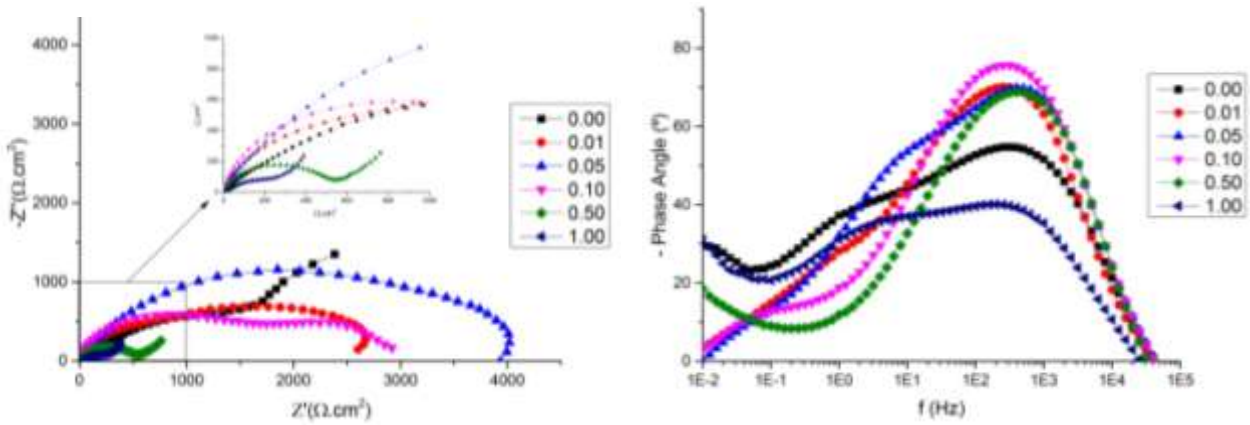
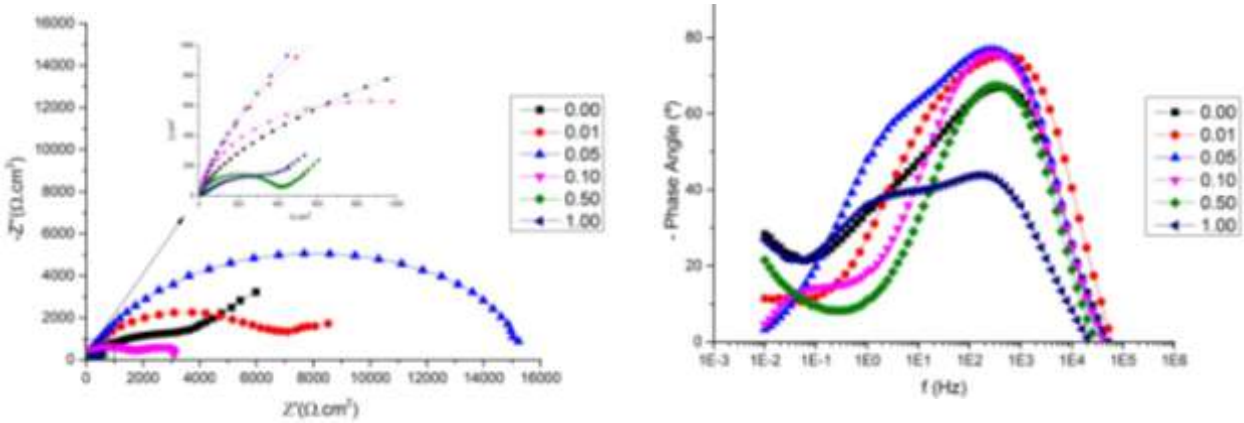


Figure 4: Cathodic polarization curves for copper samples in 0.5 mol L^{-1} sulfate solution with different amounts of ammonium ions.



(a) (b)

Figure 5: Nyquist (a) and Bode phase angle (b) plots after 3,600 s immersion of copper samples in 0.5 mol L^{-1} sulfate solution with different amounts of ammonium ions.



(a) (b)

Figure 6: Nyquist (a) and Bode phase angle (b) plots after 10,800 s immersion of copper samples in 0.5 mol L^{-1} sulfate solution with different amounts of ammonium ions.

4. Conclusions

In the present work the influence of ammonium ions in the corrosion behaviour of copper in sulphate solution was investigated, the results found allowed us to conclude that:

- Ammonium ions increases the corrosion rate of copper and hinder the development of the black tenorite (CuO) layer on the metal surface;
- The development of a compact corrosion product layer effectively blocks the corrosion of the copper samples in the studied solution;
- The results of the electrochemical tests, even though performed after only a short immersion time, corroborated with the results of the immersion tests, which took one month to be accomplished.

5. Acknowledgments

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6. References

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