

## Electrochemical Study of Soil Corrosion on an Ancient-Like Ternary Cu-Pb-Sn Alloy

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### Abstract

The progress in the scientific field of the conservation of cultural heritage metal objects is highly dependent on the understanding of the complex and heterogeneous corrosion mechanisms at different exposure conditions. The unexcavated metal cultural heritage objects are endangered by active soil corrosion, especially in sites where ancient civilizations thrived and where the soil environment has been seriously affected by recent extensive agricultural activities. The addition of some fertilizers supposedly accelerates the metal corrosion processes and many studies have proved the correlation between particular corrosion products and the soil enrichment with modern fertilizers [1,2].

In this study, two samples of soil –with and without recent addition of fertilizers– collected from arable fields in Thessaly during autumn and spring respectively, two different types of fertilizers - F1 (30%N- 4%P weight) and F2 (19%N-14%P)-extracts have been employed as electrolytic solutions (aqueous extraction from soils and soil-fertilizer mixtures as well as fertilizer dilution in deionized water). Electrochemical tests were conducted on the bronze surface in order to investigate the impact of fertilizer addition. The pH and the conductivity were measured in all solutions. A correlation has been attempted between pH measurements and the surface condition of the alloy.

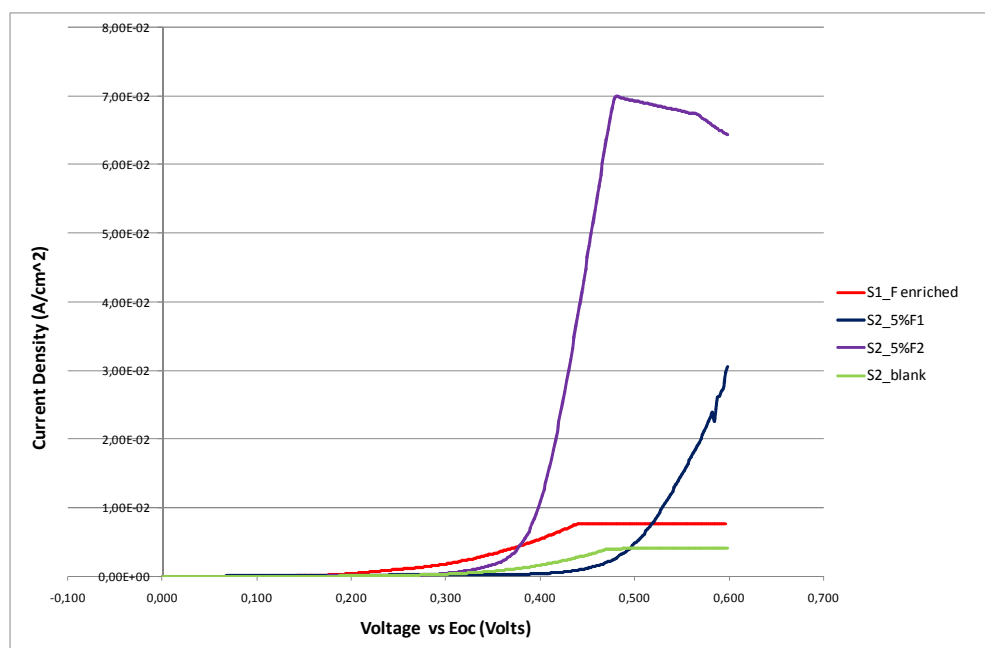
Ancient Greek type bronze cast [3], as the ancient craftsmen produced, was employed for the electrochemical measurements. The alloy tested has a composition of 88% Cu, 8% Pb and 4% Sn and a microstructure similar to the one of ancient alloys.

The electrochemical setup consists of a three-electrode cell - with the metal specimen surface as a working electrode, an Ag/AgCl electrode as reference and a Pt wire as counter electrode. The electrolyte employed was the extracted aqueous solutions of soil, fertilizers or combination. The metal surface remained for 1000 seconds at open circuit (OC) conditions and then a Tafel curve was acquired for the potential range of  $E_{oc} \pm 300$  mV, at a scan rate of 1 mV/s. The corrosion rates were calculated and the electrolyte solutions were ranked according to their corrosivity. Subsequently, the alloy was anodically polarized from open circuit potential ( $E_{oc}$ ) up to +600mV/ $E_{oc}$  in order to study the anodic dissolution and passivation behavior in the different corrosive media.

As a first indication of the corrosivity of the studied electrolytes, the corrosion rates were calculated from the initial Tafel curves. The rates were similar in all cases;

therefore a detailed investigation of the anodic behavior of the alloy is required in order to extract trustworthy conclusions. The anodic polarization curves, presented in Figure 1, indicate that the type 1 fertilized soil exhibits the earliest passivation region in comparison to the other corrosive media. Between the two extracted solutions from type 2 soil with the addition of F1 and F2 fertilizer (S2\_5F1 and S2\_5F2), S2\_5F2 presents a tendency for severe metal dissolution very close to the  $E_{oc}$ . On the other hand, S2\_5F1 presents a more prolonged Tafel region, before the evolution of the metal dissolution process which starts approximately at 0.48 Volts vs  $E_{oc}$ . The recorded dissolution slope is decreased but still very steep due to the high concentration in fertilizer compared the collected fertilized soil. The curve of the particular solution does not show a passivation behavior within the examined potential range.

A correlation between the chemical composition of the two fertilizers and the corrosion and passivation behavior will also be attempted.



**Figure 1:** Linear potentiodynamic curves after Tafel polarization for some of the studied electrolytic solutions: **S1\_F enriched** - extracted soil type 1 (already enriched with fertilizers), **S2\_blank** – soil type 2, **S2F1\_5%**- soil type 2 enriched with fertilizers of type 1, **S2F2\_5%**- soil type 2 enriched with type 2 fertilizer. The voltage values are expressed versus the open circuit potential ( $E_{oc}$ ).

## References

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