

# Evaluation of Cupronickel Alloy Used in Sodium Chloride Solutions Contaminated with Nitrogenated Fertilizers.

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**Abstract**— Cupronickel alloys have been used in the manufacture of equipment, pumps and pipes for refrigeration systems and heat exchangers, among other applications. Certain nitrogen fertilizer plants are built near seaports for the transport of products, and use seawater for refrigeration systems. However, in the case of accidental discharge, it is important that seawater capture does not cause damage to materials and equipment, preserving the integrity and guaranteeing the service life of the equipment. The present work analyses the behavior of cupronickel 90/10 alloy (Cu with 10 wt. % Ni) in relation to corrosion, through the development of gravimetric (mass loss) and electrochemical tests in solutions of 3.5 wt. % sodium chloride, with the additions of nitrogen fertilizer in several proportions. A superficial attack was observed on the surfaces of the alloy specimens, and the presence of pits was not observed. In addition, a greenish coloration on the surface developed with increased immersion time and with the greatest addition of fertilizer. The results of the mass loss tests of the cupronickel alloy with saline solution showed that for nitrogen fertilizer injection, in concentrations of 1, 3 and 5 wt. %, the corrosivity varies from low to moderate, and that despite suffering corrosion in the saline environment, cupronickel has a good resistance to this corrosive process, and can be considered the most suitable material for application in highly aggressive environments, such as in the sea water capture system.

**Keywords**— Copper-nickel alloy, corrosion, laboratory tests, nitrogen fertilizer.

## I. INTRODUCTION

Copper and copper-nickel alloys (also known as cupronickels) have been used for more than 60 years in seawater applications, typically in pipes, pumps, heat exchangers and condensers, due to their good resistance to corrosion. It is well-known from several previous reports [1-4] that the addition of nickel to copper, as a component alloy, to form cupronickel alloys gives rise to the production of corrosion-resistant material. For this reason, cupronickel alloys have been used in the construction of equipment for the chemical industry in general.

Fertilizers are products that constitute one of the main substances and/or mixtures in agricultural industry. The fertilizer industry is one of the most prosperous businesses in the agribusiness world. Industrial products such as nitrates can be used as petrochemicals and in mining, and in some cases are extremely toxic, flammable, or corrosive, bringing serious risks inherent to the population and the environment. In addition, these products have

dangerous and unhealthy manufacturing processes, generating various wastes and ensuring that any type of leak may be harmful, at least [5,6].

In the same way that nitrate-based fertilisers are a source of nitrogen for the development of agriculture, so, against society, nitrate-based compounds serve the explosives and weapons industry. Hence, the positioning of accidents in the industrial sector. Accidents in fertilizer factories have occurred over the last few decades, and have brought to light the risks surrounding these industries [7].

In the present study, a fertilizer factory was examined, which will not be identified for privacy reasons, located near the sea port for the purpose of facilitating drainage, and where sea water is reused in the refrigeration system (very common in plants of this type).

In this cooling system, sea water is captured, used to exchange heat with the piping system, heat exchangers and condensers, cooling pumps, and then returns to the sea,

without direct contact with any polluting material. Figure 1 illustrates a typical cooling system using sea water.

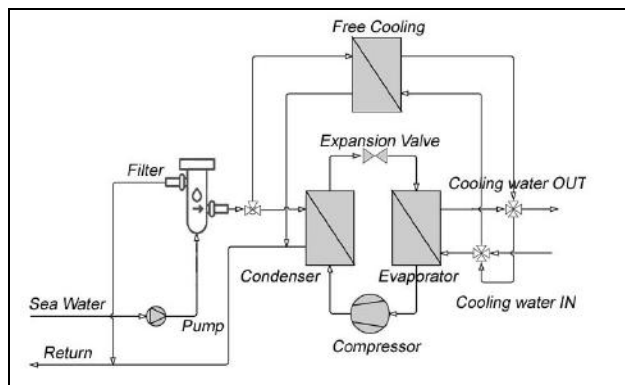


Fig. 1: Typical industrial cooling system using seawater

As the system uses sea water, cupronickel alloys are the material used to construct the equipment (pipes, pumps, compressors, and others).

However, at one point, an accidental dumping of nitrogen compounds and ammoniacal deposits occurred, and these materials may cause the corrosion process in the cupronickel alloys used in this system, and, as a result, leaks may occur that would impact the operation of the industrial unit, as well as the surrounding environment, and cause health risks to the general population.

## II. MATERIALS AND METHODS

The material used for the manufacture of the coupons used in this study was the cupronickel alloy consisting of copper (87.50%), nickel (10.4%), iron (1.51%) and manganese (0.59%), the chemical composition of which is framed in ASTM standard B171/B171M-12[8].

The coupons used in the gravimetric tests (weight loss) had the following dimensions: 3.0 cm × 1.5 cm × 0.2 cm, while the coupons for the electrochemical assays were cut in the following dimensions: 0.5 cm × 0.5 cm × 0.2 cm.

All specimens were previously treated by sanding using four sandpapers of different granulations (80, 120, 180 and 320), in order to guarantee the homogeneity of the metallic surface. The previously-cut samples were carefully sanded with the appropriate grain in one direction, and then at 90° from that direction until the first scratches disappeared, then returning to the original direction. This procedure ensured the removal of the original surfaces and provided a surface with an adequate roughness for the tests. The coupons were cleaned with acetone and ethanol, and dried with hot air.

The corrosive medium used to represent seawater was a solution of sodium chloride (NaCl) (3.5 wt. %)

containing 800 mg and 400 mg, respectively, of magnesium chloride ( $\text{MgCl}_2$ ) and calcium chloride ( $\text{CaCl}_2$ ). The pH was set between 7.2 and 8.0 by addition of sodium hydroxide (NaOH).

To represent the spill of nitrogen fertilizer in seawater, a commercial “NK” type fertilizer, consisting of a mixture of potassium nitrate ( $\text{KNO}_3$ ) and sodium nitrate ( $\text{NaNO}_3$ ), was added; thus, forming a product containing 15% nitrogen (N) and 11% potassium (K). The additions of this commercial nitrogen fertilizer were in the proportions of 1, 3 and 5 wt. %.

### 2.1 Gravimetric test (weight loss)

The test consisted of two stages, in which the performance of the specimens in a static and dynamic state was analyzed.

In the case of the static gravimetric test, the tests were performed with the placement of the coupon in polyethylene containers with a capacity of 100 mL, where the alloy specimens were completely immersed in 3.5 wt. % NaCl saline solution, containing 800 mg of  $\text{MgCl}_2$  and 400 mg of  $\text{CaCl}_2$ , with the addition of nitrogen fertilizer in 3 different proportions (1, 3 and 5 wt. %). Tests were carried out at room temperature and ambient pressure, with exposure times of 15, 30 and 60 d, and were completely static, as shown in Figure 2.

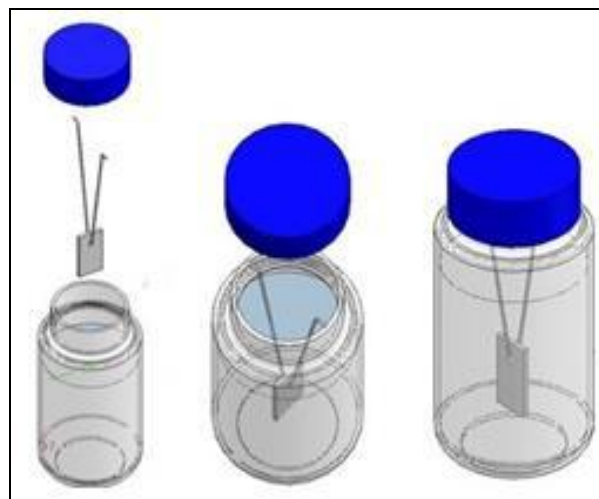


Fig. 2: Static gravimetric test

In the case of the dynamic gravimetric test, the tests were carried out by placing the coupons in plastic containers with a capacity of 55 L, where they were loaded with 40 L of 3.5 wt. % NaCl saline solution, containing 800 mg of  $\text{MgCl}_2$  and 400 mg of  $\text{CaCl}_2$  with the addition of nitrogen fertilizer in the proportion of 5 wt. %. Tests were carried out at room temperature and pressure environment, with exposure times of 15, 30 and 60 days,

choice justified as being the most critical situation of the present test. The dynamic gravimetric test setup is shown in Figure 3.

A continuous circulation system was mounted on the plastic container, using a submerged pump, and the injection of compressed air by an air compressor was used in order to keep the oxygenation rate constant, aiming to replicate conditions simulating a maritime environment, more aggressive than in the static test.

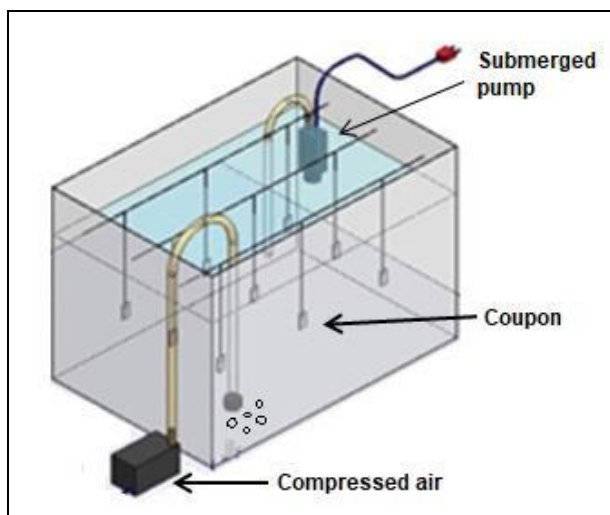


Fig. 3: Dynamic gravimetric test

Corrosion rates were calculated in mm/y, as established in ASTM standard G1-03 [10], based on the total initial surface area of the specimen and mass lost during the test, using the equation:

$$CR = \frac{K \cdot W}{A \cdot t \cdot \rho}$$

Where,

CR = Corrosion rate, mm/y;

K = constant ( $8.76 \times 10^4$ );

W = mass loss, g;

A = area, cm<sup>2</sup>;

t = exposure time, h;

$\rho$  = specific mass, 8.9 g/cm<sup>3</sup>.

## 2.2 Electrochemical test

For the polarization measurements, samples of the cupronickel alloy were cut in order to obtain an electrode surface of 0.5 cm × 0.5 cm. The alloy was then embedded in a polyester resin and the samples sanded in a polishing machine using grade 100 to 1200 sandpaper, as shown in Figure 4. After this procedure, the samples were washed and passed through ultrasonic cleaning equipment for 3

min, in order to remove residues that may have aggregated during sanding [11,12].

At this point, the samples were inserted into a conventional polarization cell with a volume of 200 mL, consisting of a working electrode, a platinum counter-electrode and a saturated calomel reference electrode (SCE), as shown in Figure 5.



Fig. 3: Electrochemical coupons

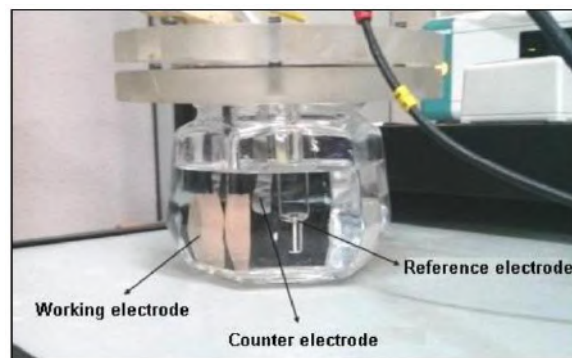


Fig. 5: Conventional polarization cell [11].

The polarization curves were recorded with an Autolab potentiostat, Type III, by varying the voltage at 60 mV/min over a range of -250mV to +250mV, with respect to open circuit voltage. All measurements were carried out at a constant temperature of 25 °C and without agitation. A solution of saline water containing 3.5 wt. % NaCl, 800 mg/L of MgCl<sub>2</sub> and 400 mg/L of CaCl<sub>2</sub>, with the pH set between 7.2 and 8.0, was used. The nitrogen fertilizer was added to the saline in concentrations of 1, 3 and 5 wt. %.

All measurements were repeated at least three times to ensure good reproducibility. The data obtained were analyzed using Origin Lab Pro software (version 7.1).

## III. RESULTS AND DISCUSSION

The results obtained in gravimetric and electrochemical tests for the cupronickel 90/10 alloy, in solutions of saline water with nitrogen fertilizer additions, are presented in the following sub-sections.



### 3.1 Static gravimetric test

As described in section 2.1, the cupronickel alloy coupons were tested statically over a period of 2 months (15, 30 and 60 days), with saline as the electrolyte and with additions of nitrogen fertilisers in concentrations of 1, 3 and 5 wt. %. The results of the averages of the corrosion rate (mm/y) are shown in Figure 6.

A superficial attack is observed on the surfaces of the specimens, without the presence of pitting, as shown in Figure 7. The possible occurrence of slight corrosion by differential aeration on the surface of the hole, where the specimen is suspended by a Teflon wire, is highlighted. In addition, there was a greenish coloration on the surface which developed with increased immersion time and with the greatest addition of fertilizer.

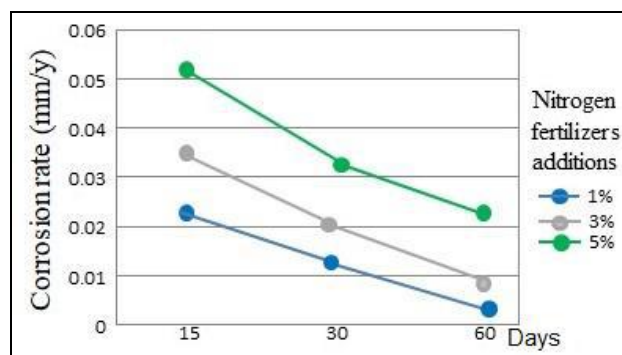


Fig. 6: Static gravimetric test results

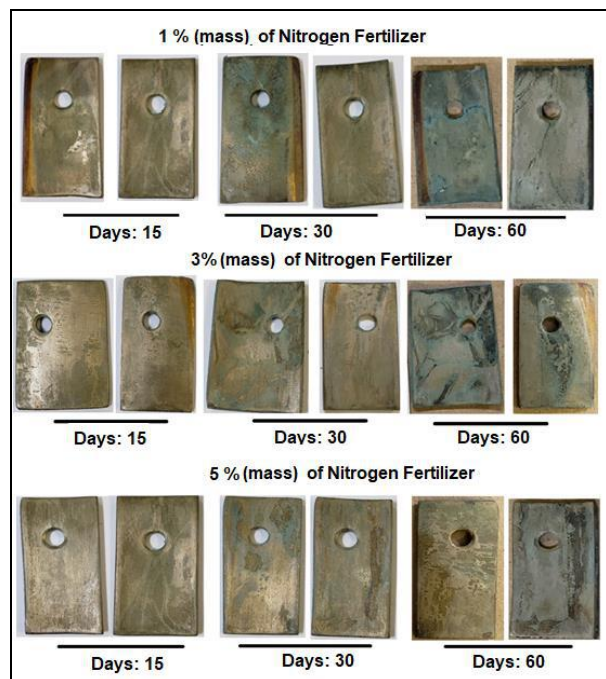


Fig. 7: Surface of the specimens removed from static gravimetric testing

### 3.2 Dynamic Gravimetric test

The results from nine coupons of cupronickel 90/10 alloy submitted for dynamic testing over periods of 15, 30 and 60 days, in saline solution with addition of 5 wt. % nitrogen fertilizer are shown in Figure 8. In Figure 9, a visualization of the specimens after the dynamic test is presented. The results show that the continuous bubbling of air and the agitation caused by the submerged pump in this assay are more aggressive conditions than those in the static assay.

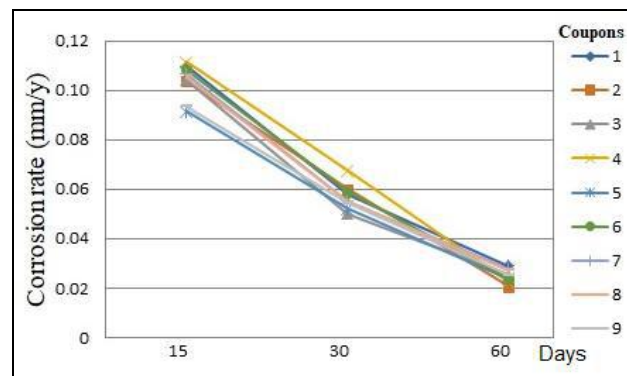


Fig.8: Dynamic gravimetric test results

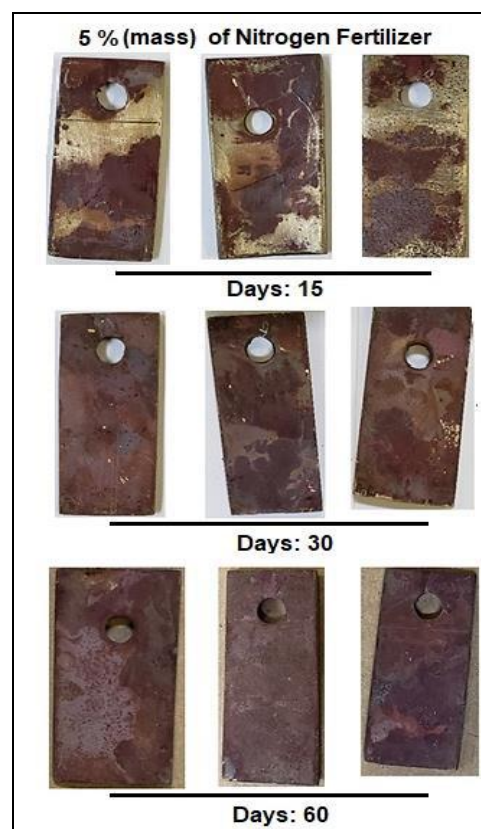


Fig. 9: Surface of the specimens removed from dynamic gravimetric test

Table 1 of Standard NACE-RP-07-05[13] below shows that the corrosion rates of cupronickel alloy coupons immersed in NaCl solutions, contaminated with nitrogen fertilizer in the mass loss tests (static and dynamic), are classified as low to moderate.

Table 1: Average corrosion rate of Standard NACE-RP-07-05[13].

Average corrosion rate, mm/y	Corrosiveness
<0.025	Low
0.025 - 0.12	Moderate
0.13 – 0.25	High
0.25	Severe

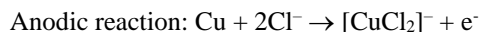
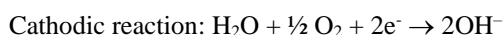
Figure 7 shows the macroscopic morphologies of the surfaces of the corroded coupons of the cupronickel 90/10 alloy, immersed in 3.5 wt. % NaCl solution without air bubbling and with additions of 1, 3 and 5 wt. % of nitrogen fertilizer for 15, 30 and 60 days. An oxidized film ( $\text{Cu}_2\text{O}$ ) is observed that darkens as the immersion time increases from 15 to 60 days. It was also observed, for some coupons with holes, a slight corrosion due to concentration differential from the Teflon wire supporting these coupons.

Figure 8 shows the macroscopic morphologies of coupons removed from the dynamic assay with the same saline solution, and the addition of 5 wt. % nitrogen fertilizer with continuous air bubbling. An adhered film with a yellow brick-red coloration is noted, which changes to brick-red and even black as the immersion time reaches 60 days.

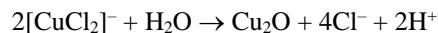
The X-ray diffraction analyses carried out on the deposits adhering to the surface of the specimens reveal that they mainly consist of cuprous oxide ( $\text{Cu}_2\text{O}$ ). In some samples, in addition to  $\text{Cu}_2\text{O}$ , cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ) and cupric hydrochloride traces were also identified. No copper or nickel nitrate compounds were observed, which is expected considering they are completely soluble.

The formation and properties of the passivating  $\text{Cu}_2\text{O}$  layer on the surface of cupronickel 90/10 alloy have been studied in several previous reports [14-19]. Importantly, in the literature, no report could be found where the concentrations of sodium nitrate and potassium could alter the properties of the  $\text{Cu}_2\text{O}$  layer.

Based on the studies mentioned above, the formation of  $\text{Cu}_2\text{O}$  on the surface in cupronickel 90/10 alloys can be explained by the following reactions:



Hydration of  $[\text{CuCl}_2]^-$  favors  $\text{Cu}_2\text{O}$  formation, based on the following reaction:



### 3.3 Electrochemical test

Figure 10 shows the polarization curves of the cupronickel 90/10 alloy in a solution of 3.5 wt. % NaCl, at room temperature without air bubbling and with addition of nitrogen fertilisers at concentrations 1, 3 and 5 wt. %. Values for the polarization resistance ( $R_p$ ), potential ( $E_{\text{corr}}$ ) and corrosion current density ( $I_{\text{corr}}$ ) were obtained by extrapolating the Tafel slope of the polarization curves, and are shown in Table 2.

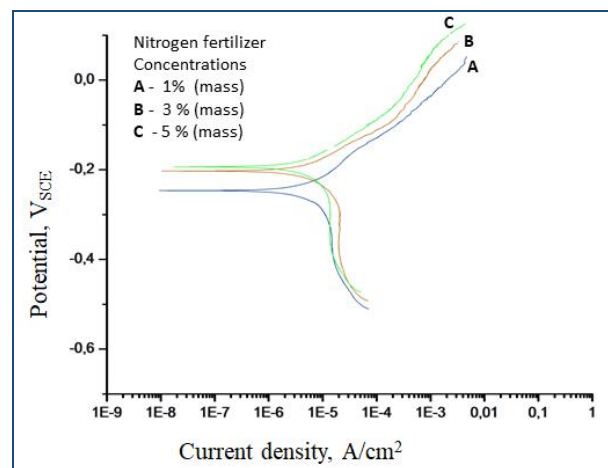


Fig. 10 :Polarization curves of the cupronickel 90/10 alloy in a solution of 3.5% NaCl, at room temperature without air bubbling, and with addition of nitrogen fertilisers in the concentrations 1, 3 and 5 wt. %.

Table 2 – Polarization resistance ( $R_p$ ), potential ( $E_{\text{corr}}$ ) and the corrosion current density ( $I_{\text{corr}}$ ) of

#### Polarization curves

Nitrogen Fertilizer	$I_{\text{corr}}$ , A/cm <sup>2</sup>	$E_{\text{corr}}$ , V	$R_p$ , $\Omega\cdot\text{cm}^2$
A – 1%	$4.8 \times 10^{-5}$	-0.240	$5.2 \times 10^4$
B – 3%	$4.5 \times 10^{-5}$	-0.210	$4.6 \times 10^3$
C – 5%	$8.1 \times 10^{-5}$	-0.190	$3.3 \times 10^3$

The potentiometric curves presented in Figure 10 show some similarity, indicating that nitrate additions do not modify the contour of the curves. The results of each parameter in Table 2 also do not show a significant difference, confirming the results of corrosion rates observed in the static tests.

According to Ezuber et al.[20], the formation of a  $\text{Cu}_2\text{O}$  protective film associated with another layer of cupric hydroxychloride favors the formation of an inert film, reducing the current density. The formation of these films is also in agreement with Mathiyarasu et al[19].

#### IV. CONCLUSION

Based on the bibliographic references and the results of the laboratory tests, it is concluded that:

- Although the cupronickel alloy with 90% copper and 10% nickel (ASTM C70600 specification) is used for the manufacture of equipment and piping for seawater collection and cooling systems, corrosion can be expected if a high injection of nitrogen fertilisers occurs;
- The mass loss tests of the cupronickel alloy with saline solution showed that, in cases of injection of nitrogen fertilisers in concentrations of 1, 3 and 5 wt. %, the corrosivity varies from low to moderate;
- The formation of a cuprous oxide ( $\text{Cu}_2\text{O}$ ) film, identified by X-ray diffraction and supported by laboratory tests, passivates the cupronickel alloy surface;
- It is essential to monitor for possible leakages of nitrogen fertilisers from industrial stations to preserve the environment and human health;
- Despite suffering corrosion in the saline environment, cupronickel has good overall resistance to the corrosive process, and can be considered as the most suitable material for application in highly aggressive environments, for example, the system for capturing sea water.

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