

Corrosion properties of copper nickel alloys in chlorinated sea water

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Summary

Copper based alloys are frequently used in marine water systems. They have indeed an attractive price and offer interesting mechanical properties associated to a relatively good resistance in sea water. Nevertheless, they can suffer from certain forms of corrosion such as localised corrosion in polluted sea water. These alloys known to have a biocide effect are also susceptible to biofilm formation and could present some fouling. Continuous treatments are then recommended to limit biofilm and fouling formation and chlorination could be a good candidate.

The present work was carried out to investigate the behaviour of CuNi 90-10 and CuNi 70-30 in natural sea water compared to chlorinated sea water. The influence of chlorination on electrochemical parameters such as the open circuit potential, the kinetics of the cathodic and anodic reactions was estimated.

The results of these studies have shown the benefic effect of chlorination to limit fouling but also biofilm and its corrosion consequences. Moreover, copper alloys seem to be more tolerant to chlorine concentration increase associated to temperature peaks.

1 Introduction

Copper based alloys are frequently used in seawater system for application such as exchangers, pumps, valves, pipes, fasteners. Despite the emergence in recent year of other alloys that offer improved properties for example stainless steels, based nickel alloys, or titanium, copper alloys continue to be widely used. They have indeed an attractive price associated to relatively good resistance to corrosion in sea water.

Nevertheless, they can suffer from certain forms of corrosion such as localised corrosion with sulphide pollution for instance [1-6]. Crevice corrosion in flanges assemblies in copper nickel alloys can also be encountered [7-9]; In this case corrosion is observed outside the metal /gasket interface, close to the gasket but not in the interface as usually observed with stainless steels.

KEYWORDS: corrosion properties; copper based alloys; chlorinated sea water

Cases of corrosion under deposit that can lead to some leaks in heat exchanger tubes are found as shown on fig. 1

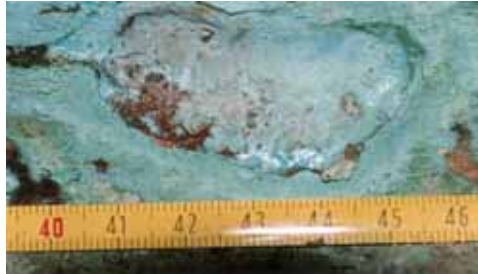


Figure 1 Corrosion under deposit on CuNi 90-10

The risk of corrosion under deposit is attributed to the biological nature of seawater that induced marine deposit, biofilm, fouling in seawater. Some exchanger tubes can be blocked with fouling and deposit that induced decrease in flowing rate of sea water in some tubes and consequently increase in sea water flowrate in other tubes. This low flowing seawater has a detrimental effect on copper nickel alloys, indeed it is well-known that flowing rate must be between 1m/s and 3 m/s for a safe use of copper alloys in seawater.

Some cases of leaks have been found in tube exchangers with period of stagnation sea water as shown on fig 2.

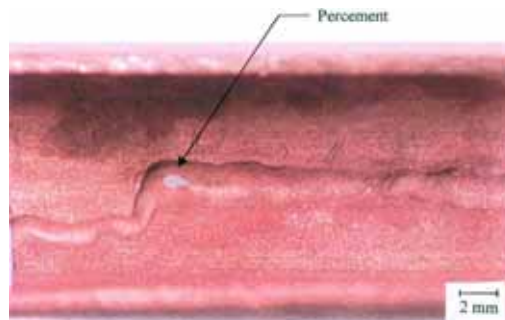


Figure 2 Leaks in copper nickel 90-10 after period of stagnation in seawater

To limit biofilm and fouling biocide treatments are recommended for copper nickel technology. Chlorination appears then to be a good candidate [10], but its oxidizing properties are susceptible to increase corrosion risk on material.

The present work was then conducted to investigate the behaviour of copper nickel 70-30 and 90-10 in natural sea water compared to chlorinated seawater. The influence of chlorination on electrochemical parameter such as potential, anodic and

cathodic polarization curves is estimated. Simulation of corrosion is also undertaken with chlorination treatments

2 Experimental procedure

2.1 Material

Nominal compositions and mechanical properties of the base materials used are found in tables 1 and 2 with reference to certificate data.

Table 1 – Chemical composition (wt. - %) of materials

	Zn	Ni	Fe	Mn	P	S	C	Pb	Sn +Pb	other	Cu
CuNi 90-10	≤0,5	9,0 11,0	1,5 2,0	0,3 1,0	≤ 0,025	≤0,02	≤0,05	≤0,02	≤0,05	≤0,1	bal
CuNi70-30	≤0,1	29,0 32,0	0,4 1,0	0,5 1,5	≤ 0,01	≤0,02	≤0,04	≤0,01		≤0,1	bal

Table 2: Typical mechanical properties

	Re 0,2% (YS) MPa	Rm (TS) MPa	A % E
CuNi90-10	≥ 100	≥ 300	≥ 30
CuNi70-30	≥ 130	≥ 370	≥ 30

2.2 Specimens conditioning

Open circuit potential (Eoc) and polarization curves specimen are machined to a surface finished of Ra 6,3 µm which is the surface finished of equipment in service. All specimens were degreased in methanol, rinsed in deionised water and then air dried.

2.3 Corrosion testing

2.1.1 Open circuit potential (EOC) measurements

Eoc measurements were conducted on specimens machined from bars with a flag shape to enable electrical connection out of sea water, the dimensions being of 25 mm in length and 25 mm in width. Eoc was measured with respect to Saturated Calomel reference Electrode (SCE). The aim of potential measurements was to estimate the possible risk of corrosion initiation on the alloys tested with regard to chlorination level. Indeed, it is well known that crevice corrosion risk increases with the level of the potential in a given medium by comparison to the potential obtained sea water without biofilm effect. The objective of the test is to estimate the increase

of the potential on the alloys considered as a function of the chlorination parameter and the oxidizing effect.

2.1.2 Anodic polarization curves

The anodic polarization curves were generated using a potentiostat, at a scan rate of 0.05 mV/s, from E_{oc} to 0.3 V vs. SCE. The tests were conducted on “flag specimen” of 25 mm in length and 25 mm in width. Conditions of tests were the same as those selected for E_{oc} measurements.

2.1.3 Cathodic polarization curves

The cathodic polarization curves were generated using a potentiostat, at a scan rate of 0.05 mV/s, from E_{oc} to about -1V vs.SCE. The tests were conducted on “flag specimen” of 25 mm in length and 25 mm in width. Conditions of tests were the same as those selected for E_{oc} measurements. The level of the cathodic threshold obtained on alloys tested was indicated the maximum propagation rate that could occur on the various alloys tested depending on the tests conditions. In the case of localized corrosion initiation, the kinetic is under oxidizing species reduction control given by the level of the cathodic threshold that is a function of chlorine dosage, the temperature and the considered surface. In the case of this study, the range of potential under interest is between around -300 mV vs.SCE and -50 mV vs.SCE respectively the potential of the alloys considered in sea water without biofilm and the maximum potential in natural sea water with biofilm settlement and autopollution of the sea water.

2.4 Chlorine dosage

Tests in chlorinated sea water were realised in tanks with flowing sea water. Sea water was heated by the use of a heat exchanger and treated with hypochlorite using a dosing pump.

Chlorine dosage were measured with the N,N- diethyl-p-phenylene diamine DPD colorimetric kit (Hach). A Pt electrode was immersed in the chlorinated sea water in order to follow the chlorination dosage along the test.

3 Result and discussion

3.1 Influence of chlorination on Eoc measurement

3.1.1 Eoc measurements in natural sea water

In natural sea water, open circuit potential of copper nickel alloys tend to increase from about -250 mV vs.SCE to -50 mV vs. SCE depending of the quality of the sea water, presence for instance of pollution such as sulphide pollution. In clean sea water this increase of the potential is not observed in laboratory conditions as shown on Fig 3.

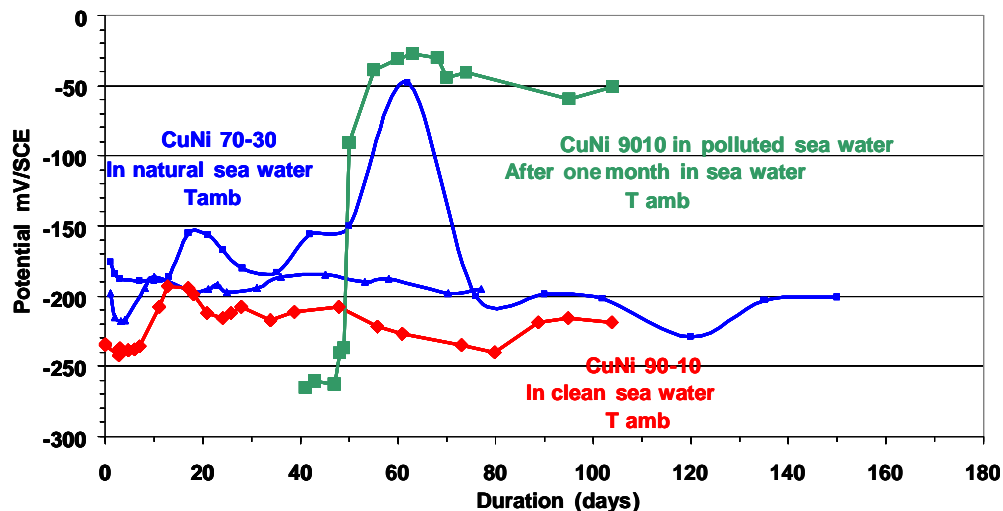


Figure 3 : Potential measurements in natural sea water laboratory tests

Nevertheless, long term test conducted on sea water test loop (see Fig 4) , have also shown an increase of the potential on CuNi 90-10 and CuNi 70-30 respectively to -100 mVvs SCE and -50 mVvs SCE. This increase was effective in renewed, low flowing sea water; it was attributed to the effect of biofilm and or the effect of auto pollution of sea water in low flowing conditions. Indeed, it was observed that the increase of the flowing rate immediately conduct to the decrease of the potential. As the decrease of flowing sea water, progressively lead to higher potential again.

These results have revealed that due to the biological nature of the sea water , high variation of potential can be observed on Copper alloys with some potential effect

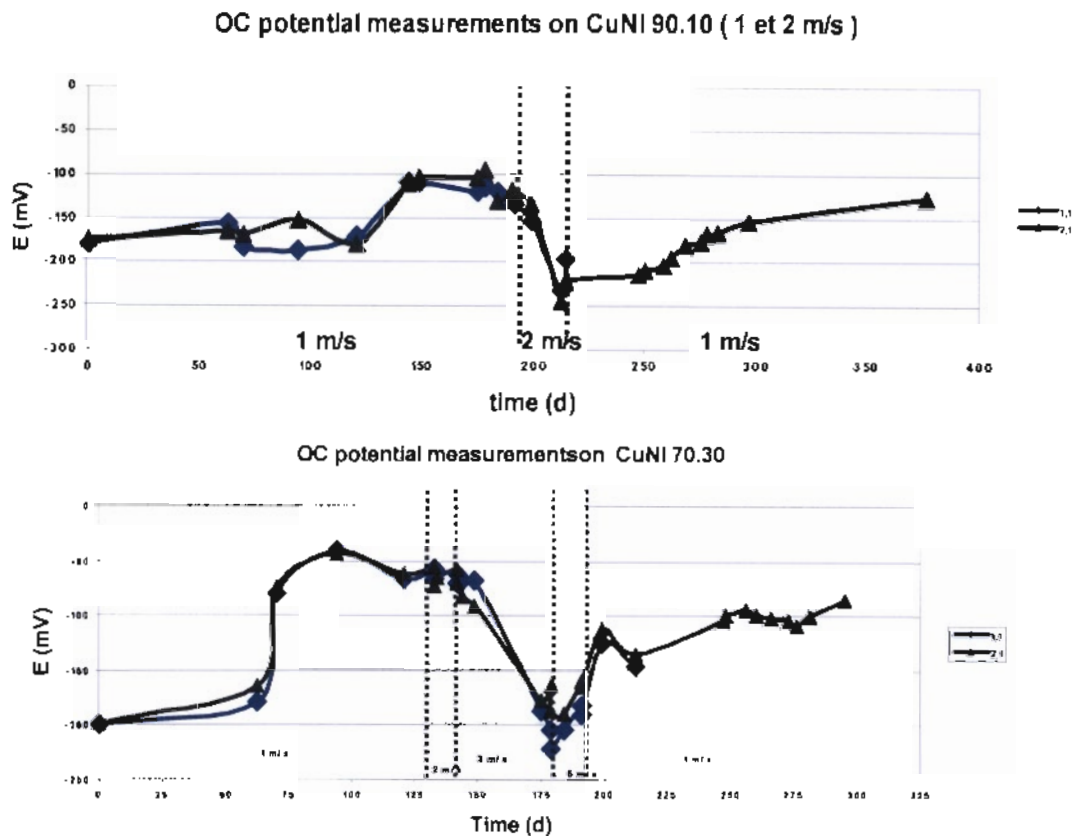


Figure 4: Potential measurements in natural sea water on corrosion test loop

on their resistance to corrosion depending on flowing parameter and the quality of the sea water.

3.1.2 *Eoc* measurements in chlorinated sea water

To prevent biofilm and biofouling effect on copper alloys, Chlorination can be used and the effect of chlorination is firstly evaluated on potential measurements

Potential measurements in chlorinated sea water on CuNi 90-10 and 70-30 are respectively presented on fig 5 and 6.

On copper nickel 90-10, the potential is maintained between -200 mV/SCE and -250 mV/SCE for a chlorination rate from 0.2 ppm to 0.5 ppm. When the temperature increases, no increase of the potential is observed, it stabilizes at a value inferior to -250 mVvs.SCE. Elsewhere, increase of the chlorination rate associated to the increase of the temperature, does not induce important variation of the potential, which is maintained in all cases inferior to -200 mVvs.SCE. Compared to potential measured in natural sea water, it was not noticed a potential

evolution to -100 mVvs.SCE after a significative test duration of 90 days. It is then considered that in these conditions localized corrosion initiation risk is low.

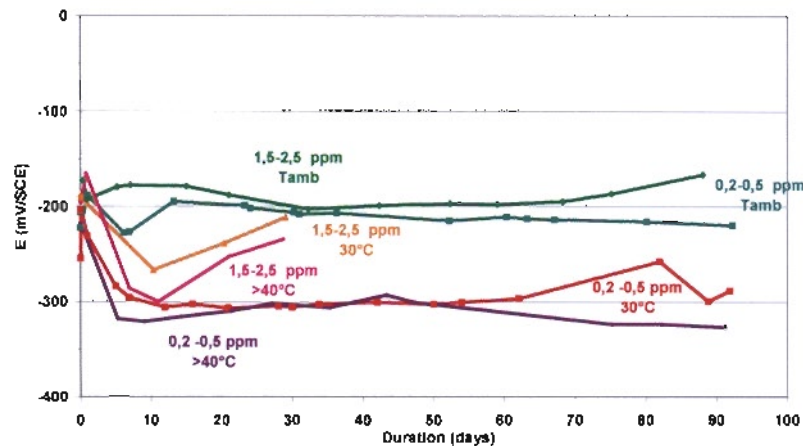


Figure 5 Potential measurements on CuNi 90-10 in Chlorinated sea water between 0.2 to 0.5 and 1,5 to 2,5 ppm

On CuNi 70-30, the potential in chlorinated sea water between 0.2 and 0.5 ppm is also maintained between -250 mVvs.SCE and -200 mVvs.SCE for a temperature inferior to 40°C. Compared to results obtained in natural sea water the increase of the potential to -50 mVvs.SCE with the risk of localized corrosion initiation. When chlorination rate is increased between 1.5 to 2.5 ppm, the potential is stabilized between -200 and -150 mV vs.SCE for a temperature inferior to 40°C. Nevertheless, an increase of the potential over -100 mVvs.SCE is noticed when the temperature is over 40°C.

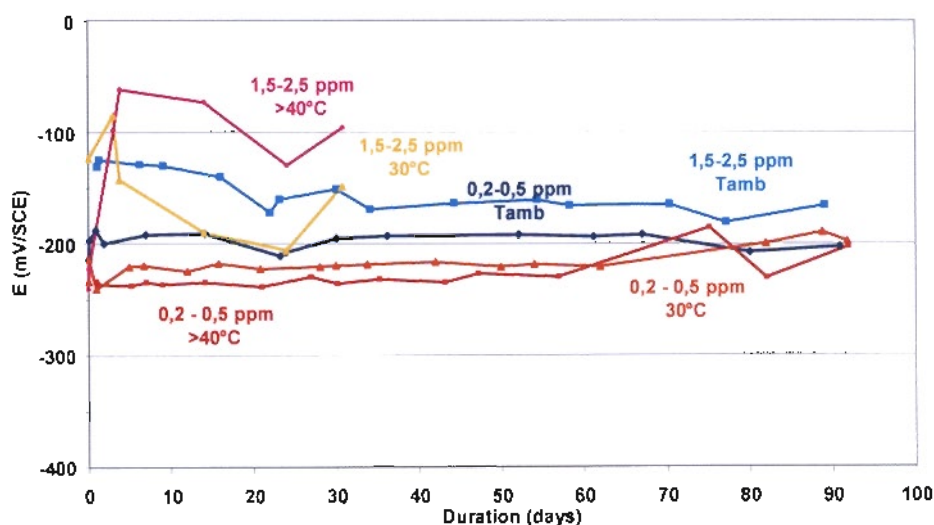


Figure 6

Potential measurements on CuNi 70-30 in Chlorinated sea water between 0.2 to 0.5 and 1,5 to 2,5 ppm

3.2 Passivation of Copper alloys in natural sea water

Anodic polarization curves are compared in clean sea water and polluted sea water. On CuNi 90-10 a large pseudo passivation threshold is observed between -230 mVvsSCE and -70 mVvs. SCE with current over 10 mA/m^2 (see fig 7). In polluted sea water, The Potential increases to -100 mVvs.SCE and no passivation threshold is shown. In these conditions the risk of localised corrosion is considered high.

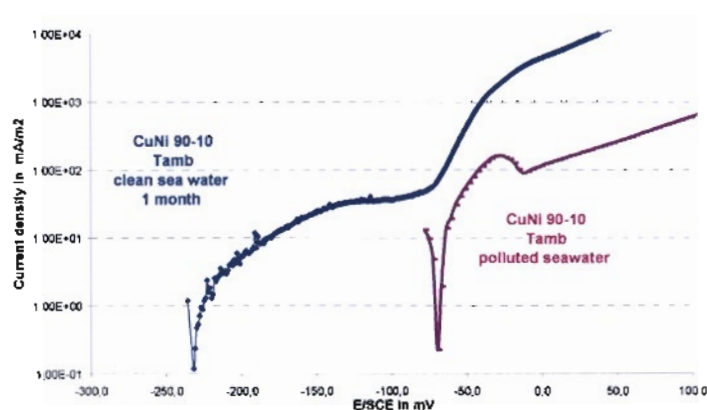


Figure 7 Anodic polarization curves of CuNi90-10 in natural sea water

On CuNi 70-30, a similar phenomenon is noticed, a large pseudo passivation threshold is shown between -200 and -50 mV/SCE with a maximum current of 10 mA/m^2 after 80 days of immersion duration. In polluted sea water the potential is increased over -50 mVvs.SCE with no passivation threshold (see fig 8).

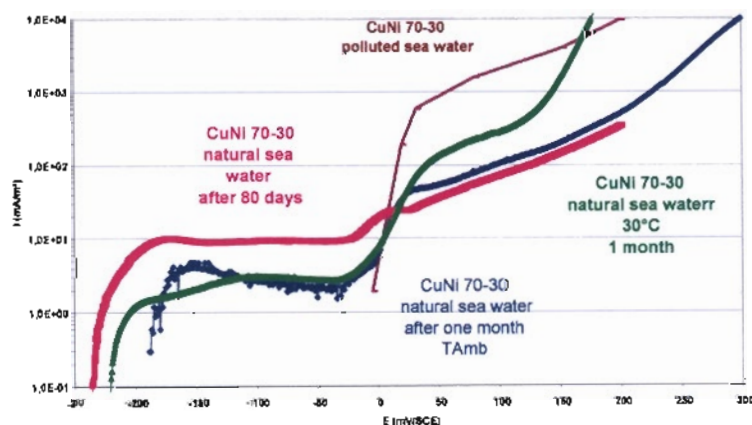


Figure 8 Anodic polarization curves of CuNi70-30 in natural sea water

3.3 Influence of chlorination on the passivation of copper alloys

On CuNi 90-10 A pseudo passivation threshold between -150 mVvs.SCE and -50 mVvs.SCE is obtained under chlorination treatment to 0.2 to 0.5 ppm. After one month of treatment the threshold progressively decreased to reach those obtained in clean natural sea water for a temperature inferior to 40°C that is between 10 and 100 mA/m². The increase of the chlorination dosage between 1.5 and 2.5 ppm have low incidence on passivation threshold obtained for a temperature inferior to 40°C (see fig 9).

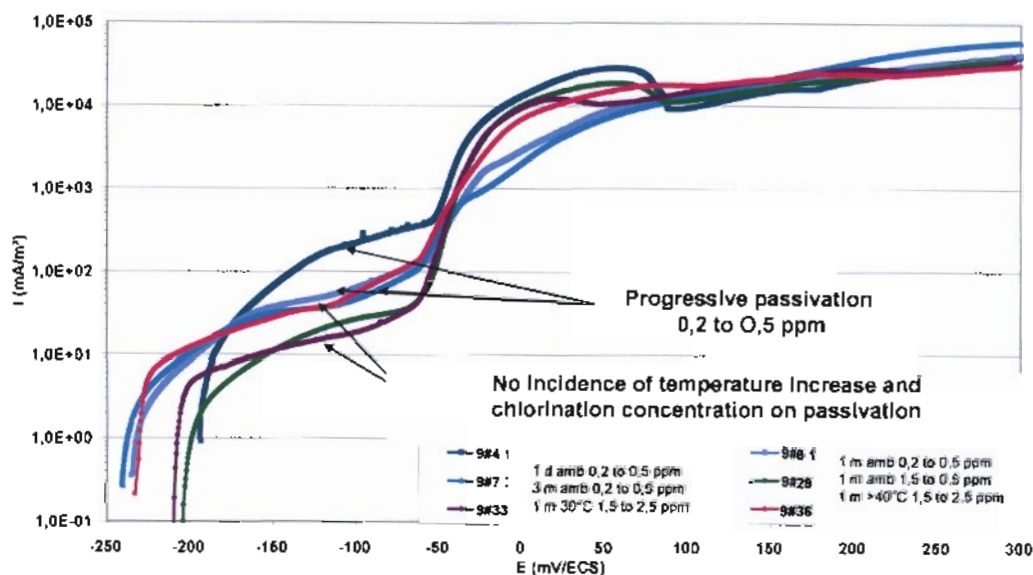


Figure 9 Anodic polarization curves of CuNi 90-10 in chlorinated sea water

When chlorination treatment is applied on CuNi 70-30 (see fig 10) , a large pseudo passivation threshold is observed between -200 and -50 mVvsSCE. The level of the threshold decreases with the duration of the treatment between 0.2 to 0.5 ppm. When the temperature is increased to 30°C, the same phenomenon is observed. Nevertheless, if the temperature is over 40°C, the pseudo passivation threshold is slightly higher. Compared to the anodic polarization curves obtained in clean sea water, the passivation threshold measured is considered as the same level after more than one month of immersion duration.

It was then considered that chlorination treatment has a beneficial effect on the passivation of Copper nickel alloy. These alloys are more tolerant to chlorination dosage increase associated with temperature peaks as long as they are maintained inferior to 40°C.

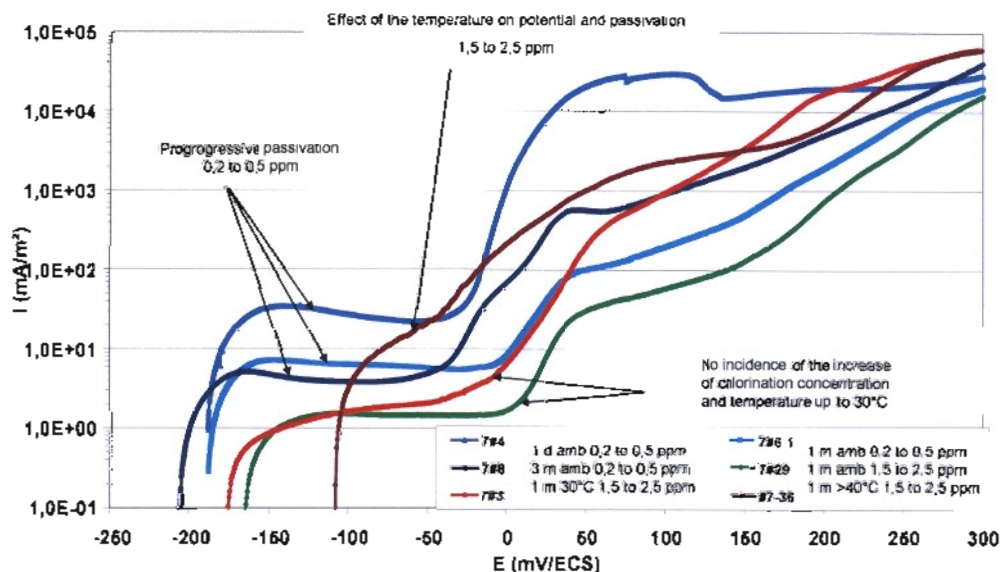


Fig 10 Anodic polarization curves of CuNi 70-30 in chlorinated sea water

3.4 Cathodic reduction rate in natural sea water

Cathodic reduction rate on CuNi 90-10 and 70-30 (see fig 11) established after long term immersion (33 months) in clean sea water have shown respectively a cathodic threshold of 10 mA/m² and 100 mA/m². The level of the current could be attributed to the effect of the biofilm on the surfaces if we consider a similitude between what is observed on stainless steels or base nickel alloys that is an increase in potential and an increase in cathodic reduction rate. As the maximum potential is obtained on CuNi 70-30 in natural sea water, the maximum reduction rate is observed also on CuNi-70-30.

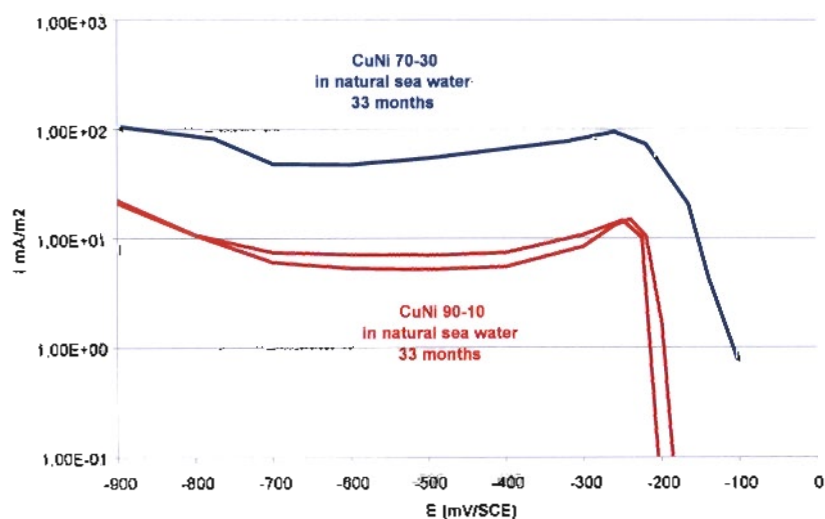


Fig 11 Cathodic polarization curves of CuNi 70-30 and CuNi 90-10 natural sea water

3.5 Influence of chlorination on cathodic reduction rate

When chlorination treatment is applied on these alloys, the cathodic reduction rate decreases progressively to about $1 \text{ mA} / \text{m}^2$ for CuNi 90-10 (See fig 12) and to $10 \text{ mA} \text{ m}^2$ for CuNi 70-30 that is 10 to 100 fold lower than those measured in natural sea water. An increase in chlorination dosage associated with an increase in temperature has no effect on the cathodic reduction rate of CuNi 90-10 and slightly effect on CuNi 70-30 in the range of potential under interest that is between -250 mVvs. SCE and -50 mVvs.SCE. Globally, it is noticed that chlorination treatment has a beneficial effect on cathodic reduction rate of copper nickel alloys. These results show that cathodic activation and consequently corrosion rates will keep low for a chlorination dosage between 0.2 to 0.5 ppm . When the dosage is increased between 1.5 to 2.5 ppm a similar observation is noticed . Nevertheless, CuNi 70 -30 presents a higher cathodic threshold when the temperature is over 30°C (see fig 13)

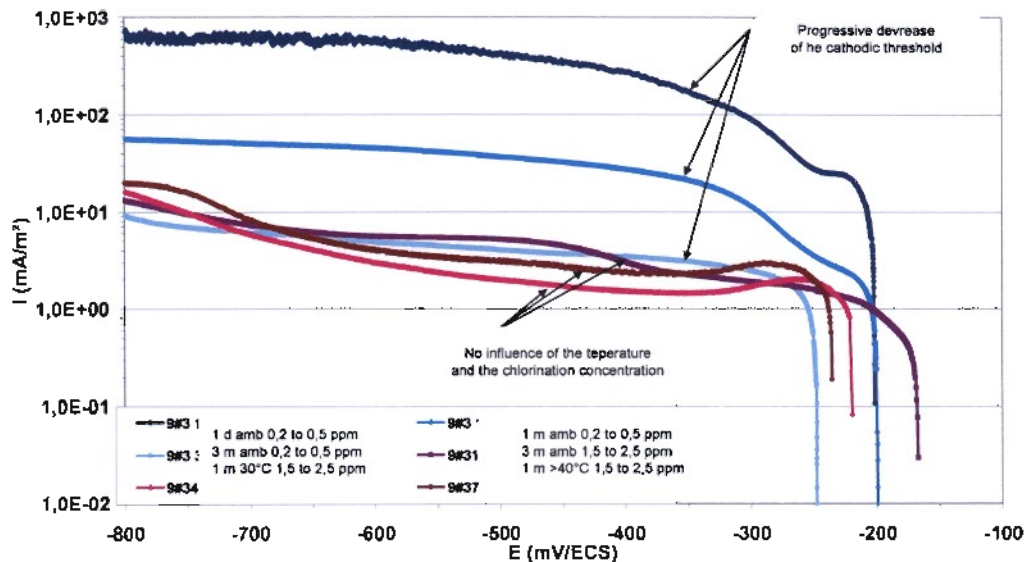


Fig 12 cathodic polarization curves of CuNi 90-10 chlorinated sea water

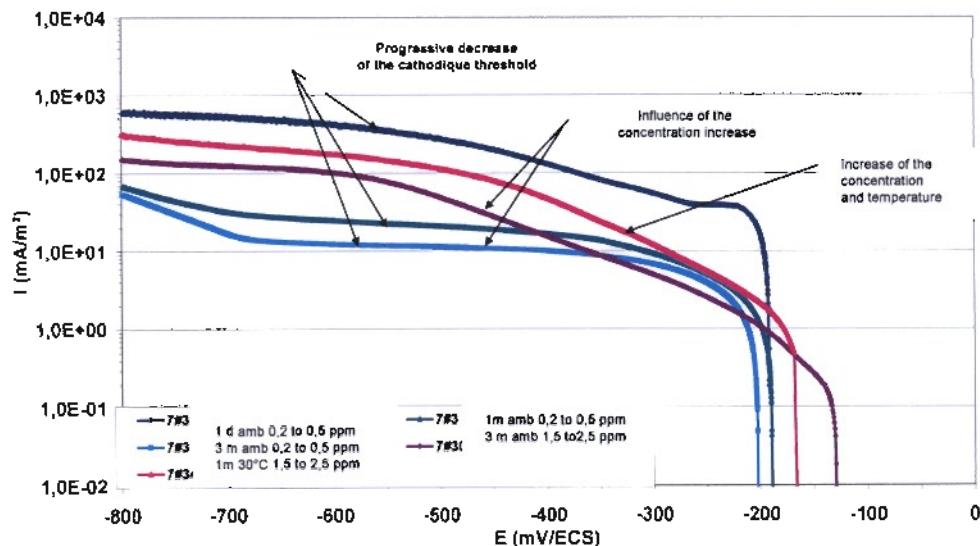


Fig 13 Cathodic polarization curves of CuNi 70-30 chlorinated sea water

3.6 Corrosion rate in chlorinated sea water

The corrosion rate estimated from weight loss measurements are given on fig 14. On CuNi 90-10, they are found inferior to 10 μm per year with chlorination treatment between 0.2 to 0.5 ppm for temperatures inferior to 40°C. On CuNi 70-30, the similar value is shown, they increase to 15 μm per year when the temperature is over 40°C. Under chlorination dosage between 1.5 to 2.5 ppm, corrosion rates are kept low inferior to 5 μm per year for all temperatures. More over, specimen examination after tests don't show any important localised corrosion after 3 months of exposure to chlorinated sea water in the various conditions, in all cases inferior to 10 μm per year. These results are considered at the level of those obtained in clean natural sea water.

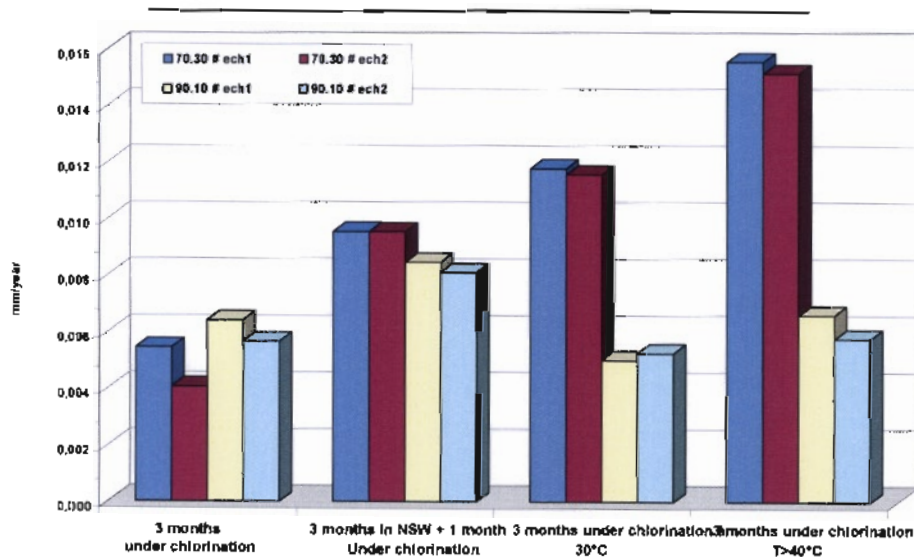


Figure 14 Corrosion rate on Copper nickel 90-10 and 70-30 in chlorinated sea water 0,2 to 0,5 ppm

4 CONCLUSION

An investigation has been conducted to better know the influence of the chlorination rate on the potential and also anodic rate and on the cathodic reduction rate on copper nickel 90-10 and 70-30.

The following conclusions can be drawn from this work.

Unlike what is observed on stainless steels and nickel based alloys, the potential of copper alloys does not increase with chlorination treatment. It was indeed maintained on Cu Ni 90-10 between -200 mV and -300 mVvs.SCE in various conditions of chlorination dosage and various temperatures inferior to 40°C. In these conditions, initiation risk of localised corrosion appeared low.

Chlorination treatment seems to improve the passivation of copper alloys according to anodic polarization curves results

The cathodic reduction rate decreases directly linked to corrosion rate with the duration of the treatment. And cathodic reduction threshold is inferior to those obtained in natural sea water in the potential range between -200 mV and -300 mVvs.SCE which is the range of potential of localised corrosion initiation risk. These results are obtained after maximum 3 months of treatment, a chlorination dosage up to maximum 2 ppm and a temperature inferior to 40°C.

In these conditions, it appears that chlorination treatment reduce the effect of biofilm on cathodic reduction rate with elsewhere low effect of oxidant species on the level of cathodic current.

Copper alloys will then be more tolerant to chlorination treatment than stainless steels or nickel based alloys and also more tolerant to the increase of chlorination dosage associated with temperature peak.

Corrosion rates measured through weight loss measurements do not show any aggravation in the presence of chlorination compared to what is observed in natural clean sea water. They are kept close to 10 µmper year corresponding to the value obtained in clean natural sea water. Else where localised corrosion is also estimated inferior to 10 µm par year.

In conclusion, the susceptibility to corrosion of Copper nickel alloys to usual sea water piping system chlorination dosage and temperature appeared low.

Chlorination treatment could then be recommended to :

Avoid micro and macro fouling in sea water piping system

Limit loss of heat transfer and maintain nominal flowing rate in piping system

Limit the risk of localised corrosion on copper nickel alloys in natural sea water

5 ACKNOWLEDGMENTS

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