

# **ELECTROCHEMICAL BEHAVIOUR OF COPPER-NICKEL ALLOY CUNI 90/10 IN CHLORINATED SEAWATER UNDER STAGNATING CONDITIONS**

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## **ABSTRACT**

The copper-nickel alloy CuNi 90/10 has been extensively used on different marine engineering structures. Its main application is piping for seawater handling and heat exchangers. Regardless of the macro fouling resistance of the material, seawater is often chlorinated. As there is only limited information available about the effect of chlorination on the corrosion rate of copper-nickel, a systematic approach is required to understand the effect of free chlorine on its corrosion behavior. The aim of the first part of this project has been the characterization of the electrochemical behavior of CuNi 90/10 in chlorinated seawater under stagnating conditions at room temperature. The results were obtained in synthetic seawater containing up to 5 ppm free chlorine using fresh and pre-exposed samples. Testing involved free corrosion potential and polarization resistance measurements, cathodic and anodic polarization as well as gravimetric and metallographic examinations. The data obtained did not reveal a distinct relationship between corrosion behavior and the free chlorine concentration. Instead, the corrosion rate was found to decrease with increasing formation of oxide layers. This fact underlines a clear advantage of CuNi 90/10 versus high alloy materials in applications where the presence of chlorine is often combined with high seawater temperatures. The data obtained is being used as the basis for a second part of the project, which compares chlorination under erosive conditions with previously reported data. This will be used to validate current practical service recommendations.

*Keywords: UNS C70600, seawater piping, chlorinated seawater, electrochemical behavior*

## INTRODUCTION

For many decades, the copper-nickel alloy CuNi 90/10 has been extensively used on different marine engineering structures. The main area of application is piping for seawater handling and heat exchangers. The single phase structure (fcc) of the CuNi-alloying system controls the excellent fabrication properties and weldability of copper-nickels. In clean oxygenated seawater, the alloy is resistant to uniform and localized corrosion. The corrosion behavior is independent of seawater temperature and together with resistance to stress corrosion cracking contributes to its wide application in the seawater desalination industry. Copper-nickel is resistant to macro fouling due to the release of copper ions and the structure of oxide layers that are established during natural corrosion processes[1]. Apart from the possibility of accelerated corrosion in water polluted with H<sub>2</sub>S and susceptibility to erosion attack under critical flow conditions, CuNi 90/10 provides reasonable technical and economical advantages when compared with other seawater piping materials.

In spite of the high macro fouling resistance of CuNi 90/10, the seawater is often chlorinated. Nevertheless, the effect of free chlorine on the corrosion behavior of copper-nickel is still little understood. In one report, the presence of 0.25 ppm free chlorine resulted in the accelerated corrosion of CuNi 90/10 during the first 30 days of exposure but decreased after that. [2]. In another report [3], it was stated that there was no negative effect of chlorine in the concentrations 0.2-0.5 ppm on the corrosion behavior of copper-nickel alloy from many years experience in coastal power and process industries.

Francis[4, 5] published the results of tests related to the effect of chlorine additions in the range between 0.3 and 4.0 ppm using electrochemical techniques and jet impingement apparatus (jet velocity 9 m/s for 2 months) in natural seawater. The main goal of this study was the evaluation of materials behavior under extremely erosive conditions, which can take place when foreign bodies become lodged in heat exchanger tubing. The corrosion products formed on CuNi 90/10 during chlorination led to appreciable anodic and cathodic polarization, and, thus, somehow to an improvement in corrosion resistance. Nevertheless, these products impaired the mechanical resistance of the copper-nickel surface leading to an increase in impingement susceptibility. For continuous and intermittent chlorine additions, the residual concentrations of 0.3 and 0.5 ppm respectively were recommended. The author pointed out that his results require more research in this area.

It should be noted that the jet impingement conditions in the last two studies [4, 5] are not common in seawater piping with bigger dimensions and, therefore, the current practical recommendations require validation. The main aim of the first part of this project has been the characterization of the electrochemical behavior of CuNi 90/10 in chlorinated seawater under stagnating conditions. The results were obtained in synthetic seawater containing up to 5 ppm free chlorine using fresh and pre-exposed samples. Testing involved free corrosion potential and polarization resistance measurements, cathodic and anodic polarization as well as gravimetric and metallographic examinations.

## EXPERIMENTAL

### ***Material under Study***

The material under study was UNS 7060X to EEMUA 144 with the nominal composition given in TABLE 1. Alloy UNS 7060X is modified from the following national designated alloys – UNS C70600, BS CN102, DIN 2.0872 being predominantly used in the offshore industry. When compared with UNS 70600, this material contains slightly higher iron content for improved erosion resistance and has lower limits of some impurities. The material was in the fully annealed as-delivered condition. Two different types of samples were used: flat plates (50 x 30 x 2 mm) and tube half shells (30 x 1.5 mm).

### **Testing Conditions**

To provide reproducible results, the experiments were carried out in synthetic seawater in accordance with ASTM D1141 at pH 8.2 at room temperature  $21 \pm 2^\circ\text{C}$ . The absence of biological activity in chlorinated natural seawater was the basis for the assumption that no difference between clean, natural and synthetic seawater is expected. Sodium hypochlorite was used to achieve free chlorine concentrations: 0, 0.3, 0.5, 1.0, 3.0, and 5.0 ppm; the upper levels cover possible high concentrations at injection points under service conditions. The chlorine concentration was determined using a colorimetric method<sup>1</sup>.

During the pre-tests in glass beakers containing CuNi 90/10 samples, a rapid decrease of the free chlorine concentration was determined indicating that the corrosion products catalyze the consumption of the free chlorine. The application of the polymer storage tanks hampered the reduction of the free chlorine concentration considerably. Although, the concentration was controlled each working day and subsequently adjusted to the nominal value, the chlorine concentration fluctuated as shown in the FIGURE 1. The chlorinated seawater was fed once-through at the rate of 10 ml/h into overflow glass beakers containing the samples. The experimental set-up is shown in the FIGURE 2. As a result, a quasi stagnating condition with relatively constant metal ion concentration was achieved.

### **Investigation Techniques**

To investigate the effect of the growing oxide layer, the samples were exposed in two different series. The material in series A was exposed for 9 weeks in seawater containing the corresponding free chlorine concentrations. The samples in series B were pre-exposed in non-chlorinated seawater for 6 weeks with subsequent exposure for 9 weeks under chlorinated conditions.

All electrochemical data were obtained using the flat samples (50 x 30 x 2 mm). The evaluation of the free corrosion potential and the polarization resistance was carried out using single samples daily versus Ag/AgCl reference electrode. The polarization resistance measurements were conducted by the non-dynamical polarization of the samples  $\pm 10$  mV vs. the free corrosion potential.

Polarization experiments were conducted starting at -300 mV at the rate of 10 mV/min to +300 mV versus free corrosion potential versus the saturated hydrogen electrode (SHE). For series A, the data was evaluated after 0, 3, 6, and 9 weeks and for series B after 5 and 9 weeks of exposure in seawater containing the corresponding free chlorine concentration.

The weight loss evaluation and the calculation of corrosion currents were carried out on the half shells (30 x 1.5 mm). Prior to the gravimetric measurements, the samples were cleaned in an ultrasonic bath containing 10 % aqueous citric acid solution.

The microscopic examination using a light microscope and a scanning electron microscope (SEM) was undertaken on flat samples after different stages of exposure for each series.

## **RESULTS**

### **Free Corrosion Potential**

The free corrosion potentials of series A are given in FIGURE 3. After approximately 100 hours of exposure, the potential of the sample without chlorine increased from about -190 mV to about -70 mV. After 400 to 800 hours, the ennoblement of the remaining samples followed to about -100 mV. During the same period of time, the material with 0.0, 0.3, and 0.5 ppm chlorine revealed potential fluctuations between -60 and -190 mV. After 800 hours, the potential of all samples stabilized at around -100 mV with a slight decrease towards the end of exposure. During the entire duration, the sample in seawater

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<sup>1</sup> Merck Microquant®

chlorinated with 1 ppm remained stable at around -200 mV. The potential of the samples used for the measurements of the polarization resistance revealed comparable behavior.

After pre-exposure of series B, the free corrosion potential of the samples experienced a rapid differentiation in the range between -250 and -25 mV (FIGURE 4), whereas the samples exposed to the seawater with lower chlorine content revealed a more negative corrosion potential. As before, the same potential distribution was confirmed by the samples used for the polarization resistance measurements.

#### ***Polarization Resistance Measurements***

The results of the polarization resistance measurements for series A are given in FIGURE 5. There was a general trend of increasing polarization resistance with time. This was particularly the case for 0.5 and 1 ppm Cl. For series B, the same trend was observed (FIGURE 6). The values of the sample which was chlorine free experienced significant fluctuations; therefore the results are not displayed here. These fluctuations were attributed to very low corrosion currents.

#### ***Polarization Experiments***

FIGURES 7-10 provide results of polarization experiments for series A and FIGURES 11-12 for series B. FIGURE 7 shows the polarization curves immediately after series A exposure begins. The cathodic branch of the curves was relatively flat. When compared with the first measurement, the slope of cathodic branches increased slightly after 3 weeks of exposure and remained unchanged (FIGURE 8, 9, and 10).

In the beginning of the exposure period of series A, the anodic metal dissolution was undisturbed by the presence of chlorine (FIGURE 7). With increasing exposure time, a passive region was observed with a sharp increase in the current at potentials of ~200 mV. This breakdown potential was evaluated at all chlorine concentrations. The presence of the oxide scale which is formed during exposure leads to a decrease in the anodic currents. For both cathodic and anodic reactions, no dependence of the chlorine concentration was evaluated (FIGURE 7, 8, 9, and 10).

As given by FIGURES 11 and 12, a dependence of the cathodic reaction on chlorine concentration was obvious for the pre-exposed CuNi 90/10 samples. After 5 and 9 weeks in chlorine containing solution, the cathodic current increased with chlorine concentration. The main characteristics of the anodic reactions were comparable with those of series A.

#### ***Evaluation of Corrosion Rates***

As given by FIGURES 13 and 14, the weight loss data of the tubular samples was used to determine the corrosion current densities depending on the time of exposure. For series A (FIGURE 13), continuously decreasing corrosion rates were obtained with time of exposure for all chlorine concentrations in the range 1.6-2  $\mu\text{A}/\text{cm}^2$  to 0.6-0.8  $\mu\text{A}/\text{cm}^2$ . Although the lowest and the highest corrosion current densities were evaluated for the 0 and 5 ppm chlorine, the intermediate concentrations did not reveal any influence of the chlorine concentration. Interestingly, the data for series B demonstrated corrosion rates further decreasing with time of exposure (FIGURE 14).

In addition, FIGURE 15 compares the corrosion current densities, which were calculated using different methods. The basis for this diagram were the data obtained from the samples exposed to seawater containing 5 ppm chlorine in series A in relation to exposure time. It is clear that the corrosion rates decreased during the first weeks of exposure and remain level between 1 and 3  $\mu\text{A}/\text{cm}^2$  until the end of exposure. It should be noted that similar comparative data which is not shown here was obtained for series A and B at all free chlorine concentrations.

### ***Macroscopic Imaging***

FIGURE 16 gives an overview of representative tubular samples in series A exposed in seawater containing 0.0, 0.5, 3.0, 5.0 ppm free chlorine after 3 and 9 weeks of exposure. The oxide layers were brown to dark brown and relatively uniform. In addition, it was observed that, depending on both the time of exposure and the free chlorine concentration, the fraction of a light green top layers increased (here displayed as a grey tone).

### ***Imaging of Cross Sections***

FIGURE 17 demonstrates a typical cross section for CuNi 90/10 after 9 weeks exposure in seawater containing chlorine. The well adhered oxide layers on all samples reached a thickness up to 15  $\mu\text{m}$ . Nevertheless, exfoliation of the oxide layer was found for samples with or without chlorine dosing due to a drying out effect which is typical for copper-nickel alloys.

### ***SEM Examination***

The SEM-Images are demonstrated by FIGURES 18 and 19. The Energy Dispersive X-Ray (EDX) analysis of the oxide film on CuNi 90/10 exposed under different conditions revealed a multi-layered structure: the porous outer layer enriched with copper, oxygen, and chlorine (presumably of copper hydroxyl-chloride) with crystalline topography which became more distinct with time and chlorine concentration. The layer below was found to be enriched with iron and nickel. The layer next to the bulk was enriched with copper and chloride. FIGURE 20 shows the representative EDX-results evaluated on the series B exposed to 5 ppm Cl for 9 weeks. Similar results were reported by other researchers after investigating the samples exposed to natural seawater [6, 7]. After 9 weeks exposure without chlorine, samples of both series showed relatively dense oxide topographies. Also with chlorine dosing, the oxide scale kept intact.

## **DISCUSSION**

### ***Free Corrosion Potential***

From the measurement of the free corrosion potential of series A, it can be assumed that the presence of chlorine hampered the oxide film formation. However, with time this effect is less distinct due to the potential ennoblement. In the case of series B, the effect of the chlorine on potential is evident. When compared with other materials such as high alloy stainless steels where corrosion potential can be altered by several hundreds of mV (0-100 mV for 0.1-0.2 ppm to 500-700 mV for 0.5-1.0 ppm free chlorine vs. SCE), the range of potential variations for CuNi 90/10 is narrower revealing a behavior with significantly reduced sensitivity towards free chlorine. Therefore, the risk of localized corrosion is reduced in contrast to high alloy materials. Moreover, as revealed by the EDX investigation and other studies, in contrast to high alloy materials, chloride anions are one of the important oxide film constituents.

### ***Polarization Resistance Measurements***

The overall results for both series, demonstrate a better performance of the samples exposed to the seawater containing intermediate chlorine concentrations of 0.5 and 1 ppm. These chlorine concentrations appear to increase polarization resistance compared with chlorine free conditions. However, the higher chlorine concentrations show comparable polarization resistance with chlorine free conditions which increases with time of exposure. This fact doesn't indicate any negative influence of the free chlorine.

### ***Polarization Experiments***

For series A, the slope of the cathodic curve increases with time indicated that the reaction mechanisms of the cathodic oxygen reduction changes from diffusion controlled to reaction controlled with

increasing exposure time, due to the growing oxide layer.

After 3 weeks exposure, the anodic reactions of both series demonstrate a distinct passive region, which is in contrast to the results given by the Ref. [4]. Independent of the free corrosion potential, the chlorine concentration as well as the duration of exposure, the passive region extends up to  $200 \text{ mV} \pm 20 \text{ mV}$ . It is suggested that this distinct breakdown potential is attributed to the oxidation of Cu(I) to Cu(II). The standard potential for this reaction is:

$$U_0 = 153 \text{ mV} (\text{Cu}^+ = \text{Cu}^{2+} + e^-) \text{ vs. SHE [8]}$$

Therefore, the presence of the passive region and the comparability of the breakdown potentials are regarded as characteristic of the oxide layers which improve with time and which are virtually independent of the free chlorine concentration.

For series B, the cathodic current increases with chlorine concentration. However, in comparison with series A, the cathodic currents of series B are clearly lower, especially for lower chlorine concentrations. It reveals that an oxide scale has a positive influence which is not degraded by the presence of chlorine. This consideration is confirmed by the measurements of the polarization resistance. It is suggested that increase of cathodic currents as such is associated with the reduction of chlorine on the cathodic sites.

#### **Effect of Chlorine on the Corrosion Rate**

A rapid decrease in corrosion rate for series A after 3 weeks of exposure is evident (FIGURE 15). For longer exposures (FIGURES 13, 14, and 15), the free chlorine concentration has no appreciable effect on the corrosion rate; the corrosion rates of both series continuously decrease with time. This means that after the exposure of 9 weeks the approximate corrosion rate of series A and series B is  $16 \mu\text{m/a}$  and  $13 \mu\text{m/yr}$  respectively ( $1 \text{ mA/cm}^2 = 23,2 \text{ mm/yr}$ ,  $1 \mu\text{A/cm}^2 = 0,0232 \text{ mm/yr}$ ). The oxide layer established during the pre-exposure of the materials was not affected by the chlorine additions. The corrosion rate is still higher than expected for tubes under practical service conditions. However, from the published data it is known that the corrosion rate continuously decreases within first years of exposure and it can be assumed that after one year exposure the corrosion rate is  $4 \mu\text{m/a}$  and after 3 years  $2 \mu\text{m/a}$  [9].

### **CONCLUSIONS**

The investigation shows that the influence of chlorine on the corrosion rate under stagnant conditions is not strong and the quality of the oxide layer is not affected by the presence of chlorine. This means as long as the oxide scale is stable, the influence of chlorine dosing on the expected lifetime of CuNi-tubes is not obvious. For CuNi90/10 systems without erosive conditions, the evaluated data reveal that actual practical recommendations are conservative and an increase up to 5 ppm free chlorine can be considered. This fact underlines a clear advantage of CuNi 90/10 in applications e.g. for fire fighting systems with predominantly stagnating conditions where the presence of chlorine is often combined with high seawater temperatures.

### **FURTHER WORK**

The data presented is being used as the basis for the second part of the project evaluating the effect of the chlorine concentrations up to 5 ppm on the critical shear stress of CuNi 90/10 using different investigation techniques. The results of the ongoing work under erosive conditions will be compared with previously reported data, and also will be used to validate the current practical service recommendations.

TABLE 1:

NOMINAL COMPOSITION OF THE MATERIAL UNDER STUDY\*

	Cu	Ni	Fe	Mn	C	Pb	P	S	Zn	Others
UNS 7060X	Rem.	10-11	1.5-2	0.5-1	0.05	0.01	0.02	0.02	0.2	0.3

\*: Composition in wt.%, single values represent the maximum content.

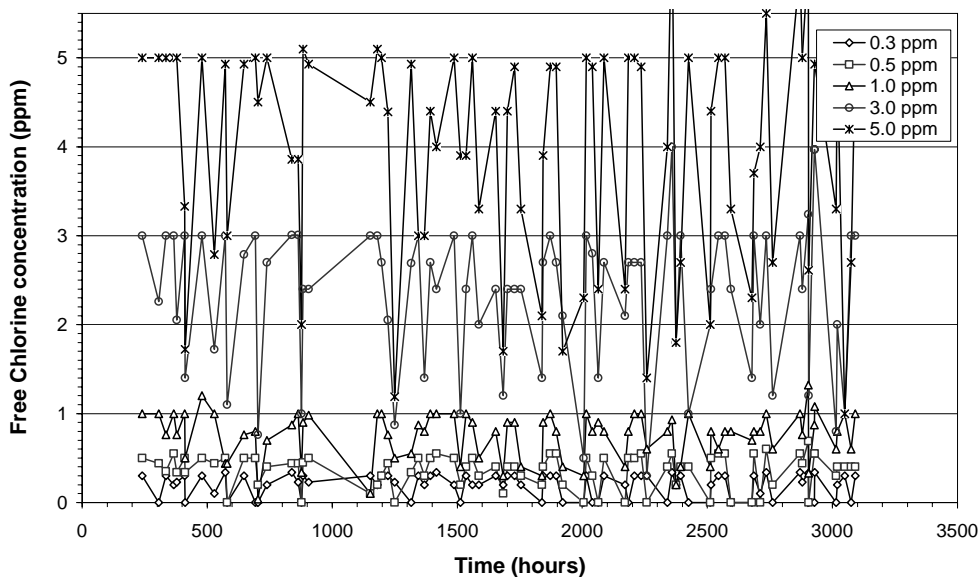


FIGURE 1: Free chlorine concentration measured in the storage tanks before adjustment to the nominal concentration.

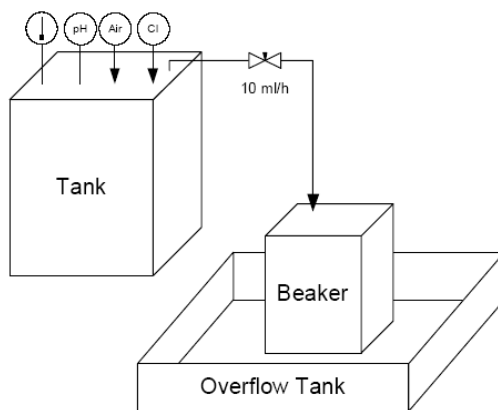
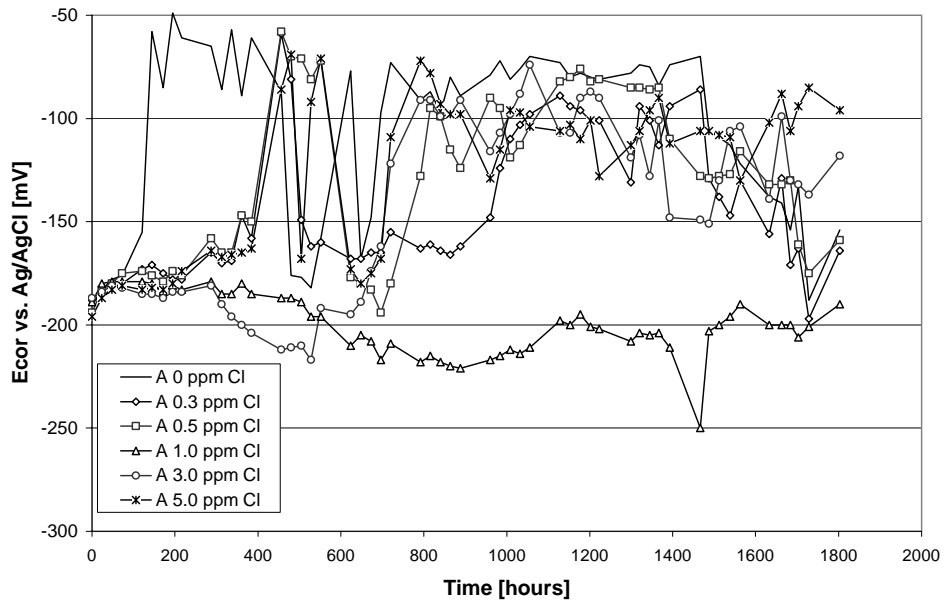
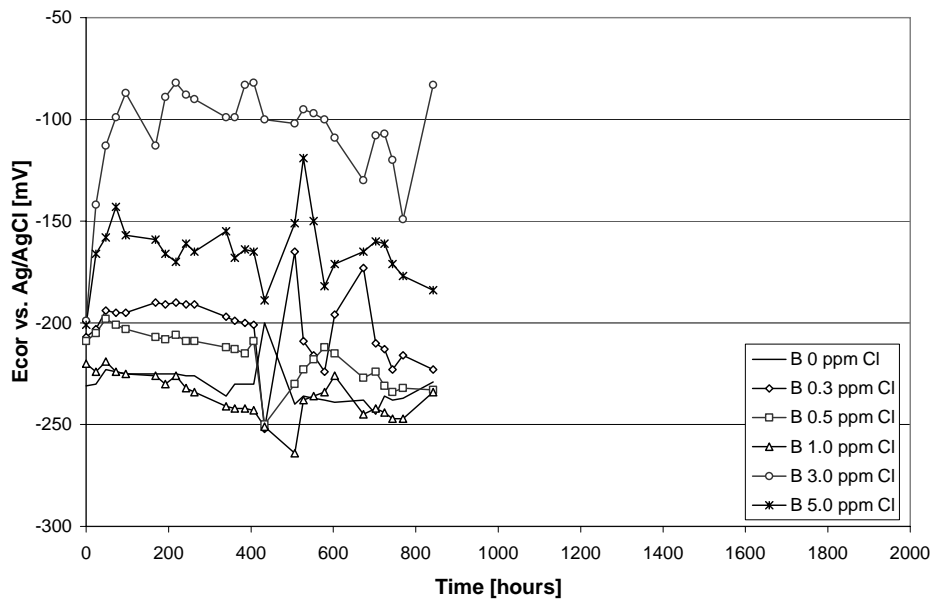


FIGURE 2: Experimental set-up.

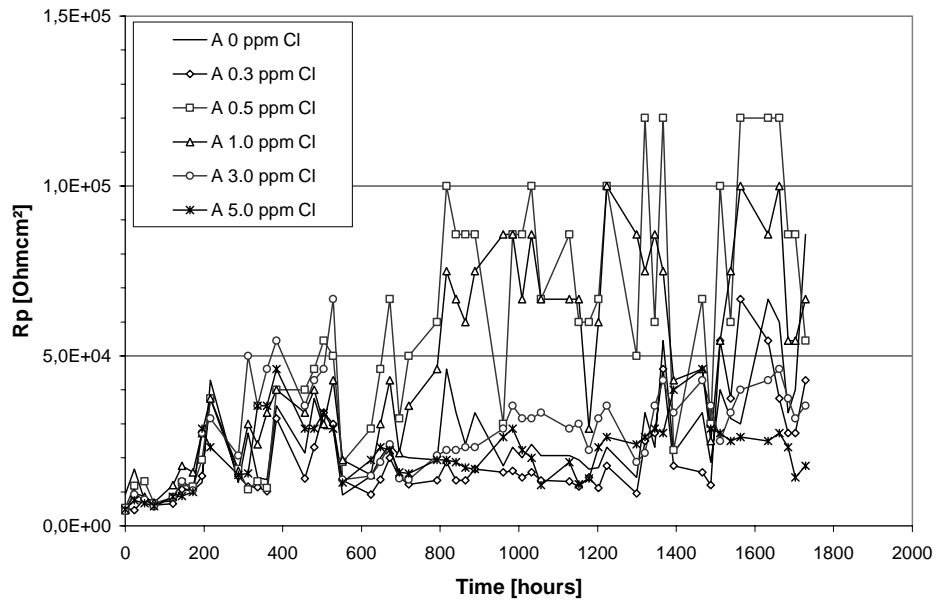


**FIGURE 3: Free corrosion potential of series A. The potential values were evaluated using single samples.**

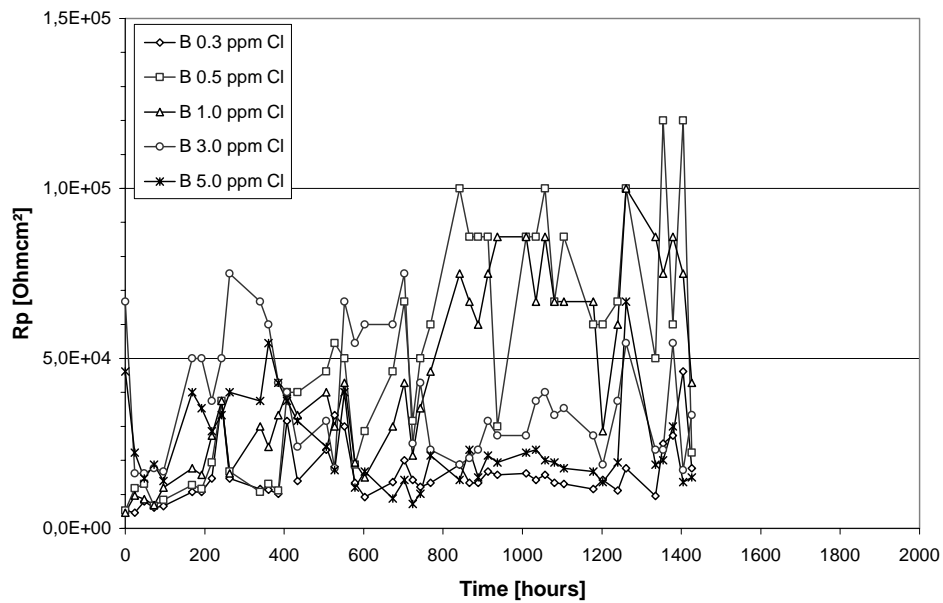


**FIGURE 4: Free corrosion potential of series B (pre-exposed). The potential values were evaluated using single samples**

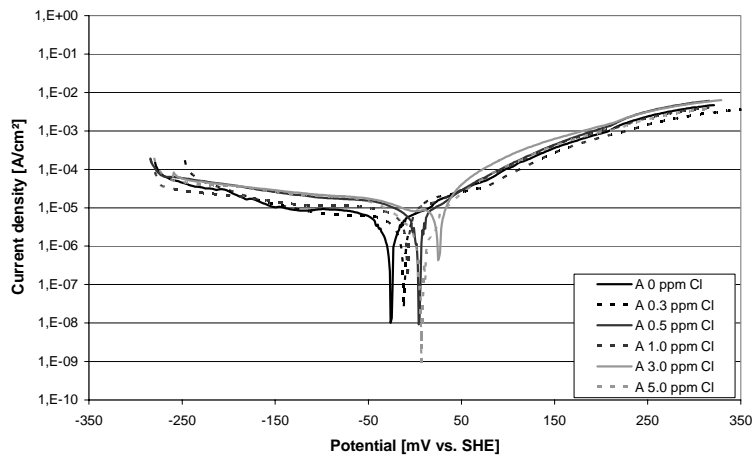




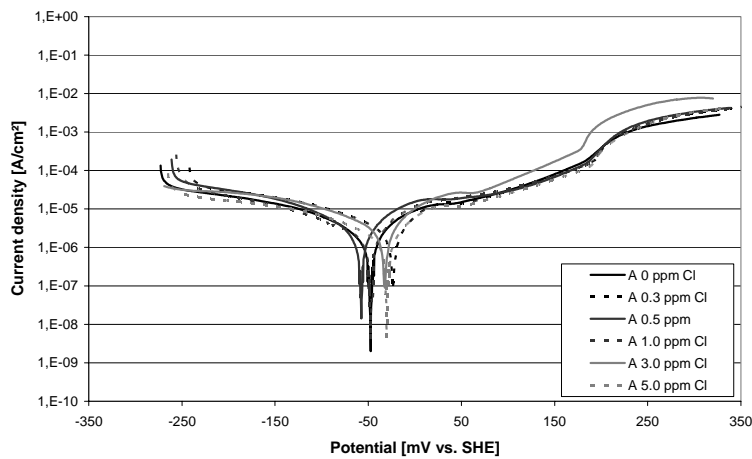
**FIGURE 5: Polarization resistance of series A. The Rp values were evaluated using single samples.**



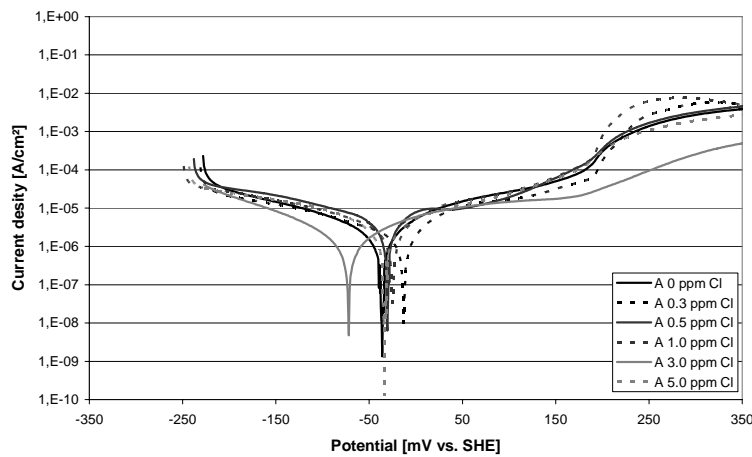
**FIGURE 6: Polarization resistance of series B (pre-exposed). The Rp values were evaluated using single samples.**



**FIGURE 7: Polarization curves from series A after exposure begin**



**FIGURE 8: Polarization curves from series A after 3 weeks of exposure**



**FIGURE 9: Polarization curves from series A after 6 weeks of exposure**

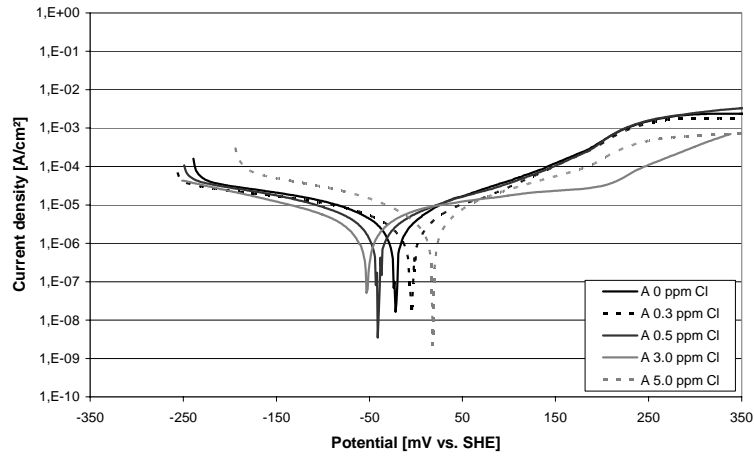


FIGURE 10: Polarization curves from series A after 9 weeks of exposure

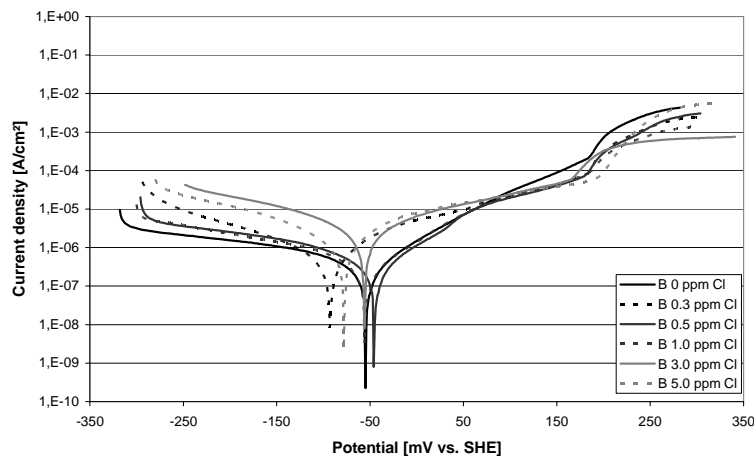


FIGURE 11: Polarization curves from series B after 5 weeks of exposure

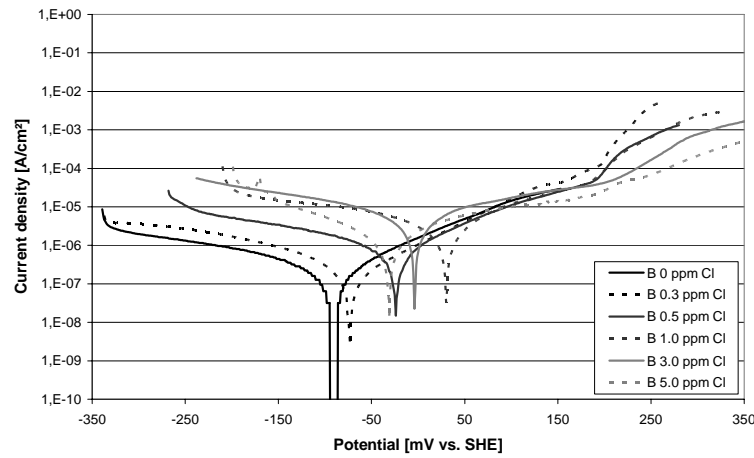
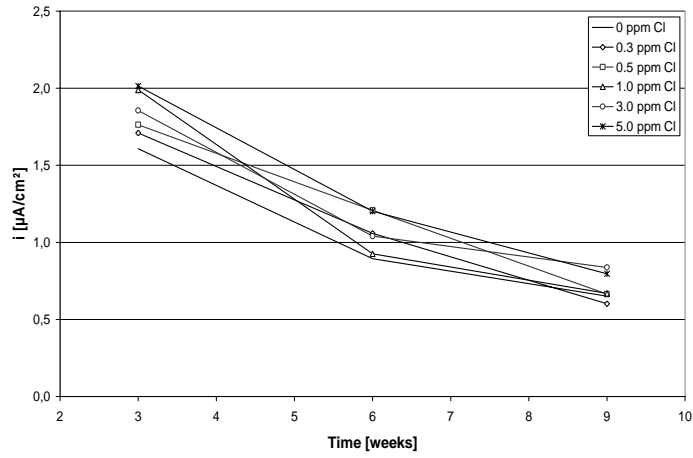
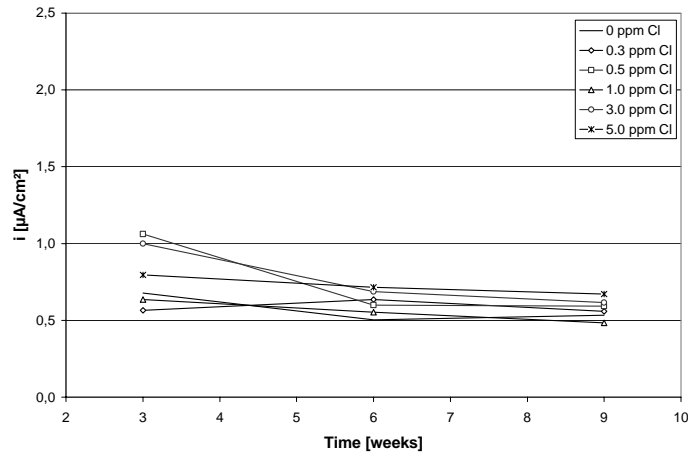


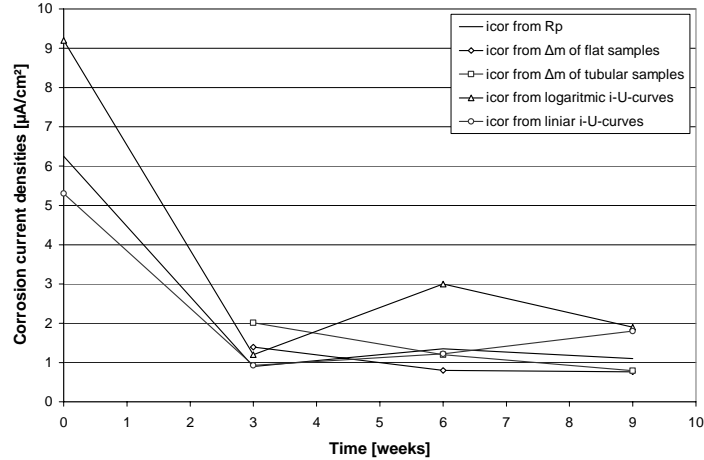
FIGURE 12: Polarization curves from series B after 9 weeks of exposure



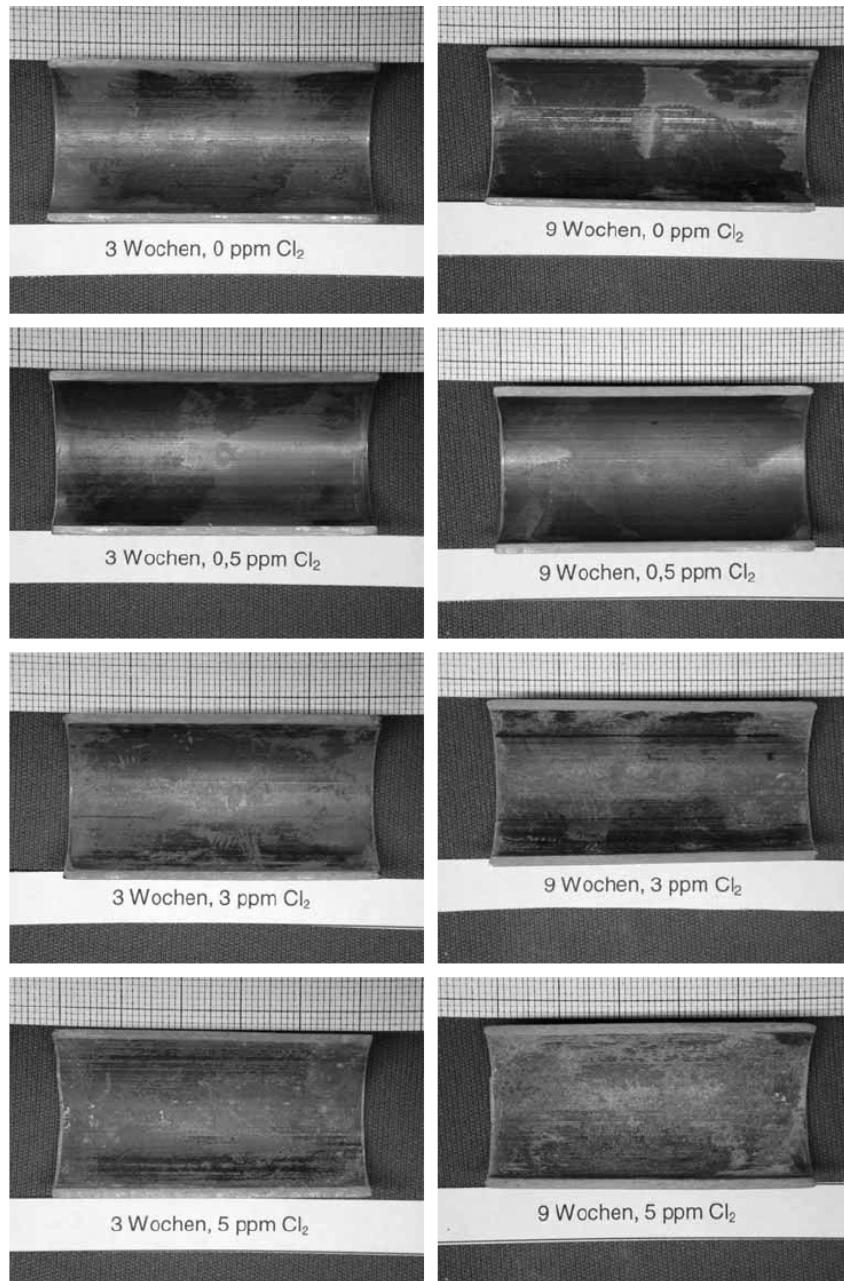
**FIGURE 13: Corrosion current densities calculated from the mass loss of tubular samples from series A ( $1 \mu\text{A}/\text{cm}^2 = 0.0232 \text{ mm/a}$ )**



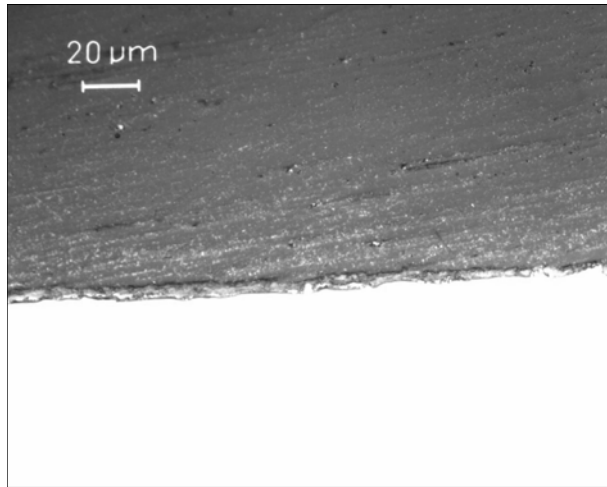
**FIGURE 14: Corrosion current densities calculated from the mass loss of tubular samples from series B ( $1 \mu\text{A}/\text{cm}^2 = 0.0232 \text{ mm/a}$ )**



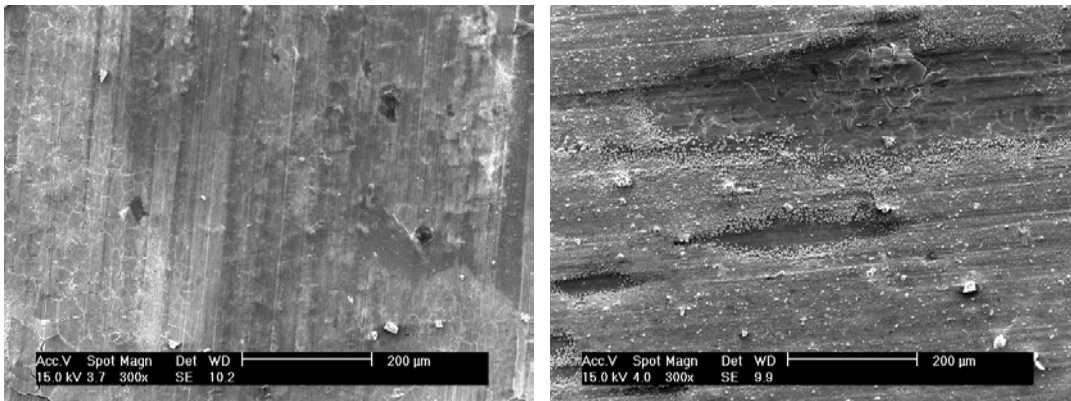
**FIGURE 15: Comparison of corrosion current densities calculated by different methods using the data of the samples exposed in seawater containing 5 ppm free chlorine from series A**



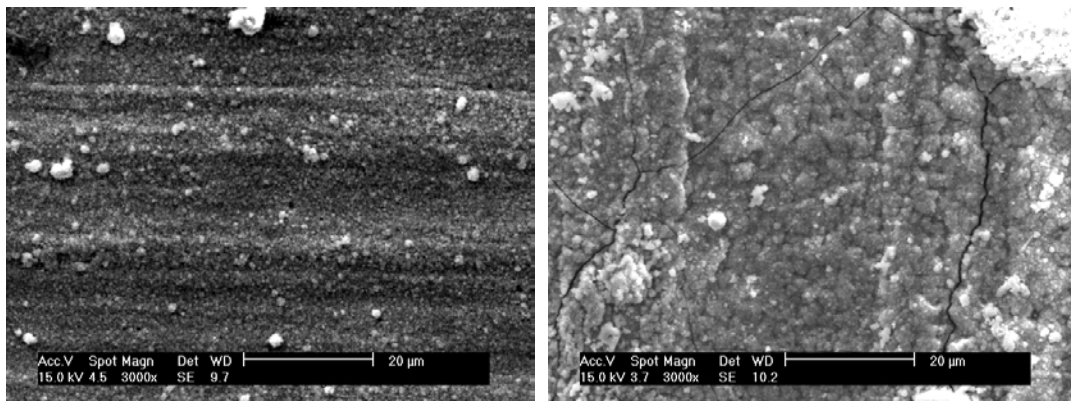
**FIGURE 16: Selected macroscopic images of series A after 3 (left) and 9 (right) weeks of exposure in seawater containing 0, 0.5, 3.0, and 5.0 (from the top to the bottom) ppm free chlorine. The fraction of light green layer, which increases with time and chlorine content, is displayed here as non-shiny grey tone.**



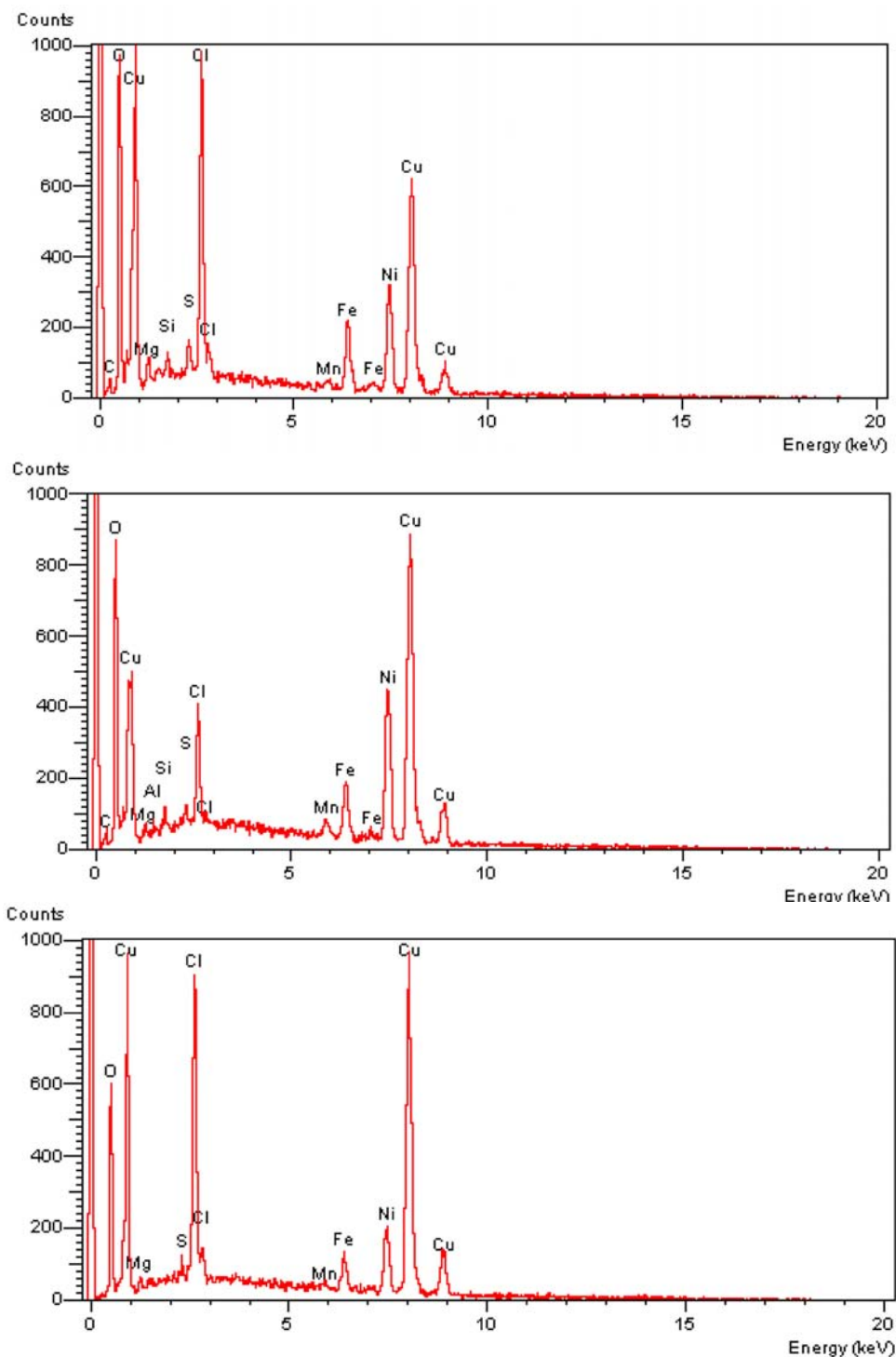
**FIGURE 17: A representative cross section of series A after 9 weeks exposure to seawater containing 5 ppm free chlorine.**



**FIGURE 18: SEM images of the surfaces after exposure to chlorine free seawater. Left: after 9 weeks (series A), right: after 15 weeks (series B).**



**FIGURE 19: SEM images of the surfaces after exposure to chlorine containing seawater. Left: 3 ppm Cl (series A), right: 5 ppm (series B).**



**FIGURE 20: Chemical composition of the outer, middle, and inner layers (from the top to the bottom) evaluated by means of EDX-analysis on series B exposed to 5 ppm Cl during 9 weeks.**

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