CEA-CONF-11272

FR9302335

APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TO MONITOR SEAWATER FOULING ON STAINLESS STEELS AND COPPER ALLOYS

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Abstract
Electrochemical impedance spectroscopy may be applied to detect and to follow seawater fouling. Experiments have been conducted with natural seawater flowing inside tube-electrodes at temperatures between 30°C and 85°C. With stainless steel tubes, mineral and organic foulings have been followed; a linear relationship between the dry weigth of the organic fouling and its electrical resistance, has been observed. On copper alloy tubes, only mineral deposits have occurred and so have been detected by impedance spectroscopy.

1-INTRODUCTION

In components exposed to seawater, mineral and organic deposits on surfaces are known as "fouling". These deposits decrease heat transfert, increase fluid frictional resistance, reduce the efficiency of cathodic protection, accelerate corrosion processes,...For instance, the presence of microbiological film (called "slime" or "biofilm") is often put forward to explain that corrosion in natural environments is higher than in artificial and sterile conditions.
The objective of this paper is to show that Electrochemical Impedance Spectroscopy (EIS) may be applied to the detection and the evaluation of seawater fouling (organic and mineral deposits)

2-BACKGROUND

EIS is a technique which has found many applications in corrosion research and which is now commonly carried out in order to collect wide informations concerning metal/solution interface.
EIS may be successfully applied to seawater fouling if this fouling can be characterized by:

- an electrical resistance, R_f
- an electrical capacitance, C_f

The addition of these fouling parameters to the parameters of the metal/solution interface leads to the equivalent circuit shown in figure 1. With such a model, the Nyquist complex plane plot is made of two semi-circles, as shown on figure 1, with time constants given by:

$$t_f = R_f . C_f \quad \text{and} \quad t_m = R_t . C_d$$

The semi-circle occurring at higher frequencies will be caused by seawater fouling if t_f is higher than t_m. The shape of the plot will appear as two distinct semi-circles if the following criterions are met:

$$0.2 < R_f/R_t < 5 \quad \text{and} \quad t_m/t_f > 20$$

These values are probably questionable, but they clearly indicate that the evidence of fouling (R_f) will be correlated to the corrosion behaviour (R_t). For instance, with titanium which is virtually immune in seawater, R_t values are very high and so the first criterion will be met only when R_f values will be high also, so only when deposits will be thick enough.

Figure 1 : Equivalent circuit model for seawater deposits and its Nyquist plot
(without diffusion)

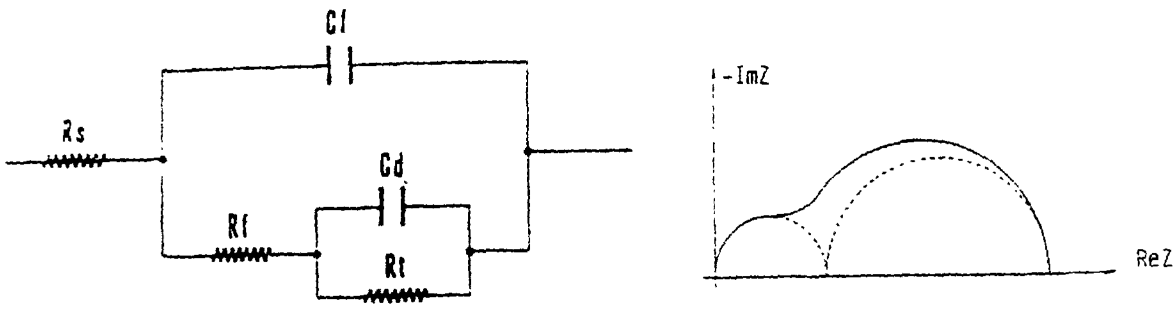


Figure 2 : Scheme of the electrochemical cell with 3 tube-electrodes

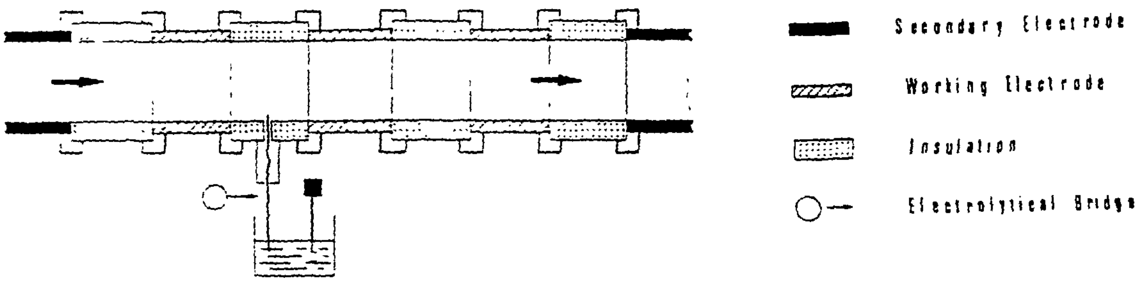
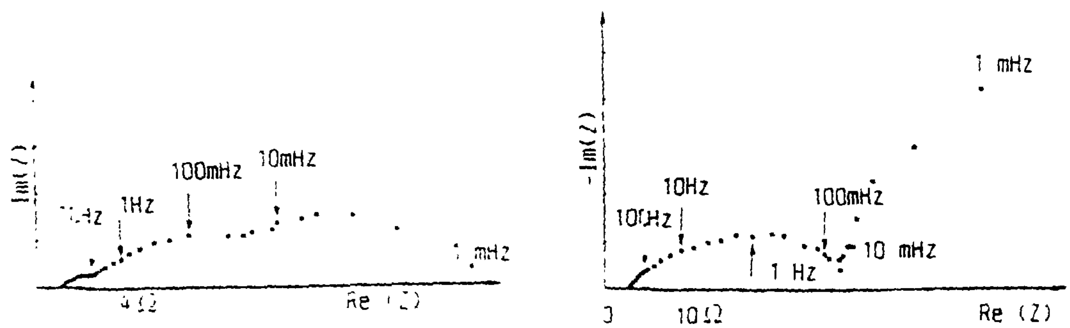


Figure 3 : EIS diagrams obtained with Cu90- Ni10 at 80°C

3-a: 3% NaCl solution **3-b: natural seawater**



3-EXPERIMENTS

Experiments have been conducted in SIRIUS facility which is located at La Hague (Normandy/France). SIRIUS is a single pass loop which operates with natural seawater at temperatures between 20°C and 150°C.
Electrochemical measurements have been made on tube-electrodes (internal diameter: 17 mm. length: 50 mm). Seawater flows inside these tube-electrodes at 2 $m.s^{-1}$. An electrolytic bridge connects the seawater flowing inside to an external saturated calomel reference electrode (figure 2).
Impedance measurements have been performed at the free corrosion potential using a potentiostat and a frequency response analyser (Solartron Schlumberger 1286 and 1250).

4-RESULTS AND COMMENTS

The experiments have included titanium, stainless steel and copper alloy electrodes covered by various seawater deposits.

In order to illustrate the results obtained with copper alloys, two EIS diagrams are shown on figure 3: they have been obtained at 80°C, after 20 hours of exposure. A 3% NaCl solution flowed inside the tube-electrode for the first diagram (figure 3a), and the observed relaxations were only due to corrosion phenomenon. With natural seawater, only one relaxation has been observed around 1 Hz and increased with time; it was due to the formation of mineral deposits which occurs under these conditions, mainly hydroxides above 70°C. The fouling resistance calculated from the EIS diagram of the figure 3b (R_f= 850 $\Omega.cm^{-2}$) is correlated to the weight of the mineral deposits (0.2 $mg.cm^{-2}$). By following the values of the fouling resistance, the increase in the precipitation of hydroxides (mainly $Mg(OH)_2$) has been pointed out up to 85°C as shown on figure 4.
On copper alloy tube-electrodes, no fouling (neither organic nor mineral) has occurred at low temperature (35°C).

On stainless steels, organic fouling has been detected and followed by EIS: figure 5 illustrates the results obtained with fresh and natural seawater flowing inside the tube-electrodes at 2 $m.s^{-1}$. At the beginning of the exposure or when the dry weight of the deposits was lower than 1 $mg.cm^{-2}$, no relaxation was visible on Nyquist diagram; when the fouling increased, a relaxation appeared around 100 Hz and increased with time as shown on figures 5b and 5c. At the end of the exposure time, the electrical fouling resistance has been measured by EIS and plotted versus the dry weight of the deposits found on the electrodes: as shown on figure 6, a linear relationship was observed.

Results on titanium were similar to those obtained on stainless steel except that bigger deposits were needed to be detected. For instance, after 3000 hours of exposure at 35°C. the EIS diagram was characteristic of a passive metal with low corrosion rate (as the diagram of the figure 5-a): it shows high R_t, but no clear evidence of fouling when the dry weight of organic deposits is 1.9 $mg.cm^{-2}$.

This interpretation of EIS data using linear coordinate plot in the complex plane (Nyquist plot) is a first step. Of course, more information and lower detection limits are available using the Bode plot and mathematical simulation. The purpose of this presentation was only to show that EIS may be useful for the detection and the evaluation of seawater fouling.

Figure 4 : Evolution of the electrical fouling resistance (R_f) on copper-nickel tube during temperature increase (natural flowing seawater, 2 $m.s^{-1}$)

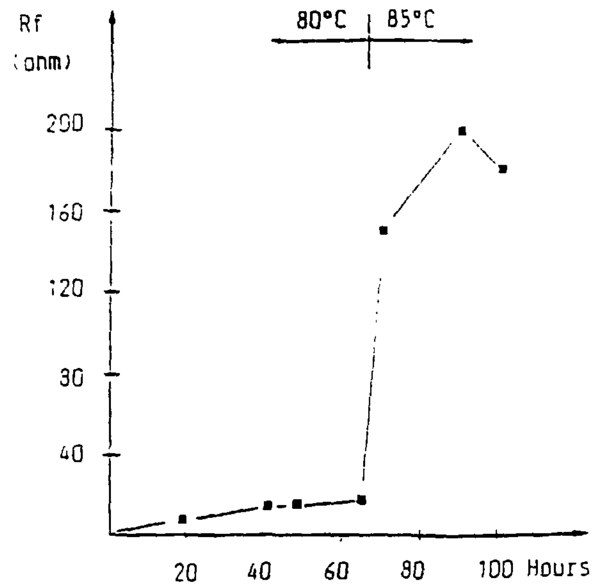
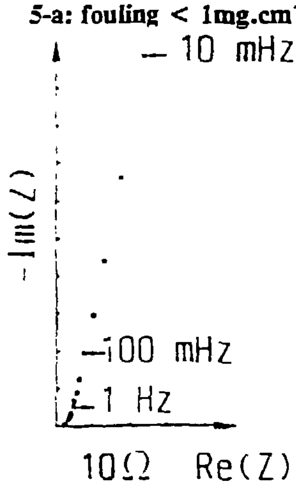
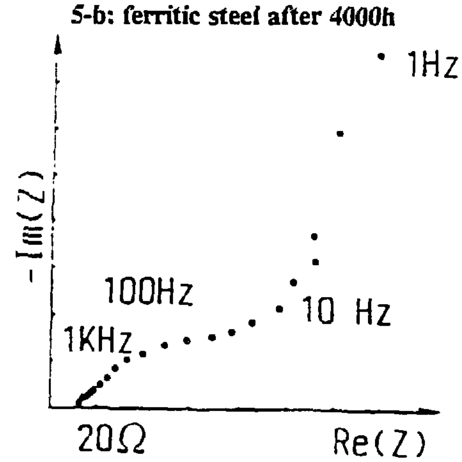


Figure 5 : EIS diagrams obtained on stainless tubes with natural seawater at 35°C and flowing at 2 $m.s^{-1}$

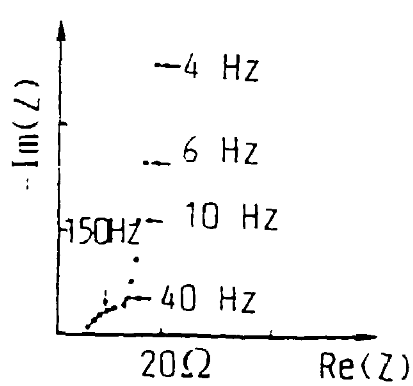
5-a: fouling < 1mg.cm^{-2}



5-b: ferritic steel after 4000h



5-c: super ferritic steel after 600h



5-CONCLUSION

The detection and the evaluation of seawater fouling have been performed on tube-electrodes at temperatures between 35°C and 85°C.
The fouling evidence by EIS is not only a function of the nature and of the thickness of deposits, but also of the materials on which fouling occurs.
From these experiments, Electrochemical Impedance Spectroscopy appears to be helpful to detect and follow seawater fouling.

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Figure 6 : Evolution of the electrical fouling resistance versus fouling weight
stainless steel tubes, natural flowing seawater (2 m.s^{-1}), 35°C