

Analysis and models of some composites corrosion evolution

ALINA BĂRBULESCU*, DANA – CRISTINA TONCU*, LUCICA ORAC**

*Department of Mathematics and Computers Sciences

“Ovidius” University of Constanța

124, Mamaia Bd., 900527, Constanta

ROMANIA

** Faculty of Metallurgy and Materials Science

“Dunărea de Jos” University of Galati

Str. Domneasca no. 111, Galati

ROMANIA

Abstract: In this paper we describe the results of the experiments concerning the behavior at corrosion of some composites materials, in saline water and in the presence of cavitation. Some models of the mass loss evolution in time are also given.

Key-Words: composites, corrosion, polarisation resistance, Tafel diagram, SEM, models.

1 Introduction

The corrosion is the phenomenon of spontaneous destruction of metallic surfaces or alloys under the action of the medium factors, as gasses, electrolytic solutions, microorganisms. The electrochemical corrosion appears in the presence of electrolytic solution. If a cavitation field is also present, the electrochemical corrosion is combined with the erosion process.

The corrosion study needs chemical, physical, metallurgical and mechanical perspectives, as well as environment aspects.

As the corrosion – erosion can dramatically affects the functioning of different machine components, the use of some resistant materials to design them, is a solution.

In the last years, the composites use increased based on their anticorrosive properties [6, 7].

(graphite) and half of them adsorbed bearing oil at high temperature (Table 1).

2 Materials analysis and experimental methods

It is assumed that in the simplest case on a corroding metal electrode, two electrochemical reactions may proceed:

- ionization of metal atoms, together with the reverse reaction
- cathodic depolarization, i.e. reduction of oxidant present in solution to reduced form, together with the reverse reaction.

The polarization current of such a corrosion system is the sum of such a corrosion system in the sum of partial current of reactions. [5]

The corrosion stage of a material can be observed by:

- qualitative methods, as microscopic observations;
- quantitative methods, as corrosion speed calculation.

Some methods of corrosion parameters determination can be mentioned: gravimetric, galvanostatic and potentiostatic methods.

Before the corrosion experiments, the materials were analyzed using a scanning electron microscope (SEM).

SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the

Table 1. Materials' composition

SAMPLE	COMPOSITION
1	0 % graphite, non-oil
2	0 % graphite, oil
3	1.5 % graphite, non-oil
4	1.5 % graphite, oil
5	2.5 % graphite, non-oil
6	2.5 % graphite, oil

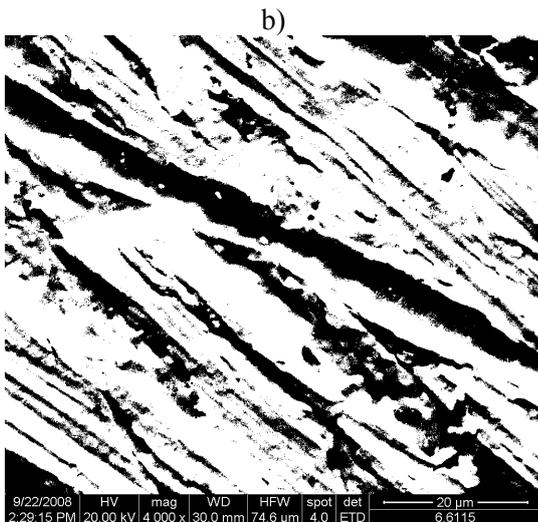
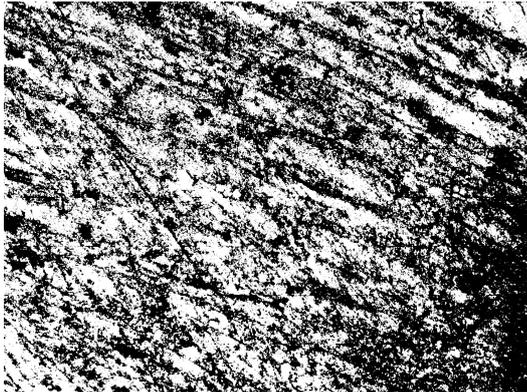
In this study we focused on the analysis of some composite materials, in saline media and in cavitation field. The materials were obtained by 87 % Cu, 7% Sn, 4% Zn, 2% Pb powder by sintering with carbon concrete

sample's surface topography, composition and other properties such as electrical conductivity [9].

The observation was repeated at the experiments end.

In Fig. 1 a) and b) the image of a sample of material 5, before the experiments is presented.

Fig.1.a) Image of a material sample with the composition 5 before the experiment (100x); b) Image of sample 5 after the erosion – corrosion experiment (4000x)



2.1 Electrochemical method

Electrochemical methods are frequently used to evaluate the metal corrosion rate in electrolytic environment in a very wide range of values from $\mu\text{A}/\text{cm}^2$ to A/cm^2 , equivalent to a linear corrosion rate from fractions of $\mu\text{m}/\text{year}$ to several mm/year [5].

In order to determine the corrosion parameters (current density, potential, corrosion speed and wear speed) the galvanostatic method was applied.

The experiments were carried out using a conventional three electrode cell having as the working electrode a composite sample with a surface of 1 cm^2 . Prior to the experiments the electrode was cleaned and

polished, wiped washed with acetone and finally with distilled water.

The counter electrode consisted of a piece of platinum wire.

The reference electrode to which all potential are referred was the saturated calomel electrode.

The measurements were carried out at the room temperature, on a Voltalab 21 system connected to a PC. The software used was VoltaMaster 4.

The working media consisted of a solution of 0.5M NaCl in distilled water.

For each sample the following sequence of experiments was performed:

- open circuit potential;
- general corrosion initial (to determine the initial polarization resistance);
- cyclic voltammetry;
- linear potential (Tafel curves determination);
- pitting corrosion.

2.2 The erosion-corrosion study in cavitation field

It is known that in a liquid, an ultrasonic field can carry along small bubbles or can produce cavitation bubbles. Their subsequent collapse/rebound cycle results in such effects as: pressure oscillations with frequency different from that of the stimulating ultrasonic field, sonoluminescence and rectified diffusion of gas dissolved in the liquid, emulsification of multiphase media and chemical reactions in cavitating liquids. Erosion and unpassivation of solid boundary surfaces are phenomena of undisputable technical significance. [8]

The experiments have been done in stationary saline water in cavitation field produced in an experimental set up specially built for this purpose that can also be used to study the corrosion – erosion in circulated media. The cavitation was produced by an ultrasound field generated by a transducer module fitted in the set up. It mainly consists of a tank for liquids, containing a transducer connected to a high frequency generator that excites the transducer to produce ultrasounds [4].

The tests were done at a power of 80 W, 120 W and 180 W. We present only the results obtained at 80 W.

As temperature determines a shift in the position of erosion zone, this parameter was kept constant: $+21^\circ\text{C}$.

Test samples were machined to suitable dimensions, after which the surfaces exposed to cavitation were ground and polished. They were stored in a desiccator between the experiments.

The samples were put on the cavitation field 24 hours, by stage of 30 minutes. Before and after each test, they were dried and weighed. The average mass loss was used to determine the erosion - corrosion rate.

To prevent temperature rises during testing, the water was cooled to the test temperature.

3 Results

3.1 Results of electrochemical investigation

We present the results of the experiments made on the samples 5 and 6 and we compare them at the end.

The first step in the electrochemical analysis done on the materials was to run an Open Circuit Potential with a duration of at least 30 minutes and a scan rate of 0.6 s. Thermodynamically, the less negative the OCP, the more sensitive to corrosion the sample is.

In Figs.2 and 3, the results of this test are given for the samples 5 and 6.

It can be seen that in the first case a slow decreasing of the potential was registered, in the first 20 minutes; in the second case, after a sudden decreasing of potential, it tends to become stable at -283 mV.

General corrosion tests with VoltaMaster4 automatic calculate the polarisation resistance (R_p) determined from cyclic (Fig.4) or linear voltammetries performed around the rest potential.

Fig.2 OCP graph – sample 5

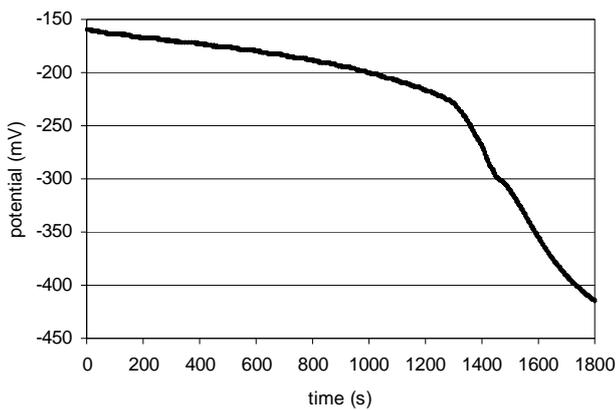
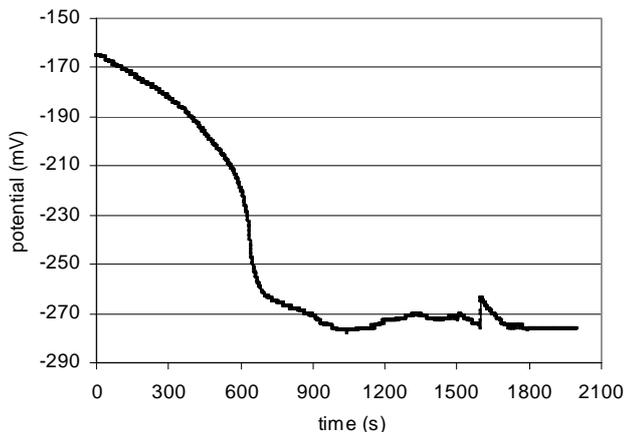


Fig.3 OCP graph – sample 6



In this case, 7 individual linear voltammetries were recorded at a scan rate of 2mV/s. Their graphs (Figs. 5 and 6) the black lines represent the polarization resistance and the grey one, the corrosion potential measurements versus time of all voltammetries.

Fig.4 The voltammogram of sample 6

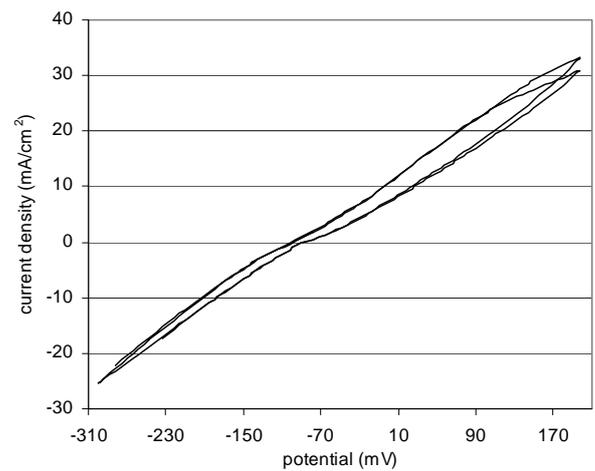


Fig.5 Polarization resistance and corrosion potential– sample 5

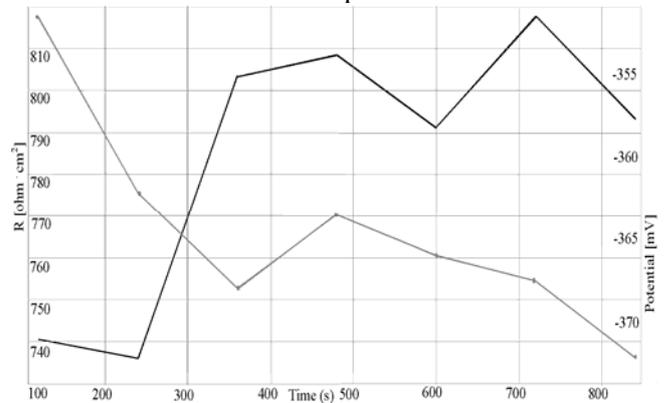
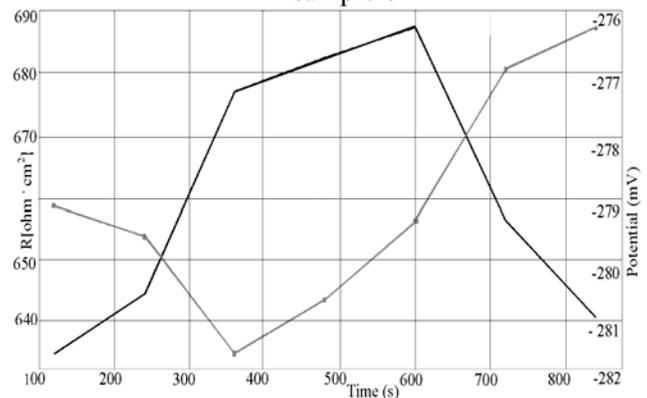


Fig. 6 Polarization resistance and corrosion potential– sample 6



The recorded mean polarization resistance was respectively 784.393 $\text{ohm} \cdot \text{cm}^2$ and 660.646 $\text{ohm} \cdot \text{cm}^2$.

The recorded the mean potential was -364.44 mV, respectively -279.549 mV.

The determination of corrosion current regularly present at the surface of a metal which is in contact with a corroding solution was made using the Tafel equation. The study was made in a interval of ± 40 mV (Fig.7) and ± 1000 mV (Fig.8) around the mean potentials, calculated at the previous step.

Fig. 7 Polarization curves (Tafel) for sample 5

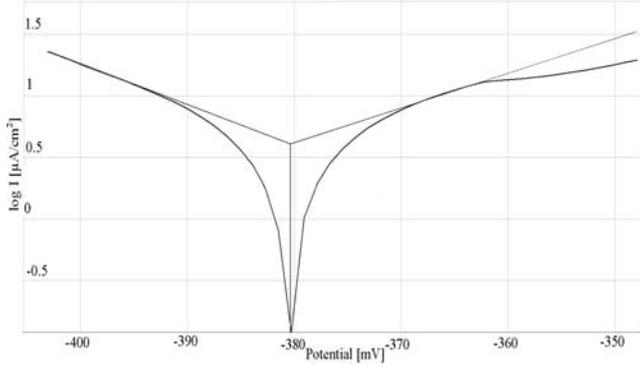
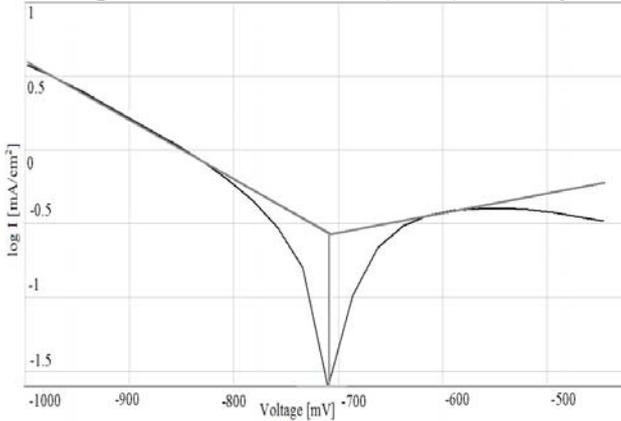


Fig. 8 Polarization curves (Tafel) for sample 6



The results were respectively:

- the corrosion potential, -380.4 mV and the corresponding current density, $4.0576 \mu\text{A}/\text{cm}^2$ – for the sample 5;
- the corrosion potential, -707.2 mV and corresponding current density $0.2674\text{mA}/\text{cm}^2$, for the sample 6.

For pitting corrosion test, the work electrode is polarised at -10 mV versus the REF potential and this potential is scanned towards anodic polarisation at a scan rate of 1 mV/s with potential steps of 2.5 mV and a 2.5 second duration. The current is measured. The more anodic the "pitting potential", the less subject to pitting the sample is [10].

The tests results prove that all studied materials were pasivating. For the sample 5, the critical pitting potential was -99.6mV and for the sample 6, -63.8mV.

4 Mathematical models

Using the experimental data, the masses loss equations in time were determined. They are respectively:

$$m = 1.24 + 1.97 \cdot 10^{-5} t - 8.36 \cdot 10^{-8} t^2 + 1.16 \cdot 10^{-10} t^3 - 5.08 \cdot 10^{-14} t^4, \quad (1)$$

$$m = 1.35 + 1.16 \cdot 10^{-6} t - 6.05 \cdot 10^{-9} t^2 + 8.52 \cdot 10^{-12} t^3 - 4.23 \cdot 10^{-15} t^4, \quad (2)$$

$$m = 1.76 - 9.34 \cdot 10^{-8} t + 3.46 \cdot 10^{-10} t^2 + 9.96 \cdot 10^{-13} t^3 -$$

$$-1.52 \cdot 10^{-15} t^4, \quad (3)$$

$$m = 1.21 + 1.47 \cdot 10^{-7} t + 3.15 \cdot 10^{-9} t^2 - 4.48 \cdot 10^{-12} t^3 + 1.2 \cdot 10^{-15} t^4, \quad (4)$$

$$m = 2.86 - 5.1 \cdot 10^{-6} t + 1.18 \cdot 10^{-8} t^2 - 9.63 \cdot 10^{-12} t^3 + 1.51 \cdot 10^{-15} t^4, \quad (5)$$

$$m = 1.29 + 2.97 \cdot 10^{-6} t - 1.45 \cdot 10^{-8} t^2 + 2.30 \cdot 10^{-11} t^3 - 1.16 \cdot 10^{-14} t^4, \quad (6)$$

where t is the time and m is the mass at the moment t . The curves' allures are presented in Figs. 9 – 14.

Fig.9 The graph of sample 1 mass loss

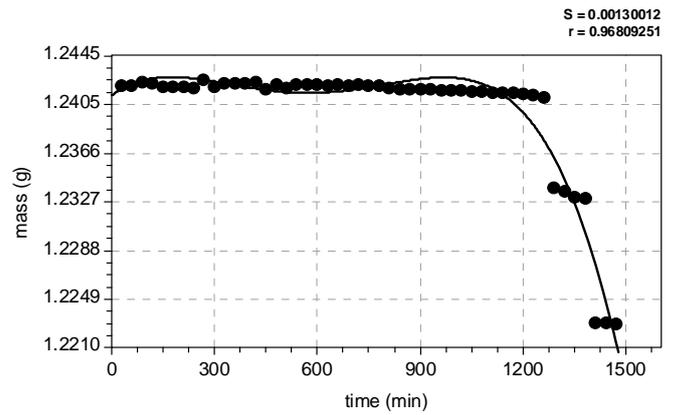


Fig.10 The graph of sample 2 mass loss

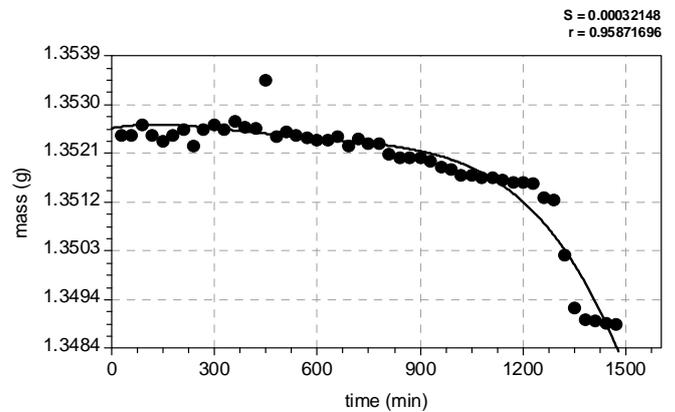


Fig.11 The graph of sample 3 mass loss

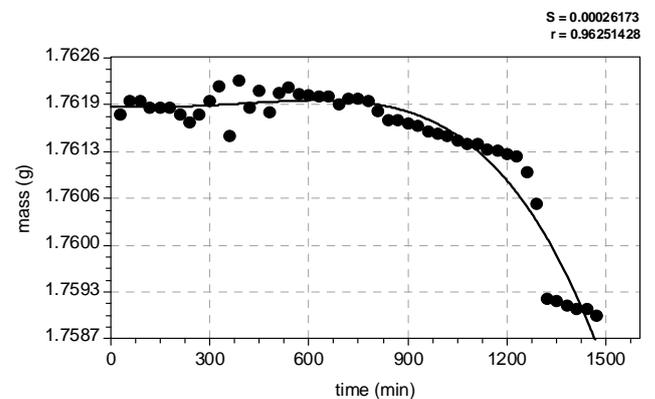


Fig.12 The graph of sample 4 mass loss

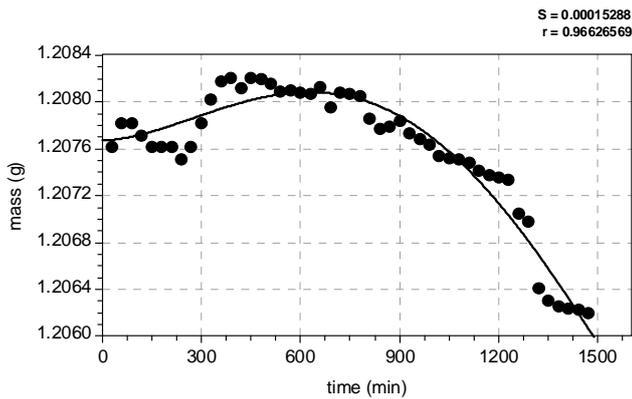


Fig.13 The graph of sample 5 mass loss

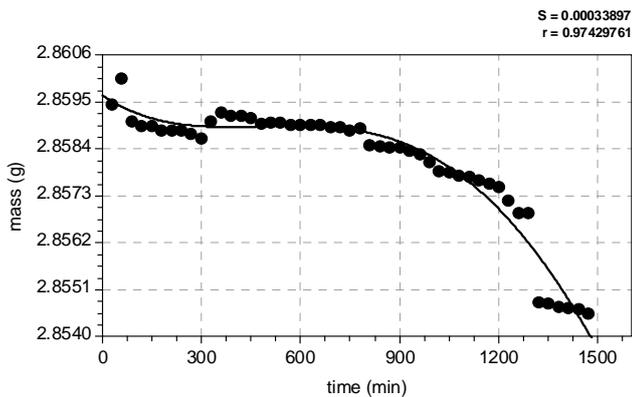


Fig.14 The graph of sample 6 mass loss

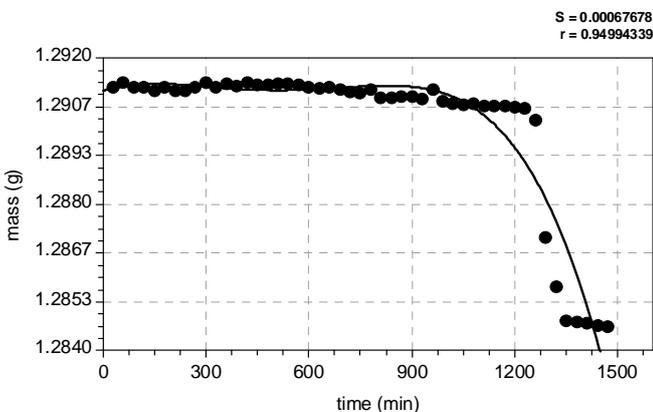


Fig.15 The graph of residual in the model (1)

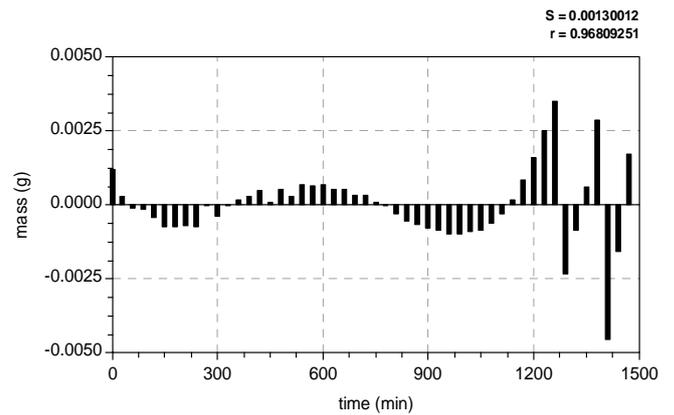


Fig.16 The graph of residual in model (2)

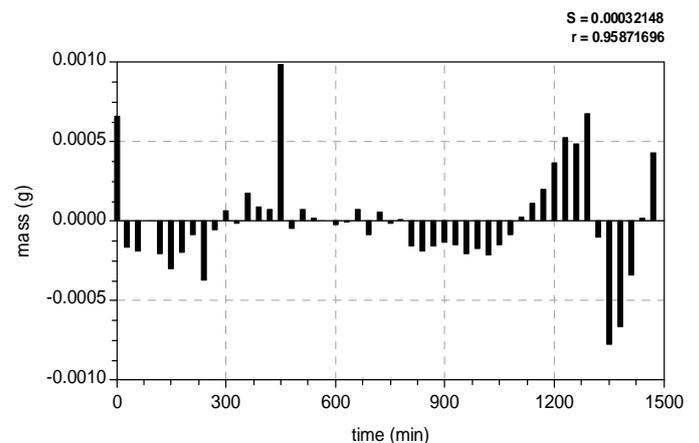
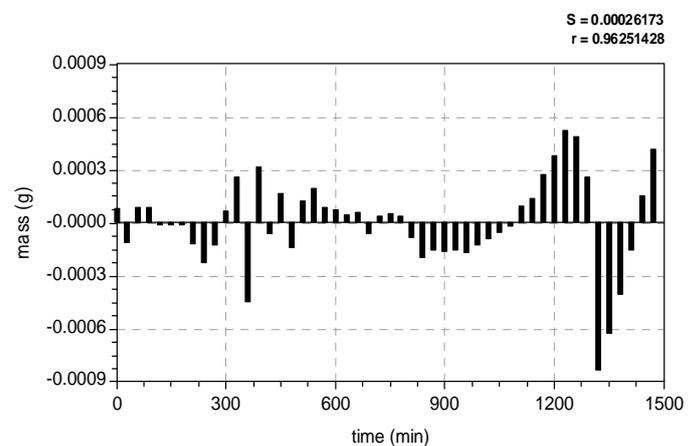


Fig.17 The graph of residual in model (3)



So, the mass variation trends of all composites samples are described by polynomial functions of fourth degree.

The standard deviation, S , is very small (between 0.00026273 and 0.00130012) and the correlation coefficient, r , is close to 1 (between 0.94994379 and 0.974297).

Point of view of statistics, the coefficients in the models are significant, i.e. the results of t-test for each coefficient in models and F-test for the coefficients ensemble lead us to accept the hypothesis that the coefficients are not zero.

The graphs of residuals from the models (1) – (6) are plotted in Figs. 15 - 20.

In order to validate the models, the residuals analysis was performed. Kolmogorov-Smirnov test and Q-Q plots, the autocorrelation function and the Bartlett test were used in order to test respectively the hypotheses of residuals normality, independence and homoscedasticity (the same variance)[1].

The results of these tests, for each model, lead us to accept the hypotheses that all the residuals are normally distributed, independent and homoskedastic, so the models describe very well the erosion – corrosion evolution in time.

Fig.18 The graph of residual in model (4)

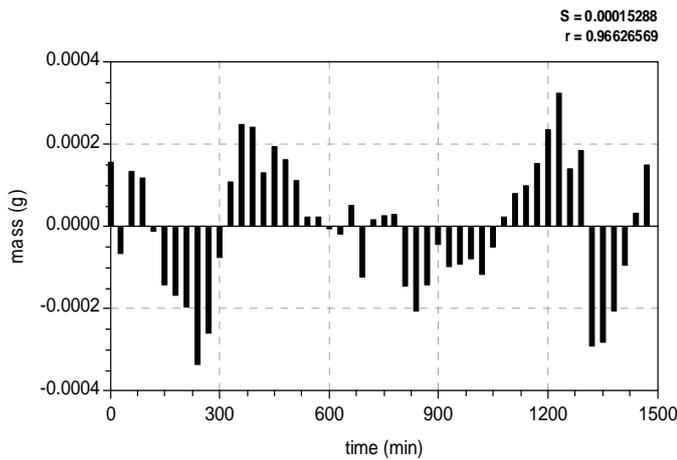


Fig.19 The graph of residual in model (5)

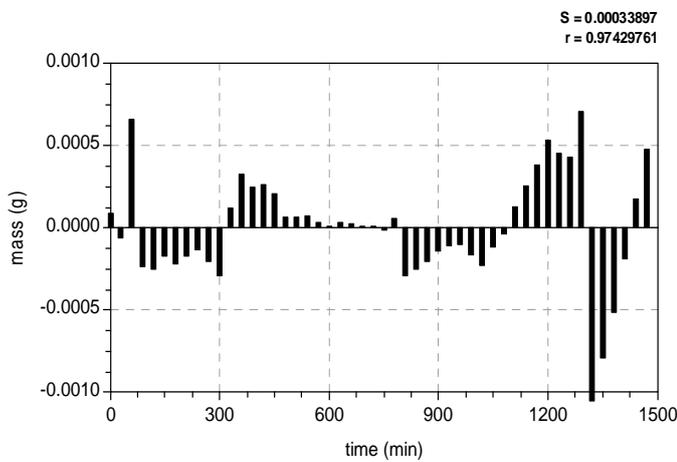


Fig.20 The graph of residual in model (6)

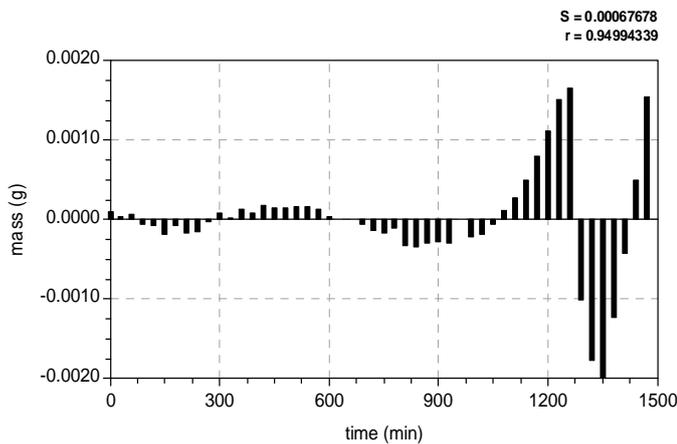


Fig.21 The graph of absolute mass loss variation

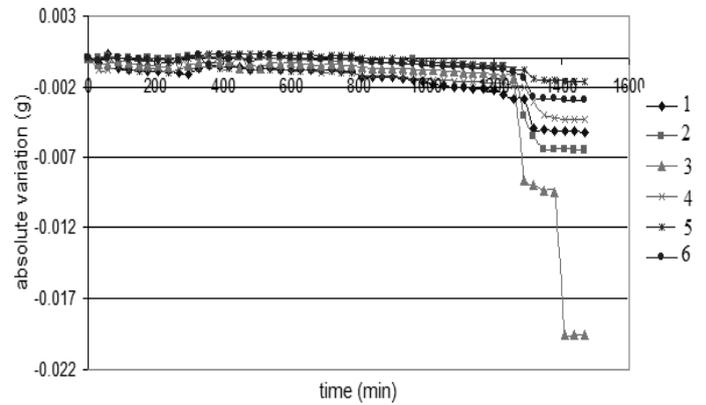
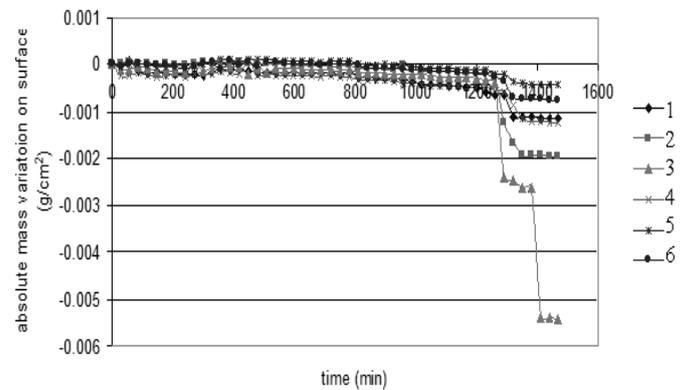


Fig.22 The graph of absolute mass loss variation with respect to time and surface



5 Conclusions

In this article the results of the studies on some copper - base composites corrosion on saline media were presented. Comparing their corrosion behavior we can conclude that:

- The samples were resistant at general corrosion in the studied media.
- The pitting test proves that the materials are not exposed at this corrosion type.
- The composite impregnated was more resistant to the corrosion comparing to the non - impregnated one, in both situation (the presence and the cavitation absence);
- The cavitation presence accentuates the corrosion speed;
- The mass loss of material in cavitation field, function of time can be described by a polynomial of 4-th degree, for all composites, and the mathematical models found are good point of view of statistic, since the coefficients are significant and the residuals are independent, homoscedastic and normally distributed. These results are concordant with the studies previously done on other materials of the same type [3, 4].

The absolute mass variation function with respect to time (Fig.21) and the absolute mass loss on time surface (Fig.22) were determined.

Taking into account the last values calculated, corrosion speeds were calculated.

For the samples 5 and 6 the values are respectively 0.46 mm per year, 0.31mm per year.

References:

- [1] A. Barbulescu, Time series with applications, Junimea, Iasi, 2002
- [2] A. Barbulescu and C.S. Dumitriu, Models of the mass loss of some copper alloys, *Scientific Bulletin of "Politehnica" University of Timisoara, Chemistry and Environment Engineering Series* (in press)
- [3] A. Barbulescu, D.-C. Toncu, Copper-Base Materials For Shipbuilding – Corrosion Behaviour, *Scientific Bulletin of "Politehnica" University of Timisoara, Chemistry and Environment Engineering Series* (in press)
- [4] C. S. Dumitriu and A. Barbulescu, *Studies concerning the copper base alloys used in naval constructions – Modeling the mass loss in different media*, Sitech, Craiova, 2007
- [5] J. Jankowski, Electrochemical methods for corrosion rate determination under cathodic polarisation conditions – A review. Part I – DC Methods, *Corrosion reviews*, Vol.20, No.3, 2002, pp.159 - 177.
- [6] V. G. Grechanyuk, V.A. Denisenko and L. Orac, *Structure and corrosive firmness of composition materials on basis of copper and molybdenum electron beam technology method*, *Anal. of "Dunarea de Jos" University of Galati, Fasc. IX Metallurgy and Materials Science*, Vol. 1, 2007 (in print)
- [7] V. G. Grechanyuk, V.A. Denisenko and L. Orac, *Studies and research on mechanical properties and the influence of structural defects for the Cu-Mo composite materials obtained using the PVD metod*, *Proceedings of 2nd International Workshop in Geoenvironment and Geotechnics, Milos Island, Greece*
- [8] R.A. Rory, *Physical aspects of sonoluminescence from acoustic cavitation*, *Ultrasonic, Sonochemistry*, Vol.1, No.1, 1994, pp. S5 - S8, 2008, pp. 237- 243
- [9] http://en.wikipedia.org/wiki/Electron_microscope
- [10] <http://www.radiometer-analytical.com/pdf/voltalab>

Acknowledgements. The research was supported by Grant CNCSIS 902/2007-2008