



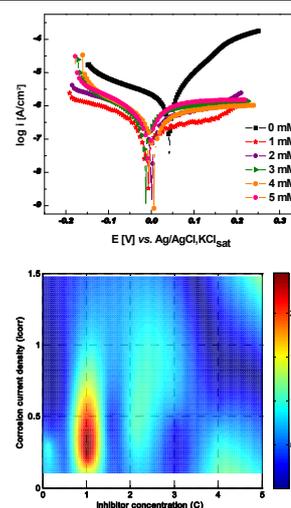
ELECTROCHEMICAL AND META-MODELLING ANALYSIS OF THE INHIBITING EFFECT EXERTED BY SULFURIC ACID DIAMIDE ON BRONZE CORROSION

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The bronze monuments exposed outdoors suffer atmospheric corrosion and depreciation because of pollution. Therefore, it is important to find efficient methods to protect them against corrosion. Due to the toxicity of commonly used corrosion inhibitors and the ever tightening environmental norms surrounding their use and disposal, there is great interest in replacing harmful inhibitors with effective non-toxic alternatives. In this context, the main aim of this paper is to investigate the protective effect of sulfuric acid diamide (SAD) at different concentrations on bronze corrosion. The inhibiting effect of the SAD on corrosion of bronze CuSn8 was investigated by electrochemical method, in a $0.2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.2 \text{ g L}^{-1} \text{ NaHCO}_3$ (pH=5) solution simulating acid rain. To extend the domain of inhibiting conditions and to reduce experimental measurements, correlated predictions of parameters based on experimental values was implemented in the paper using two methods of meta-modelling techniques.



INTRODUCTION

One of the most important methods in the protection of bronze against corrosion is the use of organic inhibitors.¹ Therefore, in the last decades, a series of organic compounds, in particular heterocyclic compounds with nitrogen, sulfur and oxygen were tested as corrosion inhibitors for bronze.^{2,3} They can act as effective inhibitors for bronze due to their ability to form protective films on the metal surface through different mechanisms involving physical adsorption, chemisorption, or polymerization. Among these, benzotriazole and

its derivatives have been shown to be most effective, but their high toxicity causes major concerns.⁴ Recently, extensive research have led to the discovery of new classes of corrosion inhibitors, and the importance of the use of several drugs as corrosion inhibitors has increased.^{5,6} Due to their availability on the market, relatively low toxicity and chemical composition, the drugs appear to be promising substitutes for toxic inhibitors.⁵ The inhibiting action of these compounds is due to their interaction with the metallic surface by adsorption. Polar functional groups stabilize the adsorption process. In general,

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the adsorption of the inhibitor on the metal surface depends on its nature, manner of adsorption, chemical structure and on the type of electrolyte solution.⁷

In this context this paper presents a study regarding the bronze corrosion in the presence of a drug from sulfonamides class, namely sulfuric acid diamide (*SAD*, also known as sulfamide). Sulfonamides represent an important class of active medicinal compounds, which are used on a large scale as antibacterial agents. Aiming to investigate the inhibiting properties of *SAD* in the corrosion process of bronze, electrochemical experiments were carried out in a $0.2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.2 \text{ g L}^{-1} \text{ NaHCO}_3$ ($pH = 5$) solution simulating acid rain in its presence.

On the other hand, to reduce the number of laboratory experiments, the time and costs of researches, the paper implements into a comparatively manner two methods of meta-modelling based on artificial intelligence techniques. A meta-modelling procedure involves at least the following steps: (a) choosing an experimental design for generating experimental data, (b) choosing a model to represent the data, and then (c) fitting the model to the observed data. Meta-models rely on input-output mapping to describe the unknown relation between values of input and output or response variables of the process. A meta-model replaces a true functional relationship $g: \mathfrak{R}^n \mapsto \mathfrak{R}$ and known values $y_i = g(x_i)$ at selected input variables usually called sampling points ($X = \{x_1, \dots, x_m\}, X \in \mathfrak{R}^n$), by an empirical mathematical expression $\hat{g}(x)$ that is much easier to evaluate. Thus surrogates of the objectives and constraint functions can replace the original functional relationship $g(x) = \hat{g}(x) + \varepsilon(x)$. Based on input-output pairs of values and simulation runs, parameters of the model are fit to approximate the original data in a best possible way. The present work implements two empirical meta-modelling procedures,

basically two-class classifiers: (1) a well known support vector machine approach and (2) a minimax decision procedure based on minimax probability machine regression approach. Both procedures are inductive learning procedure, learning from a given set of training/examples, verifying on test/ examples to induces rules/predictions from these. These procedures are used to predict trends of electrochemical parameters regarding bronze corrosion process using a reasonable-small numbers of experiments and experimental data. Support vector machine based on statistical learning theory was introduced by Vapnik in 1995, developed and studied by many others.⁹ Minimax decision procedure based on minimax probability approach were introduced and presented in detail elsewhere.^{10,11} The foundation of this decision procedures are based on minimax probability machine for binary classification and minimax probability machine regression presented and developed after 2002.^{12,13}

RESULTS AND DISCUSSION

1. Potentiodynamic polarization measurements

The experiments started with measuring the potential of the working electrode in open circuit for 1 hour, in the absence and in the presence of different concentrations of inhibitor. To determine the polarization resistance of the electrodes, linear polarization curves were recorded, in the potential domain of $\pm 20 \text{ mV}$ vs. the value of the open circuit potential (OCP). The polarization resistance values for each electrode, calculated as the inverse of the slope of each curve, are shown in Table 1.

To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of $\pm 200 \text{ mV}$ vs. OCP, some results are shown in Fig. 1.

Table 1

Corrosion process parameters for the examined samples in $\text{Na}_2\text{SO}_4 / \text{NaHCO}_3$ ($pH = 5$) solution obtained in the absence and in the presence of various concentrations of inhibitor

C [mM]	i_{cor} [$\mu\text{A}/\text{cm}^2$]	R_p [$\text{k}\Omega \cdot \text{cm}^2$]	η [%]	
			i_{cor}	R_p
0	1.46	9.05	-	-
0.5	0.41	48.30	72	81
1	0.16	176.00	89	95

Table 1 (continued)

1.5	0.27	40.49	81	78
2	0.39	44.85	73	80
3	0.48	41.36	67	78
4	0.46	50.68	62	82
5	0.39	41.29	73	78

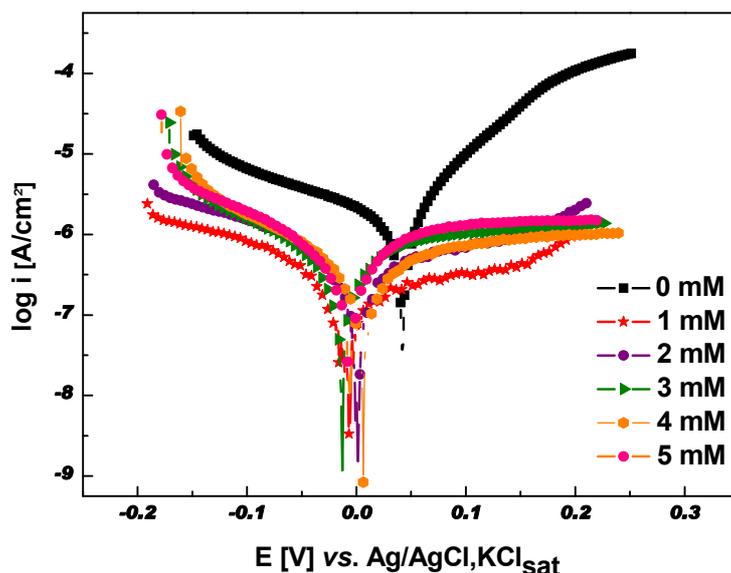


Fig. 1 – The polarization curves (± 200 mV vs. OCP) for the studied electrodes immersed in $0.2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.2 \text{ g L}^{-1} \text{ NaHCO}_3$ (pH 5) at different concentrations of *SAD*.

As shown in Table 1, the sulfuric diamide exerts a protective effect against bronze corrosion at all investigated concentrations. The best results were noticed at 1 mM *SAD*, this is suggested by the high value of the polarization resistance ($R_p=176.00 \text{ [k}\Omega\text{cm}^2]$) and the low value of the corrosion current density ($i_{\text{corr}}=0.16 \text{ [}\mu\text{A cm}^{-2}]$). It can be assumed that the beneficial action of the organic compound is due to S and N heteroatoms from its molecules determining its adsorption on the bronze surface. Based on the corrosion current density the protection conferred by inhibitor at all concentrations used was determined according to the relation:

$$\eta[\%] = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (1), \text{ where } i_{\text{corr}}^0 \text{ and } i_{\text{corr}}$$

are the values of the corrosion current densities in absence and in presence of the inhibitor at different concentrations, respectively. The results are presented in Table 1 and confirm that the highest efficiency was reached in the case of 1 mM *SAD*.

In order to validate these findings many sets of polarization curves in the presence of different inhibitor concentrations were recorded. All these electrochemical corrosion measurements were

included in the database necessary to the meta-modelling methods mentioned before.

2. SEM-EDX analysis

In order to establish if the *SAD* is adsorbed on bronze, the surface morphology and the composition of the corrosion products covering the electrode was examined by SEM and EDX. Fig. 2 presents the bronze surface morphology after 72 h of immersion in the corrosion solution in the absence and in the presence of 1 mM (*SAD*). As expected, in the absence of the inhibitor, the bronze surface appears to be completely covered with a layer of corrosion products. It can be observed that in the presence of *SAD* the layer of corrosion products is less continuous and thinner than in its absence, presenting small regions of uncovered bronze substrate. On the other hand, the EDX analysis on the bronze surface indicated the presence of S in a larger quantity when 1 mM *SAD* was used (6.01 %) as in the absence of inhibitor S (0.71 %). These results can be explained by the adsorption of the inhibitor on the bronze surface.

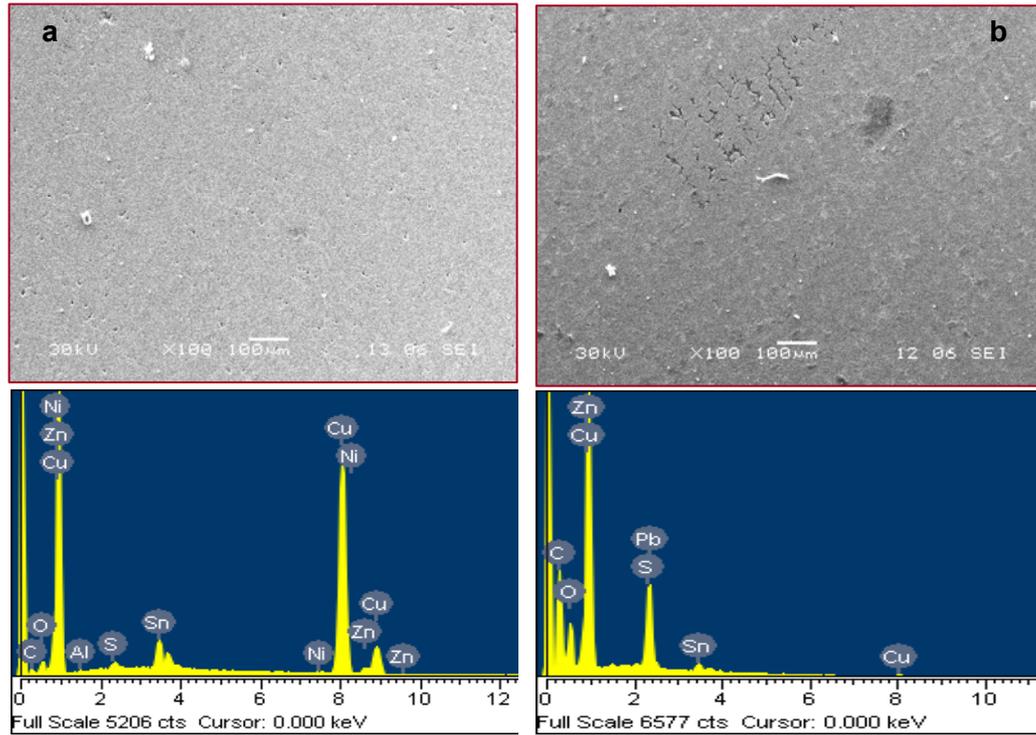


Fig. 2 – SEM / EDX of bronze surface after 72 h immersion in $0.2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.2 \text{ g L}^{-1} \text{ NaHCO}_3$ (pH 5) in the absence (a); and in the presence 1mM SAD (b).

3. Adsorption isotherm

The polarization resistance values determined from linear polarization curves ($R_p=1/\text{slope}$), recorded in the potential domain of $\pm 20 \text{ mV}$ vs. the value of the *OCP*, were used to calculate the degree of surface coverage (θ) with inhibitor molecules and the inhibition efficiency (η), according to the following equations:

$$\theta = \frac{R_p - R_p^0}{R_p} \quad (2); \quad \eta [\%] = \theta \times 100 \quad (3);$$

where R_p and R_p^0 are the polarization resistances in electrolytes with and without inhibitor at different concentrations, respectively. The results are shown in Table 1. From Fig. 3 it can be seen that the plot of $\frac{C}{\theta}$ versus C results in a straight line with nearly unit slope (1.14), confirming that the adsorption of SAD on bronze obeys Langmuir isotherm:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (4)$$

where K is the adsorption equilibrium constant and C is the inhibitor concentration. Based on K value deduced from the Langmuir adsorption isotherm the standard free energy of adsorption ΔG_{ads}^0 was calculated with following equation:

$\Delta G_{ads}^0 = -RT \cdot \ln(55.5K)$ (5), where 55.5 represents the molar concentration of water in solution (mol L^{-3}), R is the gas constant and T is the thermodynamic temperature. In this way, for $K = 1.21 \cdot 10^4 [\text{M}^{-1}]$ was obtained $\Delta G_{ads}^0 = -14.24 [\text{kJ mol}^{-1}]$. The negative value of ΔG_{ads}^0 indicate spontaneous adsorption of the inhibitor molecule on the bronze surface.¹⁴

4. Implementation of the meta-modelling procedures

Because both implemented procedures are inductive learning procedure, to ensure a good distribution of the data and stability the simulations was based on data randomly divided into a number of distinct learning and testing subsets. There are no uniquely agreed approaches to choose the suitable dimension of learn and test subsets, but is commonly agreed that the training data must be sufficiently large compared with the number of features (variables). In every random cycle of simulation, a random percentage of the database (10–30%) is set aside and used in testing step (trial and errors). The procedures were conducted in a crude manner, without outliers' detection and no

features reduction or selection. The implementation of support vector machines is based on free version of *LS - SVMlab* version 1.5. The implementation of minimax decision procedure was developed as a user-friendly computer application also in *MATLAB* software environment. The main goal of implementations is to establish the most suited inhibitor concentration to achieve the best protection against corrosion. This objective is highlighted by the highest values

of R_p . Prediction of R_p was modelled as a function of 5 input variables: the C , i_{corr} , E_{corr} , β_c , β_a , and R_p . The database with 40 sample sets of electrochemical measured parameters-input parameters was derived from the polarization curves at different values of inhibitor concentration (Table 2). Symbolic function of prediction for polarization resistance R_p was represented as, $R_p = f(C, E_{corr}, \beta_c, \beta_a, i_{corr})$.

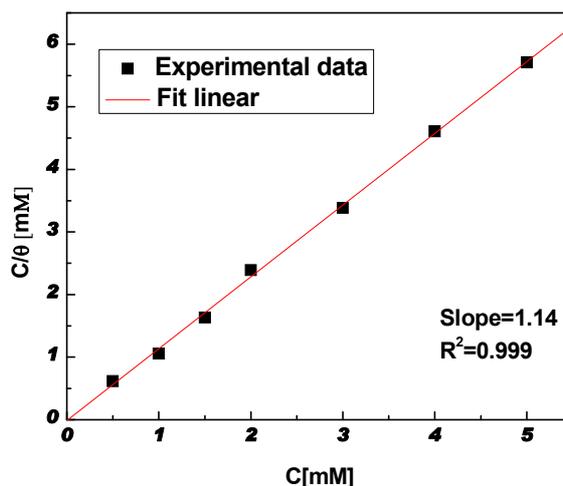


Fig. 3 – Langmuir isotherm for adsorption of *SAD* on bronze surface.

Table 2

Statistical parameters of extended database of electrochemical measurements

Parameters	C [mM]	E_{corr} [mV]	β_c [mV dec ⁻¹]	β_a [mV dec ⁻¹]	i_{corr} [μ A cm ⁻²]	R_p [k Ω *cm ²]
Range	0 ÷ 5	-158.11 ÷ 41.8	74.63 ÷ 358.04	83.59 ÷ 406.10	0.10 ÷ 1.48	7.29 ÷ 205.77
Mean value	1.715	-16.487	169.16	205.54	0.547	64.842
Standard deviation	1.767	60.509	70.062	89.141	0.446	50.102

Table 3

Partial results and some conditions of simulations for the best meta-model

	Minimax decision procedure	Support vector machines (LS-SVMlab version 1.5)
Range of relative errors on all test data subsets	-3.868 ÷ 12.281 [%]	-22.106 ÷ 64.283 [%]
Range of relative errors on the best data test subset	-4.667 ÷ 3.99 * 10 ⁻¹¹ [%] based on Fig. 7a	-4.838 ÷ 32.523 [%] based on Fig. 7b
Kernel functions	$K(\mathbf{x}_i, \mathbf{x}_j) = \exp\left(-\frac{\ \mathbf{x}_i - \mathbf{x}_j\ ^2}{2\sigma^2}\right)$	
Possible domain of polarisation resistance $R_p \geq 200$ k Ω *cm ²	200 ÷ 240	200 ÷ 245
Possible domain of inhibitor concentration C [mM]	0.85 ÷ 1.15	0.85 ÷ 1.15

Possible domain of variation validate and extend experimental conclusions ensuring also reasonable consumption and cost-effectively performance of protection at corrosion.

To be comparable, both procedures are forced to work in multiple cyclic steps on identical data sets. The error will be estimated by testing rather than by calculation. The performance of procedures was investigated based on the following criteria: (i) simple equivalent linear regression between the predicted and the corresponding targets: $Y_{predicted} = a \cdot Y_{test} + b$ (6); where Y represents predicted or test values and a and b the slope and intercept of the equivalent linear regression model, respectively. Theoretically better predictions, means b index close to zero value and a index close to unity. (ii) relative error between the predicted and the corresponding test targets:

$$RE = \left(\frac{Y_{predicted} - Y_{test}}{Y_{predicted}} \right) \times 100 [\%] \quad (7).$$

Main conditions of simulations and partial results are done in Table 3. Performing the predictions in both procedures a kernel type as an exponential radial basis function with standard width kernel

(σ) tuned using 10 - fold cross validation (Table 3) was proved to work well. The model that performs the best on predictions over cyclic simulations, according (eqs.6 - 7), was defined as the surrogate model. This best surrogate model in both procedures will be used to assess new predictions. Numerical applications addressed the following main tasks: (1) predictions of R_p as a control parameter for the effective protection at corrosion at different C and (2) assessments of a possible domain of R_p as a function of C and i_{corr} . The performance of both implemented procedures is closed (Fig. 6 and Table 3). Regarding simple equivalent linear regression between the predicted and the corresponding R_p (eq. 6, Table 3 and Fig. 4) the differences are minors. Some important differences are revealed concerning relative error between the predicted and the corresponding test targets (eq. 7, Table 3 and Fig. 5). The results of minimax decision procedure are a little better than those obtained by implementation of support vector machines.

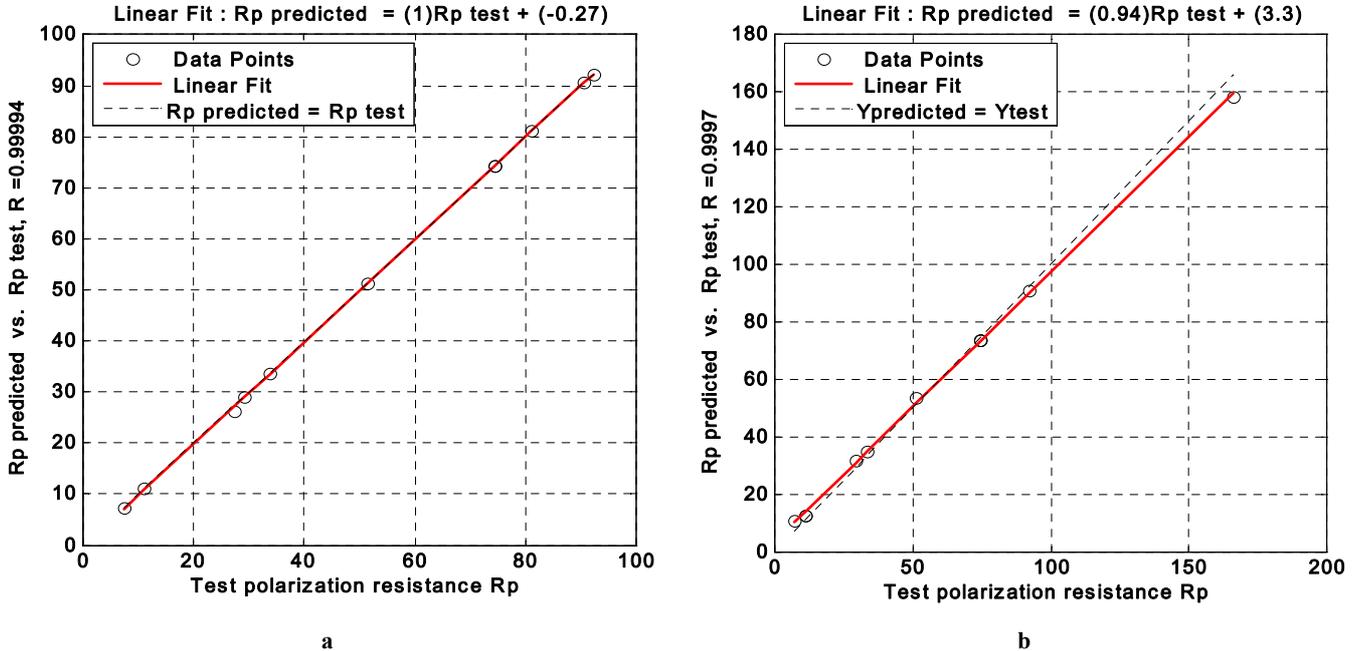


Fig. 4 – Linear dependencies in the best models between predicted and experimental values for Rp: minimax decision procedure (a), support vector machines (b).

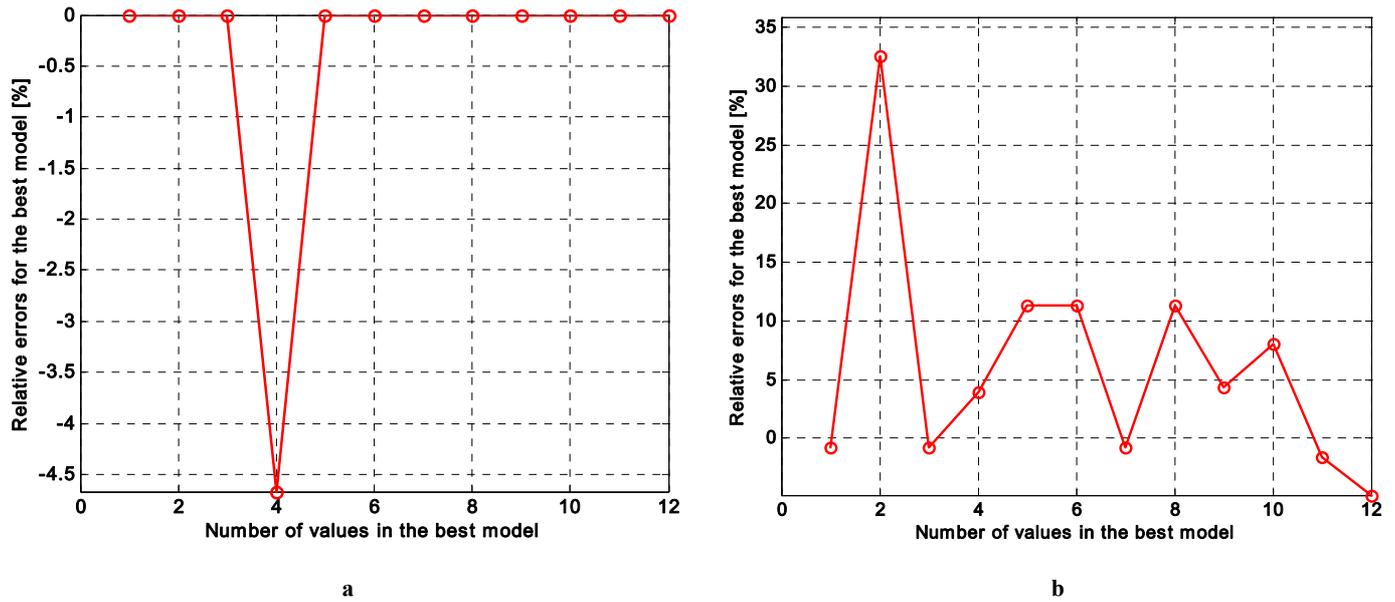


Fig. 5 – Relative errors in the best models between predicted and measured R_p : minimax decision procedure (a); support vector machines (b).

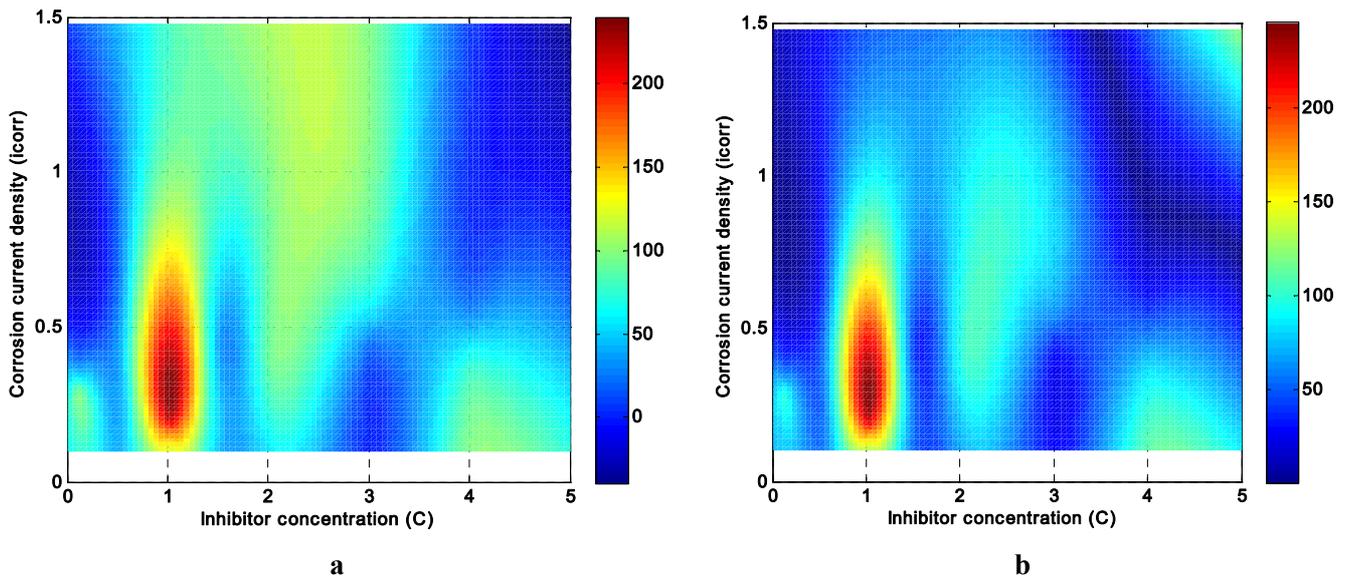


Fig. 6 – Predicted quantitatively interactions between predicted R_p , C and i_{corr} in the best models: for minimax decision procedure (a), for support vector machines (b).

Good correlation between numerical simulations and experimental values related to R_p reveal the capacity of these meta-modelling procedures. According with this good correlation we extend the predictions as correlated variation of the R_p with C and i_{corr} . From these predictions (Fig. 6), one can see much better the influence of these parameters on the effective protection at corrosion. Instead a point value for C implicitly a single experimental value of R_p , results a domain with more possible values for C which can assure a good protection at corrosion. This domains was

stated by values greater than 176 [$\text{k}\Omega\text{cm}^2$] obtained from unique experimental measurements around $C = 1$ mM (Table 1). The results related to the highest values of R_p confirm the best protection at corrosion previously established into a singular experiment. The accurate results offer a potential domain of values for the C (Table 3). Based on these extended experimental conclusions it is possible to reduce the number of detailed laboratory experiments. This fact can ensure reasonable consumptions of C , relative small number of laboratory experiments and generally a

cost-effectively performance of protection at corrosion.

EXPERIMENTAL

To conduct the electrochemical studies, a contemporary bronze CuSn8 was selected with the following chemical composition: 90.18 % Cu, 8 % Sn, 0.8 % Zn, 1 % Pb and 0.02 % Al. The working electrodes made by cylindrically shaped, were placed in a PVC tube (exposed area = 2.00 cm²), while the sealing was assured with epoxy resin. For electrical contact, a metal rod was attached. The inhibitor used in the experiments was a non - toxic sulfonamide derivative, namely sulfuric acid diamide (H₂NSO₂NH₂). The inhibitor was dissolved in the corrosive solution at different concentrations respectively: 0.5 mM L⁻¹, 1mM L⁻¹, 1.5 mM L⁻¹, 2 mM L⁻¹, 3 mM L⁻¹, 4 mM L⁻¹ and 5 mM L⁻¹. The electrolyte solution for corrosion measurements was 0.2 g L⁻¹ Na₂SO₄ + 0.2 g L⁻¹ NaHCO₃ acidified to pH = 5 by the addition of a dilute sulfuric acid at room temperature.

The electrochemical corrosion measurements were performed on a PC - controlled electrochemical analyser AUTOLAB - PGSTAT 10 using a three electrodes cell containing a working electrode (bronze), an Ag / AgCl electrode as reference electrode and a platinum counter electrode. Polarization curves were recorded in a potential range of ± 20 mV (for *R_p* determination) and of ± 200 mV vs. the value of the open circuit potential (for Tafel interpretation), with a scan rate of 10 mV / min, after 1 hour immersion in the corrosive solution.

The morphology of corrosion products layer formed on the electrodes surface was examined with a scanning electron microscope (SEM; Scanning Jeol JEM5510LV) coupled with Oxford Instruments EDX Analysis System Inca 300 at 15kV and spot size 39 μm.

CONCLUSIONS

Electrochemical investigations revealed that sulfuric acid diamide exerts a good protective effect against bronze corrosion immersed in Na₂SO₄ / NaHCO₃ (pH 5) solution. The best anticorrosive effect was noticed when 1mM inhibitor was used. Based on SEM / EDX analysis, it can be concluded that the beneficial action of

SAD is due to S atoms from its molecule determining its adsorption on the bronze surface. Adsorption of sulfuric acid diamide on bronze surface obeys Langmuir isotherm. Comparative numerical simulations demonstrate the capability of the proposed meta modelling approaches to reduce the number of laboratory experiments and to establish an appropriate experimental policy. More or less cumbersome the depicted example emphasises the utility of mixed approaches for engineers dealing with corrosion.

REFERENCES

1. R. Bostan, S. Varvara, L. Găină and L. M. Mureșan, *Corr. Sci.*, **2012**, *63*, 275-286.
2. E. Cano and D. Lafuente, "Corrosion inhibitors for the preservation of metallic heritage artifacts", Published by Woodhead Publishing Limited, 2013, p. 570-594.
3. A. Balbo, C. Chiavari, C. Martini and C. Monticelli, *Corr. Sci.*, **2012**, *59*, 204-212.
4. R. B. Faltermeier, *Stud. Conserv.*, **1998**, *44*, 121-128.
5. I. Rotaru, S. Varvara, L. Găină and L. M. Mureșan, *Appl. Surf. Sci.*, **2014**, *321*, 188-196.
6. S. H. Zaferani, M. Sharifi, D. Zaarei and M. R. Shishesaz, *J. Environ. Chemical Eng.*, **2013**, *1*, 652-657.
7. El-S. M. Sherif, *Appl. Surf. Sci.*, **2006**, *252*, 8615-8623.
8. V. N. Vapnik, "The nature of statistical learning theory", 2nd edition, Springer, New York, 2000.
9. N. Cristianini and J. Shawe - Taylor, "An introduction to support vector machines", University Press, Cambridge, 2000.
10. C. I. Anghel and A. M. Cormoș, *Rev. Chim.*, **2012**, *63*, 1278-1285.
11. L. Bizo and C. I. Anghel, *Rev. Roum. Chim.*, **2012**, *57*, 369-381.
12. G. R. G. Lanckriet, E. L. Ghaoui, C. Bhattacharyya and M. I. Jordan, *J. Mach. Learn. Res.*, **2002**, *3*, 555-582.
13. T. R. Strohmman and G. Z. Grudic, "A formulation for minimax probability machine regression, in: S. Thrun, S. Becker, K. Obermayer (Eds.), *Advances in Neural Information Processing Systems 15*", MA: MIT Press, Cambridge, 2003 p. 769.
14. C. Küstü, K. C. Emregül and O. Atakol, *Corr. Sci.*, **2007**, *49*, 2800-2814.