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A chemiometric approach for phosphate inhibition of copper corrosion in aqueous media

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Abstract The inhibition of copper corrosion in aqueous media by inorganic phosphates has been studied using a chemiometric approach (experimental and simplex designs). To achieve the objective, four steps were recognized. When submitted to aqueous aggressive media, the anion nature and its concentration were the important variables for the explanation of the mass loss variation. The most corrosive experimental conditions were: anion: chloride (Cl^-); concentration: $[Cl^-] = 1$ mol/l; exposure time: 24 h. In the second step, two inorganic phosphates, Na_3PO_4 and $Na_5P_3O_{10}$, are tested as copper corrosion inhibitors when the material is submitted to the severe conditions. The chemical structure was found to be the most influent factor. However, %IE varies between 25% and 56%. Then, we recognized a passivating treatment by submitting copper to inhibitor solution before immersion in the aggressive medium. Three parameters were studied: inhibitor structure, chemical concentration and passivation time (tp). We concluded that tp is the most influent experimental factor. The best passivating conditions are: inhibitor: $Na_5P_3O_{10}$; inhibitor concentration: [Inhibiteur] = 10^{-2} mol/l and passivation time: 3 h. The inhibition efficiency was 89%. To increase %IE, a simplex design was also performed starting by the above obtained conditions and using the polyphosphate ($Na_5P_3O_{10}$) as inhibitor. The optimum experimental conditions for phosphate inhibition of copper corrosion in aqueous media are: inhibitor: $Na_5P_3O_{10}$, $[Na_5P_3O_{10}] = 0.017$ mol/l and passivation time tp = 2.17 h. Under these conditions an inhibition efficiency of 98% was reached.

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Introduction

Copper exhibits an attractive combination of properties, e.g., good machinability, good resistance to corrosion and biofouling, and superior thermal and electrical conductivities [1]. Thus, it is widely used in industrial and microelectronic applications such as heat-exchangers, wiring technology, electromagnetic interference shielding, and electrostatic dissipation technology. With the development of portable electronic devices, copper is more and more used in corrosive conditions, for example marine or urban environments with elevated pollution level.

In spite of a relatively high standard electrode potential of this metal, corrosion process takes place in significant rate. In fact, during exposure to aggressive media, a film of corrosion products grows at the surface of the metal. The composition and structure of the patina layer depend on the composition of the environment and on the immersion time [2 and references therein].

Nevertheless, whatever the experimental conditions cuprous oxide is the main component of the surface film [3]. In neutral aqueous solution, the corrosion process of copper is controlled by the diffusion of Cu(I) ions through the oxide film [4–7]. Consequently, there is an ever-increasing interest in formulating new corrosion-control measures that would inhibit or at least diminish the corrosion of copper.

Many chemicals are used to inhibit the corrosion of copper in aqueous media. The most famous is benzotriazole that gave a high degree of corrosion protection for copper and copper alloys [8]. Although this organic compound is excellent inhibitor suitable for use in wide variety of environments, it has toxic properties. Consequently, much of the recent researches have therefore focused on formulating new and more environmentally acceptable preservation solutions [9–16].

Phosphorous compounds are commonly used to inhibit the corrosion of carbon steel [17–21] and zinc [22] in aqueous electrolytes. Their use is relatively risk free due to their low toxicity. But, they have never been applied for copper protection. What came to our knowledge is that only Edwards et al. [23] tested two inorganic phosphates, sodium orthophosphate ($NaHPO_4$) and sodium hexametaphosphate (a polyphosphate with $Na_{(n+2)}P_nO_{(3n+1)}$ $n \approx 6$ structure), to inhibit soluble copper corrosion by-product release.

In previous work [24], we tested Na_3PO_4 as inhibitor against the corrosive action of sulfates and chlorides on an archaeological copper-based alloy.

This paper presents the results of an investigation carried out seeking an optimization of the experimental conditions to be used for copper inhibition by inorganic phosphates when submitted to aqueous aggressive media.

Generally, the optimum operational conditions are established by a systematic alteration of a single variable whilst maintaining the others constant. It ensues that such a univariate optimization generates a large number of experiments to achieve the highest possible protection of copper and neglects the independence and interdependence of each experimental parameter. Thus, the only reasonable way to achieve the optimization is to use a chemiometric approach.

Experimental

Pure copper (99.999%) was used for this investigation. The specimens, (5×5) cm, were mechanically cut from a sheet 1.0 mm thick. The calculated exposed specimen surface area was 50 cm^2. The specimens were dry handpolished with emery paper up to grade 2500, degreased with acetone, rubbed with cotton wool soaked in ethanol, dried at room temperature, weighed to determine initial mass, and tested immediately according to the standard procedure ASTM G1-90 (reapproved 1999) [25]. All experiments were conducted at room temperature in aerated solutions prepared from analytical grade reagents. The pH of all corrosive electrolytes was fixed at 7 whereas it ranges between 10 and 12 for the passivating solutions.

Results and discussion

To achieve the optimization of copper inhibition, we recognized four steps:

- understanding the most corrosive conditions;
- evaluating the efficiency of two inorganic phosphates as copper corrosion inhibitors;
- determining the best chemical for copper passivation;
- optimization of the experimental conditions for metal protection.

Determining the most corrosive conditions

We wanted to select the most corrosive condition for copper when submitted to aqueous media. Hence, we consider the following experimental responses:

Δm: the response representing the mass loss; it was measured according to the standard method [25];
U_1: first factor representing the concentration of the anion in the electrolyte;
U_2: second factor representing the exposure time of copper into the aggressive medium;
U_3: third factor representing the nature of the anion.

The experimental field used in this first step is given in Table 1.

In order to compare the effects of the different factors in the experimental field concerned coded variables were used.

The factors U_1, U_2 and U_3 can be transformed into the coded variables X_1, X_2 and X_3, by the relation:

$$X_i = \frac{U_i - \overline{U_i}}{\Delta U_i} \quad (1)$$

where X_i the value taken by the coded variable i;

U_i: the value taken by the factor i;
$\bar{U}_i$: the value taken by the factor i in the center of the experimental field concerned;
ΔU_i: the range of variation of the factor i;

Table 1 Experimental field for the first step

Factor	U_1 (anion concentration) (mol/l)	U_2 (exposure time) (h)	U_3 (anion)
Lower limit (–1)	10^{-2}	1	SO_4^{2-}
Upper limit (+1)	1	24	Cl^-

$$\overline{U_i} = \frac{\text{Upper limit}(U_i) + \text{lower limit}(U_i)}{2} \quad (2)$$

$$\Delta U_i = \frac{\text{Upper limit}(U_i) - \text{lower limit}(U_i)}{2} \quad (3)$$

A mathematical approach was used where the experimental responses Δm and CR were represented by the following equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3$$

b_i represents the estimation of the main effects of the factor i;
b_{ij} represents the estimation of the interaction between the factors i and j;
b_{ijk} represents the estimation of the interaction between the factors i, j and k;

Calculation of coefficients is carried out through the least squares method by using:

$$B = (X\prime X)^{-1}X\prime Y \quad (4)$$

where:

B is the vector of the estimates of the coefficients;
X is the model matrix;
$(X'X)$ is the information matrix;
$(X'X)^{-1}$ is the dispersion matrix;
Y is the vector of experimental results.

We have chosen a full factorial design, proposed by several authors [26–28] in which l^n experiments are needed to evaluate the influence of n variables at l levels. Three variables are considered in this investigation: [Anion], exposure time and anion nature with two levels each. Thus, the experimental design consists of eight experiments and it is organized as reported in Table 2.

The experimental results are summarized in Table 3.

The responses were analyzed by regression analysis according to the proposed model. The estimated models parameters are listed in Table 4.

To explain Δm changes and to evaluate the weight of the different coefficients of the models Pareto analysis [29] was performed. Plots of the contribution of each term are displayed in Fig. 1. The percentage effect P_i of every term i, was calculated through:

Table 2 The experimental design and the corresponding experimental matrix for the first step

	Experimental design			Experimental matrix		
	X_1	X_2	X_3	U_1	U_2	U_3
1	–1	–1	–1	10^{-2}	1	SO_4^{2-}
2	1	–1	–1	1	1	SO_4^{2-}
3	–1	1	–1	10^{-2}	24	SO_4^{2-}
4	1	1	–1	1	24	SO_4^{2-}
5	–1	–1	1	10^{-2}	1	Cl^-
6	1	–1	1	1	1	Cl^-
7	–1	1	1	10^{-2}	24	Cl^-
8	1	1	1	1	24	Cl^-

Table 3 Mass losses obtained for the first experimental design

	Δm (mg)	Δm (mg/cm^2)
1	0.9	0.17
2	1.6	0.28
3	1.2	0.22
4	1.8	0.32
5	2.1	0.36
6	2.6	0.49
7	2.0	0.34
8	2.9	0.55

Table 4 Mathematical model coefficients

b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}
0.341	0.068	0.017	0.091	0.007	0.015	–0.006	0.012

$$P_i = 100x\left(\frac{b_i^2}{\sum_i b_i^2}\right) \quad (5)$$

These plots indicate that for Δm, the coefficients b_3 and b_1 could explain about 95% of the experimental response variation, the main effect is the anion nature (P_3 = 60.68%).

To find the most corrosive conditions, we have to maximize the mass loss. Then, we have analyzed the models coefficients:

- b_1 is positive: Δm increases when X_1 decreases ; the optimum level for the coded variable will be +1 ;
- b_2 is positive: Δm increases when X_2 decreases ; the optimum level for the coded variable will be +1 ;
- b_3 is positive: Δm increases when X_3 increases ; the optimum level for the coded variable will be +1.

Then, the most aggressive experimental conditions correspond to the 4th experience of the design.

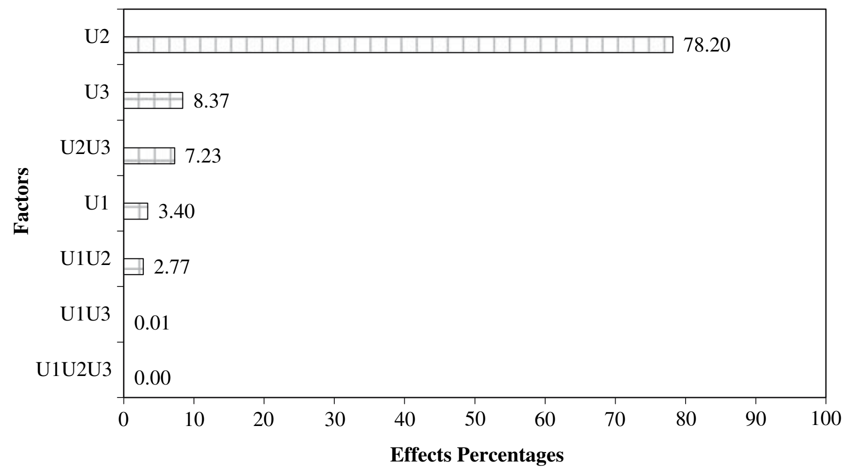

Fig. 1 Pareto chart for the first experimental design

Effectiveness of inorganic phosphates as copper inhibitors

The aim of the present study is to ensure the effectiveness of inorganic phosphates as copper corrosion inhibitors. Hence, we considered the inhibition efficiency percentage as experimental responses. It was calculated according to the following equation [29 and references therein]:

$$\%\mathrm{IE} = 100x\,\frac{(\Delta m(0)) - \Delta m(inh)}{\Delta m(0)} \tag{6}$$

where:

$\Delta m(0)$ is copper mass loss when immersed in an aggressive electrolyte;
$\Delta m(inh)$ is copper mass loss when submitted to an inhibitive treatment.

Two parameters were studied: the nature of the inhibitor (I) and its concentration ([I]). The experimental field is reported in Table 5.

The mathematical model used to describe the experimental response %IE was:

$$\%\ \mathrm{IE} = b'_0 + b'_1X_1 + b'_2X_2 + b'_3X_3 + b'_{12}X_1X_2$$

A full factorial design was used to evaluate the influence of the two parameters at 2 levels. Then, the experimental design consists of four experiments (Table 6).

The experimental results are reported in Table 7.

Then, we used the least squares method (Eq. 4) in order to calculate the model coefficients (Table 8).

Pareto analysis was performed to measure the weight of each factor (Fig. 2).

The graph indicates that the coefficients b_1 and b_2 could explain about 97% of inhibition efficiency variation, the main effect is the inhibitor nature (P_1 = 58.64%). Such result is in agreement with results achieved by Edwards et al. [23] where the most efficient

Table 5 Experimental field for the second step

Factor	U'_1 (inhibitor)	U'_2 (inhibitor concentration) (mol/l)
Lower limit (–1)	Na_3PO_4	10^{-3}
Upper limit (+1)	$Na_5P_3O_{10}$	10^{-2}

Table 6 The experimental design and the corresponding experimental matrix for the second step

	Experimental design		Experimental matrix	
	X'_1	X'_2	U'_1	U'_2
1	–1	–1	Na_3PO_4	10^{-3}
2	+1	–1	$Na_5P_3O_{10}$	10^{-3}
3	–1	+1	Na_3PO_4	10^{-2}
4	+1	+1	$Na_5P_3O_{10}$	10^{-2}

Table 7 Mass losses obtained for the second experimental design

	Δm (mg)	Δm (mg/cm^2)	%IE
1	1.3	0.24	56.4
2	1.9	0.32	41.8
3	1.6	0.29	47.3
4	2.4	0.41	25.5

Table 8 Mathematical model coefficients

b'_0	b'_1	b'_2	b'_{12}
0.315	0.100	0.020	0.070

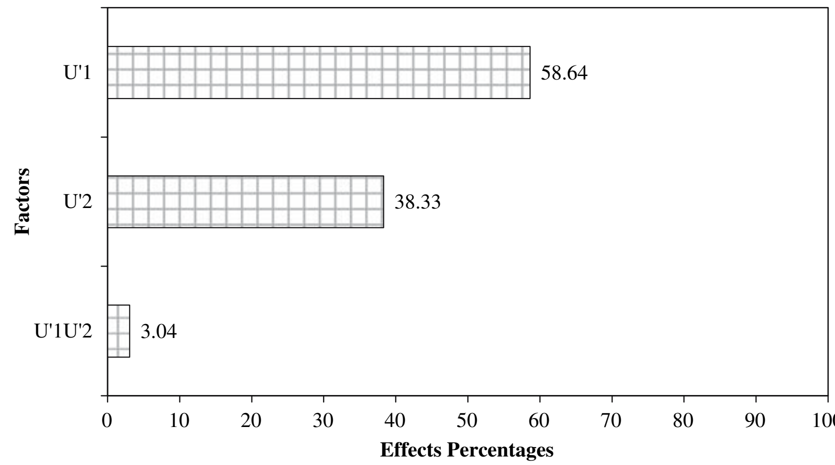

Fig. 2 Pareto chart for the second experimental design

protection was observed for phosphates. Polyphosphates increases the dissolution of the material.

When analyzing the experimental results, some inhibitive behaviour could be stated for both phosphates. Then, a passivation step is necessary to improve copper protection.

Effectiveness of passivation of copper by mean of inorganic phosphates

The objective of the following study is to explore the possibility of passivation copper using inorganic phosphates. Then, the inhibition efficiency percentage will be considered as experimental response.

Three parameters were studied: the inhibitor nature (I), the inhibitor concentration ([I]) and the time of exposure to the inhibitor electrolyte (tp).

The experimental field is reported in Table 9.

A mathematical model was used to describe the inhibition efficiency percentage. Hence, %IE could be represented by mean of the following equation:

$$\% \text{ IE} = b''_0 + b''_1X_1 + b''_2X_2 + b''_3X_3 + b''_{12}X_1X_2 + b''_{13}X_1X_3 + b''_{23}X_2X_3 + b''_{123}X_1X_2X_3$$

b_i'' represents the estimation of the main effects of the factor i;

b_{ij}'' represents the estimation of the interaction between the factors i and j;

b_{ijk}'' represents the estimation of the interaction between the factors i, j and k;

Calculation of the model coefficients is carried out through the least squares method by using Eq. (4).

A full factorial design was used to evaluate the influence of the three variables at 2 levels. Then, eight experiments are needed. Table 10 illustrates the experimental design.

The experimental results achieved are reported in Table 11.

Table 9 Experimental field for the third step

Factor	U''_1 (inhibitor)	U''_2 (inhibiteur concentration) (mol/l)	U''_3 (passivation time) (Heures)
Lower limit (–1)	Na_3PO_4	10^{-3}	1
Upper limit (+1)	$Na_5P_3O_{10}$	10^{-2}	3

Table 10 The experimental design and the corresponding experimental matrix for the third step

	Experimental design			Experimental matrix		
	X_1	X_2	X_3	U_1	U_2	U_3
1	–1	–1	–1	Na_3PO_4	0.001	1
2	+1	–1	–1	$Na_5P_3O_{10}$	0.001	1
3	–1	+1	–1	Na_3PO_4	0.01	1
4	+1	+1	–1	$Na_5P_3O_{10}$	0.01	1
5	–1	–1	+1	Na_3PO_4	0.001	3
6	+1	–1	+1	$Na_5P_3O_{10}$	0.001	3
7	–1	+1	+1	Na_3PO_4	0.01	3
8	+1	+1	+1	$Na_5P_3O_{10}$	0.01	3

Table 11 Mass losses obtained for the third experimental design

	Δm (mg)	Δm (mg/cm^2)	%IE
1	1.2	0.214	60.8
2	1.1	0.216	60.4
3	1.1	0.224	62.4
4	0.7	0.224	76.0
5	1	0.197	63.9
6	0.9	0.177	67.6
7	1.1	0.211	61.4
8	0.3	0.056	89.7

Table 12 Mathematical model coefficients

b''_0	b''_1	b''_2	b''_3	b''_{12}	b''_{13}	b''_{23}	b''_{123}
0.1897	–0.0432	–0.02215	–0.05935	–0.41	–0.0443	–0.03145	0

The response was analyzed by regression analysis according to the proposed model. The estimated models parameters are listed in Table 12.

Pareto graphical analysis (Eq. 5) was performed (Fig. 3). The results achieved are reported in Fig. 3.

It was evidenced that b_1'', b_{12}'', b_2'' and b_3'' could explain about 92% of the %IE variation. The main factor for the experimental response is b_1'' ($P_1 = 34.85\%$) corresponding to the nature of the inhibitor.

The most passivating conditions were found by maximizing %IE. Then, we have analyzed the models coefficients:

- b_1'' is positive: %IE increases when X_1 decreases ; the optimum level for the coded variable will +1;
- b_2'' is positive: %IE increases when X_2 decreases ; the optimum level for the coded variable will +1;
- b_3'' is positive: %IE increases when X_3 increases ; the optimum level for the coded variable will be +1.

Then, the best passivating conditions correspond to the 8th experience of the design. However, %IE was equal to 89.7%. An optimization step is needed to reach inhibition efficiency equivalent to those given by benzotriazole and derivatives.

Optimization of copper passivation by mean of inorganic phosphates

A simplex design [30] was used to optimize the experimental conditions of copper passivation. The simplex was constructed starting by the experimental conditions obtained in the last design. $Na_5P_3O_{10}$ was tested as copper corrosion inhibitor. Only the inhibitor concentration and the passivation time were varied. The initial simplex and the corresponding experimental design are reported in Table 13.

When performing the experiences, we obtained the resulted gathered in Table 14.

It was evidenced that the mass loss increases with decreasing of %IE, indicating an increase of the corrosion rate.

We observed that the worst point of the simplex corresponds to the 3rd experience. We calculated the coordinates of the simplex 4th point and we obtained the corresponding values of the natural variables (Table 15).

When performing the experience, we obtained the mass loss. Then, we calculated %IE (Table 16).

Δm was equal to 10 μg/cm^2 corresponding to an inhibition efficiency of 98%.

Table 13 Initial simplex

	Experimental design		Experimental matrix	
	X''_1	X''_2	U''_1	U''_2
1	0	0	0.010	3
2	0.966	0.260	0.020	3.26
3	0.258	0.970	0.013	3.97

Table 14 Mass losses obtained for the initial simplex

	Δm (mg)	Δm (mg/cm^2)	(%IE)
1	0.3	0.056	89.7
2	2.3	0.460	15.5
3	2.4	0.490	8.5

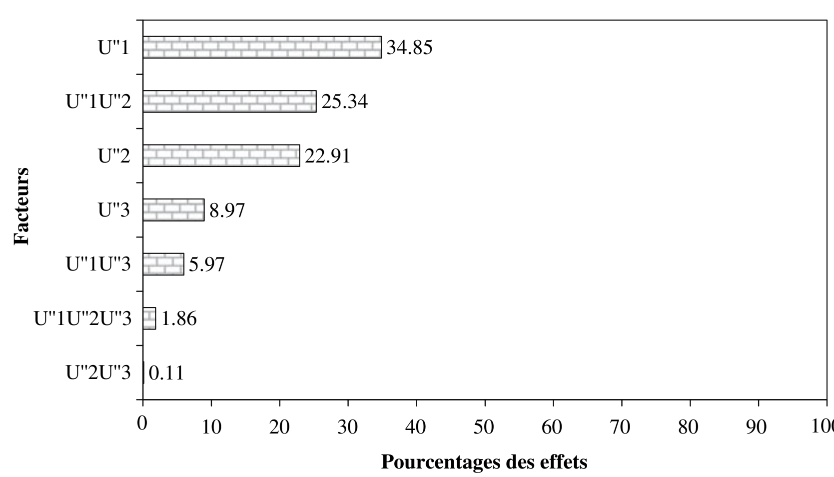

Fig. 3 Pareto chart for the third experimental design

Table 15 Coordinates of the simplex 4th point

	Experimental design		Experimental matrix	
	X_1	X_2	U_1	U_2
4	0.707	–0.710	0.017	2.290

Table 16 Mass losses obtained for the simplex 4th point

	Δm (mg)	Δm (mg/cm^2)	(%IE)
4	0.05	0.010	98.1

Conclusion

The aim of our research program was the inhibition of copper corrosion in aqueous media by inorganic phosphates. To achieve this objective a chemiometric approach was used.

When submitted to aqueous aggressive media, we noticed that the anion nature and its concentration are the important variables for the explanation of the mass loss variation.

The most corrosive experimental conditions are:

anion: chloride (Cl^-);
concentration: [Cl^-] = 1 mol/l;
exposure time: 24 h.

Under the obtained severe conditions we tested two inorganic phosphates, Na_3PO_4 and $Na_5P_3O_{10}$, as copper corrosion inhibitors.

The results achieved indicated that chemical nature is the most influent factor. Furthermore, we observed a decrease of the mass loss when adding the phosphate based chemicals (%IE varies between 25% and 56%). Inorganic phosphates could be used as copper corrosion inhibitor. But, an optimization of the experimental conditions is needed.

Then, we recognized a passivating treatment by submitting the material to inhibitor solution before immersion in the severe conditions. We studied the influence of three parameters: the inhibitor, its concentration and the passivation time. The results achieved allowed concluding that the passivating time is the most influent experimental factor (P_i = 35%). The best passivating conditions are:

inhibitor: $Na_5P_3O_{10}$;
inhibitor concentration: [Inhibiteur] = 10^{-2} mol/l;
passivation time: 3 h.

Under these experimental conditions the inhibition efficiency was about 90%. In order to reach %IE in the order of magnitude of those observed for benzotriazole and its derivatives (≥95%), we performed a simplex design starting by the above obtained conditions and using the polyphosphate ($Na_5P_3O_{10}$) as inhibitor. After four experiences, we obtained an inhibition efficiency of 98%. The chemiometric approach is a powerful tool for studying the corrosion and inhibition phenomena.

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