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# DEVELOPMENT OF A SOFTWARE APPLICATION FOR THE CONSTRUCTION OF THE SIMPLIFIED POURBAIX DIAGRAMS USED IN THE STUDY OF THE CORROSION

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## Abstract

As a result of the adaptation of the Spanish University to the European Space for Higher Education, changes in teaching-learning methodologies are required. In this context, the development of new software applications can be useful.

Pourbaix diagram, also known as a potential-pH diagram, is a graphic representation of the potential with respect to the standard hydrogen electrode (vertical axis) versus the pH (horizontal axis) for a metal under standard thermodynamic conditions (usually water at 25 °C). The diagram has in account the chemical and electrochemical equilibria and it defines the dominion of stability for the electrolyte (normally water), the metal, and compounds related, for example, oxides, hydroxides, and hydrides. Such diagrams can be constructed from calculations based in the equation of Nernst and in the equilibrium constants of different metallic compounds.

Pourbaix diagrams have proved to be very useful in corrosion as well as in many other fields, such as industrial electrolysis, plating, electrowinning and electrorefining of metals, primary and secondary electric cells, water treatment, and hydrometallurgy. Pourbaix diagrams are useful particularly in the study of the behaviour in front of the corrosion of metallic materials, since they permit predicting the zones of immunity, corrosion, and passivation of a metal in an aggressive determined means. If metal in its elementary form is the thermodynamically stable phase, this will indicate conditions of immunity. The corrosion will occur if a soluble cation of the metal is the thermodynamically stable phase. If a soluble complex anion of the cation in alkaline means is the thermodynamically stable phase, which occurs in the case of amphoteric metals, as for example, iron, aluminium, zinc, etc., this will indicate conditions of alkaline corrosion. The passivation will occur if a compound solid of the metal is the thermodynamically stable phase, as for example, oxides, hydroxides or hydrides. This is the reason for which habitually in the studies of corrosion Pourbaix diagrams appear in simplified form showing the described regions and without specifying which the stable species in each condition are.

However, manual construction of Pourbaix diagrams is a tedious and systematic task requiring a large amount of time to perform. The development of a software application able to perform Pourbaix diagrams will help to save time in the study of many corrosion problems, as well as problems in other fields cited before.

The aim of this work is to develop a new software application for the construction of the simplified Pourbaix diagrams applied to the study of the corrosion. Simplified Pourbaix diagrams with precise delineation of immunity, corrosion, alkaline corrosion, and passivation regions can be an useful tool for the study of the corrosion behaviour of metallic materials both education and research fields.

Keywords: Corrosion, pH, potential, Pourbaix diagram, software application.

## 1 INTRODUCTION

As a result of the adaptation of the Spanish University to the European Space for Higher Education, changes in teaching-learning methodologies are required. In this context, the development of new software applications can be useful.

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(normally water), the metal, and compounds related, for example, oxides, hydroxides, and hydrides. Such diagrams can be constructed from calculations based in the equation of Nernst and in the equilibrium constants of different metallic compounds [1-7].

Pourbaix diagrams have proved to be very useful in corrosion as well as in many other fields, such as industrial electrolysis, plating, electrowinning and electrorefining of metals, primary and secondary electric cells, water treatment, and hydrometallurgy. Pourbaix diagrams are useful particularly in the study of the behaviour in front of the corrosion of metallic materials, since they permit predicting the zones of immunity, corrosion, and passivation of a metal in an aggressive determined means. If metal in its elementary form is the thermodynamically stable phase, this will indicate conditions of immunity. The corrosion will occur if a soluble cation of the metal is the thermodynamically stable phase. If a soluble complex anion of the cation in alkaline means is the thermodynamically stable phase, which occurs in the case of amphoteric metals, as for example, iron, aluminium, zinc, etc., this will indicate conditions of alkaline corrosion. The passivation will occur if a compound solid of the metal is the thermodynamically stable phase, as for example, oxides, hydroxides or hydrides. This is the reason for which habitually in the studies of corrosion Pourbaix diagrams appear in simplified form showing the described regions and without specifying which the stable species in each condition are.

However, manual construction of Pourbaix diagrams is a tedious and systematic task requiring a large amount of time to perform. The development of a software application able to perform Pourbaix diagrams will help to save time in the study of many corrosion problems, as well as problems in other fields cited before.

The aim of this work is to develop a new software application, called EpHGraph, for the construction of the simplified Pourbaix diagrams applied to the study of the corrosion.

## 2 METHODOLOGY

### 2.1 Characteristics of the software

EpHGraph program is organized in the following workflow modules, as shown in Fig. 1. These modules are described below.

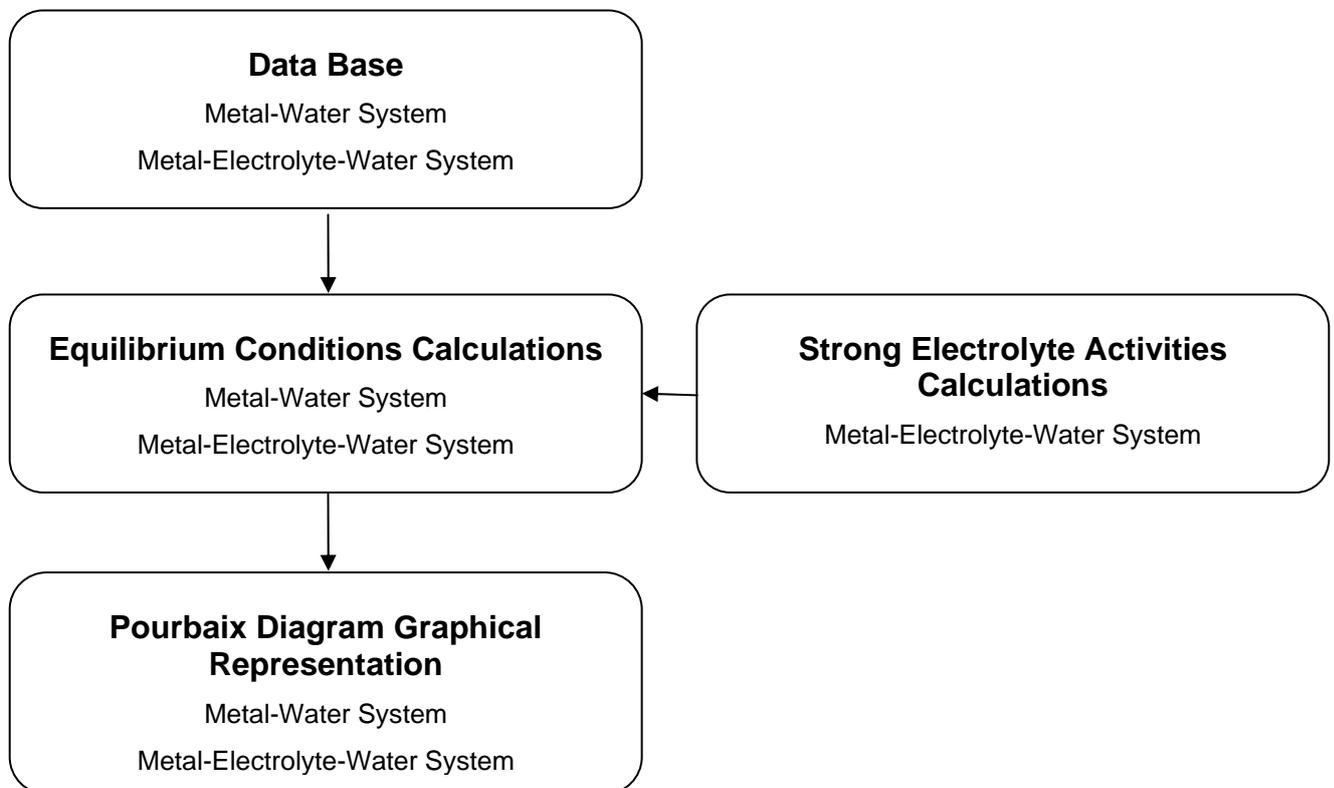


Fig.1. Workflow modules for the EpHGraph program.

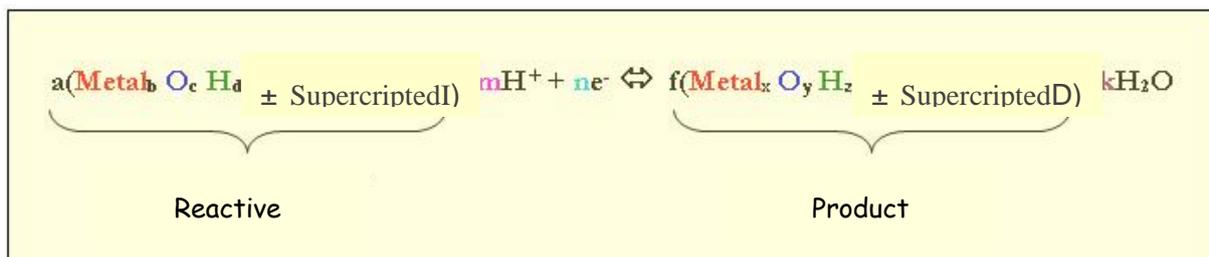
### 2.1.1 Data Base

EpHGraph works with a data base of chemical species. In this data base, there are a data table for each metal. Each table has a row for each species related to the metal, where values of standard Gibbs free energy of formation ( $\Delta G_f^\circ$ ) are defined, together the oxidation number, the state of the species, and the complete and abbreviate formula.

This information is the engine of the program, because the information on the data base is absolutely necessary to calculate the equilibrium conditions. These conditions can be calculated for two types of systems: metal-water and metal-electrolyte-system.

### 2.1.2 Equilibrium Conditions Calculations

In this module, first the equations of the different reactions between all species in the system are calculated. Pairs of species (reactive and product) were considered in each reaction together with the proton ion ( $H^+$ ), the electrical charge ( $e^-$ ), and water ( $H_2O$ ). The reaction equations have the following general form:



The calculation of the balanced equations is carried out in 4 steps:

- 1) Place the species in the right side of the equation.
- 2) Calculate the reactive and product coefficients.
- 3) Calculate the water and protons coefficients.
- 4) Calculate the electrical charge coefficients.

Once the equation is balanced, the EpHGraph program classified the reactions in three types:

- *Electrochemical reactions not involving  $H^+$* . These electrochemical reactions are dependent on the potential and independent of the pH; they are labelled "E" in the EpHGraph program.
- *Electrochemical reactions involving  $H^+$* . These electrochemical reactions depend both on the potential and the pH; they are labelled "E vs pH" in the EpHGraph program.
- *Chemical reactions involving  $H^+$* . These chemical reactions are independent of the potential and dependent on the pH; they are labelled "pH" in the EpHGraph program.

Finally, EpHGraph program realizes the calculation of the equilibrium conditions for the three types of reactions. EpHGraph program is able to show a table with all these calculated values, ordered by type of reaction, as shown in Fig. 2.

### 2.1.3 Strong Electrolyte Activity Calculations

This module calculates the activity value for strong electrolytes, which is necessary for the calculation of the equilibrium conditions. This module only is used in the case of the system metal-electrolyte-water.

### 2.1.4 Pourbaix Diagram Graphical Representation

This module implements the graphical representation of the calculations performed.

EpHGraph can perform three types of graphics: predominance zones, Pourbaix diagrams, and simplified Pourbaix diagrams.

The diagrams are represented drawing the values saved in complex structures (vectors and matrixes) by the Equilibrium Conditions Calculations Module.

Once the selected diagram by a user is shown, the user can select to rescale the X and Y axis, so that the user can zoom the chart to view a larger or smaller area of the diagram.

Reacción	Tipo	Subtipo	dG°	E	Ph	E vs Ph
1 Cu+ + OH+ + 1e- <=> 1 Cu + 0 H2O	E	continua	-50,300	0,167		
1 Cu+2 + OH+ + 2e- <=> 1 Cu + 0 H2O	E	continua	-65,700	0,163		
1 Cu+2 + OH+ + 1e- <=> 1 Cu+ + 0 H2O	E	discontinua	-15,400	0,160		
2 Cu+ + 2H+ + 1 H2O <=> 1 Cu2O	Ph	continua	-11,522		4,990	
1 Cu+2 + 2H+ + 1 H2O <=> 1 CuO	Ph	continua	37,478		6,285	
1 Cu+2 + 2H+ + 2 H2O <=> 1 Cu(OH)2	Ph	continua	49,156		7,308	
1 Cu+2 + 3H+ + 2 H2O <=> 1 HCuO2-	Ph	discontinua	149,756		8,750	
1 Cu+2 + 4H+ + 2 H2O <=> 1 CuO2-2	Ph	discontinua	224,756		9,849	
1 CuO + 1H+ + 1 H2O <=> 1 HCuO2-	Ph	continua	112,278		13,680	
1 CuO + 2H+ + 1 H2O <=> 1 CuO2-2	Ph	continua	187,278		13,413	
1 Cu(OH)2 + 1H+ <=> 1 HCuO2- + 0 H2O	Ph	continua	100,600		11,633	
1 Cu(OH)2 + 2H+ <=> 1 CuO2-2 + 0 H2O	Ph	continua	175,600		12,390	
1 HCuO2- + 1H+ <=> 1 CuO2-2 + 0 H2O	Ph	discontinua	75,000		13,146	
1 Cu + 1H+ + 1e- <=> 1 CuH + 0 H2O	E vs Ph	continua	259,400			-0,059 Ph + -2,689
1 Cu2O + 2H+ + 2e- <=> 2 Cu + 1 H2O	E vs Ph	continua	-89,078			-0,059 Ph + 0,462
1 CuO + 2H+ + 2e- <=> 1 Cu + 1 H2O	E vs Ph	continua	-103,178			-0,059 Ph + 0,535
1 Cu(OH)2 + 2H+ + 2e- <=> 1 Cu + 2 H2O	E vs Ph	continua	-114,856			-0,059 Ph + 0,595
1 HCuO2- + 3H+ + 2e- <=> 1 Cu + 2 H2O	E vs Ph	continua	-215,456			-0,089 Ph + 0,939
1 CuO2-2 + 4H+ + 2e- <=> 1 Cu + 2 H2O	E vs Ph	continua	-290,456			-0,118 Ph + 1,328
1 Cu+ + 1H+ + 2e- <=> 1 CuH + 0 H2O	E vs Ph	continua	209,100			-0,030 Ph + -1,261
1 CuO + 2H+ + 1e- <=> 1 Cu+ + 1 H2O	E vs Ph	continua	-52,878			-0,118 Ph + 0,903
1 Cu(OH)2 + 2H+ + 1e- <=> 1 Cu+ + 2 H2O	E vs Ph	continua	-64,556			-0,118 Ph + 1,024
1 HCuO2- + 3H+ + 1e- <=> 1 Cu+ + 2 H2O	E vs Ph	discontinua	-165,156			-0,177 Ph + 1,712
1 CuO2-2 + 4H+ + 1e- <=> 1 Cu+ + 2 H2O	E vs Ph	discontinua	-240,156			-0,237 Ph + 2,489
1 Cu+2 + 1H+ + 3e- <=> 1 CuH + 0 H2O	E vs Ph	continua	193,700			-0,020 Ph + -0,787
2 Cu+2 + 2H+ + 2e- + 1 H2O <=> 1 Cu2O	E vs Ph	continua	-42,322			0,059 Ph + -0,136
1 Cu2O + 4H+ + 4e- <=> 2 CuH + 1 H2O	E vs Ph	continua	429,722			-0,059 Ph + -1,113
1 CuO + 3H+ + 3e- <=> 1 CuH + 1 H2O	E vs Ph	continua	156,222			-0,059 Ph + -0,540
1 Cu(OH)2 + 3H+ + 3e- <=> 1 CuH + 2 H2O	E vs Ph	continua	144,544			-0,059 Ph + -0,499
1 HCuO2- + 4H+ + 3e- <=> 1 CuH + 2 H2O	E vs Ph	continua	43,944			-0,079 Ph + -0,270

Fig. 2. Table of all the equations of the reactions for a system metal-water.

## 2.2 Handling of the software

This section is showing an example of the use of the EpHGraph program for the construction of the simplified Pourbaix diagrams for the system copper-water at 25 °C.

When the software application is open, it appears a toolbar at the top of the visual display screen. The toolbar shows a number of buttons, as shown in Fig. 3:

“**Sistemas**”, is used for the calculation of the equilibrium conditions in the diagrams.

“**Diagramas**”, is used for the construction of the different types of diagrams: predominance zones, Pourbaix diagrams, and simplified Pourbaix diagrams.

“**Salir**”, is used for turning off the software.

“**Acerca de**”, is used as help.

For the construction of the simplified Pourbaix diagrams, select the button “Diagramas”. A window appears, and click the button “Diagramas de Pourbaix simplificados”. A new window appears to select the type of system used for the construction of the diagrams: metal-water, and metal-electrolyte-water. For example, in the case of the system copper-water, select the button “Metal-agua”, as shown in Fig. 3.

When the button “Metal-agua” is selected, a new visual display screen appears for the metal-water system, as shown in Fig. 4. It shows a window with the different metals that can be selected. For example, in the case of the system copper-water, select the button “Cu”. The visual display screen also shows the buttons “Siguiente” to pass the following screen, and “Atras” to pass the previous screen.

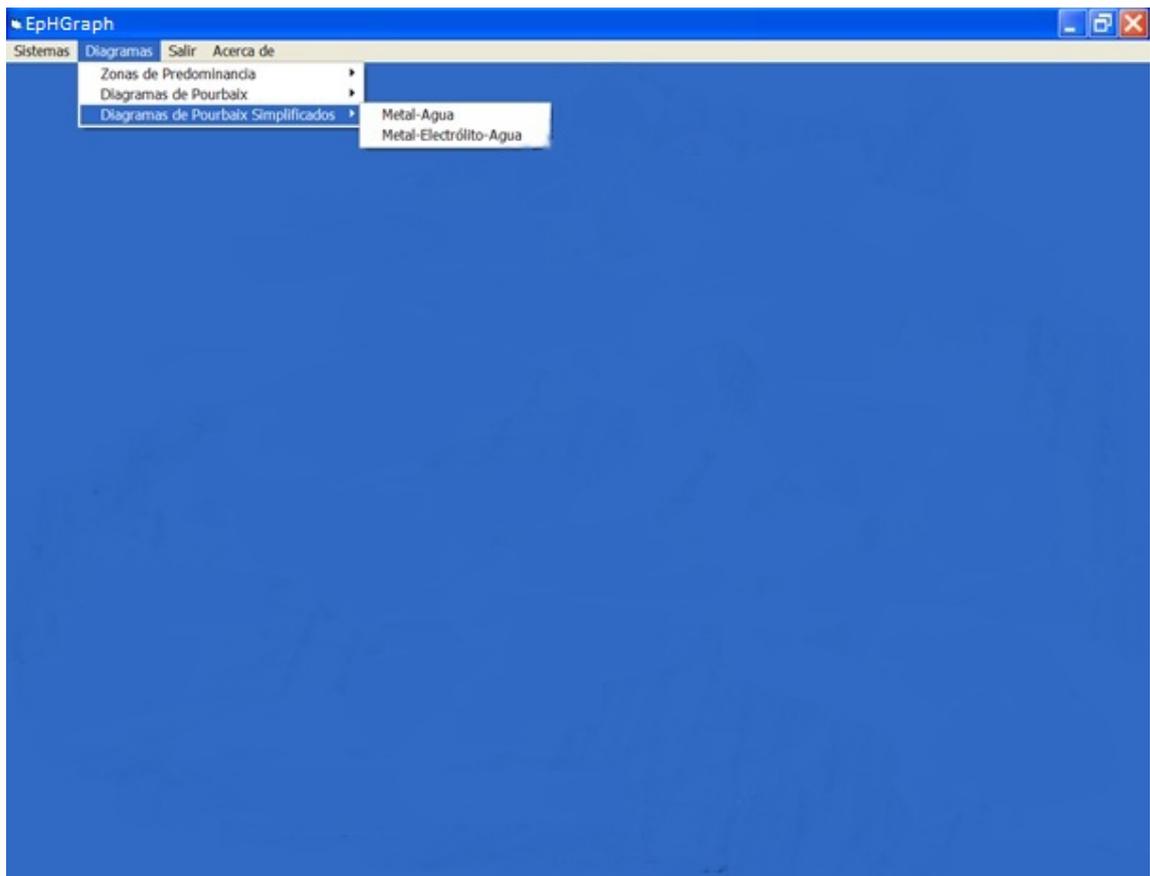


Fig. 3. Principal toolbar of the EpHGraph program.

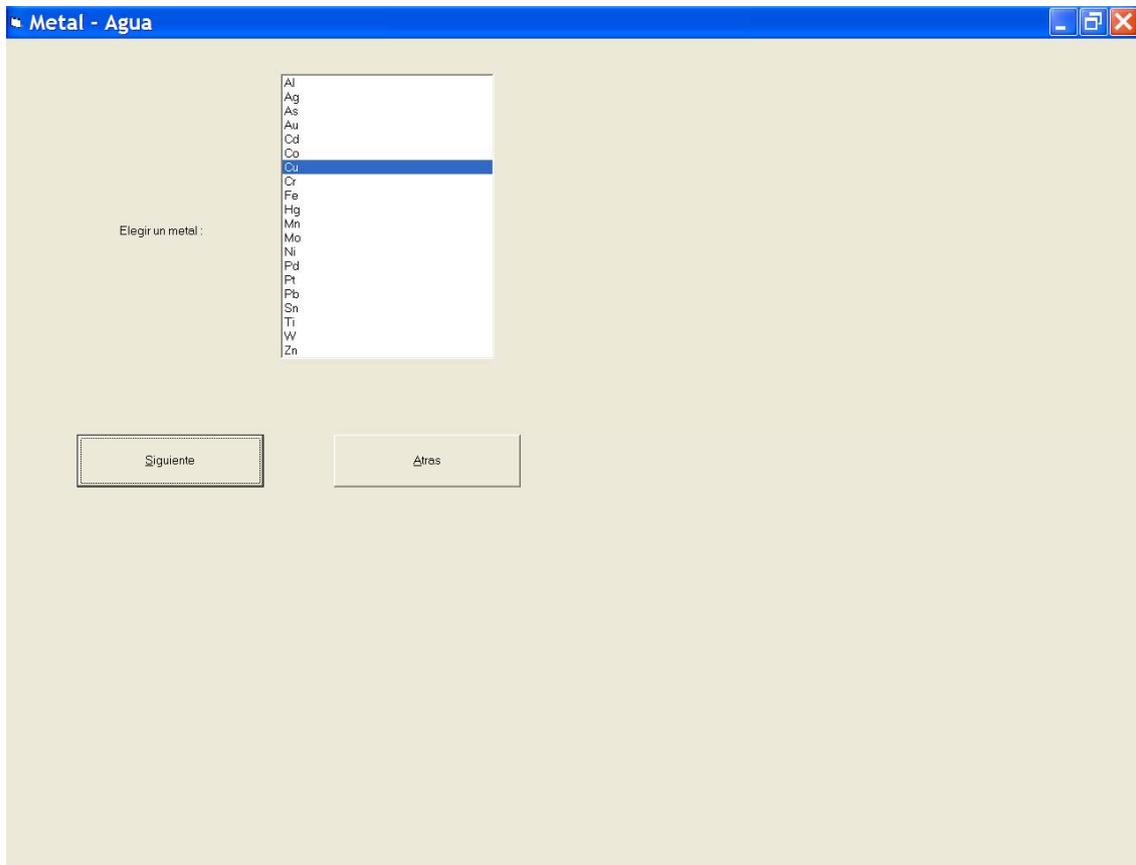


Fig. 4. Visual display screen used to select the metal in the system metal-water.

When the metal is selected, a new window appears for the metal-water system, as shown in Fig. 5. The window permits to introduce the activity value of the soluble metal species, which is necessary for the construction of the diagrams. It can be introduced in two options:

“**Valor Definido**”, used for select the activity value defined for the software application ( $10^0$ ,  $10^{-2}$ ,  $10^{-4}$ ,  $10^{-6}$ , and  $10^{-8}$ ).

“**Valor Usuario**”, used for introduce the activity value defined for the user.

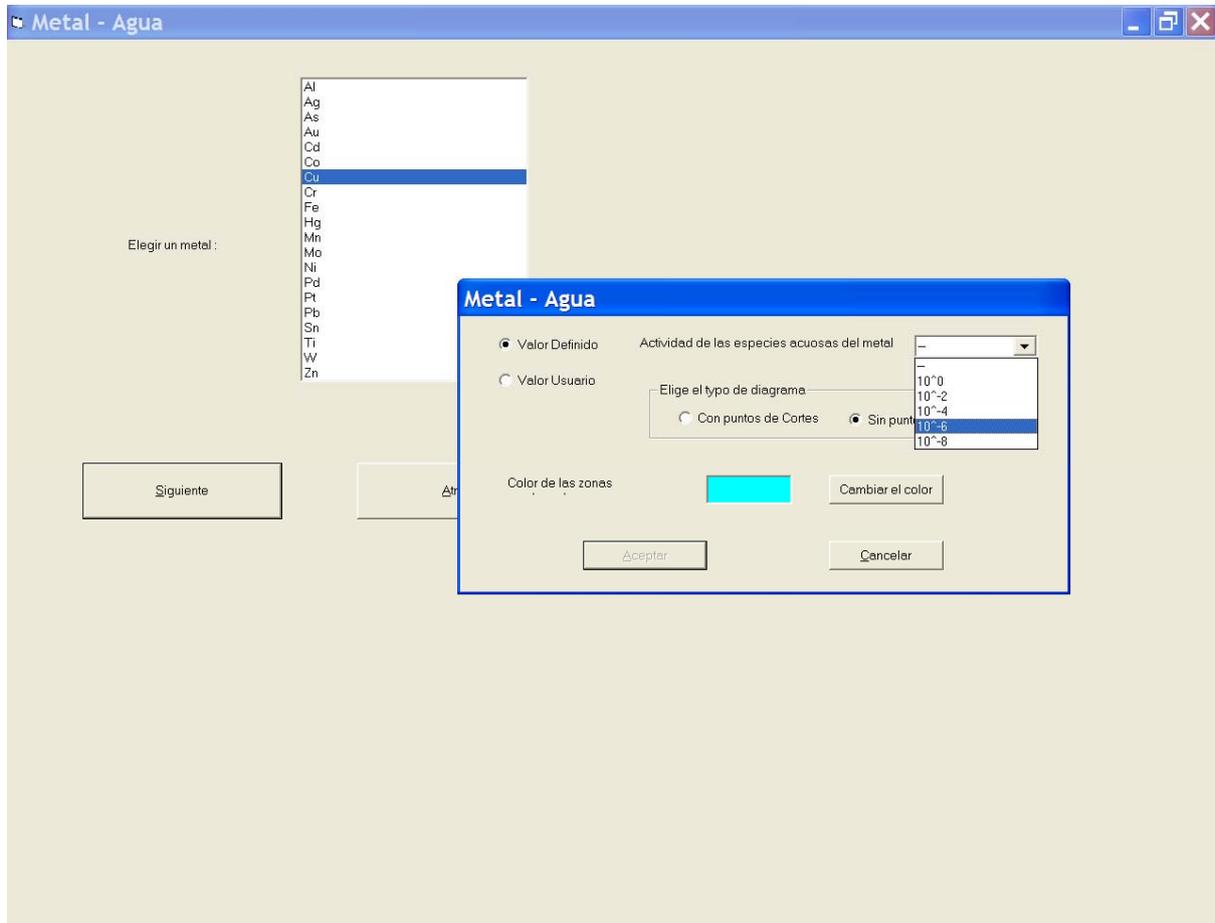


Fig. 5. Window to enter the activity value of the soluble metal species for the system metal-water.

This window also permits to change the colour of the corrosion zones in the diagrams. When the button “Cambiar el color” is selected, it appears a new window that contains the different colours that can be selected by the user, as shown in Fig. 6. In defect the corrosion zones are colored in blue.

Finally, when the activity value of the soluble metal species is introduced in EpHGraph program, the simplified Pourbaix diagram appears in a new visual display screen.

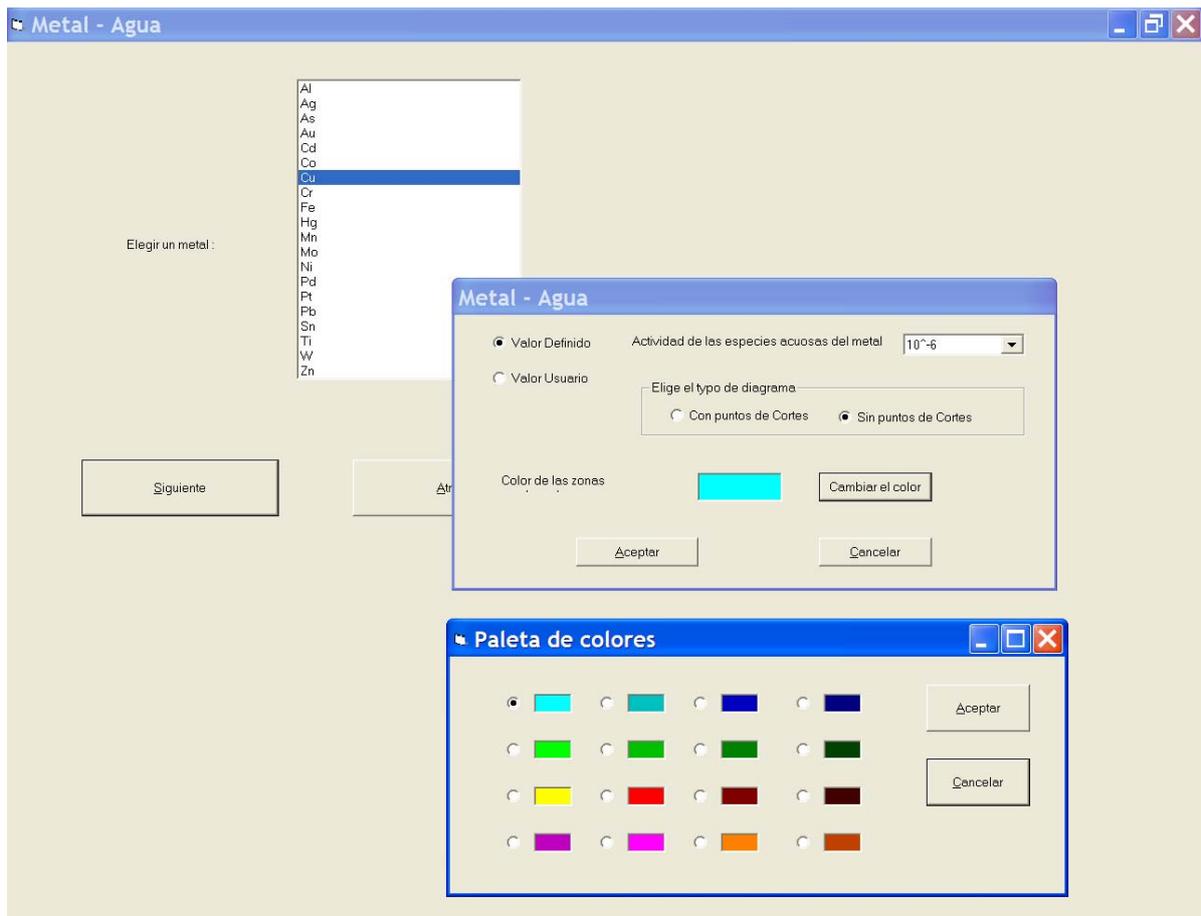


Fig. 6. Window to select the colour of the corrosion zones in the diagrams for the system metal-water.

### 3 RESULTS

Fig. 7 shows a practical example of EpHGraph program for the construction of the simplified Pourbaix diagrams. Visual display screen in Fig. 7 shows the simplified Pourbaix diagram for the system copper-water at 25 °C. The diagram was plotted for a  $10^{-6}$  activity of the soluble copper species, which was used to separate between corrosion, immunity, and passivation. The corrosion areas were shaded in blue colour to differentiate them from immunity and passivation.

In the simplified Pourbaix diagram there are three general types of lines, each one represents an equilibrium among two species:

- Horizontal lines, which indicates reactions with dependence only of the potential.
- Vertical lines, which indicates reactions with dependence only of the pH.
- Oblique lines, which indicates reactions with dependence both of the potential and the pH.

In the diagram two additional lines appear, labelled “a” and “b”, which represents the equilibrium of water decay with formation of oxygen and hydrogen, respectively. The region between the two lines represents a zone where water is stable regarding oxygen and hydrogen. Above the line “a” (oxidizing conditions), the water will be oxidised with gaseous oxygen evolution. Below the line “b” (reducing conditions), the water will be reduced with gaseous hydrogen evolution.

Visual display screen in Fig. 7 shows two buttons at the top and at the bottom of the potential vertical axis (E), which can be used to change the maximum and the minimum value of potential in the axis, respectively.

The visual display screen also shows the button “Export en jpg”, which permit to export the simplified Pourbaix diagram as image in “jpg”.

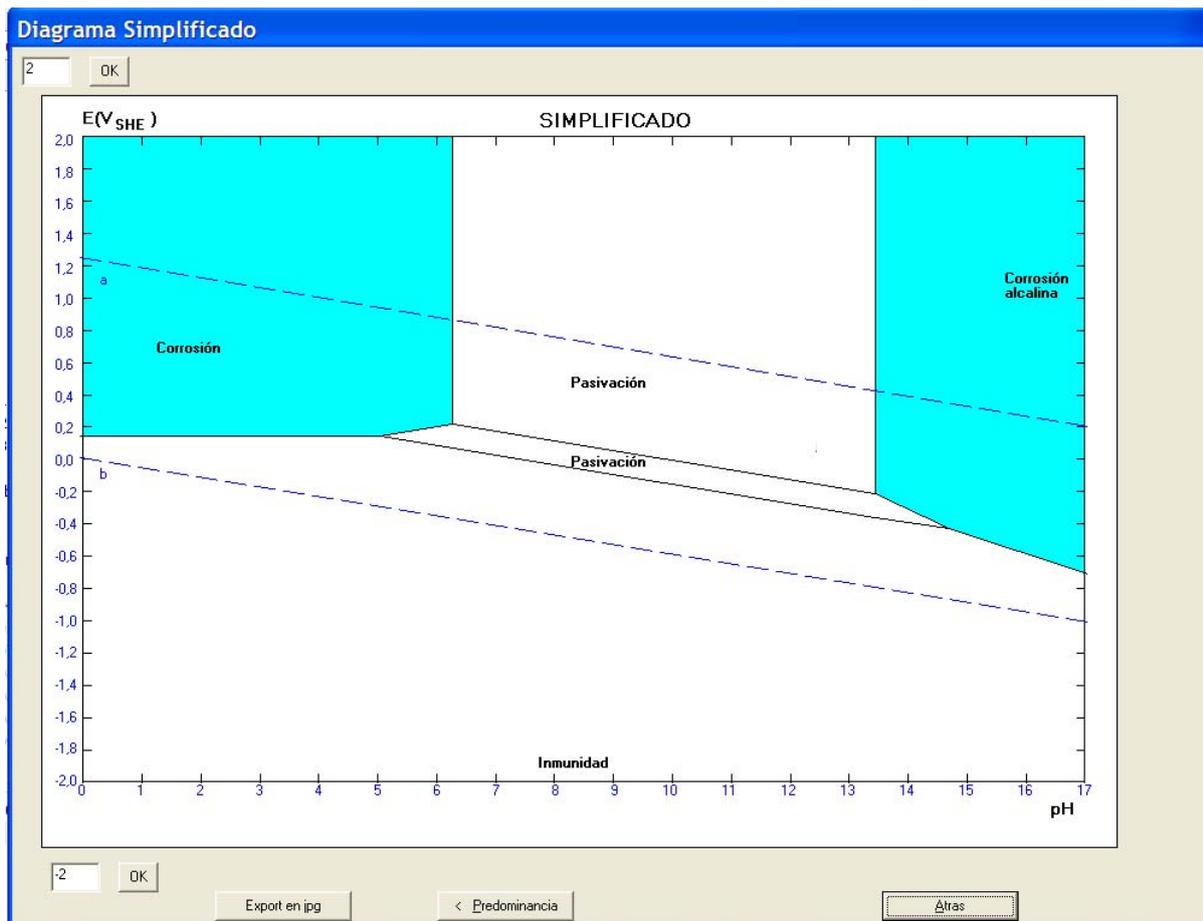


Fig. 7. Practical example of the use of EpHGraph program for the construction of the simplified Pourbaix diagram for the system copper-water at 25 °C.

Simplified Pourbaix diagrams with precise delineation of immunity, corrosion, alkaline corrosion, and passivation regions can be a useful tool for the study of the corrosion behaviour of metallic materials both education and research fields.

## 4 CONCLUSIONS

This work has described the development of a new software application, the EpHGraph program, for the construction of the simplified Pourbaix diagrams applied to the study of the corrosion. Simplified Pourbaix diagrams with precise delineation of immunity, corrosion, alkaline corrosion, and passivation regions can be an useful tool for the study of the corrosion behaviour of metallic materials both education and research fields.

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