THE EFFECT OF PH ON THE COPPER DISPLACEMENT REACTION IN SIMPLE ELECTRICAL CELLS

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ABSTRACT

A displacement reaction is an important oxidation and reduction reactions consists of those in which an element reacts with a compound, entering into combination with one of the constituents and freeing the other. This study reports on the effect of PH solution on the copper displacement reaction. Low carbon steel (0.14%c), pure aluminum (99 %), and aluminum alloy (G3/5052) used as substrate for deposition copper from its aqueous solution of varying PH.

The results show Cu deposit from its aqueous solution, and rate of deposition increase with decreasing the value of PH of the aqueous Copper solution.

INTRODUCTION:

A displacement reaction is the chemical change which occurs when a more reactive element displaces a less reactive element from its compounded, for example in displacement reaction such as:

$$M_{(s)} + Cu^{2+}_{(aq)} \longrightarrow M^{n+}_{(aq)} + Cu_{(s)} \qquad \text{if M>Cu} \qquad (1)$$

in such redox reaction, electrons are transferred from metal atoms to Copper (II) ions because the metal is more reactive than Copper (i.e., the metal is more easily oxidation) the redox half equations are:

$$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne^- \qquad \text{(Oxidation)} \qquad (2)$$

$$Cu^{n+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad \text{(Reduction)}$$

All single displacement reactions have the general form :

$$A + BC \longrightarrow B + AC \qquad \text{Here:} \qquad (3)$$

A is an element and BC is usually an aqueous ionic compound or an acid (consisting of B and C aqueous ion) . A displaces B in BC , resulting in the formation of new element B and a new ionic compound or acid , AC. If the new element B is a metal , it will appear as a metallic deposit. If it is a gas , it will appear as bubbles .

An Activity Series of elements is often used to determine if A will displace B in a single displacement reaction . As a rule , if A has a higher activity that B , a Single displacement reaction will occur . However , if A has lower activity than B , a single displacement reaction will not occur .

The rate and overall performance of displacement reaction can be dependent on :

1- Chemical composition (liqands , PH ,etc) .

The more strongly complexed an ion ,that harder it is to reduce , PH can affect complexation and overall chemical and electrochemical reaction .

2- Physical properties (temperature , agitation , or mass transport).

High temperature and agitation results in higher rates and uniformity .

3- Electrochemical properties of the metal ion (the standard potential ,the charge on the ion , the rate of electron transfer .

The independent variables known to effect on the displacement reaction include concentration, temperature, surface area, PH of solution, and the catalysts.

In simple electrical cells, a potential difference (v) is absorbed if the metal (M) is more or less reactive than copper. [....., Ca> Mg> Al > Mn > Zn > Fe > Ca > Ni> Sn > (H) > Cu > Ag] .

The metallic calcium will displace any of the other metals in the list ; whereas gold will not displace but will be displaced by any of the of others . As a corollary it may be pointed out that only those metals that precede hydrogen in the displacement series would be expectation , indeed is borne out by experiment . Hydrogen can not be obtained , for example , by the action of an acid upon metallic copper .

EXPERIMENTAL:

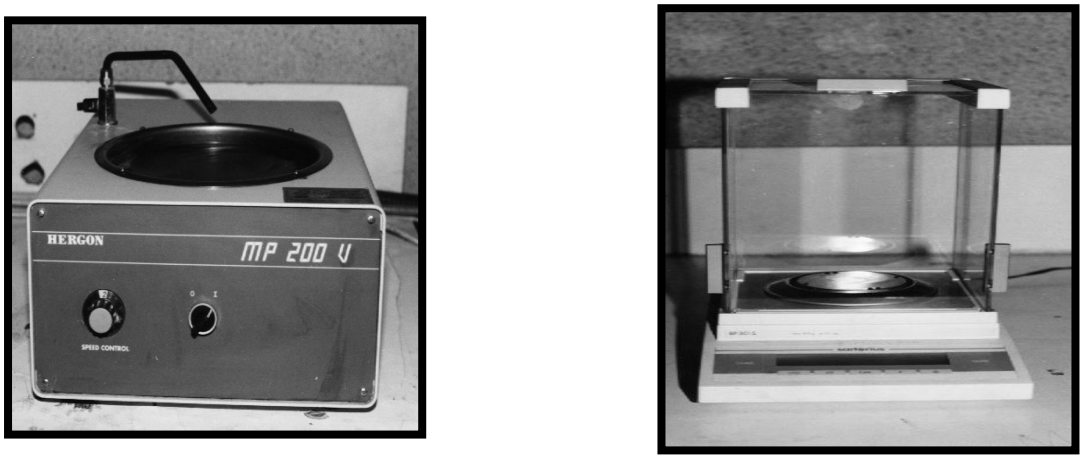
The percentage composition of the samples that used is given in the following tables as follows:

The analysis of chemical composition of low carbon steel and aluminum alloy G3/5052 used in this study examine in S.C.OF MECHANICAL INDUSTERY , by using X-ray diffraction .The pure aluminum in S.C OF GELOGICAL SURVEY AND MINING , by using volumetric method .

Table (1): Present the percentage composition

Composition , percent								
Metal	Mg	Zn	Cu	Mn	Si	Cr	C	Other
Low carbon steel	-	-	-	0.4	-	-	0.14	99.46Fe
Pure aluminum(1100)	-	-	-	-	-	-	-	99%Al
Aluminum alloy G3/5052	2.81	0.1	0.1	0.1	0.37	0.35	-	95.9%Al 0.4%Fe

The surface of the samples must be cleaning before the immersion. Surface preparation by grinding ,by using grinding instrument type Buehler – Ltp (England) , after end each stage of grinding the samples rinsed by distilled water and alcohol then dried . After grinding the samples polishing by using general polishing instrument type Hergon – mp 200v (China) , then rinsed by distilled water , alcohol and dried in hot air current by using electric drier. Figure (1- A -) show the general polishing instrument . Then the samples cleaning by alkaline and acids cleaning, for alkaline cleaning, the samples immersion in a 10% by weight sodium hydroxide at 75 C , immersion time 120 second. The acids cleaning used by immersion the samples in a 30 % by volume hydrochloric acid at room temperature , immersion time 120 second.



A **B**

Figure (1) : show A general polishing instrument ; B electric sensitive balance .

The samples of low carbon steel , pure aluminum (1100) and aluminum alloy used are rectangular parts have the dimension (2x1 cm) and thickness (4 mm) , (2x1 cm) and thickness (2mm) , (2x1 cm) and thickness (3 mm) respectively . For suspended the samples by hook , worked hole in the samples (1.5mm) in diameter ; figure (2) show the shape and dimension of samples used .

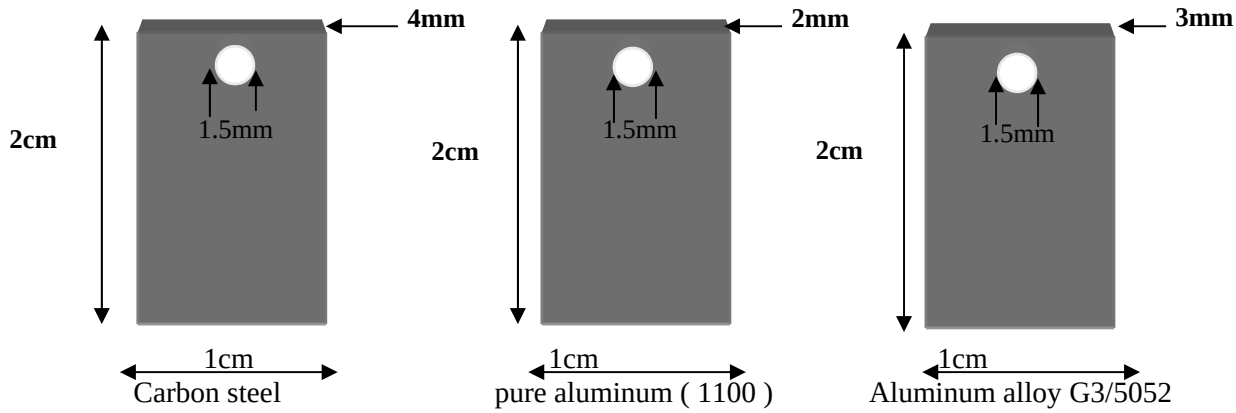


Figure (2) : Show the shape and dimension of samples used .

CuSo4 was used as metal salt, the samples of different metal was immersed in aqueous solution of varying ph containing the copper ion (Cu^{+2}) at room temperature and the samples immersion in 0.5 M CuSo4 for 5 min. PH-Meter type (HI 8314 Portable PH/ mv / C) ; range (0.00 to 14) made in Romania ,used to determine the value of PH copper solution used in this study .

The metal should be completely immersed in the solution used with single immersion, and record any change in reaction mixture, e.g., the color of the solution and of the (precipitated) solid. To determine the weight of copper deposition, the samples weighted before and after displacement reaction, by using electric sensitive balance made in German type (sartorius Bp 3015 Max 303g d= 0.1mg) ; figure (1-B) show the electric sensitive balance , and using equation to determine the rate of deposition;

$$R.D = \frac{\Delta w}{At} \qquad (4)$$

Where:
R.D = the rate of deposition ($g.min^{-1}.cm^{-2}$).
Δ w= the weight change (g)
t= time of immersion (min)
A = surface area of samples (cm^2)

RESULTS AND DISCUSSIONS:

Figures 4 , 5, 6 show the effect of PH of copper solution on the weight of copper deposition by displacement reaction on the carbon steel, pure aluminum and aluminum alloy G3/5052 respectively. From the figures, coppers was deposited from aqueous solution contaninig all Cu^{2+} ions when the value of PH solution less than nine PH and the weight of copper deposing increase with decrease the value of ph solution PH<1.

Copper could not be deposit from the solution when PH of solution a great than nine. Also figures 7, 8, 9 show the effect of PH copper solution on the rate of deposition when we use low carbon steel, pure

aluminum and aluminum alloy respectively, by displacement reaction. From the above figures, the rate of deposition increase with decrease the value of PH solution. According to above results, the differenced in copper deposition and rate of deposition can be related to the different value of PH solution of copper. When PH<9 and decrease the value PH<1 will increasing acidity of solution, and increasing the number of free ion of copper Cu^{2+}, therefore the displacement reaction of copper will occur with metal used.

$$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu \qquad \Delta G^{o} = -150kj \qquad (5)$$

$$2Al + 3Cu^{2+} \longrightarrow 3Cu + 2Al^{2+} \qquad \Delta G^{o} = -1158kj \qquad (6)$$

Fe and Al is oxidized and is the reducing agent :

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e \qquad (7)$$

$$Al(s) \rightarrow Al^{3+}(aq) + 3e \qquad (8)$$

And Cu^{2+} is reduced and is oxidizing agent :

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \qquad (9)$$

From the equation (5,6) the change in free energy ΔG^{o} negative, reaction thermodynamically favorable .

From the figure (4, 5, 6) when PH < 9 , the weight of copper deposition by displacement reaction on the pure aluminum is greater than the weight of copper deposition on aluminum alloy (G3/5052) and carbon steel (0.14 % C) , respectively , the different deposition behavior can be related to the different electrode potential of each metal , the electrode potential is driving force of displacement reaction , the potential different between copper and metal used ; Fe/Cu = 0.75 V ; Al/Cu = 2 V , There for increase the potential different increasing the rate of reaction and increasing the weight of copper deposition on the surface of metal used .

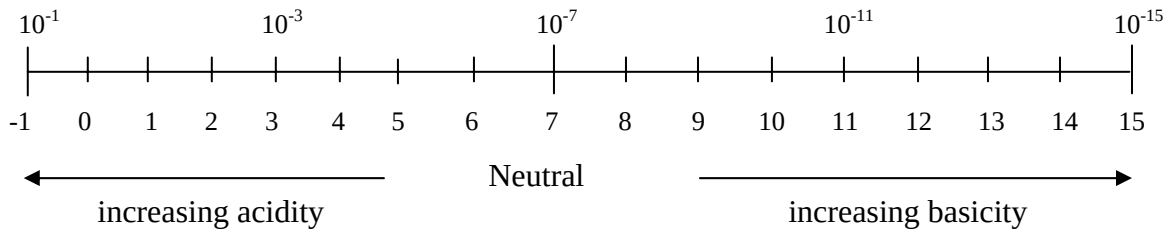
There are other factors will increase the deposition , increase the number of H+ when PH<1 and the solution attac the substrate metal (immersion metal) and product hydrogen atoms.

$$2H_{(aq)}^{1+} + 2e^{-} \longrightarrow H_{2(g)} \qquad (10)$$

the hydrogen atoms can deposit the copper from solution

$$H_2^{1+} + Cu2+ \longrightarrow Cu + 2H^{+} \qquad (11)$$

therefore, the weight and rate of deposition increase.



$$H^{1+}_{aq} > OH^{1-}_{aq} \qquad H^{1+}_{aq} = OH^{1-}_{aq} \qquad H^{1+}_{aq} < OH^{1-}_{aq}$$

when PH > 9 will increasing the basiticity of the copper solution $H^{1+}_{aq} < OH^{1-}_{aq}$ from the PH Scal above shows, and decrease the number of free ion copper Cu^{2+}; from figure 10 (pourboaix diagram for copper) ; that show the relation ship between the potential different and PH of solution ; when used carbon steel Fe/Cu = 0.75 V ; aluminum Al/Cu = 2 V ; PH > 9 ; we in the region that the number of free ion Cu^{2+} decrease and increasing formation of $Cu(oH)_2(s)$.

$$Cu^{2+}_{aq} + 2OH^{1-}_{aq} \rightarrow Cu(oH)_2(s) \qquad (12)$$

pale blue

and when increasing PH solution increasing formation $[Cu(oH)_4]^2(aq)$ (tetrashydroxocuptate (II) ion) fro the equation (13) ;

$$Cu(OH)_2(s) + 2OH_{aq} \rightarrow [Cu(oH)_4]^2(aq) \qquad (13)$$

tetrashydroxocuptate (II) ion

therefore no deposition of copper when PH>9, because the copper in solution is surrounded by a close shell of molecules or ion called " ligands", and this increases with the increasing of the value of PH copper solution, caused more strongly complexed copper ion , the harder it is to reduced and the displacement reaction of copper will not occur.

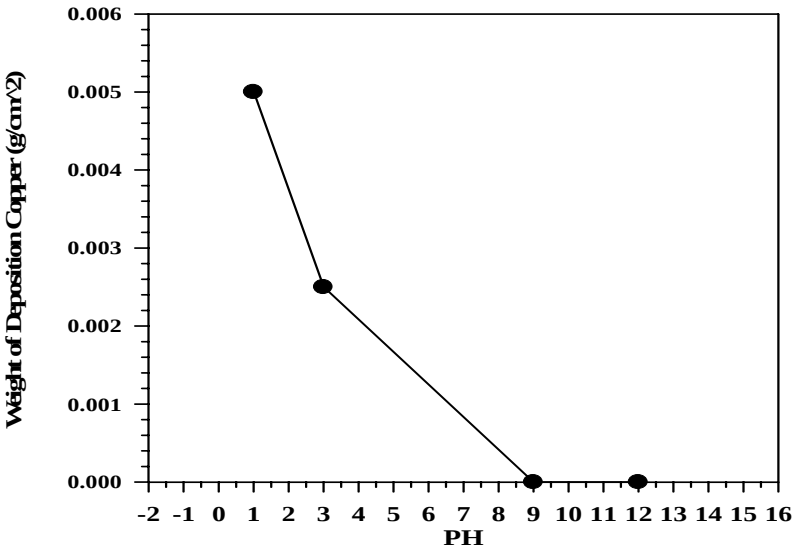


Figure (4): The relation ship between weight of copper deposition per unit area and (PH) of copper solution (carbon steel).

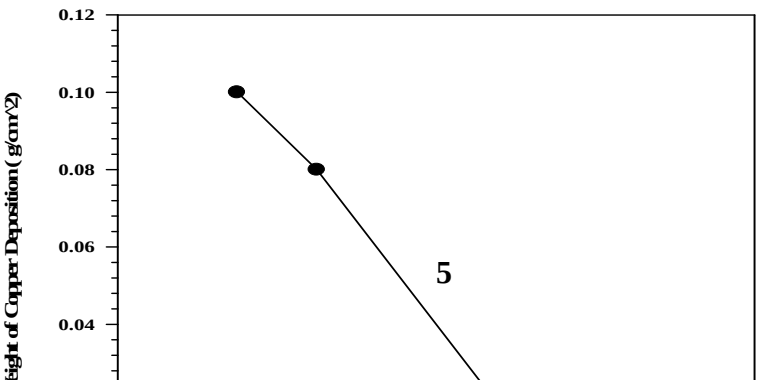


Figure (5): The relation ship between weight of copper deposition per unit area and (PH) of copper solution (pure aluminum).

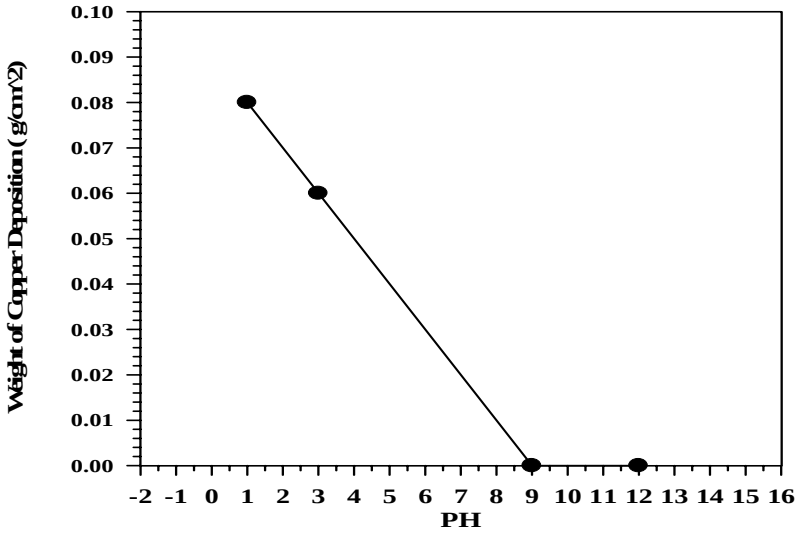


Figure (6): The relation ship between weight of copper deposition per unit area and (PH) of copper solution (aluminum alloy).

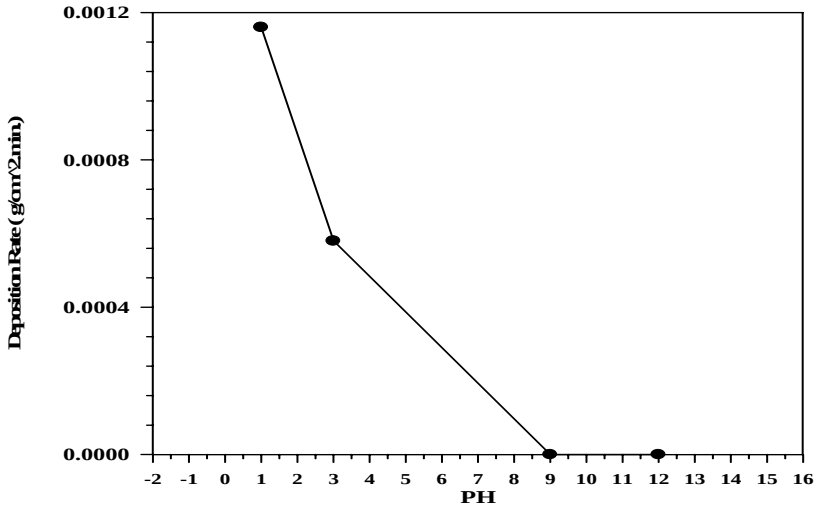


Figure (7): Effect of Ph copper solution on the rate of deposition by displacement reaction of low carbon steel

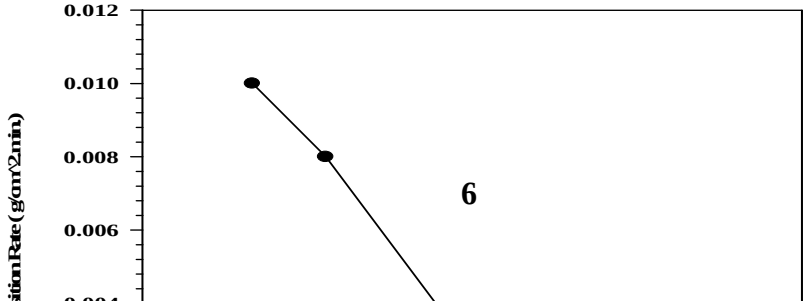


Figure (8): Effect of Ph copper solution on the rate of deposition by displacement reaction of pure aluminum.

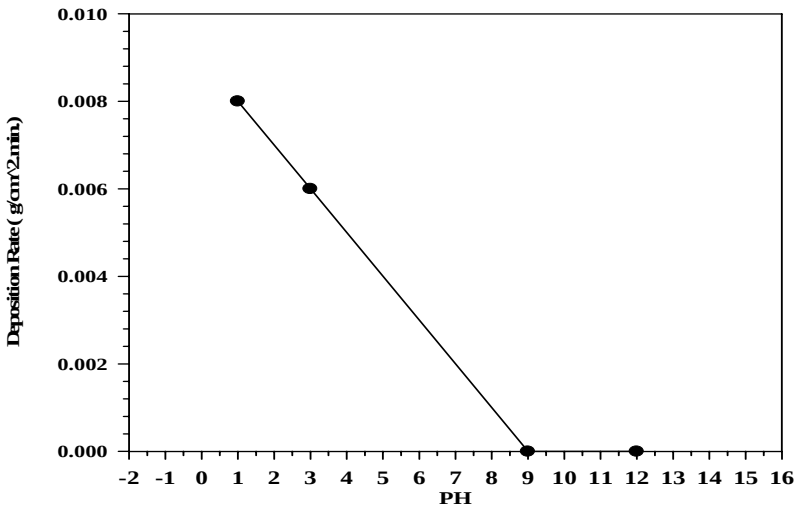


Figure (9): Effect of PH copper solution on the rate of deposition by displacement reaction of aluminum alloy.

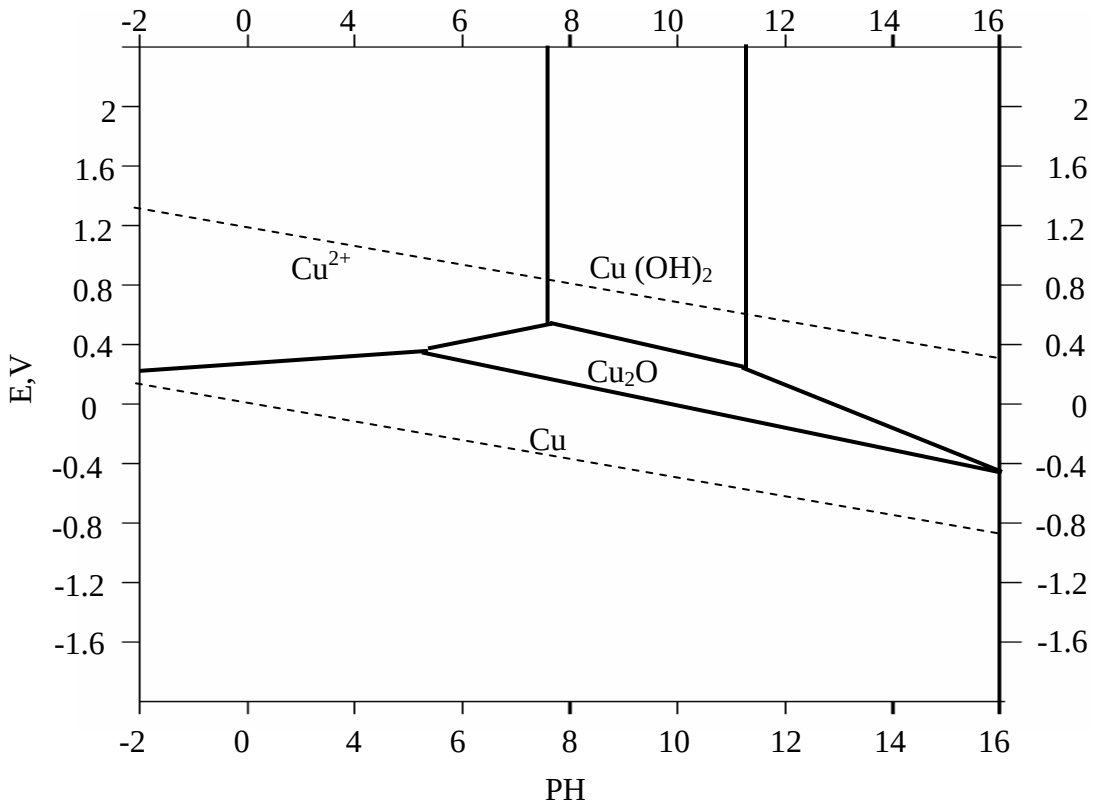


Figure (10): Pourboaix diagram for copper**.**

CONCLUSION:

Copper displacement reaction in simple electrical cells effected by PH solution used. The result show the copper displacement reaction occurs when increasing acidity of solution PH<1, because increasing the number of free ion of copper Cu. The copper reduction (cathodic reaction) is accompanied by the oxidation of metal used low carbon steel , aluminum alloy as counter reaction (anodic reaction) , the redox half equations are : (for low carbon steel and aluminum alloy respectively) .

$Fe \rightarrow Fe^{2+} + 2e$ (anodic reaction) (14)

$Cu^{2+} + 2e^{-} \rightarrow Cu$ (cathodic reaction) (15)

$Al \rightarrow Al^{3+} + 3e$ (anodic reaction) (16)

$Cu^{2+} + 2e^{-} \rightarrow Cu$ (cathodic reaction) (17)

The copper displacement reaction no occurs when increasing basicity of solution PH>9,because the copper ion in solution is surrounded by a close shell of molecules or ion. Therefore the solution not attack the low carbon steel and aluminum alloy used at the time of immersion used 5 min. ,and

the above anodic reaction (14 ,16) not occurs , and copper displacement reaction in simple electrical cell not occur .

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