Chemical Engineering Journal 152 (2009) 503–508

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Leaching of copper oxide with different acid solutions

N. Habbache, N. Alane, S. Djerad*, L. Tifouti

*Laboratory of Environmental Engineering, Department of Chemical Engineering, University of Annaba, BP 12 El Hadjar, Annaba 23000, Algeria*

ARTICLE INFO

*Article history:*
Received 9 February 2009
Received in revised form 30 April 2009
Accepted 14 May 2009

*Keywords:*
Copper oxide
Inorganic acids
Citric acid
Dissolution rate
Corundum

ABSTRACT

In this study, the dissolution of CuO in HCl, $H_2SO_4$, $HNO_3$ and citric acid solutions was investigated in a batch reactor employing parameters expected to affect the dissolution rate of copper such as stirring speed, temperature and acid concentration. It was found that 99.95% of copper was dissolved after 14 min with inorganic acids at 0.5 M, 25 °C and $l/s = 10$ ml/g while more drastic operation conditions were needed to reach the same dissolution efficiency with citric acid solution. Anions seem to be involved in the surface reaction. The dissolution kinetics of CuO was examined according to heterogeneous model and it was found that the dissolution rate was controlled by surface chemical process in all cases.

## 1. Introduction

Hydrometallurgical extraction of metals is a branch of industry for which the research work is ongoing to develop processes which are less costly, more environmentally friendly and acceptable economically. In hydrometallurgical extraction, many leaching agents are used such as HCl, $HNO_3$ and $H_2SO_4$. However, most of these leachants cause environmental pollutions. Organic acids such as citric, acetic or oxalic acids can be attractive leaching agents as the leaching is carried out at moderate acidic conditions [1–3]. However, they cannot be used as leaching agents for hard dissolving compounds due of their weak acidities, low boiling temperatures and decompositions.

Copper is used in vast variety of products in domestic and industrial domains as thermal and electrical conductor and as a constituent of various metal alloys. Copper is also used in chemical industry as catalyst in the oxidative conversion of ethyl acetate in water [4], hydrogen production by partial oxidation of methanol [5], liquid-phase oxidation of benzene to phenol [6], carbon monoxide oxidation [7] and in removal of $NO_x$ and $SO_x$ from flue gases [8]. After deactivation, the components of the catalyst can be reused as secondary sources of metals. This is considered as more beneficial from environmental and economical point of views than landfill depositing.

Leaching processes of metallic copper or ores containing copper in the divalent state have been the subject of many research works in recent years [9–13]. However, no study was found concerning the dissolution kinetics of $CuO/Al_2O_3$ catalyst in inorganic or organic acid solutions.

Copper (II) oxide is a basic oxide, so it dissolves in mineral acids according to the general reaction [14]:

$$CuO(s) + 2HX \rightarrow CuX_2 + H_2O \quad (1)$$

In case of hydrochloric acid, sulfuric acid or nitric acid the reaction becomes:

$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O \quad (2)$$

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O \quad (3)$$

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \quad (4)$$

Copper oxide can also be dissolved by a weak acid such as citric acid:

$$3CuO + 2C_6H_8O_7 \rightarrow Cu_3(C_6H_5O_7)_2 + 3H_2O \quad (5)$$

This article presents the results on copper and alumina separation from $CuO/Al_2O_3$ catalyst treated in fresh form with HCl, $HNO_3$, $H_2SO_4$ and citric acid solutions. The effects of acid concentration, stirring speed and temperature on the dissolution rate were evaluated with the four acid solutions. The dissolution kinetics were examined according to the heterogeneous reaction models and the best fitted equation to the experimental data was determined.

## 2. Experimental

The catalyst used in this study was a 10%$CuO/\alpha$-$Al_2O_3$ ($n/n$) prepared with incipient wetness method. In this method, a defined volume of $Cu(NO_3)_2{\cdot}3H_2O$ (99.6%, Fluka) with known concentration was used to impregnate a given mass of $\alpha$-$Al_2O_3$. With this

---

* Corresponding author. Tel.: +213 7 71 01 88 16; fax: +213 38 87 65 60.
*E-mail address:* s_djerad@hotmail.com (S. Djerad).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.05.020

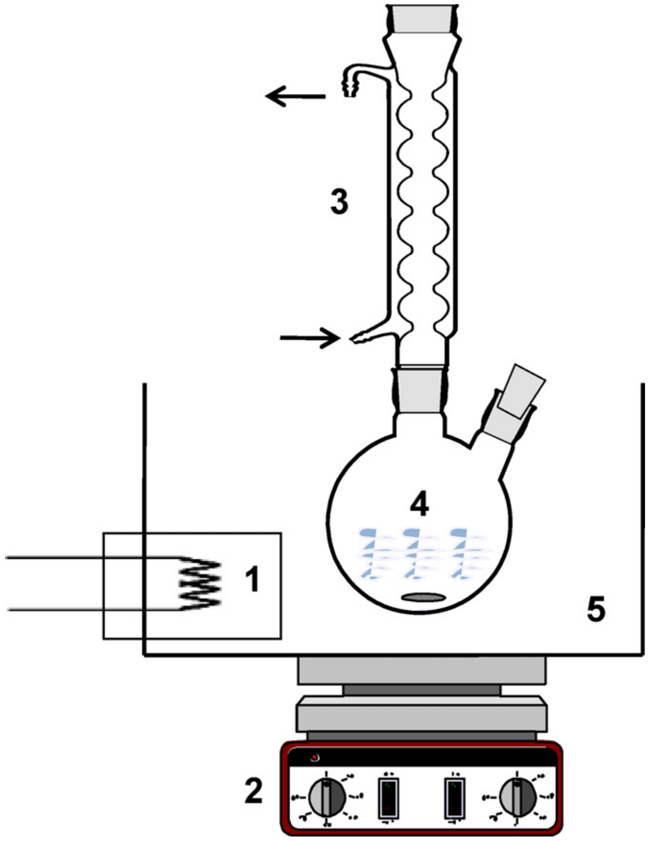

**Fig. 1.** Dissolution experiment setup: (1) temperature-controller; (2) magnetic stirrer; (3) glass condenser; (4) glass reactor; (5) water bath.

technique the load of copper can be calculated in a simple way. The sample was dried overnight at 110 °C and calcined in oven at 500 °C for 2 h. Copper composition was checked after that by atomic absorption. The obtained powder was crushed into particle size of 80 μm. $H_2SO_4$ (96–98%, Biochem), $HNO_3$ (60%, Cheminova), HCl (37%, Carlo Erba) and citric acid monohydrate ($C_6H_8O_7$, 99%, Alfa Aesar) were used as leaching reagents. Leaching experiments were carried out in a spherical glass batch reactor of 100 ml heated by a temperature-controlled water bath and equipped with a return-flow cooler (glass condenser) to minimize solution losses due to evaporation (Fig. 1). The solutions were mixed using a magnetic stirrer to eliminate the influence of mixing and mass transfer on the kinetic results. A typical experiment was conducted as follows: 0.2 g of the sample was placed into the glass flask with a desired volume of the selected acid. After the leaching process, the reaction mixture was filtered and $Cu^{2+}$ was analyzed by titration with EDTA using murexide as an indicator. The percentage of dissolution was calculated from the following equation:

$$\frac{\text{Mol number of copper in the solution}}{\text{Mol number of copper in the catalyst leached}} \times 100 \qquad (6)$$

The data presented are an average of two test replicates with an error of 5%.

Leaching behavior of CuO was tested under reaction conditions which were characterized by a relatively high excess of acids to eliminate possible effects of the changes in lixiviant composition during individual runs on the rate of leaching. The main parameters that affect the dissolution of copper oxide such as the nature of acid (HCl, $H_2SO_4$, $HNO_3$ and citric acid), acid concentration (0.1, 0.5, 1, 2 M), stirring speed (50, 200, 400 rpm) and temperature (30, 40, 50, 60 and 80 °C) were considered and the best conditions for the maximum recovery were established.

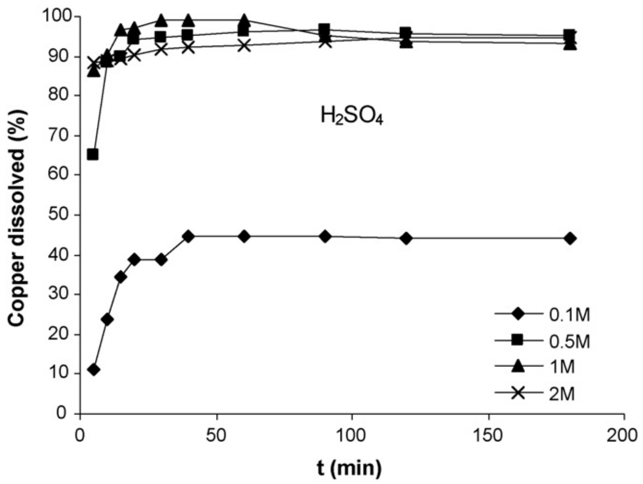

**Fig. 2.** Effect of $H_2SO_4$ concentration on copper dissolution. Operation conditions: $T$ = 25 °C, l/$s$ = 10 ml/g, without agitation.

## 3. Results and discussion

### 3.1. Inorganic acids

### 3.1.1. Effect of acid concentration

In order to investigate the effect of acid concentration, experiments were performed first with $H_2SO_4$ solution used as a reference with different concentrations (0.1, 0.5, 1, 2 M) without agitation, at 25 °C and l/$s$ ratio of 10 ml/g. The results are shown in Fig. 2 as a fraction of copper reacted vs. time. It can be seen that the fraction of copper dissolved was not changed when acid concentration was increased from 0.5 to 1 M. The concentration of 0.5 M was selected for investigating the effect of other parameters. The same experiments were carried out after that with HCl and $HNO_3$ solutions under the same operation conditions and 0.5 M of acid concentration to compare their dissolution efficiencies (Fig. 3). It can be seen that copper dissolution was very fast with HCl. It attained 85% at the first minute and reached 99.95% at 14 min. The lowest kinetic dissolution was obtained with $HNO_3$ at the start of the reaction (1–6 min) but it increased gradually attaining 99.95% at 14 min. Alumina dissolution was checked with the four acid solutions several times at different concentrations. No dissolution was observed due to its chemical inertia and its high stability against acids [15]. In

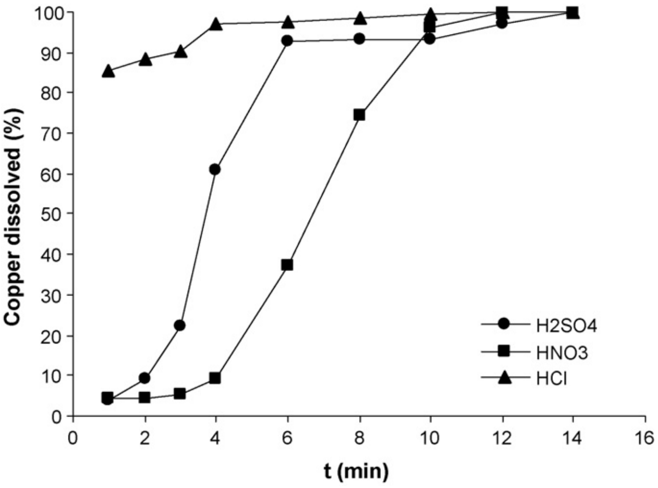

**Fig. 3.** Effect of the nature of acid on copper dissolution. Operation conditions: $T$ = 25 °C, acid concentration = 0.5 M, l/$s$ = 10 ml/g, without agitation.

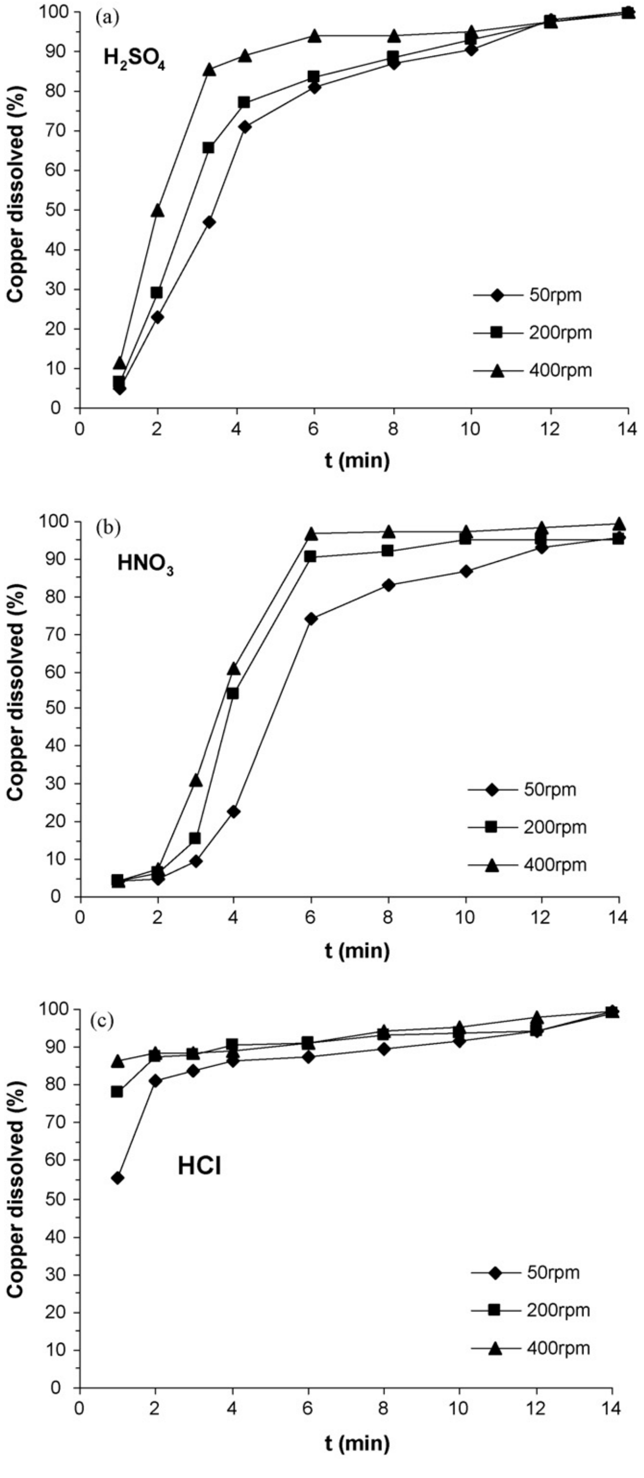

**Fig. 4.** Effect of stirring speed on copper dissolution in the presence of the three inorganic acids. Operation conditions: $T = 25\,^\circ$C, acid concentration = 0.5 M, l/s = 10 ml/g.

fact, in a parallel work, it has been observed that alpha-alumina could be dissolved only under drastic conditions such as roasting with $KHSO_4$ at high temperature (e.g. 600 °C).

### 3.1.2. *Effect of stirring speed*

The effect of stirring speed on the dissolution rate of copper was investigated using different agitation speeds (50–200 and 400 rpm) at 25 °C, l/s ratio = 10 ml/g and acid concentration of 0.5 M (Fig. 4). It can be seen that agitation speed has almost no effect on CuO dissolution with HCl. With $H_2SO_4$ and $HNO_3$ the effect of stirring was more significant in range (2–10 min).

### 3.1.3. *Effect of temperature*

The effect of temperature on the rate of copper dissolution from CuO when leached in the three inorganic acids was investigated over a temperature range of 30–50 °C at acid concentration of 0.5 M, stirring speed of 400 rpm and l/s = 10 ml/g. Fig. 5 shows that temperature has a significant effect on the acceleration of copper dissolution with $HNO_3$ followed by $H_2SO_4$. A weak effect of temperature was observed on the dissolution of copper with HCl.

## 3.2. *Citric acid*

### 3.2.1. *Effect of temperature*

Leaching experiments were carried out in a water bath with 0.5 M acid concentration at temperatures ranging from 40 to 80 °C in steps of 20 °C and with agitation speed of 400 rpm. At temperature lower than 40 °C and $l/s < 40$ ml/g, no dissolution of copper was observed. As can be seen from Fig. 6, copper dissolution with citric acid was highly temperature dependant. The reaction rate was slower than that obtained with inorganic acids since it needed hours to reach high dissolution efficiency. In fact, at a temperature of 40 °C, 32% of copper was extracted in 4 h of leaching time, whereas 76% was recovered at a temperature of 60 °C after the same period of time and 99% was dissolved after 2 h at 80 °C. A decrease in copper dissolution observed at 80 °C over 2 h was due to the decomposition of citric acid and its reaction with $Cu^{2+}$ ions forming a green precipitate corresponding to $Cu(OH)_2CO_3$ [16].

### 3.2.2. *Effect of stirring speed*

The effect of stirring speed on the dissolution rate of copper was investigated using different stirring speeds (50–200 and 400 rpm) at 60 °C, l/s ratio = 40 ml/g and acid concentration of 0.5 M (Fig. 7). The results indicate that the agitation has a more pronounced effect on the dissolution of copper with citric acid than that observed with inorganic acids.

## 3.3. *Kinetic analysis*

The rate of a reaction between a solid and a fluid such as the system considered here can be expressed by heterogeneous models. In a heterogeneous system, the overall rate expression becomes complicated because of the interaction between physical and chemical processes. To interpret the results of CuO dissolution in the different acidic media studied, the kinetic has been assessed on the basis of the shrinking core model. SCM was chosen because it approximates real particles more closely than does the other conversion models in a wide variety of situations [17]. In this model, the solid reactant is considered to be non-porous with a spherical shape and is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid. As the reaction proceeds, a product layer forms around the unreacted core. With the increase of the conversion the unreacted core of the particle shrinks and the layer of the product thickens. According to this model, the following three steps are considered to occur in succession during the dissolution:

1- Transport of the reactant through the solution to the surface of the solid ($H^+$, anions).
2- Reaction on the surface between the reactant and the solid.
3- Formation of the products on the surface layer of the reaction zone and their transport from the interface into the bulk of solution.

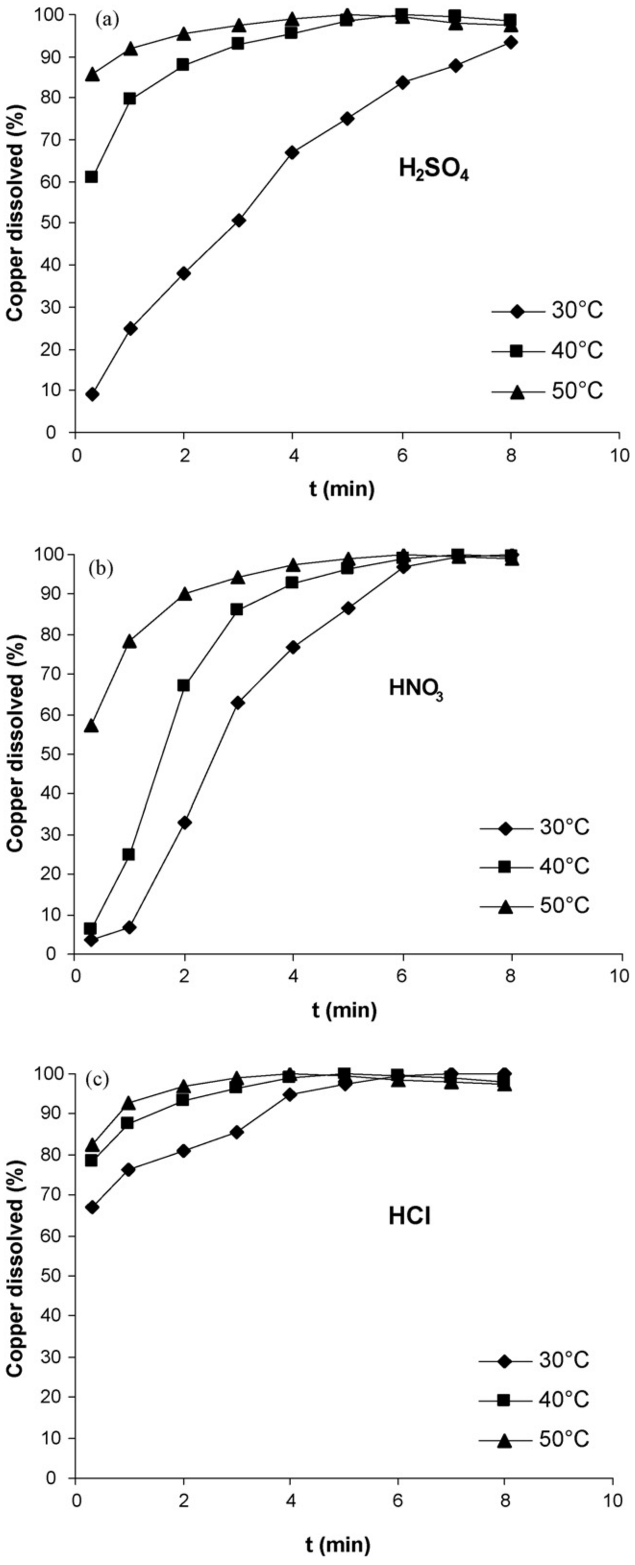

**Fig. 5.** Effect of temperature on copper dissolution in the presence of the three inorganic acids. Operation conditions: acid concentration = 0.5 M, l/*s* = 10 ml/g, stirring speed = 400 rpm.

The overall leaching process may be controlled by intrinsic chemical reaction or by external mass transfer. The following expressions can be used to describe the dissolution kinetics of the process:

$$x = kt \quad \text{for liquid film diffusion control} \tag{7}$$

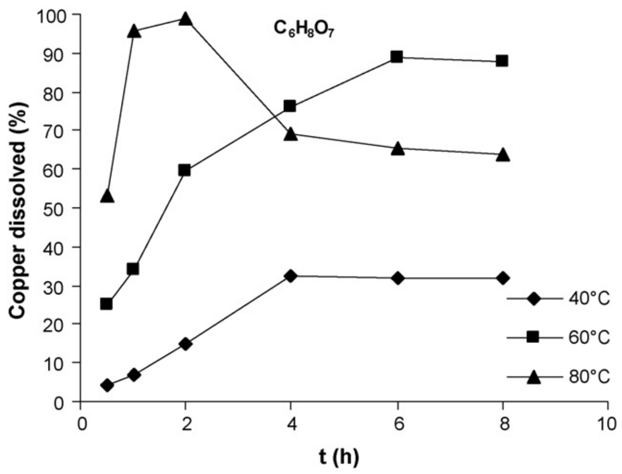

**Fig. 6.** Effect of temperature on the dissolution of copper with citric acid solution. Operation conditions: acid concentration = 0.5 M, l/*s* = 40 ml/g, stirring speed = 400 rpm.

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = kt$$

$$\text{for film diffusion control through the ash or product } \textit{layer} \tag{8}$$

$$1 - (1 - x)^{1/3} = kt \quad \text{for surface chemical reaction control} \tag{9}$$

where "*x*" is the fractional conversion of CuO, "*t*" is the reaction time (min or h) and "*k*" the apparent rate constant ($\text{min}^{-1}$ or $\text{h}^{-1}$). The rate of the process is controlled by the slowest of these sequential steps.

In order to determine the kinetic parameters and rate-controlling step of CuO leaching in the four acid solutions investigated in this study, the shrinking core model was tested at various temperatures. The validity of experimental data into the integral rate was tested by graphical method.

When the shrinking core model in which the rate limiting step is the chemical reaction (Eq. (9) was applied to the data obtained with the four acid solutions, good linear fits were obtained as shown in Fig. 8.

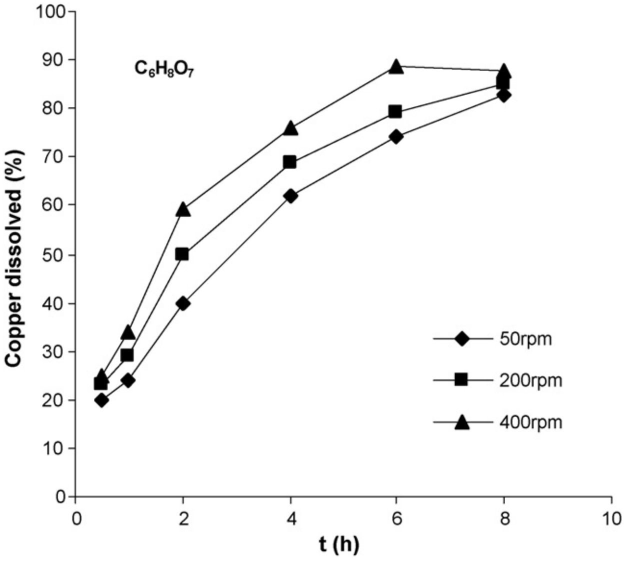

**Fig. 7.** Effect of stirring speed on copper dissolution in the presence of citric acid solution. Operation conditions: acid concentration = 0.5 M, l/*s* = 40 ml/g, *T* = 60 °C.

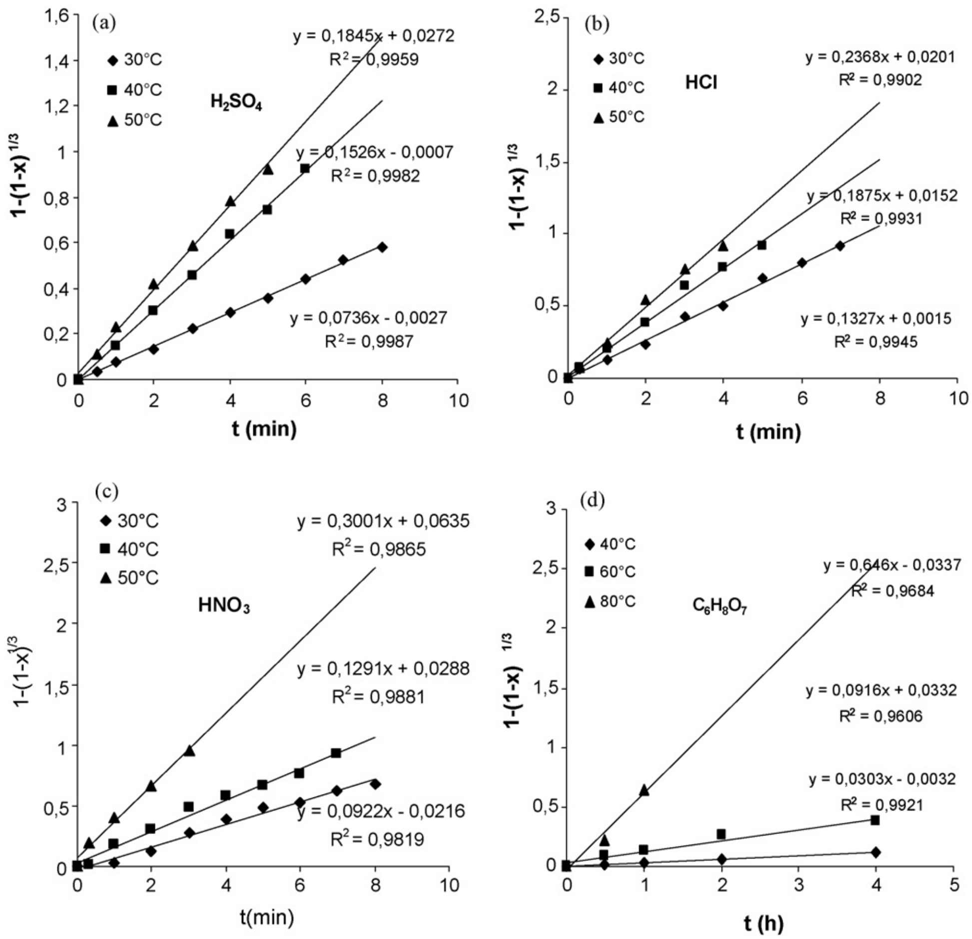

**Fig. 8.** Plots of $1-(1-x)^{1/3}$ vs. leaching time at different temperatures for the dissolution reactions of copper with $H_2SO_4$ (a), HCl (b), $HNO_3$ (c) and citric acid (d) solutions.

From the slopes of the straight lines (Fig. 8) the apparent rate constants, $k$, were evaluated. Arrhenius equation $k = k\cdot e^{-Ea/RT}$, was plotted as $\ln k$ vs. $(1/T)$ for each temperature and the activation energies were calculated from the slopes $-Ea/RT$. The following values of $k$ and $Ea$ were determined:

$H_2SO_4$: $k_{(30\,^\circ C)} = 0.073\ \text{min}^{-1}$; $k_{(40\,^\circ C)} = 0.152\ \text{min}^{-1}$; $k_{(50\,^\circ C)} = 0.184\ \text{min}^{-1}$; $Ea = 37$ kJ/mol.
HCl: $k_{(30\,^\circ C)} = 0.132\ \text{min}^{-1}$; $k_{(40\,^\circ C)} = 0.187\ \text{min}^{-1}$; $k_{(50\,^\circ C)} = 0.236\ \text{min}^{-1}$; $Ea = 24$ kJ/mol.
$HNO_3$: $k_{(30\,^\circ C)} = 0.092\ \text{min}^{-1}$; $k_{(40\,^\circ C)} = 0.129\ \text{min}^{-1}$; $k_{(50\,^\circ C)} = 0.3\ \text{min}^{-1}$; $Ea = 47.72$ kJ/mol.
$C_6H_8O_7$: $k_{(40\,^\circ C)} = 0.03\ \text{h}^{-1}$; $k_{(60\,^\circ C)} = 0.091\ \text{h}^{-1}$; $k_{(80\,^\circ C} = 0.646\ \text{h}^{-1}$; $Ea = 69.9$ kJ/mol.

Research and modeling of the leaching process has difficulties which are typical for most multiphase reaction systems. The number of physical and chemical phenomena is large and only the most relevant of them can be included in the model. Moreover, the models of these phenomena include simplifications. In fact, it is interesting to note that the value of activation energies in case of CuO dissolution with HCl and $H_2SO_4$ are lower than 40 kJ/mol while the processes are controlled by the chemical surface reaction. For pure chemical controlled process the activation energy should be rather high. However, since there is no ash formed around the unreacted particles due to the fact that the catalyst is formed by pure products and that the stirring has a weak effect on the dissolution efficiency which means that diffusion through the fluid film does not act as rate controlling step, there is no doubt that chemical process controls the CuO dissolution.

In the leaching process, $H^+$ ion should be the unique responsible of the dissolution reaction as indicated by reactions (1)–(3). Anions such as $NO_3^-$, $SO_4^{2-}$ and $Cl^-$ should be non-effective. However, it is worth noting that inorganic acids used are completely dissolved in water, which means in case of HCl and $HNO_3$ that the same mol number of $H^+$ were present in the solution leading normally to the same dissolution efficiency of CuO. Moreover, $H_2SO_4$ at 0.5 M produced 1 M of $H^+$ and in spite of that, lower dissolution efficiency of $H_2SO_4$ was observed compared to HCl. These results indicate that leaching is not a simple process and that anions may play an important role on the rate of copper oxide dissolution.

In corrosion field, chloride, sulfate and nitrate ions are considered as aggressive elements for metals that involve their corrosion [18–20].

It can be speculated that specific adsorption of these anions may occur on the solid surface with possible formation of different products leading to the dissolution of metal oxide as well as the increase in the heterogeneity of the surface. One paper was found [14] dealing with the effect of the electrolytic environment (presence of $Cl^-$) that may affect the dissolution process of CuO in acidic media. In fact, Senanayake [14] explained the dissolution of copper oxide on the basis of surface adsorption equilibria involving the formation of chloro-complexes as adsorbed species. The author reported that the adsorption of aqueous HCl onto the oxide surface releases some of the water in hydration sphere of HCl to the solution in order to establish heterogeneous (solid/surface/solution) equilibria for the oxide:

$$\text{CuO(s)} + \text{HCl(aq)} \leftrightarrow \text{Cu(OH)Cl(ad)} + \Delta h\,\text{H}_2\text{O} \qquad (10)$$

And that the adsorbed specie Cu(OH)Cl may react with HCl to complete the reaction as shown below:

$$Cu(OH)Cl(ads/aq) + HCl(aq) \leftrightarrow CuCl_2(aq) + H_2O \qquad (11)$$

The author indicated that the high stability of a chloro-complex would increase the value of $K_{ads}$ for the adsorption equilibria and thus enhance the rate of dissolution. Sulfate and nitrate ions may act also with the same manner but probably with lower strength due to their different chemical characteristics. No detailed information in the literature was found about the mechanism of metal oxides dissolution in the presence of sulfate and nitrate ions. Thus, it can be concluded that the leaching is a complicated process since several parameters such as proton activity, the tendency of anions to form complexes on the solid surface with different stabilities and temperature act simultaneously to accelerate the leaching process.

In the case of citric acid, the pH of the solution at 0.5 M and ambient temperature was 1.6 indicating that the solution was enough acid to efficiently dissolve copper oxide. This was not the case. Only increasing the temperature has effectively enhanced the dissolution rate of CuO probably due to the increase of $H^+$ ions produced under heating. This constitutes another indication that despite the strong acidic media of the citric acid solution, the anions susceptible to enhance the dissolution rate of copper oxide were not present but their absence avoids post-treatments and pollution risks.

## 4. Conclusion

Based on the results achieved in this study, it can be concluded that all inorganic acids were able to dissolve CuO from $CuO/Al_2O_3$ catalyst after 14 min using an acid concentration of 0.5 M at 25 °C while 2 h at 80 °C were necessary to reach the same dissolution efficiency with citric acid solution. Comparison between acids showed that hydrochloric acid yields the highest CuO dissolution efficiency, followed by sulfuric acid, nitric acid and citric acid. Depending on the nature of the acid solution, the combination of aggressive character of anions which is in reality a beneficial effect in leaching process and the acidic character of $H^+$ seems to play an important role on the acceleration of CuO dissolution rate.

The shrinking core model assuming rate control by chemical reaction was found appropriate to describe the reaction of CuO in the four acid solutions.

## References

[1] F. Demir, O. Laçin, B. Dönmez, Leaching kinetics of calcined magnesite in citric acid solutions, Ind. Eng. Chem. Res. 45 (2006) 1307–1311.

[2] C.E. Halim, J.A. Scott, H. Natawardaya, R. Amal, D. Beydoun, G. Low, Comparison between acetic acid and landfill leachates for the leaching of Pb(II), Cd(II), As(V), and Cr(VI) from cementitious wastes, Environ. Sci. Technol. 38 (2004) 3977–3983.

[3] M. Alkan, M. Dogan, Dissolution kinetics of colemanite in oxalic acid solutions, Chem. Eng. Process. 43 (2004) 867–872.

[4] U. Armbruster, A. Martin, A. Krepel, Hydrolysis and oxidative decomposition of ethyl acetate in sub- and super-critical water, Appl. Catal. B: Environ. 31 (2001) 263–273.

[5] Z. Wang, J. Xi, W. Wang, G. Lu, Selective production of hydrogen by partial oxidation of methanol over Cu/Cr catalysts, J. Mol. Catal. A: Chem. 191 (2003) 123–134.

[6] T. Miyahara, H. Kanzaki, R. Hamadab, S. Kuroiwa, S. Nishiyama, S. Tsuruya, Liquid-phase oxidation of benzene to phenol by $CuO-Al_2O_3$ catalysts prepared by co-precipitation method, J. Mol. Catal. A: Chem. 176 (2001) 141–150.

[7] S.H. Taylor, G.J. Hutchings, A.A. Mirzaei, Copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation, Chem. Commun. (1999) 1373–1374.

[8] C. Macken, B.K. Hodnett, G. Paparatto, Testing of the $CuO/Al_2O_3$ Catalyst–Sorbent in extended operation for the simultaneous removal of $NO_x$ and $SO_2$ from flue gases, Ind. Eng. Chem. Res. 39 (2000) 3868–3874.

[9] P.R. Kruesi, V.H. Frahm, Process for the recovery of copper from its ores, US Patent No. 4,324,582 (1982).

[10] T. Oishi, K. Koyama, S. Alam, M. Tanaka, J.C. Lee, Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions, Hydrometallurgy 89 (2007) 82–88.

[11] F. Habashi, Trends in the hydrometallurgical treatment of copper oxide ores, Arab Min. J. 4 (1983) 46–52.

[12] F.A. Forward, A. Peters, Leaching, vol. 2, SME Mineral Processing Handbook, Seeley W. Mudd Series, New York, 1985, pp. 13.12–13.6.

[13] O.N. Ata, S. Colak, Z. Ekinci, M. Copur, Determination of the optimum conditions for leaching of malachite ore in $H_2SO_4$ solutions, Chem. Eng. Technol. 24 (2001) 409–413.

[14] G. Senanayake, Review of theory and practice of measuring proton activity and pH in concentrated chloride solutions and application to oxide leaching, Miner. Eng. 20 (2007) 634–645.

[15] N.M. Al-Mansi, N.M.A. Monem, Recovery of nickel oxide from spent catalyst, Waste Manag. 22 (2002) 85–90.

[16] N. Glinka, Chimie Générale, vol. 2, Editions Mir, Moscou, 1987, p. 234.

[17] O. Levenspiel, Chemical Reaction Engineering, 3rd ed., John Wiley & Sons, New York, 1999, p. 570.

[18] M. Scendo, The influence of adenine on corrosion of copper in chloride solutions, Corrosion Sci. 50 (2008) 2070–2077.

[19] J. Datta, B. Samanta, A. Jana, S. Sinha, C. Bhattacharya, S. Bandyopadhyay, Role of $Cl^-$ and $NO_3{}^-$ ions on the corrosion behavior of 20% $SiC_p$ reinforced 6061-Al metal matrix composite: a correlation between electrochemical studies and atomic force microscopy, Corrosion Sci. 50 (2008) 2658–2668.

[20] M. Scendo, Inhibition of copper corrosion in sodium nitrate solutions with nontoxic inhibitors, Corrosion Sci. 50 (2008) 1584–1592.