Int. J. Chem. Sci.: 12(2), 2014, 679-686
ISSN 0972-768X
www.sadgurupublications.com

BEHAVIOR OF CUPRITE IN CuS –H_2SO_4–NaClO AND CuS –H_2SO_4–$KClO_3$ SYSTEMS

SH. BAYYSBEKOV, G. ZHUNUSSOVA, M. BULENBAYEV[*],
A. TAIMASSOVA and S. SERKEBAYEVA

Kaz NTU Named After K. I. Satpayev, Satpayev St. 22, 050013, ALMATY, KAZAKHSTAN

ABSTRACT

This article presents the results of the calculation of the Pourbaix diagrams and the possibility of formation of stable phases and phase transitions of iron in the aqueous phase systems CuS–H_2SO_4–NaClO and CuS–H_2SO_4–$KClO_3$, which allowed us to estimate thermodynamic probability of occurrence of oxidative leaching of pyrite. In the environment of sulfuric acid and the use of oxidants-oxychlorides of sodium and potassium, cuprite can pass into solution, with no need for a second oxidant-oxygen. The most powerful oxidant is sodium hypochlorite.

Key words: Oxychlorides of sodium and potassium, Cuprite, Diagrams of Pourbaix, Sulfuric acid, Thermodynamic analysis.

INTRODUCTION

The development of new environmentally friendly technologies for the production of gold was formerly held by thermodynamic analysis of the oxidative leaching of gold-bearing minerals in sulfuric acid in the presence of an oxidant-manganese dioxide[1,2].

In this paper, for the thermodynamic analysis of oxidative leaching of the mineral carrier gold-cuprite in sulfuric acid in the presence of oxidizing agents: sodium hypochlorite (NaClO) and potassium perchlorate ($KClO_3$), there was used the Pourbaix diagramming program method developed by "Outokumpu Ou".

The Pourbaix diagram (Eh-pH) graphically depict the boundaries of the stability region and coexistence of diverse forms and connections for a particular system, depending on the values of the redox potential and pH at fixed temperature and ion activity[3,4].

---

[*]Author for correspondence; E-mail: mbulenbaev@mail.ru; Ph.: +7702-584-42-66

RESULTS AND DISCUSSION

The results of calculations Pourbaix diagrams for the CuS-H_2SO_4-O_2-NaClO system at 298, 353, 373 and 403 K are shown in Figs. 1-4. Behavior of CuS at 298 K (Fig. 1). Stable form of copper compounds in the aqueous phase are Cu, Cu_2S, CuCl, Cu_2O, [CuCl] + and CuO. Cu phase is stable at pH = 0-14. This is oxidized to Cu_2O phase at pH = 6-14 with a change of the redox potentials at pH = 6 by E = 0.1 V to E = + 0.3 V, and at pH = 14 by E = -0.3 V to E = -0.2 V. There is also the formation of Cu_2S phase at pH = 0-12, 9 with changing redox potentials at pH = 0 to E = -0.3 V to E = + 0.1 V and 12.9 to pH = E = -0.2 V. Phase CuCl formed by dissolution and oxidation of Cu and Cu_2S. Cu in the transition CuCl performed at pH = 0-6 with changing the redox potential at pH = 0 to E = 0.1 V to E = + 0.5 V, and at pH 14 to E = + 0.1 V to E = + 0.3 V. Education cation $[CuCl]^+$ is the result of adsorption on CuCl copper cation. CuO formation occurs as a result of oxidation of Cu_2O in the range of pH = 6-14 with a change in redox potential at pH = 6 by E = 0.3 V to E = 2.0 V and at a pH = 14 by E = 0, 2 to E = + 2.0 V, and as a result of oxidation of the cation $[CuCl]^+$ at pH = 0-4 with a change of the redox potential at pH = 0 to E = 1.4 V to E = 2.0 V, and at pH 4 to E = + 0.5V to E = + 2.0 V.

Behavior of CuS at 353, 373, and 403 K (Figs. 2-4). The formation of new stable phases of copper have been found. With increasing temperature, the process is shifted above the stability region of copper in the stable phase region acidic environments, which is particularly noticeable at a temperature of 403 K. For example, the pH range for Cu_2S = 0-10, CuCl - pH = 0-5, $[CuCl]^+$ - pH = 0-2,9. pH range for CuO increased, which demonstrates the effectiveness of the oxidant.

NaClO oxidizing agent behavior at 298 K. In Purbaix diagram at this temperature (Fig. 1) sodium hydride existence domain is observed in the range of pH = 0-14 with the redox-potential change of sodium from -2.0 to -1.25 and -1.6 V respectively at pH equal 0 and 14. Dissociated sodium ion is formed by the dissociation of sodium hypochlorite in water at pH = 0-14 and redox-potentials of sodium from -1.2 to +1.75 V at pH = 0, and from -1.6 to + 0.7 V at pH = 14.

Sodium ion reacts with sulfate ion in an aqueous medium to form $[NaSO_4]$ - and $Na_2SO_4 \cdot 10H_2O$. Resilience $[NaSO_4]$ - found in the diagram in the range of pH = 7-14 with a change in potential from +0.0 to +0.25 V at pH 7 and at -0.5 to 0.4 V at pH 14. Resilience $Na_2SO_4 \cdot 10H_2O$ detected in the diagram in the range from pH 6.5-14 potential change from 0.05 to 0.25 V at pH 6.5 and from 0.4 to 0.43 V at pH = 14.

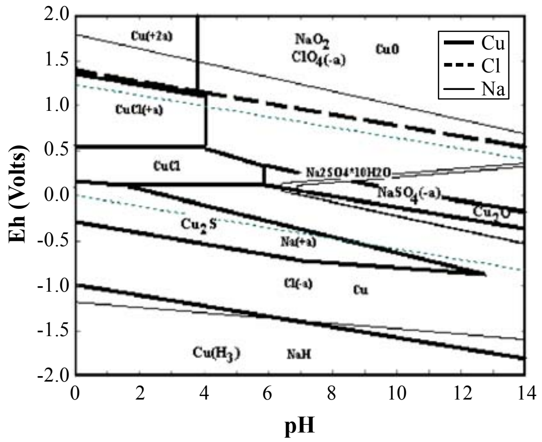

Fig. 1: The pourbaix diagram for the $CuS-H_2SO_4-O_2-NaClO$ system at 298 K

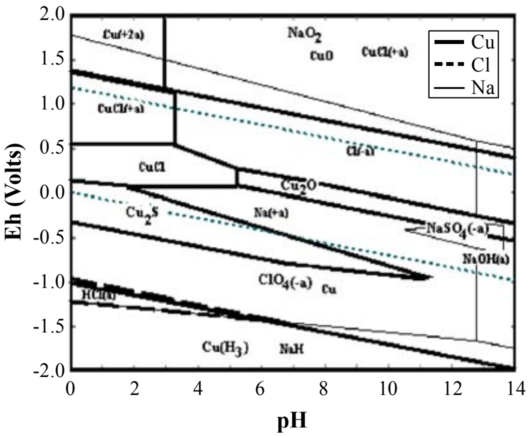

Fig. 2: The pourbaix diagram for the $CuS-H_2SO_4-O_2-NaClO$ system at 353 K

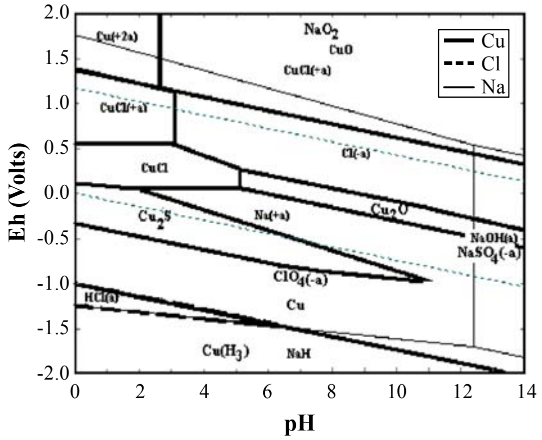

Fig. 3: The pourbaix diagram for the $CuS-H_2SO_4-O_2-NaClO$ system at 373 K

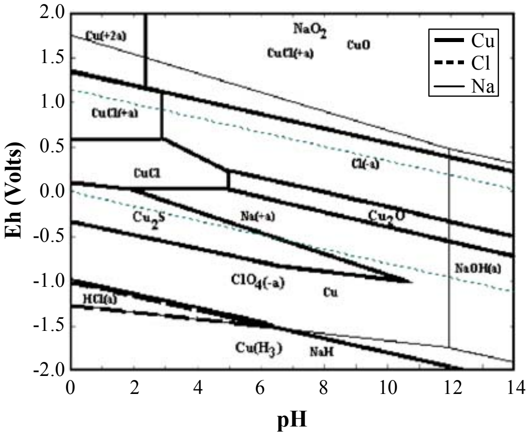

Fig. 4: The pourbaix diagram for the $CuS-H_2SO_4-O_2-NaClO$ system at 403 K

The stability region is formed by the dissociation of the hypochlorite ion to chloride ion and atomic oxygen with the change of potential from -2.0 to +1.4 V at pH = 0 and from -2.0 to +0.6 V at pH =14. $[ClO_4]^-$ is formed by the coordination of four oxygen atoms around the chloride ion with the change of potential from +1.2 to +2.0 V at pH = 0, and from +0.6 to +2.0 V at pH = 14.

NaClO oxidizing agent behavior at increasing temperature from 298 to 403 K (Figs. 1-4). As the increasing temperature from 298 K to 353 K there is no formation of sodium sulfate, and the existence domain of the anion $[NaSO_4]^-$ decreases to = pH 10.6-13.7 when the redox-potential is from E = -0.75 to -0.4 V at pH = 13.7. At this temperature Pourbaix diagram sodium ion forms NaOH at pH = 12, 8-14 ageing effect from -1.7 V to + 0.5 V at pH = 12.8 and from -1.8 V to 0 5 V at pH = 14. At further increasing temperature to 373 to 403 K, there is an increase of NaOH in acidic media to pH = 12.5 with a change of redox-potentials from -1.7 to + 0.6 V at 373 K and pH = 12 with the change of potentials - 1.7 V to 0.5 V at 403 K.

At the increasing temperatures from 298 to 403 to the stability region of chloride ion $[Cl]^-$ and chlorate ion $[ClO_4]^-$ remain in the range of pH = 0-14 with a change of redox potential $[Cl]^-$ from -2.0 V to + 1.4 V at pH = 0 and 298 K, and at 403 K from -2.0 V to +1.35. At pH = 14 and 298 K, the ageing effect from -2.0 V to +0.6 V, and at pH = 14 and 403 K from -2.0 to +0.25 V.

The behavior of the sulfate ion at increasing temperature from 298 to 403 K is demonstrated in Figs. 5-8.

The behavior of the sulfate ion at 298 K. In the diagram (Fig. 5) is the formation of stable phases of sulfur compounds in the aqueous phase with ageing effect from +0.0 to +1.35 V at pH = 0 and from -0.75 to +0.4 V at pH = 14. In this area, stable phases are the following compounds $H_2S_4O_3$, $H_2S_2O_7$ and $H_2S_2O_8$. These compounds are powerful oxidants and shear equilibrium will allocate atomic oxygen, which is an additional oxidant.

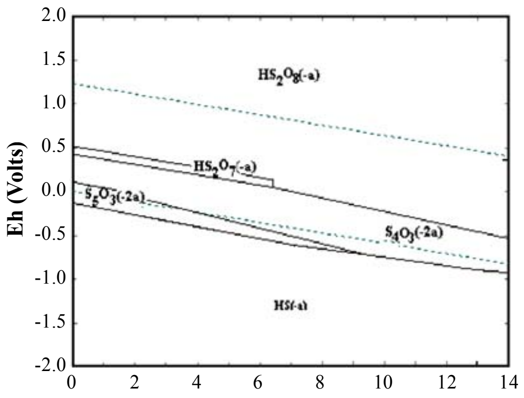

Fig. 5: The Pourbaix diagram for the H_2SO_4–O_2–NaClO system at 298 K

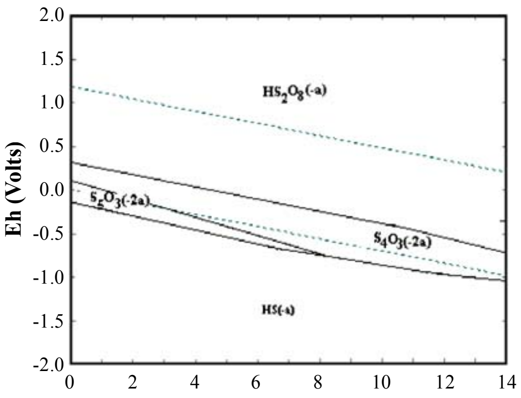

Fig. 6: The Pourbaix diagram for the H_2SO_4-O_2-NaClO system at 353 K

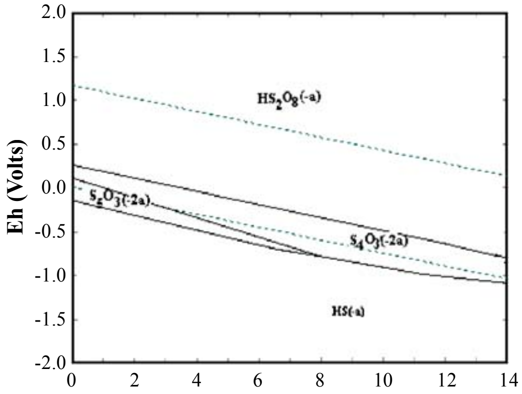

Fig. 7: The Pourbaix diagram for the H_2SO_4–O_2–NaClO system at 373 K

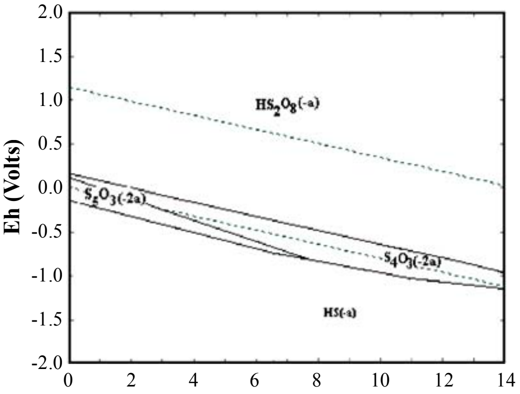

Fig. 8: The Pourbaix diagram for the H_2SO_4–O_2–NaClO system at 403 K

The behavior of the sulfate ion at 298-403 K. In the diagram (Figs. 5-8) are demonstrated the changes of formation of stable phases of sulfur compounds in the aqueous phase at the increasing temperatures from 298 to 403 K. The Pourbaix diagrams demonstrate the fact of increase of hard of pyroxide acid, which is a strong oxidizing agent with increasing temperature in the aqueous media. In this pH range is not changed and remains from 0 to 14, and a change in the redox-potential at pH = 0 and 298 K from +0.5 to +2.0 V at pH = 0 and 403 K from +0.25 to +2.0 V. In the pH = 14 area with the ageing effect -0.53 to +2.0 V at 298 K and from -0.95 to +2.0 at 403 K.

Charting the Pourbaix diagram for the CuS –H_2SO_4–O_2–NaClO system

Pourbaix diagrams for the « CuS-H_2SO_4-O_2-$KClO_3$» system at 298, 353, 373 and 403 K temperatures were also constructed according to the licensed program of Outokumpu Ou company (Figs. 9-12).

CuS behavior by the increasing temperature from 298 to 403 K (Figs. 9-12). Also, as in the Pourbaix diagrams oxidizer -NaClO, in this Pourbaix diagrams saved the same region of phase stability of copper -Cu, Cu_2S, CuCl, $[CuCl]^+$, Cu_2O, CuO and the values of their redox potentials.

Oxidant behavior-$KClO_3$ at 298 K (Fig. 9). At this temperature aqueous phase diagram Purbe stable phases are K^+, KOH, K_2SO_4, K_2SO_4, $KClO_4$, KO_3. Education K^+ is due to the dissociation of potassium hydride in the range of pH 0-9.5 with changing the redox potential of E = -1.3 V to E = +1.4 V at pH = 0 and E = -1.55 V to E = +0.8 V at pH = 9.5. KOH phase is formed by reacting potassium hydride, with water and is stable in the pH range of 9.5-14. Phase K_2SO_4 formed by reacting the potassium cation and sulfate anion and is stable in a pH range of 6-9.5, and the second stability region is potassium sulfate pH = 9.5-10.2 interval and an interval occurs in the neutralization reaction. $KClO_4$ phase is formed in two regions of pH = 0-9,5 and pH = 9.5-11.2, wherein in the first region the phase transition from the potassium cation and anion chlorate in the second region as a result of dissociation phase, and interact KOH cation potassium chlorate anion. KO_3 stable phase in two areas 0-11.2 pH and pH = 11.2-14. In the first region dissociation occurs with the formation of potassium perchlorate KO_3, the second region- as KOH dissociation to form KO_3.

$KClO_3$ oxidation behavior at 298 K (Fig. 9). In aqueous phase of Pourbaix diagrams K^+, KOH, K_2SO_4, K_2SO_4, $KClO_4$, KO_3 are hard phases. K^+ spiking is due to the dissociation of potassium hydride at pH = 0-9.5 change the redox- potential from E = -1.3 V to E = +1.4 V at pH = 0, and from E = -1, 55 V to E = + 0.8 V at pH = 9.5. KOH phase is formed by reaction of potassium hydride with water and it is hard at pH = 9.5-14. K_2SO_4 phase is formed by the interaction of potassium cathion and sulfate anion and is hard at pH = 6-9.5 range, the second hard area of potassium sulfate is the range of pH 9.5-10.2 and the reaction of neutralization occurs in this range. $KClO_4$ phase is formed in two areas of pH = 0-9.5 and pH = 9.5-11.2. In the first of the phase there is a phase transition from chlorate and potassium cathion-anion, in the second phase in the result of dissociation phases of KOH and interaction of cathion with potassium chlorate anion. KO_3 phase is hard in two areas pH = 0-11.2 pH and pH = 11.2-14. In the first area there is a dissociation of potassium chlorate with KO_3 forming, and the second area - Dissociation of KOH with forming of KO_3.

$KClO_3$ Oxidation behavior with increasing temperature from 298 to 403 K (Figs. 9-12). It's obvious from Pourbaix diagrams that there is K^+ and $KClO_4$ existence areas shift to acidic media area, $KClO_4$ phase at 403 K is absent and K_2SO_4 phase is present only at 298 K. The behavior of chloride ions and sulfate anions in the system is similarly to above discussed ones.

The Pourbaix diagrams calculated results showed that in CuS-H_2SO_4-O_2-NaClO and CuS-H_2SO_4-O_2-$KClO_3$ systems in the aqueous phase are Cu, Cu_2S, CuCl, Cu_2O, [CuCl]+ and CuO, which indicates multistage nature of oxidation under the influence of cuprite sodium hypochlorite, potassium perchlorate, and the process temperature increases the stability region shifts above stable phases of copper to acid media, which is particularly noticeable at a temperature of 403 K.

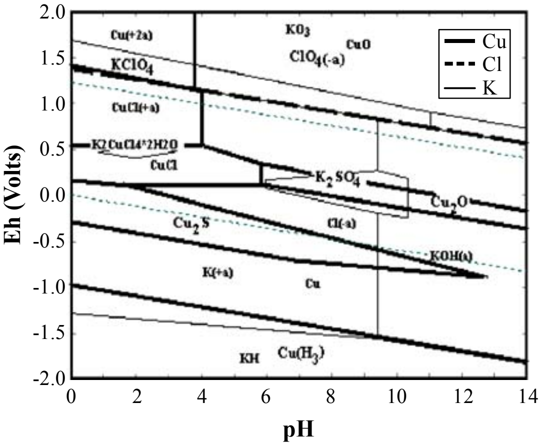

Fig. 9: The Pourbaix diagram for the $CuS-H_2SO_4-O_2-KClO_3$ system at 298 K

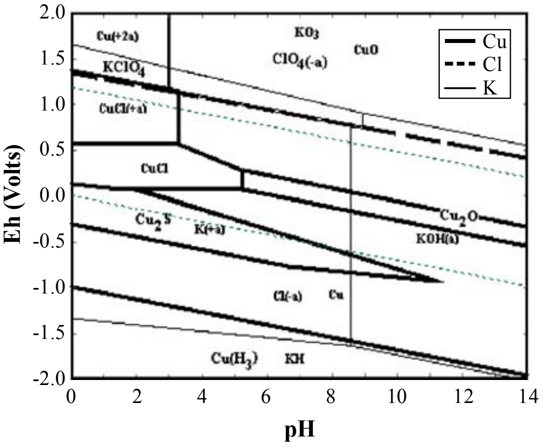

Fig. 10: The Pourbaix diagram for the $CuS-H_2SO_4-O_2-KClO_3$ system at 353 K

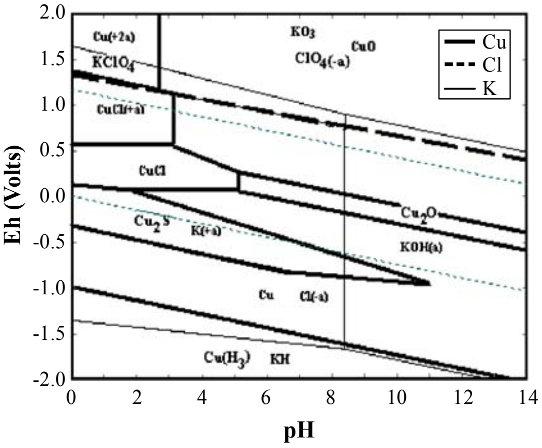

Fig. 11: The Pourbaix diagram for the $CuS–H_2SO_4-O_2-KClO_3$ system at 373 K

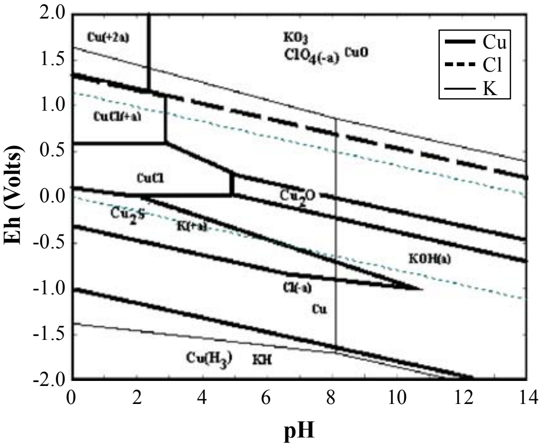

Fig. 12: The Pourbaix diagram for the $CuS-H_2SO_4O_2KClO_3$ system at 403 K

The materials in this article are the result of research according to the grant #1826/GF within budget program 055 "The scientific and/or technical activities," sub 101 "grant funding for researches" for 2012-2014 (Republic of Kazakhstan).

CONCLUSION

Achieved data indicate the that transition of cuprite into the solution may pass in the environment of the selected solvent as sulfuric acid and oxidizing agents-oxychlorides of sodium and potassium and the fact that there is no need of usage of the second oxidizer oxygen. The most strongest oxidizing agent in the abovementioned reactions is a sodium hypochlorite.

The materials in this article are the result of research according to the grant № 1826/GF within budget program 055. "The scientific and/or technical activities," sub 101 "grant funding for researches" for 2012-2014 (Republic of Kazakhstan).

REFERENCES

1. G. Zh. Zhunusova, Pourbaix Diagram Systems of the Gold Aluminides -H_2SO_4-MnO_2, Herald KazNTU-Almaty, **6(82)**, 7 (2010).
2. G. Zh. Zhunussova, N. T. Akkazina and Sh. Bayisbekov, The Studying of Pyrite Behavior in Oxidation Leaching of Hard Gold-containing Ore in Sulfuric Acid Solution in the Presence of Pyrolusite//Bulletin of the Kyrgyz-Russian Slavic University, 12 (2010).
3. V. M. Latimer, Oxidation States of the Elements and their Potentials in Aqueous Solutions, Moscow, IL (1964).
4. A. N. Zelikman, G. M. Voldman and L. V. Belyavskaya Hydrometallurgical Processes Theory, M. Metallurgiya (1987) p. 421.

Accepted : 11.03.2014