Kinetics from Reaction of Copper Extraction from Convertor Dust in Sarcheshmeh Copper Complex, Kerman

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Abstract - In this study the kinetics of copper extraction from convertor dust in Sarcheshmeh Copper Complex in Kerman has been presented based upon the shrinking core. In this research we examined different parameters such as acid, temperature, pressure, time, size of particles and stirring speed. The laboratory results show that stage of reaction control is the surface reaction on particles.
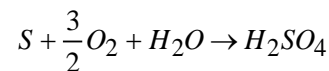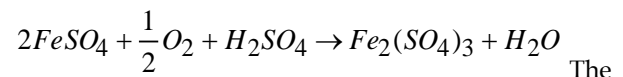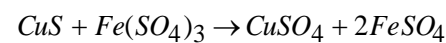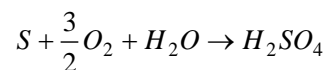
Index Terms – Acidity, Copper Complex, Extraction, Kinetics, Partial Pressure, Surface reaction, Thermodynamic parameters

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1 INTRODUCTION

FOR the optimal conditions of copper recovery by the designed pressurized reactor, it is necessary to know the kinetics of extraction reaction. For example, there are some effective factors on extraction reaction speed such as sulfuric acid 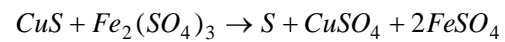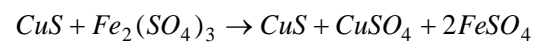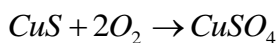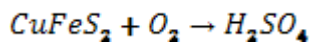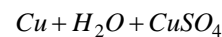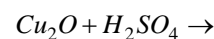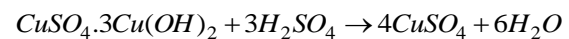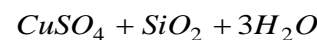concentration, reaction temperature, pressure, time, stirring speed and size of particles which their effects must be measured on isolation speed. The sample analysis showed that the dust compositions are similar to phosphoric ores and there have been a lot of works done on kinetics of reaction so far, for example, Achorjee (1) works on examining kinetics of lead sulfide extraction reaction with chloride acid and Pritker (2) works on kinetics of lead sulfide extraction reaction with chloride acid. Other researches included on the field are Nunez (5) work who studied in details on solving zinc ferric compositions in chloride acid and Lanyon (6) and his colleagues examined iron extraction from its oxide sources with chloride acid and also Olani Pekun (7) defined the effective factors in kinetics of extraction.

The mechanism of extraction reaction based upon the shrinking model:

If we have the reaction with the following equations:
The copper sulfide compositions reaction with sulfuric acid and oxygen:

$$CuFeS_2 + O_2 \rightarrow H_2SO_4$$

$$CuS + 2O_2 \rightarrow CuSO_4$$

$$CuS + Fe_2(SO_4)_3 \rightarrow CuS + CuSO_4 + 2FeSO_4$$

$$CuS + Fe_2(SO_4)_3 \rightarrow S + CuSO_4 + 2FeSO_4$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

$$S + \frac{3}{2}O_2 + H_2O \rightarrow H_2SO_4$$

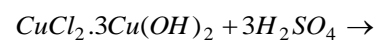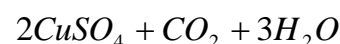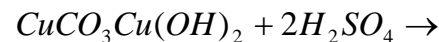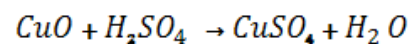$$CuS + Fe(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4$$

$$2FeSO_4 + \frac{1}{2}O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$

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$$S + \frac{3}{2}O_2 + H_2O \rightarrow H_2SO_4$$
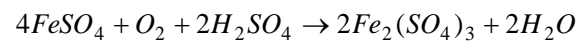
copper oxide compositions reaction with sulfuric acid:
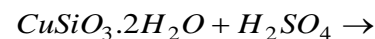
$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$CuCO_3Cu(OH)_2 + 2H_2SO_4 \rightarrow$$
$$2CuSO_4 + CO_2 + 3H_2O$$

$$CuCl_2.3Cu(OH)_2 + 3H_2SO_4 \rightarrow$$
$$3CuSO_4 + CuCl_2 + 6H_2O$$

$$CuSiO_3.2H_2O + H_2SO_4 \rightarrow$$
$$CuSO_4 + SiO_2 + 3H_2O$$

$$CuSO_4.3Cu(OH)_2 + 3H_2SO_4 \rightarrow 4CuSO_4 + 6H_2O$$

$$Cu_2O + H_2SO_4 \rightarrow$$
$$Cu + H_2O + CuSO_4$$

The direct reaction of sulfide compositions:

$$CuFeS_2 + \frac{17}{4}O_2 + \frac{1}{2}H_2O_4 \rightarrow$$

$$CuSO_4 + \frac{1}{2}Fe_2(SO_4)_3 + \frac{1}{2}H_2O$$

The indirect reaction of sulfide compositions:

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow$$
$$CuSO_4 + 5FeSO_4 + 2S$$

$$5FeSO_4 + \frac{5}{4}O_2 + 5H_2SO_4 \rightarrow$$

$$\frac{5}{2}Fe_2(SO_4)_3 + \frac{5}{2}H_2O$$

$$2S + 3O_2 + 2H_2O2 \rightarrow 2H_2SO_4$$
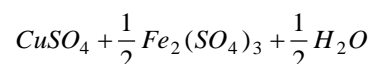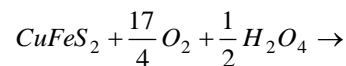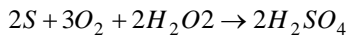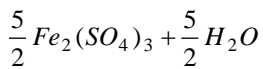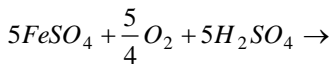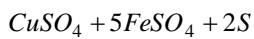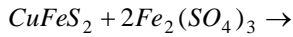
There have been many studies achieved on solid-fluid reaction which divided into two groups (8, 9, 10).

(A) – IF THE SURFACE REACTION IS CONTROLLER:

When the reaction in liquid phase produces a very soluble material, the following equation shows the reaction which takes on solid level:

$$\left(-\frac{dN}{dt}\right) = \pi d^2 R_A = \frac{6d^2 R_A V_0}{d_0{}^3}$$

in which RA is the reaction speed for area unit representing a function of fluid elements. The initial and real diameter and particles represented by d0 and d, respectively. If d3/d03 ration shows as (1-X), then X is a solid part participating in the reaction. Thus N=V0 ρ (1-X)/M and we have:

$$\frac{dX}{dt} = -\frac{dN}{dt} \cdot \frac{M}{\rho \cdot V_0} = \frac{6R_A M}{d_0 \rho}(1-X)^{2/3}$$

in which M shows the solid molecular weight and ρ is the solid density. Therefore we can see the reacted part is appropriate with the initial diameter of particles. By integration the above equation is written as the following formula:

$$t = \frac{d_0 \rho}{2R_A M}\left[1 - (1-X)^{1/3}\right]$$

$$1 - (1-X)^{1/3} = K_{S1}t$$

by which we can get the reacted part. If the X curve is perpendicular to time, then we can say that the surface reaction is controller [18,19, 20].

(B) PENETRATION FROM PRODUCT LAYER IS CONTROLLER:

In this state assuming there is a balance on surface, speed in base of surface is appropriate with concentration difference on surface and penetration into the product and if B shows the penetrated material, the reaction speed which equals to penetration speed represents by the following formula:

$$J_B = \frac{dN_B}{dt} = D_B \frac{dC_B}{ds} A$$

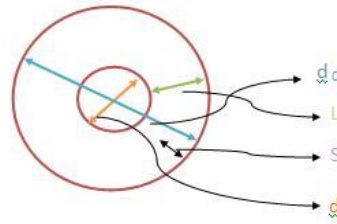in which s shows the layer thickness of product and A=π (d0 – 2s)2 shows the surface of particles.

Fig 12-3: Local view of changes in particles

Therefore the mass flux is written by the following formula:

$$\frac{dN_B}{dt} = \frac{D_B \Delta C_B}{\int_0^L \frac{ds}{A}} = \frac{\pi D_B \Delta C_B}{\int_0^L \frac{ds}{(d_0 - 2s)^2}} = \frac{2\pi D_B \Delta C_B}{(1/d) - (1/d_0)}$$

in which d is the diameter of particle and the particle value participated in the reaction is related to the particle value by the following formula:

$$\frac{dX}{dt} = \frac{12 D_B \Delta C_B M_B}{\rho_B d_0{}^2 [(1-X)^{-1/3} - 1]}$$

in which it also shows the product value is appropriate with the initial diameter of particle. If we integrated the formula then we have:

$$t = \frac{d_0{}^2 \rho_B}{4D_B \Delta C_B M_B}\left[\frac{1 - (1-X)^{2/3}}{2} - \frac{X}{3}\right]$$

$$1 - \left(\frac{2}{3}\right)X - (1-X)^{2/3} = Ks_2 t$$

If the curve of this function is a direct line by time thus the penetration from inside of product is controller. As we may know the speed chemical reactions is functional to different parameters of which the most important ones are pressure, temperature, concentration of materials, and if there is any solid particles, the size of particles. So the relationship of speed may be written as follow:

$$r = \frac{1}{A} \times \frac{dN}{dt} = K.f(C).f(T).f(P)$$

in which r shows the speed of chemical reaction in terms of mole by solid surface unit, T is temperature, P shows pressure and N is the number of moles. The Arrhenius equation shows the function of temperature.

$$f(T) = K.e^{-\frac{E}{RT}}$$

in which E shows the energy of reaction activity, R is the gas fixed value and T is temperature. Since in solid phase reactions there are three phases of external penetration, internal penetration and chemical reaction, thus there are three phases in this system too and if the surface reaction is controller, the speed equation may be written as this:

r = K. f (C)

in which K is a fixed value dependent to temperature and in this reactions due to tendency from acid ideal state, it is a better parameter for defining the speed of reaction so that we can write the above formula as this:

r = K.f (aH+)

With this value the following methods have been used for determining the speed and effective factors on reaction.

How to Do the Tests

As we said earlier, in this article we try to examine some effective factors on reaction speed of copper compositions. It is required to do some standard tests. So we used 98% sulfuric acid. In this test using a mixer with 900 rpm (fixed) mounted in a Bach reactor and reactor temperature was controlled by oil pump and reactor pressure was controlled by oxygen capsule, the effective factors have been examined on chemical reactions. Fig (2) shows how to pour a specific weight of solid sample at the time base into a container with acid and while keeping the mixed at a fixed round and temperature and container pressure are changing during testing, we took samples from the container for determining the reacted amount of copper and iron and after filtering by Atomic Absorption Spectrophotometer and some lab methods, we determine the iron and copper concentrations in samples which the results are shown as chart later in the article.

Fig (2) – The device used for determining kinetics of reaction

DISCUSSION AND CONCLUSION

1- The dust of blast furnaces at Sarcheshmeh Copper Complex in Kerman containing high amounts of oxide copper compositions and some sulfide copper compositions which we should take proper method to recover them.

2- The leaching tests under pressure results showed that the consumption of acid by dust is high at first then it lowers and reached to a fixed value.

3- With the lab data and results, we can introduce 130°C temperature, 8 bar oxygen pressure, mixer speed at 900 rpm, 3 hours of time, 0.1 gr/lit of pulp density and 200 gr/lit of acidity as the optimal conditions for pressurized dissolution of blast furnaces at work. In these optimal conditions, the recovery rate of copper is 88%.

4- Analyzing the solid products showed that the solid contains about 3%-5% of copper. These copper compositions are unrecoverable due to their unknown structure and composition.

(A) Kinetic Examination

A-1- Kinetic examinations on lab data showed that in consistent conditions with no external control, the chemical reaction of controller phase is the dissolution process for copper. In these conditions the activation energy was calculated to be 15.94 kj/mol.

A-2- Using the equation in theory section, assuming all the particles participate in chemical reaction similarly, if we draw the right side of equation (3) in terms of time, we would have:
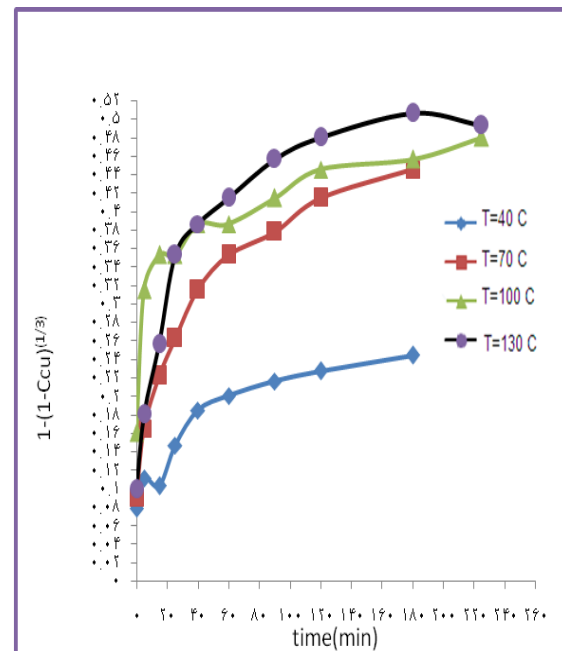

Chart (1): Determinant chart of reaction controller

This chart shows the surface reaction is controller. If we draw the right side of equation (7) in terms of time there would not any direct lines.

(B) THERMODYNAMIC EXAMINATION (HOW DIFFERENT PARAMETERS AFFECT THE REACTION)

The effect of different parameters with the controlling surface reaction and using the tests can be summarized as follow:

1- Temperature: the effect of temperature on reaction speed of dust compositions with sulfuric acid has been examined and the results show that as the temperature increases the dissolution speed is increases too. We use Arrhenius law to express the effect of temperature on dissolution speed as it has been discussed in the theory section, so as the chart (2) shows we have drawn the logarithm chart of speed in terms of temperature inverse but, of course, different references presented different activations (11).

2- Acid: We use the results from acidity tests excepting acid concentration with similar conditions to select the proper acid concentration. These tests taken placed with 100 and 200 gr/lit acid concentrations, respectively. The results from these two tests show that the copper recovery at 200 gr/lit of acidity would be higher in less leaching time.

3- Pulp Density: increasing pulp density at specific extent would increase the copper concentration and other metal ions in solution as well, but generally decreases the recovery of metals. If the pulp density goes beyond a specific limit not only decreases the recovery but the concentrations also decrease and may lowers the efficiency of process severely. Thus we use the test results with similar conditions excepting the pulp concentration to select the pulp proper concentration. These tests have been taken place in 10 and 20 gr/lit concentrations. The results from these two tests show that there would be a high recovery for copper in 10 gr/lit of pulp.

4- Mixer Speed: the external mass transfer, which its effect defined by mixer round, has an important role on controlling the process speed, so that as the mixer speed increases the copper recovery rate as well as dissolution reaction speed increase severely. But in higher speed of mixer (over 800 rpm), diffusion effect on boundary layer is removed. Therefore we used 900 rpm mixer rounds for optimal improvement and lowering the number of test phases.

5- Partial Oxygen Pressure: as oxygen pressure increases partially, copper recovery and speed of dissolution process increase considerably. The effect is too high as recovery of copper sulfide compositions in atmospheric pressure, even in high temperature, would be very trivial but as the oxygen pressure increases up to about 8 bar, most of copper enter the solution.

6- Time: the reaction time is an important factor to determine the amount of copper and also impurity of other metals in the solution. So at initial times, the solved copper increases very much and during time copper concentration and other impurities are decreased.

With the results in previous paragraphs, we can see that the salvation under pressure is a proper method for recovering copper from its sulfide compositions in dust, and if it has economic justifications, it can be a proper replacement for similar methods.
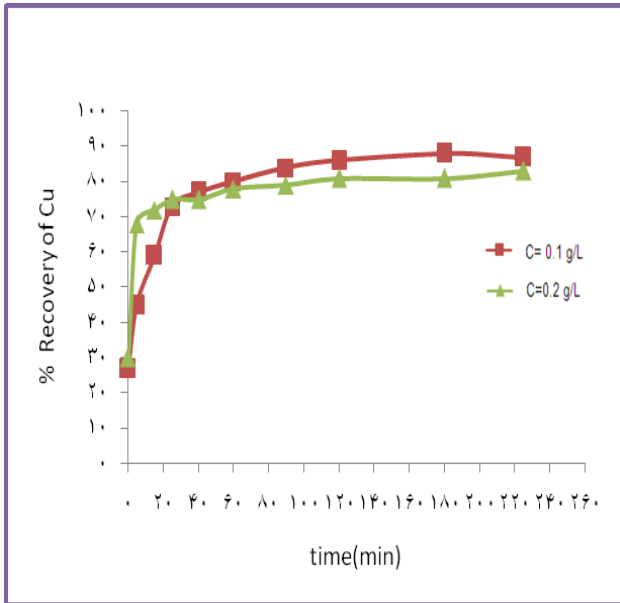
SOME RELATED CHARTS
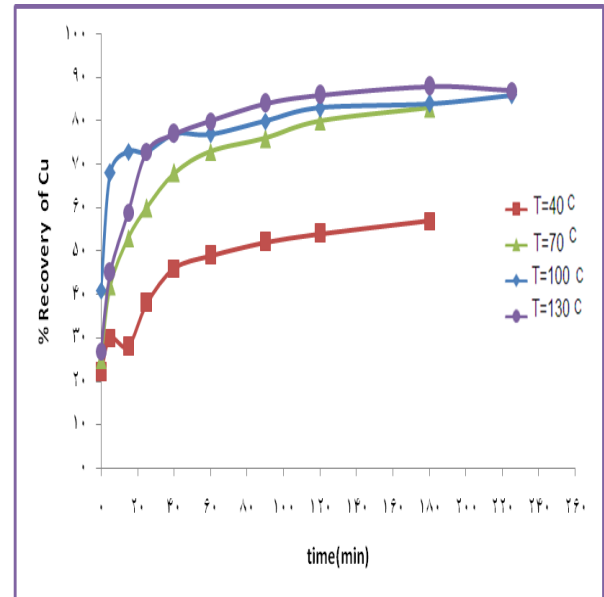
speed=900 rpm,Po2=8bar,S/L=0.1,acidite=200 g/l
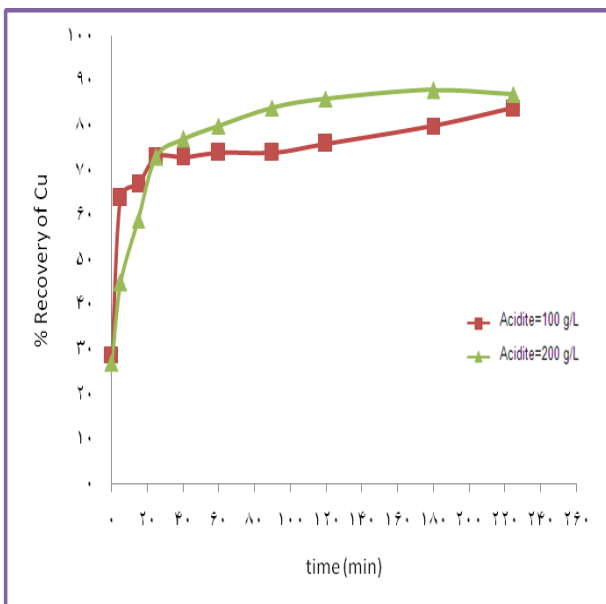
Chart 2: Temperature effect on recovery of copper
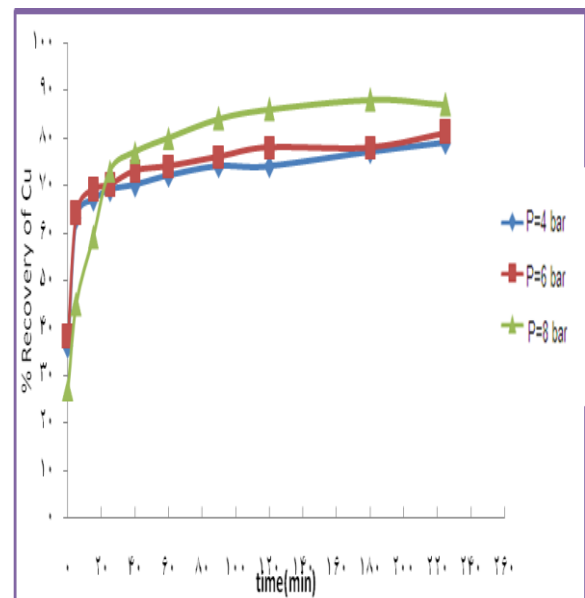
speed=900rpm,T=130 ˚C, Acidite =200 g/l, S/L=0.1

Chart 3: Oxygen pressure effect on recovery of copper

speed=900rpm,T=130˚C,Po2=8bar, Acidite =200g/l

Chart 4: Pulp density effect on recovery of copper

speed=900 rpm, T=130 C,Po2=8 bar ,S/L=0.1

Chart 5: Acidity effect on recovery of copper

From - $\dfrac{Q}{R}$ ratio we can calculate the activation energy equals to 15.94 kj/mol, which numerically shows the chemical control.
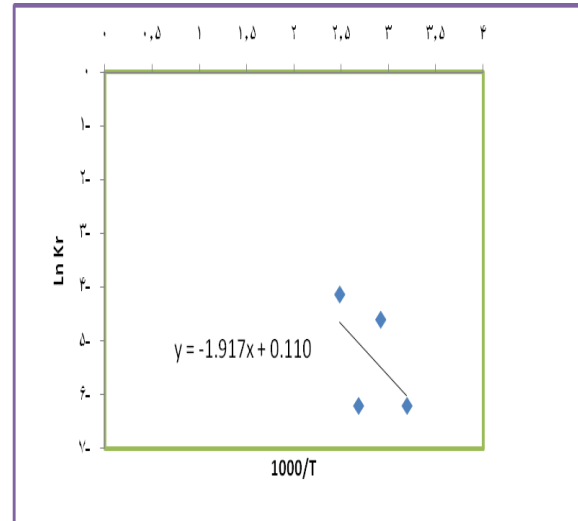

Chart 6: Speed fixed changes in terms of temperature for copper

REFERENCES

[1] Acharjee.D.K.(1989);"Recovery copper from copper concentrator tailing by leaching".*Can.J.Chem.Eng.*vol.67.pp.686-688

[2] Pritzker.M.(1998);"Model for the ferric chloride leaching of galena Metall.Trans B.,vol.29B,pp.953-960

[3] Majima H.,Awakura Y.,Mishima T.,(1985);"the leaching of hematite in acid solutions":Metal.*Trans.B,*vol.26B,pp.23-30

[4] Majima H.(1995);"Importance of fundamental study in hydrometallurgy"; *Metal.&Mat.Tras.B,*vol. 26B,pp.1109-1122

[5] Nunez C.,Vinals J.(1984):"Kinetics of leaching of zinc ferrite in aqueous hydrochloric acid solutions"; *Metal.Trans.B,*vol.15B

[6] Lanyon M.R.,Lwin T.,Merritt RR.,(1999);"The dissolution of iron inhydro choleric acid leach of an ilmenite concentrate"; *Hydrometallurgy,*vol.51(3),pp.299-323

[7] Olanipekun E.O.(2000);"Kinetics of leaching laterite"; *Int.J.Miner.process.*,vol.60.pp.9-14

[8] Smith J.,(1980);"Chemical Engineering Kinetics".New York.Mc-Graw Hill,Inc.

[9] Fogler H.S.(1992) ; "Elements of Chemical Reaction Engineering"2nd editions , New Jersey , Perentice-Hall, Engelwood cliffs.Inc.

[10] Miller.G &Newton.T, "Copper Heap Leaching Testing, Interpretation and Scale up", *ALTA* 1999.

[11] Wiess N.L, "SME Mineral Processing Hand Book" ,1985