Chapter - L

HYDROMETALLURGY & SOLUTION MINING

HİDROMETALURJİ & ÇÖZELTİ MADENCİLİĞİ

Effect of Temperature on Dissolution of Gold from Copper Anode Slime

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ABSTRACT The effect of temperature on the rate of gold dissolution from copper anode slime by chloride leaching was investigated. A series of experiments were conducted in a temperature range of 30 to 75 ˚C to evaluate the kinetics and thermodynamics of gold dissolution. The results showed that the concentration of gold increases significantly at elevated temperatures in which the maximum recovery of gold was 97.3% at 75˚C. Additionally, the formation of a product layer over anode slime particles was confirmed through SEM images. XRD, XRF and BET analysis showed that this layer is composed of silver chloride and barium sulfate. It was also found that the ash diffusion mechanism is the rate-controlling step at all temperatures. Additionally, the value of the activation energy was estimated 15.65kJ/mol.

Keywords: Copper anode slime, gold, chlorination process, Kinetics

1 INTRODUCTION

Due to the importance of gold (Au), and its dwindling sources, the recovery of Au from the secondary sources is essential. It has been reported that about 20% of all Au deposits have significant copper mineralization commonly associated with chalcopyrite and chalcocite in certain ores (Dai et al., 2012). Copper concentrates often contain precious metals like Au and Ag.

During copper electrorefining process, where the blister copper is processed to obtain copper with a purity of 99.99%, impurities accumulate in the bottom of cells as anode slimes; these slimes are the un-dissolved portion of the corroding copper anode. These slimes contain copper, gold, lead, nickel, platinum, selenium, silver and tellurium which their chemical composition depends on the composition of the anodes. Growing demand and the primary resource constraints precious metals, recovery of these metals from anode slime is economically attractive and also it is environmentally friendly (Nilanjana Das,2010).

Different methods have been proposed for recovery of Au from copper anode slimes (Hait et al., 2009; Akinori and Yoshifumi, 2000). Hydrometallurgical processes for recovery of precious metal from anode slime occurs in alternative leaching agent (Wk wang et al.,1981). Most common leaching agent used in gold salvation in anode slime in aqueous media such as aqua regia (Wk Wang et al,1981), cyanide (Su Jianhua et al, 2002), thiourea (Omer Yavuz et al, 2007), hydrochloric acid (J. Biswas et al, 1998), hydrochloric acid and hydrogen peroxide (Rw Stanley, 1987), hydrochloric acid, and chlorine gas (B.Donmez et al., 1999)

Due to the nature of the noble metal gold, using strong oxidants to encourage the dissolution of gold in aqueous medium is important. So some oxidants such as hydrogen peroxide and chlorine gas was used in different medium.

A literature survey shows that temperature plays a critical role on dissolution of gold from copper anode slime. Despite the limited increase in temperature in hydrometallurgical processes, many studies have been focused on the effect of temperature in this case (Rw Stanley, 1987; J Bertha, 1989; Wk Wang et al, 1981; B.Do¨nmez et al., 2001).

In this work, the effect of temperature on the dissolution of gold from copper anode slime via chlorine gas - hydrochloric acid leaching system is investigated form the thermodynamic and kinetic aspects.

2 MATERIALS AND METHODS

2.1 Materials

The anode slime was obtained from sarcheshmeh mine (Kerman, Iran). The sample was analyzed with XRF method and the main components sludge is reported at Table 1. Base on (XRD) analysis the main composition of anode slime was barium sulfate, some minor component same as silver selenite and copper selenite. The particle size was 120 µm (over 80%).

Commerical sodium carbonate was purchased from Razi petrochemical company, Shiraz, Iran. Also, analytical grade of hydrochloride acid (37%vol) and sulfuric acid (95–98%vol) were utilized (Baran Chemical Co., Iran). Industrial grade of calcium hypochlorite ($Ca(ClO)_2$, available Chlorine Min. 70%) was used to produce chlorine gas and was purchased from Sree Rayalaseema Hi-Strength Hypo Company, India.

2.2 Experimental procedures

Recovery of gold from copper anode slimes is a multi-stages process; at first stage selenium and copper were separated from anode slime. Then, anode slime was roasted

Table 1. The chemical composition of anode slim

Chemical composition	Weight.%
Au	0.106
SeO_2	16.1
CuO	5.90
Fe_2O_3	0.19
BaO	37.1
SO_3	22.1
PbO	2.80
Ag_2O	5.80
As_2O_3	0.88

with sodium carbonate with 15-20% weight ratio at temperature 700-800 ˚C for 1 to 3 hr. The roasted sample was leached by double distilled water at 90˚C for selenium removal (Langner, B.E., 1998). After drying of solid residue, copper leaching was conducted with a 100 gr/lit sulfuric acid solution at 90˚C for 1hr (Fabian, H., 1998). The final remained residue (copper anode slime after Se and Cu removal) was used for Au leaching study. Chlorine gas was produced by chemical reaction of calcium hypochlorite with hydrochloric acid at room temperature.

All experiments were carried out in 3L mechanically agitated reactor containing 2000 mL leaching solution at 210 RPM at varying temperatures in the range 30–75 °C. The values of liquid to solid ratio, HCl concentration and Chlorine gas flow rate are set at 12.5 L/Kg, 2 mol/lit and 2 Lit/min, respectively. The concentrations of Au, Ag, Se, Cu and Fe in all aqueous solutions were determined by atomic absorption spectrometry (AAS) model Varian AA240. Brunauer, Emmett and Teller (BET) surface area analyzer (Micromeritics, Gemini 2375) was used to determine the surface area of the concentrate before and during Chlorination process. The morphological features of the gold leaching residues and the reaction products formed during leaching were studied by scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Effect of temperature

The reactions involved in the dissolution of chlorination of gold are presented in Eq(1) (Donmez, B, 1999):

$$Au(s) + 3/2\ Cl_2\ (g) + Cl^-\ (aq) = AuCl_4^-\ (aq) \quad (1)$$

A series of experiments were carried out at temperatures in the range of 30–75 °C at a given L/S, HCl concentration and Chlorine gas flow rate. The evolution of Au concentration versus time, at different temperatures, is illustrated in Fig 1. As observed, an increase in temperature leads to a slight increase in Au Concentration and the optimum temperature for Chlorination of gold leaching is 75 °C.

Also, the results of Fig. 2 show that the maximum recovery of gold from anode slime was 97.3% after 180 min at 75˚C.

Regarding the Pourbaix diagram presented in Fig.3, at elevated temperature and for a given concentration of Cl^-, the stability region of $AuCl_4^-$ increases which is attributed to the endothermic nature of reaction.

3.2 Kinetic analysis and modeling

Many of studies on the kinetic aspect of gold chlorination suggest that the diffusion through the product layer is the rate-controlling step (M.I. Jeffrey et al 2001).

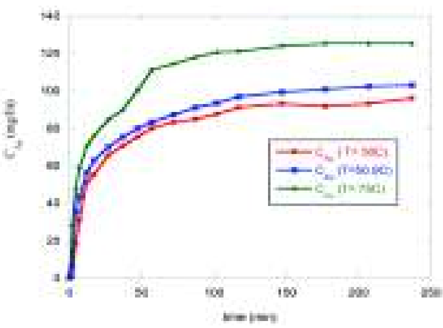

Figure 1. The evolution of Au concentration versus time, at different temperatures

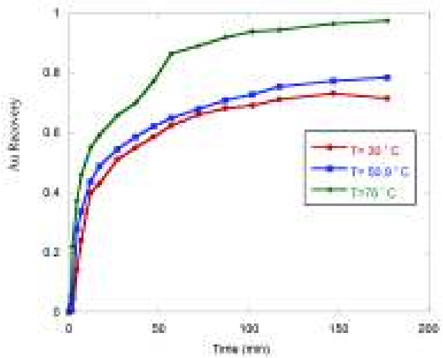

Figure 2. The maximum recovery of gold from anode slime at different temperature

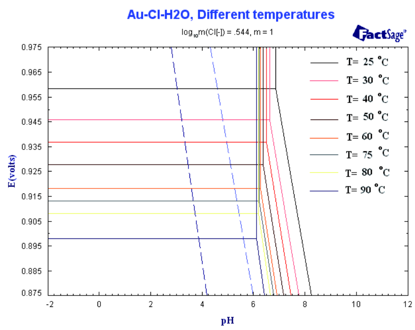

Figure 3. Pourbaix diagram at different temperature

On the other hand, Vinals et al. (1995) stated that the chemical reaction is the controlling step of the chlorination processes.

The XRF results (Table 2) indicate that the anode slime is mainly composed of silver, barium, sulfur and selenium. Also XRD analysis (Fig. 4) confirms the formation of silver choride and barium sulfate as product layer.

Additionally, SEM images (Fig. 5) shows that a layer of silver chloride, which can hinder the diffusion of Cl^- ions, covers the surface of Au particles during the chlorination process of anode slime.

Moreover, the changes in the surface area of the chlorinated residues can be used to determine whether the particle size is remained constant or not. Based on the results of BET analysis the surface area varied in the range of 7.37–7.55 (m2/g) during the chlorination process. This

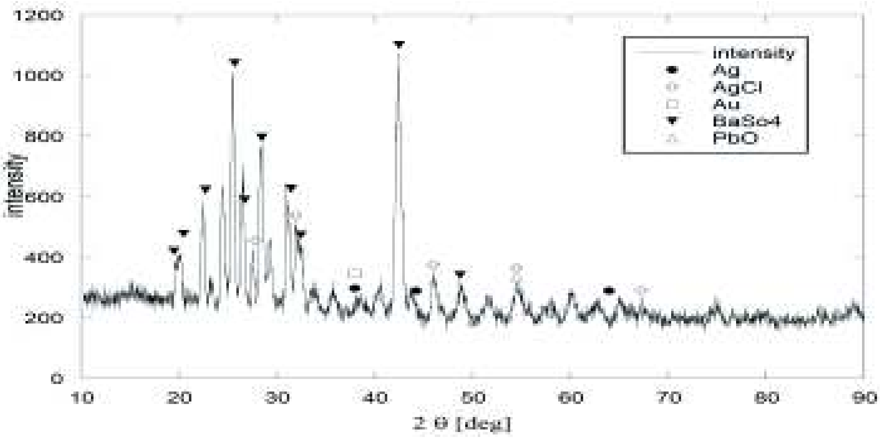

Figure 4. The XRD Pattern of anode slime after chlorination process

Table 2. The chemical composition of anode slime after chlorination process

Chemical composition	Weight.%
Au	<10 ppm
SeO_2	4.37
CuO	0.32
Fe_2O_3	0.98
BaO	54.1
SO_3	15.8
PbO	2.77
Ag_2O	8.4
As_2O_3	0.25

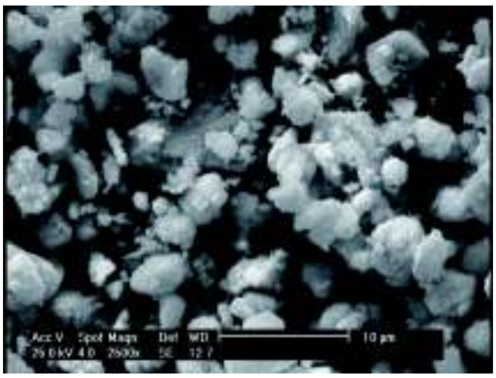

Figure 5. SEM image after chlorination process

constant specific surface area variation is indicative of unchanged particle size during process.

To sum up, based on the above evidences presented the rate of Au chlorination can be controlled by the rate of diffusion of Cl^- ions through the silver chloride and barium sulfate.

The results depicted in Fig.6 shows that the diffusion of the ions is the rate-controlling step at all temperatures. The activation energy of the dissolution process was found to be about 15.65 kJ/mol in the temperature range of 30-75 C.

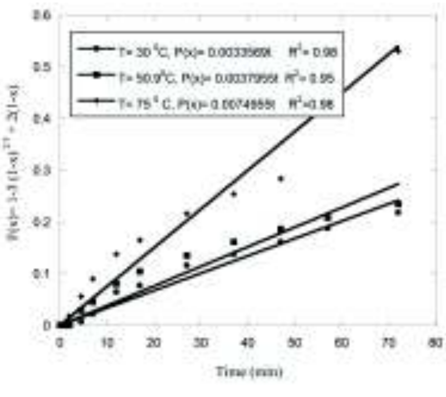

Figure 6. The plots of the p(XAu) versus F(t) at different temperatures; L/S= 12.5 , HCl= 2 mol/l, Cl_2= 2 Lit/min

4. CONCLUSIONS

Based on the obtained results, it was shown that the concentration of gold ion increases significantly during leaching by increasing the temperature. The optimum temperature for gold chlorination is found to be 75 °C. Also, the maximum recovery of gold was 97.3% at 75˚C.

The presence of the silver chloride and barium sulfate layer as the diffusion barrier was confirmed by SEM, XRD, XRF and BET analyses. It was found that the diffusion mechanism is the rate-controlling step at all temperatures. Additionally, the values of the activation energy showed that the rate of this process can be diffusion limited.

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Solvent Extraction of Gold from Chloride Solution by Tri-Butyl Phosphate (TBP)

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ABSTRACT Low concentrations of gold ion and the presence of various impurities in leaching solution is a problematic issue in hydrometallurgical production of gold. In this study, the extraction of gold from hydrochloric acid media was investigated via solvent extraction route employing tri-butyl phosphate (TBP) diluted in kerosene. Based on our findings, the extraction of gold increases at higher concentration of hydrochloric acid; however, this leads to inefficient separation of gold over iron. The results also showed that the extraction of gold is an exothermic reaction with activation energy of - 63. kJ/mol. The stripping efficiency of gold from loaded organic phases was obtained up to 90% using 0.05 M sodium thiosulfate ($Na_2S_2O_3$) solution. By the use of slope analysis method, the organo-metallic complex of gold and TBP, formed in the organic phase, was proposed as $H.AuCl_4.L_3$, where L represents the organic extractant.

Keywords: Solvent Extraction, Gold, Chloride media, TBP

1 INTRODUCTION

In hydrometallurgical production of gold, the concentration of gold in leaching solutions is low; on the other hand, various impurities are present in such solutions. Solvent extraction is a powerful technique for concentrating and purifying solutions under such existing circumstances. Several solvents have been proposed for the extraction of gold from chloride media, such as Methyl isobutyl ketone (MIBK) (Cox, 1992), di-ethylene diglycol di-n-butyl ether (DBC) (Jung et al.,2009), tri butyl phosphine oxide (TBPO) (Martfnez et al., 1996), tri-n-octylphosphine oxide (TOPO) (Martinez et al.,1997), ammonium compounds (Alguacil et al.,1993) and mono amide compounds (Narita et al.,2006).

Tri-butyl phosphate, known commonly as TBP, is relatively inexpensive with low solubility in water and appropriate extraction performance. The extraction of trace amounts of $HAuC1_4$ from aqueous solutions investigated employing TBP diluted in different diluents [Tocher et al., 1963]. It was reported that the organo-metallic macromolecules of Au-TBP-H_2O extraction system can be presented as $AuCl_4.3TBP.nH_2O$.

In the present work, extraction of gold from chloride solutions by TBP is evaluated. The effect of pertinent parameters, namely as time, temperature, and HCl, Au and TBP concentrations, on the separation process of gold are identified. Slope analysis method is employed to clarify extraction mechanism of gold with TBP diluted in kerosene. Also, different aqueous solutions are examined for effective stripping of Au loaded organic phase.

2 MATERIALS AND METHODS

Commercial tri-n-butyl phosphate (TBP) (Fluka) as extractant and kerosene (Isfahan Refinery Co) as diluents were utilized. Hydrochloric acid (35%-37%vol) and sulfuric acid (98%vol) obtained from Dr. Mojallali chemical laboratories in Iran. Also, gold and iron ions prepared by the standard metal chloride ($HAuCl_4$ and $FeCl_3$ MERCK).

Initially, kerosene was purified by washing with 3M HC1 solution then it diluted TBP. HCl diluted by gold chloride and distilled water in different ratios.

Batch experiments were carried out in a flask containing equal volumes (20 ml) of aqueous and organic solutions. Initial concentrations of gold in the aqueous phase were 500, 300, 130 and 68mg/L. The mixture was agitated at constant temperature (20 C), except in the temperature effect experiments, by a mechanical shaker at 400 rpm. Agitation was carried out for 30 min to assure equilibrium conditions then agitated samples were poured in separating funnel for 15 min to allow complete separation of the two phases. Kinetic test carried out in Erlenmeyer whereas two phases was agitated by magnetic stirrer. The metal content of the aqueous phase was determined by atomic absorption spectroscopy (varian, A240) and chemical composition of the organic phase was determined by mass balance calculations.

3 RESULTS AND DISCUSSION

3.1 Equilibrium time for extraction of gold

In order to estimate the required time for attaining the equilibrium conditions of extraction, a series of experiments were conducted at different time. Figure 1 shows

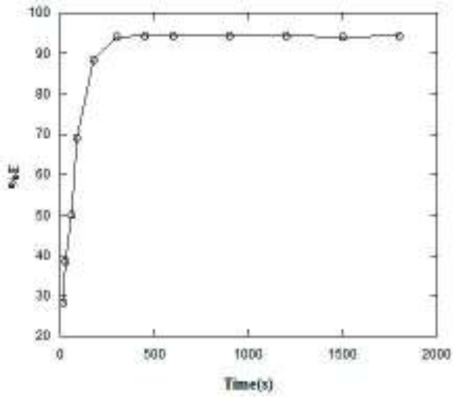

Figure 1: Extraction percent of gold versus time, T=20 °C, [Au] =67 mg/l and [TBP] = 0.1M [A]:[O]=1:1.

the results of these experimental runs; the total time needed for equilibrium extraction of gold with TBP was around 1.5 min. Therefore, a period of 30 min applied for each batch experiment to ensure attaining equilibrium conditions.

3.2 Effect of HCl concentration

Figure 2 illustrates the influence of HC1 concentration on gold extraction by TBP diluted in kerosene. As shown, an increase in hydrochloric acid concentration leads to higher extraction percent. Previous reports on this case [Alamdari et al., 2011] show that

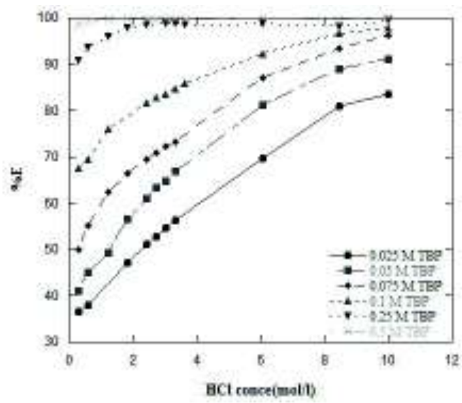

Figure 2:The influence of the HC1 concentration on gold (III) extraction by TBP (Au:500 mg/l).

the mechanism of Au extraction by TBP involves an ion association process in which the protonation of TBP molecules by H^+ (H_3O^+), brings the extraction ability for TBP to extract anionic species. The higher HCl concentration results in increasing of both H^+ and $AuCl_4^-$ in solution, and consequently, leads to further progress in gold extraction.

Moreover, by increasing the solvent (TBP) concentration in the organic phase, Au extraction percent is enhanced (Figure 2).

3.3 Effect of extract ant concentration

The extraction reaction of Au via TBP can be represented by Eq.1.

$$\mathbf{AuCl^-_{4aq} + H^+_{aq} + TBP_o = AuCl_4.H.TBP_o} \quad (1)$$

And the corresponding equilibrium constant is:

$$\mathbf{K = \frac{\gamma_{AuCl_4.H.TBP}.[AuCl_4.H.TBP]}{\gamma_{AuCl_4^-}[AuCl_4^-].\gamma_{H^+}[H^+].\gamma_{TBP}[TBP]^n}} \quad (2)$$

Where brackets stand represent concentrations, and γ for activities coefficient.

Since TBP concentration is varied in a specific range, γ_{TBP} may be considered constant. Beside, our observations indicate that pH variation in given HCl concentration is negligible, and γ_{H^+} is also constant. Furthermore, $AuCl_4^-$ is in dilute (trace) concentration, the concentrations of two gold solutes in aqueous and organic phases are very low in which $\gamma_{AuCl_4^-}$ and $\gamma_{AuCl_4.H.TBP}$ can be constant (Henry behavior).

These constant values can be considered in a term (Q) as:

$$\mathbf{Q = \frac{\gamma_{AuCl_4.H.TBP}}{K.\gamma_{AuCl_4^-}.\gamma_{H^+}.[H^+].\gamma_{TBP}}} \quad (3)$$

Regarding the definition of distribution coefficient ($D = [Au]_{org}/[Au]_{aq}$) as well as Eq. (3), Eq.4 can be written as:

$$\mathbf{D = Q.[TBP]^n} \quad (4)$$

Taking logarithm of Eq (4) leads to:

$$\mathbf{\log D = n \log[TBP] + \log Q} \quad (5)$$

the plot of log D *vs.* [TBP] yields a straight line with slope ***n***. Such plots are depicted in figure 3; the slopes are estimated in the range 2.9 to 3.2.

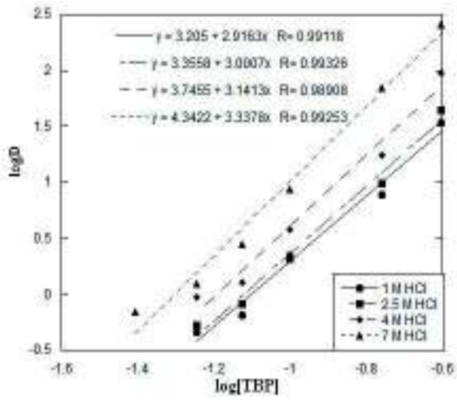

Figure 3: Variation logD of gold vs. log[TBP](Au:500mg/l).

3.4 Effect of gold initial concentration

Figure 4 illustrates the influence of intial gold concentration in the auqeous phase on the extraction percent of gold by 0.1 M TBP. The lower initial gold concentration results in an increase in gold extraction percent. It should be pointed out that when initial gold concentration in aqueous solution is set at high value (300, 550 mg/l), increasing of HCl concentration shows a desirable effect on the gold extraction percent. However, at low gold concentrations, extraction percentage decreases with acid increasing.

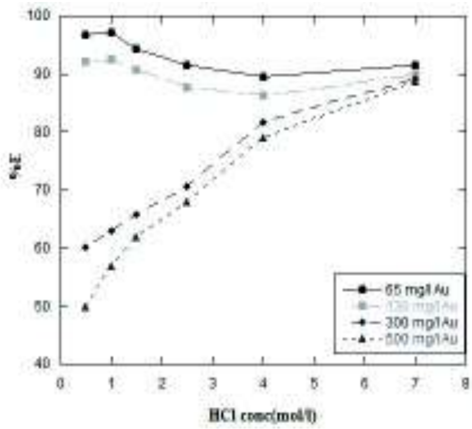

Figure 4: Influence of metal concentration on the extraction of gold by 0.1M TBP

In order to shed more light on the oxidation-reduction aspects of the process, the probable electrochemical reaction (Eqs. 6 – 9), can be written as:

$$Au + 4Cl^- = AuCl_4 \quad (6)$$

$$Au = Au^{3+} + 3e^- \quad (7)$$

$$2Cl^- = Cl_2 + 2e^- \quad (8)$$

$$H_2 = 2H^+ + 2e^- \quad (9)$$

The equilibrium concentrations of H^+ and Cl^- are also affected by the amount of HCl present in aqueous solution; the higher HCl leads to higher available H^+ and Cl^-; this issue can result in H_2 and Cl_2 releasing. In addition, the gold colloids deposited under high acidic conditions, can be accounted as an evidence for low stability of $AuCl_4^-$

3.5 Effect of temperature on extraction

To assess the effect of temperature on the extraction of gold, experiments were conducted at four different temperatures (0, 21, 40 and 60 °C). Figure 5 shows that gold extraction is endothermic reaction with enthalpy of is -63.4 KJ/mol.

3.6 Effect of chloride salt

Since the use of inorganic chloride salt in the chloride leaching step of gold bearing sources is a conventional issue, the effect of NaCl on the extraction efficiency of gold was evaluated. As observed in Figure 6, NaCl have a negative effect on the extraction percent of gold.

It seems that increasing of chloride ions in solution leads to a progress of Eq.8 in the reverse direction, free electron activity rises and gold ions concentration reduces (according to Eq. 7). Hence, the stability of gold chloride complexes decreases and the extraction percent is reduced.

Also, the existence of Na^+ in the system causes a competition between H^+ and Na^+, which drops the extraction percent of gold.

3.7 Separation of Fe

The selectivity of the extraction system over iron present in the aqueous solution was studied at different TBP concentrations (0.1, 0.25, 0.5 and 0.75 M). As observed in Figure 7, the amount of Fe extraction is low at HCl concentrations < 2.5 M.

3.8 Stripping of gold from loaded organic phase

The stripping process of Au loaded organic phase was investigated using an organic phase of 0.25 M TBP loaded with 800 Mg/l gold. Table 1 shows different reagents employed for gold stripping. Among different stripping solution (Table1) sodium

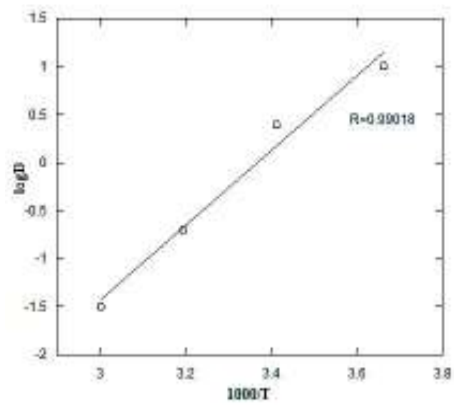

Figure 5: Arrhenius plot for the extraction of gold from 2.5M HCl aqueous solution by0.1M TBP.

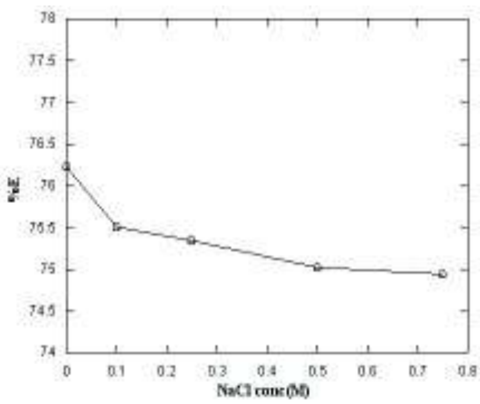

Figure 6: effect of NaCl concentration in chloride solution(3M HCl , 500 mg/l Au) on extraction by 0.1M TBP.

Table1: Effect of different compound concentration on stripping of Au from loaded organic phase

Stripping media	**Au stripping efficiency, %**						
	0.01 M	**0.05M**	**0.1M**	**0.2M**	**0.25M**	**0.5M**	**1 M**
Distilled water				1.1			
Ammonia sol.	19.4	31.6	14.2	___	___	___	___
H_2SO_4	1	0.9	0.81	0.69	____	0.5	0.15
Sodium thiosulfate sol.	___	90.9	92.1	94.8	95.7	97.7	___

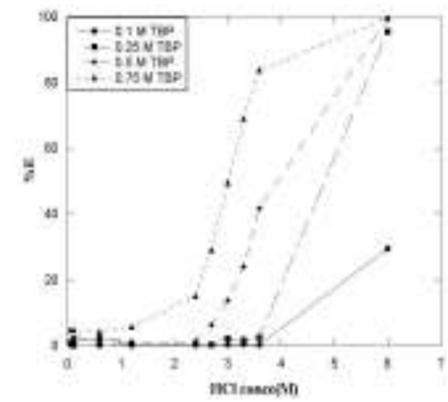

Figure 7: The influence of the HC1 concentration on Fe (III) extraction by TBP (Fe:1 g/l).

thiosulfate is the most favorable reagent for strip gold from TBP. The stripping process efficiency is higher than %90.

4 CONCLUSIONS

- Based on the obtained results, it was shown that the commercially available tri-butyl phosphate (TBP) is an appropriate extractant for the recovery of gold from chloride solution.
- The exothermic extraction reaction ($\Delta H°$=-63.4kJ/mol) of Au by TBP reaches to equilibrium conditions only after 1.5 min.
- The organo-metallic complex of Au and TBP is proposed as $HAuC1_4L_3$ where L represents the extractant molecule.
- Stripping of gold from loaded organic phases can be achieved using sodium thiosulfate solution as stripping solution.
- Au–TBP solvent extraction system shows an excellent performance; high gold loadings at low extractant concentrations, good rate of extraction and stripping, and suitable selectivity over iron.

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Simulation of Heavy Metals Transfer of Zinc Leaching Plant to the Environment

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ABSTRACT In the last decade, the presence of pollutant with human origin such as heavy metals in the ecosystem has been greatly increased, that is a serious threat to the life of the earth ecosystem. One of the solid wastes is concern about production of filter cake on hydrometallurgy process. These filter cakes were depot in open area. In this research, the behavior and solubility of heavy metals and dangerous levels of zinc, nickel, cobalt, cadmium, manganese, and lead was studied in column leaching experiments. The height of column is 40 cm. leaching filter cake depot have four important districts from viewpoint height. The heights of filter cake depot include 10 cm, 100 cm, 200 cm, and 300 cm. The obtain results were simulated to different height of depot. Two parameters were studied, the height of filter cake and time. The maximum concentration of studied element obtained in height of 300 cm.

Key words: leaching filter cake, Heavy Metals, Environmental impacts, Simulation.

1 INTRODUCTION

The amount and variety of waste material have increased in with the growing of technology and population. Of the priority pollutants, heavy metals cause adverse effects on aquatic ecosystem by entering into the food chain and accumulating in living organism (Moore and Ramamoorthy, 1984). Heavy metals continue to receive increasing attention due to the better understanding of their toxicological importance in ecosystems, agriculture, and human health. Multiple studies have been conducted to characterize the metal content in different substrates such as soil, air, food, water, paints (Hussain and Islam, 2010).

Heavy metals widely from natural and human resources enter the environment. The entrance rate of heavy metals into the environment is more than what that is omitted by natural process, so heavy metals accumulation in the environment is considerable. Soils may also be contaminated by heavy metals such as zinc (Zn), cadmium (Cd), lead (Pb) and copper (Cu), due to different environmental impacts such as sludge or urban composts, pesticides and fertilizers, emissions from municipal waste incinerators, car exhausts, residues from metallic ferrous mining and the metal smelting industry. These, and other heavy metals, are also considered to be essential micronutrients and are required in trace amounts for plants to complete their life cycles (Hussain and Islam, 2010). The first factor, affected by the metals contamination in the ecosystem, is the presence of heavy metals in the biomass of a polluted area. This endangers the human health. Accumulation of heavy metals in water, air, and soil is an extremely important environmental problem.

The heavy metals can have a pollutant effect on the environment. A part from these metals are considered microelement, they having a special importance in plant growing and animal nutrition if they don't over a maximum concentration over which they can become very toxically for the plant and animals and human health (Alfani et al., 1996).

However, the widespread accumulation of metals and other forms of soil pollutants is becoming one of the most critical challenges facing the environment.

Important environmental problems throughout the world (Doumett et al., 2008; Nouri et al., 2006) the ability of heavy metals to accumulate and cause toxicity in biological systems - humans, animals, microorganisms and plants has been reported (Nouri, 1980). As chemical hazards, heavy metals are non-biodegradable and can remain almost indefinitely in the soil environment. However, their availability to biota can change considerably depending on their chemical speciation in the soil. The adequate protection and restoration of the soil ecosystems, therefore, require the characterization and remediation of soils that are contaminated with heavy metals (Nouri et al., 2008; Nwachukwu et al., 2010).

Remediation techniques include: (i) ex-situ (excavation) or in-situ (on-site) soil washing/ leaching/ flushing with chemical agents, (ii) chemical immobilization/ stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, (iii) electro kinetics (electro migration), (iv) covering the original polluted soil surface with clean soils, (v) dilution method (mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals), (vi) phytoremediation by plants such as woody trees (GOC, 2003; Fawzy, 2008; Nouri et al., 2009; Kord et al., 2010).

In practice, leaching methods, such as hydrothermal, subcritical water treatment, fungal bioleaching, were seldom considered for the practical process due to their too strict operation conditions and high cost or too long operation time, so the process performed at ambient temperature should be preferentially considered, and the selection of the suitable lixiviant is essentially significant. Many lixiviants can be chosen for the extraction of heavy metals reported in literatures, such as inorganic mineral acids like sulfuric acid, hydrochloric acid, and nitric acid, organic acids like citric acid, oxalic acid, acetic acid, tartaric acid, or chelating reagents like nitrilotriacetic acid (NTA), ethylene diamine tetra acetate (EDTA), and diethylene triamine penta acetate (DTPA). And in some cases, alkaline solutions like ammonium and sodium hydroxides have been also investigated for this purpose.

Among the above lixiviants, synthetic chelating agents such as NTA, EDTA and DTPA exhibit good leaching efficiency. However, they are not biodegradable and also very difficult to recover the metals from their leach liquor due to their strong chelating affinity with the metals. Alkaline leaching using ammonium or sodium hydroxide solutions has the advantages that only Pb and Zn, amphoteric metals, are dissolved in alkaline solution while other impurities remain in the solid residue. However, alkaline leaching process has to be conducted together with subsequent leaching using other acidic lixiviants for further extracting other heavy metals such as Cu and Cd, which makes the whole process complex and inconvenient, resulting in the increase in the practical operation cost. Consequently, acids are more advantageous as the lixiviants. Organic acids such as citric acid, oxalic acid, acetic acid and tartaric acid are biodegradable and environmentally benign, and also exhibit good leaching behavior, but the recovery of heavy metals from these leach liquor is not necessarily easy similar to the cases of chelating agents. Although sulfuric and hydrochloric acids generally appear to be the most suitable lixiviants due to their low cost, lead in fly ash cannot be extracted because of the formation of water insoluble species, $PbSO_4$ or $PbCl_2$ (Huang et al., 2011).

For understanding the chemistry of heavy metals in their interaction with other soil components such as clay minerals, organic matter and soil solution, or to assess their mobility and retention as well as their availability to plants, the usual approach is to use selective chemical extraction. It has been shown that several soil variables other than pH, such as texture, organic matter and clay contents, cation exchange capacity and redox potential may influence the behavior and availability of heavy metals.

Limited work has been done to determine the rates of extraction, and the factors which influence the rate. This is important since extraction efficiency depends on many factors such as lability of heavy metals in soil, strength of leachates, electrolytes, pH and soil matrix(Hussain and Islam, 2010).

In zinc plant located in Zanjan, Iran, it is practiced a leach-electrolysis process for zinc production. In this process, a lot of filter cakes as by-product are generated daily. These wastes are retained for valuable elements recovery in the future and dumped in open stockpiles where they may cause heavy metal pollution problems. In this plant three types of wastes were produced including; leaching filter cake, cobalt purification filter cake and Ni-Cd purification filter cake. All of the filter cakes have a high percent of heavy metal (Hakami, 2005., Sedaghat et al., 2008).

2 MATERIALS AND METHODS

2.1 Materials and Reagents

Leaching filter cake for this study was obtained from Research & Engineering Co. for Non-ferrous Metals, Zanjan, Iran. After drying, the filter cake was ground and sieved to +200 meshes. The chemical analysis was carried out by AAS (Perkin-Elmer AA300 atomic absorption). The analytic results were given in Table 1.

Table 1. Chemical analysis of leaching filter cake

Chemical analysis (%)								
Fe	**Mn**	**Zn**	**Ca**	**Mg**	**Pb**	**Ni**	**Co**	**Cd**
2.3	0.14	7.5	7.6	0.02	8.13	0.02	0.02	0.09

In this paper, for recognizing leaching filter cake, permeable test was used. Soil always include fine particle of different mineral that make porous form of soil. These pores media include water, air or both of them. Pore volume is volume of water (V_m) and volume of air is V_a (Baker and Brooks, 1989). Soil with its three phase schematically is illustrated in figure 1.

In permeable test 10 cm of column height was filled with leaching filter cake and 20 cm of pure water was filled on it. Reaching times of outlet solution volume to cake pore volume was recorded and equation 1 was used to measure cake permeable.

$$k = \frac{Q.L}{H.A.t} \qquad (1)$$

Where:

Q: solution volume (m^3)
L: soil height (m)
H: column height (m)
A: column area (m^2)
t: water assemblage time (time)
k: permeable (m/min)

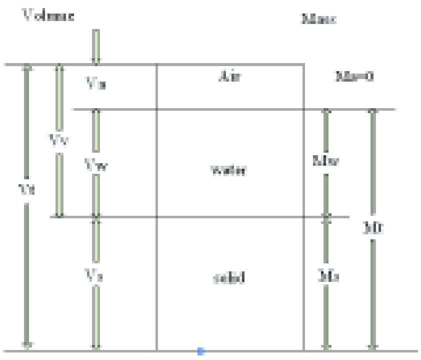

Figure 1. pore volume of soil containing air and water

Figures 2 and 3 are illustrated permeable of filter cake diagrams based on pore volume and time.

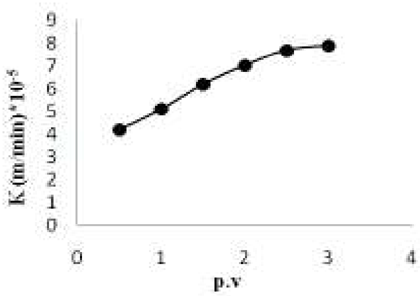

Figure 2. Effect of pore volume on filter cake permeable

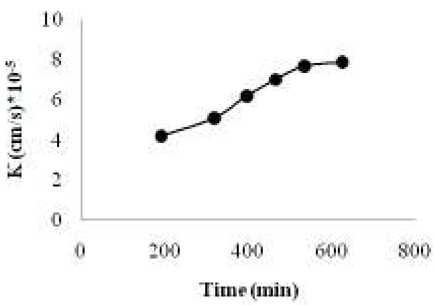

Figure 3. Effect of time on filter cake permeable

2.2 Experimental Method

For experimental design and determining the important factors which affect the leach ability of residual the conventional methods was used. In this study columns with 6 cm diameter and 50 cm length from Plaxcy glass were employed. A 2-4 cm layer of washed and dried sand with a Whatman paper was putted at the end of each column. Above it was filled of 875gr leaching filter cake. To uniform distribution of leaching solution a layer of fiber-glass between two Whatman papers were used in the top of each column. Acid sparging time was 24 hours a day. During this time output solution was collected in a container to prepare reagent samples to measurements Zn, Cd, Pb, Ni, Co and Mn concentration on 2,4,6,10,15 and 20 days. The picture of columns employed in this study is shown in Figure 4. Test condition include pH=5, inlet solution rate=1cc/min and 40 cm of soil that was felled in column. pH and solution rate are based on raining condition in Zanjan.

Figure 4. Column leaching

3 RESULTS AND DISCUSSION

3.1 Residues Depot

Located in northwestern province of Zanjan, Iran, in an electrolytic zinc plant, with a capacity of 20,000 ton Zn production per year (for leach filter cake), a major amount of Co filter cake has been stockpiled during the years and also about 50 kg of the same residue per ton of produced zinc is added to dumps daily. Depending on the composition of zinc concentrate, the composition of filter cake may vary. Leaching filter cake depot is shown in figure 5, and shows the different height of Leaching filter cake depot. filter cake depot area is more than 10,000 m^2. This waste has a lot of heavy metals such as zinc, lead, cobalt, manganese, nickel, cadmium and etc. Heavy metals transfer from this filter cake to environment is a serious problem.

Figure 5. Leaching filter cake depot in zinc plant

3.2 Modeling of Heavy Metals Transfer

Leaching filter cake height in Zinc plant is variable. Four districts are more than considerable. These districts have different heights that include: 10 cm, 100 cm, 200 cm and 300 cm. The minimum and maximum height in this depot is 10 cm and 300 cm, respectively. Experimental were done in column with height equal to 40 cm. The height of 40 cm of these columns was filled with leaching filter cake. Achieved results were used to simulation of heavy metals transfer from different height of depot to environment .

Simulation was done with the following equation:

$$R_{h1} = R_{h2} \quad (2)$$

$$[(C_1*V_1)/(G_1*M_1)] = [(C_2*V_2)/(G_2*M_2)] \quad (3)$$

$$V_1=V_2 \quad (4)$$

$$G_1=G_2 \quad (5)$$

$$[C_1/(\rho_1*\pi r^2 h_1)] = [C_2/(\rho_2*\pi r^2 h_2)] \quad (6)$$

$$\rho_1= \rho_2 \quad (7)$$

$$(C_1/h_1) = (C_2/h_2) \quad (8)$$

$$C_2 = (C_1*h_2)/h_1 \quad (9)$$

Where:
R: Metal recovery (%)
C: Concentration of metal (g/l)
V: Volume of solution (l)
G: Grade of metal (%)
M: Mass of filter cake (kg)
ρ: Density of filter cake (kg/m^3)
r: Radius of column (m)
h: Height of column (m)

3.3 Effect of Filter Cake Height

Figures 6-11 illustrate the effect of different height of filter cake on the dissolution of Zn, Pb, Cd, Co, Ni and Mn. Experimental were done with the following conditions: flow rate of 1 cc/min, input solution pH of 5 and time leaching of 2 day. The minimum concentrations of Zn, Pb, Cd, Co, Ni, and Mn for height of 10 cm were achieved 0.405 mg/l, 0.335 mg/l, 9.52 mg/l, 0.0737 mg/l, 0.35 mg/l, and 0.682 mg/l, respectively. The maximum concentrations of Zn, Pb, Cd, Co, Ni, and Mn for height of 300 cm were achieved 12.15 mg/l, 10.05 mg/l, 285.6 mg/l, 2.2125 mg/l, 10.5 mg/l, and 20.475 mg/l, respectively.

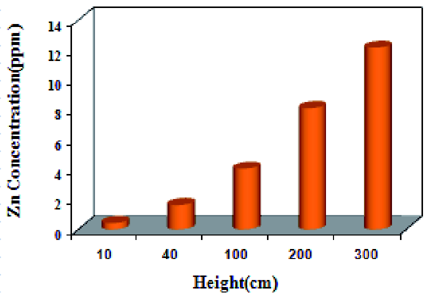

Figure 6. Zn dissolution in different height of filter cake

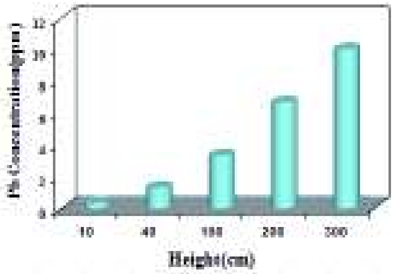

Figure 7. Pb dissolution in different height of filter cake

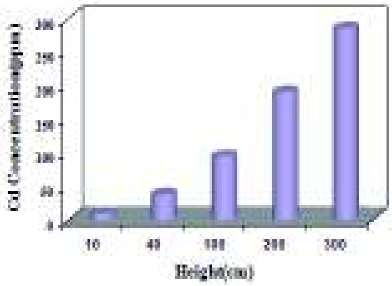

Figure 8. Cd dissolution in different height of filter cake

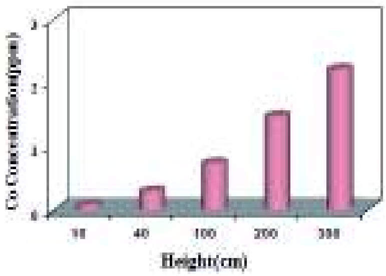

Figure 9. Co dissolution in different height of filter cake

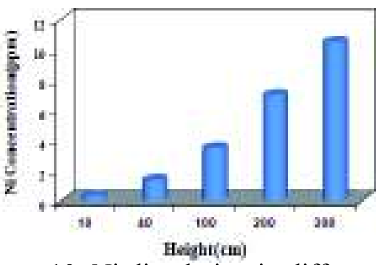

Figure 10. Ni dissolution in different height of filtercake

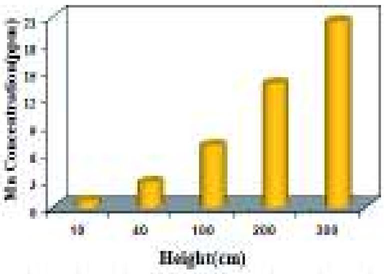

Figure 11. Mn dissolution in different height of filtercake

3.4 Effect of Leaching Time

The effect of leaching time in different height of filter cake on the dissolution of Zn, Pb, Cd, Co, Ni, and Mn are shown in figures. 12-17. The concentration of mentioned metals were measured on 2,4,6,10,15 and 20 days. The Concentration of metals decreased with the increasing of time and it reached to a minimum level after 20 days. The maximum concentration of metals was achieved after 2 days and filter cake height of 300 cm. The concentration of Zn, Pb, Cd, Co, Ni, and Mn for height of 300 cm after 20 days were achieved 23006 mg/l, 10.06 mg/l, 287.7 mg/l, 39.64 mg/l, 34.02 mg/l and 6.454 mg/l, respectively.

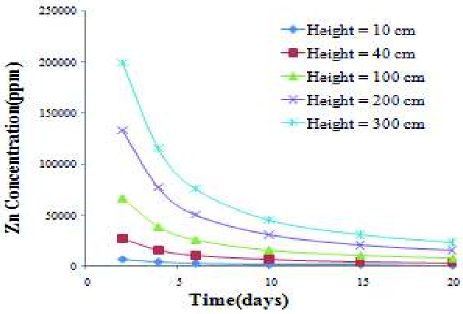

Figure 12. Effect of time on the Zn dissolution

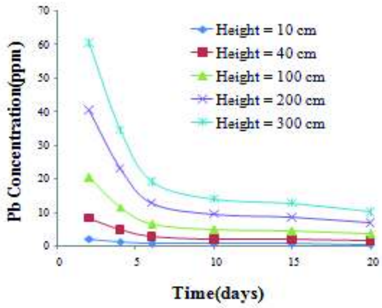

Figure 13. Effect of time on the Pb dissolution

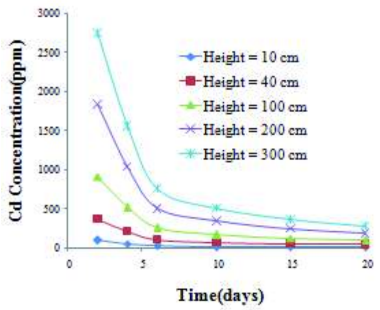

Figure 14. Effect of time on the Cd dissolution

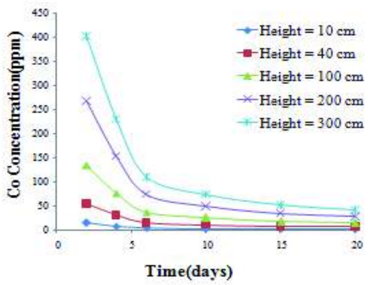

Figure 15. Effect of time on the Co dissolution

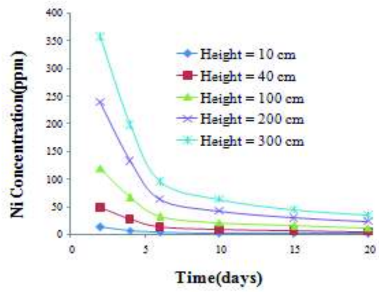

Figure 16. Effect of time on the Ni dissolution

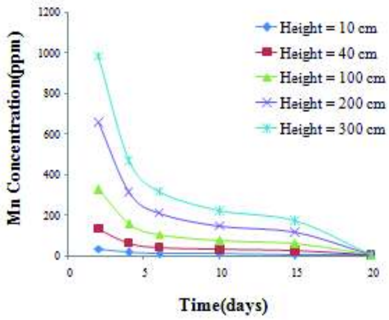

Figure 17. Effect of time on the Mn dissolution

4 CONCLUSION

Owing to industrial development and population expansion, heavy metal pollution in water environment is becoming increasingly serious in world. The transport of heavy metals such as Zn, Cd, Ni, Co, Mn and Pb from leaching filter cake was examined by using column leaching. Experimental were done in column with height equal to 40 cm and then the obtain results were simulated to different height of depot. The minimum and maximum height in this depot is 10 cm and 300 cm, respectively. Parameters studied included: different height of depot and time. The maximum concentration of Zn, Pb, Cd, Co, Ni, and Mn for height of 300 cm after 2 day was achieved 199159.43 mg/l, 60.384 mg/l, 2741.16 mg/l, 401.47 mg/l, 357.30 mg/l, and 981.28 mg/l, respectively. Thus the filter cakes, retained on open areas for recovering of valuable metals, will seriously cause heavy metal pollution problems.

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Giresun Dereli Bölgesindeki Bakır Cevherinin Çözünürlüğü Üzerine Oksitleyici Maddelerin Etkisinin İncelenmesi
Investigation of the Solubility of Giresun Dereli Copper and the Effect of Oxidising Agent on This Solubility

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ÖZET Giresun Dereli bakır cevherinin çözünürlüğü üzerine hidrojen peroksit, peroksidisülfat ve ferik sülfat gibi oksitleyici maddelerin etkisi çalışılmıştır. Çalışmada bu oksitleyici maddelerin cevherin çözünürlüğünü iyileştirmek yerine azalttığı tesbit edilmiştir. Bu sonuçlar literatürdeki sonuçları Dereli cevherinin ve literatürde çalışılan cevherin alüminyum muhtevasındaki farklılık nedeni ile doğrulamamaktadır. Çözünürlükteki bu fark Dereli cevherindeki ve literatürde çalışılan cevherdeki alüminyum muhtevasının farklılığına atfedilebilir. Çünkü Dereli cevheri literatürdeki çalışılan cevherden çok fazla Al_2O_3 ihtiva ettiği için oksitleyici maddelerin eklenmesi çözünürlüğünü azaltmaktadır. Oksitleyici maddeler alüminyumu alüminyum oksite oksitleyerek cevher yüzeyinde geçirgenliği düşük bir film oluşturmaktadır. Bu durum aynı maddelerin farklı cevherlerin çözünürlüğü üzerine ters etki yapması onların bileşimlerindeki farklılıklar ile izah edilebilmektedir.

ABSTRACT The effect of the oxidising agent such as hydrogen peroxide, peroxodisulphate and ferric sulphate on the solubility of Giresun Dereli copper ore was studied. The results of this investigation shows these oxidation agents did not improved the solubility of the ore instead it reduced it. These conclusions did not confirm with the result obtained in the literature when compared with the aluminium content of the Dereli ore and the ore studied in literature. This can be attributed to the difference between the aluminium contents of the ore studied in the literature and Dereli ore. Since Dereli ore contains much higher amount of Al_2O_3 than the ore studied in the literature, addition of oxidising agents reduces the solubility of Dereli ore. Because the oxidising agents may oxidise aluminium to Al_2O_3 resulting in less diffusible film on the ore. This shows same agent may have opposite effect on the solubility of the different ore due to the difference in their composition.

1 GİRİŞ

1.1 Bakır ve Mineralleri

Bakır, milattan önceki yıllardan beri bilinen bir metal olup, elektriği ve ısıyı iyi iletmesi, aşınma ve korozyona dayanıklılığı ve kolayca şekillendirilebilmesi nedeniyle geniş kullanım alanına sahiptir. Tabiatta metalik halde bulunabildiği gibi, oksit, karbonat ve sülfürlü mineralleri şeklinde de bulunabilmektedir. Sülfürlü minerallerinden bornit (Cu_5FeS_4), kalkopirit ($CuFeS_2$) ve enarjit ($Cu_3(As,Sb)S_4$) birincil mineraller olarak bilinmektedir. Kovallit (CuS) ve kalkozit (Cu_2S) gibi mineraller ikincil mineralleridir. Malahit ($CuCO_3.Cu(OH)_2$) ve azurit ($2CuCO_3.Cu(OH)_2$) gibi minerallerde yüzeydeki sülfürlü minerallerin oksidasyonu sonucu meydana gelmişlerdir [1].

Kalkopirit, bakır demir sülfür mineralidir ve teorik bileşimi kütlece % 34.6 Cu, %30.5 Fe ve %34. 9 S'dür. Birincil olarak magmatik kayaçlarda ve hidrotermal damarlarda pirit, sfalerit, galenit gibi cevherler ve kuvars, kalsit, dolomit gibi gang mineralleri ile birlikte bulunur. Porfiri bakır yataklarında oluşan önemli bir mineraldir[2,3].

1.2 Bakırın Elde Edilişi

Bakır, cevherlerinden veya hurdadan pirometalürjik, hidrometalürjik, biyohidrometalürjik ve elektrometalürjik yöntemlerden biri veya birkaçının bir arada kullanılması ile elde edilmektedir. Oldukça yaygın olarak kullanılan pirometalürjik yöntem, son yıllarda çevresel faktörler ve maliyet yüksekliği nedeni ile yerini hidrometalürjik yönteme bırakmaktadır. Dünya bakır üretiminin %15-20'si hidrometalürjik yöntemle üretilmektedir [4].

Hidrometalürjik yöntem, düşük tenörlü cevherin veya maden işleme atığının uygun bir sıvı veya sıvı karışımı ile çözündürülmesi yani liçine dayanır. Liç işleminden elde edilen bakırca zengin çözeltiden bakır ya ekstraksiyon veya elektroliz ile elde edilir. Belli başlı liç şekilleri şunlardır:

a) **Yerinde (in-situ) liç:** Cevher, bulunduğu yerde liç edilir.

b) **Yığma liç:** Cevher, bulunduğu yerden çıkartılıp, tabanı geçirgen olmayan bir bölgeye yığılır ve üzerine liç solüsyonu dökülerek liç edilir.

c) **Süzülme (perkolasyon) liçi:** Kırılmış cevher büyük tanklara doldurularak ve liç solüsyonu aşağıdan yukarı veya veya ters yönde hareket ettirilerek liç edilir.

d) **Karıştırma liçi:** Öğütülmüş cevher veya konsantre, tanklar içinde liç solüsyonu ile karıştırılarak liç edilir [4,5].

1.3 Bakır Liçi Çalışmaları

Kalkopiritin liçi konusunda pek çok çalışma yapılmış olup genellikle sülfirik asit veya hidroklorik asitli ortamda bir oksitleyici ile cevherin çözünmesi incelenmiştir.

Sokic ve ark. yapmış oldukları çalışmada kalkopiritin sülfirik asitte sodyum nitrat ile liçini incelemişlerdir. Sülfirik asit ve sodyum nitrat konsantrasyonunun artmasının ve tanecik boyutunun küçülmesinin bakırın çözünürlüğünü artırdığını, karıştırma hızının reaksiyon hızını azalttığını, sıcaklığın reaksiyon hızı üzerine etkisinin önemli olduğunu belirtmişlerdir. 120 dakikalık liç işleminde sıcaklığın 70°C den 90°C e çıkarılmasının çözünürlüğü %28'den %70'e yükselttiğini, en iyi liç işleminin 90°C'de 240 dakika ile yapılan işlem olduğunu ve çözünürlüğün bu şartlar altında %75.5 olduğunu belirtmişlerdir [6].

Yılmaz ve ark. Kayabaşı masif bakır cevherinin ferrik sülfat liçini incelemişlerdir. Fe^{3+} konsantrasyonunun çalışılan şartlarda metal çözünürlüğü üzerine önemli bir etkisinin olmadığını, çözünürlüğün liç işleminin ilk yarım saatinde hızlı olduğunu daha sonra çözünme hızının yavaşladığını belirtmişlerdir. Sıcaklığın çözünürlük üzerine etkisinin önemli olduğunu 8 saatlik liç işleminde 25°C'de bakırın %42'si çözünürken 80°C'de %91'inin çözündüğünü belirtmişlerdir. Ayrıca liç hızının ve veriminin reaktif yüzey alanı arttıkça arttığını bu nedenle liç sistemlerinde yüzey alanının önemli olduğunu belirtmişlerdir [7].

Dakubo ve ark. kalkopiritin peroksidisülfatla liçini incelemişlerdir. Sülfirik asit içerisinde pH=2'de kalkopiritin liçini peroksidisülfatın iyileştirdiğini, bunun kalkopiritin oksitlemesi için yük transfer direncini peroksidisülfatın azaltmasından kaynaklandığını belirtmişlerdir. Ayrıca tanecik yüzey alanı arttıkça liç kinetiğinin arttığını belirtmişlerdir [8].

Antonijevic ve ark. kalkopiritin sülfirik asitte hidrojen peroksit ile çözünme kinetiğini incelemişlerdir. Kalkopiritin sülfirik asitte hidrojen peroksitle oksitlenmesinin karıştırma hızından bağımsız olduğunu, bu nedenle reaksiyonun sıvı fazda difüzyonla kontrol edilmediğin belirtmişlerdir. Ayrıca sülfirik asitin de hidrojen peroksitin de konsantrasyonunun artırılmasının oksidasyonu artırdığını belirtmişlerdir[4].

Yapılan literatür araştırması sonunda,

-kalkopiritin tanecik boyutunun çözünme üzerinde etkili olduğu, çözünmenin daha hızlı ve etkili olabilmesi için tanecik boyutunun küçük olması gerektiği,

- kalkopiritin çözünmesinin liç ortamında karıştırma hızı ile önemli bir artış göstermediğinin tesbit edildiği bulunmuştur. Bu nedenle çalışmamızda, Giresun-Dereli bölgesindeki kalkopiritin sülfirik asitle çözünürlüğü incelenirken tanecik boyutu -75 µm'de sabit tutularak, karıştırma işlemi yapılmaksızın sadece sülfirik asit ve oksitleyici olarak hidrojen peroksit, peroksidisülfat ve $Fe_2(SO_4)_3$'in çözünürlük üzerine etkisi incelenmiştir.

2 MATERYAL VE METOT

2.1 Materyal

Giresun ili, Dereli ilçesi yakınlarında bulunan maden yatağından cevher damarını temsil edecek numuneler alınmıştır. Yaklaşık 10 kg olan toplam numune 1,0-1,5 mm ebatına kırıldıktan sonra dörtlenip azaltılarak yaklaşık 1 kg lık bir kısım halkalı değirmende -75 µm ebatına öğütülmüştür. Çalışma süresince aynı temsili numune kullanılmış olup, bez bir torba içerisinde ağzı kapalı olarak muhafaza edilmiştir. Numunenin XRF analizi Tablo 1'de verilmiştir.

Tablo 1. Cevherin XRF analizi

Bileşen	%	Bileşen	%
SiO_2	29,32	Al_2O_3	7,28
Fe_2O_3	19,41	MgO	2,22
SO_3	17,61	K_2O	0,96
CuO	10,23	CaO	0,03
PbO	0,81	MnO	0,35
ZnO	0,50	TiO_2	0,12

2.2 Metot

Deneyler ağzı kapaklı cam erlenler içerisinde yapılmıştır. Çözünme ortamı olarak 1 M, 3 M ve 5 M'lık sülfirik asit çözeltileri kullanılmıştır. Çözelti içerisinde katı madde miktarı bütün denemelerde %6,7'de sabit tutulmuştur. Yığın liçine uygulanabilir olabilmesi için sıcaklık artırılmamış ve literatürde çözünmeye karıştırmanın önemli bir etkisi olmadığı belirtildiği için herhangi bir karıştırma işlemi yapılmamıştır. Oksitleyici olarak 0,05 mM, 0,5 mM, 1,5 mM, 2,5 mM, 5,5 mM hidrojen peroksit; 0,05 mM potasyum peroksidisülfat; 0,05 mM, 0,5 mM, 1,5 mM amonyum peroksidisülfat ve 0,05 mM demir III sülfat kullanılmıştır. Liç süresi olarak 30, 60, 90 ve 120 dakikalar çalışılmıştır.

Liç işlemi sonunda numuneler süzüldükten sonra Perkin Elmer marka 3110 model alevli atomik absorpsiyon spektrometresi ile çözünen bakır miktarları tesbit edilmiştir.

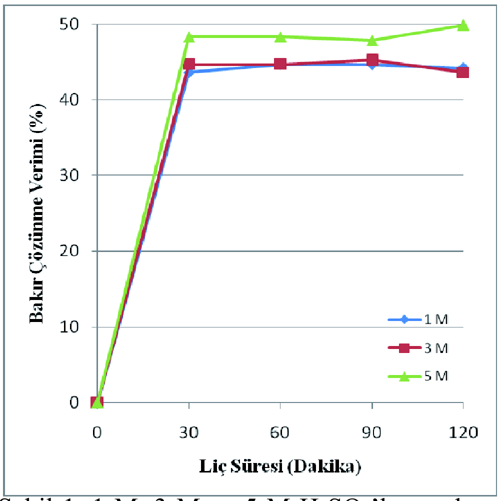
3 DENEYSEL SONUÇLAR

3.1 Bakır Çözünürlükleri

3.1.1 H_2SO_4 Konsantrasyonunun Etkisi

%6,7 katı madde oranı sabit tutularak kalkopiritin 1 M, 3 M ve 5 M H_2SO_4 içerisindeki çözünme verimleri incelenmiştir.

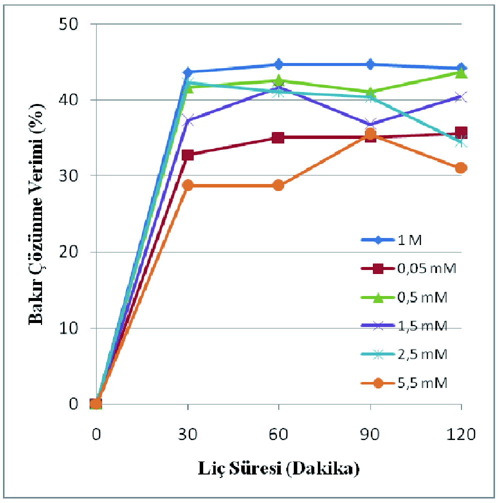
Elde edilen sonuçlar Şekil 1'de görülmektedir. H_2SO_4 konsantrasyonunun artmasının bakırın çözünmesini artırdığı, ancak çalışılan şartlarda 1 M H_2SO_4 ile 3 M H_2SO_4'in hemen hemen aynı davranışı gösterdiği görülmektedir. Ayrıca liç süresinin artmasının çözünme üzerine önemli bir etkisinin olmadığı ilk 30 dakikada ulaşılan çözünme verimi ile 120 dakika sonunda ulaşılan çözünme verimleri arasında büyük bir farklılığın olmadığı görülmektedir.



Şekil 1. 1 M, 3 M ve 5 M H_2SO_4'le yapılan liç işlemleri sonunda elde edilen bakır çözünme verimleri

3.1.2 H_2O_2'in Etkisi

H_2O_2'in çözünme üzerine etkisini belirlemek için 1 M, 3 M ve 5 M H_2SO_4'li liç ortamlarına farklı konsantrasyonlarda ilave edilmiştir.

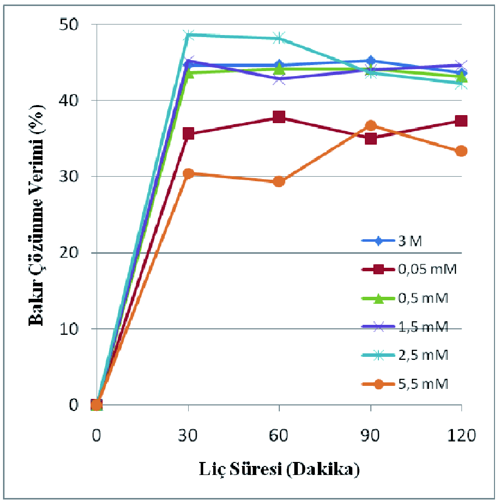


Şekil 2. 1 M H_2SO_4'li ortama sırasıyla 0,05 mM, 0,5 mM, 1,5 mM, 2,5 mM ve 5,5 mM H_2O_2 eklenmesi ile ulaşılan bakır çözünme verimleri

Şekil 2'de 1 M H_2SO_4'li ortama sırasıyla 0,05 mM, 0,5 mM, 1,5 mM, 2,5 mM ve 5,5 mM hidrojen peroksitin eklenmesi ile ulaşılan çözünme verimleri görülmektedir.

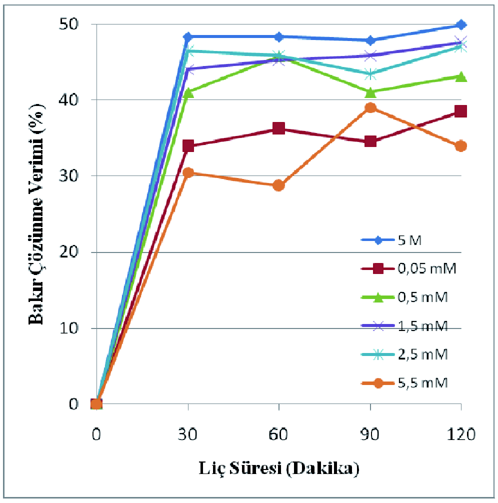
Şekil 3'de 3 M H_2SO_4'li, Şekil 4'de 5 M H_2SO_4'li liç ortamında değişen konsantrasyonlardaki H_2O_2 ile elde edilen bakır çözünme verimleri görülmektedir.

Şekil 2 incelendiğinde 1 M sülfirik asitli ortama oksitleyici olarak hangi konsantrasyonda H_2O_2 ilave edilirse edilsin, bakır çözünme verimini azalttığı görülmektedir. Hidrojen peroksitin konsantrasyonundaki artış ile çözünürlükteki azalma arasında herhangi bir doğrusal ilişki bulunamamış olup, ortamda hidrojen peroksidin en fazla olduğu 5,5 mM'lik çözeltide bakır çözünme veriminin en düşük olduğu tesbit edilmiştir.

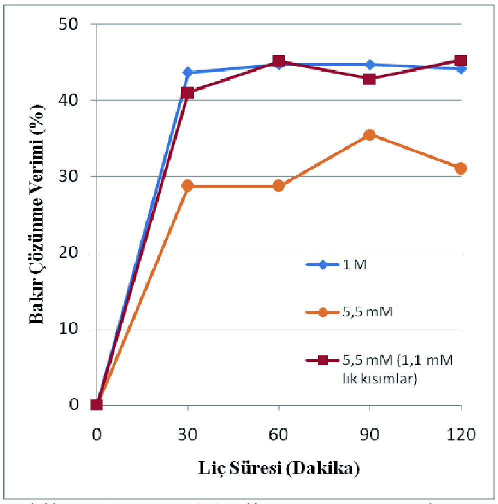


Şekil 3. 3 M H_2SO_4'li ortama sırasıyla 0,05 mM, 0,5 mM, 1,5 mM, 2,5 mM ve 5,5 mM H_2O_2 eklenmesi ile ulaşılan bakır çözünme verimleri

Şekil 3 ve 4 incelendiğinde, benzer şekilde hidrojen peroksit konsantrasyonunun en yüksek olduğu durumda bakır çözünürlüklerinin en düşük oldukları görülmektedir.



Şekil 4. 5 M H_2SO_4'li ortama sırasıyla 0,05 mM, 0,5 mM, 1,5 mM, 2,5 mM ve 5,5 mM H_2O_2 eklenmesi ile ulaşılan bakır çözünme verimleri

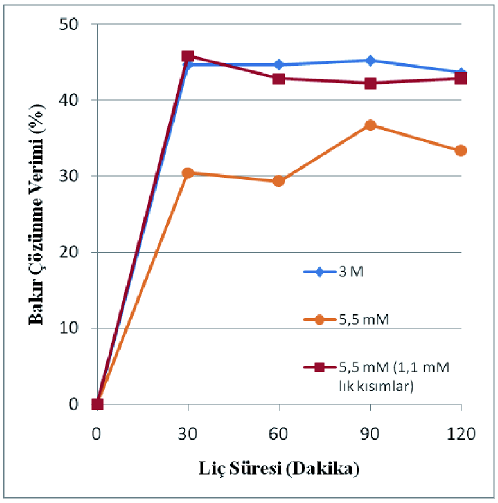


Şekil 5. 1 M H_2SO_4'li ortama sırasıyla 5,5 mM H_2O_2 bir defada ve 1,1 mM lık kısımlar halinde 5 defada eklenmesi ile ulaşılan bakır çözünme verimleri

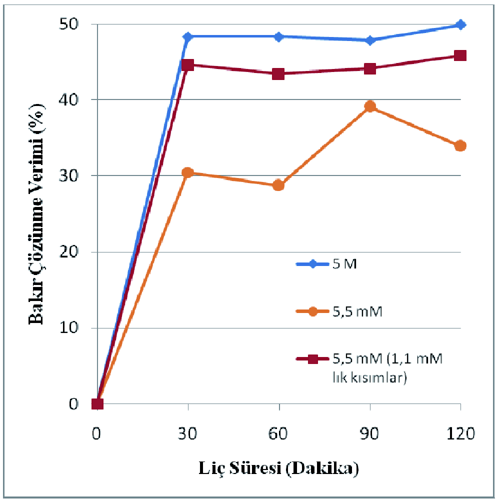
3.1.3 H_2O_2'nin Eklenme Süresi

Oksitleyici olarak kullanılan hidrojen peroksitin liç ortamına kısımlar halinde sürekli eklenmesinin çözünürlük üzerine etkisini incelemek için, en derişik konsantrasyon olan 5,5 mM'lik hidrojen peroksit ortama 1,1 mM lik kısımlar halinde 5 kez eklenerek bakır çözünürlükleri incelenmiştir.

Şekil 5'de 1 M H_2SO_4'li ortamda 5,5 mM H_2O_2'nin bir kez ve 1,1 mM lık kısımlar halinde 5 kez eklenmesi halinde bakır çözünürlüğünün değişimi görülmektedir. Benzer şekilde Şekil 6'da 3 M H_2SO_4'li ortam için, Şekil 7'de 5 M H_2SO_4'li ortam için çözünürlük değerleri gösterilmektedir.



Şekil 6. 3 M H_2SO_4'li ortama sırasıyla 5,5 mM H_2O_2 bir defada ve 1,1 mM lık kısımlar halinde 5 defada eklenmesi ile ulaşılan bakır çözünme verimleri

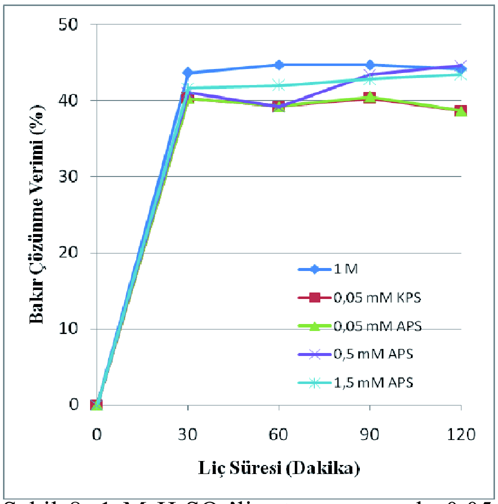


Şekil 7. 5 M H_2SO_4'li ortama sırasıyla 5,5 mM H_2O_2 bir defada ve 1,1 mM lık kısımlar halinde 5 defada eklenmesi ile ulaşılan bakır çözünme verimleri

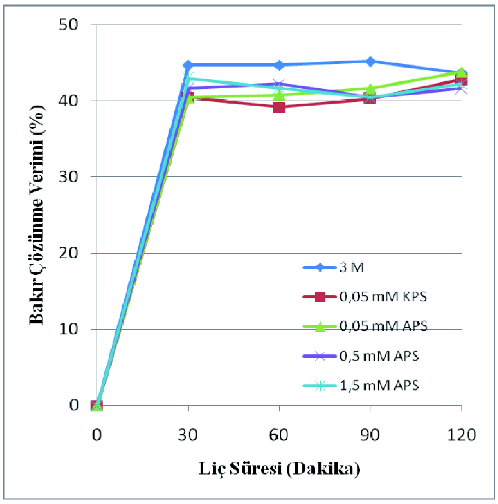
Şekil 5, 6 ve 7 birlikte incelendiğinde, hidrojen peroksitin liç süresince ortama kısımlar halinde sürekli ilave edilmesinin bir kez eklenmesine göre daha iyi sonuçlar verdiği görülmektedir. Ortama oksitleyici olarak eklenen hidrojen peroksitin bir kez ortama eklenmesi halinde çözünürlüklerin çalışılan bütün asit konsantrasyonlarında çözünürlüğü azalttığı görülmektedir. Ortama hidrojen peroksitin zamanla beslenmesinin çözünürlüğü çok az da olsa yine de azalttığı tesbit edilmiştir.

3.1.4 Peroksidisülfatın Çözünürlüğe Etkisi

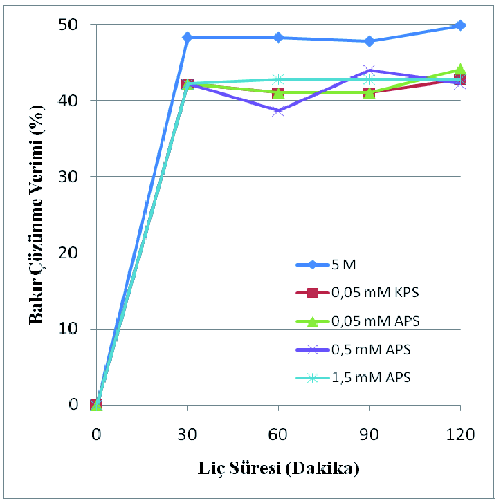
Bakır cevherinin sülfirik asit içerisindeki liç ortamına oksitleyici olarak hidrojen peroksitin katılmasının bakırın çözünürlüğünü azalttığı tesbit edildikten sonra, aynı çalışma şartlarında farklı oksitleyiciler denenmiştir. Bunun için 0,05 mM potasyum peroksidisülfat (KPS), 0,05 mM amonyumperoksidisülfat (APS), 0,5 mM amonyum peroksidisülfat, 1,5 mM amonyum peroksidisülfat ile çalışılmıştır. Şekil 8'de 1 M H_2SO_4'lü ortam için, Şekil 9'da 3 M H_2SO_4'lü ortam için, Şekil 10'da 5 M H_2SO_4'lü ortam için sonuçlar görülmektedir.



Şekil 8. 1 M H_2SO_4'li ortama sırasıyla 0,05 mM potasyum peroksidisülfat (KPS), 0,05 mM amonyum peroksidisülfat (APS), 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen bakır çözünme verimleri



Şekil 9. 3 M H_2SO_4'li ortama sırasıyla 0,05 mM KPS, 0,05 mM APS, 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen bakır çözünme verimleri

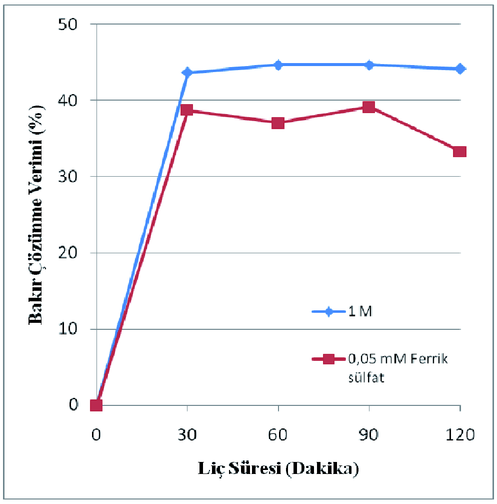


Şekil 10. 5 M H_2SO_4'li ortama sırasıyla 0,05 mM KPS, 0,05 mM APS, 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen bakır çözünme verimleri

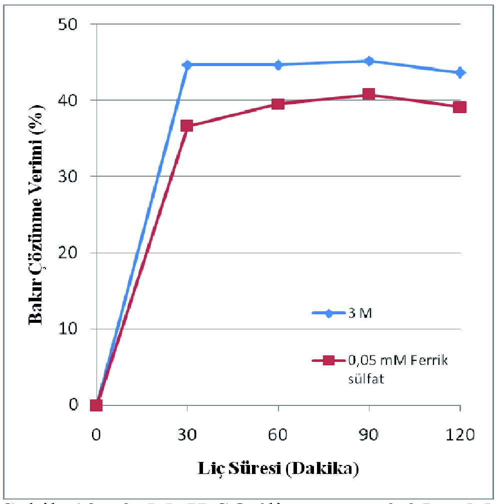
Şekil 8, 9 ve 10 bir arada incelendiğinde açıkça görüldüğü gibi, peroksidisülfatların da hidrojen peroksit gibi çözünürlüğe olumsuz yönde etki ettikleri tesbit edilmiştir. Ancak potasyum peroksidisülfat ve amonyum peroksidisülfatın sudaki çözünürlükleri düşük olduğu için daha yüksek konsantrasyonlarda çözeltileri hazırlanamamış dolayısıyla da hidrojen peroksit ile karşılaştırmaları yapılamamıştır. Çalışılan konsantrasyonlarda, konsantrasyon artışı ile çözünürlüğe etkisi arasında bir lineerlik tesbit edilememiştir.

3.1.5 Ferrik Sülfatın Çözünürlüğe Etkisi

Bakır cevherinin sülfirik asitli ortamda oksitleyici olarak hidrojen peroksit ve peroksidisülfat ile liçini inceledikten sonra diğer bir oksitleyici bileşik olan ferik sülfat ile çalışılmıştır. 0,05 mM olan en düşük konsantrasyonda denemeler yapılmıştır. Sonuçlar Şekil 11, 12 ve 13'de görülmektedir.

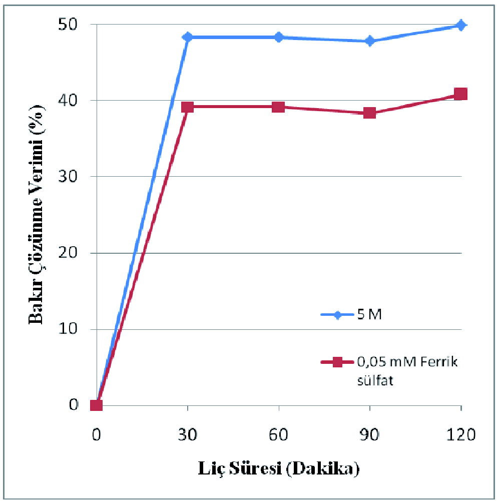


Şekil 11. 1 M H_2SO_4'li ortama 0,05 mM ferik sülfat eklenmesi ile elde edilen bakır çözünme verimleri



Şekil 12. 3 M H_2SO_4'li ortama 0,05 mM ferik sülfat eklenmesi ile elde edilen bakır çözünme verimleri

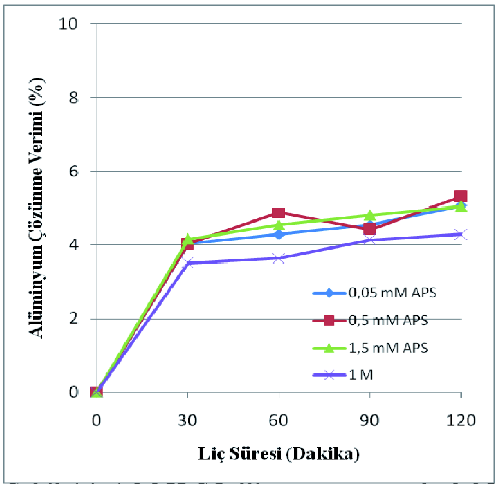
Şekil 11, 12 ve 13 birlikte incelendiğinde hidrojen peroksit ve peroksidisülfat kullanıldığında elde edilen sonuçlara benzer şekilde ferik sülfat kullanılması halinde de çözünürlük verimleri azalmıştır.



Şekil 13. 5 M H_2SO_4'li ortama 0,05 mM ferik sülfat eklenmesi ile elde edilen bakır çözünme verimleri

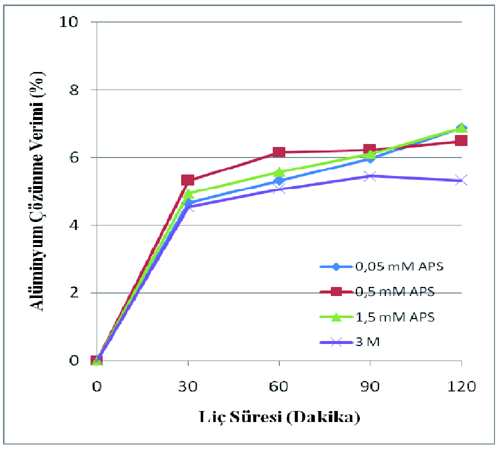
3.2 Alüminyum Çözünürlükleri

Çalışılan bakır cevherinin çözünürlüğüne, oksitleyici ortamda cevher yüzeyinde meydana gelen alüminyum oksit filminin etkili olup olmadığını inceleyebilmek için

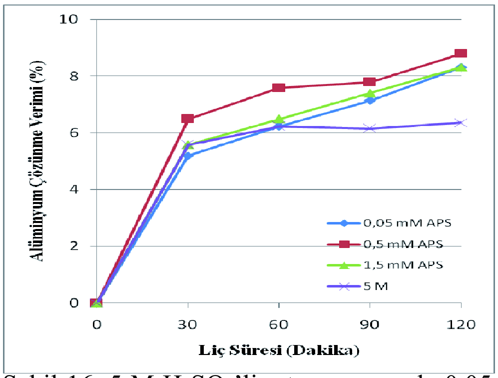


Şekil 14. 1 M H_2SO_4'li ortama sırasıyla 0,05 mM APS, 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen alüminyum çözünme verimleri

oksitleyici olarak kullanılan amonyum peroksidisülfatlı çözeltilerdeki alüminyum çözünme verimleri belirlenmiştir. Şekil 14, 1 M sülfirik asitli ortama 0,05 mM APS, 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen alüminyum çözünme verimlerini göstermektedir. Şekil 15, 3 M sülfirik asitli ortamdaki, Şekil 16, 5 M sülfirik asitli ortamdaki alüminyum çözünme verimlerini göstermektedir.



Şekil 15. 3 M H_2SO_4'li ortama sırasıyla 0,05 mM APS, 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen alüminyum çözünme verimleri



Şekil 16. 5 M H_2SO_4'li ortama sırasıyla 0,05 mM APS, 0,5 mM APS, 1,5 mM APS eklenmesi ile elde edilen alüminyum çözünme verimleri

4 SONUÇLAR

Bu çalışmada literatürde belirtilenlerin aksine oksitleyicilerin çalışılan bakır cevherinin çözünürlüğünü artırmadığı, hatta çözünürlüğü önemli ölçüde azalttığı tesbit edilmiştir. Her ne kadar diğer literatürlerin birçoğunda cevherin komple analizi verilmemiş ise de Yılmaz ve ark.[7] yapmış olduğu çalışmadaki analiz ile (Al_2O_3=%1,77) Dereli cevherinin analizi (Al_2O_3=7,28) karşılaştırıldığında, Dereli cevherinin fazla miktarda alüminyum ihtiva ettiği görülmektedir. Bu nedenle oksitleyicilerin ilavesinin cevher içerisindeki alüminyumun çözünürlüğüne etkisi amonyum peroksidisülfatlı ortamda incelenmiştir. Amonyumperoksidisülfat ilavesi ile alüminyumun çözünürlüğü çok azda olsa artmaktadır. Ancak toplam çözünürlük oldukça düşüktür. Bu nedenle cevherde bulunan yüksek orandaki alüminyumun sülfirik asitli ortamda dahi cevher yüzeyinde oksit filmleri oluşturarak, kükürtün oksitleyicilerle oluşturduğu daha az gözenekli ve sıkı filmlerle birlikte difüzyonu önemli ölçüde azalttığı, dolayısıyla da çözünürlüğü azaltmış olduğu kanaatindeyiz.

Ancak çözünürlüğün oksitleyicilerle birlikte azalmasının cevherdeki alüminyumun miktarı ile net ilişkisini ortaya koyabilmek için farklı türdeki bakır cevherleri ile benzer çalışmalara devam edilmektedir.

Sonuç olarak aynı cins cevherlerde olmuş olsa çözünürlüğe mineralin ihtiva ettiği diğer bileşenlerinde etkili olacağı gözden kaçırılmamalıdır.

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Quantitative Leaching of Nickel From Jarosite Using Sulphuric Acid

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ABSTRACT This paper deals with the extraction of nickel from jarosite precipitates. Nickel loss to these precipitates is mainly by entrainment and coprecipitation. Nickel is hazardous to the environment. In this study, an attempt has been made to extract nickel entrained in jarosite precipitates produced at Implats Base Metal Refineries. The leaching efficiency of nickel was 59% at 30^{o}C. The acid concentration of 0.5 – 1M, pulp density of 10%, leaching time of 21/2 hours was found to be optimum. High concentrations of acid and high temperatures could break the jarosite structure and release more Fe into the solution which will adversely affect the following precipitation process. The reaction is diffusion independent.

Key words: Jarosite precipitates, Leaching, Nickel, Waste and Effluent

1 INTRODUCTION

Increase in environmental alarm due to unacceptable management of both hazardous and non-hazardous wastes on the rampage from different industrial processes prioritize the need for the improved research. Nowadays, with the environmental regulations becoming more and more severe and growing pressure on the conservation of mineral resources, economically-viable refining technology in recycling has gained interest. The most serious environmental issue faced by the processing industry is the process of effluents. Mineral processing industries may contain heavy metals, organic waste, and oils, including the waste liquids from wastewater streams. Toxic metals existing in high concentrations must almost certainly be well treated (Dutrizac & Chen, 2000). On the other hand, the disposal process can bring about some complexity. Companies are also suffering from an increased disposal cost besides the environmental sensitivity.

The focus is lately on the ability to clean up waste and return or recycle a significant proportion (Kurama, 2009; Kurama, 2007). The waste which is generally regarded a hazardous could be further considered as a rich secondary source of metal such as nickel from jarosite precipitates.

Jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$) is a basic hydrous sulphate of potassium and iron, its formation is represented by the following reaction:

$3Fe_2\ (SO_4)_3 + M_2SO_4 + 12H_2O \Leftrightarrow 2MFe_3\ (SO4)_2(OH)_6 + 6H_2SO_4$……………………(1)

Where M represents any of the ions Na^+, $NH4^+$, $H3O^+$,Li^+, K^+, $0.5Pb2^+$ and ½ Hg^{2+}(Long, et al., 1992).

Nickel is not on the above list of ions that can be incorporated in a jaroiste structure neither can it substitute Fe^{3+}. Hence loss of nickel to the jarosite precipitate can either be by entrainment or co-precipitation. However with formation of Beaverite jarosite $Pb(Fe,Cu)_3(SO_4)_2(OH)_6$, Fe^{3+} can replaced by either Cu^{2+} or Zn^{2+} or both in the structure (Dutrizac & Chen, 2000; Dutrizac, et al., 1980).

Jarosite structure have been intensely researched and it is best described in the space group R-3m and has lattice parameters a~7.3 Å, c~17 Å. The kagome plane is made up of iron coordination octahedra, and the Fe octahedra are capped above and below by sulphate tetrahedral(Wills, et al., 2006).

The jarosite group of minerals has been extensively studied as a result of its importance as a by-product of the metal-processing industry as well as being very common in acid-mine waste. Minerals within the jarosite group are commonly found in acidic, high-sulfate environments associated with mine tailings(Basciano & Peterson, 2007).

Annually thousand tonnes of synthetic jarosite is produced and contains 25-36 wt% Fe(Dutrizac & Chen, 2000). Group minerals of jarosite are one of the most commonly natural occurring iron-sulfates. They usually occur as yellow crusts and coatings within the saturated zones of mine tailings and acid sulfate soils. These group of minerals consists of more than 40 different mineral species that have the general formula $AB_3(TO_4)_2(OH, H_2O)_6$ and is part of the alunite supergroup(Bigham & Nordstrom, n.d.). Minerals of the alunite-jarosite group can have Na+, K+, H_3O^+, NH_4, ^+Ag, $^+$ and ½Pb^{+2} forming the A site, Fe^{3+} (jarosite group). As the jarosite structure can incorporate a large number of elements, its chemical composition reflects the chemical compositions of the fluids from which it formed. For example: Oxygen in the SO_4 site reflects the source of oxygen during oxidation of the sulfide, this value will depend on whether water or air provides the oxygen and if any biogeochemical (microbial) processes are involved. Oxygen in the OH site is more complex and reflects the character of the parent fluid, equilibrium exchange processes, and temperature. Natural and synthetic jarosite group minerals commonly have significant quantities of hydronium in the alkali site and minor to major deficiencies in the iron site. Jarosite is also important in the base metal industry as a sink for iron; it is precipitated as a means of removing the iron that is commonly present in base metal concentrates.

Sulfuric acid is most widely used acid for leaching due to the following advantages: (i) high solubility of base metals, (ii) Low price, (iii) well established technology for solvent/electrowinning in sulphate media and (iv) regeneration of acid after solvent extraction.

2. EXPERIMENTAL

2.1 Material

The jarosite precipitate used in this study was produced at Impala Base Metal Refineries. The bulk size of the material was 93% - 45µm.

2.2 Method

2.2.1 Water Wash

10 grams was taken from the jarosite sample and washed in 200ml of distilled water to determine the amount of nickel that may have been entrained during solid liquid separation at the plant.

2.2.2 Leaching

The leaching experiments were carried out by taking required amount of sulfuric acid in a glass beaker of 500ml capacity placed under an overhead stirrer in a water bath. The concentration of sulphuric acid was varied from 0.01 M to 3M. The pulp density was varied from 5% to 30%. The temperature of all the experiments was maintained at 25 ^oC except where it was varied between 25 ^oC to 60 ^oC. Time of leaching was varied from ½ hr to 8hrs and the rate of stirring was varied from 50 to 250revs/minute. The rate of leaching was monitored in terms of leaching efficiency calculated as-

([W]t/[W]c)×100=leaching efficiency in % (2)

Where, [W]t=Wt. of the metal dissolved in solution after a particular
time period

[W]c=Total wt. of the metal in the sample taken.

3. CHARACTERISATION

The chemical composition of the jarosite precipitate was carried out using Rigaku SX Primus ii X-ray fluorescence and atomic absorption spectrometer (Thermo Scientific ICE 3000 Series) for confirmation. The mineralogical phases of the above mentioned jarosite precipitates were determined by XRD analysis, using a Rigaku Ultima IV X-ray diffractometer. The morphology of the jarosite precipitate was studied by Scanning Electron Microscope (Tescan model). The particle size distribution of the jarosite precipitates was measured by Microtrac particle size distribution analyser.

4. RESULTS AND DISCUSSION

4.1 Mineralogy

The XRF of the jarosite precipitate results are shown in Table 1. From The table, it is seen that it contains about 6.16% nickel and this is too high to be lost to the jarosite precipitate. Major component of the jarosite precipitate is iron as expected.

Further quantification of the elements was determined using an atomic absorption spectrometer and the results are shown in Table 2. Only nickel, iron and copper were analysed as they were going to be investigated in the leaching experiments. There is a huge variation with the XRF results obtained in Table 1. According to AAS results, nickel content is on average of 4.87% while iron at an average of 38.63% and copper was found to be at the lowest of 0.0197%. Being more precise AAS was used for all the chemical analysis of all the following experiments.

The XRD of the jarosite precipitate is given in Fig 1. The peaks above 100 % refers to jarosite ($K(Fe_3(SO_4)_2(OH)_6)$ and Hematite (Fe_2O_3), indicating the major phases. There are other minor phases present which are represented by smaller peaks.

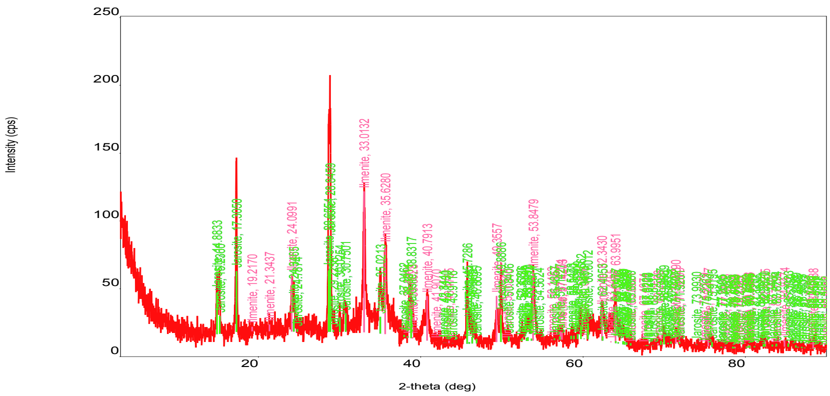

Figure 1: XRD of the jarosite precipitate.

Table 1: XRF results

Element	Mass %	Element	Mass %	Element	Mass %
Ni	6.16	Pb	1.84	K	1.00
Fe	65.98	Na	0.39	Si	10.97
Al	2.90	Cr	0.28	S	7.76
Ca	0.14	As	2.38		

Table 2: AAS results

Element	Sample 1	Sample 2	Sample 3	Average
Nickel	4.65%	4.91%	5.04%	4.867%
Iron	37.59%	39.86%	38.43%	38.63%
Copper	0.0273%	0.0197%	0.0120%	0.0197%

The morphology of the jarosite precipitate was studied and the micrographs and results are shown in Figure 2 and Table 3 respectively.

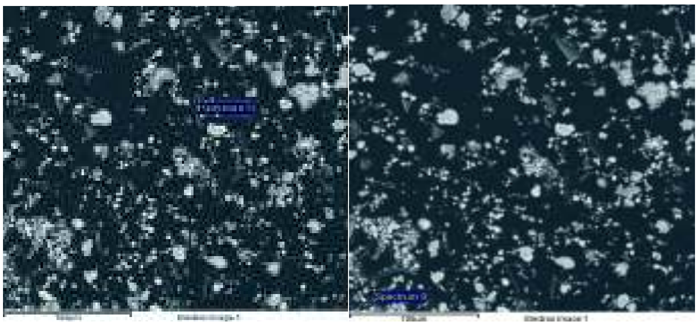

Figure 2: SEM micrographs of the Jarosite precipitate

Table 3: SEM results

Element	Fe	Al	Si	Ni	K	S	Na	As	Cl
Spectrum 5	4.36	10.58	69.25	1.99	9.37	-	1.93	-	2.51
Spectrum 8	29.62	6.25	33.88	-	2.95	-	-	-	27.30

It can be seen that a particle on spectrum 5 is rich in silicon at 69.25%, while iron and nickel are 4.36% and 1.99 % respectively. A particle on spectrum 8 has 29.62% iron and no nickel. These two results gives an indication that a particle on spectrum 8 might be a jarosite crystal and the one on spectrum 5 might be another form of precipitate which contains nickel.

4.2 Water Wash.

A water wash was carried on the jarosite precipitates at different times and the results are shown in figure 3. Figure 3 shows that the nickel recovery remained constant around 27% nickel recovery regardless of the leaching time. It can thus be deduced that 27% of nickel losses in the plant to jarosite precipitates are a result of poor washing techniques employed at Implats plant. The remaining 73% either co-precipitates with the jarosite precipitates or forms part of the jarosite crystal structure. There is evidence form literature that base metals can be incorporated in a jarosite crystal eg Beaverite jarosite ($Pb(Fe,Cu)_3(SO_4)_2(OH)_6$) where Fe^{3+} is replaced by Cu^{2+} or Zn^{2+} or both.

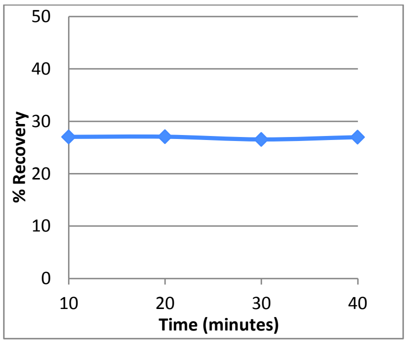

Figure 3: Water washes at different times, 25°C

4.3 Leaching

Leaching of the jarosite precipitate was carried out to extract nickel from the precipitates. This material is not a naturally occurring geological material but an industrial deposition. Therefore, its mineralogy and leaching behaviour are quite different from the normal ores and minerals. Variation of parameters were studied and optimised. The results are given in the following sections.

4.3.1 Effect of leaching time.

The jarosite precipitate was leached at different times using 1Molar H_2SO_4 and 10% pulp density at room temperature and the results are shown in figure 4. From figure 4, it follows that with the increase of leaching time from 30 minutes to 150 minutes, recovery of nickel increases from 38.9 to 51.3 %. Further increase in leaching time from 150 to 480min recovery of nickel does not significantly increase (2.4%).

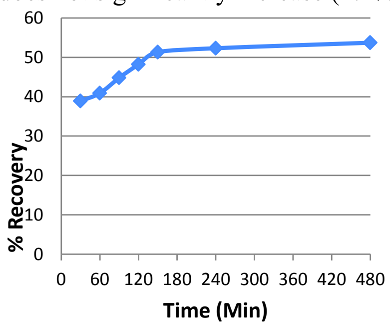

Figure 4: Effect of time on leaching of jarosite precipitate, 1M H_2SO_4, 10% PD, 25^oC

4.3.2 Effect of acid concentration.

The concentration of the acid is one of the major parameters for recovery of nickel from jarosite precipitates. Acid breaks the complex to release the metal values. In the present study, jarosite precipitate was leached at different concentrations at a constant time of 21/2hrs, 10% pulp density, 25 ^oC and the results are shown in figure 5. Figure 5 shows that the optimum leaching concentration of H_2SO_4 is between 0.5 and 1M H_2SO_4 where there is a recovery of around 48% Nickel and less than 5% Fe Recovery. With the increase in the acidity from 0.05 to 1M H_2SO_4, recovery of nickel increases from 50 to 58% and recovery of Fe from 0.4 to 1.5%. There is need to keep the concentration of Fe as minimum as possible (5%) as this will adversely affect in the following precipitation process. Further increasing H_2SO_4 concentration will only increase recovery of Ni by 10% and that of Fe will go up to 3.5%.

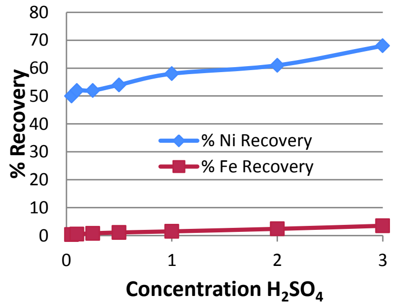

Figure 5: Effect of acid concentration on leaching of jarosite precipitate, 2 ½ hrs, 10% PD, 25^oC

4.3.3 Effect of stirring speed

The effect of stirring speed on the leaching of the jarosite precipitate was investigated and the results are shown in figure 6. Figure 6 shows that the recovery of nickel does not change much with the change in stirring speed and thus it can be concluded that the leaching reaction is diffusion independent.

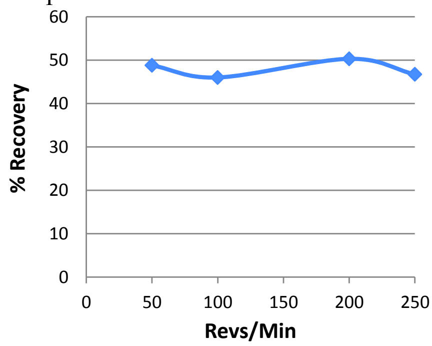

Figure 6: Effect of stirring speed on leaching of jarosite precipitate, 1M H_2SO_4, 2 ½ hrs, 10% PD, 25^oC.

4.3.4 *Effect of temperature*

The effect of temperature was studied for the liberation of nickel and Iron. Jarosite precipitate was leached at different temperatures and the results are shown in figure 7. It was found that increase in temperature increases the recovery of Ni and Fe. Increasing leaching temperature from 25 to 60 °C, recovery of Ni increases from 52 to 75% and Fe from 1.7 to 14%. Thus at high recovery of Ni (60 °C) there is also a high recovery of Fe and this will adversely affect the following precipitation process. Optimum leaching temperature will be 30°C where recovery of Ni is 59% and Fe 5.5%.

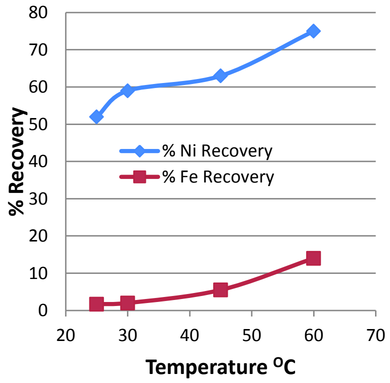

Figure 7: Effect of leaching temperature, 1M H_2SO_4, 2 ½ hrs, 10% PD.

4.3.5 *Effect of Pulp Density*

The solid to liquid ratio (w/v) is termed the pulp density. The effect of pulp density on nickel extraction is given if figure 8. It is clear that in both 5% and 10% pulp density, 48% extraction was achieved. But when the pulp density was increased to 30%, the recovery was reduced to around 43%. Hence in this case 10% may be taken as the optimum pulp density for optimal recovery of nickel.

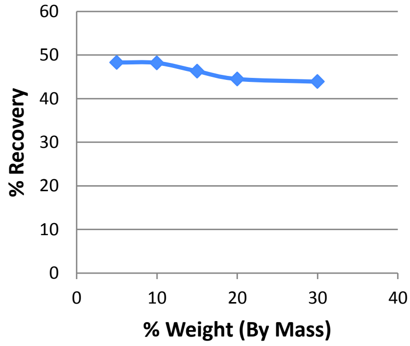

Figure 8: Effect of pulp density, 1M H_2SO_4, 2 ½ hrs, 25°C

5. CONCLUSION

The jarosite precipitate containing nickel was leached in sulphuric acid medium at different temperature and acid concentrations. The leaching efficiency of nickel was 59% at 30°C. The acid concentration of 0.5 – 1M, pulp density of 10%, leaching time of 21/2 hours was found to be optimum under the present conditions. High concentrations of acid and high temperatures could break the jarosite structure and release more Fe into the solution which will adversely affect the following precipitation process. The reaction is diffusion independent.

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Copper-Gold Ore Processing with Ion Exchange and SART Technology at Anglo Asian's Gedabek Mine in Azerbaijan

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Anglo Asian Mining plc

ABSTRACT Anglo Asian Mining has developed a 50,000 oz Au/yr open pit gold mine at Gedabek in Western Azerbaijan. The deposit at Gedabek is a copper-gold porphyry, comprising both oxide and sulphide ore mineralisation, which is being mined at the rate of about 1 million tons of ore per year. Ore processing is by conventional cyanide heap leaching, which produces a pregnant leach solution (PLS) containing 1-2 ppm of gold, together with 1000 ppm or more of copper. The PLS is treated by column ion exchange, using Dow's gold-selective MINIX resin. Loaded resin is stripped with an acidic thiourea solution, from which gold and silver are electrowon on to stainless steel mesh cathodes. Copper concentrations in the leach solutions are controlled by passing part of the PLS flow through a SART process, where the acronym stands for "Sulphidisation, Acidification, Recycling and Thickening".

1 INTRODUCTION

In May 2009, Anglo Asian Mining, a London-listed, junior gold mining company, started operations at its first mine, which it had developed near a remote town called Gedabek, high in the Lesser Caucasus mountains in western Azerbaijan. Not only was this mine the junior company's first mining operation, it was also the first metal mine to be built in Azerbaijan for over a century. In the nineteenth century, Gedabek had been a mining town, when the Siemens company from Germany operated a copper mine there for about 50 years, until the Russian revolution intervened after the end of the First World War, when the Germans closed the mine and went home. By then, oil had been discovered in Azerbaijan, both on-shore and off-shore in the Caspian Sea, and so the country rapidly became an important source of energy for the growing industrial demands of the USSR. During the Soviet era, mineral exploration continued in the Gedabek region, but no further mining development took place during the rest of the twentieth century, until some three years ago, when Anglo Asian began operating its new open pit gold mine with state-of-the-art ion-exchange processing technology to produce 50,000 oz of gold per year.

2 DEPOSIT DESCRIPTION

2.1 Regional Geology

Azerbaijan straddles the mountain ranges of the Greater and Lesser Caucasus, which are part of the Alpine-Himalayan mountain chain that marks the collision of the African and Indian continental plates with the Eurasian plate. The continental collision is manifested by the Alpine tectono-magmatic cycle, which shows a progressive development from predominantly oceanic magmatism in the Jurassic, through to predominantly continental magmatism in the Tertiary. This magmatic episode was responsible for one of the world's major metallogenic belts, the Tethyan, which can be traced from Pakistan through Iran and Turkey to the Balkans. Notable deposits within this belt include a spectrum of hydrothermal deposit types ranging from Cyprus-type massive sulphide deposits, through porphyry copper and gold deposits, to epithermal gold deposits.

2.2 Local Geology

The Gedabek deposit lies in the Lesser Caucasus mountains in western Azerbaijan at an altitude of 1600m, close to the border with Armenia and about 60km from Ganja, Azerbaijan's second city (see Figure 1). The deposit exhibits many characteristics typical of porphyry copper-gold deposits, but it is peculiar in the development of distinct bodies of massive and semi-massive sulphide, as well as the more normal 'porphyry style' disseminated and stockwork mineralization.

The Gedabek deposit is believed by Azeri geologists to be a composite ("telescoped") deposit of two contrasting types of mineralization: an older volcanogenic massive sulphide (VMS) deposit and a younger porphyry stockwork. The massive sulphide bodies are composed principally of pyrite and chalcopyrite with minor amounts of sphalerite, galena, tetrahedrite and barite. There are five known large massive sulphide bodies, with plan areas of 8,000m^2 to 26,000m^2, and several smaller ones. These bodies are distributed within the porphyry over a strike length of about 600m and over a vertical interval of up to 200m. Past production from these lenses during the Siemens period is reported to have totaled 1.7Mt of ore, with 56,000t of copper and 134t of Au-Ag-Cu doré recovered.

The porphyry-style mineralization at Gedabek consists of disseminated and stringer sulphide mineralization, dominated by pyrite with subsidiary chalcopyrite. The host intrusion has been affected by intense weathering and it is bounded to the east by a regional north-northwest trending fault and by a parallel fault to the west. Other less important faults cut the deposit in northeast, east-west and north-south directions. Weathering is highly variable, frequently extending to depths of more than 50m, particularly within the highly altered and deformed contact between the felsic intrusive and the overlying volcaniclastic lithologies. However fresh sulphides also exist near the surface where they are encapsulated by silicification, resulting in a transitional oxide-sulphide boundary

Figure 1. Map showing the location of the Gedabek Mine in Azerbaijan

2.3 Mineralogy and Gold Deportment

The sulphide mineralogy of the Gedabek deposit is dominated by pyrite, with lesser chalcopyrite and minor amounts of sphalerite, covellite, chalcocite, galena and arsenopyrite. The py/cpy ratio is generally in the 12-15 range. The gangue mineralogy is dominated by quartz (approx. 50%), with lesser feldspars, muscovite, and andalusite. Minor barite and iron hydroxyoxides are also present.

Gold is found in two main forms: (i) gold minerals, including native gold, electrum and petzite [Ag_3AuTe_2]; (ii) submicroscopic gold in sulphides and goethite. The highest concentrations of sub-microscopic gold occur in arsenopyrite (40ppm Au) and covellite (9ppm Au), but because of its dominance, pyrite is the principal sulphide carrier of sub-microscopic gold. Silver occurs as native silver, electrum, acanthite, hessite [Ag_2Te] and petzite, of which hessite is the most common, followed by native silver. Silver is also likely to occur in solid solution in covellite. Five telluride minerals are present, of which Bi-tellurides, hessite and altaite [PbTe] are the most common.

The so-called oxide ore is characterized by minerals typical of the hypogene oxidation zone of copper porphyry deposits, including malachite, azurite, goethite and other iron hydroxyoxides.

2.4 JORC Resources and Reserves

The most recent measured, indicated and inferred mineral resources of both the oxide and sulphide mineralisation based on a cut-off grade of 0.3 g/t of gold is described in Table 1, together with the proved and probable open pit ore reserve estimation, based on the same cut-off grade. The table shows that the current JORC gold resource at Gedabek is just over 1.2M oz Au in all categories, while the mineable ore reserve is 744K oz Au.

Table 1. JORC Resources and Reserves.

CLASSIFICATION	Tonnage	Grades			Products		
	(t)	Au (g/t)	Cu (%)	Ag (g/t)	Au (oz)	Cu (t)	Ag (oz)
RESOURCES							
Measured	22,349,562	1.028	0.255	8.249	738,958	57,069	5,927,487
Indicated	14,762,015	0.665	0.167	5.649	315,424	24,696	2,681,064
Measured & Indicated	37,111,577	0.884	0.220	7.215	1,054,382	81,765	8,608,551
Inferred	11,027,402	0.626	0.119	4.787	222,040	13,125	1,697,102
RESERVES							
Proved	15,586,952	1.172	0.285	9.203	587,099	44,389	4,611,806
Probable	4,725,928	1.033	0.319	10.292	156,939	15,091	1,563,725
Proved & Probable	20,312,879	1.139	0.293	9.456	744,038	59,479	6,175,531

3 MINING

The Gedabek mine is a conventional open pit, truck and shovel operation, with a current production of about one million tons of ore per year. Rock breakage is accomplished by blasting, which is carried out once per day. Blast holes are drilled on a 2.5m x 2.5m pattern in ore and 3m x 3m in waste rock, to a depth of 3m. The blast holes are each charged with 10kg ANFO/Geonit mix and detonated electrically. Grade control drilling is used ahead of blast hole drilling to delineate ore blocks and classify them as either, high grade oxide (>1 gAu/T), low grade oxide (<1>0.3gAu/T), sulphide ore, or waste rock.

4 PROCESSING

4.1 Overall Flowsheet

The Gedabek process plant, which began operation in May 2009, uses conventional cyanide heap leaching, combined with gold extraction by resin ion exchange and SART technology for copper control. A schematic flow diagram of the overall process is shown in Figure 2.

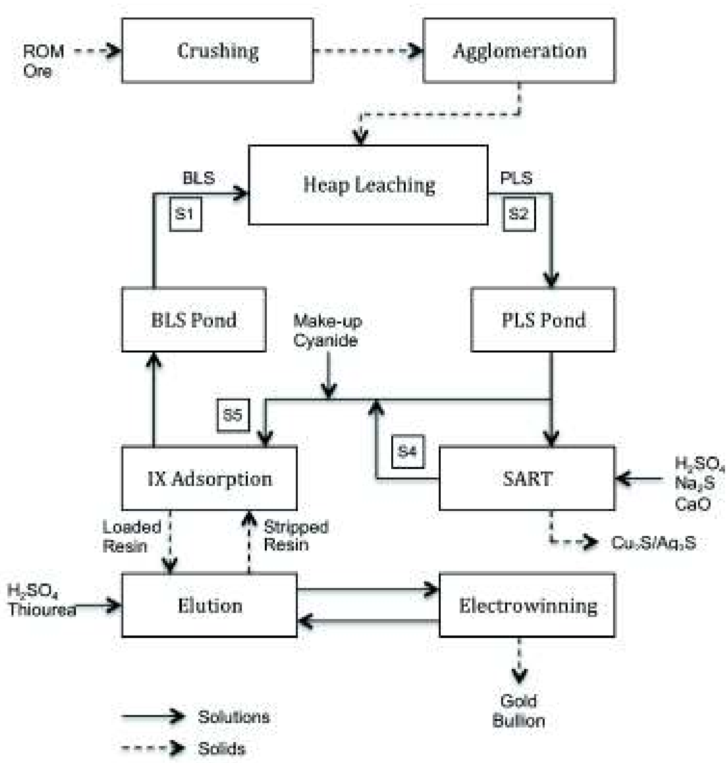

Figure 2. Flowsheet for gold ore processing at Gedabek. *(Solution compositions given in Table 2)*

4.2 Ore Preparation

ROM ore is prepared for heap leaching by three stages of crushing – primary jaw crusher, followed by secondary and tertiary cone crushers, to give a product 100% minus 25mm. The output from the primary crusher is passed over a 25mm screen and the -25mm material passes into an agglomeration drum (2.2m diam. x 10m length), together with lime (3kg/t ore) and cement (5kg/t ore). The over-size rock from the primary screen is fed to the cone crushers and, after secondary and tertiary crushing to -25mm, it is conveyed to the heaps, together with the agglomerated fines.

4.3 Heap Leaching

The crushed and agglomerated ore is stacked on the leach pads in 12m lifts by a radial arm stacker. A maximum of two and half lifts per heap are used (max. 30m high). The heaps are constructed on pre-prepared pads, which are double lined with HDPE sheet with geo-membrane between the layers for leak detection.

Barren leach solution (BLS) is pumped from the BLS pond and the solution is sprayed on to the surface of the heaps through sprinklers positioned at 2m intervals. The rate of leach solution application is 10 $l/m^2/hr$. Ore on the heaps is typically leached for a period of about 6-9 months, dependent on the time of year and weather conditions. The maximum gold extraction that can be achieved from Gedabek ore by heap leaching is around 70%, after which the ore heap is considered spent and ready for a new lift to be placed on it.

4.4 PLS Treatment – CIX

Pregnant leach solution from the heaps is collected in the PLS pond, from where it is pumped to the ADR (Adsorption/ Desorption/Recovery) process plant at a rate of 400 m^3/h. Because of the copper minerals in the Gedabek ore, the PLS contains high concentrations of copper (see Table 2); typically the Cu/Au concentration ratio in the leach solution is ~1000 and, under these conditions, it is impossible to use conventional activated carbon to adsorb the gold. The technology used at Gedabek to extract gold from the PLS is column ion exchange (CIX) using the Dowex Minix gold-selective strong base ion exchange resin (XZ-91419), produced by the Dow Chemical company. This resin, which was originally developed by Mintek in South Africa, is highly selective for gold over copper. In order to control the concentration of dissolved copper in the recirculating leach solutions, 25% of the PLS (100m^3/h) is diverted through the SART plant, where copper and silver are precipitated from solution (*see below*). The SART treated solution rejoins the main PLS flow before it arrives at the ADR plant. Make up cyanide is also added before the PLS enters the IX adsorption columns to increase the free cyanide concentration to 1000mg/l. This helps to suppress the adsorption of copper on the resin by encouraging the formation of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$, which are only weakly extracted by the resin.

The adsorption plant consists of four IX packed columns, each 2.5m in diameter and 2.1m high, with internal volumes of 9m^3. Each column contains 6.5m^3 of resin. The columns are operated in parallel in down-flow mode, with each column being fed with 130 m^3/h of PLS during its loading cycle. Each column goes through a sequence of operations, comprising charging, loading, washing and discharging. At any given time, three columns are loading, while the fourth is off-line, being washed, discharged and then re-charged with stripped resin from the elution columns. Loading is carried out for 24 hours, by which time the resin will contain about 160mg/l Au, 120mg/l Ag and 230mg/l Cu. The average adsorption efficiencies for Au and Ag are 70% and 15%, respectively, while Cu adsorption is negligible. The loaded resin in the column is then washed with fresh water and pumped to an elution column.

4.5 Elution

There are three elution columns, operated in parallel, each is 1.75m in diameter and 5.9m high, with an internal volume of 15m^3. Each elution column can treat up to 7m^3 of resin. Loaded resin is eluted with a hot, acidified solution of thiourea - 0.2 M H_2SO_4 and 1.0 M Thiourea at 50°C. Elution is carried out in series with electrowinning, with the eluate circulating between the two operations at a rate of 7.5m^3/h. Typically, the resin is eluted for 4 hours, by which time the gold concentration on the resin has dropped to 0.005 mg/l. It is then washed and returned to the adsorption columns.

4.6 Electrowinning

Electrowinning of gold from the thiourea eluate is carried using stainless steel mesh cathodes and lead anodes at a cell voltage of 5V and a current of 500-800A. The EW cells contain 6 anodes and 5 cathodes and the anodes are contained in geo-membrane bags to minimise oxidation of thiourea. Periodically the cathodes are removed from the cell and washed with high pressure water jets to recover the electrodeposited gold particles.

4.7 SART Process

The purpose of the SART process is to regenerate cyanide and recover copper from the solutions in gold heap leaching operations. The name SART arises from the core unit operations that define the process: sulphidization (S), acidification (A), cyanide recycling (R), and thickening of the copper precipitate (T). The main stages of the process are acidification and sulphidization, precipitate thickening, sulphide precipitate filtration, solution neutralization, gypsum thickening and gypsum filtration.

Figure 3 is a schematic flow diagram of the Gedabek SART process. The acidification (pH 5-6) and sulphidization stages are carried out in the nucleation reactor by the addition of concentrated sulphuric acid and sodium sulphide. In this reactor, Cu_2S and Ag_2S precipitation occurs and HCN is generated, which remains dissolved in solution, according to equations (1), (2) and (3).

$$2NaCN + H_2SO_4 = 2HCN_{(aq)} + Na_2SO_4 \quad (1)$$

$$2NaAg(CN)_2 + 2H_2SO_4 + Na_2S = Ag_2S_{(s)} + 4HCN_{(aq)} + 2Na_2SO_4 \quad (2)$$

$$2Na_2Cu(CN)_3 + 3H_2SO_4 + Na_2S = Cu_2S_{(s)} + 6HCN_{(aq)} + 3Na_2SO_4 \quad (3)$$

As shown in equation (1), dissolved HCN is formed when acid is added; acidification also promotes breakage of weak metal cyanide complexes (WAD cyanide), such as those formed with the metals Cu, Zn, Ni, Ag, and Hg. The addition of Na_2S results in the precipitation of heavy metal ions in the form of metallic sulphides, which are Cu_2S and Ag_2S in the case of the Gedabek PLS, as shown in equations (2) and (3), with an equivalent amount of cyanide being released into solution.

The solids formed by precipitation are removed using stages of thickening and filtration, while the treated solution is sent to the neutralisation stage where milk of lime ($Ca(OH)_2$) is added to raise the pH to 11. The addition of lime converts the dissolved HCN into calcium cyanide ($Ca(CN)_2$) and removes sulphate by the precipitation of gypsum.

$$2HCN_{(aq)} + Ca(OH)_2 = Ca(CN)_{2(aq)} + 2H_2O \quad (4)$$

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O = CaSO_4{\cdot}2H_2O_{(s)} + 2NaOH \quad (5)$$

A SART plant with a capacity of 100 m^3/h to process 25% of the total PLS was commissioned at Gedabek in April 2010. The PLS treated by the SART plant is pumped into the process, where concentrated H_2SO_4 and Na_2S solution are added into in-line mixers in the PLS pipeline to reduce the pH to 5.5. Approximately 20% excess sodium sulphide over the stoichiometric amount required to precipitate copper and silver according to equations (2) and (3) is used, which results in precipitation efficiencies of 90% for Cu and 97% for Ag. The PLS reagent mix flows into the nucleation reactor, where Cu_2S and Ag_2S are precipitated and dissolved HCN is generated. The slurry from the nucleation reactor discharges into the Cu_2S thickener (8m diameter) to increase the solids concentration. Part of the thickener underflow is recycled back to the nucleation reactor to serve as seed for the precipitation, while the remaining underflow fraction is sent to the filtration stage. The filtration of the sulphide precipitate is carried out by two filter presses, producing a precipitate cake having 55% final moisture. The filter cake is then dried in an oil-fired dryer.

The Cu_2S thickener overflow passes into the neutralisation reactor, where $Ca(OH)_2$ is added until the pH reaches 10.5-11, which converts dissolved HCN to $Ca(CN)_2$ and induces gypsum precipitation. The gypsum slurry is fed into the gypsum thickener (8m diameter) to separate the solids from the treated solution. In a similar manner to the precipitate thickener, part of the underflow from the gypsum thickener is recycled back to the neutralisation reactor, while the remaining underflow fraction is sent to filtration. The gypsum filtration is performed by a rotary filter, giving a gypsum filter cake with 80% final moisture, which is discarded.

The SART process plant also includes a caustic soda scrubber system connected to the main plant equipment in order to capture and treat fugitive emissions of HCN and/or H_2S gases from the reactors and thickeners. Scrubber solution containing dissolved sodium cyanide is returned to the leach circuit.

The current annual production of the Gedabek SART plant is about 600T of copper and 100,000oz of silver in a mixed sulphide concentrate that is sold into the market for smelting.

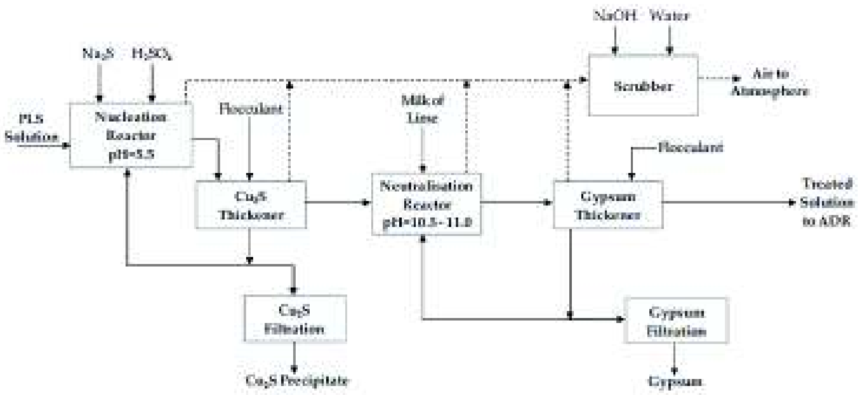

Figure 3. Block flow diagram of the SART process in the Gedabek plant.

Table 2. Typical process solution compositions.

	SOLUTION	Gold (mg/l)	Silver (mg/l)	Copper (mg/l)	CN (Free) (mg/l)	pH
S1	BLS	0.20	1.6	530	1000	10.5
S2	PLS and SART (in)	0.79	2.3	660	320	10.0
S3	SART (intermediate)	0.78	0.03	50	N/A	5.4
S4	SART (out)	0.77	0.07	65	1300	10.5
S5	ADR (in)	0.79	2.3	660	1000	10.0

5. CONCLUSIONS

The successful operation of Anglo Asian Mining's Gedabek process plant, which uses a unique combination of ion exchange for gold extraction and SART technology for copper control, has demonstrated a new route for the treatment of copper-gold ores, which in the past have proved difficult to handle with conventional gold processing technology.

Ion exchange resins offer many advantages over activated carbon for the treatment of gold-bearing solutions and pulps. Chief amongst these are: simple, low temperature stripping; elimination of thermal regeneration requirements; and physical robustness and attrition resistance. In the case of the Minix strong-base resin, there is the additional advantage of excellent selectivity for gold over copper. At Gedabek, where the Cu/Au ratio in the PLS is about 1000, the loaded Minix resin has a Cu/Au ratio of between 1 and 2, demonstrating a selectivity ratio for gold over copper of 500 to 1000. There is no indication of resin breakage or attrition losses, nor is there any noticeable decrease in the adsorbtion efficiencies of the resin due to ageing. However, the Gedabey operation shows that resin adsorption efficiencies can be negatively affected by the presence of excess flocculant in solution and by fine solid particles either precipitated from solution, e.g. gypsum, or fine ore particles carried over from heap leaching. However this is due to the use of packed bed ion exchangers at Gedabey, which at the same time act as bed filters.

Accumulation of flocculant and fine particles affects the adsorption both by disturbing the fluid flow pattern in the IX vessels and by fouling the resin surfaces. Application of remedial measures such as high pressure back washing, or periodic flow direction change from downward to upward flow can improve absorption performance to a certain extent, but does not solve the problem entirely.

The SART process at Gedabek, which is one of only half a dozen industrial applications of this technology in the world, has proved to be a reliable process that gives consistent results and that lends itself to automatic control. It produces a saleable Cu/Ag by-product that is suitable for smelting and which makes a useful contribution to the overall profitability of the mine.

After three years of operation, most of the well-oxidised, readily leachable ore in the Gedabek mine has been consumed and production is moving into the transition and sulphide ore zones. In order to cope with the changing leaching characteristics of the ore, an agitation leaching plant and associated tailings dam is now under construction. This US$50M investment is designed to treat 100t ore/hour and will be in operation by mid-2013. Like the original process plant at Gedabek, this new plant will also be ground-breaking in that it will be the first use of the Minix resin in a large scale resin-in-pulp process. Higher grade ore from the mine will be treated in the new plant, together with spent ore from the current heap leach operations, which still contains significant quantities of gold.

Lower grade ore from the mine will continue to be sent to the leach pads for heap leaching over extended periods of time.

Appendix: General process data for the Gedabek plant.

UNIT PROCESS	VALUE
Heap Leaching	
Ore feed size to agglomeration	-25 mm
Addition rate of cement and lime	5 and 3 kg/T ore
Irrigation rate	10 $l/m^2/h$
pH of BLS to heap irrigation	10.0 – 11.0
Free cyanide concentration in BLS to heap	1000 mg/l
Ion Exchange	
PLS flow rate	400 m^3/h
pH of PLS to IX	10.0
Number of IX Adsorption columns	4
PLS flow rate per IX adsorption column	133 m^3/h
IX Adsorption columns (diameter x height)	2.5 x 2.1 m
IX Adsorption column volume / resin inventory	9 / 6.5 m^3
Number of Elution columns	3
Elution columns (diameter x height)	1.75 x 5.9 m
Elution column volume / resin inventory	15 / 6.5 m^3
Eluant composition	0.2 M H_2SO_4 + 1.0 M Thiourea
Eluant temperature	50 $^{\circ}C$
Electrowinning	
EW cell dimensions (width x height x length)	0.72 x 0.72 x 1.4 m (x 4 off)
Number of electrodes (anodes x cathodes)	6 x 5
Anode material	Pb + 1% Antimony
Anode bags	Geo-felt
Cathode material	SS mesh
Eluant flow rate to EW cells	7.5 m^3/h
EW Cell Voltage/Cell Current	5V/500-800A

Using of Central Composite Design Method for Evaluation of Silver Recovery from Gold Leaching Residue

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ABSTRACT Hydrogen peroxide method – an inexpensive and safe technique – was employed for the recovery of silver from silver chloride solution. The effects of pertinent factors on the silver recovery were evaluated via Response Surface Methodology (RSM) based on a Central Composite Design (CCD). Regarding the statistical developed model, the optimized levels of the significant factors were determined for an effective Ag recovery. The statistical analyses indicated that an increase in the level of NaOH and H_2O_2 results in an enhancement in Ag recovery. The maximum recovery of Ag could be achieved at NaOH = 43.13 g and H_2O_2 = 986.66 ml after 60 minutes of chloride leaching of silver in a 3 L agitated reactor running at 210 rpm.

Keywords: Silver Recovery, Gold Leaching Residue, Central Composite Design

1 INTRODUCTION

Silver and gold are two important constituents of copper electrorefining anode slime; which during gold chlorination process, silver chloride is precipitated. Thus, recovery of silver from these chloride precipitations is economically/technically important. Different methods have been proposed for recovery of Ag metal from silver chloride, such as formaldehyde, sodium borohydride, zinc, copper, benzaldehyde, dextrose and hydrogen peroxide method (Peter C. Hsu et al, 1996). However, the recovery procedure should be environmentally friendly, cost effective and technically favorable. Typically, hydrogen peroxide method depends upon the level of NaOH and H_2O_2 used for the implementation of the process; the maximum yield of Ag dissolution would be achieved when these parameters are considered and optimized collectively.

A suitable experimental approach for optimizing a process, is the response surface methodology (RSM) which, through the use of experimental strategies such as central composite design (CCD), is able to simultaneously consider several factors at different levels, and give a second order polynomial model for the relationship between the various factors and the response (Haghshenas et al., 2012). Generally, the experimental design strategy has only been applied in limited cases to Ag recovery processes; Bard and Sobral (2008) employed a factorial design (at 2 levels) to optimize the influential factors on the extraction of Ag, Au and Cu from copper anode slimes.

In the present study, the effect NaOH weight and H_2O_2 volume on recovery of Ag from silver chloride were examined and optimized with the help of RSM. Also, the probable interactions between these factors were identified in a 3–L agitated reactor.

2. EXPERIMENTAL PROCEDURE

2.1 Silver Chloride and Reagents

Silver chloride as solid of gold chlorination process anode slime was obtained from Copper Complex Company (Sarcheshmeh, Iran). X−Ray Diffraction (XRD) analysis (Figure 1) showed the concentrate was mainly composed of silver chloride. Hydrogen peroxide, used in this study, was analytical grade and purchased from MERCK. Also, sodium hydroxide and nitric acid were utilized (Baran Chemical Co., Iran).

2.2 Methods

As received solids from anode slime chlorination process which is contain silver chloride with some other products were mixed with a certain amount of NaOH in a stirring reactor accompanied by injection of hydrogen peroxide with known concentration and constant mass flow for 1 hr. Then the solution was sent to a filtering system for solid/liquid separation. The solids which were metallic silver were then dissolved into 60 g/l nitric acid at 75 ˚C for about 20 minutes. The concentration of Ag was determined by Atomic Absorption Spectrophotometer (AAS) model Varian AA240.

Response surface methodology (RSM) was employed to investigate the effect of NaOH weight and H_2O_2 volume on Ag recovery from silver chloride. A central composite design (CCD) was adopted in this work to study two factors at three levels. Ten experimental runs consisting of 4 star points (star distance is 0) and 2 center points were generated with 2 factors and 3 levels by the principle of RSM using MINITAB Release 15. The CCD design matrix employed, which includes the levels employed for the different factors, is presented in Table 1.

3. RESULT AND DISCUSSION

3.1 Model fitting

Table 1 lists the values of Ag recovery (reaction fraction) after 60 minutes of leaching at each of the 10 combination of

Table 1. Central composite design arrangement and response (Ag recovery)

Experiment Numbe	NaOH	H_2O_2	Ag (conversion fraction)
1	10	160	50.25
2	50	160	51.07
3	10	1040	29.41
4	50	1040	90.24
5	10	600	50.45
6	50	600	85.06
7	30	160	62.82
8	30	1040	96.57
9	30	600	84.92
10	30	600	90.05

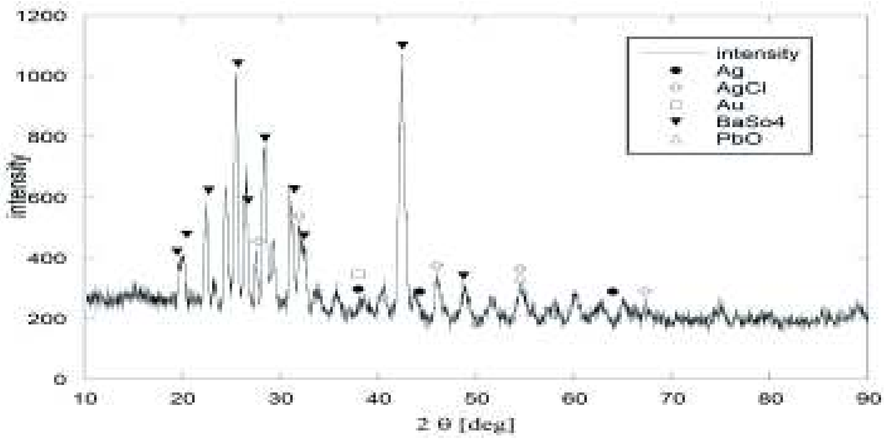

Figure 1. The XRD Pattern of anode slime after chlorination process

factor levels generated by the principles of RSM with the values ranging from as low as 0.29 to as high as 0.96. The results of the ANOVA are presented in Table 2; the low p values for the regression ($P<0.001$) and the fact that the lack of fit of the model was not significant ($P>0.05$) indicates the suitability of the model.

The value of the regression coefficients are presented in Table 3. All the linear terms and the second order of NaOH are significant, indicating that a second order polynomial model is necessary to represent the data. Based on the regression coefficients calculated for the response (Table 3) a polynomial regression model equation that fitted 95.15% of the variation in the data was proposed as follows (coded value):

3.2 Effects of parameters: Analysis of response surfaces

According to equation (1), an increase in NaOH and H_2O_2 results in an increase in the Ag recovery at the end of 60 minutes of leaching. In the cases where interaction between factors is statistically significant, surface plots give more complete information regarding the effect of a factor on the response. The curvature of the surface plots presented in Fig. 2 suggests that NaOH × H_2O_2 have interaction with each other in the leaching process. This is further confirmed by the results presented in Table 3.

As can be seen in Fig. 2, the effect of NaOH weight on the Ag recovery is more significant at high H_2O_2 volume.

$$\text{Ag recovery} = 83.593 + 16.043\ \text{NaOH} + 8.680\ H_2O_2 - 24.174\ \text{NaOH}\times\text{NaOH} + 15.003\ \text{NaOH}\times H_2O_2 \quad (1)$$

Table 2. ANOVA table

	Df*	SS**	MS***	F-values	P-values
Total	9	4787.99			
Regression	5	4555.89	911.18	15.70	0.010
Residual error	4	232.09	58.02		
Lack of fit	3	218.95	72.9	5.55	0.300
Pure error	1	13.15	13.15		
R^2	95.15				

* df, degrees of freedom
** SS, sum of squares
*** MS, mean square.

Table 3. Values of regression coefficients calculated for the Ag recovery from silver chloride.

Independent factor	Regression coefficient	Standard error	T-value	P-value
Constant	88.837	4.552	19.515	0.000
NaOH	16.043	3.110	5.159	0.007
H_2O_2	8.680	3.110	2.791	0.049
$NaOH^2$	-22.426	4.987	-4.497	0.011
$H_2O_2{}^2$	-10.489	4.987	-2.103	0.103
NaOH × H_2O_2	15.003	3.809	3.9	0.017

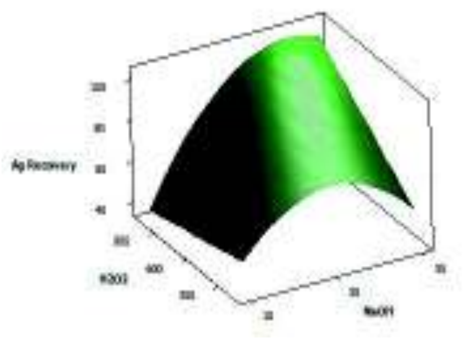

Figure 2. Surface plots for Ag recovery with respect to NaOH and H_2O_2

Furthermore, at high level of NaOH, the variation of Ag recovery due to the change of H_2O_2 volume is intensified; while at low level of NaOH the same change in H_2O_2 shows minor effect on Ag recovery.

3.3. Optimization of Ag recovery

Using the proposed second order polynomial model (equation 1) to interpolate within the levels of the two factors studied, the maximum recovery of Ag that can be achieved after 60 minutes of leaching of silver chloride, in a 3 L reactor running at 210 rpm is 0.98 under the following conditions: NaOH: 43.13 g and H_2O_2: 986.66 ml.

4 CONCLUSIONS

In the present study CCD coupled with RSM was used to study the interaction between factors in Ag recovery process from silver chloride using a 3–L agitated reactor with the following results:

- According to the statistically developed model, an increase in NaOH, H_2O_2 results in an increase in the Ag recovery. Also, it was found that NaOH and H_2O_2 have interaction with each other in the AgCl dissolution process.

- The effect of NaOH weight on the Ag recovery is more significant at high H_2O_2 volume. Moreover, there is a parabolic dependency between Ag recovery and NaOH variation at a fixed level of H_2O_2 Volume. Furthermore, at high level of NaOH, the variation of Ag recovery due to the change of H_2O_2 is intensified; while at low level of NaOH the same change in H_2O_2 shows minor effect on Ag recovery.

-The maximum recovery of Ag that can be achieved after 60 minutes of leaching of silver chloreide, in a 3 L reactor running at 210 rpm is 0.98 under the following conditions: NaOH: 43.13 g and H_2O_2: 986.66 ml.

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Harmful Components in Concentrated Phosphate and Methods of Their Djebel-Onk Algerie Example

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ABSTRACT The world phosphate industry is based on the commercial exploitation of certain deposits. Despite their extremely variable composition, phosphates are the commercial source of phosphorus used as feedstock for the manufacture of phosphate fertilizers and chemicals. The fertilizer industry consumes about 90 percent of the world production of phosphates (sulfuric acid, single superphosphate (SSP), phosphoric acid, triple superphosphate (TSP), ammonium phosphates and NPK). Phosphate is also used for industrial purposes and for the production of animal feed supplements and food products. Another important use is in the manufacture of elemental phosphorus and its derivatives, in particular sodium tripolyphosphate, an important component of detergents laundry. Most categories contain phosphates sold more than 30 percent P2O5 (65 percent of TPL). To meet this requirement, most phosphate ores undergo enrichment by washing and sieving, decarbonation.

All phosphates contain dangerous elements including heavy metals such as Cd, Cr, Hg and Pb, and radioactive elements, such as uranium (U), which are considered toxic to human and animal health. The contents of these dangerous elements vary widely among sources of phosphate and even in the same field. These additions are considered harmful. Among the hazardous heavy metals in phosphate fertilizers, cadmium is probably the most sought after, because of the potentially high toxicity to human health food from crops fertilized with phosphate fertilizers containing a significant amount of cadmium. In this study the possibility of experimenting with different leaching concentrates phosphates Djebel-Onk for the elimination of harmful elements. It has three distinct parts: The first part is a literature, the second part concerns the choice of solvents commonly used. The third part is dedicated to experiments leaching concentrates and treatment results. (BOUZENZANA. A 2007)

Keywords: Phosphate, TPL, harmful elements, hydrometallurgy, leaching

1. INTRODUCTION:

The phosphate indicates the product containing of phosphorus. Besides principal mineral containing of phosphorus, the layers of phosphates also contain additional minerals or impurities of gangue. Although considerable quantities of additional minerals and impurities are removed during enrichment, the enriched ore always contains a certain quantity of the impurities of origin.

The phosphate layers are distributed geographically and geologically in the whole world, and the very great supplyers in hand are able to satisfy the request calculated for a foreseeable future. The evaluations generally consider a total from 200 to 300 billion tons of phosphate of all the categories.

Approximately 80 percent of the worldwide productions of phosphate come from the deposits of marine sedimentary origin. The sedimentary phosphates are made up mainly of apatites. They present a great variation in their chemical composition and show a large range of properties consequently. In the sedimentary deposits, the principal phosphatic minerals are francolites (fluoroapatites microcrystalline carbonated), which are in partnership with a large variety of minerals.

The content of phosphate (or rank) is by convention expressed out of phosphorus pentoxide (P2O5). In the industry of phosphates, the content phosphate is usually expressed as a phosphate calcium and traditionally indicated under the name of BPL (Bone Phosphates lime = lime phosphate: P2O5 X 2.1853 = BPL) or (TPL: triple phosphates of lime). The manufacturers of phosphoric acid and phosphate fertilizer normally require a minimum content of 28 per cent of P2O5, and most of the categories of phosphates marketed contain more than 30 per cent of P2O5 (65 per cent of TPL). To meet this requirement, most of the phosphate ores undergo enrichment by washing and sieving, carbonate removal equipment will be provided, magnetic separation and flotation.

The results of a chemical analysis of the potentially dangerous elements in certain sedimentary phosphate samples are presented on table 1.

Table 1: Chemical analysis of the potentially dangerous elements in sedimentary phosphates

Countries	Deposit	Réactivity	**P_2O_5**	**As**	**Cd**	**Cr**	**Pb**	**Se**	**Hg**	**U**	**V**
			(%)	**(mg/kg)**							
Algéria	Djebel Onk	High	29,3	6	18	174	30	3	61	25	41
B Faso	Kodjari	Low	25,4	6	< 2	29	< 2	2	90	84	63
China	Kaiyang	Low	35,9	9	< 2	18	6	2	209	31	8
USA	Florida	Average	31,0	6	6	37	9	3	371	59	63
USA	Carolina	High	29,9	13	33	129	3	5	146	41	19
India	Mussoorie	Low	25,0	79	8	56	25	5	672	26	117
Jordan	El Hassa	Average	31,7	5	4	127	2	3	48	54	81
Mali	Tilemsi	Average	28,8	11	8	23	20	5	20	123	52
Maroccoo	Khouribga	Average	33,4	13	3	188	2	4	566	82	106
Niger	Parc W	Low	33,5	4	< 2	49	8	< 2	99	65	6
Péru	Sechura	High	29,3	30	11	128	8	5	118	47	54
Syria	Khneifiss	Average	31,9	4	3	105	3	5	28	75	140
Tanzania	Minjingu	High	28,6	8	1	16	2	3	40	390	42
Sénégal	Taïba	Low	36,9	4	87	140	2	5	270	64	237
Togo	Hahotoe	Low	36,5	14	48	101	8	5	129	77	60
Tunisia	Gafsa	High	29,2	5	34	144	4	9	144	12	27
Venezuela	Riecito	Low	27,9	4	4	33	< 2	2	60	51	32

The most toxic heavy metals including cadmium is probably Once deposited, cadmium is absorbed by plants, some of which are intended for human consumption, such as wheat or vegetables contaminated other plants used for food to animals then concentrate cadmium in their bodies. Offal (liver, kidney) are the edible parts of the animal that represent the greatest risk to humans Part of cadmium is found in the soil after the fertilizer was applied on agricultural land and the rest of cadmium are found in the waters. Cadmium can be transported over long distances when it is absorbed by the mud. This sludge rich in cadmium can both polluted surface water that soil.

Certain sources of Phosphate can contain a significant quantity of radioactive elements when one them compared to others, for example 25 mg uranium for phosphate of Djebel-Onk or 12 mg uranium per kilogramme of Phosphate of Gafsa (Tunisia) against 390 mg uranium are contained per kilogramme of phosphate of Minjingu (Tanzania). Questions are asked about the usage security of these phosphates.

2. CATCH AND PREPARATION OF THE SAMPLES

2.1 Sampling

Sampling is the process of choice and analysis of the samples. Analysis with always for object to determine the physical properties, the chemical composition and the content while composing useful in a matter to be controlled. A sample is part of substance, which has the characteristics of the matter to be analyzed. During the treatment, the mineralogical analysis of the sample makes it possible to know the structural characteristics and texturales, the composition of useful minerals and the character of association of the mineralogical components, their natural connection, the size of crystallization where dissemination.

The concentrates from the track dry and wet after drying are evacuated each one in a pile. Taking of about 1 kg is made at the end of the day for 5 days

$Q_{totale} = 1000 \times 5 = 5000g = 5kg$ Of each concentrate

For the transport each sample is packaged in a plastic bag, and then in a second bag to avoid losses during transport. (BOUZENZANA. A 2007)

2.2 Characterizations

2.2.1chemical composition of concentrated:

2.2.1.1Concentrated 66-68 % TPL. (Table 02 and 03)
2.2.1.2 Concentrated 69-72 % TPL.(Table 04 and 05)
2.2.1.3 Concentrated 73 – 75 % TPL. (Table 06 and 07)

2.2.2Grain-size distribution of the concentrated:
2.2.2.1 Concentrated 66-68TPL. (Table 08)
2.2.2.2 Concentrated 69-72 TPL (Table 09)
2.2.2.3Concentrated 73 -75 TPL (Table 10)

Table 2: Elements Major

Composants	Content of %
H_2O	0.5-0.6
Loss in ignition	1.2-1.5
P_2O_3	30.3-31
SO_3	2.4-2.9
CO_2	4.7-5.3
SiO_2	1.6-1.8
MgO	0.8-1.0
Fe_2O_3	0.3-0.4
Al_2O_3	0.4-0.5
Na_2O	0.6-0.7
K_2O	0.07-0.09
F	3.6-3.8
Organic matter	0.15-0.2
CaO	50.0-51.5
Cl	400 PPM

Table 4: Elements Major

Composants	Contend %
H_2O	0.2-0.3
Loss in ignition	0.6-0.8
P_2O_5	31.6-32.5
SO_3	2.3-2.6
CO_2	4.0-4.5
SiO_2	1.5-1.8
MgO	0.8-1.6
Fe_2O_3	0.3-0.35
Na_2O	1.1-1.3
Al_2O_3	0.4-0.47
K_2O	0.07-0.09
F	3.7-3.9
Organic matter	0.13-0.15
CaO	52.0-53.5
Cl	400 ppm

Table 3: Elements in trace

Composants	Content %
TiO_2	0.024 %
MnO	0.0012 %
Cd	18 ppm
Pb	35 ppm
Hg	5 ppm
Ni	25 ppm
Cu	30 ppm
Zn	160 ppm
Sb	10 ppm
As	10 ppm
Bi	20 ppm
U	40 ppm

Table 5: Elements in trace

Composants	Content %
TiO_2	0.026
MnO	0.0012
Cd	20 ppm
Pb	40 ppm
Hg	5 ppm
Ni	25 ppm
Cu	27 ppm
Zn	170 ppm
Sb	10 ppm
As	10 ppm
Bi	20 ppm
U	38 ppm

Table 6: Element Major

Composants	Content of %
H_2O	0.2 – 0.3
Loss in ignition	0.5 - 0.6
P_2O_3	33.4 – 34.3
SO_3	20. – 2.4
CO_2	1.5 – 2.0
SiO_2	1.2 -1.8
MgO	54.5 – 55.0
Fe_2O_3	0.08 – 1.01
Al_2O_3	0.3 -0.35
Na_2O	1.1 – 1.3
K_2O	0.4 – 0.47
F	0.04 – 0.06
Organic matter	3.8 – 4
CaO	0.1 – 0.12
Cl	200 PPM

Table 7: Elements in Trace

Composants	Content of %
TiO_2	0.024 %
MnO	0.0012 %
Cd	18 ppm
Pb	35 ppm
Hg	5 ppm
Ni	25 ppm
Cu	30 ppm
Zn	160 ppm
Sb	10 ppm
As	10 ppm
Bi	20 ppm
U	40 ppm

Table 8 :Grain-size distribution of the concentrated 66-68 % TPL.

Class (mm)	Weight (g)	partiel output(%)	Cumulated output $\Sigma\gamma\downarrow$(%)	Cumulated output $\Sigma\gamma\uparrow$(%)
- 1.56 +1.25	4.57	4.86	4.86	100
- 1.25 + 1.0	7.95	8.45	13.31	95.14
- 1.0 + 0.8	18.36	19.52	32.83	86.69
- 0.8 + 0.63	18.51	19.67	52.5	67.17
- 0.63 + 0.5	44.69	47.5	100	47.5
- 0.5 + 0.315	-	-		
- 0.315 + 0.2	-	-		
-0.2 + 0.125	-	-		
Total	94.08	100	-	-

Table 09: Grain-size distribution of the concentrated 69-72 % TPL.

Class (mm)	Weight (g)	Partial output (%)	Cumulated Output Σγ↓ (%)	Cumulated output Σγ↑ (%)
-1.56 + 1.25	5.47	5.76	5.76	100
-1.25 + 1	8.52	8.97	14.73	94.24
- 1 + 0.8	19.56	20.59	35.32	85.27
- 0.8 + 0.63	22.01	23.16	58.49	64.68
- 0.63 + 0.5	39.45	41.52	100	41.52
- 0.5 + 0.315	-	-		
- 0.315 + 0.2	-	-		
-0.2 + 0.125	-	-		
Total	95.01	100	-	-

Table 10 : Grain-size distribution of the concentrated 73 -75 % TPL.

Class mm	Weight g	partial output (%)	Cumulated output Σγ↓ (%)	Cumulated output Σγ↑ (%)
- 1.56 +1.25	5.1	5.53	5.53	100
- 1.25 + 1.0	7.78	8.44	13.97	94.47
- 1.0 + 0.8	19.53	21.2	35.17	86.03
- 0.8 + 0.63	20.04	21.76	56.93	64.83
- 0.63 +0.5	39.68	43.07	100	43.07
- 0.5 +0.315	-	-		
- 0.315 +0.2	-	-		
- 0.2 +0.125	-	-		
Total	92.13	100	-	-

2.2.3 Analysis by X-ray of the samples of phosphate

Interpretation of results:
After the peaks and the corresponding wavelengths in the diffractogrammes, one finds that for the phosphates:
* concentrated 66-68 % in TPL and 69-72 per cent in TPL, contain:

- The carbonates of magnesium (dolomite): Ca Mg $(CO_3)_2$.
- The calcium phosphate hydrate: Ca_3 $(PO_4)_2$. Carbonate
- The hydroxylapatite syn: Ca_{10} $(PO_4)_3$ $(CO_3)_3$ $(OH)_2$.

* Concentrated 73-75 % in TPL:
* Lack of carbonates of magnesium: the absence of the dolomite is due to the calcination and washing that cause

- The enrichment of phosphates with an increase of the content in TPL.
- The thermal destruction of carbonates (dolomite, calcite and magnesia), according to the reactions:
- Ca Mg $(CO_3)_2 \rightarrow CaCO_3$ + Mg CO_3.
- $CaCO_3 \longrightarrow CaO + CO_2$.
- Mg $CO_3 \longrightarrow MgO + CO_2$

  And after washing, we obtain:
- $MgO + H_2O \longrightarrow$ Mg $(OH)_2$.
- $CaO + H_2O \longrightarrow$ Ca $(OH)_2$.

3 TRACE ELEMENTS IN THE CONCENTRATES OF PHOSPHATES:

Table 11 : Summary table of the trace elements in the concentrates of "D-O"

	Eléments %			Eléments ppm									
	TiO_2	**MgO**	MnO	**Cd**	**Pb**	Hg	Ni	Cu	**Zn**	Sb	As	Bi	**U**
1	0,024	**1.61**	0.0012	**18**	**35**	5	25	30	**160**	10	10	20	**40**
2	0,026	**1.61**	0,0012	**20**	**40**	5	25	27	**170**	10	10	20	**38**
3	0,026	**1.01**	0,0012	**18**	**30**	5	25	27	**140**	10	10	20	**38**

1: 66 – 68 % TPL
2: 69 – 72 % TPL
3: 73- 75 % TPL

4. METHOD OF DISPOSAL OF HEAVY METALS AND CONDUCT OF EXPERIMENTS.

4.1 Theory. (Jean-François 2001)

Hydrometallurgy: Is a science still recent but currently very developed. Its importance in the development of non-ferrous metals is highlighted. The theoretical foundations of the hydrometallurgy are explicit.

Thermodynamics, Chemical kinetics and the electrochemistry which allow a better knowledge of the reaction process assignee are mentioned at the same time that their limits of use. An inventory of all the elementary operations allowing the constitution of the various known hydrometallurgic processes reveals the great diversity of the techniques of implementation and the requirements relating to chemical engineering.

Hydrometallurgy is the ore processing by chemical way in liquid phase. It applies to the rough ores and certain concentrates. Proceed hydrometallurgic expanded little by little they saw their applications industrial largely extending. They proved their interest in the ore processing to weak concentration, in that of the ores of which enrichment present of the difficulties, and in that of the ores which are not justiciable to physical processes of separation. Hydrometallurgy allows a true dissolution of metals by precipitation is by solvent or exchange of ions. Often for certain ores or concentrated, it is necessary to carry out a netting before the setting in solution called leaching.

A process hydrometallurgy often understands the following unit operations:

* The solution of the fraction of the ore which contains the chemical element to develop
* The purification and the concentration of solutions to treat
* The transformation to the metallic state

4.2 Leaching. (Loïc Guérin 2000)

It is the operation by which a compound or an element is solubilized in a liquid from its own solubility or by chemical reaction. Generally, one seeks a setting in solution as selective as possible metals to be extracted with a maximum concentration. The majority of the operations of leaching is held in acid medium, because the outputs of solubilization are there generally the best. The sulphuric acid is employed in the extraction of copper, zinc, cadmium, etc is generally preferred with hydrochloric acid is employed in the metallurgy of bismuth, tin, of the money, for reasons of price and aggressiveness. Other media are also employees, such as nitric acid, fluosilicique, etc. The contribution of an oxidant is sometimes necessary (placing in solution of metals, sulphides). One usually uses the air, oxygen, chlorine, manganese dioxide.

Hydrometallurgy is not unaware of the basic mediums such as soda (production of alumina), the sodium carbonate (production of uranium) or ammonia (production of nickel, of cobalt). Because of their selectivity, the basic mediums limit the operations of purification but generally give weaker outputs of extraction.

When a metal is soluble in acid environments as in the workplace basic, the nature of the gangue (acidic or basic) is a criterion of choice leading to limit to the maximum the consumptions in reagents. The selective leaching of solid particles is used to extract the metals from ores or the additions of concentrated harmful enrichment. One uses as solution of attack the acids, the alkaline ones or salts. The process of leaching consists of what the liquid (juice of attack) penetrates in the pores and dissolves the components to be extracted. Metals to dissociate pass in the solution diffused towards the surface of the body and goes in the principal mass of the liquid. Leaching is a process of mass transfer, its speed depends on several factors: forms, dimensions of the pores and the solid bodies, chemical composition etc

Choice of reagents of dissolution: The choice of solvent is determined by:

1) * selectivity of their reactions.

2)* Speed of dissolution of minerals.

3) * Rate of change of concentration and the temperature of the solution.

4) * Price of the solvent.

The study of the bibliographic research does not allow to determine of the solvents that are reliable and usable for this or that element, but on the other hand, we will limit the numbers of most solvents used in the leaching of metals in general and of heavy metals in particular has 4 (four) solvents which are:

1) The hydrochloric acid (HCl).

2) Sodium hydroxide (Na OH).

3) The sulfuric acid (H2SO4).

4) Nitric acid (HNO3).

4.3 Preparation of Solutions. . (Beatrice Levasseur 2005)

The water used in the preparation of solutions is distilled water.

a) Solution of hydrochloric acid, sulfuric acid and nitric acid: In a flask of 1000 ml, add 83 ml of acid in about 800 ml of distilled water and fill to the mark with water.

b) Solution of sodium hydroxide 0.1 N: Dissolve 2.0 g of NaOH in approximately 300 ml of water and complement to 500 ml with water.

4.4 Necessary Equipment for the Leaching:

a) Analytical Balance.
b) Series of beakers of 1 liter.
c) Graduated cylinder
d) Mechanical stirrer.
e) Vacuum filtration system.
F) Filter paper (0.45 µm) and funnel.
g) Oven at 60 ° ± 5 °C.

5 PREPARATION OF SAMPLES FOR THE LEACHING:

Samples of the three concentrated are of a particle size already fine and they do not require any prior reduction.

Conduct of the experience of the leaching:

• Weigh 20 g of solid sample (concentrated) and add 400 ml of solution (1 for 20) in a one-liter flask.

• Cap the bottle and shake on a mechanical shaker (speed 30 ± 2 rpm) for 8 hours.

• Leave the solution in the flask for 24 hours and stir manually time to time with a glass rod.

• After the leaching, decant the solid in order to facilitate the filtration.

• Filter on a filter having a porosity of 0.45 µm on a filtration system was empty.

• The cake obtained is dried in an oven for 8 hours.

• The concentrated and leached out more a gross sample of each concentrate are packed in plastic wobbling and send to the laboratory of pherphos unit of phosphate Djebel-Onk for analysis

Each type of concentrate (three concentrates) is subjected has the leaching of the four solutions with the result that the full number of the experiments is equal to 12.

6 RESULTS OF CHEMICAL ANALYZES:

Table 12: Results of chemical analyzes of the concentrated gross

Sample	P_2O_5 %	CO_2 %	CaO %	MgO %	Cd ppm	Zn ppm	Pb ppm
66-68 %	29.90	6.3	48.97	1.61	20	170	40
69-72 %	31.70	4.4	51.01	1.61	18	160	35
73-75 %	33.00	2.3	54.80	1.01	18	140	30

Results of the concentrated chemical detergents.

Table 13: Concentrated 66 - 68 % TPL

		MgO %	Cd ppm	Zn ppm	Pb ppm
	Rough sample	1.61	18	160	35
	(1)	1.81	23	170	50
solution	(2)	0.20	20	155	45
of leaching	(3)	0.20	8	10	5
	(4)	1.41	25	165	55

Table 14: concentrated 69 - 72 % TPL

		MgO %	Cd ppm	Zn ppm	Pb ppm
	Rough sample	1.61	18	160	35
	(1)	1.81	23	170	50
solution	(2)	0.20	20	155	45
of leaching	(3)	0.20	8	10	5
	(4)	1.41	25	165	55

Tableau 15: Concentrated 73 -75 % TPL

		MgO %	Cd ppm	Zn ppm	Pb ppm
	Rough sample	1.01	18	140	30
	(1)	0.75	11	125	29
Solution de	(2)	0.85	15	130	25
lixiviation	(3)	0.30	15	10	5
	(4)	1.90	20	60	50

7 INTERPRETATION OF RESULTS AND DISCUSSIONS.

It can be concluded with regard to this information:

* Additions harmful in samples treated with sulfuric acid (H2SO4) were significantly reduced compared to the other samples are treated with other solvents and to a lesser degree by hydrochloric acid.

* For cadmium the most harmful in concentrated phosphate has decreased by an average of over 50% compared to the crude concentrate (20 ppm is increased to 8 ppm).

* To lead is reduced on average by 85% compared to gross concentrated (35 ppm it is 5 ppm).

* For zinc we see a decrease of approximately 90% compared to raw concentrated (170 ppm it went to 10 ppm).

8 CONCLUSION.

* The hydrometallurgical treatment of concentrates obtained at different mining complex Djebel-Onk by dry and wet, eliminates heavy metals. these additions are considered harmful (thus penalizing merchants phosphate products across national and international), whether for the production of phosphate fertilizers or for the manufacture of phosphoric acid.

* The objective of this study is the hydrometallurgical treatment of concentrates by leaching. We try as much

as possible solvents and consequently the results of the chemical analysis of the products obtained, depending on the rate of reduction of heavy metals. We determine the most solvent blank. In our case it is sulfuric acid (H2SO4) which is the most powerful solvent from the viewpoint decrease harmful elements.

* Studies should be done to improve the quality of treatment by hydrometallurgical accurate determination of the concentration of H2SO4, and the solid-liquid ratio best suited for better dissolution of the elements and sought to facilitate the processing of the product obtained. Best suited for the treatment and make the most economical as well as the design of the pilot plant and industrial.

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Hydrochloric Acid Leaching of Ilmenite from Iranian Beach Placers

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ABSTRACT In This research an ilmenite concentrate by grading 44.5% TiO_2 was used as a raw material. This concentrate is obtained by concentration of Kahnooj beach placers ore containing 3.7% TiO_2 by combination of gravity and magnetic separation methods. The reduction of ilmenite concentrate was carried out using metallurgical coke with 10 % Wt. at different times and temperatures. The maximum reduction rate was occurred in 90 minutes retention time at 800 ºC. The effective parameters in hydrochloric acid leaching process were investigated and optimized. After reduction and iron removing by leaching, a residue containing about 77.70% TiO_2 with 88% recovery is obtained at optimal condition including 240 minutes leaching time, 90 ºC leaching temperature, 20% acid concentration, 10% solid percent and particle size of 140µ. The final reduced product was characterized using XRF, XRD and SEM.

Key word: Ilmenite, hydrochloric acid leaching, reduction, titanium dioxide.

1 INTRODUCTION

Titanium dioxide is an important intermediate in the manufacture of paints, pigments, welding-rod coatings, ceramics, papers, and in other areas of chemical industry (Diebold, 2003). The manufacture of pigment is via two main routes; namely, the sulfate route and the chloride route. Each of these two routes requires different feedstock.

One of the main commercial processes for the production of titanium dioxide pigment from ilmenite minerals is the Sulfate Process (Barksdale, 1966; Mackey, 1994; Lasheen, 2009). It accounts for about 40% of world production for pigment titanium dioxide (Adams et al., 1997; Wang et al., 2009; Liang et al., 2005). In response to increasing environmental pressures, numerous investigations have been carried out and innovative techniques developed to improve the process (Kamala et al., 2006; Smith et al., 2006; Kretschmer and Derler, 2004; Welham and Llewellyn, 1998).

The other main commercial process for the production of titanium dioxide pigment from ilmenite minerals is Chloride Process which utilizes rutile (TiO_2) as a raw material and presently enjoys more favorable economics and also generates less waste materials (Mackey, 1994)

In order to produce high grade TiO_2 feedstock for these two processes, we have to remove impurities such as iron with different methods.

According to Ogden (1961) and Stamper (1970), iron can be selectively removed from ilmenite ore by acid treatment. Some authors have indicated that the rate of ilmenite dissolution is strongly affected by both acid strength and the acid/ilmenite molar ratio (Jackson and Wadsworth, 1976; Hussein et al., 1976). Others have studied the kinetics of ilmenite dissolution in HCl (Van Dyk et al., 2002).

The acid consumption could be high in these processes but recent advances in acid regeneration technology from the spent leaching liquor have made acid leaching processes more attractive (Walpole, 1995; Newman and Balderson, 1993).

Recently, Mahmoud et al. (2004) have studied the treatment of Abu Ghalaga massive-type ilmenite ore to prepare synthetic rutile by HCl and in the presence of metallic iron. These authors indicated that the dissolved Fe^{3+} would be reduced to the Fe^{2+} state, improving the ilmenite dissolution.

Most leaching studies of ilmenite by hydrochloric acid were performed in order to obtain optimum conditions for upgrading the ilmenite into synthetic rutile. Addition of phosphate and fluoride to hydrochloric acid was found to enhance the leaching of ilmenite (Duncan and Metson 1982). The leaching of ilmenite has also been reported to occur at a much faster rate in alcoholic hydrochloric acid solutions than in aqueous ones (Girgin and Turker 1986, Girgin 1990).

The purpose of this research was to HCl leaching of the reduced concentrate in order to produce synthetic rutile and comparing two different conditions i.e., determination of conditions permitting maximum iron leaching with minimum possible titanium dissolution. For this target, reduction experiments of ilmenite concentrate was carried out using metallurgical coke with 10% Wt. at different times and temperatures; and a second series of leaching experiments was carried out with reduced ilmenite concentrate.

2 EXPERIMENTAL

2.1 Kahnooj Ilmenite Concentrate

The material used in this study was ilmenite concentrate of Kahnooj which was prepared by combination of gravity and magnetic separation methods.

The chemical and mineralogical compositions of these materials were carried out using X-ray fluorescence (XRF) and X-ray diffraction (XRD). Polished sections were studied using optical microscopy and scanning electron microscopy (Philips, model XL30). XRD pattern of ilmenite concentrate and its chemical composition analyzed by XRF are shown in Fig. 1 and Table 1, respectively.

Table 1. Results of XRF analysis of ilmenite concentrate

Composition	TiO_2	Total Fe	MnO	V_2O_5	P_2O_5	CaO	MgO	SiO_2	Al_2O_3	Cr_2O_3
Wt.%	44.5	46.1	0.83	0.26	0.21	0.68	3.76	2.57	0.58	0.42

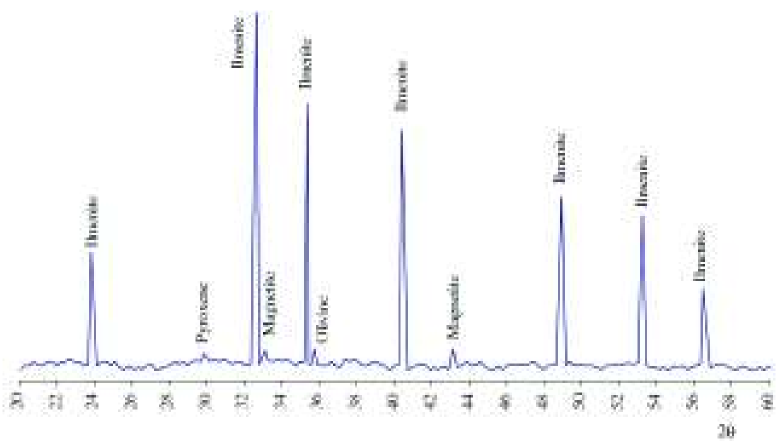

Figure 1. XRD pattern of ilmenite concentrate

The results indicate that the concentrate by grading of 44.5% TiO_2 contain about 90% ilmenite. The other minerals in the concentrate are magnetite and minor amount of hematite and some silicate minerals.

Back-scattered electron (BSE) images prepared using scanning electron microscopy is shown in figure 2.

Figure 2a shows the ilmenite-liberated grains in the concentrate. Also, some locked and free grains of gangue minerals such as pyroxene and olivine are observed. The content of gangue or rock-forming minerals (mainly pyroxene) in the concentrate does not exceed 5%. The other mineral which is observed in ilmenite concentrate is magnetite as locked particles. Figure 2b, c show that hematite is in the form of ex-solved lamellae, and particles range in size from 0.1 to 1 μm inside ilmenite. Hematite lamellae are generally considered to represent solid state ex-solution of originally homogeneous hematite–ilmenite solid solutions.

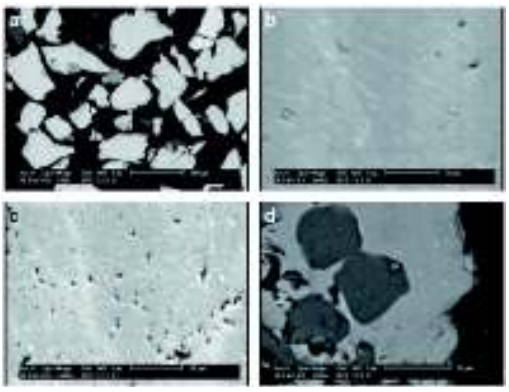

Figure 2. Mineralogical and textural features of ilmenite concentrate taken by SEM (BSE detector). **a** Ilmenite grains of concentrate and some locked and free grains of gangue minerals. **b** Hematite ex-solved lamellae inside ilmenite. **c** Hematite ex-solved fine particles inside ilmenite. **d** Apatite inclusion inside ilmenite

2.2 Leaching Procedure

Leaching tests were conducted in a 500 mL cylindrical glass reactor, with the slurry being agitated by a glass bladed overhead stirrer. The stirrer was rotated at a constant speed such that the ilmenite particles were completely suspended. The reactor was heated using a hotplate equipped with a temperature control (±2 ˚C) system.

For each run, 200 ml of HCl solution of predetermined molarity was charged into the reactor and heated to the required temperature. Thereafter, ilmenite concentrate was added to the reactor and the contents were well agitated. At the end of each leaching experiment, the slurry was filtered, washed with distilled water, and dried at 110˚C. The obtained filtrate was then analyzed for iron and titanium to calculate their leaching efficiencies by equation (1):

$$R = (N/M) \times 100 \quad (1)$$

In which N is iron/titanium content in filtrate (%), M is iron/titanium content in concentrate (%) and R is the leaching efficiency (%).

2.3 Reduction of Concentrate

According to reactions (2) and (3), in order to make all oxygen from Fe_2O_3 and FeO convert to CO, the molar ratio of C to double O ($n(C)/n(O_2)=2$) from iron oxides should be 2.

$$Fe_2O_3+3TiO_2+3C \rightarrow 2Fe+3TiO_2+3CO \quad (2)$$

$$FeO+TiO_2+C \rightarrow Fe+TiO_2+CO \quad (3)$$

According to that, the ilmenite-coke (10% Wt.) mixtures were adjusted for converting all the oxygen to carbon monoxide. The experiment was conducted in an electric furnace. The ilmenite-coke mixtures were heated in a ceramic crucible suspended in the air ambience furnace tube. When the experiments were finished, the samples were withdrawn from the furnace and mass loss was determined. XRD analysis of reduced concentrate was done and the result is shown in figure 3.

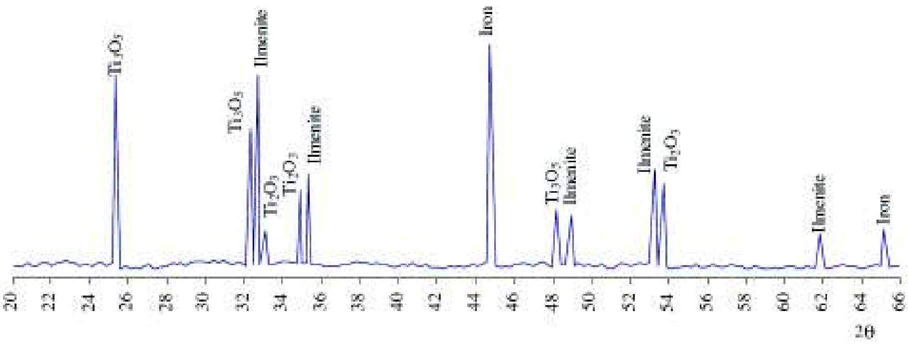

Figure 3. XRD pattern of reduced ilmenite concentrate

According to figure 3, XRD revealed the presence of phases such as $FeTiO_3$, Ti_3O_5, Ti_2O_3, and metallic iron. The back-scattered images of ilmenite reduction were obtained with SEM and are shown in figure 4. The light particles are metallic iron and iron carbide, which is produced by reduction of iron oxides at the earlier stages of reduction process. The partial reduction of Ti^{4+} to Ti^{3+}forming a secondary oxide phase also took place in this stage (figure 4a, b). With proceeding of reduction reactions, some Ti^{3+} is converted to Ti^{2+}.

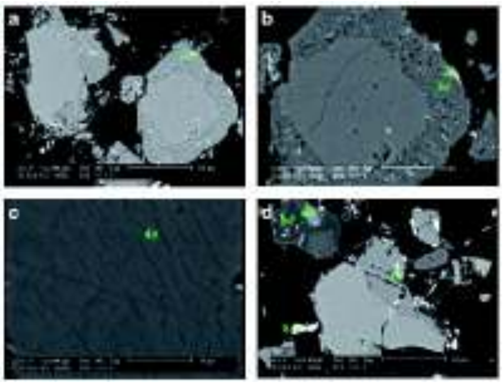

Figure 4. Mineralogical and textural features of reduced ilmenite concentrate taken by SEM (BSE detector). **a** Reduced particles of ilmenite. **b** Ilmenite reduction and formation of secondary oxide phase. **c** The oriented pits inside ilmenite due to reduction and forward out of hematite lamellae. **d** Reduction of ilmenite particles and forward out of metallic iron

Figure 4c shows that all of the hematite lamellae inside ilmenite disappeared and forwarded out as metallic iron due to its higher reduction kinetics than ilmenite and now appear as oriented pits. The reduction of ilmenite proceeded not only from grain boundaries but also from these pits. These oriented pits affect the reduction of ilmenite positively. So, the hematites lamellae do not have negative effects on next stages of titanium dioxide production and then chlorination process

3 RESULTS AND DISCUSSION

Several studies have been performed to illustrate the mechanism of ilmenite leaching in hydrochloric acid (Van Dyk et al., 2002; Lanyon et al., 1999; Jackson and Wadsworth, 1976; Sinha, 1984). Most of these studies include reduction or oxidation pretreatment. But here we will investigate the direct leaching of ilmenite concentrate and leaching of reduced ilmenite concentrate in order to compare the two conditions and also investigate the mineralogical and textural features of reduced ilmenite concentrate.

3.1 Leaching Of Ilmenite Concentrate

3.1.1 Effect of acid concentration

Several leaching experiments were performed using HCl, with concentrations varying from 10% to 25% (Wt.). In these experiments, leaching was performed at 105˚C for 180 min agitation and particle size of 140 microns using solid percent of 10%.

From the results obtained and plotted in Figure 5, it is clearly evident that, with increasing acid concentration, the total iron leaching efficiency increased steadily. On the other hand, the TiO_2 leaching efficiency was negligible. Thus, iron leaching from ilmenite mineral grains was directly correlated with the acid concentration. An increase in acid concentration favors higher iron removal from the structure lattice of the mineral.

Figure 6 indicates the effect of acid concentration on TiO_2 and Fe_2O_3 grades. As the acid concentration increases, the grade of Fe_2O_3 decreases but it has inverse effect on TiO_2 grade. The optimum acid concentration was obtained 20% Wt. of HCl acid.

3.1.2 Effect of time

Leaching experiments were carried out for different periods (120, 180 and 240 min) at 20% HCl concentration, 105˚C and solid percent of 10%. It is clear from figure 7 that increasing retention time decreased the rutile recovery but increases Fe removal efficiency. The selected optimum retention time was 240 min, corresponding to 84.24% and 59.30% for rutile recovery and Fe removal efficiency, respectively. Also figure 8 shows the effect of time on TiO_2 and Fe_2O_3grade.

3.1.3 Effect of temperature

The effect of temperature on the dissolution of titanium and iron was investigated in 20% HCl concentration with 140 µ particle size and solid percent of 10% at temperatures of 90, 100 and105 ˚C for 240 minutes. From the results shown in figure 9 and 10, it can be observed that both metals were largely dissolved at 90 ˚C. Tests at higher temperatures would be less suitable due to increased corrosion rates and loss of HCl vapor.

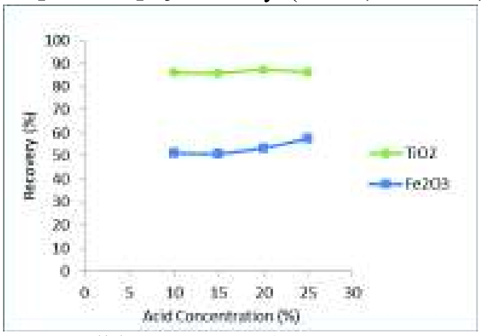

Figure 5. Effect of acid concentration on TiO_2 and Fe_2O_3 recovery (105˚C, 180 min, 140 µ, solid percent: 10%).

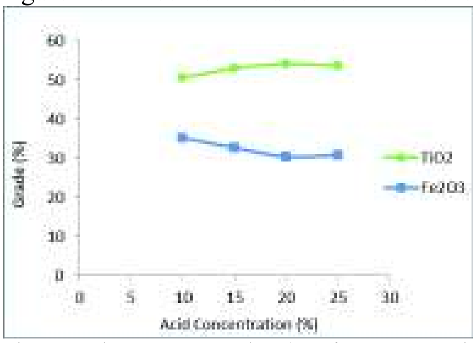

Figure 6. Effect of acid concentration on TiO_2 and Fe_2O_3 grade (105˚C, 180 min, 140 µ, solid percent: 10%).

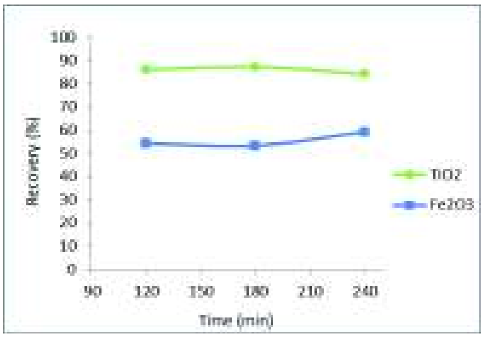

Figure 7. Effect of time on TiO_2 and Fe_2O_3 recovery (105˚C, 20% acid conc., 140 µ, solid percent: 10 %).

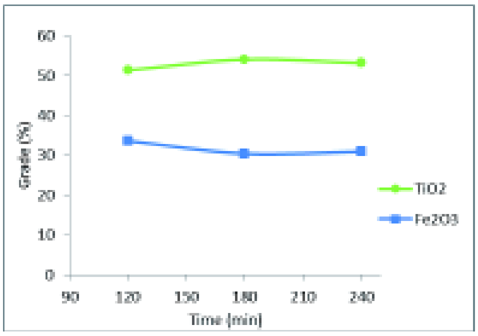

Figure 8. Effect of time on TiO_2 and Fe_2O_3 grade (105˚C, 20% acid conc., 140 µ, solid percent: 10%).

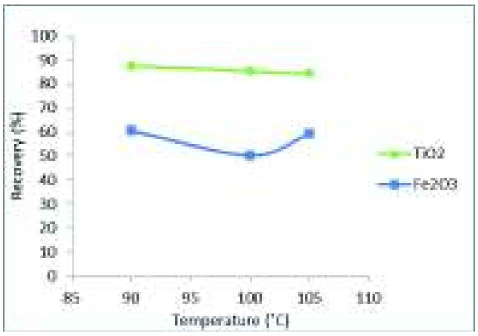

Figure 9. Effect of temperature on TiO_2 and Fe_2O_3 recovery (20% acid conc., 240 min, 140 µ, solid percent: 10%).

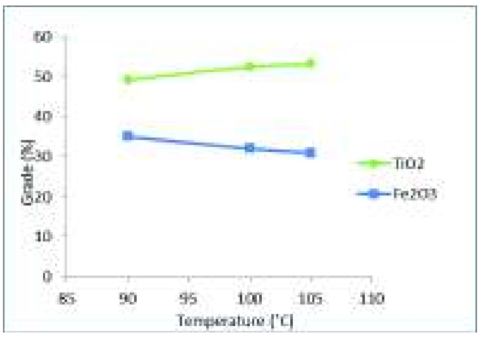

Figure 10. Effect of temperature on TiO_2 and Fe_2O_3 grade (20% acid conc., 240 min, 140 µ, solid percent: 10%).

3.1.4 Effect of particle size

The effect of particle size on the dissolution of titanium and iron was investigated in 20% HCl concentration at 105 ˚C, using three particle sizes: 75, 110, and 140 microns for 240 minutes. Based on figure 11, it is obvious that increasing the particle size does not bring about any perceptible increase in the dissolved iron and titanium percentage. While results presented in figure 12 show that the grade of TiO_2 and Fe_2O_3 are inversely proportional to the average initial diameter of the particles.

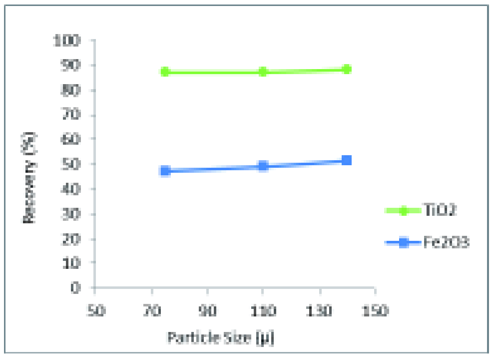

Figure 11. Effect of particle size on TiO_2 and Fe_2O_3 recovery (20% acid conc., 240 min, 105˚C, solid percent: 10%).

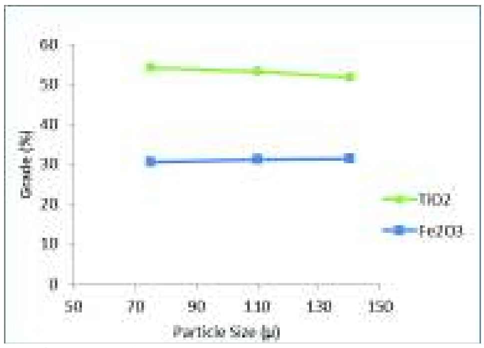

Figure 12. Effect of particle size on TiO_2 and Fe_2O_3 grade (20% acid conc., 240 min, 105˚C, solid percent: 10%).

3.1.5 Effect of solid percent

The effect of solid percent on recovery and grade of TiO_2 and Fe_2O_3 was also studied using 20% acid concentration directly as illustrated in figures 13 and 14. It was found that an increase of the initial solid percent would increase the acid content and in turn the acid/ilmenite ratios, which would have a great influence upon both iron and titanium dissolution. From the results shown in figure 13, it appears that the rates of dissolution of titanium are low for the lower solids content, but the rate is higher at the highest solids content. It is obvious that the dissolution of iron in 10% solid percent is more than other amounts so 10% solid percent considered as optimum level.

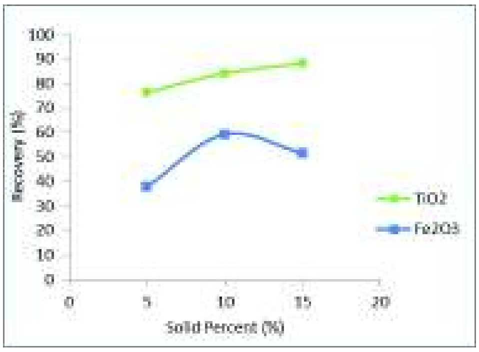

Figure 13. Effect of solid percent on TiO_2 and Fe_2O_3 recovery (20% acid conc., 240 min, 105˚C, 140 µ).

3.2 Leaching Of Reduced Ilmenite

From the results of leaching under normal conditions, it is clearly evident that, although almost complete dissolution of Ti has been realized, iron leaching efficiency did not exceed about 40%. Failure to improve iron removal beyond about 40% under these conditions required reduction of ilmenite concentrate. This view is based on the assumption that the leached iron is in the bivalent state in the ilmenite concentrate. In other words, although both Fe (II) and Fe (III) form soluble chlorides, but the Fe (III) doesn´t tend to leaching.

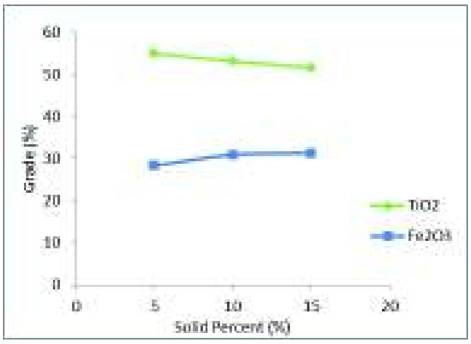

Figure 14. Effect of solid percent on TiO_2 and Fe_2O_3 grade (20% acid conc., 240 min, 105˚C, 140 µ).

3.2.1 Effect of reduction on TiO_2 and Fe_2O_3 recovery

Figures 15 and 16 show the effects of reduction temperature and time on TiO_2 and Fe_2O_3 recovery. It concluded that reduction of iron in 800 ˚C for 90 minutes cause better dissolution of iron. The recovery of TiO_2 and removing iron were obtained 88% and more than 80%, respectively.

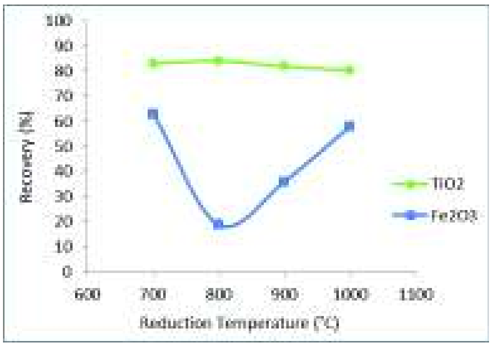

Figure 15. Effect of reduction temperature on TiO_2 and Fe_2O_3 recovery (leaching condition: 20% acid conc., 240 min, 90 ˚C, 140 µ).

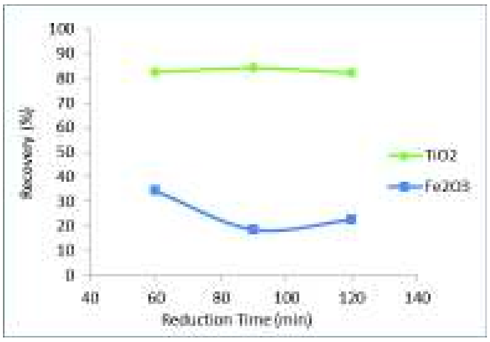

Figure 16. Effect of reduction time on TiO_2 and Fe_2O_3 recovery (leaching condition: 20% acid conc., 240 min, 90 ˚C, 140 µ).

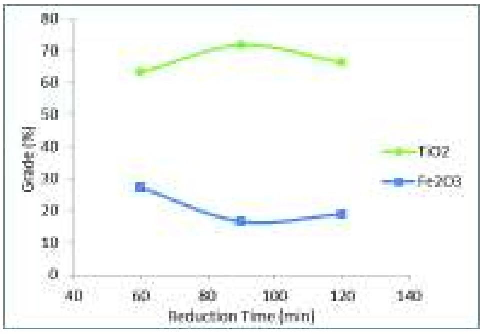

Figure 18. Effect of reduction time on TiO_2 and Fe_2O_3 grade (leaching condition: 20% acid conc., 240 min, 90 ˚C, 140 µ).

3.2.2 Effect of reduction on TiO_2 and Fe_2O_3 grade

Figures 17 and 18 show the effects of reduction temperature and time on TiO_2 and Fe_2O_3 recovery. As can be seen from the figures the optimum temperature and time of reduction cause impressive effect on leaching efficiency mainly grade of TiO_2 in residue. As it clear the grade of Fe_2O_3 is reduced mainly in optimum conditions of reduction.

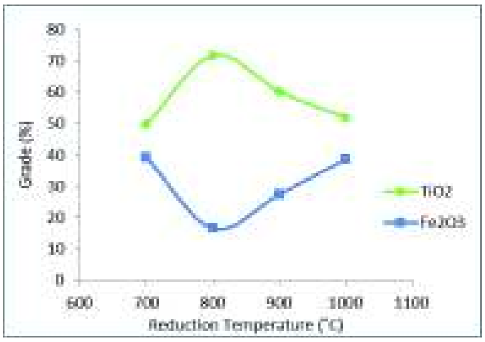

Figure 17. Effect of reduction temperature on TiO_2 and Fe_2O_3 grade (leaching condition: 20% acid conc., 240 min, 90 ˚C, 140 µ).

4 CONCLUSIONS

The optimization of HCl leaching parameters of Kahnooj ilmenite concentrate has been studied. High acid concentration and pre-reduction of concentrate facilitate the removal of iron from the concentrate and avoid titanium dissolution. The study and comparing of mineralogical features of ilmenite concentrate was also done before and after reduction. Finally the leaching test of reduced concentrate in 800 ºC for 90 minutes, was done under optimum conditions of leaching parameters including 240 minutes leaching time, 90 ºC leaching temperature, 20% acid concentration, 10% solid percent and particle size of 140µ. The product was a residue containing about 77.70% TiO_2 with 88% recovery.

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Asetik Asit/Amonyum Asetat Çözeltilerinde Malahit Cevherinin Liç Özelliklerinin İncelenmesi

Examination of Leaching of Malachite Ore in Acetic Acid/Ammonium Acetate Solutions

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ÖZET Organik asitler son yıllarda bazı cevherlerin hidrometalurjik yöntemle işlenmesinde liç reaktifi olarak kullanılmaktadır. Bu çalışmada asetik asit ile amonyum asetat içeren çözeltilerin malahit cevherinin liç işleminde kullanılabilirliği incelenmiştir. Asetik asit/amonyum asetat oranı, sıcaklık, katı/sıvı oranı ve tane boyunun malahit cevherinin liç hızına olan etkileri araştırılmıştır. Asit derişiminin fazla tuz derişiminin ise düşük olduğu durumda liç veriminin daha yüksek olduğu belirlenmiştir. Malahit cevherindeki bakırın hemen hemen tamamının çözelti ortamına geçtiği tespit edilmiştir. Liç prosesinin kinetik analizi yapılmış ve ürün tabakasından difüzyon kontrollü modele uyduğu bulunmuştur.

ABSTRACT Organic acids have been used as leach reagent in hydrometallurgical processing of some ores in recent years. In this study, the usability of the solutions containing acetic acid and ammonium acetate for the leaching of malachite ore was investigated. The effects of acetic acid/ammonium acetate ratio, temperature, solid to liquid ratio, and particle size on the leaching rate of malachite ore were examined. It was determined that the leaching efficiency was higher in case of high acid and low salt concentrations. It was determined that almost all copper in malachite ore was passed into solution medium. The kinetic analysis of the leaching process was done, and it was found that it followed the diffusion model through the product layer.

1 GİRİŞ

Bazik karakterli cevherlerin liçinde kuvvetli asitlerin kullanılması durumunda cevher matrisinde bulunan başta demir olmak üzere bazı safsızlıkların da çözünerek çözeltiye geçtiği ve kirlilik oluşturdukları bilinmektedir. Bu safsızlıkları uzaklaştırmak için uygulanan ayırma ve saflaştırma işlemlerinin sayısının mümkün olduğu kadar az olması prosesin ekonomisini yakından etkilemektedir. Bazik karakterli cevherlerin çözündürülmesinde hafif asidik veya bazik liç reaktiflerinin kullanılması bu bakımdan bazı avantajlar sağlayabilir. Bu amaçla son yıllarda organik asitler gibi zayıf asitlerin çeşitli cevherlerin hidrometalurjik olarak işlenmesinde çözücü olarak kullanıldığı görülmektedir (Alkan ve Doğan, 2004; Demir vd., 2006; Şengül vd., 2006; Hurşit vd., 2009; Ekmekyapar vd., 2010).

Malahit bazik karaktere sahip oksitli bir bakır cevheridir. Değişik kaynaklardan elde edilen malahit cevherleri genellikle düşük tenörlü olmalarına rağmen sülfürlü bakır cevherlerine alternatif olarak bakır üretiminde kullanılabilir. Bunun için ilk olarak malahit cevherinin uygun bir çözücü yardımıyla liç edilmesi gerekir. Farklı bileşimlere sahip malahit cevherlerinin çözündürülmesinde bazı avantajlarından dolayı özellikle amonyak içeren çözeltilerin liç reaktifi olarak kullanıldığı görülmektedir

(Künkül vd., 1994; Ekmekyapar vd., 2003; Bingöl vd., 2005; Ekmekyapar vd., 2012).

Asetik asit zayıf bir organik asit olup sulu çözeltileri bazı cevherler için çözücü olarak kullanılmıştır (Özmetin vd., 1996; Laçin vd. 2005; Ekmekyapar vd., 2008). Bunun yanı sıra asetik asidin bir tuzu olan amonyum asetat nötral bir karaktere sahiptir ve liç işlemlerinde özellikle bazik cevherler için çözücü olarak kullanılabilir (Demirkıran, 2008). Önceki çalışmalarımızda bu iki kimyasal madde malahit cevherinin çözündürülmesinde kullanılmıştır (Tanaydın, 2010; Gulezgin, 2010). Özellikle düşük derişime sahip asetik asit çözeltilerinde malahit cevheri çözündükçe çözeltinin pH değerinde bir artış olduğu ve reaksiyon hızının yavaşladığı gözlenmiştir. Amonyum asetatlı ortamda ise çözeltilerin pH değerlerinin yüksek olduğu, çözünme için uzun süreler gerektiği ve fazla madde harcandığı belirlenmiştir. Bu iki çalışmadan elde edilen bulgulardan hareketle asetik asit ve amonyum asetat tampon çözeltilerinde malahitin çözündürülmesinin sabit pH değerlerinde (hafif asit ortamlarda) yapılmasının hem reaksiyon kinetiği hem daha az madde harcanması ve asetik asitli ortama göre daha temiz bir liç çözeltisi elde edilmesi bakımından avantajlı olabileceği düşünülmüştür.

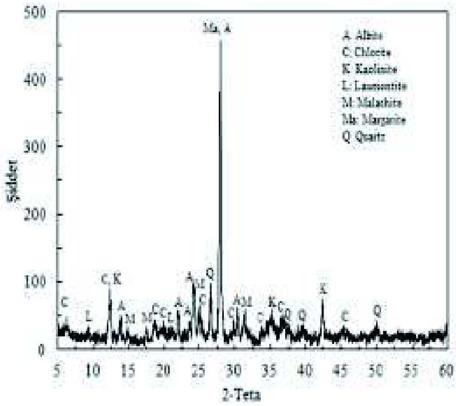
Böylece, bu çalışmada asetik asit ve amonyum asetat içeren sulu çözeltiler kullanılarak malahit cevherinin liç özellikleri incelenmiştir.

2 DENEYSEL ÇALIŞMA

Deneylerde kullanılan malahit cevheri Elazığ bölgesinden temin edilmiştir. Cevher kırılıp öğütüldükten sonra faklı tane boyuna sahip örnekler elde etmek için standart eleklerle elenmiştir. Cevherin kimyasal analizi yapılmış ve %46.40 SiO_2, %17.00 Al_2O_3, %7.30 MgO, %6.87 Fe_2O_3, %5.20 CuO, %3.30 CaO, %2.30 Na_2O, %3.63 diğer oksitler olarak belirlenmiştir. Cevherin 800 °C'de yapılan kızdırma kaybı sonucunda %8.00'lik bir kütle kaybı tespit edilmiştir. Deneylerde kullanılan malahit cevherine ait X-ray grafiği Şekil 1'de verilmiştir.

Liç deneyleri 1 L hacimli ceketli bir cam reaksiyon kabında yapılmıştır. Asetik asit ve amonyum asetat derişimleri bilinen çözeltilerin 500 mL'si reaktöre konulduktan sonra sıcaklık değerinin çalışılacak olan sıcaklığa ulaşması için beklenmiş ve daha sonra bilinen miktarlarda malahit örnekleri reaktöre ilave edilmiştir. Reaktör içeriği bir mekanik karıştırıcı vasıtasıyla belirlenen karıştırma hızlarında karıştırılmış ve çeşitli zamanlarda çözeltiden örnekler alınarak cevherden çözeltiye geçmiş olan bakır miktarı kompleksometrik yöntemle belirlenmiştir. Çözeltiye geçen ve cevherdeki bakır miktarları arasındaki orandan bakırın çözünme kesri (X) hesaplanmıştır.

Asetik asit ve amonyum asetat derişimi, reaksiyon sıcaklığı, tane boyu ve katı/sıvı oranı gibi bazı parametrelerin cevherin çözünürlüğü üzerine olan etkileri incelenmiştir. Elde edilen deneysel verilere heterojen reaksiyon modelleri uygulanarak kinetik analiz yapılmıştır.



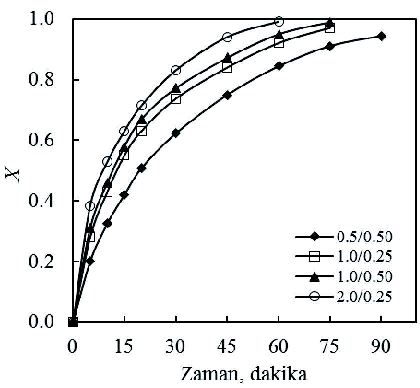
Şekil 1. Çalışmada kullanılan malahit cevherinin XRD grafiği

3 SONUÇLAR VE TARTIŞMA

3.1 Konsantrasyon Etkisi

Malahit cevherinin çözünürlüğü üzerine CH_3COOH-CH_3COONH_4 derişiminin etkisi farklı derişimlerde asetik asit ve amonyum asetat içeren çözeltiler kullanılmak suretiyle incelenmiştir.

Bu deneyler, asetik asit ve amonyum asetat derişimlerinden biri sabit tutulurken diğerinin derişiminin değiştirilmesi suretiyle yapılmıştır. Hazırlanan çözeltilerin başlangıç pH değerleri, çözelti hazırlanmasında kullanılan kimyasal madde miktarları ve deneyler sırasında belirlenen çözünürlük değerleri dikkate alındığında asetik asit derişiminin yüksek, amonyum asetat derişiminin ise düşük olduğu çözeltilerin kullanılmasının daha uygun olduğu belirlenmiştir. Her iki kimyasalın derişimininde yüksek olduğu durumlarda çözünürlükte azalma olduğu gözlenmiştir. Elde edilen deneysel sonuçlardan malahit liçi için asetik asit/amonyum asetat derişimi oranı 0.5/0.5, 1/0.25, 1/0.5 ve 2/0.25 (M/M) olan çözeltilerin kullanılmasının daha uygun olabileceği sonucuna varılmıştır. Bu çözeltilerin başlangıç pH değerleri sırasıyla 4.63, 4.11, 4.33 ve 3.87 olduğu ve deneyler sonunda bu pH değerlerinde önemli bir değişimin olmadığı belirlenmiştir. Malahitin çözünürlüğü üzerine derişim etkisinin incelendiği deneylerde reaksiyon sıcaklığı, ortalama tane boyu, karıştırma hızı ve katı/sıvı oranı ise sırasıyla 50 °C, 120 µm, 450 rpm ve 2/500 g/mL değerlerinde sabit tutulmuştur. Belirtilen derişim değerlerinde elde edilen deneysel sonuçlar Şekil 2'de verilmiştir.

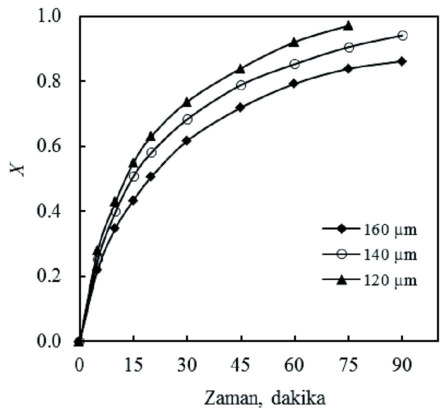


Şekil 2. Malahitin çözünürlüğüne asetik asit/amonyum asetat derişim oranının etkisi

Asetik asit/amonyum asetat oranının 2/0.5 olduğu çözeltilerle yapılan deneylerde 60 dakikalık sürede % 99.12 çözünürlüğe ulaşılmıştır. Derişim oranları 1/0.25 ve 1/0.5 olan çözeltilerle elde edilen çözünme değerlerinin birbirine oldukça yakın olduğu belirlenmiştir. Bu derişim oranları için 75 dakikalık sürede çözünürlük değerleri sırasıyla %97.05 ve %98.20 olarak tespit edilmiştir. 0.5/0.5 derişim oranına sahip çözelti için ise 90 dakikalık sürede %95.31 çözünürlük değerine ulaşılmıştır. Kullanılan kimyasal madde miktarları ve ulaşılan çözünürlük değerleri dikkate alındığında asetik asit/amonyum asetat oranı 1/0.25 olan çözeltilerin liç işleminde kullanılmasının prosesin ekonomisi açısından daha uygun olacağı ifade edilebilir. Bu sebepten, diğer deneylerde asetik asit/amonyum asetat derişim oranı 1/0.25 olan çözeltiler kullanılmıştır.

3.2 Tane Boyunun Etkisi

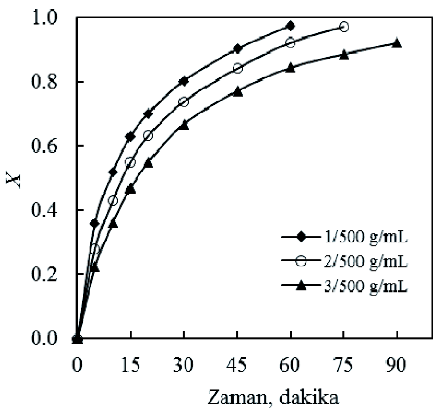
Malahitin çözünürlüğü üzerine ortalama tane boyunun etkisi 120, 140 ve 160 µm'lik örnekler kullanılarak incelenmiştir. Bu deneylerde asetik asit/amonyum asetat derişim oranı, reaksiyon sıcaklığı, karıştırma hızı ve katı/sıvı oranı sırasıyla 1/0.25, 50 °C, 450 rpm ve 2/500 g/mL değerlerinde sabit olarak alınmıştır. Bu deneylerden elde edilen sonuçlar Şekil 3'de gösterilmiştir. Deney sonuçlarına göre tane boyunun azalmasıyla malahitin çözünürlüğünün arttığı belirlenmiştir. Tane boyu azaldıkça yüzey alanının artması sebebiyle çözünürlük değerinin yükselmesi beklenen bir sonuçtur.



Şekil 3. Malahitin çözünürlüğüne tane boyunun etkisi

3.3 Katı/Sıvı Oranının Etkisi

Katı/sıvı oranı birim hacim başına düşen katı miktarıyla ilişkili olup prosesin ekonomisini etkileyebilecek önemli bir parametredir. Bu sebeple liç çalışmalarında sıklıkla incelenir ve genellikle katı/sıvı oranının azalmasıyla çözünme hızında artış gözlenir. Bu çalışmada, malahit cevherinin liçi üzerine katı/sıvı oranının etkisi 1/500 g/mL, 2/500 g/mL ve 3/500 g/mL değerlerinde incelenmiştir. Deneylerde derişim oranı 1/0.25, sıcaklık 50 °C, karıştırma hızı 450 rpm ve ortalama tane boyu 120 µm olarak alınmıştır. Şekil 4'de verilen sonuçlardan katı/sıvı oranının azalmasıyla malahitin çözünürlüğünün arttığı görülmektedir.



Şekil 4. Malahitin çözünürlüğüne katı/sıvı oranının etkisi

3.4 Reaksiyon Sıcaklığının Etkisi

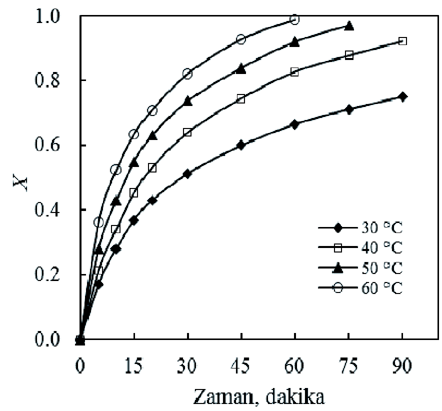
Kimyasal reaksiyonların hızları genellikle sıcaklığın artmasıyla artar. Derişim oranı 1/0.25, karıştırma hızı 450 rpm, ortalama tane boyu 120 µm ve katı/sıvı oranı 2/500 g/mL değerlerinde sabit tutularak, malahitin cevherinin çözünürlüğüne sıcaklığın etkisi 30, 40, 50 ve 60 °C değerlerinde incelenmiştir. Bu deneyler sonucunda elde edilen veriler Şekil 5'de gösterilmiştir. Şekilden görüleceği gibi reaksiyon sıcaklığının artmasıyla malahit cevherinden bakırın çözünme hızının arttığı görülmektedir.

3.5 Liç Kinetiği

Liç reaksiyonları heterojen reaksiyonlar olduğundan bu tür reaksiyonların kinetik analizi genellikle katalitik olmayan heterojen reaksiyon modelleri kullanılarak yapılır. Liç reaksiyonları çoğu zaman akışkan filminden difüzyon, kimyasal reaksiyon veya ürün tabakasından difüzyon modellerinden birine uyar. Bu çalışmada elde edilen deneysel verilere yukarıda sözü edilen modeller uygulandığı zaman ürün tabakasından difüzyon modeline uyduğu belirlenmiştir. Bu model için matematiksel ifade eşitlik 1'de verilmiştir.

$$1\text{-}3(1\text{-}x)^{2/3}+2(1\text{-}x)=k.t \qquad (1)$$

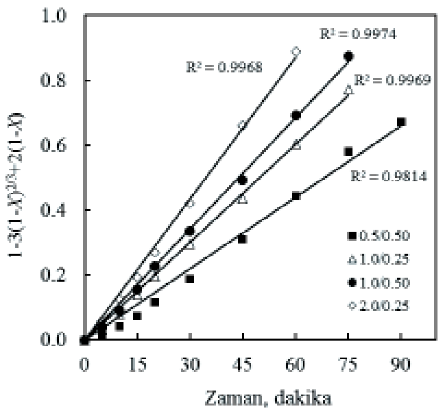
Bu eşitlikte x dönüşüm kesrini, k reaksiyonun görünür hız sabitini ve t reaksiyon süresini temsil etmektedir. Eşitlik 1'in sol tarafının zamana karşı grafiğinin çizilmesiyle yüksek korelasyon katsayılı düz doğrular elde edilmiştir. Bu grafik Şekil 6'da gösterilmiştir.



Şekil 5. Malahitin çözünürlüğüne sıcaklığın etkisi

YORUM VE ÖNERİLER

Bakır yüksek elektrik iletkenliği özelliği sebebiyle teknolojinin en çok kullandığı metallerden biridir. Günümüzde modern hayatın vaz geçilmez parçaları haline gelen elektronik cihazların çeşitliliğinin ve sayısının artması başta bakır olmak üzere birçok metalin kullanımını arttırmış ve buna bağlı olarak metal fiyatları yükselmiştir. Metalik bakırın öneminden başka, bazı bakır bileşiklerinden de tarımsal uygulamalardan katalizör olarak kullanılmalarına kadar çok geniş bir alanda faydalanılmaktadır. Bu sebeple bakırın yanı sıra ülkemizin sahip olduğu diğer metal kaynaklarının da değerlendirilerek kullanılabilir ürünlere dönüştürülmeleri ve ekonomiye kazandırılması gerektiği açıktır. Literatürde oldukça düşük bakır içeriğine sahip olan cevherlerin bile değerlendirildiği görülmektedir. Liç işlemi hidrometalurjik işlemlerin ilk basamağını oluşturmaktadır. Böylece, değişik kaynaklardan temin ettiğimiz bakır cevherlerinin liçi üzerindeki çalışmalarımızdan biri olan bu çalışmanın ilerleyen dönemde geliştirilerek çeşitli bakır bileşiklerinin laboratuvar ölçeğinde üretilmesi hedeflenmektedir.



Şekil 6. Farklı derişim oranları için ürün filminden difüzyon model grafiği

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Amonyak/Amonyum Klorür Çözeltilerinde Malahit Cevherinin Liçinin İncelenmesi

Examination of Leaching of Malachite Ore in Ammonia/Ammonium Chloride Solutions

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ÖZET Bu çalışmada, oksitli bir bakır cevheri olan malahitin amonyak/amonyum klorür çözeltilerinde liçi incelenmiştir. Malahitin liçi üzerine reaksiyon sıcaklığı, amonyak ve amonyum klorür derişimi ile karıştırma hızının etkileri araştırılmıştır. Elde edilen bulgulara göre, amonyak/amonyum klorür oranının cevherin çözünmesi üzerinde önemli bir etkiye sahip olduğu belirlenmiştir. Sıcaklığın artmasıyla çözünme hızının arttığı, karıştırma hızının ise önemli bir etkiye sahip olmadığı gözlenmiştir. Heterojen reaksiyon modelleri uygulanarak liç prosesinin kinetik analizi yapılmış ve karışık kinetik modele uyduğu tespit edilmiştir. Liç reaksiyonunun düşük sıcaklıklarda difüzyon kontrollü, yüksek sıcaklıklarda ise kimyasal reaksiyon kontrollü olduğu belirlenmiştir. Bu iki basamak için aktivasyon enerjileri sırasıyla 19.5 ve 50.8 kJ/mol olarak hesaplanmıştır.

ABSTRACT In this work, the leaching of malachite, an oxidized copper ore, in ammonia/ammonium chloride solution was studied. The effects of the reaction temperature, ammonia and ammonium chloride concentration, and stirring speed on the leaching of malachite were examined. According to findings obtained, it was determined that ammonia/ammonium chloride ratio has a considerable effect on the dissolution of ore. It was observed that the dissolution rate increased with increasing temperature, and the stirring speed has not a considerable effect. The kinetic analysis of the leaching process was performed by applying the heterogeneous reaction models, and it was found that the leaching reaction followed the mixed kinetic controlled model. It was determined that the leaching reaction was controlled by diffusion at low temperatures, while it was controlled by chemical reaction at high temperatures. The activation energies for two consecutive mechanisms were calculated to be 19.5 and 50.8 kJ/mol, respectively.

1 GİRİŞ

Düşük tenörlü cevherlerin hidrometalurjik yöntemle işlenmesi pirometalurjik yönteme göre daha avantajlı olmaktadır. Sülfürik asit ucuzluğundan dolayı birçok cevherin hidrometalurjik olarak değerlendirilmesinde çoğu zaman tercih edilen bir liç ajanıdır. Ancak sülfürik asit kullanıldığı durumlarda cevherlerin içerdikleri gang mineralleri de çözünmekte ve safsızlık oluşturan türlerde çözelti ortamına geçmektedir. Bu durumda, istenen metali kazanmak için uygulanacak olan saflaştırma proseslerinin sayısı artabilir ve prosesin ekonomisi bundan olumsuz yönde etkilenebilir. Hidrometalurjik proseslerde alternatif liç reaktiflerinin kullanılmasına yönelik çalışmalarda amonyak ve bileşiklerinin oldukça fazla kullanıldığı görülmektedir. Amonyağın bir çok metal iyonu ile kompleks oluşturması ve sağladığı yüksek pH değerleri ile amonyak bileşiklerinin çözeltilerinin sahip olduğu hafif asidik özellik liç işlemlerinde bazı avantajlar sağlayabilir. Özellikle demir iyonlarının liç esnasında hidroksit halinde çökmesi daha temiz bir liç çözeltisi elde edilmesine imkân tanımaktadır (Bingöl ve Canbazoğlu, 2004; Ekmekyapar vd. 2003; Ekmekyapar vd., 2012).

Malahit cevheri oksitli bir bakır cevheri olup, sülfürlü bakır cevherine alternatif bakır kaynakları olarak değerlendirilebilirler. Günümüzde yüksek tenörlü sülfürlü bakır cevherlerinin azalmış olması, malahit gibi bakır cevherlerin işlenmesini zorunlu hale getirmiştir. Dolayısıyla düşük tenörlü olsa bile malahit türü cevherlerin ve bakır içeren çeşitli atıkların hidrometalurjik metotlarla işlenmesine yönelik çalışmaların sayısında artış olmuştur. Literatürde, malahitin cevherinin liçi için çeşitli liç reaktifleri kullanılmıştır. Bu çözücüler içerisinde amonyak içeren çözeltilerin daha fazla olduğu görülmektedir (Künkül vd., 1994; Arzutuğ vd., 2004; Bingöl vd., 2005; Ekmekyapar vd. 2003; Ekmekyapar vd., 2012).

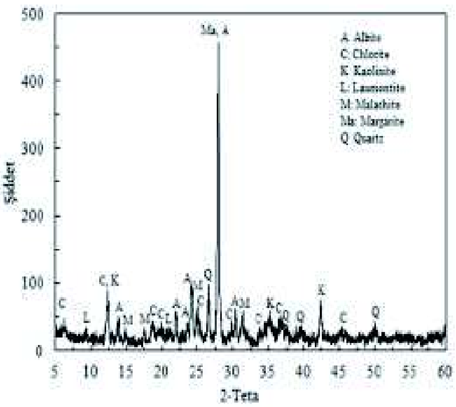
Bu çalışmada, malahit cevherinin amonyak-amonyum klorür içeren sulu çözeltilerde liçi incelenmiş ve kinetik analiz yapılmıştır.

2 DENEYSEL ÇALIŞMA

Deneylerde kullanılan malahit cevheri Elazığ bölgesinden temin edilmiştir. Cevher kırılıp öğütüldükten sonra farklı tane boylarına sahip örnekler elde etmek için standart eleklerle elenmiştir. Cevherin kimyasal analizi yapılmış ve %46.40 SiO_2, %17.00 Al_2O_3, %7.30 MgO, %6.87 Fe_2O_3, %5.20 CuO, %3.30 CaO, %2.30 Na_2O, %3.63 diğer oksitler olarak belirlenmiştir. Cevherin 800 °C'de yapılan kızdırma kaybı sonucunda %8.00'lik bir kütle kaybı tespit edilmiştir. Deneylerde kullanılan malahit cevherine ait X-ray grafiği Şekil 1'de verilmiştir. Şekilden görüleceği gibi cevher, kuvars ve malahitin yanı sıra sodyum alüminyum ve kalsiyum alüminyum silikatlardan oluşmaktadır.

Liç deneyleri 1 L hacimli ceketli bir cam reaksiyon kabında yapılmıştır. NH_3-NH_4Cl derişimleri bilinen çözeltilerin 500 mL'si reaktöre konulduktan sonra sıcaklık değerinin çalışılacak olan sıcaklığa ulaşması için beklenmiş ve daha sonra bilinen miktarlarda malahit örnekleri reaktöre ilave edilmiştir. Reaktör içeriği bir mekanik karıştırıcı vasıtasıyla belirlenen karıştırma hızlarında karıştırılmış ve çeşitli zamanlarda çözeltiden örnekler alınarak cevherden çözeltiye geçmiş olan bakır iyonları miktarı kompleksometrik yöntemle belirlenmiştir. Çözeltiye geçen ve cevherdeki bakır miktarları arasındaki farktan bakırın çözünme oranı hesaplanmıştır.

Reaksiyon sıcaklığı, amonyak ve amonyum klorür derişimi ve karıştırma hızının malahitin çözünmesi üzerine olan etkileri belirlenmiştir.

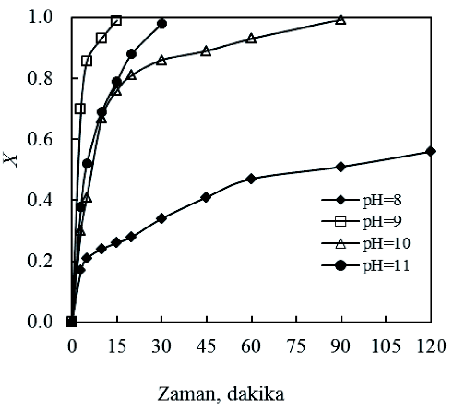


Şekil 1. Çalışmada kullanılan malahit cevherinin XRD grafiği

3 SONUÇLAR VE TARTIŞMA

3.1 Derişimin Etkisi

Malahit cevherinin çözünürlüğü üzerine NH_3 ve NH_4Cl derişiminin etkisi farklı derişimlere sahip amonyak ve amonyum klorür içeren çözeltiler kullanılarak incelenmiştir. Bu deneylerde molarite olarak $[NH_3]/[NH_4Cl]$ oranları 0.05/1.00, 0.50/0.95, 0.60/0.10 ve 1.00/0.02 olup, bu derişimlerdeki çözeltilerin pH değerleri sırasıyla 8, 9, 10 ve 11 olarak belirlenmiştir. Bu deneylerde, reaksiyon sıcaklığı, ortalama tane boyu, karıştırma hızı ve katı/sıvı oranı ise sırasıyla 50°C, 120 µm, 450 rpm ve 2/500 g/mL değerlerinde sabit tutulmuştur. Deneylerden elde edilen sonuçlar Şekil 2'de gösterilmiştir. Bu şekilden görüleceği gibi pH değeri 9 ve 11 olan çözeltiler kullanılarak yapılan deneylerde daha kısa sürelerde yüksek çözünme hızlarına ulaşılmıştır. pH=9 olan çözeltiyle yapılan deneyde 15 dakikalık sürede %99'luk dönüşüme ulaşılmışken, pH=11 olan çözelti kullanıldığında %98'lik dönüşüme 30 dakikada ulaşılmıştır. pH değeri 8 olan çözeltilerle yapılan deneyde ise 120 dakikalık reaksiyon süresinde %56'lık bir dönüşüm değerine ulaşılmıştır. pH değeri 10 olan çözelti kullanılarak yapılan deneyde ise 90 dakika sonunda malahit cevherindeki bakırın %99'luk bir kısmının çözünerek çözeltiye geçtiği belirlenmiştir. Kullanılan kimyasal maddelerin miktarları, oluşan çözeltilerin pH değerleri, reaksiyon sırasında kompleks oluşumları ve kinetik değerlendirmeler dikkate alındığında pH=10 olan çözeltilerin liç işlemi için kullanılmasının daha uygun olabileceği düşünülmüştür. Böylece sonraki deneylerde pH değeri 10 olan çözeltiler liç amacıyla kullanılmıştır.



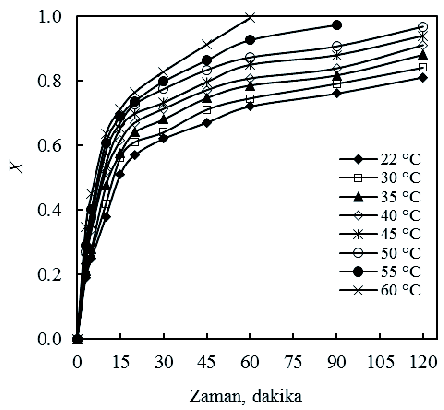
Şekil 2. Malahit cevherinin liç hızına derişimin etkisi

3.2 Reaksiyon Sıcaklığının Etkisi

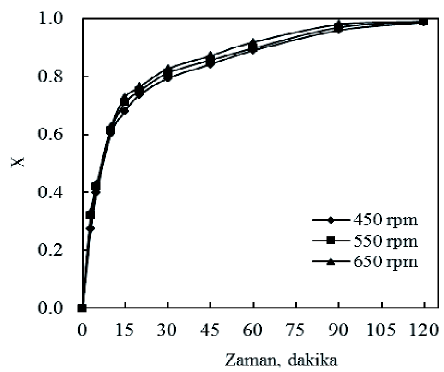
Malahit cevherinin liçi üzerine reaksiyon sıcaklığının etkisi 22, 30, 35, 40, 45, 50, 55, 60 °C sıcaklık değerlerinde incelenmiştir. Bu deneylerde pH10 olan çözelti kullanılmıştır. Karıştırma hızı, ortalama tane boyutu, katı/sıvı oranı ise sırasıyla 450 rpm, 120 µm ve 2/500 g/mL değerlerinde sabit tutulmuştur. Deneyler sonucunda elde edilen veriler Şekil 3'de grafiksel olarak gösterilmiştir. Bu şekilden görüleceği gibi sıcaklığın artmasıyla malahit cevherinin çözünürlüğü de artmaktadır. 22 °C'de 120 dakika reaksiyon süresi sonunda %81'lik çözünürlük elde edilmişken 60 °C'de %99 çözünürlük değerine 60 dakika sürede ulaşılmıştır.

3.3 Karıştırma Hızının Etkisi

Karıştırma hızının malahitin çözünürlüğüne olan etkisinin incelendiği deneyler 450, 550 ve 650 rpm karıştırma hızı değerlerinde incelenmiştir. Deneylerde reaksiyon sıcaklığı 50 °C, pH=10, ortalama partikül boyutu 120 µm olarak alınmıştır. Deneysel sonuçlar Şekil 4'de verilmiştir. Çalışılan karıştırma hızı aralığında, karıştırma hızının arttırılmasının malahitin çözünürlüğü üzerinde çok önemli bir etkiye sahip olmadığı Şekil 4 den gözlenmektedir.



Şekil 3. Malahit cevherinin liçing hızına reaksiyon sıcaklığının etkisi



Şekil 4. Malahit cevherinin liç hızına karıştırma hızının etkisi

3.4 Liç Kinetiği

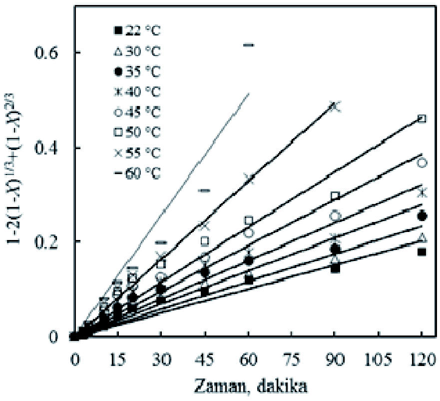
Liç proseslerinin kinetik analizi genellikle katalitik olmayan heterojen reaksiyon modelleri kullanılarak yapılır. Bu tür reaksiyonların kinetik analizi için literatürde büzülen çekirdek modelinin uygulandığı görülmektedir. Bu modele göre katalitik olmayan bir katı-akışkan reaksiyonun hızı akışkan filminden difüzyon, ürün filminden difüzyon veya kimyasal reaksiyonla kontrol edilir (Levenspiel, 1972). Sözü edilen bu modeller deneysel verilere uygulandığı zaman orijinden geçen düz doğruların elde edilmediği görülmüştür. Literatürde, yukarıdaki modeller haricinde bu tür heterojen reaksiyonların kinetiğini açıklamak için karışık kinetik modeller de geliştirilmiştir. Bu modeller deneysel verilere uygulandığı zaman, amonyak amonyum klorür çözeltilerinde malahitin liçi için en uygun modelin Eşitlik 1'deki gibi yazılabilecek karışık kinetik modelin olduğu görülmüştür.

$$1-2(1-x)^{1/3} + (1-x)^{2/3}=k.t \qquad (1)$$

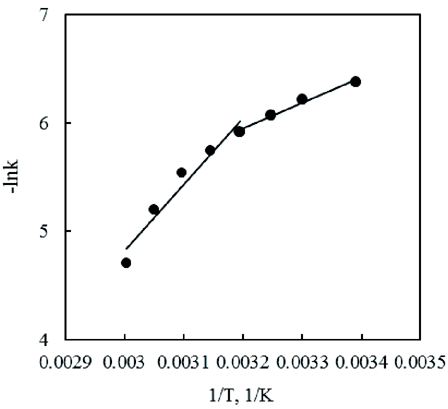
Bu eşitlikte x dönüşüm kesrini, k reaksiyonun görünür hız sabitini ve t reaksiyon süresini temsil etmektedir. Farklı reaksiyon sıcaklıkları için Eşitlik 1'in sol tarafının t'ye karşı grafiğe geçirilmesiyle Şekil 5 elde edilmiştir. Bu şekilden görüldüğü gibi orijinden geçen yüksek korelasyon katsayılı düz doğrular elde edilmiştir.

Liç prosesinin aktivasyon enerjisini hesaplamak için Şekil 5'de görülen düz doğruların eğimlerinden görünür hız sabitleri belirlenmiş ve Şekil 6'da görülen Arrhenius grafiği oluşturulmuştur.

Şekil 6'da elde edilen doğruların eğimlerinden ardışık iki basamağın aktivasyon enerjisi hesaplanmıştır. 22-40 °C arasında proses difüzyonla kontrol edilmektedir ve aktivasyon enerjisi 19.5 kJ/mol olarak hesaplanmıştır. 40-60 °C arasında ise mekanizma değişmekte ve bu sıcaklık aralığında proses kimyasal reaksiyonla kontrol edilmektedir. Bu basamak için aktivasyon enerjisi 50.8 kJ/mol olarak hesaplanmıştır.



Şekil 5. Farklı sıcaklıklar için karışık kinetik model grafiği



Şekil 6. Liç prosesi için Arrhenius grafiği

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