1. INTRODUCTION

Cyanidation has been a predominant gold extraction process of more than a century. The primary advantages of the cyanidation process in comparison with other methods are its higher chemical stability and lower cost [1, 2]. However, toxic nature of cyanide compounds, cyanidation process problems of ores containing carbonaceous materials, and excessive consumption of cyanide due to the formation of metal cyanide species in presence of impurities have caused an increased focus on the application of non-cyanide processes. Recently, the use of cyanide process of gold extraction has been restricted resulting from the growing environmental and public concerns in many regions of the world. Therefore, various chemicals like thiosulfate, thiourea, chloride, thiocyanate, ferric chloride and bromide have been proposed for gold extraction. Among them, ammoniacal thiosulfate leaching has received much attention as an alternative technology in the extraction of gold [3-5]. Non-toxic, low consumption, little interference with foreign cations, extraction of gold from refractory ores, and short residence times are the particular benefits of thiosulfate leaching process [6-9].

Another recent problem with gold extraction industry is that with reduction of oxidized free-milling gold reserves, most of the important new deposits that being mined today; do not respond to direct leaching because the gold is very finely disseminated and encapsulated in host matrixes that are inert minerals. For this reason, these matrixes must be broken down prior to leaching to improve the accessibility of gold particles. The physical and chemical pretreatments such as mechanical activation and pre-oxidation are used on the solid phase to change the particle size and composition of the gold-bearing material and thus to facilitate the subsequent leaching process [10-13].

Mechanical activation as a pre-treatment process has improved the gold and silver extraction processes. Generally, the mechanical activation of a mineral leads to a positive influence on the leaching kinetics. The breaking of bonds in the crystalline lattice of the mineral brings a decrease
in the process activation energy and an increase in the rate of leaching. The leaching rate of a disordered mineral is greater than that of an ordered mineral [14-17]. Various researchers have confirmed that mechanical activation accelerates the leaching kinetics [18-22].

Following text reviews the important researches about thiosulfate leaching of gold and mechanical activation effect on it. Breuer and Jeffrey [23] studied the effect of various parameters on the kinetics of gold thiosulfate leaching by using a rotating electrochemical quartz crystal microbalance. They found that the chemical reaction mechanism controls the gold leaching kinetics and the leaching rate decreases in time as the copper (II) concentration decreases. Aylomore and Muir [6] found that thiosulfate leaching is a non-toxic process, cheaper and faster than cyanidation, and due to the decreased interference of foreign cations, high gold recoveries are achievable from the thiosulfate leaching of complex and carbonaceous-type ores. According to Aylomre research [24], pre-treating a refractory gold-copper sulfide concentrate by ultra-fine milling followed by thiosulfate leaching resulted in 94% gold recovery after 48 h.

Ficeriova et al. [25] studied the leaching of gold from a mechano-chemically pretreated Cu₆PbZn complex sulfide concentrate using ammonium thiosulfate. They demonstrated that it was possible to achieve 99% gold recovery within 45 minutes for a sample mechanically activated at an energy input of 403 kWh.t⁻¹, while the gold recovery from as-received concentrate was only 54% in 120 minutes. In addition, Jeffrey [26] found that the leaching of gold decreases because of the presence of a transient film. In addition, he reported that under most experimental conditions, the reaction is chemically controlled.

Hashemzadeh et al. [10] investigated the effect of mechanical activation to enhance the gold recovery from a CuPhZn complex sulfide concentrate. They showed that gold extraction increases from 17.4 % in the non-activated sample to 73.26 % in 1 h-activated sample under milling time of 1 h, sample to ball weight ratio of 15, and mill speed of 600 rpm. Ghobeti et al. [11] studied the effect of mechanical activation on the chloride–hypochlorite leaching of gold from a refractory pyritic concentrate containing ca. 27 g/t gold. They found that gold extraction value of 45 minutes milled sample was 100% after 30 minutes leaching, while it was only 37.2% in the un-milled sample after 480 minutes leaching at 25 °C. Aazami et al. [27] investigated the effect of different additives on the thiosulfate leaching of gold from Zarshouran refractory gold ore and indicated that gold recovery and thiosulfate consumption in the presence of EDTA (ethylene diamine tetraacetic acid) are higher and lower than that achieved in the presence of ammonia, respectively. Xu et al. [28] and Liu et al. [29] considered the effect of sulfide minerals on the thiosulfate leaching of gold and found that addition of sulfide minerals including chalcopyrite, galena, sphalerite, pyrite, and arsenopyrite could accelerate the thiosulfate consumption and hinder the gold recovery. Yang et al. [30] studied the effect of arsenopyrite on the thiosulfate leaching of gold. The results showed that the thiosulfate consumption slightly raises with increasing the concentration of arsenopyrite, but the gold dissolution markedly declines. This may mainly attribute to the catalytic effect of arsenopyrite on the thiosulfate decomposition and the formation of a passive layer on the gold foil surface. Mohammadi et al. [31] studied the ammoniacal thiosulfate leaching of a refractory oxide gold ore and found that leaching under optimum conditions shows a transition after a leaching time of 2 h indicating a change in the process mechanism. Ha et al. [32] studied the thiosulfate leaching of gold from waste mobile phones. They found that gold extraction increases by using the leaching solutions containing 15–20 mM cupric, 0.1–0.14 M thiosulfate, and 0.2–0.3 M ammonia.

To the best of author’s knowledge, the effect of mechanical activation on the ammoniacal thiosulfate leaching of Sarigunay refractory oxide gold ore has not been studied. Moreover, the mechanical activation effect on the kinetics of gold extraction from refractory oxide gold ore by ammoniacal thiosulfate leaching has not been reported. The aim of this research was to study the effect of mechanical activation on the kinetics of gold extraction by ammoniacal thiosulfate leaching from a refractory oxide gold ore.
2. MATERIALS AND METHODS

The gold-bearing ore, used in this study, was obtained from Sarigunay mine of Iran. The bulk chemical analysis of the ore is given in Table 1. The gold content (2.8 ppm) of the ore was determined by fire assay method. X-ray diffraction analysis (Fig. 1) showed that the ore has an oxide nature and quartz, epidote, muscovite and orthoclase are the major minerals. The mineralogical studies using polished and thin sections confirmed that quartz and epidote were the main phases, while oxides such as goethite and jarosite were minor phases. Studies of a polished section of the ore by scanning electron microscopy (SEM) revealed that beyond the arsenical pyrite grains with the size of 2-20 µm and probably host to gold, the ore microstructure contains coarse grains (20-80 µm) that are early brassy pyrite surrounded by a layer of arsenical pyrite with the thickness of about 5 µm. The previous work [31] provides more details about the ore microstructure.

The ore was crushed to less than 10 mm by a jaw crusher (Retsch BB 200) and subsequently ball milled. Screen analysis showed that the d80 value of the sample after ball milling was 300 µm.

A cyanide leaching test was used to determine the refractory nature of the ore. For this purpose, 10 g of the milled ore (d80 of 300 µm) further ball milled to d80 value of 74 µm (200 mesh) and was dissolved during 2 h in the solution containing 3 g/L sodium cyanide (≥95%, Merck), pH of 10.5, stirring speed of 400 rpm, liquid/solid ratio of 5, and temperature of 50 °C. The gold recovery of 74 % was achieved by cyanide leaching test. Therefore, the result of cyanide test categorized the ore in the refractory gold ore group due to the gold recovery value of (less than 80 %) and the presence of arsenopyrite particles (host to gold) [33, 34].

Mechanical activation of the samples was carried out by a high-energy ball mill (PM 100) using a milling vial with a volume of 250 ml, the ball to powder weight ratio of 20, stainless steel balls with diameter of 20 mm and 10 mm, and rotating speed of 400 rpm. The ore was milled in different times of 15, 30, 45, and 60 minutes and the pre-

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ti</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>33.01</td>
<td>8.53</td>
<td>3.04</td>
<td>0.13</td>
<td>0.02</td>
<td>7.26</td>
<td>0.24</td>
<td>0.27</td>
<td>0.22</td>
<td>0.07</td>
<td>0.04</td>
<td>2.8 ppm</td>
</tr>
</tbody>
</table>

Table 1. Chemical analysis of the refractory oxide gold ore

Fig.1. XRD pattern of the refractory oxide gold ore.
pared samples were nominated as 15BM, 30BM, 45BM, and 60BM, respectively. In addition, the non-activated ore was coded with 0BM.

A thiosulfate leaching solution was prepared according to findings of various researchers [6, 24, 26, 27, 31, 35, 36] by dissolving of 0.1 M sodium thiosulfate pentahydrate (≥ 97%, Merck), 3 M ammonia (25%, Merck), 0.0125 M anhydrous copper sulfate (≥ 99%, Merck) in 1 L distilled water. Subsequently, 50 mL of the prepared solution and 10 g of the ore were poured into a 200 mL glass reactor located in a water bath equipped with a thermometer and then leaching experiments were carried out at 25 °C. A magnetic stirrer-heater (IKA, RH Basic 2) was used for heating and stirring the solution. The initial pH, pulp density, and stirring speed of all experiments were adjusted to 10, 20%, and 400 rpm, respectively. Sodium hydroxide (≥99%, Merck) and hydrochloric acid (37%, Merck) were used as pH adjusting reagents.

The gold concentration of the leaching solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista-PRO). X-ray powder diffraction (XRD, Philips X’pertpro diffractometer) with Cu-Kα radiation, X-ray fluorescence (XRF, Philips PW1480), scanning electron microscopy (SEM, CamScan MV2300), and fire assay analyses were utilized for the ore characterizing.

3. RESULTS AND DISCUSSION

3.1. Effect of mechanical activation on the gold extraction

The effect of mechanical activation time on gold extraction is shown in Fig.2. In all the leaching curves, two leaching stages (different line slopes) are recognizable. The first stage appeared at the beginning of the leaching process (less than 2 h) and the second stage arrived between 2-16 h. It is seen that the gold extraction proceeds rapidly with stage one and maximum extraction is attained after 2 h for all samples. Then, the gold extraction rate decreases due to the dropping of thiosulfate in the solution resulting from its consumption and kinetically problems [37, 38].

Fig.2 demonstrates that mechanical activation has a positive effect on gold extraction. This effect on the 15BM, 30BM, and 45BM samples is negligible as the gold extraction value of these samples is between 55-65 % and close to the gold extraction value of sample 0BM after 16 h. On the contrary, the gold extraction value of 60BM sample was about 100 % after the same time. The different gold extraction values of the samples are due to the particle size decreasing with raising the activation time and consequently increasing the gold accessibility. In addition, the gold extraction is improved by increasing both lattice strain and structural disorder (residual stresses) caused by mechanical activation [10, 11, 20]. Although the residual stresses have a positive effect on the gold dissolution, the role of reducing particle size generated by mechanical activation is considerable.

Optical microscopy images of the OBM and activated samples are illustrated in Fig.3 and Fig.4, respectively. These images obviously confirmed
that the mechanical activation decreases the particle size of the ore. The d80 value of the non-activated ore was 300 µm, while it declined to 240, 130, 90, and 45 µm for the 15BM, 30BM, 45BM, and 60BM samples, respectively. Therefore, it is concluded that the mechanical activation causes an increase in the samples surface area. The higher surface area obtains the greater gold accessibility and increases the leaching rate and gold extraction as it is seen in Fig.2. The higher gold recovery value of sample 60BM in comparison with sample 45BM and other samples suggested that significant change has taken place with the sample during the 60 minutes mechanical activation. In fact, some encapsulated gold in relatively large silicates, oxides, and sulfide minerals (arsenopyrite) have liberated and the gold accessibility with the leaching solution has increased. In addition, the mechanical activation creates microscopic cracks at the mineral particles that also improve the solution-diffusion into particle cores resulted in complete gold extraction (Fig. 5).

It should be noted that the effective role of the particle size in gold dissolution occurs when the particle size reaches the level of gold minerals liberation. That is why the reduction in particle size in the range of 0-45 minutes mechanical activation is not very significant on the gold extraction since the particle size has not yet reached the level of gold minerals liberation. But, in the case of sample 60BM, since its particle size has reached the limit of the liberation, its gold extraction is much higher than that of the other samples.

Fig. 5 shows the SEM images of the 0BM, 45BM, and 60BM samples. It is seen that the particle size of the sample 60BM is much finer than that of sample 0BM. Moreover, the SEM images
reveal that sample 60BM has more cracks in particle surfaces in comparison with sample 45BM. In fact, in addition to small particle size, the cracks are also an effective factor in achieving the full gold extraction in sample 60BM. These are the main effects of mechanical activation on the ore morphology that explains the difference between gold extraction values of sample 60BM (~ 100 %) and other samples (55-65%) after 16 h leaching.

3.2. Kinetics of the leaching

Various researchers [26, 39, 40] have studied the kinetics of gold leaching and shown that overall dissolution reaction of gold from an ore exhibit shrinking core model indicating the formation of a surface ash layer on dissolving materials. In the shrinking core model, a reaction occurs first at the outer surface of a particle, then moves into the solid core and leaves behind completely converted material and inert solid that is referred to “ash layer”. Thus, at any time an un-reacted core shrinks in size during leaching reaction [41].

In the present research, the shrinking core model (SCM) was used to describe the ammoniacal thiosulfate leaching of the refractory oxide gold ore. To establish the kinetics parameters and rate-controlling step for the dissolution of gold in the solution, the experimental data in Fig.2 were fitted to the shrinking core model (spherical constant particles size). According to this model, the reaction rate of a heterogeneous process may be controlled by one of the following steps and equations [41]:

Liquid film diffusion:

\[
\frac{t}{\tau} = X_b
\]  

Chemical reaction:
t/τ = 1 - (1 - X_B) \frac{1}{3} \quad (2)

Ash layer diffusion:

\frac{t}{\tau} = 1 - 3(1 - X_B)\frac{2}{3} + 2(1 - X_B) \quad (3)

Where X_B is the fraction of reacted gold after time t and \( \tau \) is the time for complete conversion of a particle.

As it was said earlier, Fig.2 shows the presence of two stages; stage one that occurs at the beginning of the leaching process (less than 2 h) and stage two that appears between 2-16 h leaching. The rate of leaching at these two stages is considerably different suggesting a different controlling step in each stage. Moreover, when any of the equations related to different controlling regimes (Eq. 1, 2, and 3) was examined with the experimental data for the whole leaching period, a significant change in the trend before and after 2 h was observed. This also indicates that the whole leaching process is not governed by a single mechanism. The controlling regime equations in the SCM were examined for 0-2 h and 2-16 h, separately. For this purpose, the results obtained from the ore leaching were fitted to equations 1, 2, and 3. The regressed model and dominant mechanisms in this study were determined by using the logical discussion and attention to previous research works [26, 39, 40] along with correlation coefficients (R^2) values (Table 2 and Table 3). To summarize, only the best-fitted mechanisms were plotted in Fig. 6 to Fig. 9. The mechanisms discussed in this study are based only on the mathematical equations. In practice, the control mechanisms of the leaching reaction may be different.

3.2.1. Kinetics of the leaching between 0-2 h

According to the correlation coefficients of fitted mechanisms in Table 2 and Fig.5, there is a considerable agreement with the proposed kinetic mechanism and the experimental data for the 0BM, 15BM, 30BM, and 45BM samples between 0-2 h. Therefore, it is concluded that the leaching kinetics of the ore is controlled by diffusion through an ash layer for these samples. The sample 60BM showed different behavior kinetically at the same time. According to Table 2 and Fig.7, the best-fitted mechanism for sample 60BM is chemical reaction control. It seems that the particle size reduction has a particular role in the changing of the mechanism from the ash layer diffusion to the chemical reaction. In fact, thickness and volume of the ash layer around the small particles do not cause any kinetic problems because before reaching to a critical value, the reaction of leaching in stage one is completed.

Therefore, the ash layer diffusion is not the dominant mechanism in the case of sample 60BM, and the changing of reaction mechanism from the ash layer diffusion to the chemical reaction seems logical. The reactions that are controlled by the ash layer diffusion have a slight rate compared to reactions that are controlled by chemical reaction. Therefore, the gold recovery of a sample’s leaching being controlled by a chemical reaction is higher than gold recovery in all other samples.

3.2.2. Kinetics of the leaching between 2-16 h

Table 2. Correlation coefficients (R^2) of the lines fitted to 0-2 h leaching data

<table>
<thead>
<tr>
<th>Milling time (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid film diffusion</td>
<td>0.920</td>
<td>0.913</td>
<td>0.914</td>
<td>0.931</td>
<td>0.982</td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>0.935</td>
<td>0.930</td>
<td>0.932</td>
<td>0.95</td>
<td>0.997</td>
</tr>
<tr>
<td>Ash layer diffusion</td>
<td><strong>0.980</strong></td>
<td><strong>0.992</strong></td>
<td><strong>0.992</strong></td>
<td><strong>0.992</strong></td>
<td><strong>0.997</strong></td>
</tr>
</tbody>
</table>

Table 3. Correlation coefficients (R^2) of the lines fitted to 2-16 h leaching data

<table>
<thead>
<tr>
<th>Milling time (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid film diffusion</td>
<td>0.980</td>
<td>0.985</td>
<td>0.964</td>
<td>0.985</td>
<td><strong>0.979</strong></td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>0.978</td>
<td>0.980</td>
<td>0.975</td>
<td>0.986</td>
<td>0.946</td>
</tr>
<tr>
<td>Ash layer diffusion</td>
<td><strong>0.989</strong></td>
<td><strong>0.999</strong></td>
<td><strong>0.988</strong></td>
<td><strong>0.990</strong></td>
<td>0.954</td>
</tr>
</tbody>
</table>
Table 3 and Fig. 8 demonstrate the dominant mechanism is diffusion through an ash layer for the 0BM, 15BM, 30BM, and 45BM samples between 2-16 h. It means the diffusion through an ash layer is the controlling step in gold dissolution. Therefore, the dominant mechanism in the leaching process of the 0BM, 15BM, 30BM, and 45BM samples in both stages are the same. According to Table 2 and Fig. 9, the dominant kinetics mechanism for sample 60BM in stage two (2-16 h) is the liquid film diffusion. Although, stirring the solution reduces the liquid film layer but cannot completely eliminate it. Because the size of the particles is very small, a layer with very low thickness can also be very effective at the process rate. Moreover, according to SEM images in Fig. 5, particles of the 60-minutes mechanically activated sample had cracks in the structure that stirring is not capable of removing the film layer from cracks.

Being said earlier, particle size plays an important role in changing the kinetics mechanism from the ash layer diffusion to liquid film diffusion mechanism. Liquid film diffusion mechanism is usually observed when using very fine particles because here the liquid film is thick in comparison with particle size [41]. Table 4 summarizes the leaching kinetics mechanisms of the samples in the two stages.

Since the layer of ash is thick enough for the 0BM, 15BM, 30BM, and 45BM samples during the two-leaching stages, so the ash layer diffusion controls the gold dissolution reaction in both stages. It should be noted that although the reaction mechanism of 0BM, 15BM, 30BM, and 45BM samples is the same in the first and second stages, the reaction rate of each sample is different (slope of a curve in Fig. 2) in each stage. That is because the ash layer in stage two is thicker than that in stage one. Therefore, the reactants must diffuse more distances in stage two that result in longer reaction time (lower reaction rate). In the case of sample 60BM, also there are two stages of leaching, because in the first stage the leaching mechanism is a reaction controlled (high rate), while the leaching mechanism in the second stage is liquid film diffusion (low rate). Therefore, two different rates make two leaching stages.
3.2.3. Relation between the mechanical activation and complete conversion time (τ)

Fig. 10 shows the relation between the mechanical activation time and calculated complete conversion time. To calculate the complete conversion time, the value of $X_B$ was considered equal to one (therefore $y$ value in the line equations will be one) and based on the equation of the lines in Fig. 8 and Fig. 9, the $τ$ was calculated for different samples. As it is seen in Fig. 10, the $τ$ of leaching reaction for the 0BM sample is about 190 h, while it reaches to about 189 h, 156 h, 116 h for the 15BM, 30BM, and 45BM samples, respectively. The $τ$ of the leaching reaction of sample 60BM is about 17 h. According to the Fig. 2, the real value of $τ$ for sample 60BM is about 16 h. Comparison of these two values, i.e. 17 h and 16 h, confirms that the calculated (Fig. 10) value and real value (Fig. 2) of the $τ$, at least, are in good agreement for sample 60BM.

4. CONCLUSIONS

The main findings of this work are summarized as follows:

1. The d80 value of the non-activated sample was 300 µm, while it was declined to 240, 130, 90, and 45 µm for the samples activated for 15, 30, 45, and 60 minutes, respectively.
2. Mechanical activation had a positive influence on the rate and gold recovery. The gold recovery of 99.81% was achieved by 16 h leaching of the 60 minutes activated sample. This value was very favorable in comparison with the gold extraction of 55% achieved by using the non-activated sample in the same leaching time.
3. Kinetics of the leaching was controlled by diffusion through an ash layer for the non-activated sample and samples activated up to 45 minutes between 0-2 h leaching, while the sample activated for 60 minutes showed the chemical reaction control mechanism at the same leaching time.

<table>
<thead>
<tr>
<th>Mechanical activation time (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching time (h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Kinetics mechanisms of the two leaching stages

- Ash layer diffusion
- Chemical reaction
- Liquid film diffusion
4. The dominant kinetics mechanism was diffusion through an ash layer for the non-activated sample and samples activated up to 45 minutes between 2-16 h leaching, while it was liquid film diffusion for the sample activated for 60 minutes in the same leaching time.

5. The calculated complete conversion time ($\tau$) for the non-activated and 15 minutes activated samples was about 190 h, while it was decreased to about 155 h, 50 h, and 19 h for the samples activated for 30, 45, and 60 minutes, respectively.

6. The real complete conversion time ($\tau$) for the sample activated for 60 minutes was about 16 h that was close to the calculated value (17 h).

5. ACKNOWLEDGMENTS

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