GOLD LECHING FROM A SAUDI ORE
BY THE NONPOLLUTING THIOSULFATE PROCESS

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Abstract: In all working Saudi gold mines, ores are treated using the hazardous cyanidation process. Some Saudi gold ores, such as Al-Amar, is known to be refractory to cyanidation. In this work, we have examined the extraction of gold from Al-Amar gold ore by the much environmentally safer and efficient thiosulfate process. The run of mine (ROM) and carbon-in-leach (CIL) feed, that is obtained after separation of copper concentrate from ROM samples were found to contain 6.5 and 3.6 ppm gold, respectively. The mineralogical microscopic investigations of ROM samples confirmed that fine gold specks were scattered and encapsulated inside sulfide or quartz base minerals. This could explain the expected reason of the difficult leaching of gold by cyanidation. The X-ray diffraction analysis showed that the CIL feed contained quartz, pyrite, sphalerite and chlorite minerals. After detailed leaching studies of CIL feed, almost 70% of gold could be extracted at 0.2 M ammonium thiosulfate and 0.3 M ammonium hydroxide after 24 h. Addition of copper(II) as <0.2 mM only slightly enhanced the gold leaching in the ammoniacal thiosulfate solution. Gold leaching drastically decreased as the concentration of copper(II) increased 0.2 mM due to the degradation of \(S_2O_3^{2-}\).

Keywords: gold, extraction, leaching, thiosulfate, Saudi ore

Introduction

Gold dissolution in an alkaline cyanide solution was first reported by Elsner in 1846. About 92% of all gold metal in the world is produced using the hazardous cyanidation process [McNulty, 2001]. The major problems of the cyanidation process are: (i) the use of cyanide, an extreme toxic chemical, that has been banned in many countries (Rainforest Information Centre, 2005), (ii) its reduced efficiency, i.e. high reagent
consumption and/or low gold leaching, during the treatment of refractory and complex ores (La Brooy et al., 1994). Due to environmental concerns, mining companies are now applying the stringent regulations and codes on the transportation, handling, usage and disposal of cyanide containing materials. A list of recent cyanide spillage disasters suggested that the only ultimate solution for this problem is to replace cyanide with a lixiviant that is significant environmentally friendly (Rosenhek, 2007). It is believed that the use of cyanidation process will be increasingly restricted in the near future.

Several alternative lixiviants were investigated to provide a solution for the treatment of refractory ores and to develop an environmentally friendly gold leaching process. Au(I) forms strong complexes with different non-cyanide reagents such as thiourea, halogens, thiocyanate and thiosulfate (Wan et al., 1993). Some of processes based on these reagents have a higher overall production cost and/or difficult to control. For instance, thiourea is requiring an acidic leaching conditions; where high reagent consumption, gold passivation problems, and high capital costs have hindered further developments (Tremblay et al., 1996). Furthermore, thiourea is considered to be a potential carcinogen.

On the other hand, Au(I) forms strong complex with thiosulfate, which is more stable than the thiourea and the thiocyanate complexes. Compared to thiourea, thiosulfate has demonstrated greater potentials in both leaching performance and environmental considerations. One significant advantage of thiosulfate leaching is its ability to treat preg-robbing ores containing carbonaceous materials (Wan, 1993; West-Sell and Hackl, 2005). It is also thought that thiosulfate leaching might provide an alternative option for the leach of copper-bearing ores, which are not economical in cyanidation. Compared to cyanide, thiosulfate is a much more safer chemical. Thiosulfate salts, including ammonium thiosulfate, ATS, are regarded as nonhazardous by Worksafe Australia (NOHSC, 1999). They are also classified as “General Recognized as Safe” in the US and not considered as dangerous substances by European standards (Bean, 1997, EEC/FDA, 2001 ). Another fact that has to be considered is that ATS (US$0.1-0.15/kg) is about 10 times cheaper than sodium cyanide (US$1.8-2.0/kg) in bulk chemical market. Moreover, thiosulfate leaching has similar or faster kinetics compared to cyanidation (Jeffrey, 2001). Therefore, thiosulfate has become the most promising noncyanide lixiviant and is receiving extensive attentions from both academic and industrial points of view. However, there are numerous obstacles those hinder the industrial application of thiosulfate process such as high consumption of chemicals in treating copper bearing sulfidic ores, and gold recovery problems by the popular CIP/CIL (carbon-in-pulp/carbon-in-leach) technologies (Aylmore, 2001). However, solvent extraction, ion exchange, zinc and copper cementation were found to be effective recovery techniques (Navarro, 2004, Liu, 2004, Zhang and Dreisinger, 2004). The interferences of associated minerals may in some cases increase the complexity of the reaction chemistry and the instability of thiosulfate. Developing has been made to find alternative leaching catalysts in
thiosulfate media other than copper and ammonia (Zhang et al., 2005; Chandra et al., 2005). Carbonaceous sulfide ores after oxidative pre-treatment are typically very easy to leach with thiosulfate, while complex metal sulfide ores are much more difficult to treat. The presence of various amount of pyrite, pyrrhotite, chalcopyrite, arsenopyrite, chalcocite, bornite, and some lead species, has significant detrimental effects on thiosulfate leaching of gold (Chen, 2008). This shows how much a mineralogical investigation is important to be performed before leaching study of any gold ore by the thiosulfate process.

Several gold localities are scattered in the Arabian Shield of the kingdom of Saudi Arabia which has about 20 million tons of recoverable gold ores. In working gold mines, ores are treated using the hazardous cyanidation process through the CIL or heap leaching. Although several Saudi gold mines are in operation since 1980s, very few published studies were found in the literature dealing with Saudi gold ores (Madani et al., 2012, Khandaker et al., 1997, Salpeteur et al., 1989, Huckerby et al., 1982, Hakim 1982, Al-Hobaib et al., 2010). All these studies are of geological, mineralogical or environmental nature. Tailings (mining wastes) are stored in the dumping area as a dam that contains residual cyanide. Moreover, no published work was found concerning with leaching of gold from Saudi ores with the thiosulfate process. Thus, a comprehensive detailed studies are needed to investigate the suitability of Saudi gold ores to the thiosulfate leaching and to develop a leaching strategy for gold leaching. The study should include the several factors affecting the efficiency of gold leaching.

The aim of this research is to investigate the mineralogical nature and study the optimum leaching conditions of a selected Saudi gold ore using the thiosulfate process. Leaching time and concentrations of main reagents were studied to reach the optimum concentrations.

### Experimental

#### Samples collection and preparation

Three types of samples were collected from Al-Amar gold mine and processing plant those are located West Riyadh city, Saudi Arabia. Rough block samples from run of mine, ROM, were selected for the microscopic petrography investigation, and thin section and polished samples were prepared and the nature of the minerals and gold inclusion have been identified. Another rock samples from ROM were collected in the form of midsize boulders and crushed to the size of approximately 1 x 1 cm using Jaw crusher and then a 20 kg were taken and divided two times to obtain a well representative sample which was ground to the size of 100% - 100 mesh and kept in plastic bags. These samples were used for chemical and X-ray diffraction analyses. Another wet sample was collected from CIL feed, that is obtained after separation of copper concentrate by flotation of ROM in the plant. The sample was filtered off and washed with fresh water. The wet cake was dried at about 50 °C for 72 h, broken
down, ground and packed in plastic bags. These samples were used for chemical and mineralogical analyses and also for the leaching experiments.

**X-ray diffraction and chemical analysis**

X-ray diffraction (XRD) analysis was performed on ROM and CIL feed samples using an automated diffractometer (Philips type: PW1840), at a step size of 0.02°, scanning rate of 2° in 2θ/min, and a 2θ scale range from 4° to 80°.

Chemical analysis was performed on ROM and CIL feed after opening of 2 g finely ground representative samples in aqua regia and dilution to 250 cm³ with de-ionized water. Inductively Coupled Plasma-Atomic Emission Spectrometer, ICP-AES (Type: Perkin Elmer Optical Emission Spectrometer 2100 DV) was used for elemental analysis in solutions. SiO₂ contents were performed gravimetrically, and referred as Si.

**Mineralogical studies**

Both thin and polished sections of the studied ROM rocks were used for petrographic studies. Also, the environmental scanning electron microscopy (ESEM) technique was used to identify some opaque minerals in the studied samples to support the microscopic identification. Polished sections of selected samples of the studied rocks were examined with a Philips XL30 environmental scanning electron microscope (ESEM), operating at 25 kV and equipped with EDAX energy dispersive analytical X-ray sensitivity.

**Leaching**

Leaching experiments were carried out in a sealed 100 cm³ conical flask glass reactor at room temperature (~ 25 °C). A 10 g ore sample and a 20 cm³ solution containing all reagents (e.g. ammonium thiosulfate, ammonium hydroxide, copper sulfate, etc.) was added into the flask and the mixture was horizontally shaken at 480 rpm using an electric shaker. After the required time, the slurry was filtered off and the filtrate was chemically analyzed to determine the Au content.

**Results and discussion**

Gold dissolution in ammoniacal thiosulfate can be described as shown in Fig. 1.

Leaching of gold in thiosulfate solutions is a metal oxidation process as described in Eq. 1 (Chen, 2008)

\[
4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} = 4[\text{Au(S}_2\text{O}_3)_2]^3^- + 4\text{OH}^-.
\]
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The reaction chemistry using cupric amine as an oxidant can be explained by the intermediate reactions as shown in Eqs. 2 and 3:

$$\text{Au} + 5 \text{S}_2\text{O}_3^{2-} + [\text{Cu(NH}_3\text{)}_4]^{2+} = [\text{Au(S}_2\text{O}_3\text{)}_2]^{3+} + 4\text{NH}_3 + [\text{Cu(S}_2\text{O}_3\text{)}_3]^{5-}$$  \hspace{1cm} (2)

$$16 \text{NH}_3 + 4[\text{Cu(S}_2\text{O}_3\text{)}_3]^{5-} + \text{O}_2 + 4\text{H}^+ = 4[\text{Cu(NH}_3\text{)}_4]^{2+} + 2\text{H}_2\text{O} + 12\text{S}_2\text{O}_3^{2-}.$$  \hspace{1cm} (3)

According to this theory, the dissolution of gold is a “corrosion” process. The ultimate oxidant is oxygen or any other oxidative chemicals that are capable of oxidizing Cu(I) amine to Cu(II) amine. Unlike cyanidation, thiosulfate leaching of gold does not require a diffusion of oxygen onto the solid-liquid interface of gold, which can be very slow under atmospheric conditions. The direct oxidant of gold is Cu(II) amine after it is adsorbed on to the surface of gold in the cathodic area. After accepting one electron, Cu(II) amine is reduced to Cu(I) amine, which is desorbed and diffused into the bulk solution phase. In the anodic area of gold surface, a gold atom loses one electron and produces an aurous ion. It is then complexed with ammonia. The aurous ammonia complex diffuses to the bulk solution phase where ammonia is substituted and aurous ion is stabilized as a more stable complex, $\text{Au(S}_2\text{O}_3\text{)}_2^{3-}$. There are four diffusion steps: the diffusions of ammonia and Cu(II) amine to the gold solid-liquid interface and the diffusions of Cu(I) amine and Au(I) amine complex to the bulk solution phase. In all these diffusion steps, ammonia plays important roles. This partially explains the slow dissolution rates in the absence of sufficient ammonia ligand. First of all, ammonia works as ligand of copper, which stabilizes copper and forms the oxidation catalyst in the anodic area. Also, free ammonia must be present, so it can be adsorbed on the surface of gold and form an aurous complex.
Mineralogical studies

Environmental Scanning Electron Microscopy (ESEM) showed noticeable concentrations of opaque minerals, especially in the sheared or contact samples as well as silica-rich samples. The opaque minerals in the studied rocks are represented as Fe-Ti oxides and sulfides together with gold specks as well as small amounts of goethite (FeO(OH)) and malachite. Sulfides are represented by pyrite (FeS₂), chalcopyrite (CuFeS₂) and galena (PbS). Figures 2a and b show the microscopic images of pyrite-gold association and its ESMS. Magnetite (Fe₃O₄) occurs as eu-hedral homogeneous crystals. Ilmenite (FeTiO₃) is found as homogeneous sub-hedral crystals or form composite texture with magnetite. Pyrite occurs as cubic crystals or as aggregates of subhedral crystals altered to goethite which shows colliform texture. Chalcopyrite (CuFeS₂) is less abundant than the pyrite.

![Image of pyrite-gold association and ESEM of pyrite](image1)

**Fig. 2.** (a) Pyrite-gold association, and (b) ESEM of pyrite

![Image of gold specks in sulfides and ESEM of gold](image2)

**Fig. 3.** (a) Gold specks in sulfides and (b) ESEM of gold
Gold occurs as inclusions in the sulfides or as small irregular specks along the fractures. There are noticeable amounts of gold, especially in the samples which are rich in quartz. Figures 3 and 4 show the microscopic images and the ESMS of gold in sulfide and quartz minerals.

![Gold specks in quartz and ESEM of gold](image)

**Fig. 4. (a) Gold specks in quartz and (b) ESEM of gold**

### X-ray diffraction analysis and chemical analysis

Figure 5 shows the X-ray diffraction patterns of ROM and CIL feed samples. The main peaks in ROM are referring to quartz, sphalerite, pyrite and chalcopyrite. The CIL feed sample shows the absence of chalcopyrite peaks and a new peak of chlorite. Table 2 shows the detected minerals with their chemical composition and card number. Table 3 shows the chemical analysis of representative samples of ROM and CIL feed. These samples contain SiO$_2$ as a major constituent (about 30% as Si). The ROM sample contains about 6.5 ppm Au which is considered as a low grade gold ore, while the CIL feed contains only 3.6 ppm Au. On the other hand, the ROM and CIL contain small amounts of silver of 11.7 ppm and 6 ppm, respectively.

**Table 2. Detected minerals in X-ray diffraction analysis of ROM and CIL feed samples**

<table>
<thead>
<tr>
<th>Detected mineral name</th>
<th>Chemical composition</th>
<th>Card number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>[99-101-1988]</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>[99-200-5214]</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>[99-201-6098]</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>[99-100-8979]</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Mg$<em>{2.25}$Fe$</em>{0.255}$ Al$<em>{0.865}$ Si$</em>{1.588}$ O$_3$ H$_4$</td>
<td>[99-100-4282]</td>
</tr>
</tbody>
</table>


Fig. 5. X-ray diffraction patterns of ROM and CIL feed. Q: quartz, Ch: chalcopyrite, Py: pyrite, Sp: sphalerite, Cht: chlorite

Table 3. Chemical analysis of ROM and CIL feed samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROM</td>
</tr>
<tr>
<td>Au</td>
<td>6.47 ppm</td>
</tr>
<tr>
<td>Ag</td>
<td>11.7 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>28.0</td>
</tr>
<tr>
<td>Zn</td>
<td>13.1</td>
</tr>
<tr>
<td>Fe</td>
<td>12.8</td>
</tr>
<tr>
<td>Cu</td>
<td>5.09</td>
</tr>
<tr>
<td>Pb</td>
<td>0.96</td>
</tr>
<tr>
<td>Cd</td>
<td>0.02</td>
</tr>
<tr>
<td>V</td>
<td>0.56</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Appreciable amounts of iron is present in both samples, 12.8 and 6.5% in ROM and CIL feed, respectively. ROM contains 5.1% copper which is separated by flotation in the following steps. That is why the CIL feed contains neglected amount of copper (0.16%). Zinc is a major constituent; about 13%, in all samples.

Gold leaching

Effect of \((\text{NH}_4)_2\text{S}_2\text{O}_3\) concentration

As discussed above, extraction of gold is usually performed by leaching with a solution containing an oxidizing and a complexing agents. The thiosulfate concentration in the leaching slurry is an important factor affecting the leaching process from the effectiveness and economical points of view. A series of experiments was conducted to study the effect of ammonium thiosulfate (ATS) concentration (from
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0.05 M to 0.8 M) on the leaching of gold from Al-Amar CIL feed in absence of an additional oxidizing agent. The equilibrium pH was about 3. The results under the condition of 0.3 M ammonium hydroxide (AH), for 24 h are shown in Fig. 6. At 0.05M ATS, the gold leaching was as low as 24%. The leaching of gold was greatly improved with increasing the ATS concentration and reached its maximum at 0.2 M where about 66% gold was extracted. In the range of 0.2 M and 0.6 M ATS, the gold leaching stayed at a plateau of 66%. Thus, ATS concentration of 0.2 M is considered to be a minimum concentration to maximize the gold leaching performance under the above mentioned conditions. A sharp drop in leaching was observed at higher thiosulfate concentration than 0.6 M. This behavior is probably due to the possible degradation of thiosulfate at this high concentration forming elemental sulfur and other degradation products which cause passivation of gold and minerals surfaces.

![Fig. 6. Effect of ATS concentration on gold leaching. 0.3 M AH, pH = 9.3, 24 h](image)

**Effect of NH₄OH concentration**

It is known that ATS is stable in alkaline medium and quickly dissociates in acidic medium where fine elemental sulfur is formed. Thus, an alkaline condition is important to keep the ATS un-dissociated during gold leaching. The effect of AH concentration (from 0.05 M to 1 M) on gold leaching from Al-Amar mine CIL feed was studied and the results under the conditions of 0.2 M ATS, 24 h, are represented in Fig. 7. The equilibrium pH was also measured at the end of each experiment and shown in the same figure. It is clear that gold leaching was gradually improved with increasing AH concentration mostly. At 0.05 M AH about 45% of the Au was extracted at which the equilibrium pH was 9, where about 66% of Au was extracted at 0.3 M AH where the pH was 9.3, but the leaching leveled off at higher concentrations. It appears that the improvement of leaching with increasing AH concentration is due to the increasing stability of the thiosulfate S₂O₃²⁻ ions where the accompanied pH increased to 9.3 at 0.3 M AH. The result supports that 0.3 M of AH is the optimum concentration with the combination of the mentioned conditions.
Effect of shaking time

Figure 8 shows the effect of shaking time on the leaching of gold from Al-Amar CIL feed at 0.2 M ATS and 0.3 M AH. It can be seen that more than 40% of gold was extracted after only 2 hours. At longer times, the gold leaching slightly increased. About 70% of gold was extracted after 20 hours and almost stayed at this level at longer times.

Effect of CuSO$_4$ concentration

Oxidation of gold with the naturally dissolved oxygen in thiosulfate solution is not favorable due to the very slow reaction kinetics. Therefore, an oxidizing agent such as copper(II) may enhance the rate of gold leaching. Cupric ion has been previously used as an effective oxidizing agent during ammoniacal thiosulfate leaching of gold.
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reduction of Cu(II) amine to Cu(I) thiosulfate, i.e. Cu(II) oxidizes Au(0) to Au(I) in presence of $S_2O_3^{2−}$ as a complexing agent. The formed Cu(I) is re-oxidized to Cu(II) by the dissolved O₂. These half-cell reactions are shown in Eqs. 4 and 5, respectively (Breuer and Jeffrey, 2000).

$$Au + 2 S_2O_3^{2−} → Au(S_2O_3)_2^{3−} + e^−$$ (4)

$$Cu(NH_3)_4^{2+} + 3S_2O_2^{−2} + e^− → Cu(S_2O_3)_3^{5−} + 4NH_3.$$ (5)

However, the thiosulphate leaching system is complicated by the side reaction of reduction of Cu(II) by the thiosulfate ions in solution as shown in Eq. 6 (Breuer and Jeffrey, 2003):

$$2Cu^{2+} + 2 S_2O_3^{2−} → 2 Cu^+ + S_4O_6^{2−}.$$ (6)

We have examined the effect of CuSO₄ on leaching of gold from pure gold wires. Figure 9 shows the dissolution rate of pure gold wires (0.1 g) at different time intervals in presence and absence of CuSO₄ (0.1 mM) in 0.3 M AH, 0.2 M ATS. It can be seen that the gold dissolution was very slow at the first 10 hours and then more faster increased at longer times. It is also noticed that the dissolution percentage of gold in presence of Cu(II) ions was usually higher than that in its absence. This is in good agreement with the expected catalyzation of gold oxidation in presence of Cu(II) as explained above.

Figure 10 shows the leaching of gold from Al-Amar CIL feed at different time intervals in presence and absence of Cu(II) (as 0.2 mM CuSO₄) at 0.3 M AH and 0.2 M ATS. It can be seen that Cu(II) could only slightly enhance the leaching kinetics of gold. This little improving effect of Cu(II) on leaching of gold may be explained by the existence of small residual amount of chalcopyrite in the CIL feed (0.16% as Cu). This may dissolve as Cu(II) ions in leaching medium and cause the catalyzing effect on oxidation of gold. Thus, the effect of additional Cu(II) would be limited. It is worth mentioning that at prolonged time such as 24 h (not seen in the figure) the leaching percentages of gold is almost similar in presence and absence of Cu(II) reaching near to 70%. Figure 11 shows the effect of Cu(II) concentration on leaching of gold. It is clear from this figure that addition of Cu(II) very slightly enhanced gold leaching at low concentration and the leaching gradually decreased as the concentration of Cu(II) increased. The maximum leaching of gold was near to 70% at 0.2 mM Cu(II) where excessive amounts of Cu(II) blocks the gold leaching; that is no gold practically extracted at Cu(II) concentration as high as 0.1 M. This deteriorative effect of Cu(II) can be explained by the oxidative degradation of $S_2O_3^{2−}$ with increasing Cu(II) concentration as explained in Eq. 6.
Fig. 9. Dissolution of pure gold wires (0.1 g) in presence and absence of CuSO$_4$ at different time periods. Leaching solution: 200 cm$^3$ containing 0.1 mM CuSO$_4$, 0.3 M AH, 0.2 M ATS. Shaking speed: 480 rpm at ambient temperature and sealed vessel.

Fig. 10. Leaching of gold in presence and absence of Cu(II). 0.3 M AH, 0.2 M ATS, pH 9.3

Fig. 11. Effect of Cu(II) concentration on gold leaching. 0.3 M AH, 0.2 M ATS, 24 h, pH 9.3

**Conclusion**

The microscopic examinations of rocks from Al-Amar mine proved the presence of fine gold specks and granules inclusions within sulfide and quartz base minerals which may be the reason of the expected difficulty of leaching of gold. About 70% of the gold could be extracted under the following condition: 0.3M NH$_4$OH, 0.2M (NH$_4$)$_2$S$_2$O$_3$, 24 h, 480 rpm, Liquid : Solid = 1:2.
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Acknowledgement
The authors would like to thank Ma'aden company in KSA for allowing them to visit their Al-Amar mine and processing plant and for providing the rock samples.

References


