Microanalysis study of Al-Amar rock and leaching behavior of its tailings for recovery of gold and silver

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Abstract: Some Saudi gold ores, such as that at Al-Amar mine, suffer from low leaching efficiency using the toxic cyanidation process. Only about 60% of the gold and 26% of the silver in the feed ore can be extracted at 0.2% CN− after 24 h and the rest percentages of these metals remained in leaching residues (tailings). These tailings contained 1.1 ppm Au and 4.3 ppm Ag. Reprocessing of tailings serves both for economic and environmental reasons. A petrography analysis of the mineral constituents indicated that the rock samples consisted primarily of sphalerite, chalcopyrite, pyrite and galena in decreasing order of abundance. An electron probe microanalysis quantitatively showed that gold and silver were finely distributed in the grain boundaries and within sphalerite, chalcopyrite, pyrite, and quartz. The dissemination of gold and silver in these hard minerals may be the main reason for their low recovery by cyanidation. Open air roasting of the tailings can release amounts of the disseminated gold and silver which can be extracted during leaching with the harmless thiosulfate ion S2O32−. After studying the different parameters, we found that the maximum possible extraction of gold and silver from the tailings roasted for 2 h at 400°C reached about 50% at 0.2 M ammonium thiosulfate, 0.3 M ammonium hydroxide, solid–liquid ratio ½ for 24 h. These achievements represent a possible exploitation of the accumulated 1.65 million Mg tailing waste containing significant amounts of gold and silver valued at about $73 million.

Keywords: gold, silver, tailings, mineralogy, extraction, thiosulfate

1. Introduction

Exploration and exploitation of gold in Saudi Arabia has attracted many researchers and mining companies in the last few decades (Harbi et al., 2006; Surour et al., 2014). Operating gold mines currently use the toxic cyanidation process for gold extraction. Of these, the Al-Amar goldfield is one of the major sources of gold in Saudi Arabia (Surour and Bakhsh, 2013). However, it is one of the mines producing refractory ore for cyanidation and thus suffers low gold recovery. This has led to appreciable amounts of gold and silver remaining in rejected tailings (Mahmoud et al., 2015).

Al-Amar mine currently processes gold-rich polymetallic ore at a production rate of 200 ktpa, to produce gold doré as well as copper and zinc concentrates. About three-quarters of this amount (i.e. 150,000 t) is dumped annually as tailings with an average gold and silver content of about 1 and 5 g/t, respectively. A rough estimate shows that the quantity of tailings accumulated since the mine commenced production in 2006 up to now totals about 1.65 million Mg containing gold and silver valued at about $73 million. This considerable amount of lost precious metals encouraged a study of the reasons for the refractory nature of the ore and how to reprocess the tailings and extract the valuable metals. Once the most easily treated ore has been consumed, the gold industry in future may
have to treat ores with increasing degrees of refractoriness (La Brooy et al., 1994), or recover the wasted precious metals in tailings.

Tailings reprocessing is increasingly carried out in South Africa, Australia and Russia both for economic and environmental reasons (Kondrat’eva et al., 2012; Salinas-Rodríguez 2016). Malusel et al. (2012) proposed a process for the chemical extraction of gold and silver from tailings and from low-grade and refractory pyritic concentrates containing a minimum of 1 ppm gold in a sodium thiosulfate medium. The suggested process avoids the major problems of cyanidation: (a) cyanide is an extremely toxic substance that has been banned in many countries; (b) cyanidation is relatively inefficient (high reagent consumption for low gold extraction); (c) slow reaction kinetics of the cyanide ion with gold ore, 24–72 h (Ayata and Yildiran, 2001). Recent cyanide spillage disasters would suggest that the only ultimate solution for this problem is to replace cyanide with an environmentally friendly lixiviant.

Alternative non-cyanide lixiviants have been investigated for the treatment of refractory ores. Thiosulfate, thiourea, halogens and thiocyanate have received most attention (Wan et al., 1993). Most of these have a higher overall production cost and/or utilize processes that are relatively difficult to control. Thiosulfate is the most promising noncyanide lixiviant and is receiving extensive attention from both academic and industrial points of view (Mahmoud et al., 2015). Thiosulfate salts are known to be a much harmless chemical than cyanide, and are regarded as nonhazardous. They have been classified as “generally recognized as safe” (GRAS) by the U.S. Food and Drug Administration, and are not considered to be dangerous by European standards (Bean, 1997).

The aim of this work is to study the reason for the inefficient gold and silver extraction by cyanidation and to recover as much as possible of the lost metals in the tailings. Electron probe microanalysis (EPMA) has long been used in geological applications (Agangi et al. 2015). In the present work, the distribution of common and trace elements in the rock minerals was mapped using EPMA in order to find out the surrounding of gold and silver that blocking extraction. Cyanidation of the raw ore was first carried out and a detailed leaching study using thiosulfate was then performed to optimize the factors affecting the extraction of gold and silver from tailings. It is worth mentioning that reprocessing of the tailings did not require any grinding or concentration other than slight crushing, since the raw ore had already been finely ground and concentrated for cyanidation.

2. Material and methods

Samples were collected from different locations at the Al-Amar mine and its cyanidation plant (located 210 km west of Riyadh, KSA). Rough block samples of run-of mine (ROM) ore were selected for investigation of microscopic petrographic properties. A wet 50 L sample was collected from carbon in bulk feed stream (designated CIL feed) of the cyanidation plant, filtered and washed with fresh water. The wet cake was dried at 60 °C, and then broken down and used for leaching experiments by cyanide. The particle size of this material was as fine as 100% -100 mesh and 70% - 200 mesh. Five 10 kg samples of tailings waste (TW) were collected from different locations in the tailings dam, where the rejected filter cakes after CIL operation had been dumped. These were dried at 60 °C, then broken down, mixed and quartered to obtain a representative sample. This sample was packed in plastic bags for later use in chemical analysis, and for detailed leaching experiments by thiosulfate. The particle size of this material was almost same as CIL feed. Representative samples of ROM, CIL feed and TW were chemically analyzed through aqua regia digestion (using a microwave digester, MARS6–CEM), dilution with water and detection of major cations using inductively coupled plasma optical emission spectrometer, Optima 2000 DV, PerkinElmer (ICP-OES).

The chemical composition of the rock slices was determined using a Jeol electron probe microanalyzer JXA-8200 at the Department of Mineral Resources and Rocks, Faculty of Earth Sciences, King Abdulaziz University, KSA. Thin sections were prepared by polishing the samples to identify the ore minerals by reflected light microscopy. Distribution maps of selected elements were generated by the COMPO analysis of EPMA. The color legend in the distribution maps indicates decreasing order of percentage abundance of each element: red →orange → yellow → green → blue → black. Some minerals are readily recognized by matching the high color intensities of their components in the same areas (e.g., Zn and S for sphalerite; Fe and S for pyrite; Cu, Fe and S for chalcopyrite). The intensity of
gold and silver distribution in these minerals can thus be recognized by observing the color intensities of these metals in each mineral area.

Thermo-gravimetric differential thermal analysis (TG-DTA) of ROM and TW was performed using Shimadzu DTG-60/60 H thermal analyzer.

Extraction of Au and Ag was performed in an open sintered Pyrex conical flask reactor fitted in an electrical horizontal shaker. Ten grams of Al-Amar mine TW was placed in the reactor and a weighed amount of ammonium thiosulfate (ATS) was added. A 0.1 M CuSO₄ solution was prepared and the required volume was added to the reactor, if required. Then 20 mL of ammonium hydroxide (AH) at the required concentration (or water if needed) was added to the above mixture and the resulting slurry was shaken at 480 rpm for the necessary time periods. After the extraction time had elapsed and the slurry was filtered. Samples of leaching liquor were periodically taken, diluted with water and directly analyzed by ICP-OES. Similar experiments were performed following the same sequence of leaching, filtration and chemical analysis, but using CIL feed instead of TW with added NaOH and NaCN as leaching solutions. Double distilled water was used in the whole work and all chemicals used were of pure chemical grade.

3. Results and discussion

3.1 Mineralogical study of rock samples

Mineralogical studies were carried out prior to extraction experiments to give an overview of the mineral constituents and metal inclusions.

3.1.1 Petrography of sulfide mineral constituents

Two types of sphalerite Sph (ZnS) were optically observed: (i) Twinned euhedral to subhedral crystals (Fig. 1a), and containing exsolved particles of Chalcopyrite Ccp (CuFeS₂) (Fig. 1b); and (ii) subhedral to anhedral crystals (Figs. 1c, d). Ccp occurred in large aggregates as fracture infill in pyrite Py (FeS₂) crystals, (Figs. 2a, b). Ccp usually surrounded and filled fractures in large Py crystals (Figs. 2a, c) and occasionally forming intergrowths with large Sph crystals (Fig. 2b). It was also seen as exsolved Ccp within the Sph (Fig. 2d). Chalcocite Cc (Cu₂S) was found as crack infill within the Ccp masses (Fig. 2e, f). Py, the third-most abundant sulfide mineral, was found as small cubes (Figs. 3a, b) containing Py crystals with Ccp. Fine-grained Py occurred mostly as perfect cubes (Fig. 3a).
It can be concluded that the samples consisted of the following sulfide ore minerals in decreasing order of abundance: Sph, Ccp, Py and some galena (PbS). Other minor ore minerals were also recorded: covellite (CuS), chalcocite (Cu$_2$S) and bornite (Cu$_5$FeS$_4$). Sphalerite (the most abundant sulfide mineral) represented more than 40% of the total volume of sulfides in most cases. The sulfide minerals are mostly exsolved in different shapes and forms.

Fig. 2. Petrography of chalcopyrite in Al-Amar rock samples

3.1.2 Mineral chemistry using EPMA

Three ROM rock samples ("a", "b" and "c") were selected for EPMA investigation. Element distribution maps were generated to show the relative distributions of some selected elements on mineral crystals (Figs. 3a, b, c). Table 1 lists the chemical analyses of the identified minerals.

The map of sample “a” shows more gold in Sph than in Ccp (Fig. 3a). Silver is scattered fairly evenly in all the Sph and Ccp areas but in lower extent than that of gold. It is obvious from the map of sample “b” (Fig. 3b) that more of both gold and silver occur in Ga than in Sph. The map of sample “c” (Fig. 3c) shows both gold and silver distributed homogeneously in Sph, with reasonable amounts of iron and copper evenly scattered throughout the Sph, suggesting a small amount of disseminated Ccp. It is concluded here that gold and silver are very finely disseminated inside the crystals of some complex sulfide minerals, with varying metal content. Neither gold nor silver were observed in large accretions within the mineral textures.
Fig. 3. Elemental distribution map of Al-Amar rock samples a, b and c

Quantitative EPMA results (estimated averages of multiple readings, wt %) of major and trace elements in the analyzed areas of minerals identified in Al-Amar rock samples “a”, “b” and “c” are listed in Table 1. These readings showed that the Sph had average of S and Zn contents of 35.3% and 62.7% approaching the theoretical values of 32.9% and 67.1%, respectively. The average value of gold content in Sph was 0.022%, and that of silver was 0.004%. These values are somewhat low but generally consistent with the distribution maps (Fig. 3a, b, c), which also show much more gold than
silver in Sph. Notable average amounts of Fe and Cu (1.06% and 1.08%) were also detected in the Sph matrix of samples, suggesting the inclusion of small quantities of Fe and Cu along with the gold and silver. The average Fe and S contents of the pyrite are 44.95% and 54.93% approaching the theoretical values of 46.7% and 53.3%, respectively. The average gold and silver contents in Py were 0.02% and 0.004%, respectively. The Ccp contained 32.86% Cu, 30.12% Fe and 36.79% S on average, compared with the theoretical values of 34.6%, 30.50% and 34.90%, respectively. The average gold and silver contents in Ccp of this sample were 0.016% and 0.01%, respectively.

Table 1. EPMA of identified minerals in Al-Amar rock samples (wt.%)

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<th>S</th>
<th>Cu</th>
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<th>Co</th>
<th>Pb</th>
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<th>As</th>
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<td>0.006</td>
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<td>0.785</td>
<td>13.388</td>
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<td>0.000</td>
<td>0.053</td>
<td>0.026</td>
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3.2 Thermal analysis (TGA- DTA)

Thermal analysis was selected to examine the behavior of ROM ore (Fig. 4a) and TW (Fig. 4b) during the roasting process. As shown in Fig. 4a, a sharp exothermic peak is evident in the DTA curve at temperatures around 480.1 °C. A mass loss of 3.1% was detected on the TGA curve for a temperature increase from 58.1 to 482.5 °C. It is supposed that the heat release and weight loss is connected with the oxidation of sulfur in some sulfide minerals such as pyrite in the sample. This is followed by a mass gain, then a further mass loss of 12.2% in the temperature range 585.1 to 969.6 °C. This mass loss may be due to oxidation of sphalerite (Földvári M., 2011). The maximum mass loss appeared at 1000 °C. As shown in Fig. 4b, a mass loss of 2.7% was detected on the TGA curve of TW for a temperature increase from 28.5 to 583.2 °C and another mass loss of 4.89% was detected for a temperature increase from 583.2 to 983.4 °C. Reasons of these two mass losses in TW may be same as those of ROM mentioned above.

3.3 Chemical analysis

Silicon was the major component of TW sample (Si = 39.6%) which suggest that the main gangue minerals are silica and silicates. The sample contained gold and silver in amounts of 1.12 ppm and 4.3 ppm, respectively. These contents were not extracted with cyanidation and expected to be left encapsulated within the TW sulfide minerals. Copper content was as low as 0.11%, hence the contained copper was already separated from ROM by flotation. Zinc and iron are the major metal constituents (about 13% and 6.3%, respectively). The sample contained minor elements such as vanadium (0.4%), manganese (0.35%) and lead (0.04%).
3.4 Extraction of Au and Ag from CIL feed by cyanidation

To verify the limited efficiency of cyanidation of Al-Amar ore, CIL feed was first investigated. The cyanide dissolution of gold is described by the Elsner equation to be:

$$4\text{Au} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Na}[\text{Au(CN)}_2] + 4\text{NaOH}. \quad (1)$$

In this redox process, oxygen eliminates one electron from each gold atom to form the complex [Au(CN)$_2$]$^-$ ion (Srithagavavut et al., 2011). A series of experiments was performed to study the effect of NaCN concentrations from 0% to 0.2% on the extraction of gold and silver from CIL feed at S/l = ½ for 24 h. It can be noticed in Fig. 5 that only 60% of the gold and 26% of the silver were extracted at 0.2% CN$^-$ concentration. It was predicted and later confirmed by the above petrographic investigations that the inclusion of fine gold and silver particles within the hard sulfide minerals may be the major reason for the low metal recovery. Releasing the disseminated gold would require the mineral crystal substrates to be broken up, which is known to be very difficult or impossible to achieve by fine grinding. Thus, there is no direct contact between the leaching agent and the trapped gold and silver, and they are therefore retained in the leaching residue, TW. We have found that cyanidation of fine ground CIL feed gave very limited improvement on extraction of gold and silver. Ultra-fine grinding may break the sulfidic mineral crystal and increase the extraction efficiency of gold and silver. However, this would be associated with extensive power consumption making the whole process uneconomical (Celep et al., 2015).

As discussed, extraction experiments were carried out on the accumulated tailings for possible recovery of the residual valuable metals. The following subsection describes the use of the harmless thiosulfate medium to extract the gold and silver from the TW, modified for releasing the trapped metals.

3.5 Extraction of Au and Ag from TW by thiosulfate

Leaching of gold in a thiosulfate solution is a metal oxidation process described by (Feng and Van Deventer, 2010).

$$4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Au(S}_2\text{O}_3)_{2}^{3-} + 4\text{OH}^{-}. \quad (2)$$

In ammoniacal thiosulfate gold leaching using cupric ammine as an oxidant, the reaction chemistry is explained by the intermediate reactions:

$$\text{Au} + 5\text{S}_2\text{O}_3^{2-} + \text{Cu(NH}_3)^{4+} \rightarrow \text{Au(S}_2\text{O}_3)_{2}^{3-} + 4\text{NH}_3 + \text{Cu(S}_2\text{O}_3)_{5}^{3-} \quad (3)$$

$$16\text{NH}_3 + 4\text{Cu(S}_2\text{O}_3)_{5}^{3-} + \text{O}_2 + 4 \text{H}^+ \rightarrow 4\text{Cu(NH}_3)^{4+} + 2\text{H}_2\text{O} + 12\text{S}_2\text{O}_3^{2-}. \quad (4)$$

Unlike cyanidation, thiosulfate leaching of gold does not require a diffusion of oxygen onto the solid–liquid interface of the gold, which is very slow under atmospheric conditions. The direct oxidant of gold is Cu(II) ammine after it is adsorbed onto the surface of the gold in the cathodic area. Silver coexists in most gold ores in the form of the alloy electrum, or as acanthite (Ag$_2$S) or other minerals (Zhang et al., 2008). Silver interacts with thiosulfate as follows:
Ag₂S + 2S₂O₃²⁻ → 2Ag(S₂O₃²⁻)²⁻ + S²⁻. \hspace{1cm} (5)

3.5.1 Effect of ammonium thiosulfate (ATS) concentration

Extraction of gold and silver from TW was carried out using ATS concentrations between 0.05 and 1.6 M, and 0.3 M AH, S/l = ½, for 6 hrs (Fig. 6a). The results showed that there was almost no extraction in the absence of ATS, then continuously improved with increasing ATS concentration up to 0.2 M where about 23% Au and 27% Ag were obtained. Then the extraction slowly decreased at higher concentrations possibly due to the decomposition of ATS and deposition of elemental sulfur on surface of ore grains. The extraction of Ag was consistently slightly higher than Au. Thus 0.2 M ATS was selected as the optimum concentration and was utilized in the following experiments.

3.5.2 Effect of AH concentration

It is known that ATS is stable in alkaline mediums and quickly dissociates in acidic mediums, forming fine elemental sulfur (Holleman and Wiberg, 2001). The presence of an alkaline medium such as AH is therefore important to ensure that the ATS remains undissociated during gold leaching. AH is also important for keeping the Cu²⁺ ion stable in solution (Eqs. (3) and (4)). Extraction of gold and silver from the TW was carried out at AH concentrations of 0.0 – 0.5 M and 0.2 M ATS, S/l = ½, for 6 h (Fig. 6b). The pH values of the reaction mixture before the extraction experiments ranged from 11.3 to 11.9 at AH concentrations between 0.1 and 0.5 M, resulting in equilibrium values of 8.7 and 9.6 respectively after the experiment. The decrease in pH after extraction may have been due to the acidic nature of certain byproducts. As shown in Fig. 6b, the gold and silver extraction were as low as 5% and 10%, respectively, when no AH was present in the leaching solution. The extraction efficiency continuously increased with increasing AH concentration for both metals, with the amount of silver usually higher than that of gold. At 0.3 M AH, about 23% and 27% of gold and silver were extracted, respectively, and the amounts almost stabilized at higher AH concentrations. It appears that the improved leaching performance with increasing AH concentration was due to the increasing stability of the thiosulfate (S₂O₃²⁻) ions, and the leached copper from the ore in solution. The results were evidence that 0.3 M AH concentration was the optimum value.

3.5.3 Effect of CuSO₄ concentration

Copper(II) is known to be a very effective catalyst for the gold oxidation reaction (Marsden and House, 2006). The leaching of gold in thiosulfate solutions is an electrochemical reaction, with the constituent half reactions being the oxidation of gold to gold thiosulfate, and the reduction of Cu(II) amine to Cu(I) thiosulfate — that is, Cu(II) oxidizes Au(0) to Au(I) in the presence of S₂O₃²⁻ as a complexing agent. The Cu(I) so formed is then re-oxidized to Cu(II) by the dissolved O₂ (see Eqs. (3) and (4)).

The effect of adding Cu²⁺ (as CuSO₄) during extraction of gold and silver from the TW of Al-Amar mine was investigated for 0.2 M ATS and 0.3 M AH, 6 h, S/l = ½ (Fig. 6c). An unexpected finding was
that the extraction efficiency for both metals was almost unaffected when the CuSO₄ concentration was increased. This behavior may be attributed to the presence of residual natural copper in the TW which may have acted as a self-catalyst, in such case the addition of an external catalyst of the same nature would have had no significant effect. For this reason, no copper was added in the following extraction experiments.

3.5.4 Effect of roasting temperature

The host matrices of Al-Amar ore are inert and/or impermeable to the leaching solution. The thermal analysis charts for the TW (Fig. 4b) show that high temperature at open air atmosphere caused exothermic DTA peaks accompanied by weight loss. This is particularly clear around 400°C, and may indicate that some structural change (e.g., oxidation of certain sulfide minerals) had occurred. Such behavior may release the encapsulated gold and silver inclusions and make them available for contact with the extraction reagent in the reaction medium. The roasting of Al-Amar TW was tested at temperatures from 200 to 1000°C for 2 h. The brownish coloration of the roasted samples became stronger at higher roasting temperatures, most likely indicating the oxidation of a sulfide mineral such as Py to hematite (Fe₂O₃).

The effect of roasting temperature on the extraction of gold and silver at 0.2 M ATS, 0.3 M AH, 6 h, S/l = ½ is shown in Fig. 6d. A continuous increase in the extraction of both metals with increasing roasting temperature up to 400°C was observed, beyond which the amounts extracted sharply declined. This may have been due to the agglomeration of ore particles, evident from the formation of visible bulk and hard dark grains following roasting. About 45% of the gold and 46% of the silver were extracted from the roasted TW at 400 °C.

3.5.5 Effect of contact time

Gold and silver were extracted from the TW of Al-Amar mine for different contact time periods (from 2 to 24 h) and 0.2 M ATS, at 0.3 M AH, S/l = ½, with and without roasting. The results (Fig. 6e) show that extraction from the unroasted TW continuously increased with increasing contact time, but were insignificant for contact times longer than 6 h. After 24 h about 30% of the gold and 35% of the silver had been simultaneously extracted.
For roasted TW the extraction amounts increased significantly with contact time, continuing to increase very slightly beyond 6 h. About 50% of both gold and silver were extracted from the roasted ore after 24 h.

4. Conclusions

Detailed petrographic investigations demonstrated that the Al-Amar ore in Saudi Arabia contains gold and silver distributed in grain boundaries and within sulfide minerals. The fine dissemination of gold and silver within hard sulfide minerals was the major reason for the refractory nature of the ore in cyanide. Considerable amounts of Au and Ag are lost in the accumulated tailing waste (TW) of cyanidation in the tailing dam of Al-Amar mine since 2006 till the moment.

We have carried out two leaching experiments of Au and Ag, one by cyanidation from CIL feed, and the other by the harmless ammonium thiosulfate (AT) from TW. Cyanidation of the ore extracted 60% of Au and 26% of Ag, meaning that 40% of Au and 74% of Ag remained in the TW mainly encapsulated within the hard sulfide minerals. Roasting of the TW at 400 °C, for 2 h and subsequent leaching with 0.2M AT in 0.3 M ammonium hydroxide could extract 50% of the trapped Au and Ag. These achievements represent a possible utilization of the accumulated 1.65 Mg TW containing gold and silver valued at about $73 million.

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