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The potential of Sudanese Refractory Gold Ores Characterization and Pre-treatment in Ariab Mines (VMS) in Red Sea (Sudan)

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Abstract

This laboratory work demonstrates the ability to characterize and pretreat Sudanese refractory gold ores at Ariab mines to extract the gold with optimal parameters. Characterization studies were performed by AAS, XRF and XRD analysis to assess the abundance of elements and mineral phases. In addition, the acidity of the ore was examined to estimate the effective amount of lime. The ore was subjected directly to cyanidation without any pre-treatment. High oxidation reagent processes were carried out to pre-treat the ore. Chemical analysis results show the gold grade to be 1.37 g/t. In addition, the ore contained 51.78% Fe₂O₃, 43.40% SO₃, 2.39% CuO, 1.47% SiO₂, 0.35% Cr₂O₃, 0.17% CaO, 0.08% As₂O₃, 0.06% ZnO and 0.06% MnO. The XRD result shows that the ore phases are Pyrite (FeS₂), Chatkaite (Cu6Fe+2Sn₂S₂) and Quartz (SiO₂). The investigations of direct cyanidation elucidated that the ore can consume a high amount of cyanide with unsatisfactory recoveries for gold (Exgold \leq 39.41%). The influence of the cyanide concentration, pulp density (% by weight), leaching time hr, agitator speed and pH were examined in direct cyanidation experiments. In pre-treatment experiments, the effect of hydrogen peroxide (H₂O₂) and concentrations on gold recovery was studied. The pre-treatment of the ore with H_2O_2 achieved a good impact on the gold extraction performance. The higher gold extraction was obtained at hydrogen peroxide (H₂O₂) 300 ppm, cyanide concentration 3500 ppm, leaching time 10 hr, pH=10.5 and pulp density 40%.

Keywords

Refractory gold ores, Characterization, Cyanidation, Leaching, Preoxidation, Recovery.



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Introduction

Volcanic Massive Sulphide deposits (VMS) hold invaluable minerals and metals such as Pyrite (FeS₂), Pyrrhotite (FeS), chalcopyrite (CuFeS₂), Chalcocite (CuS₂), Sphalerite (ZnS), Galena (PbS), Gold (Au) and silver (Ag)(Mercier-Langevin, Hannington, Dubé, & Bécu, 2011). Its typically high gold concentration in VMS deposits is deemed an important target for gold mining exploration and prospecting as its gold grade contributes significantly to the overall value. Sudan ranked 2nd among the gold-productive countries in Africa and within twenty countries around the world. Thus, the gold mining sector has and will continue to make a good contribution to the Sudanese economy (Sasmaz, 2020). Red Sea Hills occur in the shield of Arabian-Nubian in the east of Sudan, which is presently considered favourable for additional gold exploration. The gold in this area associates with massive volcanic sulphide deposits(Abu-Fatima, Marignac, Cathelineau, & Boiron, 2021).

The gold-bearing ores can be divided into free milling and refractory depending on the metallurgical efficiency to dissolve by cyanidation as is seen in ((1) and (Fig.) (Celep, Alp, & Deveci, 2011; Free, 2021; Medina & Anderson, 2020).



$$4Au + 8CN^{-} + 2H_2O + O_2 \to 4Au(CN)_2^{-} + 4OH^{-}$$
(1)

Fig. 1 Pourbaix diagram for gold and cyanide (Free, 2021).

Free-milled gold ore is defined as the ore that has a high gold extraction (90%) without high consumption of reagents for the reaction, i.e. (cyanide and oxygen), which means that sufficient cyanide is added to leave a concentration of 100-200 ppm at pH 10 at the end of the leach (La Brooy, Linge, & Walker, 1994). The term "refractory" refers to ores for which extraction by direct leaching yields poor recoveries or excessive leaching times. The common reason for refractory ores is gold locked inside a host mineral matrix. Usually, the host mineral matrix is most sulphuric (Lunt & Briggs, 2005; Udupa, Kawatra, & Prasad, 1990). Examples of these sulphurous minerals are pyrite (FeS₂), pyrrhotite (FeS), chalcopyrite (CuFeS₂), chalcocite (CuS₂), sphalerite (ZnS) and galena PbS. Therefore, the recovery of gold in the cyanidation process is decreased because the ions cyanide and oxygen are which are necessary for dissolving gold are consumed via sulphuric mineral as seen in ((2) ,((3) and ((4) (Abdollahi, Karimi, Amini, & Akcil, 2015; Coronado et al., 2012; Peter D. Kondos, Griffith, & Jara, 1996).

$$S^{2-} + CN^{-} + \frac{1}{2}O_2 + H_2O \to CNS^{-} + 2OH^{-}$$
 (2)

$$2S^{2-} + 2O_2 + H_2O \leftrightarrow S_2O_3^{2-} + 2OH^- \tag{3}$$

$$S_2 O_3^{2-} + 20H + 2O_2 \leftrightarrow 2SO_4^2 + H_2 O_2 \tag{4}$$

Refractory gold ore is generally classified into two types, but the fact that ores achieve acceptable economic gold recoveries using only height levels of oxygen and cyanide requirements are sometimes referred to as (complex),

as illustrated in (Fig.2 Fig.) (Adams, Liddell, & Smith, 2020; La Brooy et al., 1994; Ofori-Sarpong & Osseo-Asare, 2013; Sauer, Rintala, & Roth-Berghofer, 2013). Preg-robbing behaviours may present from natural carbonaceous materials in the ore that may adsorb the gold (La Brooy et al., 1994).



Fig. 2 The classification of gold ores by processing.

In the chemical extraction of free-ground gold ores, pre-treatment is usually limited to the beneficiation of the ore (crushing and milling), making the gold accessible to cyanide ions. Consequently, the rate of cyanidation depends on the fineness of the ground ore (Amankwah, Khan, Pickles, & Yen, 2005). In contrast, the primary goal of refractory pre-treatment is to remove or reduce the sulfur from the sulfur-bearing ore via physical treatment (ultrafine grinding), chemical pre-treatment, thermal pre-treatment, biological pre-treatment and pressure oxidation pre-treatment. In the fine, the ore is ground to (>38 micro) using a conventional mill or in size in range (1-20 micro) via vibratory mills, stirred mills and jet mills. In order to liberate the physically locked gold and improve its recovery, as is discussed above, the gold becomes more accessible to the cyanide solution (Celep et al., 2011; Ellis, Mines, & Kalgoorlie, 2003; González-Anaya, Nava-Alonso, & Pecina-Treviño, 2011). For example, for chemical pre-treatment, the oxygen peroxide is often used to oxidize the mineral sulphide (MS) to oxide or sulphate prior to cyanidation, as is presented in ((5) and ((6) (Nunan et al., 2017). As well as, sodium hydroxide is utilized in alkaline leaching for pre-treatment, and the recovery results of both methods can be

reached to (Re_{gold} ≤90%) of gold (Alp, Celep, Paktunc, & Thibault, 2014).

$$MS + 4H_2O_2 \to MO + H_2SO_4 + 3H_2O$$
 (5)

$$MS + 4H_2O_2 \rightarrow MSO_4 + 4H_2O \tag{6}$$

Thermal treatment can be applied to break down the sulphide phase to access gold. The sulphide is converted to oxide in the presence of oxygen ((7); this process is called roasting (Qin, Guo, Tian, Yu, & Zhang, 2021).

$$MS + \frac{3}{2}O_2 \to MO + SO_2 \tag{7}$$

The roasting of pyrite is usually carried out at 650-700°C; the pyrite transforms into hematite, which is insoluble in cyanide solution as seen in ((8) (La Brooy et al., 1994).

$$4FeS_2 + 11O_2 \to 2Fe_2O_3 + 8SO_2 \tag{8}$$

In this study, direct cyanidation of refractory gold ore at Ariab mines was performed. The influence of the cyanide concentration, pulp density (% by weight), leaching time, agitator speed, and pH value influence were examined. In addition, the ore was pre-treated with hydrogen peroxide (H₂O₂), and the effects of hydrogen peroxide and concentrations on gold recovery were studied.

Materials and methods

Raw material preparation

A systematic sampling producer collected a representative sample of 200 kg of refractory gold ore from Ariab's mines in Sudan (Fig. 3). The sample was prepared for less than 2.25 mm using two stages of a jaw crusher and then a roll crusher. About four kilograms were taken using the rifling, coning, and quartering method and then prepared to -75 μ m for experimental test using a laboratory ball mill. Also, 100 grams of a representative sample were taken carefully and then ground for less than 75 μ m by desk mill for sample characterization.



Fig. 3 The study area (Ariab mines)

Ore characterization

For characterization, the mineralization of the test sample was complicated by X-ray Diffraction analysis (XRD) to define the phases for each mineral in the sample. X-ray Fluorescence (XRF) and Atomic Absorption Spectrophotometer (AAS) analyses were carried out to identify the grades of elements and mineral oxides.

pH examinations

Five representative samples of about 84 grams were placed in different 250 ml beakers and then mixed with distilled water at a temperature of 25°C at different pulp densities (wt%) of 35%, 40%, 45%, and 50%. The mixed sample was mixed using a mixer (Multi-Function Leaching Mixing Machine), and then pH at variance time was measured via JENWAY 3505 pH-meter.

Lime consumption

For the required lime to condition pH value of cyanidation experiments, five samples were prepared at a pulp density of 40%, and then different amounts of lime Ca $(OH)_2$ were added for each sample. Finally, the pH was read as a function of time by JENWAY 3505 pH meter.

Direct cyanidation experiments

Approximately 4 kg of a representative sample (-2.25 mm) was prepared for the cyanidation tests using a laboratory ball mill down to -75 μ m and then analyzed (1.92 g/t) (Fig. a). The tests were carried out in a 500 ml beaker with a mixer (Multi-Function Leaching Mixing Machine) (Fig. b). The vacuum filter was used to separate the pregnant salutation from the solid. JENWAY 3505 pH meter was used to control the pH, and slaked lime and

hydrochloric acid of concentration (5%) were used to adjust the pH of the pulp. Sodium cyanide (NaCN) was a solvent of the cyanidation process. For each experiment, 84 grams of sample and distilled water (ppm) were prepared to obtain the desired pulp at the known dilution ratio and cyanide concentration; then, the pulp pH was adjusted. The pulp was mixed for a known time (leach time), and the agitator was set to a desired speed (rpm). The effect of cyanide concentration, pulp density, leach time, pH and agitator speed were examined. At the end of the test, the pulp was discharged, filtered and dried (tailing). The gold content in the sample before and after leaching was analyzed by AAS to calculate gold recovery using (9.

$$RE(\%) = 100 * \left(\frac{A_{gold} - B_{gold}}{A_{gold}}\right)$$

$$RE(\%) \equiv gold \ recovery$$

$$A_{gold} \equiv gold \ content \ in \ the \ sample$$

$$(9)$$

 $B_{gold} \equiv gold \ content \ in \ tailing$



Fig. 4 (a) Laboratory ball mill, (b) Agitation system

Pre-treatment experiments

Gold ore pre-oxidation experiments were performed using hydrogen peroxide (H_2O_2) in a 250 ml glass beaker using a mechanical agitator (Multi-Function Leaching Mixing Machine) at 160 rpm. For each experiment, 84 grams of sample was mixed with distilled water at a known dilution ratio and hydrogen peroxide concentration ppm. The effect of hydrogen peroxide concentration ppm was studied. The pulp was leached for 2 hours, then discharged, washed with distilled water and subjected to cyanidation.

Results and discussions

Mineralogical and chemical analyses

Tab. 1 X-ray fluorescence analysis of the ore.

Component	Fe ₂ O ₃	SO ₃	CuO	SiO ₂	Cr ₂ O ₃	CaO	As ₂ O ₃	ZnO	MnO	Pb	Se	Ag
%	51.57	43.40	2.39	1.47	0.35	0.17	0.08	0.06	0.06	0.05	0.017	0.003



The X-ray fluorescence results in Tab. 1 show that the content of the sample is dominated by sulphurous minerals, which are shown in the result of the X-ray diffraction analysis in Fig.5. The sample contains pyrite (FeS₂), chatkaite ($Cu_6Fe+2Sn_2S_2$) and quartz (SiO₂).

Size and gold distribution

Fig. shows the size and gold distribution analyses for the representative sample using the sieve analysis test and AAS. The head sample analysis is 1.37 g/ton. It presents the gold concentrates in size (-425+150) μ m.



Fig. 6 Size and gold distribution analyses

pH examinations

Fig. shows the pH test as a function of various time and pulp densities. The test results revealed that the oxidation rate of sulphuric minerals decreases when the solid percentage increases, and this attributes to the dissolved oxygen in the water at 8 ppm/l. This amount of oxygen is consumed to convert the sulphur to sulphate (Peter D. Kondos et al., 1996).



Fig. 7 The pH test as a function of different time and pulp density

Lime consumption

Fig. shows the pH test as a function of various make-up limes and time at 45% solids. The results show that an optimal (pH = 10.6) for cyanidation was obtained at 45 g/kg added lime.



Fig. 8 The pH test as a function of different additive lime and time at a solid percentage of 45%

Direct cyanidation experiments

The effect of cyanide concentration:

- Cyanidation at low cyanide concentration:

Tab. 2 shows the gold extraction (%) as a function of normal cyanide concentration at pulp density 45%, pH=10.5, leaching time 4 hours and 450 rpm. The results showed that at low cyanide concentration, gold's recovery or extraction (%) is zero because the dissolved cyanide is consumed by the sulphuric mineral, as seen in (2.

100.2 Gold extraction 70 as a function of low cyanide concentration at pulp density 4570, p11-10.3, leacning time 4 nours and 450 rp	Tab. 2 Gold extraction % as a	function of low cyanide concentration	n at pulp density 45%, pH=10.5, leac	hing time 4 hours and 450 rpn
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NaCN (ppm)	200	400	600	800	1000
Free NaCN (ppm)	5	5	10	10	10
Au Extraction (%)	0	0	0	0	0

- Cyanidation at high cyanide concentration:

Tab. 3 shows the gold extraction % as a function of high cyanide concentration at pulp density 45%, pH=10.5, leaching time 4 hours and 450 rpm. It shows that with high cyanide concentration, the extraction rate of gold increases but is still very low and unsatisfactory.

Tab. 3 Gold extraction % as a f	unction of high cyanic	le concentration at pulj	o density 45%, pH=10.	5, leaching time 4 hou	rs and 450 rpm.
NaCN (ppm)	1500	2000	2500	3000	3500
Free NaCN (ppm)	30	35	35	40	40
Au Extraction (%)	11.31	14.12	23.63	31.42	39.42

The effect of leaching time

Fig. shows the gold extraction % as a function of various leaching times at cyanide concentration 3500 ppm, pulp density 45%, pH=10.5 and 450 rpm. It reveals that the optimal time for extracting the gold is 10 hours.



Fig. 9 Gold extraction % as a function of various leaching times at cyanide concentration 3500 ppm, pulp density 45%, pH=10.5 and 450 rpm

The effect of pulp density

Fig. 10 shows the gold extraction % as a function of various pulp densities at cyanide concentrations of 3500 ppm, leaching time 10 hr, pH=10.5 and 450 rpm. It illustrated that the optimum condition for best gold recovery was achieved at a solid percentage of 45%.



Fig. 10 Gold extraction % as a function of various pulp densities at cyanide concentration 3500 ppm, leaching time 10 hr, pH=10.5 and 450 rpm

The influence of pH

Fig. 2 shows gold extraction % as a function of pH various at cyanide concentration 3500ppm, leaching time 10 hr, agitation speed 450 rpm and pulp density 40%. It demonstrated that the extraction rate increases at the rate of extraction increase at pH higher than 10 because, as seen in the pH diagram in Fig. , at pH=10, the gold can be oxidation at low potential E (v) \approx -0.2V, so the reaction affinity of gold ions Au⁺² with cyanate CN⁻ has been increased to produce cyano-gold Au(CN)⁻₂. But above pH 12, the gold extraction rate decreases because when we add lime Ca (OH)₂, CaO₂ is generated on the surface of the gold, so the cyanide ions cannot reach it.



Fig. 2 Gold extraction % as a function of pH various at cyanide concentration 3500 ppm, leaching time 10 hr, agitation speed 450 rpm and pulp density 40%.

The influence of agitation speed (rpm):

Fig. 3 shows the gold extraction % as a function of agitation speed (rpm) at cyanide concentration 3500 ppm, leaching time 10 hr, pH=10.5 and pulp density 40%. The performance of cyanidation improves when the agitation speed is higher than 300 rpm because the pulp does not allow for settling at this speed.



Fig. 3 Gold extraction % as a function of agitation speed (rpm) at cyanide concentration 3500 ppm, leaching time 10 hr, pH=10.5 and pulp density 40%.

Pre-treatment experiments

Fig. 4 shows the gold extraction (%) of the pre-treated sample as a function of hydrogen peroxide (H_2O_2) ppm at cyanide concentration 1500ppm, leaching time 10 hr, pH=10.5 and pulp density 40%. It revealed that a higher

extraction rate of gold was achieved at a hydrogen peroxide concentration of 300 ppm. The function of hydrogen peroxide in refractory gold ore is to oxidize the sulphurous mineral to the sulphate mineral, as shown in Eq. 5 and Eq. 6, and this leads to a reduction in cyanide consumption (Nunan et al., 2017). But at high concentrations of hydrogen peroxide, the rate of gold extraction decreases because a high concentration of dissolved oxygen rolls to generate Au (OH) $_3$ on the surface of the gold particle. AuO₂ does not allow the cyanide in the presence of oxygen to dissolve the gold.



Fig. 4. Gold extraction % of the pre-treated sample as a function of hydrogen peroxide (H₂O₂) ppm at cyanide concentration 1500ppm, leaching time 10 hr, pH=10.5 and pulp density 40%

Fig. 5 shows the effect of cyanide concentration on gold recovery in pre-treated gold ore using hydrogen peroxide at a pulp density of 40%, hydrogen peroxide concentration of 300 ppm, leach time of 10 hours and agitation speed of 450 rpm. The results showed that the gold recovery was improved. For example, under the same conditions and a cyanide concentration of 3000, the gold extraction percentage was 31.42% in the direct cyanidation test and 90.02% after the pre-treatment. As well as the use of high cyanide concentration negatively affected the gold extraction rate because, generally, it dissolves at (CN^2/O_2) 4.7-7.6 mg/l (P. D. Kondos, Deschênes, & Morrison, 1995).



Fig. 5 Effect of cyanide concentration on gold recovery in pre-treated gold ore

Conclusions

- The ore in the study area is considered high sulphuric minerals and contains Pyrite (FeS₂), Chatkaite $(Cu_6Fe+2Sn_2S_2)$ and Quartz (SiO₂). The concentration of gold in the ore is 1.92 g/ton.
- Studies on direct cyanidation show that the recovery of gold from this ore is not economical and satisfactory because the cyanidation process consumes a large amount of cyanide and, moreover, the percentage of gold extraction is very low. Therefore, a pre-treatment process is required.
- Hydrogen peroxide H₂O₂ is widely used in the pre-treatment of refractory and semi-refractory gold ore as it has a high concentration of dissolved oxygen, which is considered very important for the cyanidation mechanism.
- The results of the pre-treatment experiments show that adding a high H₂O₂ concentration of more than 300 ppm negatively impacts the extraction performance.

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