Metallurgy and materials
Metalurgia e materiais

Effectiveness acidic pre-cleaning for copper-gold ore

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Abstract

The presence of copper-bearing minerals is known to bring on many challenges during the cyanidation of gold ore, like high consumption of cyanide and low extraction of metal, which are undesirable impacts on the auriferous recovery in the subsequent process step. The high copper solubility in cyanide prevents the direct use of classical hydrometallurgical processes for the extraction of gold by cyanidation. Additionally, the application of a conventional flotation process to extract copper is further complicated when it is oxidized. As a result, an acid pre-leaching process was applied in order to clean the ore of these copper minerals that are cyanide consumers. The objective was to evaluate the amount of soluble copper in cyanide before and after acidic cleaning. From a gold ore containing copper, the study selected four samples containing 0.22%, 0.55%, 1.00% and 1.36% of copper. For direct cyanidation of the ore without pre-treatment, copper extraction by cyanide complexing ranged from 8 to 83%. In contrast, the pre-treatment carried out with sulfuric acid extracted 24% to 99% of initial copper and subsequent cyanidation extracted 0.13 to 1.54% of initial copper. The study also showed that the copper contained in the secondary minerals is more easily extracted by cyanide (83%), being followed by the copper oxy-hydroxide minerals (60%), while the copper contained in the manganese oxide is less complexed by cyanide (8% a 12%). It was possible to observe that minerals with low acid solubility also have low solubility in cyanide. Cyanide consumption decreased by about 2.5 times and gold recovery increased to above 94% after acidic pre-cleaning.

Keywords: copper, mineral, gold, acid cleaning, cyanidation, copper-gold ore.

1. Introduction

Cyanidation is the most common method employed to recover gold and silver from their respective ores. In this process, other metals, besides gold and silver, can be dissolved in certain circumstances and interfere with the extraction efficiency of these targets. Copper is one of these metals, being able to reach concentrations as high as 1,000mg/L. When the cyanide solution contains a high concentration of copper, extraction of precious metals reduces and operational costs increase (Hsu and Tran, 1996; González *et al.*, 2009).

Copper minerals, either as oxides, sulfides or metallic copper, may be responsible for the significant consumption of cyanide. Although chalcopyrite is the most abundant of the copper minerals, it is poorly soluble in cyanide. However, other minerals such as azurite, malachite, cuprite and chalcocite exhibit a high solubility (Dai and Jeffrey, 2006; Habashi, 1967; Nguyen *et al*, 1997).

For most operations, the cut-off grade for direct cyanidation of oxidized gold ore is that of a copper content below 0.5%. Above this value, the cyanide consumption by copper minerals becomes significant (Dai *et al*, 2012) because a high concentration of free cyanide is required for extraction of gold from the ore (Costello *et al* 1992; Muir *et al.*, 1989).

The cyanidation of bivalent copper minerals results in loss of cyanide in the ratio of $0.5molCN^-/molCu^{2+}$ leached, i.e., $0.39kgNaCN/kgCu^{2+}$ (Muir, 2011; Mendes, 1999).

The solubilization of copper by the cyanide process differs from gold and silver. In copper mineral leaching, it is not necessary to employ an oxidizing agent and the time required for dissolution of the mineral species is much smaller; however, the required cyanide concentrations reach higher values. When subjected to cyanidation, ores containing soluble copper minerals dis- solve forming various complexes, such as $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. This distribution depends greatly on the pH and the cyanide to copper concentration ratio (Nguyen *et al*, 1997).

Copper oxide ores (oxides, carbonates, silicates and sulfates) have poor responses to concentration by flotation. However, they are effectively treated by hydrometallurgical processes such as acid leaching. Sulfuric acid is an extensively used reagent in traditional hydrometallurgy to leach copper minerals, with the advantages of relatively low cost, availability, reaction with oxidized minerals and possibility of partial regeneration. Furthermore, it is also used in the leaching of a wide variety of metal-bearing minerals, including sulfides, tellurides, silicates, phosphates, and others. Sulfuric acid is successfully used in the extraction of metals from oxidized minerals such as copper, zinc, nickel, manganese, aluminum and to a lesser degree, uranium,

niobium, tantalum and titanium (Gupta e Mukherjee, 1990).

The objective of this study was to evaluate the amount of copper soluble in cyanide before and after acidic pre-cleaning, defining leaching parameters that can be applied to different ore lithology, such as oxidized, sulfide, or transition ores. It also applies to the different types of gold bearings, both refractory and non-refractory. As a result of this acidic pre-cleaning, there is an increased recovery of gold, since gold bearing or associated minerals were destroyed. However, it is only a secondary effect and the technique does not aim to maximize this effect, only to minimize cyanide consumption by eliminating cyanides, especially copper. This study was done using transition ore (oxidized and sulfide).

2. Material and method

2.1. Sample preparation

The ore used in this study was obtained from drill core samples from the northern region of Brazil. Four samples were used from four different holes: FS001-53, FS002-56, FS003-78, and FS004-87. The last two digits identify the maximum depth, in meters, of the sample.

The samples were crushed separately until particle size was less than 1.0mm. A sample of 100g of this material was taken for mineralogical analysis and the leftover material was crushed to particle sizes below 0.074mm. Then three samples were taken from this leftover material: i) 50g were selected for the pre-acid leaching assay (cleaning) and subsequent cyanidation of the residue; ii) 5g for the direct cyanidation ore assay and; iii) 50g went on for chemical analysis.

2.2 Reagents

Chemical grade reagents were used: NaCN 1%, NaOH 5% (Sigma-Aldrich) and H_2SO_4 98% (F.Maia).

2.3 Acid cleaning assay

The copper cleaning test consisted of solubilization in an acidic environment of 50g of ore containing copper. This mass was leached in a flat-bottomed flask containing 500ml of acid solution (pH<1.0) for 48h at room temperature with stirring rate at 300rpm. After the leaching time, the residue was filtered through a vacuum funnel using blue ribbon filter paper (Prolab 3552). The solution was collected in a volumetric flask of 1,000mL; the residue was washed with 200ml of sulfuric acid solution at pH 2.0; and the filtrate was collected in the same flask. Then, the residue was washed with 250ml deionized water and stored together with the above solution. The flask volume was completed until 1,000mL and 100mL of that volume was sent for analysis of the soluble copper in acid. The residue was dried in an oven at 100°C for 6h. The dried solid was crushed to 100% of particle smaller than 0.074mm using mortar and pestle and then headed for the soluble copper in cyanide step (Mendes, 1999).

2.4 Soluble copper in cyanide assay

The soluble copper in cyanide test was applied to the ore and to the waste generated during acid cleaning, using the same procedure. Assays were performed in triplicate and the amount recorded was the arithmetic mean of the three tests.

The dried samples were homogenized, disaggregated by mortar and pestle and divided using Rotary Micro Riffler, generating three samples of 1g per sample.

The test was performed with 140ml of the solution of NaCN 1% and NaOH 5% (Sigma- Aldrich) to 1,000g of the solid (residue or ore). The solution was transferred to a beaker with stirring rate of 250rpm, under a temperature of (23±2)°C and then, the solid mass was added, maintaining the stirring for 1 hour. After this period, the mixture was vacuum filtered using a funnel, blue ribbon filter paper (3552 Prolab), and a 250ml flask to collect the filtrate. To the cake washing, 100ml of deionized water were used and collected into the same solution flask. The volume was completed to 250ml, homogenized and an aliquot taken for chemical analysis to quantify the soluble copper cyanide.

2.5 Chemical and mineralogical characterization

The chemical analysis for copper of the filtered solutions was made by ICP OES -Inductively Coupled Plasma Optical Emission Spectrometry - (Agilent 725). For the mineralogical characterization, the samples of ore and residue were comminuted (100%<1mm) and for each one, a polished section was prepared for analysis by QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy) and by scanning electron microscope. This electron microscope consists of a set of backscattered electron signal detectors and X-ray dispersive energy (EDS), which allow the identification of the mineral by its brightness and chemical composition.

The QEMSCAN 650 system was used, equipped with two EDS (Energy Dispersive x-ray Spectroscopy) spectrometers, a Bruker 5030 SDD (Silicon Drift Detector), running at 25kV and 10nA. For the measurements, used were the internal standard conditions of quartz and metallic copper in terms of backscattered electron signal calibration.

Cyanide consumption and gold extraction were measured for the stages before and after the acidic pre-cleaning of the ore.

3. Results and discussion

3.1 Chemical and mineralogical characterization

The chemical analysis of the 4 samples is presented in Table 1. The copper content ranged from 0.22% to 1.36%, and noteworthy are the contents of Si (11% to 34%), Fe (9% to 46%), Al (2% to 3%), S (0% to 0.38%), and Au (1 a 5 ppm), as well

as the loss on ignition varying between 3% and 6%. The sulfur and carbon levels were very significant, proving the presence of sulfides and carbonates in the samples.

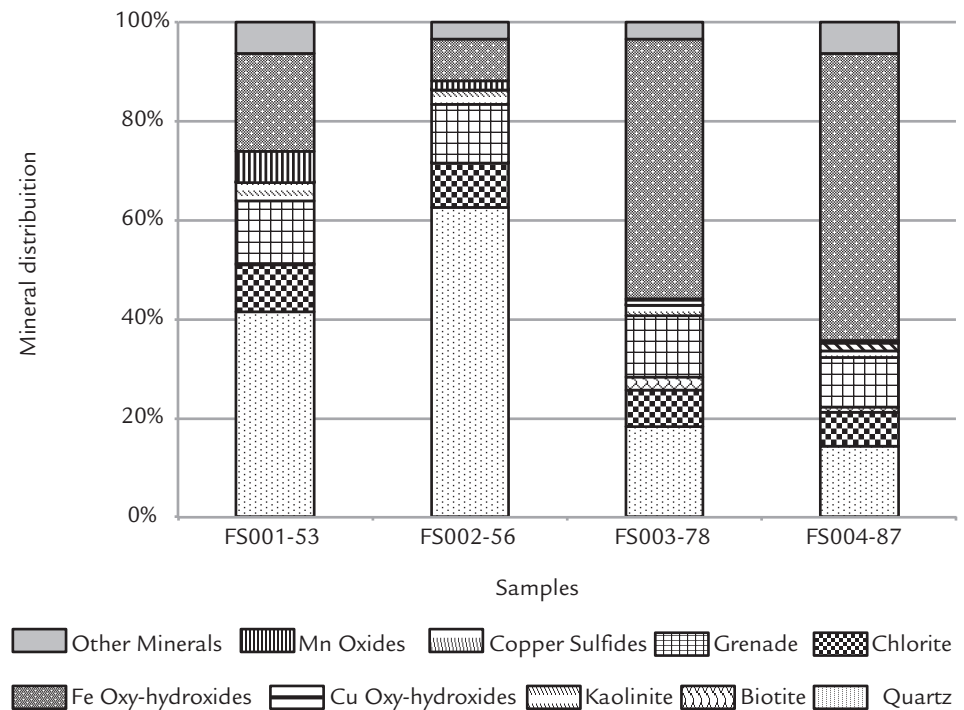| Parameter	FS001-53	FS002-56	FS003-78	FS004-87
Si (%)	25.66	33.54	13.98	10.68
Al (%)	3.38	2.50	2.90	2.03
Fe (%)	17.07	9.54	39.38	45.73
Mg (%)	< 0.17	< 0.17	0.18	0.37
K (%)	0.04	< 0.04	< 0.04	< 0.04
Mn (%)	3.31	0.97	0.35	0.24
PF (%)	6.44	4.03	3.08	3.16
Cu (%)	0.55	0.22	1.00	1.36
Co (%)	0.05	0.03	< 0.03	< 0.03
C (%)	0.05	0.04	0.14	0.23
S (%)	< 0.01	< 0.01	0.04	0.28
S^{2-} (%)	< 0.01	< 0.01	0.01	0.25
SO_4^{2-} (%)	< 0.61	< 0.61	< 0.61	< 0.61
Au ppm	1.7	1.2	4.1	5.5

Table 1
Chemical composition.

Figure 1
Mineral composition of samples.

The results (Figure 1) indicate that the samples are essentially composed of quartz, chlorite, biotite, garnet, kaolinite, copper sulfides, iron and copper oxy-hydroxides, and manganese oxides. The mineralogical analysis, as shown in Figure 1, shows that FS001-53 and FS002-56 are oxidized ores, while FS003-56 and FS004-87 are sulfide ores which contain secondary (chalcocite, covellite) and primary (chalcopyrite) minerals.

In terms of copper bearing minerals, Figure 2 shows the metal presence in biotite containing between 0.5% and 10.3% of the metal content of FS001-87 and FS001-78 samples, respectively. In this mineral, copper replaces cations of magnesium (Mg^{2+}) or iron (Fe^{2+}), which have been described for porphyry ores (Ilton e Verblen, 1993). The manganese oxide was identified as the main copper bearer for the samples FS001-56 and FS003-53 representing 98.3% and 99.5% of total copper, respectively. For these oxides, copper may occur adsorbed or replacing Co^{2+} and/or Ni^{2+} cations (Guimarães, 2007).
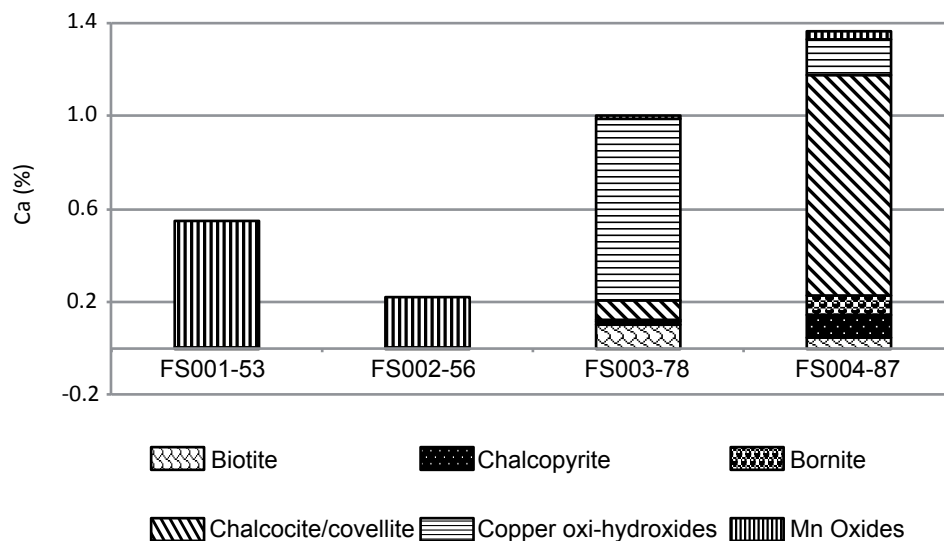
Figure 2
Copper-bearing minerals composition.

The Figure 3 shows images of textures and common mineral associations in the samples. The manganese oxides generally appeared filling fractures and other discontinuities in the rock, while the biotite formed aggregates and filaments.
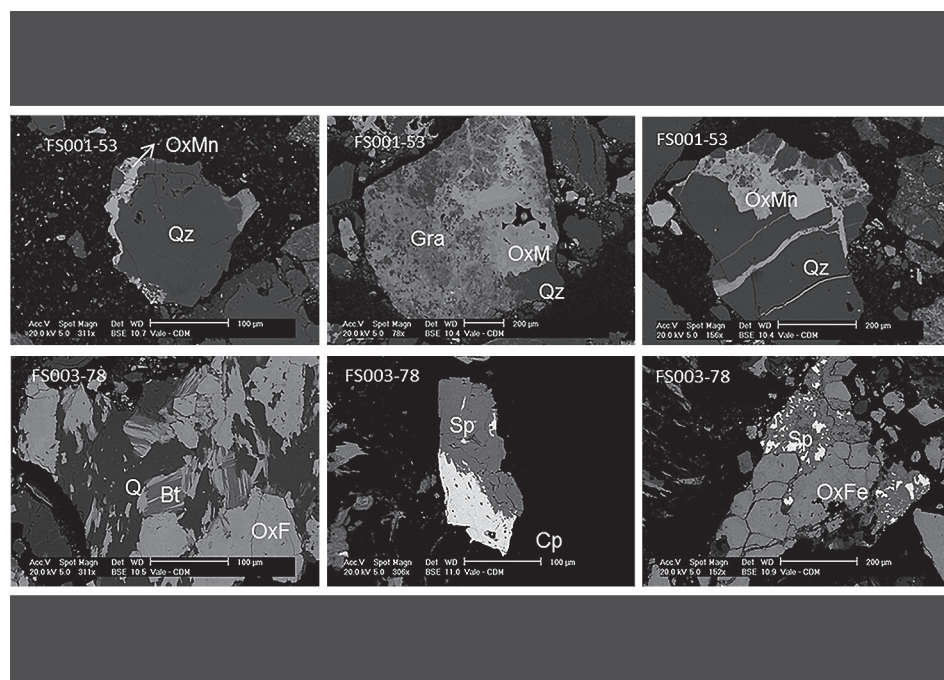

Figure 3
Backscattered electron images obtained through a scanning electron microscope showing textures and most common mineral associations within the copper diagnosed samples. Mn oxides encountered in sample FS001-53 and biotite lamellae associated with iron and copper oxi-hydroxides occurred at the interfaces and along the fractures and cleavage planes of the mineral in sample FS003-78. Subtitles: Bt – Biotite; OxFe – Iron oxi-hydroxides; OxMn – Manganese oxides; Sp – Spertiniite (Copper hydroxide: $Cu(OH)_2$); Cp – Cuprite (Copper oxide: Cu_2O; Gra – Garnet; Qz – Quartz.

3.2 Direct cyanidation assay: measuring the copper soluble in cyanide

Several copper minerals are soluble in cyanide but there are exceptions, such as chrysocolla and chalcopyrite. The main effect of copper on the cyanidation is to increase cyanide consumption due to the formation of the complex $Cu(CN)_3^{2-}$ under typical conditions (Osseo-Asare *et al*, 1984).

Considering the above mentioned and based on the chemical composition of the ore, the assessment of soluble copper in sodium cyanide aims to quantify the maximum solubilization of this metal in NaCN solutions.

When applying the methodology of Subsection 2.4, the soluble copper in cyanide was quantified for the four samples, as shown in Table 2. The fraction of copper soluble in cyanide was very high for FS003-78 and FS004-87; samples which contained sulfide minerals and copper oxy-hydroxides. The copper extractions were 60% and 83%, respectively. The lower extraction for FS003-78, relative to the sample FS004-87, might be related to the following reasons: greater biotite content (10.3% versus 3.5%), in which copper is less soluble in cyanide, and also the copper associated with iron hydroxides (Osseo-Asare *et al*, 1984). The high solubility of copper in cyanide in FS004-87 is due to the high composition of secondary copper sulfide minerals (around 70%), which are very soluble in cyanide (Hedley and Tabachnick, 1968; Dai and Simons, 2012). The behavior for FS001-53 and FS002-56 samples, with copper barely present in manganese oxides, showed relatively low extraction (8% and 12%), but still significant when considering the use of cyanide, even with lower initial copper contents (0.55% and 0.22%). Except for the sample FS003-78, where gold extraction was low (74%), the extractions of the other samples exceeded 97%, showing that gold is accessible to cyanide complexation and the ore is not considered refractory. However, there was a high consumption of cyanide between 1,200 and 2,300g/tROM.

Sample	Initial Cu	Sol Cu CN⁻	Au Extraction	NaCN consumption (g/tROM*)	Obs
FS001-53	0.55%	8.11%	99.35%	1,296	oxidized ore
FS002-56	0.22%	12.12%	97.30%	2,011	
FS003-78	1.00%	59.82%	74.65%	2,298	Transition ore
FS004-87	1.36%	83.41%	98.00%	1,518	

Table 2
Results for direct cyanidation.

*ROM: Run Of Mine.

3.3 Acid cleaning assay

The purpose of this step was to evaluate the copper extraction in the acidic stage in order to minimize the impact of this copper content on the consumption of cyanide. Table 3 shows the copper extraction results when applying a preliminary stage of ore cleaning with sulfuric acid, as described in Subsection 2.3.

The analysis of the copper extraction results in the acidic stage (Table 3) shows two groups: the samples formed by FS002-56 and FS001-53 where extraction was low (25 and 40%) and another group, represented by the samples FS003-78 and FS004-87 where the extraction was high (99% and 74%). Based on the mineralogical characterization, this behavior is in agreement with the forms of copper occurrence in these groups.

In FS002-56 and FS001-53, copper is present in manganese oxides (Figure 2), which demonstrates refractory to solubilization (Sahoo, *et al*, 2001; Pagnanelli, *et al*, 2004). On the other hand, samples FS003-78 and FS004-87 that have copper minerals in other forms, such as adsorbed on phyllosilicates (biotite) and secondary sulfides (Figure 3), show a different response in an acidic environment (Mendes, 1999). Part of the copper present in secondary sulfides is soluble, even without the presence of an oxidizing agent. The sample FS003-78 has copper adsorbed on biotite, chalcocite, covellite and oxyhydroxides of copper while the copper from FS004-87 is basically associated with secondary sulfide minerals and a small part with chalcopyrite. Secondary minerals, such as chalcocite, react with cyanide and therefore increase its consumption. The values in the table show that the pre-cleaning acid releases gold not accessible to the cyanide, as evidenced by the sample FS0003-78, where the extraction increased from 74% to 94%. Sodium cyanide consumption was reduced to values around 2.5 times, normalizing around the 800g/tROM value, improving process parameters for the processing of this ore.

Sample	Initial Cu	Sol Cu CN⁻	Au Extraction	NaCN consumption (g/tROM*)
FS001-53	0.55%	24.45%	99.34%	811
FS002-56	0.22%	39.51%	99.80%	785
FS003-78	1.00%	98.68%	94.30%	764
FS004-87	1.36%	73.65%	99.08%	793

Table 3
Results of copper extraction on acid cleaning.

3.4 Cyanidation of the residue assays

In the residue of the acid stage, produced due to the copper cleaning treatment, the cyanidation was applied according to the procedure described in Subsection 2.4. The results are shown in Table 4 and were highly positive for both classes of ore, oxidized, and sulfide. The cyanide soluble copper went from critical values between 8% and 83% to almost insignificant values between 0.13% and 1.54%.

Sample	Initial Cu	Sol Cu Without Acid Cleaning	Soluble Cu With Acid Cleaning
FS001-53	0.55%	8.11%	0.13%
FS002-56	0.22%	12.12%	0.25%
FS003-78	1.00%	59.82%	0.25%
FS004-87	1.36%	83.41%	1.54%

Table 4
Comparison of soluble copper cyanide before and after acid cleaning.

The results of soluble copper after acid pre-cleaning (Table 4) show that minerals with low acid solubility, such as manganese and chalcopyrite minerals present in samples FS001-53, FS002-56 and FS004-87 also have low solubility in cyanide. Therefore, this procedure is efficient for the purpose of reducing cyanide consumption.

4. Conclusions

The use of pre-conditioning of the gold ore proposed in this study was able to show the extraction potential of copper cyanide, reaching highly satisfactory values, allowing the cyanidation of gold and expressive lower complexation of copper by cyanide.

The final values of cyanide-soluble copper reached a peak of 1.54% with the preliminary acid cleaning step, and the direct cyanidation values reached 99% of cyanide-soluble copper. It was possible to observe that minerals with low acid solubility also have low solubility in cyanide. Cyanide consumption decreased by about 2.5 times and gold recovery increased to above 94%. The results also showed that there is a great difference in the amount of cyanide soluble copper from sulfide and oxide ores; however the pre-cleaning technique using acid meets the two classes of ores. Considering the conditions of the pre-cleaning with diluted acid at room temperature (25°C), it is possible to adapt the application for leaching in stockpiles.

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