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Treatment for gold ores with high content of carbonaceous matter

Paulo Valdivieso-Bermeo [a], Isabel Peñaloza [b] & José Moreno-Chávez [b]

[a] *Laboratorio Geológico Minero Ambiental, Grupo Minero Bonanza, Guayaquil, Ecuador. pvaldivieso@grupominerobonanza.com*
[b] *Facultad de Ingeniería en Ciencias de la Tierra, Escuela Superior Politécnica del Litoral, Guayaquil, Ecuador. ipenaloz@espol.edu.ec, josmoren@espol.edu.ec*

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Abstract
Gold ores associated with carbonaceous matter present several difficulties in their extraction due to the ability of this matter to adsorb the aurocyanide complex from gold pregnant solutions, resulting in low extractions by direct cyanidation. This phenomenon is known as preg-robbing. In the present work, a process to effectively recover Au from a highly carbonaceous ore from Colombia is proposed, combining froth flotation using the organic polymer maltodextrin as a depressant of the carbonaceous matter and a pretreatment with a cationic surfactant (benzalkonium chloride) prior cyanidation in conjunction with activated carbon (CIL). The preg-robbing % (PR%) was reduced from the initial 39.5 % to 3.96 % in the flotation concentrates and a maximum of 87.26 % extraction of Au was achieved during cyanidation.

Keywords: Preg-robbing; cyanidation; surfactant; flotation; carbonaceous matter; activated carbon.

Tratamiento para menas auríferas con alto contenido de materia carbonosa

Resumen
Las menas de oro asociadas con materia carbonosa presentan varias dificultades en su extracción debido a la capacidad de esta materia para adsorber el complejo aurocianuro de las soluciones ricas en oro, lo que resulta en bajas extracciones de oro por cianuración directa. Este fenómeno se conoce como preg-robbing. En el presente estudio, se propone un proceso para recuperar efectivamente oro de un mineral altamente carbonoso de Colombia, combinando la flotación mineral usando el polímero orgánico maltodextrina como un depresor de la materia carbonosa y un pretratamiento con un surfactante catiónico (cloruro de benzalconio) previa cianuración en conjunto con un proceso de carbón activado en lixiviación (CIL). El porcentaje de preg-robbing (% PR) se redujo del 39.5% inicial al 3.96% en los concentrados de flotación y se logró un máximo de 87.26% de extracción de Au durante la cianuración.

Palabras clave: Preg-robbing; cianuración; surfactante; flotación; materia carbonosa; carbón activado.

1. Introduction

Gold ore is referred to as refractory when gold extraction in a direct cyanidation process is less than 80%, even after fine grinding [1]. In other words, gold ore is refractory when the metal of interest cannot be optimally recovered by conventional methods (Fig. 1).

The refractoriness of gold ores occurs by occlusion or entrapment of subatomic gold particles in matrices of sulfide minerals (pyrite, arsenopyrite, stibnite, etc.) and insoluble siliceous gangue, by association with tellurides, clays and carbonaceous matter [2]. The carbonaceous material can adsorb gold, an effect

known as preg-robbing, from the solution similar to activated carbon, which is used in the purification and concentration of gold from cyanide solutions for the subsequent desorption and recovery of gold. The ability of the carbonaceous material to adsorb aurocyanide complex from the solution has been widely documented [3-8].

Figure 1. Generic process diagram for treating minerals that contain gold.
Source: The Authors.

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Characterization experiments on carbonaceous material associated with gold ores from Carlin (United States), Prestea (Ghana), Natalksink and Batkyrchik (Russia) suggest that carbonaceous matter generally consists of three components: hydrocarbons, humic acid and activated elemental carbon [9].

Additionally, sedimentary or metamorphic rocks with a high content of carbonaceous material such as carbonaceous schists, black or carbonaceous shales, and bituminous shales, carbonates of different types, can be considered; therefore it can be said that the term is used to refer to several materials [10].

Rees and van Deventer also reported that the aurocyanide complex may also be removed from the solution by the minerals themselves. This may occur by a physical adsorption process, or by the reduction of aurocyanide at the mineral surface [11].

The most known preg-robbing minerals are pyrophyllite, khaki shale, pyrite, chalcopyrite and thucholite, which is a mixture of hydrocarbons, uraninite and sulphides [12]. Gold ores with preg robbing are common in north of Colombia in the surroundings of the zone of study, however there are no detailed studies about the characterization of this ores.

The metamorphic complex San Lucas in the municipality of Puerto Berrío, has been studied and characterized. This complex is formed by schists and other metamorphic rocks were the predominant minerals are quartz, calcite, clay minerals and carbonaceous matter. The formation La Cristalina near the San Lucas complex also shows an important presence of black slate with carbonaceous matter in its compositions [13].

There are several mechanisms proposed in which carbonaceous matter adsorbs gold from pregnant solutions. Adams and McDougall proposed an electrostatic attraction for the Au(CN)2- complex paired with metallic cations [14]. Other authors found a correlation between total pore volume and gold adsorption suggesting a physical entrenchment of gold particles in carbon matrix [15]. The extraction of gold is reduced depending on the type of carbonaceous matter, the maturation of the coal and the quantity available [16]. The carbonaceous ores can be classified into two main categories: i) Mildly carbonaceous ores with a total content of organic and graphitic carbon less than 1%. ii) Highly carbonaceous ore, typically containing more than 1% carbon in a form that has a high tendency to adsorb gold [17].

On the other hand, there are several methods commonly used to treat ores with a high percentage of preg-robbing [18], among which are flotation, roasting, blanking or blinding [19] or suppression with chemical agents such as surfactants [20], use of highly competitive adsorbent materials with the carbonaceous matter in the ore, chemical and bacterial oxidation. For the low to medium levels of preg-robbing activity, its recommended to use the carbon in leach (CIL) route or pre-treatment of the ore with blinding agents to minimize the gold losses [16,17].

Mineral flotation has been tested with different reagents, such as organic polymers, to depress the carbonaceous matter. In the gold fields of Prestea and Ashanti in Ghana, starch was used as a depressant for carbonaceous matter [11] and a reagent produced by Bayer and commercially known as G4, , which was used in mines located in Mount Isa, Australia, whose 55% is composed of organic polymers [21].

For the suppression or "blanking" of the carbonaceous matter, reagents that can be selectively adsorbed by the carbonaceous matter until it is saturated and that cannot adsorb the gold in solution are used; however, this method is not used when there are large amounts of gold associated with carbonaceous matter. Diesel oils, kerosene and natural oils have been used, as well as cationic and anionic surfactants [22].

The aim of this study is to evaluate the maltodextrin organic polymer as a depressant of carbonaceous matter in the flotation of gold ores, and the cationic surfactant (benzalkonium chloride) as an additive in the cyanidation, in conjunction with activated carbon (CIL), of flotation concentrates obtained from carbonaceous gold ore to establish optimum conditions for gold recovery.

2. Materials and Methods

2.1. Characterization and preparation of samples

The samples were obtained from a mine located near the municipality of Puerto Berrío in the department of Antioquia of Colombia. The maximum particle size was 20 mm, samples which were reduced to a size 100% passing through a 10-mesh size (2 mm) and then were carefully divided up in sub samples according to Ceczott methodology [23]. A quartering was performed to obtain samples for the flotation tests of approximately 1 kg, and also to perform x-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. The samples used for flotation tests were wet ground in a 7-liter laboratory ball mill to a D_{80} of 70% passing #200 mesh (75 µm). Thin sections were made from hand samples to determine the mineral species present in them, and they were made in a Metzon cutting and polishing machine (Geoform model) and later analyzed in a Leica polarization microscope (DM2500P model). The analysis (Fig. 2) showed that the ore was composed of a matrix of metamorphic rocks with carbon content (graphitic schist - black slate), quartz and sulfides scattered throughout the matrix (pyrite).

The scanning electron microscopy analysis was performed in an equipment FEI Inspect S50, for which 10 g of sample was prepared and pulverized to D_{80} of 75 µm. A powdered sample of 1 g was taken which is placed in an aluminum frame with carbon adhesive. In several samples, it was observed that the carbonaceous matter was composed of a high percentage of carbon, aluminum, and silicates, common elements in the metamorphic rocks of sedimentary origin with carbon content. This indirectly corroborates the petrographic characterization of the ore (graphitic schists - carbonaceous slates). For the XRD analysis, the sample was

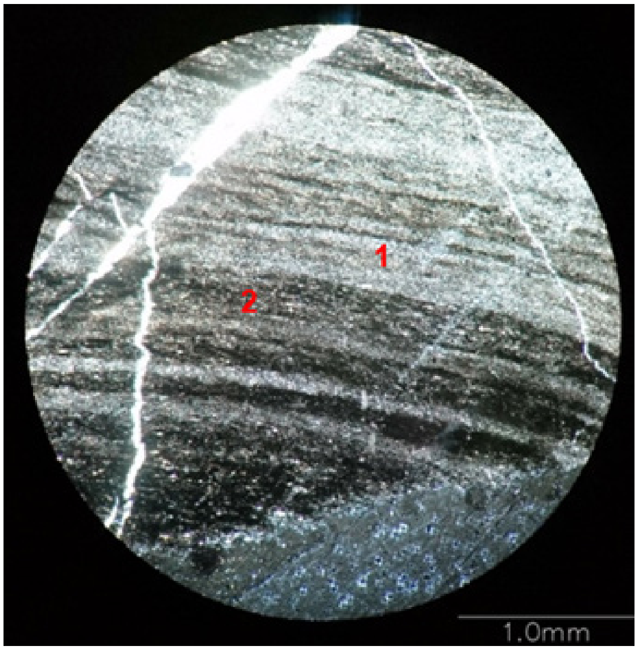

Figure 2. Mineralogical analysis by optical microscopy of the sample showing stratification of silica minerals (1) and carbonaceous matter (2).
Source: The Authors

Table 1.
Mineralogical composition of the studied ore.

Component	%
Quartz	59.6
Graphite	17.2
Pyrite	6.5
Muscovite	6.5
Amorphous	10.2

Source: The Authors.

also finely pulverized to D_{80} of 75 µm. This analysis was performed in a PANalytical XPert Pro equipment. The composition of the sample is as follows in Table 1.

2.2. Preg-robbing tests

The preg-robbing was determined using a modified test from the one developed by Barrick Gold Mines Incorporated (BGMI). The experiment consists of placing 5 g of sample in contact with a 10-ml solution of 2 g/L of NaCN and 5 ppm of Au. After 15 minutes of exposure of the sample to the solution, it is centrifuged and the concentration of Au is measured.

Simultaneously, 5 g of sample is placed in contact with 10 ml of a caustic cyanide amenability solution (2 g/L of NaCN) to observe the leaching behavior of the ore. The preg-robbing (PR %) is calculated with the following equation:

$$PR\% = \frac{(Ci_{Au} + C_{Au\,lix}) - Cf_{Au}}{Ci_{Au}} \times 100 \quad (1)$$

In eq. (1) Ci_{Au} and Cf_{Au} are the initial and final gold concentrations of the solution with 5 ppm of gold. The $C_{Au\,lix}$ is the concentration of gold leached in the solution without the addition of a standard solution of gold (cyanide amenability solution). This test was done only for the concentrates obtained in the cleaner stage, as it was considered the product with the lowest carbon content.

2.3. Flotation tests

The flotation tests were carried out using 2 Kg of the sample in an Agitair LA-500 machine with acrylic cells with a capacity of 5 L for rougher and scavenger stages and 3 L for the cleaner stage, respectively. Potassium amyl xanthate (PAX Z6) was used as a primary collector, and dithiophosphates such as AR-1208 and AR-1404 were employed as secondary collectors. Methyl isobutyl carbinol (MIBC) was employed as frother and maltodextrin as depressant. Flotation reagents were obtained from RENASA, a Peruvian industry supplier of mining reagents. The maltodextrin was obtained from Laboratorio Cevallos (Guayaquil-Ecuador).

A total of 10 tests were carried out for this research, all with the same flotation reagent dosages displayed in Table 2. The tests were carried out in three flotation stages: rougher, scavenger and cleaner. The conditioning times were the same for all tests: 3 minutes for depressant, 2 minutes for primary collector and 2 minutes for secondary collectors. Two control tests (FP-1 and FP-2) were carried without the use of maltodextrin.

In the tests from FD-1 to FD-3, maltodextrin was added only in the cleaning stage. From the FD-4 test onwards maltodextrin was added in the rougher stage in varying dosages for each test and maintaining the dosage in the cleaner stage constant (0.2 Kg/t).

2.4. Cyanidation tests

Cyanidation tests were carried using different dosages of benzalkonium chloride (cationic surfactant), with a particle size of 77% passing through #200 mesh using the concentrates obtained from flotation tests with the conditions used in FD-4 test.

Also, tests were carried with activated carbon (CIL) in conjunction with the surfactant. The dosages of surfactant were 0, 200, 400, 800 g/t for both, the standard and CIL cyanidation tests. The following parameters were used for all tests: 30% solids by weight, 1.5 g/L of NaCN and 24 hours of agitation. Additionally, control tests were carried for flotation concentrates obtained without the addition of maltodextrin in standard and CIL cyanidation experiments.

Table 2.
Reagents use and dosages in flotation tests.

Reagents	Dosage (g/t)
PAX	800
AR 1404	66.10
AR 1208	66.10
MIBC	69.56

Source: The Authors.

3. Results and discussion

3.1. Effects of maltodextrin in flotation and preg-robbing

The recoveries of the flotation tests are shown in Table 3. The average of the gold recovery for the tests is 95.62 % (Table 3), which shows that the maltodextrin in the dosages used in this study does not have a detrimental effect in the flotation of sulphide minerals associated with gold, which was one of the main concerns prior to the experiments. Also, the grade of the cleaner concentrates was above 70 g Au/t in all tests, showing that even in tests where the maltodextrin dosage was high, the grade of the cleaner concentrates did not decrease comparing them with the grades obtained in the tests without the addition of maltodextrin.

The addition of maltodextrin helped in reducing the preg-robbing effect in all the tests done in this study (Fig. 3). For the 3 first tests (FD-1, FD-2, FD-3) the addition of maltodextrin only in the cleaner phase did not result in a significant reduction of the preg-robbing (PR%). However, better results were achieved when the maltodextrin was added in both the rougher and cleaner stages, it reduced the PR% from 39.5 % to 3.96 %. As the dosage of maltodextrin was increased in the tests, the preg-robbing % decreased proportionally. Also, by visual inspection, the concentrates were cleaner when the maltodextrin was added initially in rougher stages compared to the ones where the maltodextrin was added only in cleaner stages, this was corroborated when the concentrated sample was analyzed by scanning electron microscopy (Fig. 4).

Table 3.
Metallurgical results for the flotation tests.

Test	Head grade (g Au/t)	Weight sample (g)	Cleaner conc. grade (g Au/t)	Cleaner tail (g Au/t)	Scavenger conc. grade (g Au/t)	Recovery %	Tails grade (g Au/t)
FP-1	8.23	1977.63	82.50	35.25	14.75	94.00	0.60
FP-2	8.23	1997.89	75.45	5.1	11.38	90.92	0.70
FD-1	8.03	1999.96	75.63	19.38	4.6	94.30	0.58
FD-2	7.58	1969.13	78.13	28.00	4.33	96.21	0.38
FD-3	7.63	1987.15	72.81	36.5	6.4	95.70	0.43
FD-4	7.69	1979.18	71.57	45.63	6.59	96.00	0.38
FD-5	7.52	1986.55	68.76	50.28	5.34	95.50	0.41
FD-6	7.15	1946.39	73.75	34.75	4.55	95.13	0.43
FD-7	7.66	1970.06	75.22	50.20	5.45	95.72	0.40
FD-8	7.77	1980.36	75.00	60.00	11.50	96.04	0.38

Source: The Authors.

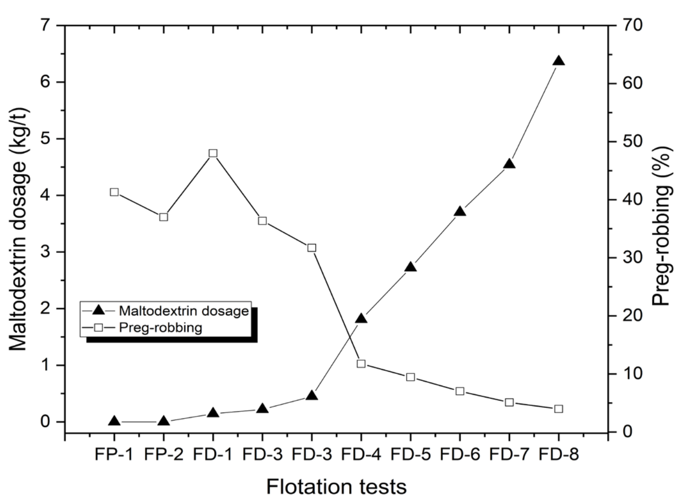

Figure 3. Comparison between PR % and the maltodextrin dosage used in the test.
Source: The Authors.

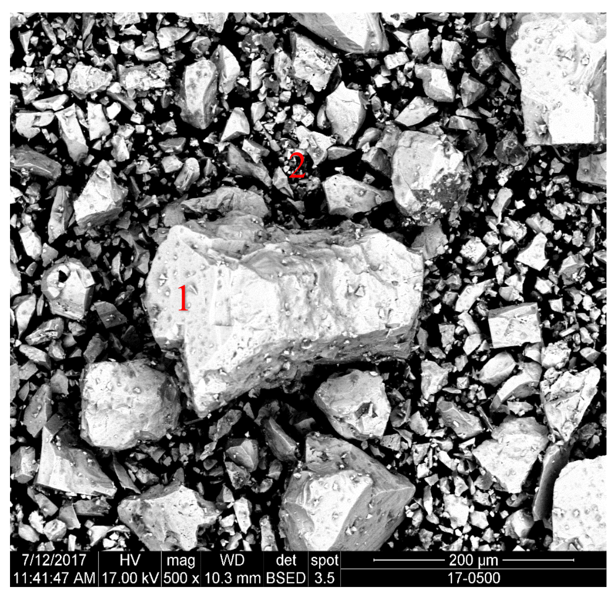

Figure 4. SEM micrograph of the cleaner concentrate obtained using maltodextrin as a depressor for carbonaceous matter. (1) We can observe clean pyrite grains. (2) Carbonaceous matter asssociated with pyrite grains in cleaner concentrate.
Source: Authors.

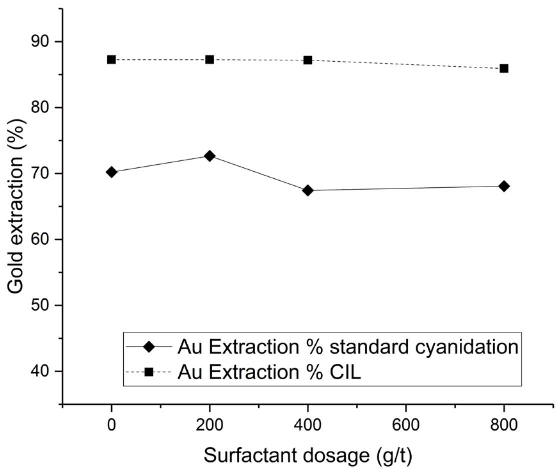

Figure 5. Gold extraction at different surfactant dosages for standard cyanidation and CIL tests.
Source: The Authors.

3.2. *Effect of surfactant in standard cyanidation and CIL process tests.*

The results of the cyanidation tests corroborate the ones obtained in the preg-robbing tests done for the flotation concentrates. The extraction of gold for the control test without the use of maltodextrin was 12.76% for standard cyanidation and 63.19 % for CIL cyanidation, as for the concentrates obtained using maltodextrin the gold extraction was 70.21% and 87.26 %, respectively. This shows the positive effect of maltodextrin as a depressant for the carbonaceous matter.

The addition of surfactant shows little improvement for gold extraction (Fig. 5). For the dosage of 200 g/t the extraction at conventional cyanidation slightly increased from 70.21% to 72.65% and decreased as the surfactant dosage was increased. In CIL tests, recovery did not improve even at a concentration of 800 g/t of surfactant.

4. Conclusions

It was demonstrated that the maltodextrin is a reagent capable of depressing the carbonaceous matter in the gold ore during froth flotation, reducing the preg-robbing effect from 39.95 % to 3.96 % without affecting grade or recovery. The maltodextrin shows better results if it is added in the initial stages of flotation, resulting in a higher reduction of the preg-robbing %.

Froth flotation tests using maltodextrin in combination with CIL process result in the best alternative for processing this gold ore associated with graphitic schist, achieving a maximum gold extraction of 87.26 % in contrast with the concentrates floated without the addition of maltodextrin (63.19 %).

The pretreatment of the gold ore using the cationic surfactant benzalkonium chloride did not passivate the carbonaceous matter resulting in a negative effect in the subsequent cyanidation, as the gold extraction slightly diminished as the dosage of surfactant in standard cyanidation tests increased.

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P. Valdivieso-Bermeo, received the BSc. Eng. in Mining Engineering in 2017 from the Escuela Superior Politécnica del Litoral, ESPOL, Ecuador. He is currently working in the R&D department of metallurgy for Grupo Minero Bonanza which is a small-scale mining company based in Ecuador with projects also in Colombia and Bolivia. His research interest includes processing of refractory and carbonaceous ores, flotation of polymetallic ores, development of eco-friendly processes for mineral processing.
ORCID: 0000-0001-9998-1512

I.Peñaloza, is student in Mining Engineering at the Escuela Superior Politécnica del Litoral, ESPOL, Ecuador. Exchange student in Mining Engineering at USP Universidade de São Paulo, Brasil in 2018, pursuing scientific initiation with MSc. José Moreno in Mineral Processing. SME member since 2015 and active participant at the Mining Engineering field.
ORCID: 0000-0002-8982-7383

J. Moreno-Chavez, received a BSc. Eng. in Mining Engineering in 2015 from ESPOL, Ecuador and a MSc. of Applied Science in Mining Engineering and Mineral Processing in 2018, from the University of British Columbia, Canadá. Currently, he is working as a Plant Operations Manager for Titan Minerals Ltd in Ecuador and as an instructor at ESPOL University. He has worked at Orenas S.A. which is a small-scale gold mining company, at Norman B. Keevil Institute of Mining Engineering of the University of British Columbia, at Canadian International Resources and Development Institute (CIRDI), and at Oroconcent S.A which is a mineral processing plant. He is a member of the Society for Mining, Metallurgy and Exploration (SME), and of the Canadian Institute of Mining, Metallurgy and Petroleum (CIM).
ORCID: 0000-0001-7955-4679