

Leaching of a Gold Bearing Partially Roasted Sulphide. Laboratory Scale Studies

*M.F. Almeida**

*Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias s/n,
4200-465 Porto, Portugal*

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This research aimed at defining a route for recovering precious metals from a very heterogeneous gold bearing sulphide and arsenide concentrate that was partially roasted and dumped by the 1960s when Santo António mine closed. Gold occurs in this concentrate as free particles in the range of 10-100 μm , most of them still enclosed in the pyrite and arsenopyrite matrix. Its content varies from 20 to 150 g of Au/ton, being higher at the dump upper levels and in the finer concentrate fractions.

Preliminary tests demonstrated the refractoriness of this product, since the leaching with conventional cyanide solutions and with other leaching solutions gave very low recoveries. However, high concentrated cyanide solutions recover more than 60% of Au, although with high NaCN and lime consumptions and poor settling characteristics. Iron was shown to be highly dissolved in these solutions.

Some prior treatments clearly favoured the cyanidation process, in particular a roasting step. Thus, a large number of roasting experiments was carried out to define the most favourable conditions for recovering gold. However, no clear relationship between roasting conditions and gold dissolution was found due to the heterogeneity of the product and high variance of gold experimental recoveries. These recoveries were calculated considering gold contained in both the leaching residues and leachates, and uncertainties of these results are relatively high.

Roasting the product at 450-700 °C for 1 h guarantees a high probability to dissolve at least 74% Au in a highly concentrated NaCN solution stirred for 24 h. The 600-700 °C roasting range is clearly preferable for consuming less cyanide and lime. Pre-washing the roasted product seems not to reduce the cyanide consumption.

Regarding the silver recovery, the NaCN and lime consumption are higher while using the products roasted at the lowest tested temperatures. Products roasted at higher temperatures have better settling performance.

Keywords: *precious metals, cyanide, thiourea, roasting, recovery estimation*

1. Introduction

Santo António gold mines are situated in the North of Portugal and were already explored in the 1st century A.D. by the Romans. These mines were reactivated around 1950 and closed 10 years later. The following two reasons explain to some extent such unsuccess: (i) an optimistic estimate of higher gold content was made; (ii) the flowsheet including a roasting step was based in few experimental tests. Thus, some unexpected surprises in the operation performance arose, namely low gold recoveries by cyanidation and poor gold cementation using Merrill-Crowe process, with no de-aeration. Around 1980, two other soli-

tary unsuccessful trials took place without continuity, perhaps due to the same intrinsic main causes, *i.e.*, high refractoriness of the ore and very random gold content. One of those trials processed all the stocked ore by milling it up to a very fine grain size followed by cyanidation, adsorption of gold onto activated carbon, burning it and melting the resulting ashes¹. The other is the core of this work carried out between 1984-1986, that aimed at recovering the gold content in a 2000 ton dump of partially roasted sulphide concentrate by adopting a batch operation in a small own-built plant².

*e-mail: mfa@fe.up.pt

Cyanide is still the most used reagent for recovering gold from its ores. In the case of refractory ores containing complex minerals, gold dissolution is not a simple process and its rate becomes depressed after a certain time of cyanidation³. Mineralogical identification of the ore and diagnostic leaching are alternative methods for establishing and designing a metallurgical flowsheet for refractory ores⁴. Some alternative leaching agents, namely thiourea, have been tried due to the environmental concerns, generally without economic success⁵. An usual approach for processing complex refractory gold ores is a pre-oxidation treatment prior the gold leaching step and the most known options are roasting, pressure oxidation and biooxidation⁶⁻⁸. Pressure oxidation is a technology where sulfuric acid can play an important role for oxidising arsenopyrite effectively⁹⁻¹¹. Biological processes are a reality as production technologies chosen for a significant refractory gold treatment plants worldwide. Several references discuss its application as bioextractor and bioheap leaching methods for refractory gold bearing sulphides and arsenides, where cyanide, as well as ammonium thiosulfate, are used as leaching agents¹²⁻¹⁷.

With the objective of designing a feasible flowsheet for recovering gold from those 2000 ton dump of partially roasted sulphide concentrate, following its mineralogical and chemical characterisation, some trials to concentrate gold by using magnetic separation and froth flotation processes were carried out without success. Then, several leaching screening tests were carried out using conventional cyanide concentrations of 0.5% w/v NaCN, conditioning the pulp and testing some treatments prior to cyanidation. Thiourea was tested as leaching agent, too. As general conclusion one can point out the failure of all those foreseen routes, except either leaching the concentrate with higher cyanide concentration or roasting it followed by cyanidation. Therefore, much more effort was invested in these two last lines of research.

2. Gold Recovery Estimation

Gold recovery is usually computed by using the following expression:

$$\eta = \frac{m_s Au_s}{m_s Au_s + m_r Au_r} \quad (1)$$

where m_s is mass of solution, m_r of residue and Au_s and Au_r are the gold contents (w/w) in solution and residue, respectively. The results obtained are expressed in percentage. However, if the gold bearing product is sufficiently uniform and the gold particles are very fine, a small variance in gold ore content is expected and gold recovery can be very well estimated by using the following expression:

$$\eta = \frac{m_s Au_s}{m_p Au_p} \quad (2)$$

where p stands for product. It means that the ratio between the gold determined in the leachate and average gold content in the ore well estimates gold recovery and there is no need to determine gold in residues.

However, in the case of gold ores, the use of expression (1) is frequently a must. In this case, the estimate of recovery variance as a function of the different factors present in expression (1) is given by:

$$s_\eta^2 = \left(\frac{\partial \eta}{\partial m_s}\right)_0^2 s^2(m_s) + \left(\frac{\partial \eta}{\partial Au_s}\right)_0^2 s^2(Au_s) + \left(\frac{\partial \eta}{\partial m_r}\right)_0^2 s^2(m_r) + \left(\frac{\partial \eta}{\partial Au_r}\right)_0^2 s^2(Au_r) \quad (3)$$

where $()_0$ means the derivative to be computed at the mean value of the variables. The development of this equation gives:

$$s_\eta^2 = \left(\frac{m_r Au_r Au_s}{Au_t^2}\right)^2 s^2(m_s) + \left(\frac{m_r m_s Au_r}{Au_t^2}\right)^2 s^2(Au_s) + \left(\frac{m_s Au_r Au_s}{Au_t^2}\right)^2 s^2(m_r) + \left(\frac{m_r m_s Au_s}{Au_t^2}\right)^2 s^2(Au_r) \quad (4)$$

where $Au_t = m_r Au_r + m_s Au_s = m_p Au_p$.

If one considers $s^2(m_s) \approx s^2(m_r) \approx 0$, since they are variance estimates of volume and mass measurements, generally less than $(\pm 0.01 * \text{magnitude measured})^2$, expression (4) reduces to:

$$s_\eta^2 = \left(\frac{m_r m_s Au_r}{Au_t^2}\right)^2 s^2(Au_s) + \left(\frac{m_r m_s Au_s}{Au_t^2}\right)^2 s^2(Au_r) \quad (5),$$

showing dependency on the gold solution and residue contents. Assuming optimistic errors of 3% for gold determination in solution by atomic absorption spectrometry (A.A.S.) and 15% for the laboratory way of sampling the residue, sample digestion, consequent dilutions of solutions up to A.A.S. determination, and substituting accordingly, the expression (5) becomes:

$$s_\eta^2 = \left(\frac{m_r m_s Au_r}{Au_t^2}\right)^2 (\pm 0.03 Au_s)^2 + \left(\frac{m_r m_s Au_s}{Au_t^2}\right)^2 (\pm 0.15 Au_r)^2 = \left(\frac{m_r m_s Au_r Au_s}{Au_t^2}\right)^2 (0.03^2 + 0.15^2) \quad (6)$$

With recoveries expressed as percentages these estimates shall be multiplied by 10000, or the square root of them (*i.e.*, its standard deviation, taken as the normal error) multiplied by 100. The magnitude of the uncertainty about the recovery created by those influences is sensible and can

be illustrated by considering the following data: $m_r = 1$ kg; $m_s = 2$ kg; $Au_r = 15$ g/ton; $Au_s = 27.5$ g/ton. Sample average recovery is about 78.6% and estimated standard deviation is around 25.8%. If $Au_r = 7$ g/ton then the calculated value for recovery is 90% and the standard deviation is 13.8%.

These results indicate that uncertainty about true recovery values is much more affected by gold residue uncertainty than gold solution uncertainty, and it decreases as both gold content in the product and its recovery increase.

Based in these considerations and (i) assuming normal distribution for the recovery variable; (ii) estimating recovery variance by the above expression; (iii) considering t Student statistic defined as:

$$t = \frac{\bar{\eta} - \mu_{\eta}}{s_{\bar{\eta}}} \quad (7)$$

where μ_{η} is the true mean recovery and $s_{\bar{\eta}}$ is the sample standard deviation of the mean recovery; and (iv) respective t value at t-Student tables, then intervals can be built where the true recovery value is contained with a given degree of confidence, generally taken as 95%.

3. Experimental

A sample of about 100 kg was taken from the dumped sulphides and considered as a representative sample. Due to the known randomness of gold in the product, all the leaching tests used either 0.5 or 1 kg of ore. Experimental recoveries were computed through gold and silver values in both the final leachate and corresponding leaching residue. For this purpose the final leaching residue was first sampled, then the sample digested with hot aqua regia solution, followed by water washing the residue and then analysing the gold content in that solution by atomic absorption spectrometry (A.A.S.). This method of analysis was also used to determine other metals in the leachates and other solutions. In the case of gold determinations the background correction was used.

Commercial reagents and tap water were used for all the experimental work. In the leaching tests the pulp was agitated in a 5 L glass beaker and experiments were controlled by sampling leachates at predetermined times. Electrode immersion in the stirred pulp was used for monitoring pH, and readings were taken only after stable pH values were achieved. For the cyanidation tests, lime was used to raise the pH to an alkaline level, and at the end of each experiment, the residue was washed with constant volumes of a stock lime solution. Free cyanide was determined by titration with silver nitrate using potassium iodide as indicator.

Carbon and sulphur in solid products were determined using an oxygen combustion method followed by absorption of the resulting gases. Carbon was quantified by the

percentage of CO_2 absorbed in a sodium hydroxide solution and sulphur was titrated as sulphate.

In order to simulate the industrial scale conditions, sulphides were roasted by using a 40 cm diameter x 100 cm length rotary kiln where the feed was directly heated by an air-propane flame that was turned on-off according to a temperature control device.

4. Results and Discussion

4.1. Characterisation

Gold occurs in the original ore generally in arsenopyrite that is associated with iron sulphides, mainly pyrite and chalcopyrite. Galena and sphalerite are also usual minerals and native bismuth occurs sometimes as small inclusions in arsenopyrite². In the partially roasted sulphides bearing ore, gold was observed by microscopy as particles whose size was in the 10 to 100 μm range, either as completely free or still inserted in grains containing sulphur and arsenium. Most of these grains still contain a few altered core that is bounded by a very porous surface resulting from both the industrial roasting step performed in a rotary kiln directly heated by a fuel-air flame, according to the old mine reports, and weathering. Grains of wolframite and pecheblend were also observed at the microscope. The only gold particle semi-quantitative analysis carried out revealed 63.6% Au and 36.3% Ag².

Table 1 shows the size distribution analysis of 8 samples. Most of the coarser particles retained in the sieves are, in fact, agglomerates of finer particles, perhaps produced at the roasting step by rolling and binding the concentrate particles of sulphides. According to a previous analysis, the overall chemical composition of the product is 65.0 and 72.4 g/ton Ag and Au, respectively; and in percentage, $SiO_2 = 17.50$; $Fe = 32.74$; $S = 8.10$; $As = 5.00$; $Cu = 0.10^{18}$.

Table 2 presents the results obtained by analysing 14 different size fractions from about 8 kg sample. Gold, silver and most of the usual non-ferrous metals increase in the finer fractions, mainly those smaller than 0.150 mm. Considering both the gold content in the 14 fractions and the respective mass percentage, computed average gold content is around 65 g/ton, less than 72.4 g/ton Au referred before. Due to the large relative variation of the finer and gold richer percentage sizes, a considerable scatter of the gold content of the samples is expected. In addition, it was also verified that average gold values corresponding to the deeper levels of the dump were unfortunately around 20 g/ton.

Carbon in the product was 1.95%, probably due to the deposited organic matter from the vegetation at the dump surroundings. Sulphur was found to be 3.70%.

Table 1. Product size distribution analysis.

Size (μm)	\bar{X} = mean oversize (%)	s = standard deviation (%)	100 \bar{X}/s	$\bar{X} \pm t_{95\%} s\bar{X}$ (%)	Cumulative oversize (%)	Cumulative undersize (%)
2360	22.16	3.35	15.11	18.81-25.51	22.16	100.00
1700	7.60	0.44	5.79	7.16-8.04	29.76	77.84
1180	6.42	0.54	8.48	5.88-6.96	36.18	70.24
850	6.81	0.26	3.87	6.55-7.07	42.99	63.82
600	5.45	0.21	3.93	5.24-5.66	48.44	57.01
425	7.37	0.39	5.26	6.98-7.76	55.81	51.56
300	8.91	0.43	4.84	8.48-9.34	64.72	44.19
212	13.07	3.16	24.17	9.91-16.23	77.79	35.28
150	11.77	2.00	17.01	9.77-13.77	89.56	22.21
106	6.90	1.28	18.53	5.62-8.18	96.46	10.44
75	2.44	0.99	40.74	1.45-3.43	98.90	3.54
53	0.74	0.60	80.62	0.14-1.34	99.64	1.10
38	0.32	0.17	52.28	0.15-0.49	99.96	0.36
0	0.04	0.02	57.86	0.02-0.06	100.00	0.04

Table 2. Chemical composition of several product fractions.

Oversize (μm)	Au (g/ton)	Ag (g/ton)	Cu (g/ton)	Bi (g/ton)	Zn (g/ton)	Pb (g/ton)	Fe (%)
2360	42.0	59.0	1161	238	1613	770	26.16
1700	43.8	20.0	1009	238	1383	800	22.98
1180	54.9	42.0	983	236	1335	809	25.73
850	50.4	24.0	984	235	1392	821	23.76
600	75.7	44.3	628	220	1002	830	24.07
425	50.6	41.4	618	203	1328	746	25.77
300	67.2	53.3	839	205	1210	675	22.36
212	51.9	58.8	832	196	1351	640	24.24
150	76.3	59.4	989	210	1494	718	26.98
106	102.3	63.0	1083	230	1542	639	30.53
75	169.1	77.3	1164	241	1474	754	30.95
53	293.0	97.7	7468	244	1686	786	31.47
38	497.8	138.8	8043	273	1628	876	30.53
0	2058.7	947.1	5179	269	1938	1595	34.26

The product is naturally acid, and the aqueous suspension (solid/water = 1) has a pH ranging from 2.8 to 2.9, 9 to 11 g/L Fe and around 0.2 g/L Cu.

4.2. Screening tests

Only about 9.5% of the product remained insensible to a weak magnetic field whereas 6% was strongly magnetic. Chemical analysis of 7 different magnetic fractions revealed no remarkable differences in Au, Ag, Cu, Bi, Zn and Pb contents. Therefore, it was not possible to take advantage of this property to concentrate the product.

Froth flotation at pH range of 9 to 10 using Na_2CO_3 , reagent 3477® and Aerofloat 25® gave the results presented in Table 3. As shown in that table, despite an evident concentration, the tailings were not poor enough to be rejected.

Figures 1 and 2 summarise the product behaviour under normal cyanide leaching solutions of 0.5% w/v NaCN. In the second case, shown in Fig. 2, the leaching conditions were essentially equal but the product was dry milled to <0.3 mm. At the times assigned A and B more sodium cyanide was added to the pulp, respectively 0.17 and 4.32 g

Table 3. Results of product froth flotation tests.

Type of product	Relative (%)	Content (g/ton)		Recovery (%)	
		Au	Ag	Au	Ag
Concentrate	26.4	136.3	81.7	49.3	38.6
Tailings	73.6	50.3	46.5	50.7	61.4
Feed	100.0	73.0	55.8	100.0	100.0

in the first experiment and 0.13 and 3.93 g in the second leaching test.

The main indications of these tests were the following:

- the lime needed to achieve adequate alkalinity is very high, and despite of that, the pulp pH decreases with time;
- the settling and filtering pulp behaviour is clearly poor;
- the dissolved iron is lower than in acidic solutions, as expected, but it increases with stirring time;
- the initially small amount of dissolved gold is progressively lost by the solution, thus the overall gold recovery is very low;

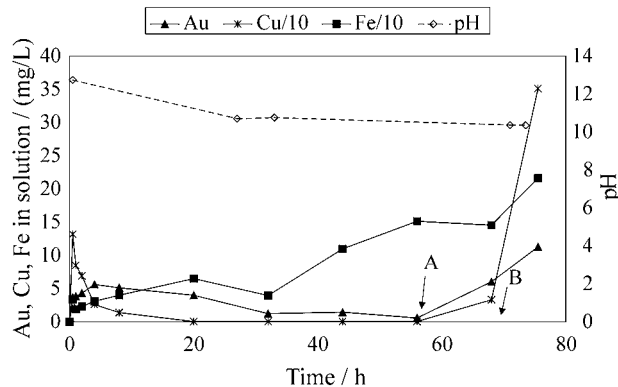


Figure 1. Product cyanidation using 0.5% NaCN solution; 1 kg of product, 1 L of solution, 50 g of lime; 0.17 and 4.32 g NaCN were added to the pulp at times A and B, respectively.

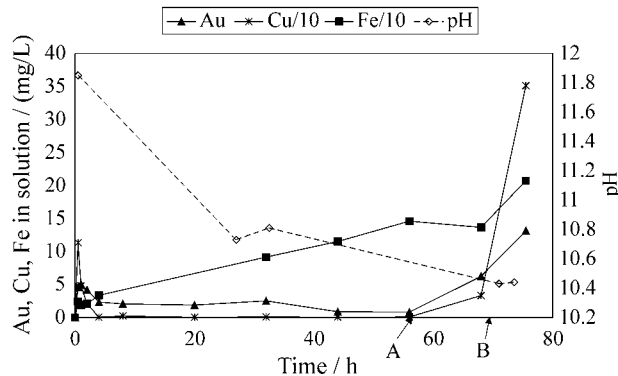


Figure 2. Cyanidation using 0.5% NaCN solution and the product milled to <0.3 mm; 1 kg of product, 1 L of solution, 50 g of lime; 0.13 and 3.93 g NaCN were added to the pulp at times A and B, respectively.

- further sodium cyanide additions to the stirred solutions immediately promote a visible increase in copper, gold and iron concentrations;

- size reduction does not affect substantially the product leaching behaviour.

It seems that cyanide degradation occurs in the bulk solution having gold losses as consequence. Thus, some alternatives to improve gold dissolution can be suggested: (a) the addition of much more cyanide, *i.e.*, the use of higher concentrated cyanide solutions; (b) to submit the product to some specific treatments that either remove chemical species accounting for degrading cyanide or speeding up their transformation; and (c) use other leaching agents that can be expected to advantageously replace cyanide, such as thiourea.

4.3. High concentrated cyanide solutions

Figures 3 and 4 refer to two of those experiments carried out with high cyanide concentration. The general conclusion of these tests is that recoveries higher than 60% of Au are possible under the following leaching conditions: (i) adding 50-70 kg of lime per ton of product; (ii) stirring the pulp for 72 h; (iii) maintaining not less than 0.2% of free cyanide in solution. However, high NaCN consumption, of around 70 kg/ton, is expected, and in order to avoid such NaCN consumption, the frequent monitoring of pH and free cyanide is recommended, since both decrease very fast at the first 15-20 h of leaching. Besides, maintaining high alkalinity, a good practice is having free cyanide concentration as low as possible so as to keep gold dissolving.

4.4. Treatments prior to cyanidation

Several treatments prior to cyanidation were tried, in general with no substantial success: dry milling all the product to <0.3 and <0.1 mm; prolonged pulp conditioning using lime; oxidising the pulp by an extended air bubbling; using lime rather than caustic soda for pH adjustment;

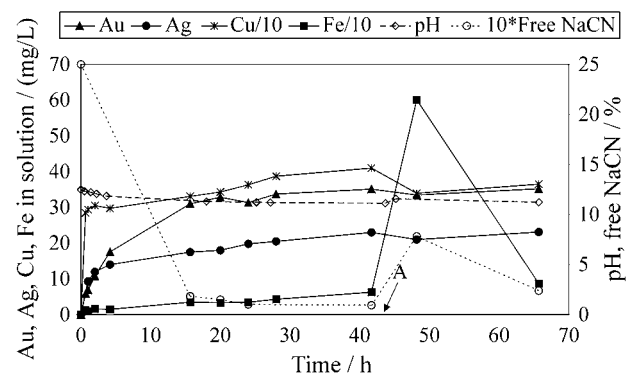


Figure 3. Product cyanidation using 2.5% NaCN solution; 1 kg of product, 1 L of solution, 71 g of lime; 25 g NaCN were added to the pulp at time A. Au recovery = 61.2%.

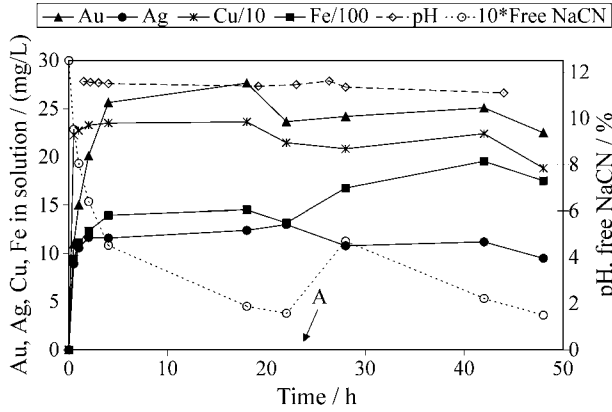


Figure 4. Product cyanidation using 1.25% NaCN solution; 1 kg of product, 2 L of solution, 54 g of lime; 20 g NaCN were added to the pulp at time A. Au recovery = 64.3%.

pre-washing the product with water, HCl, HCl + NH₄Cl, HNO₃ and H₂SO₄ solutions. These last two hot acid solutions improved cyanidation recoveries: 58% of the gold was recovered from the product previously hot washed with HNO₃ 10% solution for 2 h at 65 °C; and, as shown in Fig. 5, about 56% Au and 73% Ag were recovered from the product previously hot washed with 7% v/v hot H₂SO₄ solution at 70-80 °C. A sensible decrease in lime and NaCN consumption as well as in dissolved Cu and Fe relative to cyanidation with no acid washing treatment were also observed.

Figure 6 shows roasting as a very effective treatment prior to cyanidation, since 93% Au was recovered in the product heated to 700 °C for 1 h. Moreover, a spectacular improvement in the settling and filtering capabilities of the pulp was achieved, as well as a reduced consumption of lime and NaCN, and, in addition, much less iron was dissolved, too.

4.5. Other leaching reagents

Stirring the product for 24 h in a 20% dilute HCl + HNO₃ 3:1 solution, under 1:3 solid:liquid ratio, around

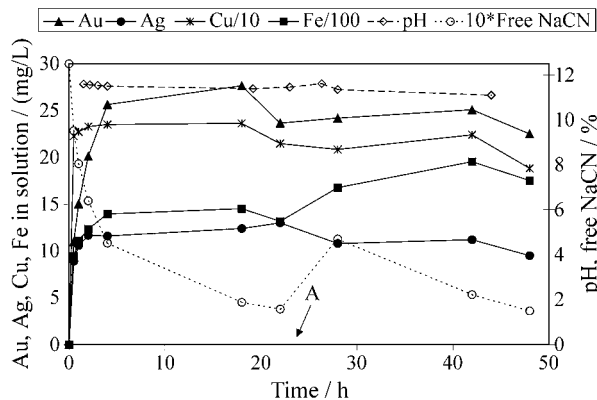


Figure 5. Product cyanidation using 0.67% NaCN solution; 1 kg of product, 3 L of solution, 30 g of lime; 10 g NaCN were added to the pulp at time A. Au recovery = 55.7%; Ag recovery = 72.7%.

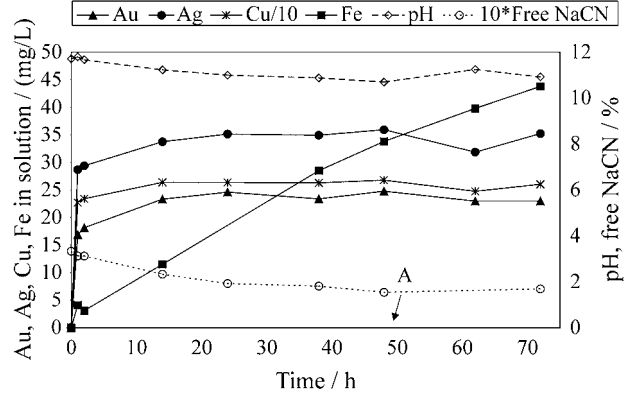


Figure 6. Product cyanidation using 0.5% NaCN solution; 1 kg of product roasted at 700 °C, 2 L of solution, 18 g of lime; 400 mL of water and 2 g NaCN were added to the pulp at time A. Au recovery = 93.4%.

51% of Au was recovered. Further cyanidation of the residue contributed to add 15% to the already recovered gold, thus the overall Au recovery was 66%.

By simultaneous stirring and electrolysis a pulp with a 10% NaCl solution, thus producing chlorine, as a result of the oxidation of chloride ions, about 35% of Au was dissolved. Additionally, 28% of Au is recoverable in 24 h by cyanidation of the residue. This result confirms an already reported partial dissolution of gold using sodium hypochlorite solutions¹⁸.

Thiourea was not an effective leaching agent for this product. In fact, by using a thiourea leaching solution of 4% v/v at pH = 1, obtained by adding H₂SO₄, only 30% of the gold content was recovered and the resulting leachate contained more than 50 g/L of iron. As in the cyanidation tests, the phenomena of losing gold already dissolved was also observed during the thiourea leaching experiment. As shown in Fig. 7, even with the roasted product, thiourea leaching offers no remarkable advantage over cyanidation, since both gold and silver recoveries in such experiment

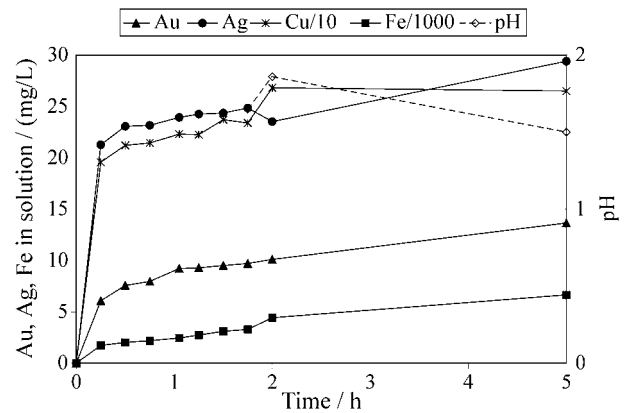
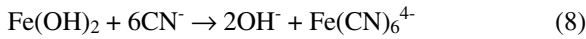


Figure 7. Product leaching using 2.67% thiourea solution; 1 kg of roasted product, 3 L of solution, 20 mL H₂SO₄. Au recovery = 71.9%; Ag recovery = 71.8%.

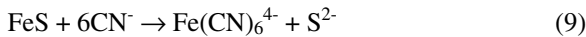
were about 72%. Perhaps high thiourea concentration solutions and longer stirring times are needed.

5. Development of a Cyanidation Route

From the above results it is reasonable to assume that one of the cyanide consuming secondary reactions involves iron, perhaps through the following mechanisms:



and



Iron hydroxide, Fe(OH)_2 , with $K_s = 4.8 \times 10^{-16}$, probably forms, as a very fine precipitate, at the beginning of the experiments, after adding lime to the pulp. The high surface area of this precipitate turns reaction (8) quite possible to take place followed by the further oxidation of Fe(CN)_6^{4-} to Fe(CN)_6^{3-} , whose $E^\circ = -0.358 \text{ V(SHE)}$, thus increasing iron dissolution and cyanide consumption. Iron is also dissolved from sulphides minerals through reactions similar to (9) pushed by further oxidation of $\text{S}^{2-} \rightarrow \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$ and the low solubility of calcium sulphate formed by calcium from added lime. Moreover, the reaction between sulphate and cyanide ions produces thiocyanate ions, which contribute to increase cyanide consumption¹⁹.

Anyway, either dissolving iron by acid pre-washing the product or increasing iron (III) and decreasing sulphur content by roasting it, both treatments reduce iron in leachates and decrease cyanide consumption.

Thus, in view of the preliminary results of gold recovery by the cyanidation of the roasted product, and due to the existence in the plant of two gas fired furnaces, one rotary kiln and one hearth furnace, it was decided to proceed by developing a metallurgical route involving roasting prior to cyanidation.

5.1. Selection of roasting conditions

The criteria adopted to select the conditions for roasting the product were the subsequent cyanidation gold and silver recoveries as well as sodium cyanide and lime consumption. Thus, some roasting tests were carried out at 450, 500, 550, 600, 650 and 700 °C where the product was held for 1 h. An additional two-step roasting cycle at 500 °C for 1/2 h and 625 °C for 1/2 h was carried out to generate maximum porosity in the pyrite and arsenopyrite mineral matrix²⁰.

Figure 8 shows that the sulphur content decrease as the temperature and roasting time increase. Arsenium was not analyzed but must be meaningful, since sometimes it was visible as white As_2O_3 even after finishing the roasting process. The product changed to a red bloody color for

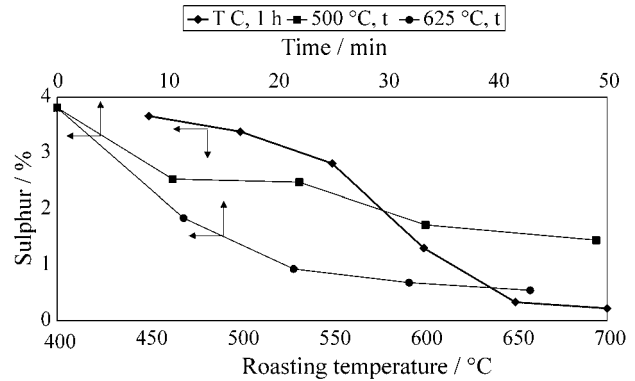


Figure 8. Sulphur in the products roasted under different conditions.

roasting temperatures higher than 600 °C due to Fe_2O_3 generation. For roasting temperatures ≥ 600 °C the obtained products were much less acid than the original one. Consequently, much less lime is needed to obtain correct alkalinity for cyanidation; conversely, if the product was roasted at temperatures ≤ 550 °C, the lime needed for achieving correct alkalinity is still high and approximately the one needed at the initial condition when the roasting process was carried out at 450 °C. The pre-washing can reduce the lime consumption mainly at these lower roasting temperatures, according to the data shown in Table 4.

The roasted products were leached for 24 h in stirred triplicate tests with an initial addition of 50 kg NaCN/ton of product and a 1:3 solid:liquid ratio. The perspective of using an excessively high cyanide concentration intended: (i) a correct basis of comparison with those preliminary cyanidation tests where original product was used; (ii) to guarantee an excess of reagent during the stirring time, to have a permanent dissolution capacity to all the leaching solutions.

Figure 9 shows the free cyanide concentration against time for some tests with no pre-washing but with pre-conditioning step, except the 500/625 °C case. Table 5 shows the cyanide consumption for some leaching tests. The

Table 4. Lime consumption with roasted products, kg/ton.

Roasting temperature (°C)	No pre-washing	Pre-washing
450	60-65	45-50
500	50-55	25-30
550	46-51	27-32
600	<10	n.d.
500, 625	3-5	2-4
650	n.d.	<4
700	n.d.	<2

n.d. - not determined.

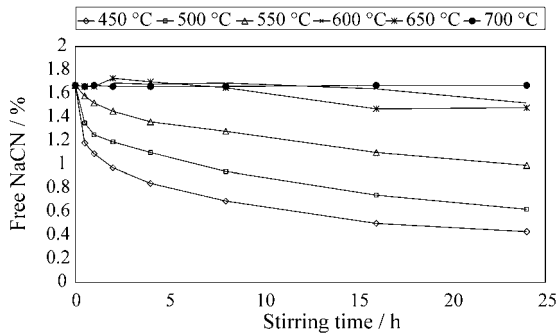


Figure 9. Free cyanide in the leaching tests using products roasted at different temperatures for 1 h; 1.67% NaCN initial concentration, 1:3 solid:liquid ratio.

Table 5. NaCN consumption in cyanidation of the roasted products.

Roast. temper- ature ¹⁾ (°C)	Pre-washi ng	Condi- tioning	NaCN (kg/ton)	b ₁ value (x 10 ⁵)
450	no	yes	37.1	-30.5
450	yes	yes	37.2	-41.4
500	no	yes	31.3	-23.2
500	yes	yes	37.4	-33.6
550	no	yes	25.0	—
550	no	yes	20.4	-13.9
550	yes	yes	22.4	-13.9
600	no	yes	9.0	—
500, 625 ²⁾	no	no	15.4	-10.3
500, 625 ²⁾	yes	no	22.8	-14.2
650	no	yes	5.7	-4.9
650	yes	yes	11.4	-6.9
700	no	yes	0.1	—
700	yes	yes	8.1	—

Holding time: ¹⁾ 1 h; ²⁾ 1/2 h at 500 °C, 1/2 h at 625 °C.

conclusions are the following: (i) NaCN needed to leach the roasted products is less than that to leach the non-roasted product; and, (ii) the NaCN consumption increases for products roasted at lower temperatures, and surprisingly, for products pre-washed. This anomalous fact was attributed to the very strongly contamination of the water used at the washing step that was collected from a well strongly contaminated by leachates from some tons of product.

A linear regression model as $\log(\text{free NaCN, \%}) = b_0 + b_1 (\text{time, min})$ fitted to all the experiments, explains, reasonably, the free cyanide changes for most of the experiments carried out, mainly after the beginning of the leaching process. Therefore, this model could be used for

Table 6. Au and Ag average recoveries in roasted products cyanidation, %.

Roasting temperature (°C)	Au	Ag
450	79.8	73.2
500	84.2	64.8
550	81.2	57.8
600	78.4	35.9
500, 625	77.5	35.0
650	86.3	46.1
700	79.4	42.3

monitoring the free cyanide concentration with time. The fact that NaCN consumption increases inversely to the roasting temperature and with pre-washing is reflected by the time coefficient in the regression expression as it is presented in the last column of Table 5 for 10 average experiments.

Two statistical hypothesis tests using the differences between either the Au or Ag recovery values, from the cyanidation of the pre-washed and non-pre-washed roasted products, were done in order to assess meaningful different leaching behaviour. Despite the average Au and Ag recoveries in pre-washed products have mean differences of 2.07 and 7.75% respectively, higher than in the non-washed products, the hypothesis test based on the t-Student statistic gives no evidence to reject the null hypothesis of equal Au or Ag recoveries for both washed and non-washed products. In consequence, Table 6 shows the pooled Au and Ag average recoveries ranked by the roasting temperatures. Clearly, the highest Ag recoveries are related to the lowest roasting temperatures in the range and the highest Au recovery is found for the 650 °C product, although not very different from other values. However, those mean values do not reflect the large variability for both Ag and Au recoveries, a characteristic shown better in Figs. 10 and 11 where true mean Au and Ag recoveries 95% confidence intervals were built for different experiments with the roasted products. The product roasted at 650 °C has the highest mean Au recovered value of 92.1%. Similar gold recoveries even higher than 81% were obtained for the 500 °C product. Therefore, these values do not assign clearly the best roasting conditions for recovering gold in the ore; and looking at the recoveries frequency distribution, it can only be said that cyanidation has a probability of about 60% to recover at least 80% of gold (or around 93% to recover more than 74% of Au) in the products roasted under any of the tested conditions. In consequence, other criteria, as silver recovery, cyanide and lime consumptions must decide among all the experiments. By

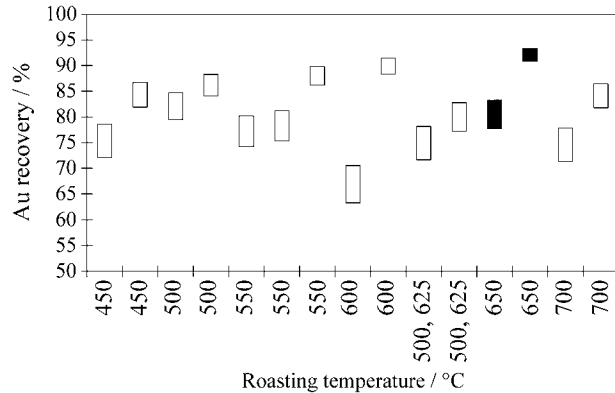


Figure 10. Mean gold recovery 95% confidence intervals from cyanidation tests with different roasted products.

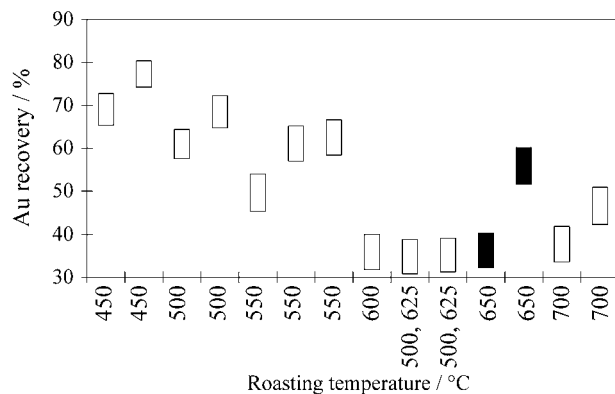


Figure 11. Mean silver recovery 95% confidence intervals from cyanidation tests with different roasted products.

weighing the value of silver recovered and NaCN and lime costs, roasting temperatures in the range of 600 to 700 °C seem to be preferable. Additionally, the resulting residues settle and filter better.

Despite the evident possibility of increasing precious metals recoveries, by increasing stirring time, the overall results are not that high. In fact, gold and silver in the roasted products were in the range of 35.2 to 153.4 g of Au/ton of product, with a 78.1 g/ton mean average, and 25.4 to 69.3 g of Ag/ton of product, with a 45.4 g/ton mean average. However, the respective leaching residues were in the range of 4.1 to 36.5 g of Au/ton of residue, with a 11.0 g/ton mean average, and 10.2 to 38.4 g of Ag/ton of residue with a 21.6 g/ton mean average. That is, residues are not still a worthless raw material.

6. Conclusions

In this gold sulphide concentrate three main reasons explain most of the variability response found at leaching tests: (i) gold exists as free and non-free particles with sizes of <10 µm to >100 µm; (ii) the product has completely roasted particles, as well as partially and almost intact sulphides particles; and (ii) the granulometric composition

of the samples is quite different and gold in finer fractions is higher than in coarse ones. As consequence, the samples of sulphide concentrate used in the tests showed a sensible gold content scattering.

Even using either 0.5 or 1 kg samples of sulphide concentrate, in the experiments carried out, and computing gold recoveries considering the gold content in both the corresponding solutions and residues, significant differences in gold recoveries were still found under similar leaching conditions.

The cyanidation of this product, using conventional NaCN concentration of 0.5% w/v, was not feasible, since the small amount of gold initially dissolved, was easily lost, and final gold recovery was very low. Some of the added cyanide was spent reacting with copper and iron, but other secondary reactions that consume cyanide may occur, such as those producing thiocyanate ions. Additionally, very high lime amount, of about 50 to 70 kg/ton of product, was needed for adjusting pulp alkalinity, and the solutions obtained, settle and filter poorly.

Thiourea showed to be a non-effective reagent to recover the gold contained in this partially roasted sulphide material and offered no visible advantages over cyanide, a less expensive leaching reagent.

By using highly concentrated cyanide solutions, about 60% of Au in the concentrate was leached with no prior treatments. However, both poor settling and filtering characteristics remained. With these solutions long stirring time of about 72 h is recommended and high cyanide consumption of around 70 kg of NaCN /ton of product must be expected. Carefully monitoring the leaching process in order to maintain free cyanide around 0.2%, as NaCN, can reduce substantially the amount of such reagent used during the leaching process.

As expected, milling the partially roasted sulphide did not benefit gold recovery, due to the non-significant relative increase of surface exposed to cyanidation in this already porous and weathered product.

Among prior treatments, HNO₃ and H₂SO₄ acid pre-washing were effective for improving settling capability, for reducing iron and copper dissolution and affording NaCN.

The roasting process has made substantial modifications in the product: (i) improved settling behavior; (ii) less iron was dissolved; (iii) lime and NaCN consumption were reduced; and (iv) more gold was dissolved in less stirring times.

The effect of roasting conditions on this heterogeneous product, as evaluated by the cyanidation experiments carried out, was the following: (i) silver recoveries are higher for the lowest roasting temperatures at the 450-700 °C range; (ii) lime and NaCN consumption are lower for

products roasted at the upper temperatures in that range; (iii) pre-washing the roasted products reduces lime required for adjusting pH of the pulp, mainly for those roasted at 550 °C or below; (iv) after roasting the product for 1 h at any temperature, in the 450-700 °C range, one can say that there is a probability of about 93% that highly concentrated cyanide solutions leach at least 74% of the Au, in 24 h; (v) there is no evidence for believing that pre-washing the roasted products improves either gold or silver recoveries.

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