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# Roasting and chlorine leaching of gold-bearing refractory concentrate: Experimental and process analysis



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# ABSTRACT

This paper deals with gold extraction from a refractory concentrate by chlorine leaching. The process considers a pre-treatment of refractory materials by low temperature oxidation carried out with low oxygen concentration. The oxidized material is treated by leaching with brine. After gold adsorption/ reduction onto activated carbon, iron and base metals can be precipitated by NaOH. Roasting tests show the necessity to carry out a thermal pre-treatment at least at 550 °C to obtain a reduction of sulfur and mercury in the material (50% and 90%, respectively). Highest gold extraction yield (around 93%) is obtained in the leaching test performed with material sample treated at 650 °C. This result confirms the necessity to optimize the thermal pre-treatment to improve Au recovery and to reduce chlorine consumption. A comparison with conventional cyanidation confirms that chlorination could be an useful alternative: in fact, gold extraction yield is quite low: 57% in non-pre-treated material and 25% in pre-treatment material.

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## 1. Introduction

Cyanidation is the conventional process used for gold recovery, as reported by Kirk–Othmer Encyclopaedia and Ullmann's Encyclopaedia [1,2]. Although gold cyanidation plant practice has been improved significantly in recent years, process optimization is still under development. Cyanidation is a relatively simple and cheap technology for treating a wide range of gold-containing ores [3].

Ores that are naturally resistant to recovery by standard cyanidation, and carbon adsorption processes are called as refractory gold ores.

A refractory ore, generally, contains sulfide minerals, organic carbon, or both. Sulfide minerals (pyrite, pyrrhotite, or arsenopyrite) often trap or occlude gold and other precious metal particles [4]. Organic carbon present in gold ore may adsorb dissolved gold cyanide complexes in much the same way as activated carbon (AC). This so called "preg-robbing" carbon is washed away, because it is significantly finer than the carbon recovery screens which is typically used to recover AC.

A host of arsenic-bearing minerals, including arsenopyrite and its weathering product scorodite, have also been identified in ore

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deposits, so arsenic can be easily found in natural gold-bearing ores, not only in industrial wastes [5,6]. The presence of arsenic in mineral concentrates drastically diminishes their value, and results in two types of problems [7]. On one hand, arsenic produces metallurgical problems, making it difficult for the metal extraction and the recovery of a final product of high purity. On the other hand, arsenic is regarded as a highly toxic contaminant, which can result in environmental problems due to its atmospheric release and possible water contamination in processing of arsenic bearing ores and concentrates.

Refractory concentrates need oxidative pre-treatments, such as roasting, bacterial or pressure leaching in order to improve recoveries and achieve the economic feasibility. Roasting is used to oxidize both sulfur and organic carbon at high temperatures using air or oxygen. A two-stage roasting is a conventional industrial practice for arsenopyritic ore. The removal of arsenic from arsenopyrite is described as follows:

$$4\text{FeAsS}_{(s)} + 3\text{O}_{2(g)} \rightarrow 4\text{FeS}_{(s)} + 2\text{As}_2\text{O}_{3(g)} \tag{1}$$

Arsenopyrite roasting is rather complicated since the formation of a large number of volatile and non-volatile species (e.g.,  $As_2O_3$ ,  $As_2O_5$  and  $As_2S_3$ ) is possible. If the partial pressure of oxygen is too high, arsenic is converted into arsenate and becomes fixed as ferric arsenate in the calcine. This should happen, and reagent consumption increases [8,9].

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The main problem related to cyanidation is its environmental impact: in fact, both cyanide compounds and process wastes are dangerous pollutants. For this reason, many studies focused on environmentally friendly processes, like chlorination or combined bio-hydrometallurgical processes [10–17].

Chlorination is one of the oldest ways to leach ores containing valuable and precious metals (the first application of this process dates back to 1600). There are many works in literature focusing on gold chlorination. Dönmez et al. performed a study to determine optimum conditions for chlorination of gold in decopperized anode slime with chlorine gas in aqueous medium [18]. Vinals et al. studied the kinetics of the gold dissolution by chlorination in aqueous solution [19]. An in situ electrochemical slurry oxidation by chlorine in acidified salty water has been evaluated at laboratory-scale level as a potential processing route [20].

The present study is related to the supply of gaseous chlorine which is provided by electrolytic way. Chlorine is locally generated by electrolysis of NaCl solution in the required amount to avoid gas storage. This is a great advantage because it reduces problems (and costs) associated with regulations about storage of dangerous materials. Furthermore, NaOH, which is required for iron and arsenic precipitation and for the recovery of base metals, is produced during chlorine electrowinning from brine. By means of this process, it is possible to extract gold from concentrates of industrial wastes.

The aim of the present work is to improve the efficiency of gold recovery from refractory ores or industrial wastes difficult to be treated by conventional process of cyanidation. The alternative process selected, i.e., chlorination, may allow the sustainability of gold extraction both for environmental (reduction of reagents and waste toxicity) and economical aspects (high capital investment related to electrolytic cell purchase cost): it should be possible to reduce the cost of storage of dangerous materials, waste management and raw materials. Moreover, chlorination allows the use of conventional techniques (carbon in pulp or carbon in leach) for the recovery of gold [21].

## 2. Materials and methods

#### 2.1. Gold concentrate

The refractory gold bearing material was supplied by Institute of Environmental Geology and Geoengineering (IGAG); and it is an industrial waste with a significant content of mercury (about 0.1%) and arsenic (about 0.26%).

The elemental analysis was performed by means of inductively coupled plasma mass spectrometry (ICP-MS, Varian 810-MS). Mineralogical analyses were performed by X-ray diffraction (XRD, diffractometer Philips X-Pert).

Tables 1 and 2 show composition and mineralogical forms of the concentrate. Before tests, samples were ground at  $\leq 104 \,\mu m$  granulometry by Retsch laboratory hammer mill.

#### 2.2. Oxidation experiments

Oxidation of the concentrate was performed by means of low temperature roasting in a fluidized bed reactor. The concentrate was put in a Pyrex tube (diameter=30 mm) at a constant temperature. Gas flow with 10% of  $O_2$  (obtained by mixing 50% air and 50%)

 $N_2$ ) was sent into the reactor. At the end of the test, the gas flow was interrupted and the solid material was cooled.

Experimental conditions are reported in Table 3. Different tests were carried out to check the effects of some process parameters: particle size ( $80 \mu m$ ,  $210 \mu m$  and unsifted material); temperature (ranging from 450 to 650 °C); roasting time and amount of solid treated.

Roasted samples were weighed to evaluate mass change and volatilization of oxides. Table 4 shows the chemical characterization of the concentrate after the thermal treatment.

The gas effluent, mainly consisted of air excess,  $SO_2$  and volatilized oxides, was gurgled in a 10% NaOH solution to reduce the emission of pollutants. Different acid solutions were used to wash the experimental equipment that showed residues of condensation on the glass walls (see Table 3).

### 2.3. Leaching experiments

Leaching tests were carried out on the solid coming from the oxidation treatments (see previous paragraph). Main operating conditions adopted in the leaching tests were as follows: pulp concentration 5%; process temperature 40 °C; process time 5 h. The experimental sequence for chlorination is described below, according to the Lalancette's patent [22].

- (1) Brine (370 g/L of NaCl) is prepared in a stirred reactor (1000 mL) equipped with heating shell to stabilize brine temperature at 40 °C; and brine volume is 500 mL.
- (2) NaBr (20 g/L), which acts as catalyst, and 5% w/w of the oxidized concentrate sample are added in the reactor.
- (3) Gaseous chlorine is gurgled into the reactor for a few minutes by means of a small pipe immersed into the suspension. Gas consumption (Cl<sub>2</sub>) is evaluated by weight decrement of the gas cylinder.
- (4) No further inlets are carried out in order to let local reactions take place. The presence of chlorine is firstly manifested by the liquid phase, which becomes yellow in color. Thus, the liquid phase color changes from yellow to red, as a consequence of bromide oxidation (Eq. (2)) to bromine, Br<sub>2</sub>:

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2 \tag{2}$$

Bromine acts as oxidant of metals. It is further reduced to bromide due to the metal dissolution, and the red coloration changes to yellow. When  $Cl_2$  has been consumed as a consequence of reaction (2), the yellow coloration disappears and an additional amount of chlorine must be added in order to allow further oxidant leaching.

- (5) Points (3) and (4) have to be repeated (4 or 5 times) until the red coloration is definitively permanent: this indicates the end of the leaching.
- (6) The suspension is then filtered by vacuum pump with a paper filter. The cake is washed four times with saturated brine (35 g of NaCl in water of 100 mL) and once with distilled water to remove NaCl. Solid residue (tailings) is dried at 105 °C for 24 h, weighed to evaluate the mass loss and then analyzed for the metal content.
- (7) Filtered solution and washing solutions are blended together in order to obtain the "pregnant solution", and diluted with saturated brine (volume of dilute solution: 1000 mL).

Table 1

Elemental composition of gold concentrate: mean value ± standard deviation.

Au (g/t)	Ag (g/t)	Pb (%)	Zn (%)	Cu (%)	Fe (%)	As (%)	Sb (%)	Hg (10 <sup>-6</sup> )	S (%)
60 ± 10	$5100 \pm 200$	$5.3 \pm 0.2$	$8.4 \pm 0.4$	$1.19 \pm 0.06$	$5.62 \pm 0.05$	$0.24\pm0.02$	$1.96 \pm 0.04$	$1000 \pm 100$	$12.2 \pm 0.3$

#### Table 2

Mineralogical composition of gold concentrate and roasted ore.

Gold concentrate			Roasted ore		
Mineral	Formula	(%)	Mineral	Formula	(%)
Sphalerite	ZnS	45	Bianchite	(ZnFe) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	30
Quartz	SiO <sub>2</sub>	16	Franklinite	ZnFe <sub>2</sub> O <sub>4</sub>	19
Galena	PbS	15	Ematite	Fe <sub>2</sub> O <sub>3</sub>	14
Pyrite	FeS <sub>2</sub>	7	Cubante	CuFe <sub>2</sub> O <sub>3</sub>	12
Chalcopyrite	CuFeS <sub>2</sub>	6	Quartz	SiO <sub>2</sub>	11
Litharge	РЬО	3	Tridymite	SiO <sub>2</sub>	5
Chlorite (ferrous clinochlore)	(MgAlCrFe) <sub>5</sub> (SiAl) <sub>4</sub> O <sub>10</sub> (OH)	3	Wurtzite	ZnS	5
Mica (muscovite)	KAl <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>	3	Mica (muscovite)	KAl <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>	2
Senarmontite	Sb <sub>2</sub> O <sub>3</sub>	2	Senarmontite	Sb <sub>2</sub> O <sub>3</sub>	2

Table :	3
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Oxidation process: experimental conditions.

Test	dp (µm)	Ore (g)	Temperature (°C)	Time (h)	Washing solution	Weight loss (g)
R1		100	450	5	HCl 20%	
R2	210	50	450	5	HCl 20%	1.1
R3	80	50	450	6	HNO3 25%	1.4
R4	80	50	550	4	Aqua regia	0.6
R5	80	50	650	4		5.3

#### Table 4

Solid characterization of gold concentrate after thermal treatment (see Table 3).

	R1		R2		R3		R4		R5	
	С	$\Delta\%$	С	$\Delta\%$	С	$\Delta\%$	С	$\Delta\%$	С	$\Delta\%$
Au	n.d	n.d	n.d	n.d	63.6 g/t	n.d	52.5 g/t	-12	52.0 g/t	-21
Ag	n.d	n.d	n.d	n.d	5214 g/t	-1	4791 g/t	-7	4939 g/t	-14
Pb	n.d	n.d	n.d	n.d	5.68%	n.d	5.35%	0	n.d	n.d
Zn	n.d	n.d	n.d	n.d	8.67%	0	8.16%	-4	n.d	n.d
Cu	n.d	n.d	n.d	n.d	1.20%	-2	1.17%	-3	n.d	n.d
Fe	n.d	n.d	n.d	n.d	5.91%	n.d	n.d	n.d	n.d	n.d
As	n.d	n.d	n.d	n.d	0.24%	-2	0.25%	n.d	0.23%	-13
Sb	n.d	n.d	n.d	n.d	1.95%	-3	1.86%	-6	n.d	n.d
Hg	n.d.	n.d	n.d.	n.d	$292\times 10^{-6}$	-71	$57.9\times10^{-6}$	-94	$54.4\times10^{-6}$	-95
S	n.d	n.d	6.30%	-49	6.28%	-50	6.10%	-50	n.d	n.d

Note: C is the concentration; n.d. means not determined.

(8) Precious metals (gold and silver) in "pregnant solution" are then recovered by absorption onto activated carbon.

#### 2.4. Analytical determination

Thermo-gravimetric analysis (TG) and thermo-differential analysis (DTA) were carried out in air flow with constant temperature rate (10 °C/min) from 20 to 800 °C (NETZSCH STA 409).

Metal concentration was detected by a Varian absorption spectrophotometer (Apectra AA-200, Varian).

A solvent extraction by MIBK was carried out to measure gold by atomic absorption spectrometry (AAS). Gold solution (100 mL) was acidified with HCl 37% (43 mL) prior to extraction into MIBK (10 mL). The sample was shaken for 5 min, then the stirring was stopped until the phase separation took place. The organic phase was recovered and stored in glass test tubes.

This preparation procedure assures dissolution of the gold contained in the solution and provides an universal method for measurement by AAS.

## 3. Results and discussion

### 3.1. Thermal analyses

The material underwent TG and DTA, in order to evidence main temperature ranges where fundamental reactions take place. These analyses are important to establish roasting operating temperature. Results are shown in Fig. 1. When the temperature increases, the sample weight (dotted line) decreases, with a low slope and then with a higher slope in the range 450–550 °C: that indicates oxidation processes and volatilization of some substances initially contained in the solid sample. In particular, sulfide oxidation takes place in the second zone. At higher temperatures, the diagram shows a weight increment, probably due to the formation of non-volatile sulfates, principally bianchite, of those metals contained in the sample, as shown by XRD analyses of the roasted sample (see Table 2).

An exothermic process can be observed (positive values of the ordinate axis in Fig. 1, continuous line), when the temperature



Fig. 1. TG and DTA results

increases. The exothermic process catches up the highest values of heat around 500 °C, in the same interval of the oxidation process (exothermic reaction). Around the maximum peak, the behavior of that line indicates the presence of simultaneous processes: an exothermic reaction and an endothermic one, which prevails after 600 °C.

These results permitted to select a suitable roasting temperature. The thermal pretreatment is a fundamental step when performing the chlorination process: the greater the amount of sulfides in the original ore is, the greater the Cl<sub>2</sub> consumption during the leaching stage is.

## 3.2. Low temperature roasting and leaching

The variation of elemental composition ( $\Delta$ %) was evaluated after roasting with respect to the elemental mean composition, as reported in Table 1. These results are shown in Table 4. The change of composition was calculated according to the following equations:

$$\Delta\% = \frac{C_{\rm RC} \cdot {\rm RC}}{C_{\rm GC} \cdot {\rm GC}} - 1 \tag{3}$$

$$RC = GC - WL \tag{4}$$

where  $C_{RC}$  is the concentration of one element in the roasted concentrate; RC the mass of roasted concentrate;  $C_{GC}$  the concentration of one element in the gold concentrate; GC the mass of gold concentrate; and WL the weight loss due to roasting.

Analysis of composition variation is important to evaluate the efficiency of the thermal process for the removal of elements/compounds that determine chlorine consumption (reagents consumption related to dissolution of contaminants, e.g., As and S).

Comparing tests R3 and R5 (carried out at 450 °C for 6 h and 650 °C for 4 h, respectively), it is possible to observe that mercury removal by oxidation pre-treatment improves from 70% to 95%. An important issue connected to Hg removal is the treatment of gaseous emissions coming from the roasting process; the Italian Directive (D.M. 12 July 1990) fixes the limit of emission for different compounds: this limit is 0.2 mg/m<sup>3</sup> for Hg and 1 mg/m<sup>3</sup> for As.

Moreover, it can be observed that sulfur removal (test R3) is about 50% and residual sulfide causes high chlorine consumption [23]. Therefore, a roasting test in two steps (test R4 of Table 4: first step at 550 °C for 2 h with low  $O_2$  air (10% of  $O_2$ ); second one at 550 °C for 2 h with air) were performed in order to reduce sulfur content; nevertheless, sulfur removal did not exceed 50%, but the XRD analyses (here not reported) demonstrated only the presence of sulfate.

To check the effect of the pre-treatment conditions on gold extraction, leaching tests were carried out with roasted samples obtained by the five different thermal treatments described before. Table 5 shows the composition of leaching tailings. These data show that Cu, Pb and Zn are completely dissolved during chlorination. The leaching environment is oxidative as well: this justifies the complete dissolution of these metals. Moreover, it is possible to observe that the percentage of these metals (Pb, Zn, Cu and Fe) are highest in the tailings coming from leaching test L4 (Table 5), which is carried out with material pretreated at 550 °C (Table 4).

Dissolution of As and Sb is about 67% and 30% (test L3). The extraction yields were evaluated using the following equation:

% Extraction Yield = 
$$1 - \frac{C_{SR} \cdot SR}{C_{RC} \cdot SL}$$
 (5)

$$SL = PC \cdot V$$
 (6)

where  $C_{SR}$  is the concentration of a certain element in the solid residue of leaching; SR the mass of solid residue; SL the mass of

roasting concentrate treated by leaching; PC the pulp concentration; and V the liquid volume.

Table 6 shows the composition of the pregnant solutions coming from leaching tests, whereas Table 7 shows the extraction yields evaluated with respect to the tailings content. It is possible to evaluate the extraction yields with respect to the pregnant solution contents by the following equation:

% Extraction yield = 
$$\frac{C_{PS} \cdot V_{PS}}{C_{RC} \cdot SL}$$
 (7)

where  $C_{PS}$  is the concentration of one element in the pregnant solution; and  $V_{PS}$  the volume of pregnant solution.

These data were not reported, because incoherent with respect to those evaluated by Eq. (5): this could be due to loss of metals during the storage of samples [24,25].

During test L5, the pregnant solution was not stored, but it was immediately put in contact with granulated activated carbon (GAC). Table 8 shows the results of this last test, where the GAC residual is 19.7 g and the adsorption efficiency is calculated by the following equation:

% Adsorption efficiency = 
$$\frac{C_{GAC} \cdot R_{GAC}}{C_{RC} \cdot SL - C_{SR} \cdot SR}$$
(8)

where  $C_{GAC}$  is the concentration of one element onto GAC after adsorption; and  $R_{GAC}$  the residue of GAC recovered.

From these data, it possible to conclude that adsorption of Au onto GAC is very efficient (100%), whereas for Ag the efficiency is only 18%. Gold recovery yield (ratio between Au onto GAC and Au in the roasted material) is about 97%: this means that the gold extracted by chlorination is completely adsorbed onto GAC (the difference between extraction and global recovery yield is probably due to operating errors).

From above analysis, this study results in the following conclusions:

- (1) Roasting temperature increases and the percentage of  $O_2$  in the gas flow does not improve sulfur removal from the concentrate (XRD showed the formation of metals sulfate), whereas Hg removal increases: this last aspect is very important when looking at emission treatments in an industrial-scale plant.
- (2) Roasting temperature and percentage of  $O_2$  in the gas flow do not seem to show any effect on the gold extraction yield, whereas at highest temperature (650 °C) the silver extraction yield decreases to around 40%.
- (3) Cu, Pb and Zn are contained in the concentrate as sulfides (see Table 2), whereas As is present as arsenopyrite. After the thermal treatment under oxidative conditions, these compounds were converted into oxides, and then, in nonrefractory compounds that can easily react with chlorine.
- (4) Dissolution of Cu, Pb and Zn is complete, whereas Fe is partially dissolved.
- (5) High roasting temperature reduces Pb, Zn, Cu and Fe dissolution.
- (6) After roasting, the residual Hg is completely dissolved apart from pre-treatment conditions.
- (7) After roasting the residual S is completely dissolved (like As).
- (8) Gold recovery by adsorption onto GAC is very efficient.

## 3.3. Cyanidation

The aim of this test was to demonstrate the roasting ability to reduce or eliminate the refractoriness of the material studied. Cyanidation treatments were carried out on both original and roasted material. Two tests were performed in a stirred reactor

Ta	able	5			

Solids residue	composition	after	leaching	by	chlorine.	
				~		

Test	Au (g/t)	Ag (g/t)	Pb (%)	Zn (%)	Cu (%)	Fe (%)	As (%)	Sb (%)	Hg	S (%)	Solid residue (g)
L1	11.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	17.6
L2	n.d.	n.d.	< 0.05	< 0.05	0.06	6.13	0.12	n.d.	n.d.	n.d.	17.1
L3	6.73	1092	0.12	0.08	0.09	6.90	0.11	1.94	$0.6 imes 10^{-6}$	0.44	17.8
L4	3.52	1447	0.97	0.89	0.43	8.00	0.16	n.d.	$0.7 imes10^{-6}$	0.24	16.3
L5	4.36	3904	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	$\textbf{0.4}\times 10^{-6}$	n.d.	18.4

Note: n.d. means not determined.

#### Table 6

Composition of	pregnant solution	recovered from	leaching tests	(mg/L).
				\ DI /

Test	Au	Ag	Pb	Zn	Cu	Fe	As	Sb	Hg	S
L1 L2 L3	0.48 0.86 0.50 1.27	n.d. 90.5 94.3 95 2	n.d. 1320 1290 1100	n.d. 1990 1990 1720	n.d. 283 263 215	n.d. 375 174 101	n.d. 38.5 41.2 26.5	n.d. n.d. 133.00 2 73	n.d. n.d. 1.21 2.35	n.d. n.d. 1560 n.d

Note: n.d. means not determined.

#### Table 7

Gold and silver extraction yields (%).

Test	Evaluated with respect to tailings content				
	Au	Ag			
L3	92	85			
L4	96	80			
L5	94	42			

#### Table 8

Characterization of currents coming from adsorption onto GAC (see Fig. 1): leaching carried out on the solid coming from roasting test 5 (see Table 4).

	Au (g/t)	Ag (g/t)	As (%)	Hg (g/t)
Active coal Barren solution (mg/L) Extraction yield (%) Adsorption efficiency (%)	64.0 <0.01 93.4 100	479.0 44.7 41.8 18 3	<1	0.008
Global recovery yield (%)	97%	7.6		

(240 r/min) with a volume of 500 mL, according to the standard parameters of cyanidation with a residence time of 24 h [26].

Tables 9 and 10 report experimental data and results for cyanidation tests, performed with a S/L ratio of 1:2 kg/kg.

At the end of the leach test, the suspension was filtered. The solid was neutralized by sodium hypochlorite, dried and finally analyzed. The filtrate was also analyzed by titration with  $AgNO_3$  at 4.33 g/L and KI 5% as indicator.

From these results, it is possible to state that after thermal oxidation the precious metals recovery decreases, while reagent consumption is higher. This fact can be explained by the interpretation of the chemical and mineralogical analyses of roasted samples (data is not shown here): the effect of temperature involves a S decrease, and with generation of sulfates (such as bianchite) and

Table 9				
Experimental	data	for	cyanidation	tests.

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### Table 10

Cyanidation process: reagents consumption (Titration Test results) and precious metals recovery (process time: 24 h).

Item	Starting concentrate	Roasted concentrate
NaCN (g/kg of concentrate)	12.20	18.00
Ca(OH) <sub>2</sub> (g/kg of concentrate)	0.63	256.13
Au (%)	57.37	24.14
Ag (%)	25.57	18.63

oxides (such as franklinite and hematite), and causes the formation of compounds that hamper the leaching kinetics. In particular, gold and silver particles may be incapsulated into minerals such as cubanite and wurtzite.

Furthermore, gold extraction yields obtained in these tests are lower than those obtained by chlorination.

#### 3.4. Process analyses

Process analyses and simulation were developed starting from the experimental results and literature data. Flow-sheet of the proposed process is shown in Fig. 2. It is possible to note the different steps of this process and, in particular, the hydrolysis stage by which chlorine and sodium hydroxide are produced. The first process step is  $Cl_2$  adsorption on brine;  $Cl_2$  is also insufflated in the leaching reactor, together with gold concentrate coming from low temperature oxidation treatment. The liquor leach (pregnant solution) is sent to the Au/Ag recovery section. After this unit operation, the solution (barren solution) undergoes precipitation sections where Fe and base metals are removed. A material balance was carried out for each unit operation.

Tables 11–13 report data about thermal oxidation (type of oven selected: rotary kiln), H/D ratio and grade of filling were fixed to 10% and 20% respectively; these data were used to design the equipment.

The feed capacity of the plant is about 4 t/h (100 t/d) of roasted concentrate. Five reactors are present in the leaching section (cross-leaching): in the first four reactors (adsorption section)  $Cl_2$  is insufflated (about 221 kg/h per reactor), whereas in the last one air is insufflated (de-gassing section). Global leaching time is 5 h (for each reactor the residence time is 1 h). The chlorate brine and the roasted concentrate feed the first reactor. Solid to liquid ratio chosen is equal to 200 g/L.

Item	Starting concentrate	Starting concentrate		Roasted concentrate	
	Concentration (g/kg)	Weight (g)	Concentration (g/kg)	Weight (g)	
Sample weight		111.5000		119.0000	
Au	0.017	0.0019	0.017	0.0020	
Ag	3.520	0.3925	3.520	0.4189	
starting NaCN	20.000	2.2300	20.000	2.3800	
starting Ca(OH) <sub>2</sub>	0.630	0.0700	256.130	30.4800	



Fig. 2. Block flow diagram of the chlorination process

#### Table 11

Process condition of oxidation: rotary Kiln

Item	Value
Ore flowrate (kg/h)	4167
Ore density (kg/m <sup>3</sup> )	1500
Ore flowrate (m <sup>3</sup> /h)	2.8
Air flowrate (kg/h)	419
Combustible flowrate (CH <sub>4</sub> ) (kg/h)	6
Thermal power of burner (kJ/h)	2.83E+05
Temperature (°C)	450-550
Pressure (Pa)	101,325
Inlet gas flowrate (re-circulated exhaust gas+air) (kg/h)	837
Residence time (h)	5
Diameter (m)	2
Length (m)	21
grade of filling of section (%)	20

#### Table 12

Leaching section data

Inlet stream	Flow rate (kg/h)	Outlet stream	Flow rate (kg/h)
Roasted concentrate Brine	4167 25.000	Slurry (to filtration)	30,000
$Cl_2$ gas	871	Air + $Cl_2$	77
Chiorate Driffe	23,082	(to torch tower)	

Tables 11–13 also report a summary of the results of leaching and electrolysis sections.

Starting from the process results, an economic analysis was carried out. The incidence of different process costs shows that

Table 13

Electrolysis data

electricity has the highest incidence (37%) on the total cost due to electrolytic cell, followed by depreciation (27%), others (17%), NaC1 (9%), labor (8%) and mine operation and flotation (3%). The cost of this process is about  $60 \in$  per ton of material treated. The estimated total plant cost is about 9 million  $\epsilon$ , assuming a straight line amortization schedule, thus under these hypotheses the incidence of depreciation charge is 27%.

## 4. Conclusions

Experimental results have highlighted that the largest gold extraction was obtained by chlorination process of roasted concentrate; increasing roasting temperature is possible to improve Hg removal (about 94%). This issue is very important in considering the design and instalation of a section for treatment of gaseous emissions: in fact, Italian environmental directives gives strict limits (D.M. 12 July 1990). This aspect influences both the initial investment and the operating costs.

However, the optimization of the roasting process is required to improve sulfur removal. The reduction of chlorine consumption, in the leaching section, is very important in order to reduce operating costs related to the chlorine production: this will ensure the economical feasibility of the chlorination process. Moreover, the improvement of sulfur removal has to be pursued in order to improve the As and Sb removal by calcinations.

Another aspect highlighted by the experimental campaign is the impossibility to stock the pregnant solution and the necessity to send it immediately to the adsorption unit to for reducing the gold loss.

Cyanidation tests showed that gold extraction yields (nearly 27%) depend on gold sintering, while gold sintering has not effect on gold extraction by chlorination (around 93%). Moreover, chlorination showed higher kinetics than cyanidation. This last conclusion confirms that cyanidation is not suitable to extract Au from refractory ores, whereas chlorination shows high versatility as well as lower environmental impacts.

Process analysis showed the high incidence of electricity and depreciation charge on the annual operating costs: this is due to the high cost of investment for purchasing the electrolytic cell and the relative operating costs. However, these costs are justified by the high added value of the final product and the very high concentration of gold in the concentrate (about 58 g/t).

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NaCl concentration (M)	pН	EMF (theoretical) (V)	EMF (applied) (V)	Power (kW)	Process cost (€/kW h)	Process cost (€/t of concentrate)
5.1	7	1.817	3	3290	0.075	59.2

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