

Technical Note

Gold extraction by chlorination using a pyrometallurgical process

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ABSTRACT

The feasibility to recover the gold present in alluvial material, by means of a chlorination process, using chlorine as a reactive agent, has been studied. The influence of temperature and reaction time was studied through changes in the reactant solid. The techniques used to characterize the mineral samples and the reaction residues were stereomicroscopy, X-ray diffraction, X-ray fluorescence and scanning electronic microscopy. Results indicate that gold extraction is favored by increasing, both, the temperature and the reaction time. The best recovery values were of 98.23% at 873 K and 3600 s and of 98.73% at 873 K and 5400 s, with very low attack of the matrix containing the metal. The powder of pure gold was not chlorinated at this temperature level.

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1. Introduction

Over the last years, gold recovery has been the central issue in a wide range of studies as a consequence of its high demand and value. These circumstances make the treatment of low-grade raw materials or refractory materials an interesting area of research. The most frequently used method for gold recovery is the cyanidation processes. Although this processes is profitable, it has environmentally-related disadvantages.

Pyrometallurgical processes, and especially selective chlorination processes, have proved to be more efficient and cheaper for the extraction and refined of metals, such as Ti, Zr, Nb, Ta, Mo, etc., generating a growing interest in the application of these procedures (Gaballah et al., 1994, 1995; Jena and Brocchi, 1997; Ojeda et al., 2002; González et al., 2004).

One of the most widely used chlorinating agents for gold recovery is calcium chloride. The non-ferrous and precious metals react with chlorine to form the corresponding chlorides, which are volatile at the temperature required for the process (1273–1473 K) (Panias and Neou-Syngouna, 1990; Deng and Li, 1987).

Dunn (1982) and Dunn et al. (1991) have extracted gold by chlorination using pyrometallurgical processes at temperatures lower than the ones mentioned above, from refractory minerals and alloys, with a previous roasting process.

The objective of this research was, on one hand, to study gold extraction from an alluvial material, through a pyrometallurgical process, using chlorine gas as a reactant, and, on the other hand, to characterize the initial material and chlorination residues, using

X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electronic microscopy (SEM) techniques.

2. Experimental

2.1. Reactants and equipment

The reactants used were the following: alluvial material from Arroyo Cañada Honda in the Province of San Luis (Argentina); gold, in powder, 99.99%, Sigma-Aldrich; chlorine, 99%, Indupa; nitrogen, 99.9%, La Oxígena. All gases were dried in suitable traps before entering the reaction zone.

A diagram of the experimental device used in chlorination is shown in Fig. 1.

The treatment and physicochemical characterization of the original material and chlorination residues was performed with the following equipment: Knelson centrifugal concentrator of high gravity at laboratory scale; Franz isodynamic magnetic concentrator Birmingham; ring mills Fritsch, model Pulverisette; stereomicroscope Leitz, equipped with an ultraviolet lamp Mineralight, model UVSL-58; X-ray diffractometer Rigaku, model D-MAX IIIC, operated at 30 kV and 20 mA, using Cu-K α radiation ($\lambda = 0.154178$ nm); X-ray fluorescence spectrometer Philips, model PW 1400, dispersive in wavelength and equipped with Rh, W and Cr tubes; and scanning electronic microscope LEO, model 1450VP.

2.2. Preparation of the material for chlorination

The material used in this work was extracted following the criteria established for simple collection for the type of ore used. The original sample (m_0) was sieved to sizes lower than 1×10^{-3} m, which is the right size for heavy mineral concentrations. The light

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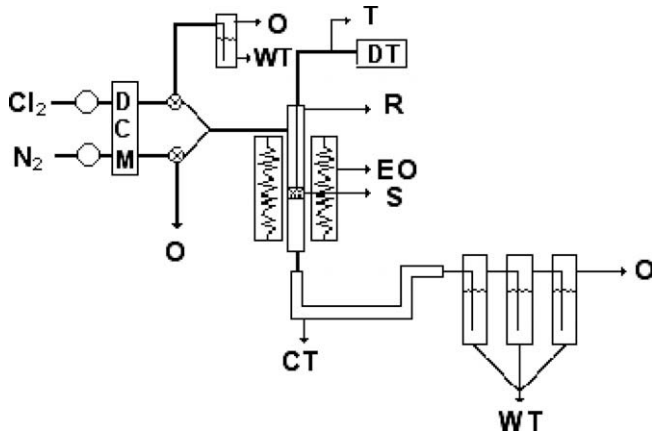


Fig. 1. Schematic representation of the experimental equipment. DCM: Drying, measuring and gas-flow control device; EO: Electric oven; S: Sample holder; R: Reactor; T: Thermocouple; CT: Collecting tube; DT: Digital thermometer; WT: Washing traps; O: Outlet.

material was eliminated using a Knelson concentrator. The magnetite was separated using a Franz electromagnetic concentrator. This material was then moved in a ring mills and sieved again, selecting the fraction over 200 mesh and retaining 325 mesh.

The low gold concentration in this sample (m_1), below 5 ppm, permitted its use as a matrix, upon which finely divided pure gold was dispersed, thus obtaining the material for chlorination tests (m_2) (Ojeda et al., 2003). The preparation was carried out by mixing 500 g of m_1 with 0.700 g of pure gold, with particle sizes in the 1.5–3 μm range. The mixing was carried out by mechanical stirred for 30 min until a homogeneous mixture was obtained. The sample homogeneity was corroborated by the analysis of four aliquots, obtaining an average value of 1416 ppm of gold with an error of 4.7%. Fig. 2 shows a flow sheet of the sample preparation.

2.3. Chlorination procedure

The system was operated as follows: approximately 0.5×10^{-3} kg of the sample to be chlorinated (m_2) was placed on the sample holder and N_2 was passed until the working temperature was reached; at this temperature the N_2 flow was stopped and the chlorinating agent was circulated, which was interrupted when the programmed reaction time finished; N_2 was circulated again at room temperature during 1800 s in order to remove the remaining chlorinating agent and cool the reactor. At the end of each experiment, the residue remaining in the sample holder was weighed to determine the total attack undergone by the sample. The quantity of reacted gold was determined quantitatively on these residues by the XFR technique.

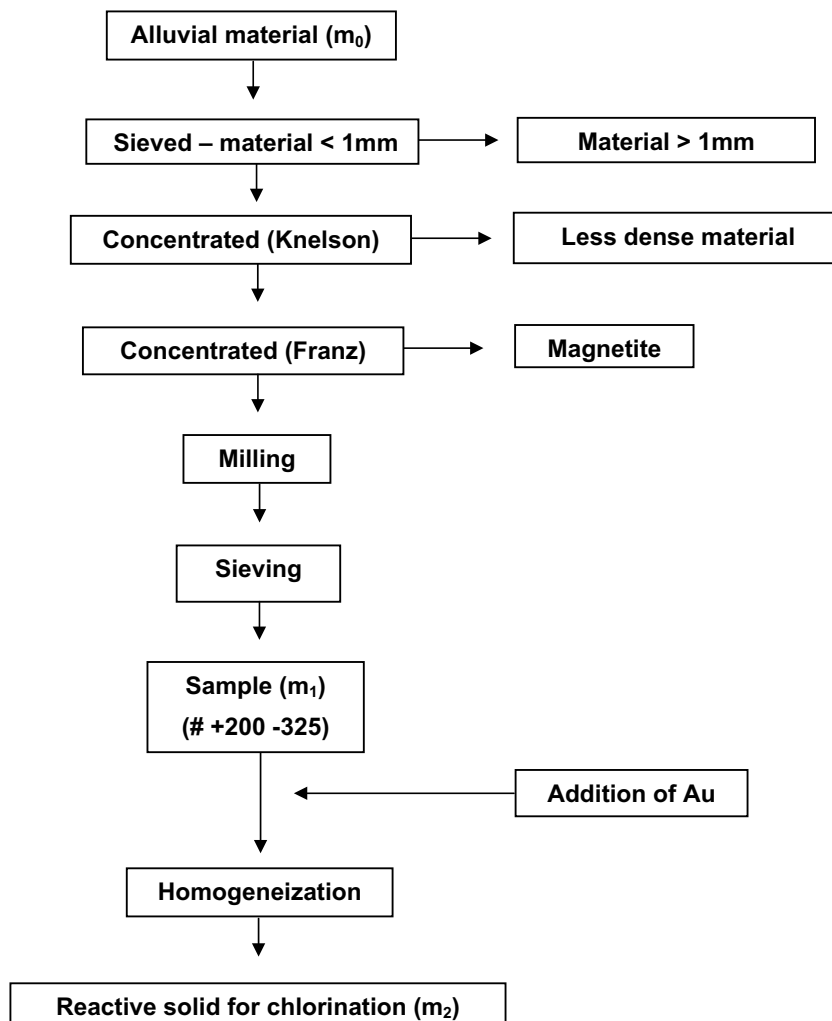


Fig. 2. Flow sheet of the stages involved in the sample preparation.

Table 1
Results of gold extraction at different temperatures and reaction times

| Run | Temperature (K) | Time (s) | Extraction (X%) | Mass loss (%) |
|-----|-----------------|----------|-----------------|---------------|
| 1 | 623 | 3600 | 0.00 | – |
| 2 | 673 | 3600 | 19.32 | 0.82 |
| 3 | 723 | 3600 | 29.75 | 0.92 |
| 4 | 773 | 3600 | 74.24 | 1.29 |
| 5 | 823 | 3600 | 88.72 | 1.08 |
| 6 | 873 | 3600 | 98.23 | 1.73 |
| 7 | 873 | 5400 | 98.73 | 2.20 |

3. Results and discussion

A practical way to express the results obtained in all the assays is as a function of the percentual extraction, X , which was defined as:

$$X (\%) = 100(M_0C_0 - M_fC_f)/(M_0C_0)$$

being C_0 the initial gold concentration in the sample (m_2), C_f final gold concentration in chlorination residue (m_3), both concentrations expressed in ppm, M_0 initial mass of the sample without chlorination (m_2) and M_f final mass of the chlorination residues (m_3), both expressed in mg.

3.1. Chlorination assays

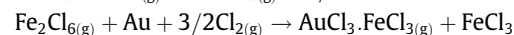
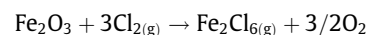
Chlorination of the sample m_2 was performed under isothermal conditions, with a descending dynamic flow at atmospheric pressure. Temperature and reaction time were investigated between 573 and 873 K and 1800 and 2700 s, respectively, operating in all cases with a flow of $1.67 \times 10^{-3} \text{ m}^3/\text{s}$ and with a molar fraction of chlorine equal to one.

Results are shown in Table 1, where for a reaction time of 3600 s, a recovery of metal of 18.5% can be observed at 673 K and it is not produced at 623 K. We may appreciate that the extraction of the precious metal considerably increases with an increase of the temperature and the reaction time, achieving a 98.2% of gold recovery at 873 K in 3600 s.

The direct chlorination of a pure gold was also studied up to a temperature of 1223 K. These experiments demonstrated that the precious metal is not attacked at that temperature, in agreement with the literature, which indicates that the reaction of direct chlorination of gold is produced at high temperatures (Panias and Neou-Syngouna, 1990).

The fact that gold chlorination is reached at lower temperatures might be explained by the formation of binary gold chloride in the vapor phase, which might be extracted from the reaction zone (Heinen and Eisele, 1974; Habashi, 1986). The previous characterizations carried out on sample m_2 indicated the presence of iron oxide, which has a great affinity with chlorine at working temperatures (573–673 K). In the case of gold, this fact might be responsible for the increase in the gold volatilization from mineral since

in the presence of iron chloride, a binary complex $\text{AuCl}_3 \cdot \text{FeCl}_3$ would be formed. Then, the following reactions for gold extraction might be proposed



4. Conclusions

The results of this study allow to conclude that it is possible to recover gold from alluvial materials by an alternative process such as chlorination, preventing environmental pollution problems generated by gold extraction and concentration by other conventional methods.

Extractions of gold close to 99% were achieved, at a temperature of 873 K and at a reaction time of 5400 s, with no significant attack to the matrix.

The characterization of the alluvial material and the chlorination residues can be performed using physical–chemical techniques available in any research laboratory.

The characterization of residues corroborated that the matrix undergoes little attack, which means an important saving in chlorine reagent and a simplification of gold separation and purification.

The chlorination equipment used in the laboratory has a simple design and permits a safer use of chlorine gas.

References

- Deng, H., Li, X., 1987. Chloride roasting of a complex gold ore and treatment of chlorine fume for precious-metal recovery-experimental results. *Transactions Institution of Mining and Metallurgy (C: Mineral Processing Extractive Metallurgy)* 96, 44–46.
- Dunn Jr., W.E., 1982. Chlorine extraction of gold. United States Patent, 4,353,740.
- Dunn Jr., W.E., Carda, D.D., Storbeck, T.A., 1991. Chlorination process for recovery gold values from gold alloys. United States Patent, 5,004,500.
- Gaballah, I., Allain, E., Djona, M., 1994. Chlorination kinetics of refractory metal oxides. *Light Metals*, 1153–1161.
- Gaballah, I., Djona, M., García-Garcedo, F., Ferrera, S., Siguín, D., 1995. Recovery of the metals contained in spent catalysts using a thermal treatment followed by a selective chlorination. *Revista de Metalurgia* 31 (4), 215–221.
- González, J., Rivarola, J., Ruiz, M.del C., 2004. Kinetics of chlorination of tantalum pentoxide in mixture with sucrose carbon by chlorine gas. *Metallurgical and Materials Transactions B* 35, 439–448.
- Habashi, F., 1986. *Principles of Extractive Metallurgy, Pyrometallurgy*, vol. 3. Gordon and Breach Science Publishers S.A., Glasgow. p. 223.
- Heinen, H.J., Eisele, J.A., 1974. United Status Patent Office, 4,825,651.
- Jena, P.K., Brocchi, E.A., 1997. Metal extraction through chlorine metallurgy. *Mineral Processing and Extractive Metallurgy Review* 16 (4), 211–237.
- Ojeda, M.W., Rivarola, J.B., Quiroga, O.D., 2002. Study on chlorination of molybdenum trioxide mixed with carbon black. *Minerals Engineering* 15 (8), 585–591.
- Ojeda, M.W., Perino, E., Ferretti, J., Ruiz, M., Rivarola, J.B., 2003. Estudio preliminar sobre la cloración de oro. Preparación del Material Aurífero. *Jornadas SAM/ Congreso CONAMET/Simposio MATERIA*, Argentina, Tomo 1, pp. 10–13.
- Panias, D., Neou-Syngouna, P., 1990. Gold extraction from pyrite cinders by high temperature chlorination. *Erzmetall* 43 (1), 41–44.