

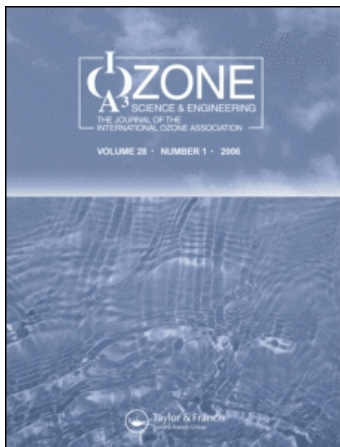
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# Pretreatment with Ozone for Gold and Silver Recovery from Refractory Ores

F. Nava-Alonso, E. Elorza-Rodríguez, A. Uribe-Salas, and R. Pérez-Garibay

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*In this work ozonization was studied as pretreatment for two Mexican refractory ores in order to increase the gold and silver extraction. Two methods for contacting ozone with the mineral were studied (indirect and direct). The indirect method did not change the precious metals recoveries for mineral sample A, but increased those of mineral B (from 53 to 88% for gold and from 26 to 78% for silver). The direct pretreatment, only tested in mineral A, did not affect gold and silver recoveries but decreased the extraction time from 40 to 24 hours for maximum metal recovery.*

**Keywords** Ozone, Refractory Gold Ores, Cyanidation, Gold and Silver Extraction

## INTRODUCTION

Although alternative leaching reagents like thiourea, thiosulfate and chlorine have been used for gold and silver extraction, the cyanide process remains the most efficient, economic and common method: it is capable of recovering up to 99% of the gold and silver present in the ore at room temperature and pressure making use of a dilute alkaline cyanide solution (Haque, 1992). The process involves two operations: the oxidative dissolution of gold and silver, and the reductive precipitation of these metals from the solution.

When gold and silver cannot be extracted efficiently by conventional cyanidation, even after fine grinding, the ore is classified as “refractory.” There are a number of reasons that explain why ores can be refractory, the most common being the occlusion of the submicroscopic gold within the sulfide minerals. In order to recover the precious metals contained in refractory ores it is necessary to modify the matrix of the ore by an oxidative pretreatment

to expose the metals to cyanide. The common alternatives for the pretreatment of refractory ores are roasting, high or low-pressure oxidation, bacterial oxidation and chemical oxidation (Fernandez et al., 2000), but these processes often imply environmental problems, excessive capital requirements, high operating and maintenance costs, or the need of highly trained operating personnel. These disadvantages, coupled with the depletion of the easily leachable ores, are forcing the mineral industry to explore new options to treat the refractory gold and silver ores. Since ozone is a strong oxidant, it may be regarded as a promising alternative in the treatment of refractory ores.

Some research work has been done regarding the use of ozone in the mineral industry, mainly on the treatment of effluents containing cyanide (Mathieu, 1977; Rowley and Otto, 1980), and on the oxidative leaching of copper ores (Roca et al., 2000). In this research work the use of ozone is proposed as oxidative pretreatment for gold and silver refractory ores with the aim of modifying the pyritic matrix and thus exposing the precious metals to cyanide.

## MATERIAL AND METHODS

The ores used in this work were the flotation tailings of two industrial operations of base metal sulfides in Mexico. Both minerals were of pyritic matrix (sample A, 68% of pyrite; sample B, 38% pyrite). In sample A, 60% of gold is free (6 – 20 microns) and the rest is associated with pyrite and quartz. Silver is present as silver sulfides (pyrargyrite and freibergite). In sample B, 14% of gold is free (8  $\mu\text{m}$ ) and the remaining is associated with pyrite, sphalerite and quartz. Silver in sample B is in the form of pyrargyrite and freibergite. Table 1 presents the chemical composition of the ores.

Two methods for contacting ozone with the mineral were tested: the indirect pretreatment, which consists in washing the mineral three times with ozone saturated water, and the direct pretreatment: bubbling the ozone

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**TABLE 1.** Chemical Composition of Mineral Samples Used in This Work

|                         | Sample A    |  | Sample B   |   |
|-------------------------|-------------|--|------------|---|
| Au                      | 1.67 g/t    | 100% native                            | 0.85 g/t   | 100% native                                       |
| Ag                      | 47 g/t      | 68.4% freibergite<br>31.6% pyrargyrite | 153 g/t    | 77.8% freibergite<br>22.2% pyrargyrite            |
| Pb                      | 0.30%       |  | 0.54%      |   |
| Cu                      | 0.18%       |  | 0.78%      |   |
| Zn                      | 1.08%       |  | 3.21%      |   |
| Fe                      | 34.4%       |  | 18.11%     |   |
| Gangue                  | 28%         | 100% SiO <sub>2</sub>                  | 49.5%      | 56.4% SiO <sub>2</sub><br>43.6% BaSO <sub>4</sub> |
| Size (D <sub>80</sub> ) | 120 microns |  | 45 microns |   |

directly into the mineral slurry. For the indirect pretreatment, the water was saturated with ozone in a column by bubbling 3 L/min of an oxygen/ozone mixture (94 g O<sub>3</sub>/Nm<sup>3</sup>) for 5 minutes. Once saturation was reached, the water was transferred to a 3 L reactor containing 200 grams of mineral; the slurry was agitated for one minute at 800 rpm and, after decanting the solids, the solution was drained off for chemical analysis. The above procedure was repeated three times. The solid content of the remaining slurry was adjusted by adding distilled water, and a standard cyanidation was performed (0.2% sodium cyanide, 25% w/w solids and pH = 11 adjusted with lime).

For the direct pretreatment, 300 grams of the mineral sample and 2.5 L of distilled water were placed into the reactor. While agitating at 800 rpm, 3 L/min of oxygen/ozone mixture (50 g O<sub>3</sub>/Nm<sup>3</sup>) was fed to the reactor for 15 minutes. After sampling for chemical analysis and discarding the solution, the desired solid content was adjusted with distilled water and a standard cyanidation was performed. During the pretreatment with ozone/oxygen, on-line measurements of pH, redox potential (ORP), dissolved oxygen, dissolved ozone and ozone in gas phase were recorded.

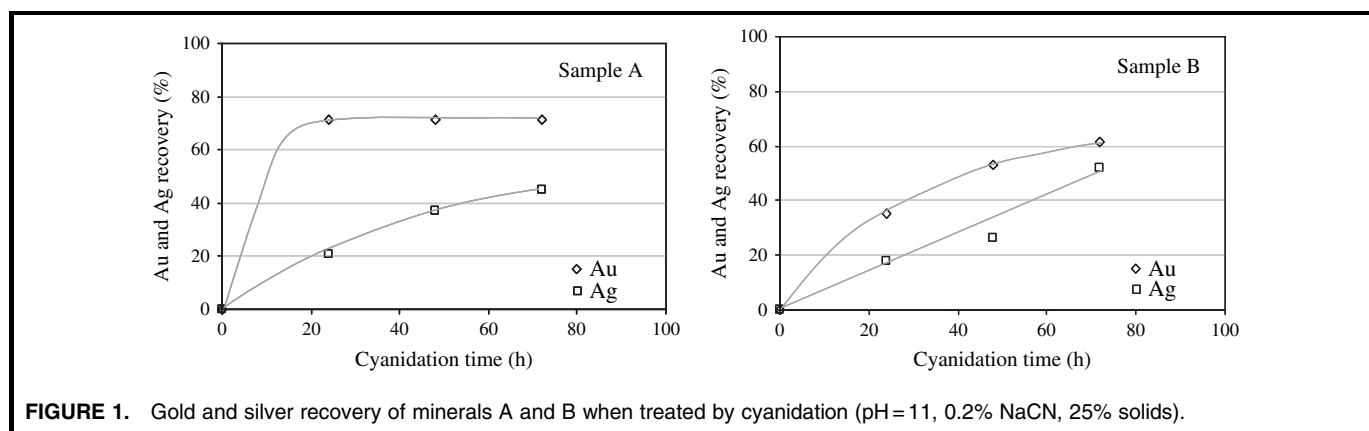
Ozone was produced from dry oxygen with a Pacific Ozone Technology (L22) generator (Benicia, CA, USA). The water used was distilled, and reagents were analytical

grade. Metals in solution were analyzed by atomic absorption in a PerkinElmer 2380 spectrometer (Wellesley, PA, USA); gold and silver were analyzed by fire assay and free cyanide in solution by volumetric titration.

## RESULTS AND DISCUSSION

Standard cyanidation was performed in both mineral samples for 24, 48 and 72 hours, giving a maximum recovery of 71.4% for gold and 45% for silver in sample A, and 61.2% for gold and 51.9% for silver in sample B, as may be observed in Figure 1. These low recoveries obtained confirm the fact that the mineral samples were refractory to conventional cyanidation.

When mineral samples are contacted three times with ozone saturated water and submitted to standard cyanidation, the recovery of gold and silver (48 hours) in sample A remains in the same range, but in sample B the recovery increases from 52.9 to 88.2% for gold, and from 26 to 78.3% for silver, as shown in Table 2. It was demonstrated by mineralogical studies of the cyanidation tailings of both samples that the remaining gold was very small sized (probably encapsulated), and that the non-dissolved silver was mostly pyrargyrite. Silver present as freibergite can be recovered with the ozonization



**TABLE 2.** Gold and Silver Recoveries and Cyanide Consumption for Standard Cyanidation of Mineral Samples A and B with and without Ozone Pretreatment (Indirect Ozone Addition, 48 Hours Cyanidation: 0.2% NaCN, pH = 11, 25% Solids)

|                       | Sample A             |                          | Sample B             |                          |
|-----------------------|----------------------|--------------------------|----------------------|--------------------------|
|                       | Standard cyanidation | Ozonization + Std. cyan. | Standard cyanidation | Ozonization + Std. cyan. |
| Au recovery (%)       | 71.43                | 71.43                    | <b>52.94</b>         | <b>88.24</b>             |
| Ag recovery (%)       | 37                   | 34.6                     | <b>26.01</b>         | <b>78.27</b>             |
| CN consumption (kg/t) | 1.46                 | 1.06                     | 6.0                  | 6.99                     |

pretreatment. It is worth mentioning that this pretreatment decreases the cyanide consumption for sample A, but increases that of sample B. This behavior can be explained in terms of the copper and zinc dissolution by cyanide, which is determined by the pretreatment method, as can be observed in Table 3.

Contacting the mineral three times with ozone-saturated water implies intensive use of equipment and labor work. In order to find out if ozone pretreatment could be simplified, some tests of direct addition of ozone to the mineral pulp were performed. At the time of this second series of tests, the industrial operation of mineral B was shut down and the direct addition of ozone to the mineral slurry was studied only with mineral A.

Ozone was directly bubbled into the mineral slurry for 15 minutes without modifying the pH, and then a conventional cyanidation was carried out. For this mineral the natural pH of the slurry was 3. Figure 2 shows the pH, redox potential (ORP), and dissolved oxygen and ozone profiles for the oxidative pretreatment with ozone. A typical composition of the water discarded after ozonization (and before cyanidation), is 1300–2000 mg/L sulfate, 100 mg/L zinc and iron, 5 mg/L lead and 15 mg/L copper, thus indicating that ozone reacts with the sulfide minerals mainly oxidizing the sulfide into sulfate ion.

The effect of cyanidation time of the mineral samples pretreated with direct addition of ozone onto gold and silver recoveries is shown in Figure 3. It can be observed that 15 minutes of ozone pretreatment and 6 hours of

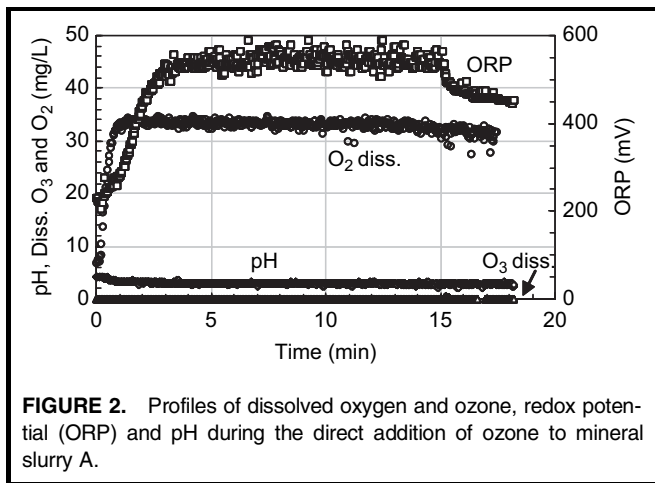
cyanidation yield a similar silver recovery than 40 hours of standard cyanidation: the silver dissolution rate is increased. Gold dissolution rate appears to be less sensitive to this pretreatment. Table 4 shows the metal recoveries for 6, 12 and 24 hours' cyanidation. From this table it is clear that copper and zinc are more soluble in cyanide after the ozone addition, thus increasing silver recovery.

Since precious metals must be first oxidized in order to form soluble cyanide complexes, the dissolution rate of gold and silver is directly related to the concentration of dissolved oxygen in the solution. Some tests were performed in order to determine if the increase in gold and silver recoveries when ozone/oxygen pretreatment is used is due solely to the increase of dissolved oxygen in solution. The pretreatment in these tests consisted in bubbling the mineral pulp with oxygen for 15 minutes. Figure 4 shows gold and silver recoveries for mineral sample A under the following conditions: (a) standard cyanidation, (b) feeding oxygen for 15 minutes to the mineral slurry before cyanidation and (c) feeding ozone/oxygen for 15 minutes to the mineral slurry before cyanidation. Other cyanidation parameters were: 2.5 L water, 0.10% NaCN, 25% w solids, pH = 11 and 6 hours.

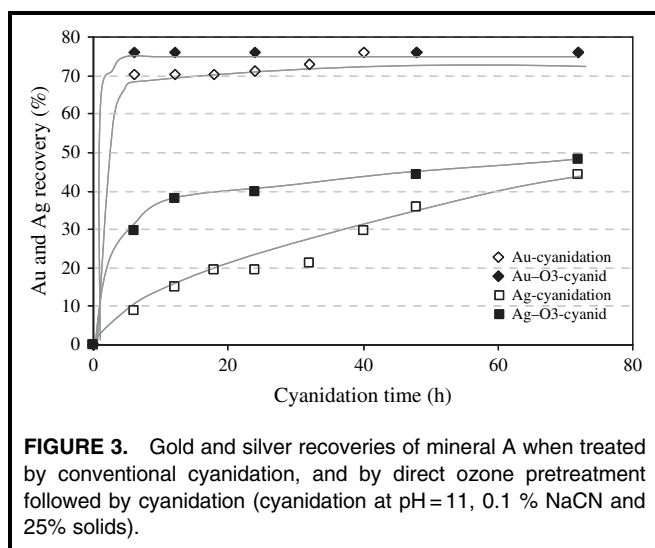
From this figure it is clear that oxygen by itself does not increase the recoveries of precious metals in the same magnitude as ozone addition. In this mineral sample, silver extraction was improved by oxygen addition before or during cyanidation, but the ozone oxidation step did give better results for both gold and silver.

**TABLE 3.** Dissolved Metals in the Cyanidation Solution and in the Ozone-Washing Solution of Mineral Samples A and B (Indirect Ozone Addition, Cyanidation: 0.2% NaCN, pH = 11, 25% solids and 48 hours)

|   | Cyanide Consumption(kg/t) | Cu           | Metal dissolution (%) |       |       |
|---|---------------------------|--------------|-----------------------|-------|-------|
|   |                           |              | Zn                    | Fe    | Pb    |
| Cyanidation solution mineral A                          | 1.46                      | <b>13.54</b> | <b>4.44</b>           | 0.002 | 0     |
| Ozone washing solution A                                |                           | 4.09         | 6.74                  | 0.05  | 3.38  |
| Cyanidation solution mineral A after ozone pretreatment | 1.06                      | <b>8.21</b>  | <b>1.16</b>           | 0     | 0.99  |
| Cyanidation solution mineral B                          | 6.0                       | <b>29.55</b> | <b>2.66</b>           | 0.001 | 0.006 |
| Ozone washing solution B                                |                           | 3.48         | 10.68                 | 0.021 | 1.78  |
| Cyanidation solution mineral B after ozone pretreatment | 6.99                      | <b>31.53</b> | <b>1.0</b>            | 0     | 0.44  |

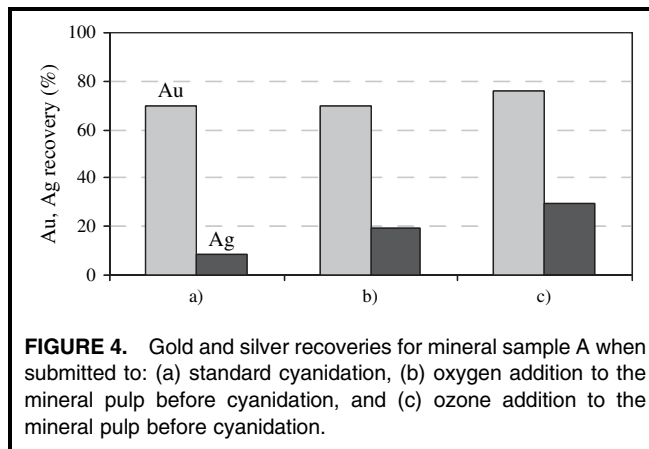


**FIGURE 2.** Profiles of dissolved oxygen and ozone, redox potential (ORP) and pH during the direct addition of ozone to mineral slurry A.



**FIGURE 3.** Gold and silver recoveries of mineral A when treated by conventional cyanidation, and by direct ozone pretreatment followed by cyanidation (cyanidation at pH=11, 0.1 % NaCN and 25% solids).

It is known that the presence of some metal ions (mainly lead) added to the cyanidation solution has an important effect on the dissolution rate of gold and silver (Habashi, 1967; Tshilombo et al., 2001; Wan-Tai et al., 1998). These ions may have either an accelerating or a retarding effect, depending on their concentration in the



**FIGURE 4.** Gold and silver recoveries for mineral sample A when submitted to: (a) standard cyanidation, (b) oxygen addition to the mineral pulp before cyanidation, and (c) ozone addition to the mineral pulp before cyanidation.

solution. The effect of ozone addition on the accelerating-retarding effect of ions such as lead, bismuth or mercury, on the precious metals dissolution kinetics was not addressed in this work.

### CONCLUSIONS

Two refractory ore minerals from Mexican sites were submitted to ozone pretreatment in order to break the pyritic matrix and to increase gold and silver recoveries. Two ozone addition methods were studied: the indirect method (contacting the ore three times with ozone saturated water), and the direct method (direct addition of ozone to the mineral slurry). When the indirect method was used, mineral sample A did not show any significant change in precious metals recovery; mineral sample B increased its gold recovery from 53 to 88% and silver recovery from 26 to 78%. The maximal gold and silver recoveries obtained with the direct addition of ozone were in the same range of those obtained without pretreatment; however, the extraction time for maximum silver recovery was reduced from 40 to 24 hours. The gold recovery is less sensitive to this pretreatment.

The high concentration of sulfate, copper and zinc in the ozonization solutions (direct or indirect addition) may be an evidence of the sulfide oxidation into sulfate, thus the exposure of precious metals to the cyanide.

**TABLE 4.** Metal Recoveries and Reagent Consumption for the Cyanidation of Mineral A with and without Ozone Pretreatment (Direct Ozone Addition, Cyanidation: 0.1% NaCN, pH=11 and 25% Solids)

| t(h) | Cyanidation          |              |      |      |      |      | Ozone addition-cyanidation |              |      |      |      |      |
|------|----------------------|--------------|------|------|------|------|----------------------------|--------------|------|------|------|------|
|      | Metal recoveries (%) |              |      |      | kg/t |      | Metal recoveries (%)       |              |      |      | Kg/t |      |
|      | Au                   | Ag           | Cu   | Zn   | NaCN | Lime | Au                         | Ag           | Cu   | Zn   | NaCN | Lime |
| 6    | <b>70.15</b>         | <b>8.90</b>  | 0.02 | 0.01 | 0.83 | 10   | <b>76.12</b>               | <b>29.61</b> | 7.45 | 2.89 | 1.06 | 8.0  |
| 12   | <b>70.15</b>         | <b>15.11</b> | 0.02 | 0.02 | 1.01 | 10   | <b>76.12</b>               | <b>37.89</b> | 7.59 | 2.98 | 1.14 | 9.5  |
| 24   | <b>71.34</b>         | <b>19.25</b> | 0.02 | 0.01 | 1.08 | 10   | <b>76.12</b>               | <b>39.96</b> | 7.65 | 3.45 | 1.34 | 14.5 |

In gold and silver minerals where the recoveries are low due to the occlusion of the precious metals into the sulfide matrix, the pretreatment with ozone could be a promising option to improve the extraction efficiency. The process is non-contaminating and is carried out at room temperature and pressure. Depending on the associations of gold and silver in the matrix, the recovery of precious metals can be either improved or the cyanidation time shortened.

## ACKNOWLEDGMENTS

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