Copper Extraction from Black Copper Ores through Modification of the Solution Potential in the Irrigation Solution

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Abstract: This article presented the behavior of ores containing black copper under acid leaching. The solution potential was modified by adding agents, and five leaching conditions were evaluated, one as a control based on sulfuric acid leaching (conventional), and the others by changing the solution potential with: ferrous sulfate (FeSO₄), white metal (Cu₂S), sulfur dioxide (SO₂), and ozone (O₃). Leaching behavior was evaluated with laboratory bottle (ISO-pH) and column leaching tests. Two ores samples from the Lomas Bayas mine were used. The samples, identified as low (LG) and high grade (HG), were characterized as 0.13–0.25% Cu and 0.15–0.38% Mn, respectively. The mineralogical analysis indicated that black copper represented around 20% of total Cu (0.05% Cu). The results of the bottle tests indicated that the solution potential decreased with the addition of reducing agents, while the copper extraction rate with the HG sample increased to 83.7%, which exceeded the extraction rate obtained by conventional acid leaching by 25%. Ozone did not favor the extraction of Mn and Cu extraction when the solution potential increased. Cu and Mn extraction were directly related. The results of the column leaching tests showed that it was possible to maintain the solution potential at values below 600 mV (SHE) with the addition of white metal and sulfur dioxide while obtaining the highest copper extraction rate of approximately 60%, which was 18% higher than the rate obtained with conventional leaching. Sulfuric acid consumption was 11 kg/t over 45 days of leaching.

Keywords: leaching; black copper ore; copper wad; copper pitch

1. Introduction

The presence of exotic ore bodies is an important characteristic of the porphyritic systems in the central Andes [1,2]. These exotic deposits vary widely in size, reaching up to 3.5 million tons of fine Cu as copper oxide [3,4]. Together with green oxides are present the black copper minerals, which are difficult to identify darkly colored mineraloid compounds with complex mineralogy and polymetallic associations [5]; black copper ores are refractory to acid leaching, with slow dissolution rates in conventional hydrometallurgical systems.

The Lomas Bayas deposit in northern Chile includes a large area with the presence of exotic copper known as black oxides or black coppers. According to geological and mineralogical studies, 30% of the non-soluble copper in the Lomas Bayas deposit is due to the presence of black copper.
Previous research by the authors [6] determined the possibility of treating this type of deposit under reducing conditions.

Geologists have traditionally identified black copper as rich in iron and manganese silicate hydrate. It is found as “copper wad” or “copper pitch” in compact earthy botryoidal masses, or filling fractures and cementing gravel. When it appears alone in an earthy state, it is called wad; if it is associated with chrysocolla, it is called pitch or black chrysocolla [1,8,9]. The term black copper silicate refers to both mineraloids, which, according to transmission electron microscopy (TEM), have non-crystalline structures and compositions [1,9]. These studies reveal varying concentrations of Cu, Mn, Fe, Al, and Si, as major elements, along with trace elements like Ca, Na, K, Mg, S, P, Cl, Mo, Co, Ni, As, Zn, Pb, U, and V. Considering relative Cu-Mn-Fe content, black copper has two distinct varieties, one rich in Mn and relatively high copper content, and the other rich in Fe and relatively poor in copper. According to [1,5], there are even more specific subgroups, such as wad-type substances, black copper oxides, polymetallic oxides/silicates, and (Fe, Cu).

There is now more information about the characteristics of black copper [1,5,6], but there have been few studies about processing them at the industrial or semi-industrial scale [6]. In general, technical chemical and kinetic data are limited. This makes it difficult to predict the leaching potential of resources with these characteristics.

Hydrometallurgical techniques applied to manganese minerals and marine polymetallic nodules are relevant to the treatment of black copper ore, given the similarities in composition and the resistance to conventional acid leaching [7]. Manganese nodules are mainly composed of two mixed metallic oxides: manganese dioxide and hydrous ferric oxide, and relative quantities of copper, nickel, cobalt, zinc, and molybdenum are also found. The presence of these metals has drawn the attention of researchers who consider manganese nodules a future source of these metals [10–13].

The dissolution of marine nodules and manganese oxides requires leaching in hydrochloric acid, sulfuric acid, or an ammonia medium, preferably in the presence of reducing agents, such as sulfur dioxide [6,14–18], ferrous sulfate or solutions of iron chloride [19], iron sulfides [20], sponge iron [21], nitrous acid, organic acids like EDTA and oxalic acid [22,23], hydrogen peroxide [24,25], and foundry slag [13].

The aim of this study was to evaluate the leaching of minerals with black copper content originating from the Lomas Bayas deposit. A conventional leaching approach was compared to one involving the addition of a strong oxidant (O3) and also reducing agents, either iron sulfate (FeSO4), white metal (Cu2S), or sulfur dioxide (SO2). Tests were performed in bottles and columns.

## 2. Materials and Methods

### 2.1. Materials

Two minerals samples from different areas of the Lomas Bayas deposit were used. The samples were identified as high (HG) and low grade (LG). The samples were subjected to three types of leaching conditions: (1) a conventional leaching media using H2SO4 without changing the oxidation/reduction condition of the solution; (2) an oxidizing media generating adding ozone (O3); and (3) reducing media, using SO2, white metal (Cu2S), and FeSO4. These media were replicated in column leaching tests for each mineral sample (2 samples, 5 tests, respectively).

### 2.1.1. Sample Characterization

The chemical composition of the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Optima 2000DV (Perkin-Elmer, Überlinge, Germany). The mineralogy of the samples was determined by X-ray powder diffraction (XRD), for which the samples were ground in an agate mortar to a size of less than 45 μm and analyzed in an automatic and computerized X-ray diffractometer (Siemens model D5600, Bruker, Billerica, MA, USA), with an analysis time of one hour. The ICDD (International center for diffraction data, Version
PDF-2, Bruker, Billerica, MA, USA) database was used to identify the species present, and the TOPAS (total pattern analysis software, Version 2.1, Bruker, Billerica, MA, USA) was used for quantification. The samples were also studied under a BX-51 reflected-light microscope (Olympus, Tokyo, Japan). Morphology was characterized by scanning electron microscopy (SEM) with a JSM-6360 Lv microscope (JEOL USA Inc., Peabody, MA, USA) with a energy-dispersive X-ray spectroscopy (EDS) microanalysis system (Zeiss Ultra Plus, Zeiss, Jena, Germany) and operated at 30 kV under high vacuum conditions. Mineral samples were metalized with a thin carbon layer to improve their conductivity.

2.2. Experimental Procedure

Ten bottle (ISO-pH) and column leaching tests were conducted to determine the behavior of black copper ore under acid leaching with different modifying potential agents.

2.2.1. ISO-pH Experiments

The ISO-pH tests were performed in leaching bottles. The ore samples were mechanically prepared by reducing their size to 100%-10 mesh (1.70 mm) and pretreated by sulfuric acid curing with 7 kg/t of H2SO4, 8% moisture, and 5 days resting time. The sulfation tests were evaluated daily to define the optimal resting time for the bottle and column tests. A preliminary evaluation was performed in a 1-L reactor with 10 g/L of sulfuric acid, mechanically stirred at 350 min⁻¹ to establish the conditions and effect of different redox potential modifiers on the leaching solution. The solution potential was measured every 10 s. The evaluated agents were FeSO4 (2, 4, 6, 10, 20, 40, 60, 100, and 140 g/L), Cu2S (2, 6, 10, 20, and 40 g/L), and the flow added of SO2 and O3.

The bottle tests evaluated the ores in conventional acid leaching conditions (ore pretreated and 10 g/L of H2SO4, simulating the Lomas Bayas leaching solution). The oxidizing condition was achieved by injecting O3 gas into the bottle. The reducing condition was achieved by adding FeSO4, Cu2S, and SO2 to the initial leaching solution (raffinate); the first two in solid-state and the third injected directly into the bottle until the solution potential stabilized. Samples were taken at 0.5, 1, 2, 4, 8, 24, 48, and 72 h, and the volume extracted was replaced with a fresh raffinate solution. Samples were analyzed for Cu, Fe, and Mn. The residues were drained, dried, and subjected to ICP-AES analysis for CuT, CuSol, Mn, and Fe.

2.2.2. Column Leaching Test

The leaching columns tests evaluated the two ores samples (HG and LG) under the same five conditions as studied in the bottle tests. Each column was 1.6 m high and 15.4 cm in diameter. The columns were filled with 40 kg of pretreated ore (100% under ¾”, 6% moisture, 7 kg/t of H2SO4, and 72 h of resting time). The column tests operated in a closed circuit using a batch solvent extraction (SX) plant, in order to treat the rich solution (PLS) from each leaching condition separately. The raffinate leaching solution, before being irrigated to the columns, was treated in a redox potential modification stage with the addition of agents to adjust the solution potential to the condition to be evaluated. Figure 1 shows the schematic of the circuit.
3. Results and Discussion

3.1. Mineral Characterization

The two ore samples (LG and HG) were chemically characterized by ICP-AES analysis, the results of which are shown in Table 1.

| Sample | Cu(T) % | Cu(Sol) % | Cu(Ins) % | Fe % | Mn % |
|--------|---------|-----------|-----------|------|------|
| LG     | 0.13    | 0.12      | 0.010     | 4.0  | 0.15 |
| HG     | 0.25    | 0.20      | 0.050     | 2.4  | 0.38 |

The mineral samples had low copper concentrations, which is characteristic of the material from the Lomas Bayas mine, with a total copper content of 0.1–0.4% [6]. The chemical analysis by mesh established the distribution of total, soluble, and insoluble copper through the particle size distribution of the samples. According to the analysis, the ore sizes were 15,460 μm in sample LG and 14,840 μm in sample HG. The analysis indicated that there was a preferential distribution of total copper in smaller sizes (75 μm) but not of insoluble copper (see Figure 2).

Table 2 shows the results of the optical mineralogical analysis. The mineralogical analysis indicated that the presence of black copper was closely associated with limonite. It was present in...
sheets and fine coliform bands (<60 μm) in limonite and as impregnation veinlets in rock. Black copper did not show internal reflection, as observed in cuprite (Cu₂O), goethite (FeOOH), hematite (Fe₂O₃), and magnetite (Fe₃O₄). The coliform texture suggests low temperatures and a high degree of supersaturation of the components [26].

Table 2. Mineralogical analysis of the black copper sample using polarized light microscopy.

| Mineral        | LG  | Proportion | Size (μm) | Mineral       | HG  | Proportion | Size (μm) |
|----------------|-----|------------|-----------|---------------|-----|------------|-----------|
| Hematite       | abundant | <760      |           | Limonite      | abundant | <140       |           |
| Magnetite      | abundant | <300      |           | Black copper  | abundant | <60        |           |
| Limonite       | abundant | -         |           | Atacamite     | abundant | -          |           |
| Black copper   | Minor  | ~10       |           | Hematite      | Minor  | ~10        |           |
| Rutile         | Minor  | <50       |           | Rutile        | Minor  | <50        |           |
| Pyrite         | Trace  | ~30       |           | Chalcopyrite  | Minor  | <20        |           |
| -              | -     | -         |           | Pyrite        | Trace  | ~50        |           |

The SEM analysis showed that the phase associated with black oxides in both samples was a homogenous mixture of copper and manganese oxides without silica. Figure 3A,B shows particles containing black copper in samples LG and HG, respectively. The bands marked as zone 1 were black copper, composed principally of Cu-Mn-Fe-O, with minor amounts of K. Zone 2, surrounding these bands, was composed of Si-O, and Al-K-O could be detected in zone 3. The SEM-EDS analysis of the oxidized copper areas of the LG and HG samples showed homogeneous black copper associated with copper oxide, iron, and manganese, with varying levels of silica.

Figure 3. Scanning electron microscope (SEM) image (X 300) of samples LG (A) and HG (B). Association of (1) Cu-Mn-Fe-O (2) Si-O (3) Fe-O.

The quantitative elemental analysis, as shown in Table 3, indicated that zone 1 consisted of oxidized Mn-Cu and low concentrations of Si (bands of black copper). Copper pitch is a silica-rich Cu-bearing phase closely associated with chrysocolla, (often called “black chrysocolla”), while the copper wad is primarily Cu-bearing manganese oxyhydrates. Furthermore, it has been noted that the Cu-Wad, while containing Cu and Mn in significant quantities, also has Fe, Si, and Al as major or minor concentrations, as well as Ca, Na, K, Cl, P, Pb, Zn, Mg, S, P, Mo, Co, As, U, V, and Ni as minor or trace elements [5]. This information indicated that the samples contained both types of black copper—wad and pitch.
Table 3. SEM-EDS (Scanning electron microscope - Energy Dispersive X-Ray Spectroscopy) analysis of zone 1 in LG (A) and HG (B) shown in Figure 3.

|       | Wt % |
|-------|------|
| Samples | O  | Mn | Cu | Fe | K  | Si |
| LG     | 64  | 18 | 1.1| 5.7| 1.7| 3.9|
| HG     | 42  | 38 | 4.2| 7.5| 2.5| 5.9|

Table 4 shows the XRD analysis. The samples were mainly oxides in which the major compounds were silica and aluminum silicates, with low concentrations of copper sulfides and tenorite. The analysis did not detect Cu-Mn-Fe minerals, which were observed by optical and electronic microscopes, because they could not be detected by XRD due to the amorphous character of black copper.

Table 4. X-ray powder diffraction (XRD) analysis of initial samples LG and HG.

| Mineral       | Formula          | LG (%) | HG (%) |
|---------------|------------------|--------|--------|
| Quartz        | SiO₂             | 24.1   | 25.4   |
| Orthoclase    | KAlSi₃O₈         | 14.0   | 20.4   |
| Pyrite        | FeS₂             | 0.15   | 0.13   |
| Muscovite     | KAl₃(SiAlO₃)(OH)₃| 4.93   | 5.21   |
| Djurleite     | Cu₃S₄Si₆        | 0.13   | -      |
| Kaolinite     | Al₂Si₂O₅(OH)₄   | 20.4   | 16.8   |
| Albite        | NaAlSi₃O₈       | 19.9   | 13.5   |
| Chalcoelite   | Cu₃S             | 0.18   | 0.13   |
| Chlorite      | (Mg,Fe)₆(Si,Al)₄O₁₀(OH)₈ | 10.9 | 15.3 |
| Jarosite      | KFe(SO₄)₂(OH)₆  | 0.11   | 0.43   |
| Digenite      | Cu₃S₄           | -      | 0.12   |
| Gypsum        | CaSO₄·2H₂O      | -      | -      |
| Anhydrite     | CaSO₄           | 4.95   | 2.48   |
| Chalcopryite  | CuFeS₂          | 0.13   | -      |
| Tenorite      | CuO             | 0.10   | 0.15   |

3.2. Leaching Test Pretreatment

3.2.1. Eh Modifying Agents

Preliminary tests determined the appropriate concentrations of each modifying agent, which allowed selecting the doses: 40 g/L of FeSO₄ and 6 g/L of Cu₂S and (0.4 L/min) of SO₂ and (5 Nm³/h, 45% O₂) of O₃. Solid ferrous sulfate dissolved rapidly and completely, establishing test times of approximately 1 to 2 min. The reducing capacity was compared to that of the solution potential of the Lomas Bayas raffinate leaching solution (654 mV SHE), which was termed the Eh reference. It was possible to decrease the solution potential to 588 mV (see Figure 4) by adding 140 g/L of FeSO₄, modifying the potential by only 66 mV. Finally, it was decided to use 40 g/L of FeSO₄, which was capable of lowering the potential to 605 mV. Concentrations over 40 g/L did not significantly decrease the solution potential.
Figure 4. Reduction capacity of FeSO₄ in a solution with 10 g/L of H₂SO₄ at room temperature.

The highest Cu₂S concentration decreased the solution potential, more than FeSO₄. Its high capacity to reduce the solution potential of the refining solution was reflected in the decrease from 654 mV (reference Eh, Lomas Bayas refining) to 427 mV with the addition of 40 g/L of Cu₂S (see Figure 5). It was decided to use a concentration of 6 g/L, given that reagent dissolution becomes complex at concentrations above 10 g/L, and the effect on the solution potential is no longer significant.

Figure 5. The reducing capacity of Cu₂S in a solution with 10 g/L of H₂SO₄ at room temperature.

3.2.2. Curing Test

The optimal acid curing time was determined based on the results of the sulfation tests, which present copper extraction and sulfuric acid consumption rates over time. Figure 6 shows that the Cu extraction rate of 35% did not change significantly after the second day of curing. Sulfuric acid consumption reached approximately 90% of the acid added for curing. Three days of curing were applied for the column leaching test to ensure the sulfation of the minerals. According to [27], an adequate curing time results in a homogeneous distribution of the acid in the mineral bed, increases copper dissolution kinetics, and helps inhibit aluminum-silicate minerals. The effect of curing time in the column leaching tests could be compared to those of [28], who performed column leaching tests for a secondary copper sulfide ore and obtained a maximum copper extraction rate at 50 days of curing. [29] also used extended curing times in leaching pretreatment in columns of a primary sulfide copper ore and obtained a maximum copper extraction rate at 100 days of curing. According
to the results shown in Figure 6, there was no need to extend the curing time beyond 5 days with the samples evaluated in this study.

![Figure 6](image)

**Figure 6.** Effect of curing time on copper dissolution and H$_2$SO$_4$ consumption in the LG (A) and HG samples (B) at room temperature.

### 3.3. Leaching Test

#### 3.3.1. Leaching Bottle Test

Figures 7 and 8 show the Cu and Mn extraction rates, respectively, under the evaluated conditions. The copper and Mn extraction rates were similar, confirming the relationship between the extraction of the two elements. Figure 7 shows that the use of the reducing reagent (SO$_2$) resulted in the highest copper extraction rates of 62% and 84% for the LG and HG samples, respectively. The difference in copper extraction rates obtained with conventional leaching and leaching with reducing agents could be attributed to the dissolution of copper from the Cu-Mn-Fe matrix of black copper oxides. The use of Cu$_2$S as a reagent resulted in extraction rates of 57.6% (LG) and 75.8% (HG), which were lower than the rates obtained with SO$_2$. However, the speed and ability to modify the solution potential and its low toxicity made Cu$_2$S a great candidate. The use of FeSO$_4$ resulted in a high copper extraction rate with the HG sample (76.6%), but a lower rate of only 49.5% with the LG sample. The higher extraction rate with the HG sample using FeSO$_4$ could be due to the higher grade of Mn in the mineral and the high concentration of Fe$^{2+}$ ions in the leaching media, which was the result of adding ferrous sulfate as a reducing agent. The dissolution of manganese in diluted sulfuric acid media in the presence of abundant ferrous ions was described by oxide-reduction and consisted of manganese going from the state (IV) to (II) by generating ferric ions as the product of the oxidation of ferrous ions in solution.

![Figure 7](image)

**Figure 7.** Copper extraction in the bottle leaching test in conventional, oxidizing, and reducing media at room temperature (A) LG and (B) HG.
Figure 8 shows that the manganese extraction rates reached maximums of 99% and 95% with the LG and HG samples, respectively, when SO\textsubscript{2} was used. The dissolution efficiency of manganese is more strongly affected by the concentration of the reducing agent than by the PH level [30]. Manganese behaved similarly to what was described by [17], with a dissolution rate of 71% at three hours of leaching.

![Figure 8. Manganese extraction in bottle leach test in conventional, oxidizing, and reducing media at room temperature (A) LG and (B) HG.](image)

Figure 9 shows the Cu, Mn, and Fe extraction rates regarding the solution potential for the different media evaluated. The copper extraction rate was directly related to manganese extraction due to the rupture of the Cu-Mn-O matrix, in which the copper was released. There were no significant differences in the Cu and Mn extraction rates between the conventional and oxidizing (ozone) leaching, with results in the order of 67% Cu and 20% Mn. Copper and manganese dissolution were favored by reducing conditions, while the oxidizing condition had no effect. SO\textsubscript{2} had the best performance of the reactive agents, achieving extraction rates of 83.7% for copper and 94.8% for manganese. For the HG sample, the addition of Cu\textsubscript{2}S to the leaching system resulted in copper and manganese extraction rates of 75.8% and 84%, respectively, which were similar to the rates obtained with FeSO\textsubscript{4} (reducing agent). The best results were obtained by adding SO\textsubscript{2} to the raffinate solution. However, white metal (a by-product of copper smelting) was found to be an interesting reducing agent because of the dissolution rate, its ease of handling, capacity to modify the potential, availability, and the generation of Cu\textsuperscript{2+} as a product.

![Figure 9. Cu, Mn, and Fe extraction rates as a function of the modifying agent with the LG (A) and HG samples (B).](image)

Table 5 shows sulfuric acid consumption rates under different leaching conditions. These results showed higher acid consumption rates were obtained under reducing conditions. The difference in acid consumption rates under standard and oxidizing conditions compared to those
under the reducing condition was due to the higher degree reactivity of the mineral species containing Mn, which was reflected in the higher Mn extraction rate. The evaluations with SO2 presented a low level of acid consumption, due to the injection of gaseous SO2, which reacted with the H2O in the leaching system, generating acid in situ according to the following reaction (1) [17]:

\[
\text{SO}_2(aq) + \text{H}_2\text{O}(l) = \text{H}^+ + \text{HSO}_3^{-(aq)}
\]  

(1)

### Table 5. Sulfuric acid consumption rates obtained in the bottle tests with different agents expressed as kilograms of sulfuric acid per ton of treated ore (kg/t).

| Samples | Conventional | O3 | FeSO4 | Cu2S | SO2 |
|---------|--------------|----|-------|------|-----|
| LG      | 13.3         | 16.8| 13.5  | 11.6 | 9.20|
| HG      | 8.80         | 14.7| 26.5  | 21.8 | 12.0|

#### 3.3.2. Leaching Column Test

Copper and manganese extraction rates were evaluated by leaching column tests using the same modifying agents as used in the bottle tests. The columns were loaded with 45 kg of cured mineral using 7 kg/t of sulfuric acid and leached with 10 g/L of sulfuric acid (raffinate) for 42 days. The results presented in Figure 10 show the direct correlation between the solution potential and the copper extraction rate. The copper extraction rates were higher with the columns operated under reducing conditions (low Eh) compared to under conventional and oxidizing conditions. With conventional and O3 leaching, the solution potential in the irrigation was 650 mV, and this value increased in the solution, reaching 790 to 760 mV (SHE) during the cycle, which means that the Fe3+ concentration in conventional and O3 leaching increased and remained stable. The PH level was stable at approximately 1.5.

When a reducing agent was added (Cu2S), the irrigation solution achieved an Eh in the range of 450 to 500 mV (SHE). This value increased to 760 mV (SHE) in the solution obtained as a consequence of Fe2+ consumption due to black copper dissolution generating Fe3+. Eh then decreased and stabilized at 600 mV. Eh stabilization was the consequence of running out of black copper.

The results showed that the extraction rates with conventional and ozone leaching (660 and 788 mV) were practically the same (42% and 51%) for the LG and HG samples, respectively. The highest copper extraction rates for the LG and HG samples of 62% and 66%, respectively, which were 19% and 15% higher than the rates obtained under standard conditions, were obtained when Cu2S was added as a reducing agent (517 mV). The increased copper extraction rate was directly related to the dissolution of manganese, these two elements being closely associated with black copper mineralization according to the initial SEM characterization of the samples.

![Figure 10. Copper extraction and solution potential behavior according to the leaching media. Tests with leaching columns at room temperature.](image)
Table 6 shows acid consumption for the mineral sample in the column tests with the addition of different Eh modifying agents. Acid consumption ranged from 10 to 13 kg/t, which is a characteristic of the Lomas Bayas process.

Table 6. Sulfuric acid consumption obtained in column tests with different agents expressed as kilograms of sulfuric acid per ton of treated ore (kg/t).

| Samples | Conventional | O₃ | FeSO₄ | Cu₂S | SO₂ |
|---------|--------------|----|-------|------|-----|
| LG      | 14.78        | 13.29 | 14.37 | 13.97 | 16.66 |
| HG      | 12.60        | 10.80 | 13.93 | 10.31 | 11.12 |

The results obtained showed that the solution potential played a key role in the copper extraction from black copper, within a range of 400 to 500 mV. In this research, the dissolution of black copper ore allowed the extraction of manganese and copper, using three reducing agents. Firstly, white metal (Cu₂S) is more likely to be used in an industrial operation due to its strong performance to decrease the solution potential. Furthermore, Cu₂S incorporates copper and sulfur (already existing into the system) to the leach solution as a reaction product, and copper can be recovered by the same process. The use of FeSO₄ as a reducing agent, has the operational disadvantages of increasing the Fe concentration in solution. Finally, the use of SO₂ is associated with the inconvenience of gas handling.

4. Conclusions

The solution potential played a key role in the black copper treatment as copper ore. For Eh lower than 500 mV, the manganese could be dissolved, exposing the copper to the acid allowing its dissolution.

In the bottle test, the reducing agents FeSO₄, Cu₂S, and SO₂ respectively, increased copper extraction from mineral with black copper by 4.7%, 18.9%, and 16.6% over the extraction rates with conventional acid leaching.

The reducing agents Cu₂S and SO₂ increased the copper extraction rate in column leaching by 10% to 20%. Extraction rates of 62% and 51%, respectively, were obtained with the LG sample, and 66% and 60%, respectively, with the HG sample.

Acid consumption in the column tests was low, between 10 and 14 kg/t. The low acid consumption rate is a characteristic of the Lomas Bayas process, which facilitates evaluation at an industrial scale.

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References

1. Fernández-Mort, A.; Riquelme, R.; Alonso-Zarza, A.M.; Campos, E.; Bissig, T.; Mpodozis, C.; Carretier, S.; Herrera, C.; Tapia, M.; Pizarro, H.; et al. A genetic model based on evapoconcentration for sediment-hosted exotic-Cu mineralization in arid environments: the case of the El Tesoro Central copper deposit, Atacama Desert, Chile. *Miner. Depos.* 2018, 53, 775–795.

2. Riquelme, R.; Tapia, M.; Campos, E.; Mpodozis, C. Supergene and exotic Cu mineralization occur during periods of landscape stability in the Centinela Mining District, Atacama Desert. *Basin Res.* 2017, 30, 395–425.

3. Munchmeyer, C. Los depósitos exóticos: productos de migración lateral asociada a sistemas porfiricos In Proceedings of the VII Congreso Geológico Chileno, Concepción, Chile, 17–21, October, 1994; Universidad de Concepción: Concepción, Chile, 1994, pp. 1602-1606.

4. Lillo, J.; Oyarzun, R.; Rivera, S. Giant versus small porphyry copper deposits of Cenozoic age in northern Chile: adakitic versus normal calc-alkaline magmatism. *Miner. Depos.* 2001, 36, 794–798.

5. Menzies, A.; Campos, E.; Hernández, V.; Sola, S.; Riquelme, R. Understanding Exotic-Cu Mineralisation Part II: Characterization of “ Black Copper ” ore (“ Cobre Negro ”). In Proceedings of the 13th SGA Biennial Meeting, Nancy, France, 24–27 August 2015.

6. Benavente, O.; Hernández, M.; Melo, E.; Núñez, D.; Quezada, V.; Zepeda, Y. Copper Dissolution from Black Copper Ore under Oxidizing and Reducing Conditions. *Metals* 2019, 9, 799.

7. Pérez, K.; Toro, N.; Campos, E.; González, J.; Jeldres, R.I.; Nazer, A.; Rodríguez, M.H. Extraction of Mn from black copper using iron oxides from tailings and Fe2+ as reducing agents in acid medium. *Metals* 2019, 9, 1112.

8. Chávez, W. Supergene Oxidation of Copper Deposits: Zoning and Distribution of Copper Oxide Minerals. *Soc. Econ. Geol.* 2000, 41, 10–21.

9. Pincheira, M.; Dagnini, A.; Kelm, U.; Helle, S. Copper Pitch Y Copper Wad: Contraste Entre Las Fases Presentes En Las Cabezas Y En Los Ríos En Pruebas De Mina sur, Chuquicamata. In Proceedings of the X Congreso Geológico Chileno, Concepción, Chile, 6–10 October 2003.

10. Madhuchhanda, M.; Devi, N.B.; Rath, P.C.; Rao, K.S.; Paramguru, R.K.; Devi, N.B.; Rath, P.C.; Rao, K.S.; Paramguru, R.K. Leaching of Manganese Nodule in Hydrochloric Acid in Presence of Sphalerite. *Can. Metall. Q.* 2013, 44, 43–43.

11. Saldaña, M.; Toro, N.; Castillo, J.; Hernández, P.; Trigueros, E.; Alessandro, N. Development of an Analytical Model for the Extraction of Manganese from Marine Nodules. *Metals* 2019, 9, 903.

12. Sparenberg, O. The Extractive Industries and Society Original article A historical perspective on deep-sea mining for manganese nodules, 1965–2019. *Extr. Ind. Soc.* 2019, 6, 842–854.

13. Toro, N.; Herrera, N.; Castillo, J.; Torres, C.M. Initial Investigation into the Leaching of Manganese from Room Temperature with the Use of Sulfuric Acid and the Addition of Foundry Slag—Part I. *Minerals* 2018, 8, 565.

14. Senanayake, G.A. mixed surface reaction kinetic model for the reductive leaching of manganese dioxide with acidic sulfur dioxide. *Hydrometallurgy* 2004, 73, 215–224.

15. Naik, P.K.; Sukla, L.B.; Das, S.C. Aqueous SO2 leaching studies on Nishikhal manganese ore through factorial experiment. *Hydrometallurgy* 2000, 54, 217–228.

16. Acharya, R.; Ghosh, M.K.; Anand, S.; Das, R.P. Leaching of metals from Indian ocean nodules in SO2-H2O-H2SO4-(NH4)2SO4 medium. *Hydrometallurgy* 1999, 53, 169–175.

17. Sun, D.; Xin, G.; Yao, L.; Yang, L.; Jiang, X.; Xin, G.; Yao, L. Manganese leaching in high concentration flue gas desulfurization process with semi-oxidized manganese ore. *Chinese J. Chem. Eng.* 2019, In Press.

18. Sinha, M.K.; Purcell, W. Reducing agents in the leaching of manganese ores: A comprehensive review. *Hydrometallurgy* 2019, 187, 168–186.

19. Jana, R.K.; Singh, D.D.N.; Roy, S.K. Alcohol-modified hydrochloric acid leaching of sea nodules. *Hydrometallurgy* 1995, 38, 289–298.

20. Kanungo, S.B. Rate process of the reduction leaching of manganese nodules in dilute HCl in presence of pyrite. Part II: leaching behavior of manganese. *Hydrometallurgy* 1999, 52, 331–347.

21. Bafghi, M.S.; Zakeri, A.; Ghasemi, Z.; Adeli, M. Reductive dissolution of manganese ore in sulfuric acid in the presence of iron metal. *Hydrometallurgy* 2008, 90, 207–212.
22. Stone, A. Microbial metabolites and the reductive dissolution of manganese oxides: Oxalate and pyruvate. *Geochim. Cosmochim. Acta* 1987, 51, 919–925.
23. Sahoo, R.N.; Naik, P.K.; Das, S.C. Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution. *Hydrometallurgy* 2001, 62, 157–163.
24. Hazek, M.N.E.; Lasheen, T.A.; Helal, A.S. Reductive leaching of manganese from low grade Sinai ore in HCl using H₂O₂ as reductant. *Hydrometallurgy* 2006, 84, 187–191.
25. Jiang, T.; Yang, Y.; Huang, Z.; Zhang, B.; Qiu, G. Leaching kinetics of pyrolusite from manganese-silver ores in the presence of hydrogen peroxide. *Hydrometallurgy* 2004, 72, 129–138.
26. Kojima, S.; OHMOTO, H. Hydrothermal synthesis of Wurtzite and Sphalerite at T = 350–250°C. *Min. Geol.* 1991, 41, 313–327.
27. Dhawan, N.; Safarzadeh, M.S.; Miller, J.D.; Moats, M.S.; Rajamani, R.K. Crushed ore agglomeration and its control for heap leach operations. *Miner. Eng.* 2013, 41, 53–70.
28. Quezada, V.; Velásquez, L.; Roca, A.; Benavente, O.; Melo, E.; Keith, B. Effect of curing time on the dissolution of a secondary copper sulphide ore using alternative water resources. *IOP Conf. Ser. Mater. Sci. Eng.* 2018, 427, 012030.
29. Velásquez-Yévenes, L.; Quezada-Reyes, V. Influence of seawater and discard brine on the dissolution of copper ore and copper concentrate. *Hydrometallurgy* 2018, 180, 88–95.
30. Zakeri, A.; Bafghi, M.S.; Shahriari, S.; Das, S.C.; Sahoo, P.K.; Rao, P.K. Dissolution kinetics of manganese dioxide ore in sulfuric acid in the presence of ferrous ion. *Iran. J. Mater. Sci. Eng.* 2007, 8, 22–27.