



Article Dissolution of Black Copper Oxides from a Leaching Residue

Víctor Quezada *^D, Oscar Benavente, Cristopher Beltrán, Danny Díaz, Evelyn Melo and Antonio García

Laboratorio de Investigación de Minerales Sulfurados, Departamento de Ingeniería Metalúrgica y Minas, Universidad Católica del Norte, Avenida Angamos 0610, 1270709 Antofagasta, Chile; obenaven@ucn.cl (O.B.); beltran.leon@live.com (C.B.); d.diaz533@live.cl (D.D.); emelo@ucn.cl (E.M.); agarcia@ucn.cl (A.G.) * Correspondence: vquezada@ucn.cl; Tel.: +56-552-651-024

Received: 2 July 2020; Accepted: 25 July 2020; Published: 28 July 2020



Abstract: This article presents the behavior of black copper minerals in reducing acid leaching using FeSO₄ as reducing agent. The original sample, which was a blend of green and black copper minerals, was treated first by an oxidizing acid leach using O_3 to dissolve the soluble phase (green copper oxides). The residue (mainly black copper) was evaluated by agitated leaching under three different solution potentials, with respect to the standard hydrogen electrode (SHE) (450, 500, and 600 mV (SHE)) at 25 °C. The original sample and the leach residue were characterized by scanning electron microscope (SEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The O₃ leach residue was 1.43% copper, with 50% of the insoluble phase associated with copper pitch, copper limonites, and unreacted chrysocolla. The results of leaching using FeSO₄ demonstrate that it is possible to obtain 90% copper extraction using a solution with a potential of 450 mV, while leaching at 600 mV resulted in 65% copper extraction. Acid consumption was 40 kg/t in the test at 450 mV, followed by 30 kg/t in the 500 mV test, and finally 25 kg/t in the 600 mV test, showing that reactivity decreases with increased solution potential. The results show that retreatment of a leaching residue is possible, considering the presence of copper pitch, copper limonites, and chrysocolla as the main copper contributing minerals. Modeling of copper extraction with nonlinear regression is proposed. The retreatment of residues resulting from conventional acid leaching can be an alternative to make use of the treatment capacity of hydrometallurgical plants.

Keywords: copper pitch; copper wad; manganese; leaching

1. Introduction

Chile produced 5.83 million metric tons of copper in 2018, making it the leading copper supplier in the world [1]. However, there are numerous challenges to copper production in Chile owing to the location of the deposits and their natural conditions—among them, energy costs, environmental impacts, and water shortages [2–4]. According to [1], one of the challenges is decreasing copper production by oxide mineral leaching, resulting in unused installed capacity, which is expected to reach 1.3 million tons by 2030. The decrease is mainly due to a change in mineralogy from oxides to secondary and primary sulfides, which in turn obliges a shift from hydrometallurgical plants to flotation plants. Consequently, there is a great opportunity to give continuity to hydrometallurgical facilities through new processes, especially for the treatment of low-grade copper sulfides [5] or non-soluble oxides like black copper ores [6].

Black copper ore is associated with exotic-type copper deposits [7] that originate from porphyry copper, which is generally found within approximately 8 km of the "parent deposit" [8]. Exotic deposits can be found in northern Chile near copper porphyry systems from the Paleogene period, such as

Huanquintipa (Collahuasi), Quebrada Ichuco (El Abra), Mina Sur (Chuquicamata), and Damiana (El Salvador) [9,10]. Black copper appears in "wad" or "pitch" form in compact earthy botryoidal masses, or filling fractures and cementing gravel [11]. When it appears alone in an earthy state, it is called wad, while when it is associated with chrysocolla, it is called pitch or black chrysocolla [12,13].

It is well known that black coppers leach with the use of reducing agents to dissolve the mineraloid matrix, mainly manganese [13,14]. As there are similarities in terms of chemical composition and refractory behavior to conventional leaching, marine nodules are used as a reference in treating black copper ore [15]. Although reducing conditions facilitate the dissolution of black copper, dissolution increase Mn²⁺ in the aqueous system. In conventional solvent extraction and electrowinning, Mn²⁺ can be transferred and subsequently raised to a highly oxidized state (IV) in electrowinning. This is associated with the deterioration of the phase separation characteristics of the organic and aqueous mixtures, resulting in lengthening the phase separation time, the formation of stable mixed phase, and organic loss [16,17].

Some reducing agents proposed for dissolving refractory minerals under conventional conditions are white metal (Cu_2S) [11], sulfur dioxide (SO_2) [6,11,18–22], ferrous sulfate (FeSO₄) [23–25], sponge iron [26], hydrogen peroxide [27,28], and even pyrite [29], several of which have been evaluated for industrial application as treatment alternatives. The SO₂ and Cu₂S present better performance, although the use of SO₂ is complex from the safety and environment point of view and Cu₂S availability is limited for small-scale mining; the reagent to be evaluated is FeSO₄, which is easy to access and manage. The purpose of this article is to evaluate the dissolution of black copper ore from leaching residue accumulate over time in a small mining operation in the north of Chile. The eventual use of these mineral resources opens the possibility of extending the operational life of hydrometallurgical plants facilities.

2. Materials and Methods

The residue from an oxidizing acid leaching (which initially contained copper oxide mineral, mainly chrysocolla) was used to evaluate the dissolution of black copper ore using a reducing leaching. The original copper oxide mineral and the residue of the acid oxidizing leaching (black copper) were characterized by SEM (JEOL USA Inc., Peabody, MA, USA). The oxidative leaching test employed O_3 at room temperature and 50 g/L of H_2SO_4 . The residue, containing black copper was dissolved using FeSO₄ following the considerations of [6,11]. The solution potential was controlled by adding O_3 or FeSO₄, depending on the value to be controlled. The acid consumption obtained in the leaching tests were measured. Copper, iron, and manganese extraction rates are reported.

2.1. Experimental Procedure

2.1.1. Sample Characterization

The oxide sample was collected near the La Famosa mine, located in the Third Region of Atacama, Chile. The sample was manually selected according to the criteria of [10,13], considering black streaks, massive habit, earthy luster, and an amorphous character. Feed samples were crushed and milled to a particle size 100% below 1.6 mm. The chemical composition was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) model Optima 2000 DV (PerkinElmer, Überlinge, Germany). For the determination of total and soluble copper, the solid sample has been digested in two different ways: soluble copper using a 2.5 g sample in a 50 mL solution with 5% sulfuric acid, and total copper using 1 g sample in 20% aqua regia solution and reaching the boiling point. The morphology was characterized by scanning electron microscopy (SEM) using JEOL 6360-LV equipment (JEOL USA Inc., Peabody, MA, USA) an energy-dispersive X-ray spectroscopy (EDS) microanalysis system (Zeiss Ultra Plus, Zeiss, Jena, Germany) and operated at 30 kV under high vacuum conditions. For SEM analysis, the mineral samples were treated with epoxy resin and metallized with a thin carbon layer to improve their conductivity.

2.1.2. Leaching Experiments

Four leaching tests were conducted. The first test involved acid leaching in an oxidizing media using O_3 in order to remove the oxide minerals while the other three tests were the black copper leaching obtained on the residue of the first test. The first test was performed with a particle size 100% below 1.6 mm at a temperature of 25 °C, a leaching time of 72 h, 50 g/L of H₂SO₄, 500 min⁻¹ of mechanical agitation, and 1000 g of sample added in 2 L of leaching solution using 3 L/min of O_3 (at 50%). The O_3 gas was added by injection to the leaching solution until obtaining an Eh of 1000 mV (SHE) using an ozonator model L21 (Pacific Ozone, Benicia, CA, USA) fed with oxygen through an oxygen generator system. The solution potential was controlled at 1000 mV throughout the test. The solid residue obtained in test 1 was divided into three homogeneous samples and leached to three different solution potentials under reducing conditions.

The three tests under reducing conditions were performed using 250 g of sample in 0.3 L of leaching solution at 25 °C, 40 g/L of FeSO₄, 50 g/L of H₂SO₄, with a leaching time of 8 h, and 500 min⁻¹ of mechanical agitation at three different solution potentials: 450, 500, and 600 mV (SHE). FeSO₄ or O₃ was used to control the solution potential as required. All potentials shown are quoted with respect to the standard hydrogen electrode (SHE).

The aliquots obtained at different leaching times were filtered (0.2 μ m) and Cu²⁺, Mn²⁺ and Fe concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) model Optima 2000 DV (PerkinElmer, Überlinge, Germany). Figure 1 shows a representation of the system.



Figure 1. Experimental setup.

3. Results

3.1. Sample Characterization

The sample had a high copper grade, with a high solubility of 92.3%, indicating the presence of highly soluble copper oxides like atacamite or chrysocolla. The non-soluble fraction is associated with the presence of black oxides. The high iron content and low manganese content indicate the presence of copper limonites [11]. The feed sample characterization can be observed in Table 1.

Table 1. Chemical composition of the copper oxide sample (initial sample).

Sample	(%) Cu (total)	(%) Cu _(soluble)	(%) Fe	(%) Mn
Feed sample	7.84	7.24	4.09	0.12

The feed sample contained copper oxide minerals like chrysocolla ($(Cu,Al)_4H_4(OH)_8Si_4O_{10}\cdot nH_2O$)) and dioptase ($Cu_6Si_6O_{18}\cdot 6H_2O$) (See Figure 2, particles 2 and 3). The distribution of the copper oxide minerals shows a clear relationship with the alteration, so chrysocolla and copper pitch prevail over atacamite in propylitized rock, while atacamite and copper wad predominate in argilized rock [13]. Thus, the presence of copper pitch, Cu-bearing manganese oxyhydrates is evidenced, which concurs with [30], who described the Cu-Mn-Si matrix as a black oxide mineral (Figure 2, particle 1). Gangue minerals associated with potassium feldspar were also identified (Figure 2, particle 4). Figure 3 shows the EDS information associated with the particles.



Figure 2. Scanning electron microscopy (SEM) image (×50) of the feed sample. Particles identified: copper pitch (1); chrysocolla (2); dioptase (3); and potassium feldspar (4).



Figure 3. EDS analysis associated with Figure 2. Particles identified: copper pitch (1); chrysocolla (2); dioptase (3); and potassium feldspar (4).

3.2. Leaching Test With O_3

The copper in the feed mineral was 83% dissolved at 72 h (Figure 4). Oxidizing conditions were favorable for the dissolution of oxide minerals such as chrysocolla and dioptase [6,11]. The main objective of the first leaching was to remove the soluble phases present in the mineral (chrysocolla and dioptase). It was assumed that the undissolved copper mineral was mainly associated with the

Cu-Mn-Si phases. According to [22,31], manganese oxides are relatively insoluble in a conventional acid medium. Under these conditions, the dissolution of soluble copper is nearly total (92.3%). Figure 5 shows that close to 80 kg of sulfuric acid was consumed per ton of mineral, which was due to the high grade of copper in the sample. The presence of k-feldspar, which [32] described as a low reactivity gangue mineral, was identified by SEM. Other low reactivity gangues like quartz, biotite, and muscovite were not found in this sample [33].

The residue from leaching with O_3 was characterized by SEM to identify non-soluble solid phases. A chemical analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) model Optima 2000 DV (PerkinElmer, Überlinge, Germany) showed the residue was copper-depleted and that there was an increase in the non-soluble phases (51% soluble), mainly associated with black copper ores or green copper oxide phases that did not react completely. Table 2 shows the chemical composition of the solid residue.



Figure 4. Copper extraction under oxidizing conditions using O_3 . Solution potential controlled at 1000 mV and 25 °C and using 50 g/L H₂SO₄.



Figure 5. Sulfuric acid consumption rate under oxidizing conditions using O_3 . Solution potential controlled at 1000 mV and 25 °C and using 50 g/L H₂SO₄.

Table 2. Chemical composition of the solid residue obtained from leaching with O₃.

Sample	(%) Cu _(total)	(%) Cu _(soluble)	(%) Fe	(%) Mn
Feed sample	1.23	0.63	2.91	0.085

In addition to the chemical characterization, the solid residue was analyzed by SEM. Image 6 shows the presence of copper pitch that does not react under oxidizing conditions [11] (Figure 6, particle 1). Unreacted chrysocolla is also observed, but in the context of copper depletion (Figure 6,

particle 2). The presence of chrysocolla explains the soluble phase that still evident in the residue. Figure 7 shows the EDS information relating to the particles.



Figure 6. Scanning electron microscopy (SEM) image (×100) of the residue sample. Particles identified: copper pitch (1); chrysocolla (2).



Figure 7. EDS analysis associated with Figure 6. Particles identified: copper pitch (1) and chrysocolla (2).

Figure 8 shows the presence of copper limonites (lim-Cu). This type of contributor, which is associated with black copper oxides, was also reported by [34]. These authors also noted the copper content of limonites is not constant, owing to inclusions and ion exchange, among other causes. Unleached chrysocolla is also identified (Figure 8, particle 2). The minerals identified in the residue are associated with black copper oxides, according to the classifications of [6,13,34]. Figure 9 shows the EDS information associated with the particles.

3.3. Black Copper Leaching Using FeSO₄

The residue obtained from O_3 with higher insoluble copper content was leached using FeSO₄ at three distinct solution potentials: 450, 500, and 600 mV (SHE). The highest copper dissolution of 90% was obtained at 450 mV after 8 h of leaching. The test with 500 mV yielded 77% copper extraction, while the test at 600 mV yielded 65%. The reducing conditions used in these tests (FeSO₄) demonstrate the possibility of leaching insoluble copper minerals. This is important considering the age of some deposits and the accumulation of residues, products of oxidizing acid leaching containing insoluble

copper. Figure 10 shows the results of the copper dissolution under reducing conditions. According to [11], the authors obtained similar results with reducing conditions (up to 432 mV (SHE)) that favored dissolving copper from black copper oxides. The maximum acid consumption obtained in the tests was 40 kg/t in the test at 450 mV, followed by 30 kg/t in the test at 500 mV, and finally 25 kg/t in the test at 600 mV (Figure 11). According to [11], an industrial mineral with a copper grade between 0.13 and 0.25% can consume between 10 and 14 kg/t, as obtained in column leaching tests using FeSO₄.



Figure 8. Scanning electron microscopy (SEM) image (×100) of the residue sample. Particles identified: limonite (1); chrysocolla (2).



Figure 9. EDS analysis associated with Figure 8. Particles identified: limonite (1) and chrysocolla (2).



Figure 10. Copper extraction under reducing conditions using FeSO₄ (40 g/L). Solution potential controlled at 450 mV (\blacklozenge); 500 mV (\blacktriangle) and 600 mV (\blacklozenge), at 25 °C and using 50 g/L H₂SO₄.



Figure 11. Sulfuric acid consumption under reducing conditions using FeSO₄ (40 g/L). Solution potential controlled at 450 mV (\blacklozenge); 500 mV (\blacktriangle); and 600 mV (\blacklozenge), at 25 °C and using 50 g/L H₂SO₄.

Figure 12 shows the summary of the solution associated with Cu, Mn, and Fe in the tests applying different solution potentials. The Cu dissolution (almost 90%) was highest at 450 mV. It is evident that breaking the manganese matrix associated with black oxides favors copper dissolution. The leaching proceeded on active sites present on the surface of MnO_2 particles and controlled by Fe^{2+} ion diffusion [22]. Similar results, favored by the minimal presence of FeSO4 and small amounts of sulfuric acid, have been reported by [25]. According to the characterization of the residue, the dissolution of chrysocolla-type species in copper is also favored. Iron dissolution rates varied little (between 10 and 12%) with variation in potentials. According to [35], copper limonite dissolution is limited in acid media.

Mineral residue retreatment can contribute to new sources of copper in mining operations like Spence, Lomas Bayas, Mina Sur, Centinela, and Chuquicamata that involve black copper oxides [6,30,36]. The search and development of new treatment alternatives for refractory copper, concentrate, or tailings is necessary for the utilization of the free capacity that hydro-metallurgical plants will have in the year 2030, according to [1].



Figure 12. Dissolution of Cu, Mn, and Fe under reducing conditions using FeSO₄ (40 g/L). Solution potential controlled at 450 mV; 500 mV; and 600 mV, at 25 °C and using 50 g/L H₂SO₄.

3.4. Modeling of Copper Extraction with Nonlinear Regression

For the modeling of copper dissolution, the support of statistical software was necessary, since the experimental curves show strongly nonlinear behavior. In this work, the Minitab 18 computational tool (Minitab LLC, State College, PA, USA) was used. After extensive model testing, the following (Equation (1)) was chosen, due to its better fit:

%, Cu dissolution = (theta0 + theta1 * Potential + theta2 * Potential²)
*
$$(1 - e^{(-beta1*time)} + beta2 * time^{0.5})$$
 (1)

with coefficients theta0, theta1, theta2, beta1, and beta2, and where solution potential is measured in mV (SHE), and time in hours. The Gauss—Newton algorithm was applied to the model for calculating its parameters or coefficients. Table 3 shows estimate, standard error, and confidence interval of each coefficient of the model. The resulting equation is exposed in Equation (2).

Parameter	Estimate	SE of Estimate	IC of 95%
theta0	328.506	35.0742	(255.666; 402.563)
theta1	-0.9431	0.1333	(-1.224; -0.666)
theta2	0.0008053	0.0001	(0.001; 0.001)
beta1	6.081	0.8765	(4.796; 10.951)
beta2	0.1115	0.0129	(0.085; 0.139)

Table 3. Parameter calculations associated with Cu dissolution model.

%, Cu dissolution = $(328.506 - 0.943076 * Potential + 0.0008053 * Potential^2) * (1 - e^{(-6.08079*time)} + 0.111461 * time^{0.5})$ (2)

With a confidence level of 95%, therefore, there is a 95% that the confidence interval contains the value of the parameter for the population. The parameter is statistically significant if the range excludes the value of the null hypothesis (that the term containing the parameter has no effect). For reference, in the case of linear regression, the null hypothesis value for each parameter is 0, so there is no effect. Table 4 exhibits a summary of statistical parameters of the model fit. Since the average of the measured values is 61.60%, the relative error is 2.55%, a low value; therefore, the mathematical model fits well with the experimental data, as seen in Figure 13.

Table 4. Statistical	l summary	of the	model	fit.
----------------------	-----------	--------	-------	------

Parameter	Value	Meaning
SSE	46.9365	Sum of the squared residuals.
DFE	19	Degrees of freedom for error, are equal to the sample size plus 1.
MSE	2.47034	Mean square of the error, is the variance around the fitted values. MSE = SSE/DFE
S	1.57173	Distance (or error) between the data values and the fitted values is measured in the units of the response. $S = MSE^{1/2}$

From the plot of residuals vs. fits, it is verified that the residuals are randomly distributed and have a limited variance. The points are located randomly on both sides of 0, but a point that is far from the others is observed on the left, which means that it is an influential point. The plot of residuals vs. order shows that the residuals are independent of each other. The residuals show no trends or patterns when displayed in chronological order. From the normal probability plot of the residuals, it is verified that the residuals are normally distributed. The normal probability plot of the residuals follows approximately a straight line. This is also manifested in the histogram of residuals (Figure 13).



Figure 14 shows that the modeled curves of the Cu dissolution reproduce well the behavior of the experimental ones, especially the abrupt change in slope in the first hour of the experiment.

Figure 13. Residual plots for copper dissolution.



Figure 14. Experimental and modeled copper dissolution vs. time.

4. Conclusions

The dissolution of insoluble copper like copper pitch, copper limonites, and chrysocolla can result in 90% copper extraction under reducing dissolution conditions (450 mV), while the copper extraction is only 65% under oxidizing leaching conditions (600 mV).

Gross acid consumption increased from 25 to 40 kg/t with a decrease in potential from 600 to 450 mV, as a consequence of copper dissolution associated with the disruption of the Cu-Mn-Si matrix.

Reducing acid leaching using FeSO₄ is an alternative for retreating solid residues containing black copper minerals (copper pitch and limonite) for the treatment and continuity of operation for hydrometallurgical plants.

With an error of 2.55%, Table 4 shows that the experimental results are in good agreement with the modeled equation (Equation (2)). Therefore, the mathematical model fits well with the experimental data.

Author Contributions: Conceptualization, V.Q. and O.B.; methodology, V.Q. and O.B.; validation, O.B.; formal analysis, E.M.; investigation, V.Q. and O.B.; resources, V.Q., O.B., A.G., C.B. and D.D.; data curation, V.Q., O.B., A.G. and E.M.; writing—original draft preparation, V.Q., O.B. and E.M.; writing—review and editing, V.Q. and O.B.; visualization, V.Q. and O.B.; supervision, V.Q., O.B., C.B. and D.D.; project administration, V.Q., O.B., C.B. and D.D.; funding acquisition, V.Q., O.B., C.B. and D.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors are grateful to the Scientific Equipment Unit (MAINI) at the Universidad Católica del Norte, Antofagasta, Chile, who supported this research by providing the SEM analysis of the samples. Special thanks to Marina Vargas Aleuy and Andrew Menzies.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Proyección de la Producción de Cobre en Chile 2019–2030. Available online: https://www.cochilco.cl/ Listado%20Temtico/Proyecci%C3%B3n%20de%20la%20producci%C3%B3n%20esperada%20de%20cobre% 202019%20-%202030%20Vfinal.pdf (accessed on 8 April 2020).
- Cruz, C.; Reyes, A.; Jeldres, R.I.; Cisternas, L.A.; Kraslawski, A. Using Partial Desalination Treatment to Improve the Recovery of Copper and Molybdenum Minerals in the Chilean Mining Industry. *Ind. Eng. Chem. Res.* 2019. [CrossRef]
- 3. Cánovas, M.; Valenzuela, J.; Romero, L.; González, P. Characterization of electroosmotic drainage: Application to mine tailings and solid residues from leaching. *J. Mater. Res. Technol.* **2020**, *9*, 2960–2968. [CrossRef]
- 4. Valenzuela-Elgueta, J.; Cánovas, M.; García, A.; Zárate, R. Electrocoalescence of emulsions in raffinate from the solvent extraction phase under AC electrical fields. *J. Mater. Res. Technol.* **2020**, *9*, 490–497. [CrossRef]
- 5. 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. [CrossRef]
- 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. [CrossRef]
- 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; pp. 3–6.
- Zambra, J.; Kojima, S.; Espinoza, S.; Definis, A. Angélica copper deposit: Exotic type mineralization in the tocopilla plutonic complex of the Coastal Cordillera, Northern Chile. *Resour. Geol.* 2007, 57, 427–434. [CrossRef]
- 9. 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; pp. 1602–1606.
- 10. Pinget, M.; Dold, B.; Fontboté, L. Exotic mineralization at Chuquicamata, Chile: Focus on the copper wad enigma. In Proceedings of the 10th Swiss Geoscience Meeting, Bern, Swiss, 16–17 November 2012; pp. 88–89.
- Benavente, O.; Hernández, M.C.; Melo, E.; Ardiles, L.; Quezada, V.; Zepeda, Y. Copper extraction from black copper ores through modification of the solution potential in the irrigation solution. *Metals* 2019, *9*, 1339. [CrossRef]
- 12. Chávez, W. Supergene Oxidation of Copper Deposits: Zoning and Distribution of Copper Oxide Minerals. *SEG Newsl. Soc. Econ. Geol.* **2000**, *41*, 9–21.
- 13. Pincheira, M.; Dagnini, A.; Kelm, U.; Helle, S. " Copper Pitch Y Copper Wad ": Contraste Entre Las Fases Presentes En Las Cabezas Y En Los Ripios En Pruebas De Mina sur, Chuquicamata. In Proceedings of the X Congreso Geológico Chileno, Concepción, Chile, 6–10 October 2003.
- 14. Mehta, K.D.; Das, C.; Pandey, B.D. Leaching of copper, nickel and cobalt from Indian Ocean manganese nodules by Aspergillus niger. *Hydrometallurgy* **2010**, *105*, 89–95. [CrossRef]
- 15. Jana, R.K.; Pandey, B.D. Premchand Ammoniacal leaching of roast reduced deep-sea manganese nodules. *Hydrometallurgy* **1999**, *53*, 45–56. [CrossRef]
- 16. Miller, G.M.; Readett, D.J.; Hutchinson, P. Experience in operating the Girilambone copper SX-EW plant in changing chemical environments. *Miner. Eng.* **1997**, *10*, 467–481. [CrossRef]
- 17. Cheng, C.Y.; Hughes, C.A.; Barnard, K.R.; Larcombe, K. Manganese in copper solvent extraction and electrowinning. *Hydrometallurgy* **2000**, *58*, 135–150. [CrossRef]

- 18. Senanayake, G. A mixed surface reaction kinetic model for the reductive leaching of manganese dioxide with acidic sulfur dioxide. *Hydrometallurgy* **2004**, *73*, 215–224. [CrossRef]
- 19. 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. [CrossRef]
- 20. 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. [CrossRef]
- 21. 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. *Chin. J. Chem. Eng.* **2019**. [CrossRef]
- 22. Sinha, M.K.; Purcell, W. Reducing agents in the leaching of manganese ores: A comprehensive review. *Hydrometallurgy* **2019**, *187*, 168–186. [CrossRef]
- 23. 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.
- 24. Villinski, J.E.; Saiers, J.E.; Conklin, M.H. The Effects of Reaction-Product Formation on the Reductive Dissolution of MnO₂ by Fe(II). *Environ. Sci. Technol.* **2003**, *37*, 5589–5596. [CrossRef]
- 25. Das, S.C.; Sahoo, P.K.; Rao, P.K. Extraction of manganese from low-grade manganese ores by FeSO₄ leaching. *Hydrometallurgy* **1982**, *8*, 35–47. [CrossRef]
- 26. 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. [CrossRef]
- 27. Jiang, T.; Yang, Y.; Huang, Z.; Qiu, G. Simultaneous leaching of manganese and silver from manganese-silver ores at room temperature. *Hydrometallurgy* **2003**, *69*, 177–186. [CrossRef]
- 28. 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. [CrossRef]
- Kholmogorov, A.G.; Zhyzhaev, A.M.; Kononov, U.S.; Moiseeva, G.A.; Pashkov, G.L. Production of manganese dioxide from manganese ores of some deposits of the Siberian region of Russia. *Hydrometallurgy* 2000, 56, 1–11. [CrossRef]
- 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. [CrossRef]
- 31. Han, K.; Fuerstenau, D. Acid leaching of ocean floor manganese at elevated temperature. *Int. J. Miner. Process.* **1975**, *2*, 163–171. [CrossRef]
- 32. Deshenthree Chetty Acid-Gangue Interactions in Heap Leach Operations: A Review of the Role of Mineralogy for Predicting. *Metals* **2018**, *8*, 47. [CrossRef]
- 33. Bai, X.; Wen, S.; Liu, J.; Lin, Y. Response surface methodology for optimization of copper leaching from refractory flotation tailings. *Minerals* **2018**, *8*, 165. [CrossRef]
- González, S.; Quintana, K.; Belmar, M.; Riquelme, R. Modelo Mineralógico de mena para Proyecto Óxidos Encuentro. In Proceedings of the XIV Congreso Geológico Chileno, La Serena, Chile, 4–8 October 2015; pp. 315–318.
- 35. Jansen, M.; Taylor, A. Overview of gangue mineralogy issues in oxide copper heap leaching. In Proceedings of the ALTA Conference, Perth, Australia, 19–24 May 2003; p. 32.
- Helle, S.; Kelm, U.; Barrientos, A.; Rivas, P.; Reghezza, A. Improvement of mineralogical and chemical characterization to predict the acid leaching of geometallurgical units from Mina Sur, Chuquicamata, Chile. *Miner. Eng.* 2005, *18*, 1334–1336. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).