

Article

Extraction of Mn from Black Copper Using Iron Oxides from Tailings and Fe^{2+} as Reducing Agents in Acid Medium

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Received: 13 September 2019; Accepted: 16 October 2019; Published: 18 October 2019



Abstract: Exotic type deposits include several species of minerals, such as atacamite, chrysocolla, copper pitch, and copper wad. Among these, copper pitch and copper wad have considerable concentrations of manganese. However, their non-crystalline and amorphous structure makes it challenging to recover the elements of interest (like Cu or Mn) by conventional hydrometallurgical methods. For this reason, black copper ores are generally not incorporated into the extraction circuits or left unprocessed, whether in stock, leach pads, or waste. Therefore, to dilute MnO_2 , the use of reducing agents is essential. In the present research, agitated leaching was performed to dissolve Mn of black copper in an acidic medium, comparing the use of ferrous ions and tailings as reducing agents. Two samples of black copper were studied, of high and low grade of Mn, respectively, the latter with a high content of clays. The effect on the reducing agent/black copper ratio and the concentration of sulfuric acid in the system were evaluated. Better results in removing Mn were achieved using the highest-grade black copper sample when working with ferrous ions at a ratio of Fe^{2+} /black copper of 2/1 and 1 mol/L of sulfuric acid. Besides, the low-grade sample induced a significant consumption of H_2SO_4 due to the high presence of gangue and clays.

Keywords: waste treatment; reducing agent; manganese

1. Introduction

Copper mining is Chile's most important economic activity, accounting for 10% of the gross national product (GNP) [1]. According to the latest figures from the Chilean Copper Commission, 5.83 million metric tons of copper were produced in 2018, making Chile the leading copper producer, accounting for 27.7% of global copper production. Experts from the Chilean Association of Geologists have stated that Chile has the largest copper deposits in the world [2], with a total copper reserve of 170 million metric tons [3].

Porphyry minerals in deposits like pyrite oxidize when submitted to geological agents. When pyrite reacts with water, it generates sulfuric acid, promoting the mobility of metals like copper that can be transported under certain potential and pH conditions, precipitating downstream and forming what are termed exotic deposits [4–8].

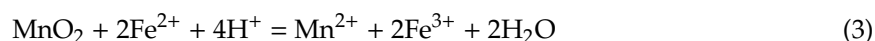
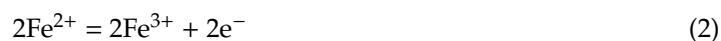
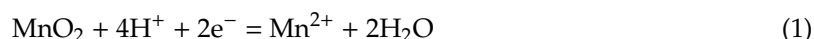
These deposits are composed of different copper containing phases such as chrysocolla, atacamite, copper pitch, and copper wad [6,9]. The latter two are defined as mineraloids because they crystallize amorphously [2]. They are also termed silicates rich in Si-Fe-Cu-Mn [10].

Some examples of exotic deposits in Chile are Mina Sur in Chuquicamata [11], Damiana in El Salvador [7], Huanquintipa in Collahuasi [12], and La Cascada, Lomas Bayas Spence, El Tesoro [2], and Angélica in Tocopilla [13]. The copper and manganese of this type of deposit are often associated with oxidized minerals, mainly chrysocolla, which, in turn, are associated with gangue that can negatively affect leaching [11]. Silicates and aluminosilicates, like mica and clay minerals, have the capacity to consume some of the acid generated by oxidization [14]. Clay minerals, like montmorillonite, kaolinite, and smectite, easily absorb acid [15]. Other minerals, like chlorites and biotite, also consume large amounts of acid over the long term [15]. Helle et al. [11] studied the effect of gangue and clay minerals on the leaching of copper oxides such as atacamite, chrysocolla, and malachite. The copper oxides were treated with a strong solution of sulfuric acid (265 g/L) in small columns at ambient temperature (18 to 21 °C), with the addition of synthetic rocks composed of 57% quartz, 1% phase mineral, and 42% reactive gangue. The authors concluded that copper retention and acid consumption were the result of the presence of smectite, mordenite gangue, kaolinite, illite, and quartz.

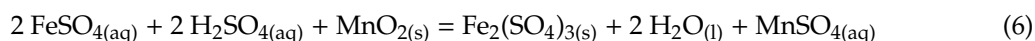
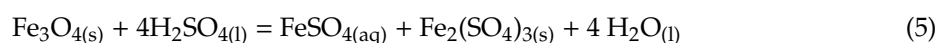
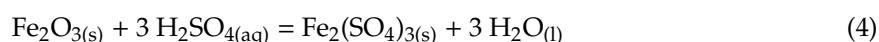
Researchers have indicated that it is not possible to recover copper associated with these silicates using conventional hydrometallurgical methods for oxidized copper because of their non-crystalline or amorphous structure [16]. However, recent studies on techniques for extracting manganese have found that silicates can be recovered by treating them in a similar manner to treatment for manganese, owing to the similarity in their metallurgical behavior [17].

It has been demonstrated that a reducing agent is required to extract Mn from MnO₂ in acid media [18,19]. Other studies have obtained good results dissolving MnO₂ with different reducing agents like H₂SO₃ [20], SO₂ [21], wastewater from producing molasses-based alcohol [22], and various iron-based reducing agents [20,23,24]. Iron, which is abundant and inexpensive, has proven to be a good alternative when working with MnO₂ in acid media.

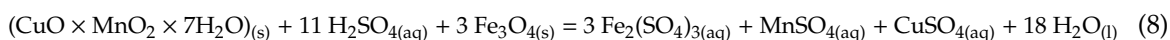
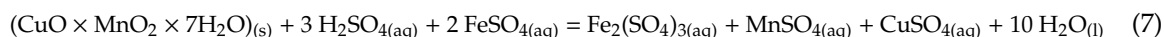
Zakeri et al. [25] obtained an Mn extraction rate of 90% in 20 min at ambient temperature with the addition of ferrous ions to the system, with an Fe²⁺/MnO₂ molar ratio of 3.0 and H₂SO₄/MnO₂ ratio of 2.0. They proposed the following series of reactions for MnO₂ dissolution:



Toro et al. [26] leached Mn nodules using tailings with high Fe₃O₄ contents (58.52%) from slag flotation for the recovery of Cu from the Alto Norte Foundry Plant and optimized the working parameters (Fe₂O₃/MnO₂ ratio and H₂SO₄ concentration). They found that for short periods of time (5 to 20 min), the optimal MnO₂/Fe₂O₃ ratio is 1/3, with H₂SO₄ concentration of 0.1 mol/L, giving Mn extraction rates of approximately 70%. The authors proposed the following reactions to dissolve MnO₂ with the addition of iron oxides:



The following reactions are proposed to dissolve manganese from black copper:



Equation (5) gives the reaction of magnetite with sulfuric acid forming ferrous sulfate, which is a good reducing agent for the leaching of MnO_2 . This is shown in Equation (6), where Mn^{4+} is reduced to Mn^{2+} . In Equation (7), the solution of manganese from black copper (copper wad) is proposed, using ferrous sulfate expressed in Equation (5). In general, Equation (8) represents the dissolution of manganese with iron oxide as a reducing agent, which demands high concentrations of sulfuric acid to first form FeSO_4 from Fe_3O_4 and then continues to dissolve manganese until a manganese sulfate solution is obtained.

In Chile, big copper mining poses new challenges and needs. It seeks to diversify the extractions of other elements (besides the Cu) in order to boost the export of commodities and raise employment. Black copper ores are resources that are generally not incorporated into the extraction circuits or left untreated, whether in stock, leach pads, or waste [27]. These exotic minerals have considerable amounts of Mn (approximately 29%), which represent a commercial appeal. Besides, according to the study conducted by Benavente et al. [27], by dissolving black copper ores in a reducing condition, the decrease in redox potential favors the dissolution of manganese. This would allow the subsequent extraction of the Cu present in black copper, given the potential commercial value of these “wastes”.

This work aimed to study the dissolution of MnO_2 from black copper in acid media comparing the use of iron and iron oxide tailings as reducing agents.

2. Methodology

2.1. Black Oxide Samples

Two samples of black copper, obtained from different mines in northern Chile, were used in this investigation. One sample, black copper sample-1 (BCS-1), was from a high-grade vein and was almost 100% pure, while the other, black copper sample-2 (BCS-2), was low-grade and taken from the mine dumpsite. The black oxides ores were ground in a porcelain mortar to sizes ranging from -173 to $+147 \mu\text{m}$. Chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Table 1 shows the chemical composition of the samples. A QEMSCAN analysis was applied, which is an electronic scanning microscope that was modified both in hardware and software. This performed the identification and automated quantification of ranges of elementary definitions that can be associated with inorganic solid phases (minerals, alloys, slags, etc.). To determine the mineralogical composition, the samples were mounted on briquettes and polished. The identification, mapping of 2-D distribution, and quantification of inorganic phases, was done by combining the emissions of retro-dispersed electrons (BSE) with a Zeiss EVO series, a Bruker AXS XFlash 4010 detector (Bruker, Billerica, MA, USA) and the iDiscover 5.3.2.501 software (FEI Company, Brisbane, Australia). The QEMSCAN analyses are based on the automated obtaining of EDS spectra (dispersed energy from X-rays) in hundreds of thousands or millions of collected analysis points, each in a time of milliseconds. The classification of mineralogical phases is done by classifying each EDS spectrum in a hierarchical and descending compositional list known as the “SIP List”. The BSE image is used to discriminate between resin and graphite in the sample, to specify entries in the SIP list, and to establish thresholds for acceptance or rejection of particles. As a result, pixelated, 2-D and false color images of a specimen or a representative subsample of particles are obtained. Each pixel retains its elementary and BSE brightness information, which allows subsequent offline data processing. Through software, customized filters are generated that allow the quantification of ore and gangue species, mineral release, associations between inorganic phases, and the classification of particles

according to criteria of shape, size, texture, etc. Figure 1 shows the chemical species to black oxides using QEMSCAN.

Table 1. Chemical composition of black oxide samples.

Sample	Mn (%)	Fe (%)
Black Copper Sample-1	22.01	7.92
Black Copper Sample-2	0.51	3.88

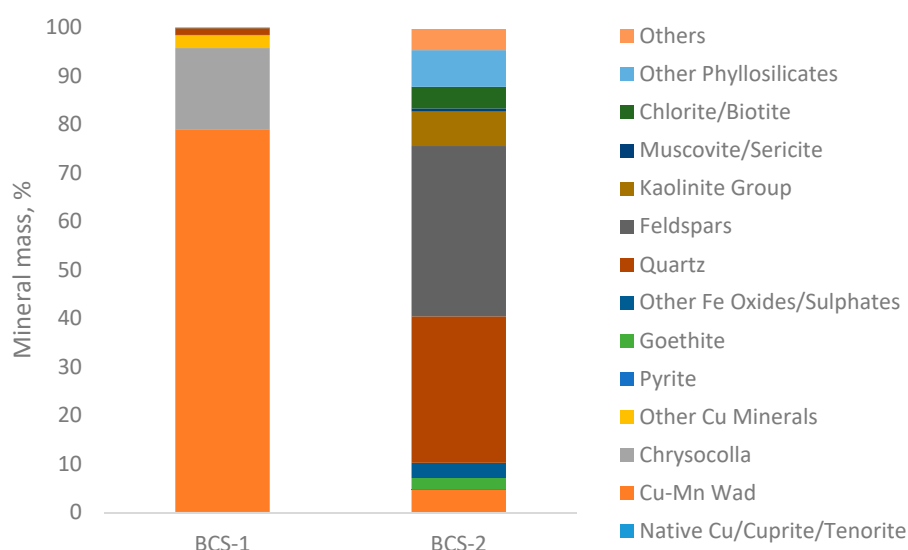


Figure 1. Detailed modal mineralogy.

Table 2 shows the mineralogical composition of the black copper samples. Copper wad refers to a subgroup of copper composed of manganese and copper hydroxides, as well as also traces of other elements such as Co, Ca, Fe, Al, Si, and Mg.

Table 2. The mineralogical composition of the black copper samples as determined by QEMSCAN.

Mineral (% Mass)	Black Copper Sample-1	Black Copper Sample-2
Native Cu/Cuprite/Tenorite	0.12	0.00
Cu-Mn Wad	78.90	4.64
Chrysocolla	16.72	0.03
Other Cu Minerals	2.69	0.03
Pyrite	0.00	0.01
Goethite	0.01	2.39
Other Fe Oxides/Sulphates	0.00	3.15
Quartz	1.41	30.20
Feldspars	0.02	35.11
Kaolinite Group	0.01	7.08
Muscovite/Sericite	0.01	0.67
Chlorite/Biotite	0.01	4.45
Montmorillonite	0.00	4.56
Others	0.09	7.35
Total	100	100

2.2. Ferrous Ions

The ferrous ions used for this investigation ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$) were WINKLER brand, with a molecular weight of 278.01 g/mol.

2.3. Iron Oxide Tailings

The iron oxide tailings used were from the Altonorte Smelting Plant. The particle sizes were in a range between -75 to $+53$ μm . The methods used to determine its chemical and mineralogical composition were the same as those used in black copper ores. Table 3 shows the minerals (and chemical formulas) from QEMSCAN analysis, noting that several iron-containing phases were present from which the Fe content was estimated at 41.9%. As the Fe was mainly in the form of magnetite, the most appropriate method of extraction was the same as that used by Toro et al. [26].

Table 3. Mineralogical composition of tailings, as determined by QEMSCAN.

Mineral	Amount % (w/w)
Chalcopyrite/Bornite ($\text{CuFeS}_2/\text{Cu}_5\text{FeS}_4$)	0.47
Tennantite/Tetrahedrite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}/\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$)	0.03
Other Cu Minerals	0.63
Cu–Fe Hydroxides	0.94
Pyrite (FeS_2)	0.12
Magnetite (Fe_3O_4)	58.52
Specular Hematite (Fe_2O_3)	0.89
Hematite (Fe_2O_3)	4.47
Ilmenite/Titanite/Rutile ($\text{FeTiO}_3/\text{CaTiSiO}_5/\text{TiO}_2$)	0.04
Siderite (FeCO_3)	0.22
Chlorite/Biotite ($\text{Mg}_3(\text{Si})_4\text{O}_{10}(\text{OH})_2(\text{Mg})_3(\text{OH})_6/\text{K}(\text{Mg})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$)	3.13
Other Phyllosilicates	11.61
Fayalite (Fe_2SiO_4)	4.59
Dicalcium Silicate (Ca_2SiO_4)	8.30
Kirschsteinite (CaFeSiO_4)	3.40
Forsterite (Mg_2SiO_4)	2.30
Barite (BaSO_4)	0.08
Zinc Oxide (ZnO)	0.02
Lead Oxide (PbO)	0.01
Sulfate (SO_4)	0.20
Others	0.03
Total	100.00

2.4. Reagent and Leaching Test

The sulfuric acid used for the leaching tests was grade P.A., with 95–97% purity, a density of 1.84 kg/L, and a molecular weight of 98.80 g/mol. The leaching tests were carried out in a 50 mL glass reactor with a 0.01 solid/liquid ratio. A total of 200 mg of black oxide ore was maintained in suspension with the use of a five-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. The tests were conducted at a room temperature of 25 °C, while variations were iron additives, particle size, and leaching time. The tests were performed in duplicate and measurements (or analyses) were carried out on 5 mL undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5 to 10%. The measurements of pH and oxidation-reduction potential (ORP) of the leach solutions were made using a pH-ORP meter (HANNA HI-4222 (HANNA instruments, Woonsocket, Rhode Island, USA)). The solution ORP was measured in a combination ORP electrode cell composed of a platinum working electrode and a saturated Ag/AgCl reference electrode.

2.5. The Effect of the Fe/MnO₂ Ratio

Other investigations have shown that variables of particle size and stirring speed do not have significant effects when working with a high Fe/MnO₂ ratio [26,28]. Given this result, we decided to work with the following parameters: Fe/MnO₂ ratios of 1/1, 2/1 and 3/1, a particle size range of -75 – $+53$ μm , a stirring speed of 600 rpm, 1 mol/L sulfuric acid, and room temperature (25 °C).

2.6. The Effect of the Acid Concentration on the System

The present research studied the effect of the sulfuric acid concentration on the system, working with H_2SO_4 concentrations of 0.5, 1, 2, and 3 mol/L under the following operating conditions: Reducing agent/black copper ratio of 1/2, particle size range of $-75 + 53 \mu\text{m}$, stirring speed of 600 rpm, and a temperature of 25 °C.

3. Results

3.1. The Effect of the $\text{Fe}^{2+}/\text{MnO}_2$ Ratio

Figure 2a,b show the results for the dissolution of two black copper samples using Fe^{2+} in acid media. As can be seen, better results were achieved with the sample BCS-1, which was due to the high presence of clay in sample BCS-2. It was observed that high Mn extraction rates can be achieved in short periods of time using $\text{MnO}_2/\text{Fe}^{2+}$ ratios of 1/2 or less, achieving dissolution rates of over 78% in 5 min with sample BCS-1, and 65% in 5 min with sample BCS-2. The results shown in Figure 2a are similar to the 90% recovery obtained by Zakeri et al. [25] in 20 min leaching MnO_2 from manganese nodules with an $\text{Fe}^{2+}/\text{MnO}_2$ ratio of 3, and an $\text{H}_2\text{SO}_4/\text{MnO}_2$ molar ratio of 2/1. A 1/1 $\text{Fe}^{2+}/\text{MnO}_2$ ratio resulted in a lower MnO_2 dissolution kinetics, with an extraction of 40% in 5 min with sample A and 31% in 5 min with sample B. In general, Mn dissolution rates were similar with a longer period (30 min). However, the dissolution kinetics were slower for the sample BCS-2.

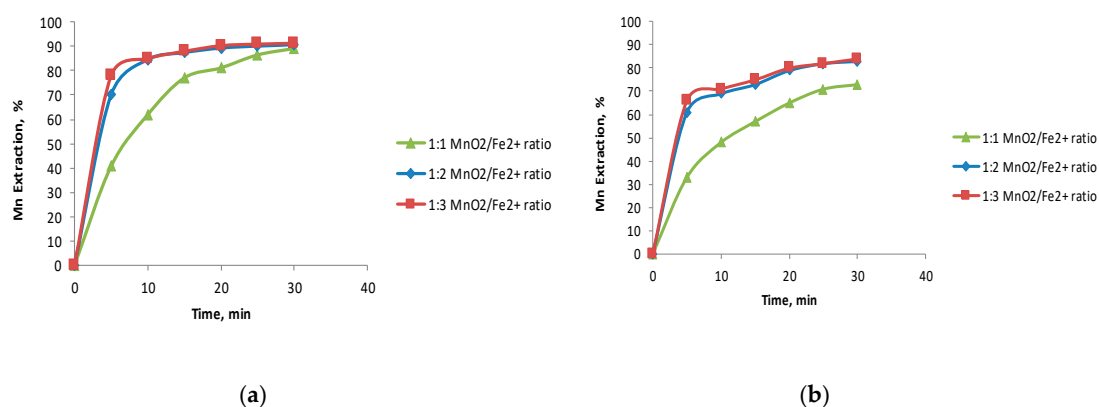


Figure 2. The effect of the Fe^{2+} concentration on MnO_2 dissolution (a) Black copper sample-1 (BSC-1); (b) Black copper sample-2 (BCS-2), 25 °C, particle size range of $-75+53 \mu\text{m}$, 1 mol/L H_2SO_4 .

3.2. The Effect of the $\text{Fe}_2\text{O}_3/\text{MnO}_2$ Ratio

Figure 3a,b show Mn dissolution with two black copper samples using Fe_2O_3 in acid media. As in earlier investigations by Toro et al. [26,28], working with an $\text{Fe}_2\text{O}_3/\text{MnO}_2$ ratio of 2/1 or higher significantly increased MnO_2 dissolution kinetics. There was little difference in the Mn extraction rates working with $\text{Fe}_2\text{O}_3/\text{MnO}_2$ ratios of either 2/1 or 3/1, while the Mn extraction fell significantly when the quantity of Fe_2O_3 was reduced. Potential and pH levels were respectively in the ranges of -0.5 to 1.3 V and -1.5 to 0.4 in all the tests in this study.

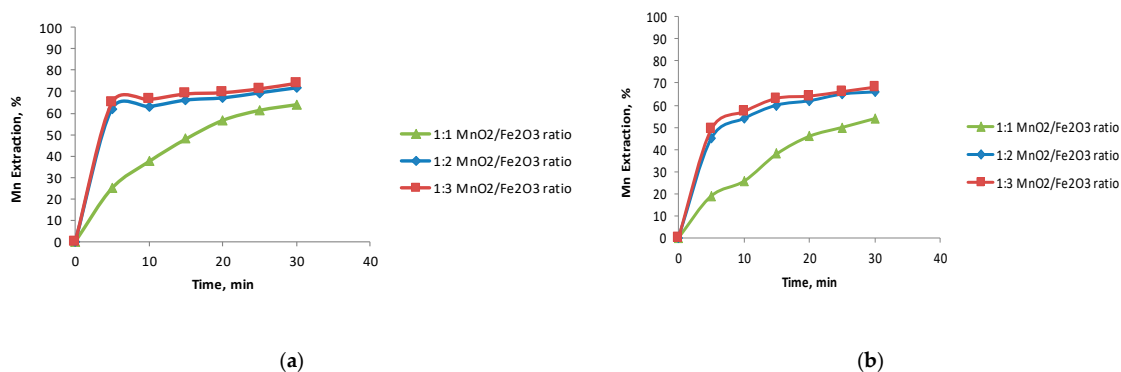


Figure 3. The effect of the iron oxide tailings concentration on MnO₂ dissolution (a) BSC-1; (b) BSC-2, 25 °C, particle size range of -75-+53 μm, 1 mol/L H₂SO₄.

3.3. The Effect of the H₂SO₄ Concentration

Figure 4 shows the effect of the acid concentration on dissolving Mn dissolution from the two black copper samples with the addition of high concentrations of iron oxides from tailings or ferrous ions. It can be seen from Figure 4a,c that for sample BCS-1, the sulfuric acid concentration was not significant in either case when working with high concentrations of the reducing agent. Differences in the effect of the acid concentration could only be noted with very low concentrations of iron oxide tailings (0.5 mol/L). The above concurs with findings of previous studies by Toro et al. [24,26] on extraction of MnO₂ from manganese nodules. The Mn extraction rate from the BCS-2 sample increased with higher concentrations of H₂SO₄, possibly owing to the high consumption of acid generated by the presence of mineral impurities in this sample, mainly montmorillonite, kaolinite, and chlorite. This is consistent with what was previously found by Helle and Kelm [29], where the leaching of exotic Cu minerals (atacamite, chrysocolla, and malachite) required higher acid consumption by incorporating reactive bargains into the system. This was driven by smectites, mordenite bargain, and the presence of kaolinite, illite, and quartz.

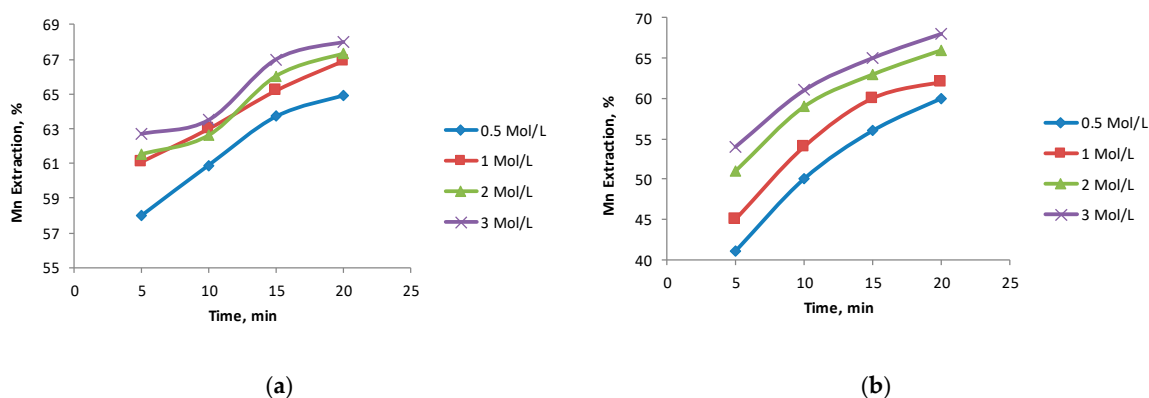


Figure 4. Cont.

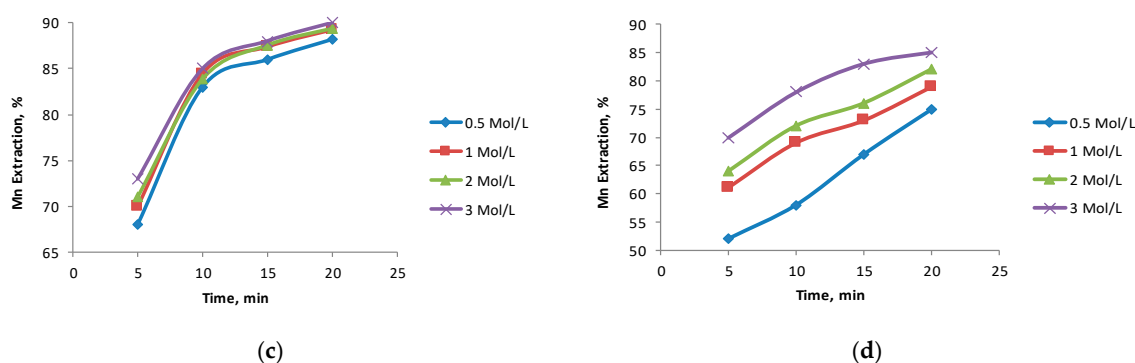


Figure 4. The effect of the sulfuric acid concentration on the system (a) BSCe-1; (b) BSC-2, $\text{MnO}_2/\text{Fe}_2\text{O}_3$ ratio of 1/2; (c) BSC-1; (d) BSC-2, $\text{MnO}_2/\text{Fe}^{2+}$ ratio of 1/2.

4. Conclusions

This study presents the results obtained for dissolving Mn from black copper using iron oxides (and specifically magnetite) from tailings and Fe^{2+} as reducing agents in acid media. Both reducing agents yielded good results with the two samples studied. Similar behavior was observed with the two samples in relation to Mn extraction, with the best results obtained in all the experiments with the BCS-1 sample. These encouraging results give new options to extract the Cu present in these exotic minerals, which are considered as industrial waste today. The main findings are the following:

- (1) The ferrous ions were a better reducing agent than iron oxides to dissolve MnO_2 in black copper.
- (2) The optimal reducing agent/black copper ratio was 2:1 for the studied reducing agents studied.
- (3) High concentrations of H_2SO_4 had a positive effect on the dissolution of Mn with the BCS-2 sample owing to the high content of clay (montmorillonite and kaolinite) and gangue (chlorite), which consume significant amounts of acid. The acid concentration was not significant with the BCS-1 sample.
- (4) The best results in this study were obtained working with the sample with fewer impurities (BCS-1), with an Fe^{2+} /black copper ratio of 2:1, and 1 mol/L of sulfuric acid.

Despite the good results obtained with BCS-1, BCS-2 was more like the mineralogy found at the industrial scale. It should be noted that although lower Mn extraction rates are obtained using tailings instead of ferrous ions, tailings can be a more attractive additive for leaching black copper because they are an industrial waste with no economic value. Given the above results, future investigations should aim to optimize operational parameters for leaching black copper minerals with high gangue content using industrial waste or wastewater as reducing agents, with the aim of taking this process to the industrial scale.

Author Contributions: K.P. contributed in research and wrote paper, N.T. and R.I.J. contributed in project administration, E.C. and A.N. contributed resources, J.G. contributed in review and editing and M.H.R. contributed in data curing.

Funding: This research received no external funding.

Acknowledgments: The authors are grateful for the contribution of the Scientific Equipment Unit- MAINI of the Universidad Católica del Norte for aiding in generating data by automated electronic microscopy QEMSCAN® and for facilitating the chemical analysis of the solutions. We are also grateful to the Altonorte Mining Company for supporting this research and providing slag for this study, and we thank to Marina Vargas Aleuy and María Barraza Bustos of the Universidad Católica del Norte for supporting the experimental tests. Also, we Conicyt Fondecyt 11,171,036 and Centro CRHIAM Project Conicyt/Fondap/15130015.

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

References

1. Servicio Nacional de Geología y Minería (SERNAGEOMIN). *Anuario de la Minería de Chile*; Servicio Nacional de Geología y Minería: Santiago, Chile, 2018; p. 274.
2. 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.
3. U.S. Geological Survey and U.S. Department of the Interior, Mineral. *Commodity Summaries*; U.S. Geological Survey: Reston, Virginia, 2018.
4. Ossandon, C.G.; Freraut, C.R.; Gustafson, L.B.; Lindsay, D.D.; Zentilli, M. Geology of the Chuquicamata Mine: A Progress Report. *Econ. Geol.* **2001**, *96*, 249–270. [[CrossRef](#)]
5. Mote, T.I.; Becker, T.A.; Renne, P.; Brimhall, G.H. Chronology of Exotic Mineralization at El Salvador, Chile, by ⁴⁰Ar/³⁹Ar Dating of Copper Wad and Supergene Alunite. *Econ. Geol.* **2001**, *96*, 351–366. [[CrossRef](#)]
6. Cuadra, C.P.; Rojas, S.G. Oxide mineralization at the Radomiro Tomic porphyry copper deposit, Northern Chile. *Econ. Geol.* **2001**, *96*, 387–400.
7. Mora, R.; Artal, J.; Brockway, H.; Martínez, E.; Muhr, R. El Tesoro exotic copper deposit, Antofagasta region, northern Chile. *Econ. Geol. Spec. Publ.* **2004**, *11*, 187–197.
8. 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, Switzerland, 16–17 November 2012; pp. 88–89.
9. Kojima, S.; Astudillo, J.; Rojo, J.; Tristá, D.; Hayashi, K.-I. Ore mineralogy, fluid inclusion, and stable isotopic characteristics of stratiform copper deposits in the coastal Cordillera of northern Chile. *Miner. Deposita* **2003**, *38*, 208–216. [[CrossRef](#)]
10. 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*; X Congreso Geológico Chileno: Concepción, Chile, 2003; p. 10.
11. Hellé, 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](#)]
12. García, C.; Garcés, J.P.; Rojas, C.; Zárate, G. Efecto sinérgico del tratamiento de mezcla de minerales conteniendo copper wad y sulfuros secundarios. In Proceedings of the IV International Copper Hydrometallurgy Workshop, Viña del Mar, Chile, 16–18 May 2007.
13. 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](#)]
14. Consejo Minero. *Guía Metodológica sobre Drenaje en la Industria Minera*; Subsecretaría de economía Consejo Nacional de Producción Limpia: Santiago, Chile, 2002.
15. Sequeira, R. A note on the consumption of acid through cation exchange with clay minerals in atmospheric precipitation. *Atmos. Environ. Part. A Gen. Top.* **1991**, *25*, 487–490. [[CrossRef](#)]
16. Helle, S.; Pincheira, M.; Jerez, O.; Kelm, U. Sequential extraction to predict the leaching potential of refractory. In Proceedings of the XV Balkan Mineral Processing Congress, Sozopol, Bulgaria, 12–16 June 2013; pp. 109–111.
17. Hernández, M.C.; Benavente, O.; Melo, E.; Núñez, D. Copper leach from black copper minerals. In Proceedings of the 6th International Seminar on Copper Hydrometallurgy, Viña del Mar, Chile, 6–8 July 2011; pp. 1–10.
18. Randhawa, N.S.; Hait, J.; Jana, R.K. A brief overview on manganese nodules processing signifying the detail in the Indian context highlighting the international scenario. *Hydrometallurgy* **2016**, *165*, 166–181. [[CrossRef](#)]
19. Saldaña, M.; Toro, N.; Castillo, J.; Hernández, P.; Trigueros, E.; Navarra, A. Development of an Analytical Model for the Extraction of Manganese from Marine Nodules. *Metals* **2019**, *9*, 903. [[CrossRef](#)]
20. Kanungo, S. Rate process of the reduction leaching of manganese nodules in dilute HCl in presence of pyrite. *Hydrometallurgy* **1999**, *52*, 313–330. [[CrossRef](#)]
21. Kanungo, S.; Das, R. Extraction of metals from manganese nodules of the Indian Ocean by leaching in aqueous solution of sulphur dioxide. *Hydrometallurgy* **1988**, *20*, 135–146. [[CrossRef](#)]

22. Su, H.; Liu, H.; Wang, F.; Lu, X.; Wen, Y.-X. Kinetics of Reductive Leaching of Low-grade Pyrolusite with Molasses Alcohol Wastewater in H₂SO₄. *Chin. J. Chem. Eng.* **2010**, *18*, 730–735. [[CrossRef](#)]
23. 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](#)]
24. Toro, N.; Saldaña, M.; Gálvez, E.; Cánovas, M.; Trigueros, E.; Castillo, J.; Hernández, P.C. Optimization of Parameters for the Dissolution of Mn from Manganese Nodules with the Use of Tailings in An Acid Medium. *Minerals* **2019**, *9*, 387. [[CrossRef](#)]
25. Zakeri, A.; Bafghi, M.; Shahriari, S. Dissolution Kinetics of Manganese Dioxide Ore in Sulfuric Acid in the Presence of Ferrous Ion. *Iran. J. Mater. Sci. Eng.* **2007**, *4*, 22–27.
26. Toro, N.; Saldaña, M.; Castillo, J.; Higuera, F.; Acosta, R. Leaching of Manganese from Marine Nodules at Room Temperature with the Use of Sulfuric Acid and the Addition of Tailings. *Minerals* **2019**, *9*, 289. [[CrossRef](#)]
27. Benavente, O.; Hernández, M.C.; Melo, E.; Núñez, D.; Quezada, V.; Zepeda, Y. Copper Dissolution from Black Copper Ore under Oxidizing and Reducing Conditions. *Metals* **2019**, *9*, 799. [[CrossRef](#)]
28. Toro, N.; Herrera, N.; Castillo, J.; Torres, C.M.; Sepúlveda, R. Initial Investigation into the Leaching of Manganese from Nodules at Room Temperature with the Use of Sulfuric Acid and the Addition of Foundry Slag—Part, I. *Minerals* **2018**, *8*, 565. [[CrossRef](#)]
29. Helle, S.; Kelm, U. Experimental leaching of atacamite, chrysocolla and malachite: Relationship between copper retention and cation exchange capacity. *Hydrometallurgy* **2005**, *78*, 180–186. [[CrossRef](#)]



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