

## Article

# Comparative Study of MnO<sub>2</sub> Dissolution from Black Copper Minerals and Manganese Nodules in an Acid Medium

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**Abstract:** The low grade of copper deposits and the use of the froth flotation process have caused excessive tailing production. In recent years, experts have looked for new alternative methods to improve this situation. Black copper minerals are abundant resources not exploited by large-scale copper mining and possess high Mn concentrations. On the other hand, manganese nodules are submarine resources and show high concentrations of Cu, Ni, Fe, and, mainly, Mn. However, both mineral resources are refractory to conventional leaching processes, and so a reducing agent is necessary for their treatment. We studied the use of tailings obtained from the flotation of foundry slags with a high content of Fe<sub>3</sub>O<sub>4</sub> as reducing agents at different MnO<sub>2</sub>/tailings ratios and H<sub>2</sub>SO<sub>4</sub> concentrations. Mn dissolution was compared in marine nodule and black copper minerals samples. It was found that higher Mn dissolutions are obtained from marine nodules, likely due to the acid consumption created by Cu dissolution from black copper minerals. The remnant elements in manganese nodules were leached under an oxidant condition.

**Keywords:** leaching; reducing agent; MnO<sub>2</sub>

## 1. Overview

Due to the decrease in copper grades in the earth's crust, mining countries such as Chile have been forced to change their production systems, which were mainly based on copper sulfides treated by froth flotation methods [1–3]. New alternatives are sought, such as the extraction of other elements such as copper ore byproducts (black copper minerals), waste generated by the industry, and even the exploitation of sea resources (manganese nodules), which has become a promising solution [4,5].

Nowadays, leaching and flotation are the most commonly used processes for extracting copper in Chile. Nevertheless, flotation processes raise environmental concerns due to the volume of tailings they produce and the acid drainage created by pyrite oxidation in tailing tanks, causing heavy element mobilization in the environment [6]. Therefore, momentum must be built to overcome the impasse facing the growth capability of the mining industry [7].

Leaching is an adequate method to treat low- and medium-grade ores at an industrial scale. Heap leaching has typically been used in mining with promising results [7,8]. In the past years, agitation leaching (reactors) has been added to industrial processes to tackle the new demands created by more refractory minerals and the appearance of impurities, which are hard to eliminate through conventional processes.

Several Chilean sectors have excellent potential for submarine mining [9,10]:

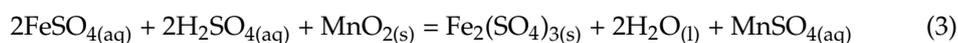
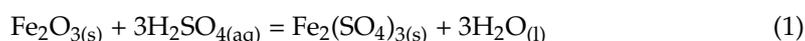
- (i) Marine phosphorites are abundant in the Caldera Basin, Bahia Inglesa, and Mejillones Peninsula.
- (ii) Massive submarine sulfide deposits are found in the Eastern Cordillera, and north and south of Easter Island.
- (iii) Manganese nodules are found around Robinson Crusoe Island and the mouth of the Loa River.
- (iv) Ferromanganese crusts are in the volcanic belt (Salas y Gomez, San Felix, and San Ambrosio Islands).

Of the above resources, manganese nodules are attractive to the industry because of the average Mn content (24%) [11], the large amounts of metals they contain (principally cobalt, copper, nickel, and iron), and the small concentrations of tellurium, titanium, platinum, and rare earth elements [12,13].

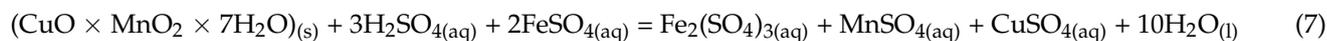
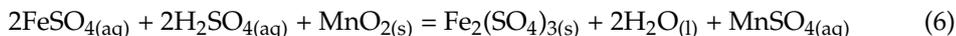
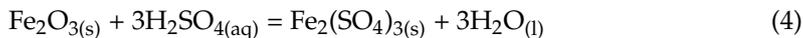
Black copper minerals are considered waste by large-scale copper mining and thus are not added to heap leaching. These are found in deposits known as “exotic copper deposits”, created by the interaction with geological agents, which oxidizes porphyry minerals such as pyrite (Py) [14–16]. When the latter reacts with water, it creates sulfuric acid, producing metals such as copper. Under certain conditions, these metals can be transported downstream, creating deposits [17–19]. Black copper minerals, also known as Si-Fe-Cu-Mn-rich silicates, have a complex structure that is neither crystalline nor amorphous [20]. Commercially important, they contain considerable amounts of manganese and copper [19]. Minerals with high MnO<sub>2</sub> contents (such as the ones above) have proven to be refractory to conventional leaching processes. Thus, to dissolve marine nodules it is necessary to work at low redox potential values [3,20,21]. Bafghi et al. [21] used sponge iron in a manganese nodule study. They evaluated different MnO<sub>2</sub>/Fe ratios and H<sub>2</sub>SO<sub>4</sub> particle sizes and concentrations. They found that the Fe concentration in the system was the most critical variable in fast Mn dissolution kinetics.

Toro et al. [22] evaluated the use of tailings obtained from smelting slag by flotation and with a high content of magnetite. The authors found that tailings are a good source when working with high concentrations of a reducing agent (Fe<sub>3</sub>O<sub>4</sub>/MnO<sub>2</sub> at 3/1). Saldaña et al. [23] created an analytical model for evaluating several variables key to the dissolution of manganese nodules, using Fe<sub>3</sub>O<sub>4</sub> as a reducing agent. The authors found that when an Fe<sub>3</sub>O<sub>4</sub>/MnO<sub>2</sub> ratio of 2/1 or higher is used, other variables (H<sub>2</sub>SO<sub>4</sub> concentration, particle size, agitation speed, leaching time) are irrelevant when obtaining Mn dissolutions of around 80%. There are few studies on black copper minerals, and recent studies report Cu and Mn recovery when Fe-reducing agents are added [3,20,24]. Benavente et al. [24] added ferrous ions to acid in order to reduce leaching of black copper minerals and found that the dissolution of MnO<sub>2</sub> immediately promoted Cu dissolution in black copper minerals. Pérez et al. [20] proved that the Fe<sub>3</sub>O<sub>4</sub> in tailings can be an efficient reducing agent of MnO<sub>2</sub> in black copper minerals when working with high concentrations, but showed lower dissolution kinetics regarding ferrous ions.

To dissolve manganese nodules using tailings, the following reactions are proposed:



To dissolve black copper minerals using tailings, the following series of reactions is proposed:



There are a few studies on black copper minerals leaching. Most of them claim that dissolution behaviors of Mn are similar to those of other minerals with high MnO<sub>2</sub> concentrations, such as marine nodules. However, no studies have proven such a statement. Despite the fact that Mn is abundant in the earth's crust, high-grade deposits are increasingly scarce. For example, in Chile all mining companies that exploit manganese are in the process of being closed, due to the drop in mineral grades. On the other hand, the deposits on the seabed have the highest concentrations of Mn on the planet and have two main advantages: (i) the minerals are concentrated in small areas, and (ii) marine nodule mining is two-dimensional, while land-based mining is three-dimensional, which generates more pollution [10]. Nonetheless, it is important to continue researching tailings reuse in metallurgical processes to provide a commercial value to this environmental liability. Currently, 151 tons of tailings are produced for every ton of copper generated by flotation processes. In addition, the tailings produced by the flotation of foundry slags are carried to tailings dams and do not represent a commercial value in the industry.

A comparative study was made between the acid-reducing leaching of Mn between black copper minerals and marine nodules in the present investigation. It evaluates tailings as a reducing agent at different MnO<sub>2</sub>/tailings ratios and uses H<sub>2</sub>SO<sub>4</sub> concentrations to identify the difference between MnO<sub>2</sub> dissolution speeds. For this, we worked under the same operational conditions to discover the difference between the dissolution rates of MnO<sub>2</sub> in both mineral resources.

## 2. Materials and Methods

### 2.1. Manganese Nodule

The marine nodules used in this research were collected on the Blake Plateau, Atlantic Ocean, in the 1970s. The sample was ground using a porcelain mortar and classified using mesh until reaching a grained fraction of (−140)–(+100) μm. It was then chemically analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Bruker, Billerica, MA, USA) at the Applied Geochemistry Laboratory, Geological Sciences Department, Universidad Católica del Norte in Chile. Its chemical composition was 0.12% Cu, 0.29% Co, and 15.96% Mn. The mineralogical analysis is shown in Table 1. Micro X-ray fluorescence spectrometry (Micro-XRF, Fremont, CA, USA) is a method used for the elemental analysis of non-homogeneous or irregular samples, small samples, and inclusions. The sample material was analyzed in a Bruker® M4-Tornado μ-FRX table (Fremont, CA, USA). This spectrometer includes an X-ray tube (Rh-anode), and the system contains polycapillary X-ray optics that focus the tube radiation on small areas, reaching 20 μm spots for Mo K. The elementary maps created with the built-in software ESPRIT of M4 Tornado™ ((FEI Company, Brisbane, Australia)) indicate that nodules contained fragments of preexisting nodules, forming the nucleus and concentric layers precipitating around the nucleus in later stages.

**Table 1.** Mineralogical analysis of the manganese nodule.

Component	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
Mass (%)	3.54	3.69	2.97	7.20	1.17	0.33	22.48	1.07	25.24	26.02

## 2.2. Black Copper Minerals Sample

In this research, we worked with the same mineral sample (high grade, nearly 100% pure) used in the study of Torres et al. [3] from a mining company in the north of Chile. Black oxide minerals were ground in a porcelain mortar until reaching sizes of (−173)–(+147)  $\mu\text{m}$ . The chemical composition of the samples was assessed by ICP-AES, as shown in Table 2. A QEMSCAN analysis using a modified (hardware and software) scanning electron microscope identified and automatically quantified ranges of elemental definitions that can be linked to inorganic solid phases (minerals, alloys, slags, and others). The samples were mounted on briquettes and polished to identify the mineralogical composition. The identification, 2-D distribution mapping, and quantification of inorganic phases were carried out, combining the backscattered electron (BSE) emissions with a Zeiss EVO, a Bruker AXS XFlash 4010 detector ((Bruker, Billerica, MA, USA), and iDiscover 5.3.2.501 software ((FEI Company, Brisbane, Australia)) (see Table 3).

**Table 2.** Chemical analysis of the mineral.

Mn (%)	Cu (%)
22.01	40.24

**Table 3.** Mineralogical composition of the black copper mineral.

Mineral (% Mass)	Black Copper Minerals
Native Cu/Cuprite/Tenorite	0.12
Copper Wad	78.90
Chrysocolla	16.72
Other Cu Minerals	2.69
Goethite	0.01
Quartz	1.41
Feldspars	0.02
Kaolinite Group	0.01
Muscovite/Sericite	0.01
Chlorite/Biotite	0.01
Others	0.09
Total	100

## 2.3. Tailings

The tailings used in this research were obtained by Cu slag flotation in a copper smelting plant. The methods used to assess their chemical and mineralogical composition were the same as those used with the marine nodule. Table 4 shows the detailed mineralogical composition of the tailings used.

## 2.4. Leaching Test

The leaching tests were carried out in a 200 mL glass reactor at 0.1 solid to liquid ratio (100 mL of acid solution). A total of 10 g of the mineral (black copper minerals/manganese nodule) was kept under agitation and suspension using a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at 600 rpm and a particle size of (−75)–(+53)  $\mu\text{m}$ . The temperature was controlled using an oil-heated circulator (Julabo, St. Louis, MO, USA). The temperature range tested in the experiments was 25 °C. All tests were performed in duplicate, and analyses were carried out using 5 mL undiluted samples and ASS with a  $\leq 5\%$  variation quotient and 5–10% relative difference. The pH and oxidation–reduction potential were measurements of the leaching solutions and were carried out in a pH-ORP meter (HANNA HI-4222, St. Louis, MO, USA). The ORP solution was measured using an ORP electrode cell composed of a platinum-employed electrode and a saturated Ag/AgCl reference electrode.

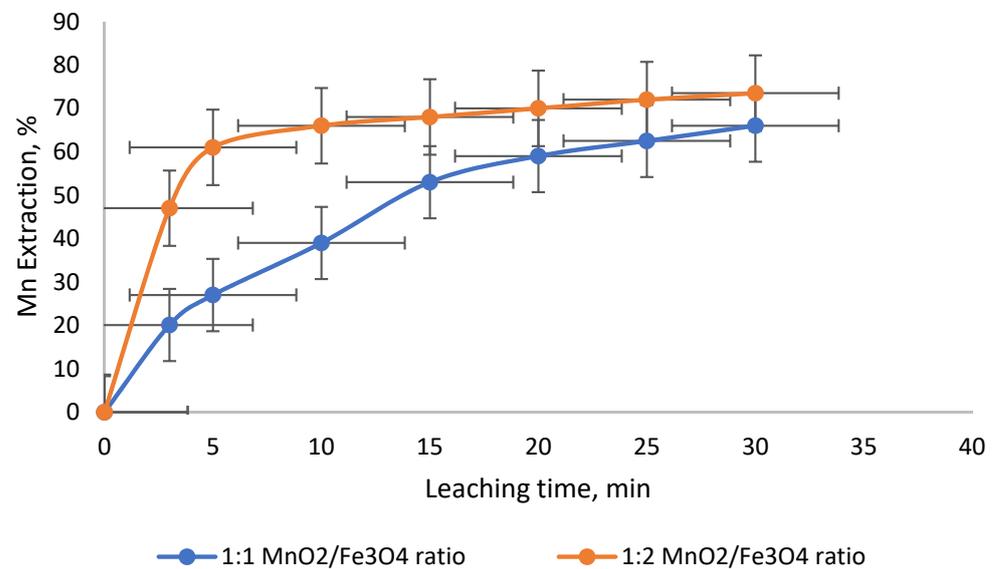
**Table 4.** Mineralogical composition of tailings assessed by QEMSCAN.

Mineral	Amount % w/w
Chalcopyrite/Bornite	0.47
Tennantite/Tetrahedrite	0.03
Other Cu Minerals	0.63
Cu-Fe Hydroxides	0.94
Pyrite	0.12
Magnetite	58.52
Specular Hematite	0.89
Hematite	4.47
Ilmenite/Titanite/Rutile	0.04
Siderite	0.22
Chlorite/Biotite	3.13
Other Phyllosilicates	11.61
Others	18.90
Total	100.00

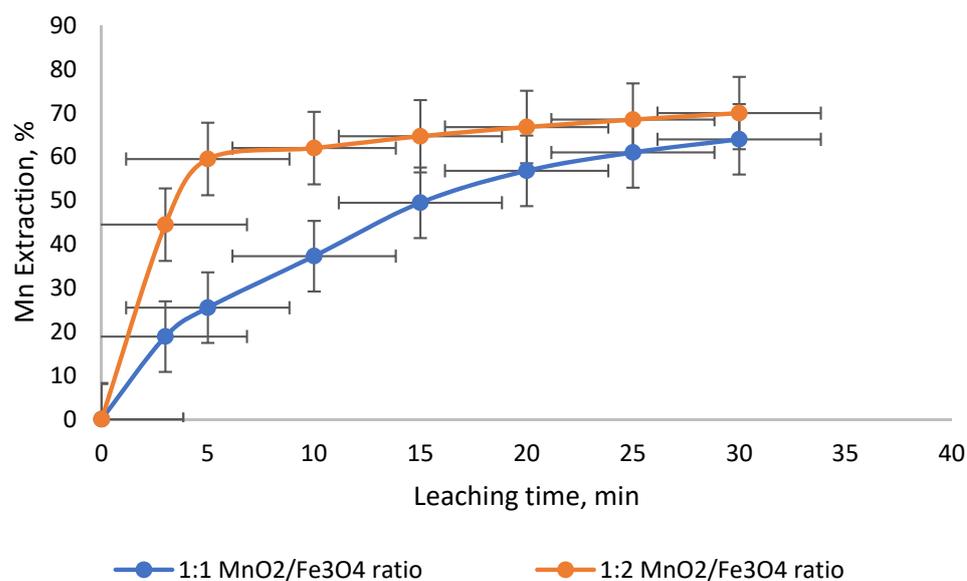
### 3. Results

#### 3.1. Reducing Agent Concentration in the System

Figures 1 and 2 show the same behavior over time for the  $\text{MnO}_2$  dissolution. In both cases, fast dissolution kinetics were obtained at high reducing agent/ $\text{MnO}_2$  ratios, reaching extractions of above 60% in 5 min. In contrast, lower concentrations of  $\text{Fe}_3\text{O}_4$  in the system led to a slower Mn dissolution, although similar extractions were obtained at longer times (30 min). This agrees with the findings of Bafghi et al. [21], which indicate that times of Mn dissolution from marine nodules can be significantly shortened by using twice the concentration of reducing agent as the amount of  $\text{MnO}_2$  in the system. The authors obtained extractions above 90% Mn in 20 min, working with sponge iron at an iron/ $\text{MnO}_2$  ratio of 1/1 and a molar concentration of acid to  $\text{MnO}_2$  of 2.



**Figure 1.** Manganese dissolution from marine nodule at different ratios of  $\text{MnO}_2/\text{Fe}_3\text{O}_4$  and 0.1 mol/L  $\text{H}_2\text{SO}_4$ .



**Figure 2.** Manganese dissolution from black copper minerals at different ratios of  $\text{MnO}_2/\text{Fe}_3\text{O}_4$  and 0.1 mol/L  $\text{H}_2\text{SO}_4$ .

In general, slightly superior extractions were obtained when dissolving Mn from marine nodules regarding black copper minerals. Both tend toward passivation at high concentrations of reducing agents, likely due to the tailings used. Tailings were reactive to acid leaching because they were previously treated in flotation processes and exposed to other chemical reagents [22,23]. They were obtained from smelting slag, which has an amorphous vitreous structure that could encapsulate  $\text{Fe}_3\text{O}_4$  and prevent contact with  $\text{MnO}_2$ .

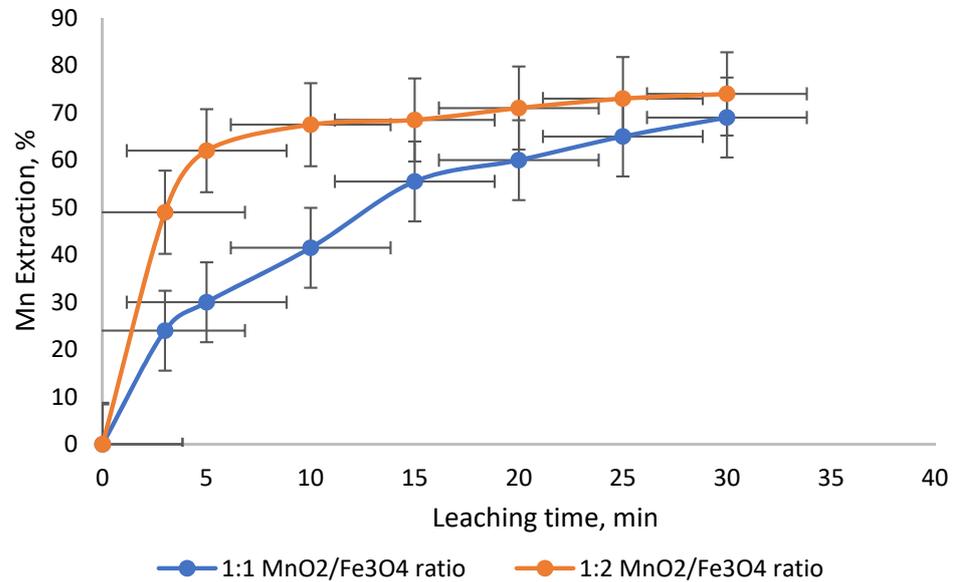
### 3.2. Effect of Acid Concentration in the System

The results shown in Figures 3 and 4 are similar for Mn dissolution from marine nodules and black copper minerals when working with high concentrations of  $\text{H}_2\text{SO}_4$ . Previous studies have proven that the concentration of  $\text{H}_2\text{SO}_4$  does not significantly affect  $\text{MnO}_2$  dissolutions in acid-reducing leaching [21,25]. However, in previous results (Figures 1 and 2), there was an appreciable difference in Mn extractions between the two minerals studied. This is likely due to the higher consumption of protons from acid when dissolving the Cu present in black copper minerals. The amorphous structure of black copper minerals prevents copper dissolution through conventional methods; this is resolved when the  $\text{MnO}_2$  present is dissolved [26]. Therefore, better results in Mn dissolution from black copper minerals are obtained when working with high acid concentrations.

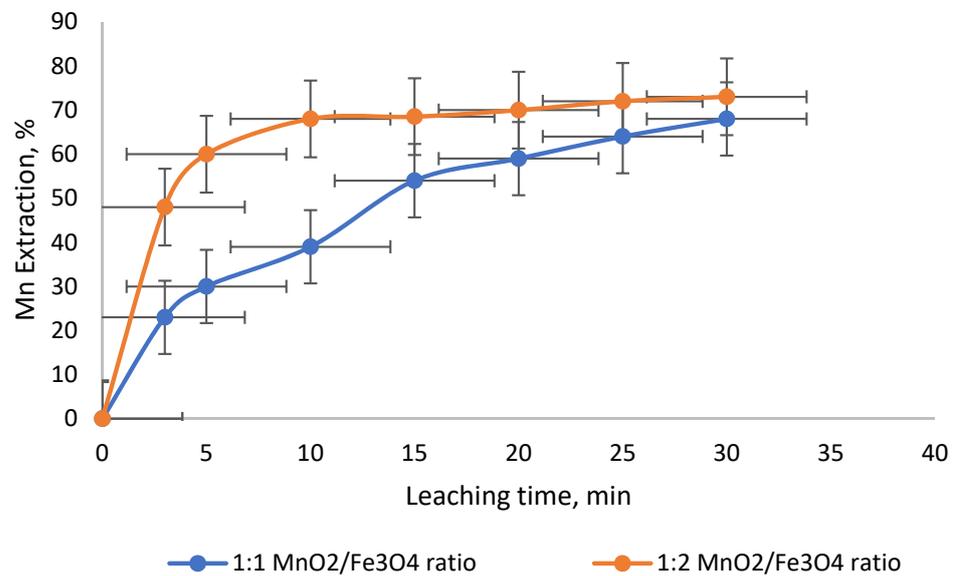
Figure 5 shows the potential and pH values during the dissolution of manganese nodules and black copper minerals when working at a concentration of 1 mol/L sulfuric acid and changing the ratios of  $\text{MnO}_2/\text{Fe}_3\text{O}_4$  (Figures 3 and 4). According to Senanayake [27], potential and pH values must be between  $-0.4$  and  $1.4$  V and  $-2$  and  $0.1$  in an acid-reducing dissolution of  $\text{MnO}_2$ , using Fe-reducing agents [28]. This is consistent with the results presented in Figure 5. Komnitsas et al. [29] indicate that when working in these ranges and keeping a low potential in an acid medium, Mn ions remain in the solution. This prevents their precipitation by oxidation–reduction reactions due to the presence of ferric and ferrous ions (for example,  $\text{MnO}_2$  or other minerals such as  $\text{CuFeO}_2$ ).

It is evident that high concentrations of a reducing agent in the system (1:2  $\text{MnO}_2/\text{Fe}_3\text{O}_4$ ) allows better dissolution kinetics of Mn from  $\text{MnO}_2$  for both minerals, compared to a lower ratio of reducing agent (1:1  $\text{MnO}_2/\text{Fe}_2\text{O}_3$ ). This is observed in Figures 1–4, where Mn extractions close to 70% are achieved in a time of 15 min for ratios of 1:2, while ratios of 1:1 double the time taken to extract 70%. By having a higher concentration of magnetite, a more significant amount of ferrous sulfate is observed in a short time (see Figure 5). For both cases, the Mn extraction curves show an asymptotic behavior, although at different

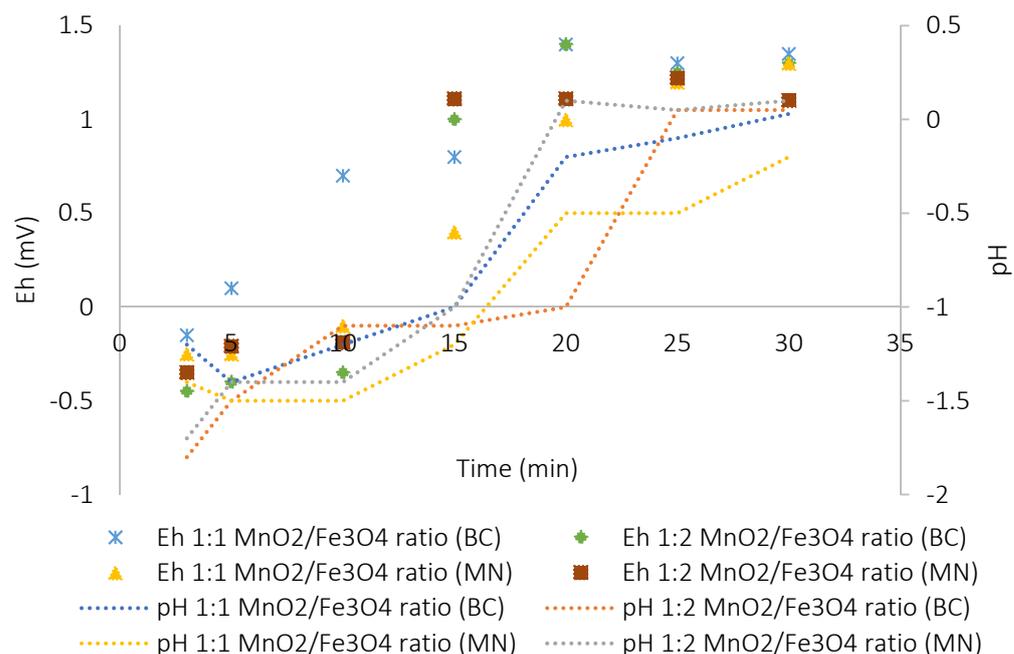
times (15 and 30 min). This may be explained by the vitreous structure of the tailings used, which prevented contact between  $\text{MnO}_2$  and ferrous sulfate, making the concentration of the reducing agent at a longer amount of time irrelevant.



**Figure 3.** Manganese dissolution from marine nodule at different ratios of  $\text{MnO}_2/\text{Fe}_3\text{O}_4$  and 1 mol/L  $\text{H}_2\text{SO}_4$ .



**Figure 4.** Manganese dissolution from black copper minerals at different ratios of  $\text{MnO}_2/\text{Fe}_3\text{O}_4$  and 1 mol/L  $\text{H}_2\text{SO}_4$ .



**Figure 5.** Effect of potential and pH in solution at different ratios of  $\text{MnO}_2/\text{Fe}_3\text{O}_4$ .

#### 4. Conclusions

This study presents comparative Mn extractions from two different raw materials (marine nodules and black copper minerals) by acidic leaching using tailings as the reducing agent. Similar behaviors were observed in both minerals while working under the same conditions, both in extraction rates and dissolution speed. The main findings of this work are:

1. In general, greater Mn dissolutions are obtained from marine nodules.
2. Tailings obtained from smelting slag by flotation show positive results in leaching at high concentrations and short periods (20 min). However, they tend toward passivation likely due to their vitreous structure.
3. Black copper minerals have lower dissolutions in Mn than in marine nodules. This is because of the consumption of protons from the acid when dissolving Cu, while other elements of the nodules dissolve in oxidizing conditions.
4. The best operational condition for dissolving  $\text{MnO}_2$  from both minerals is to work at a high concentration of reducing agent (1:2  $\text{MnO}_2/\text{Fe}_3\text{O}_4$ ), low concentration of sulfuric acid (0.1 mol/L), and for a short period of time (15 min).

In future works, it will be necessary to study the elimination of impurities from the leaching liquor (including the oxidized Fe if reduced forms of iron are used as the reductant). This problem has prevented an advance in the commercialization at an industrial level of manganese nodules and black copper minerals.

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

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