Treatment of black copper with the use of iron scrap - Part l

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Abstract

Currently, there is a large amount of mineral resources not being exploited in large copper minings, a clear example are black copper minerals. These resources are generally not incorporated into the extraction circuits or are not treated, either in stocks, leach pads, or debris. These exotic minerals have considerable amounts of Cu and Mn, which are commercially very attractive. They are refractory to conventional leaching processes, therefore, the use of reducing agents is necessary for treatment of these minerals in order to dissolve the present MnO_2, which in turn allows Cu extraction. In this research, iron scrap Fe^0 was used as a reducing agent for the dissolution of Mn from a black copper mineral in an acidic medium and compared to previous studies of the use of Fe^{2+} under the same conditions. In addition, the effects of a pretreatment process (agglomeration and curing) by adding NaCl are investigated in order to favor the reduction of MnO_2. Finally, it was discovered that there is a higher kinetics of dissolution of Mn when working with Fe^0 in short periods of time, although similar extraction efficiencies are obtained after prolonged times. The pretreatment process by adding NaCl resulted in increased Mn extraction in short periods of time (30 min). At applying high concentrations of the reducing agent, the effect of particle size on the dissolution rate of MnO_2 was shown to be insignificant.

Keywords: MnO_2; reducing agent, leaching; Fe^0.

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1. INTRODUCTION

Currently, 19.7 Mt of copper are produced worldwide [1]. In Chile, large-scale copper mining is the main economic activity, generating 10 % of GDP (gross domestic product) [2] as Chile is the largest producer of copper in the world (27.7 % of the world production) [3]. Among the possible treatment processes, pyrometallurgical processes are mainly used (75 %), and to a lesser extent hydrometallurgical processes (25 %) [4]. However, pyrometallurgical processes generate more pollution to the environment because flotation processes generate the tailings dams [5], where acid drainage is generated by oxidation of minerals with high pyrite contents. And, along with large emissions of sulfur dioxide, NOx and CO_2 are generated in the smelting plants [6,7]. Furthermore, it should be mentioned that hydro-metallurgical methods have lower operating, energy, and water consumption costs [8–10].

The deposits, being subjected to geological agents, cause oxidation of porphyry minerals such as pyrite. When reacting with water, it generates sulfuric acid, promoting mobility of metals, such as copper, which under certain conditions of potential and pH, can be transported, precipitating downstream and forming deposits called Exotics [11,12]. The existing mineralization in these deposits includes different species of copper minerals such as, atacamite
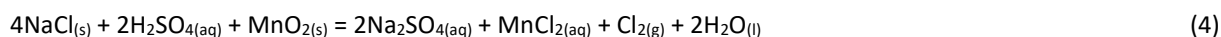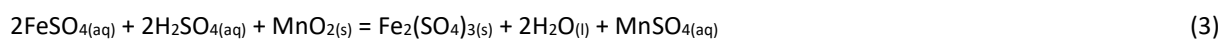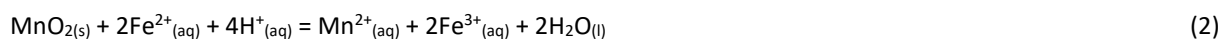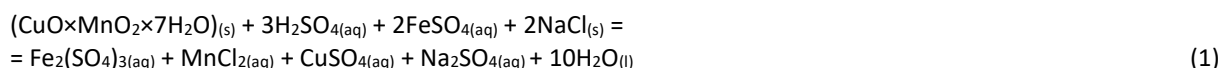
chrysocolla and black copper (copper pitch and copper wad) [11,13]. The latter are defined as mineraloids, because their structure is amorphous [14]. They are also called Si-Fe-Cu-Mn rich silicatoids [15].
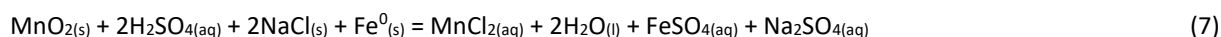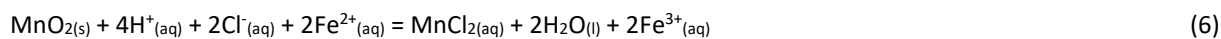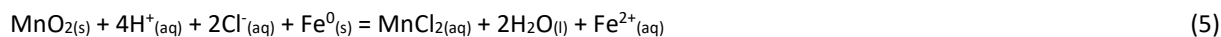
Black copper minerals are abundant in Chile, being present in large deposits such as: Mina sur Chuquicamata, Damiana in El Salvador, Lomas Bayas Spence, and El Tesoro and Huanquintipa in Collahuasi [16]. Even though these minerals contain considerable amounts of Cu and Mn [17], they are not commonly incorporated in the leach pads, being considered waste [18]. This is due to its amorphous, which prevents treating these mineral resources by means of conventional hydrometallurgical processes [16].

There are few studies that investigated leaching of black copper minerals [16–19]. In the investigations carried out by Benavente *et al.,* [18] and Pérez *et al.,* [16] it was discovered that working in an acid-reducing leaching favors dissolution of MnO_2, thus favoring the extraction of copper. Subsequently, Torres *et al.,* [17] demonstrated that it is possible to considerably increase concentrations of Cu and Mn in solutions obtained from black copper in short periods of time (20 min) when working in stirred reactors and carrying out pre-treatment processes (agglomeration and curing) by adding a reducing agent (NaCl in that study). Furthermore, it should be noted that various studies have been carried out with the aim of MnO_2 dissolution from manganese nodules [20–28], which provided multiple alternatives for extraction of Mn and Cu from black copper, as they have are similarly processed in leaching systems.

For dissolution of Mn from black copper with the use of sulfuric acid, chloride and Fe^{2+}, the following reactions are proposed [17]:

$$(CuO \times MnO_2 \times 7H_2O)_{(s)} + 3H_2SO_{4(aq)} + 2FeSO_{4(aq)} + 2NaCl_{(s)} =$$
$$= Fe_2(SO_4)_{3(aq)} + MnCl_{2(aq)} + CuSO_{4(aq)} + Na_2SO_{4(aq)} + 10H_2O_{(l)} \tag{1}$$

$$MnO_{2(s)} + 2Fe^{2+}_{(aq)} + 4H^+_{(aq)} = Mn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} + 2H_2O_{(l)} \tag{2}$$

$$2FeSO_{4(aq)} + 2H_2SO_{4(aq)} + MnO_{2(s)} = Fe_2(SO_4)_{3(s)} + 2H_2O_{(l)} + MnSO_{4(aq)} \tag{3}$$

$$4NaCl_{(s)} + 2H_2SO_{4(aq)} + MnO_{2(s)} = 2Na_2SO_{4(aq)} + MnCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)} \tag{4}$$

On the other hand, for Mn dissolution from black copper with the use of sulfuric acid, chloride and Fe^0, the following reactions are proposed:

$$MnO_{2(s)} + 4H^+_{(aq)} + 2Cl^-_{(aq)} + Fe^0_{(s)} = MnCl_{2(aq)} + 2H_2O_{(l)} + Fe^{2+}_{(aq)} \tag{5}$$

$$MnO_{2(s)} + 4H^+_{(aq)} + 2Cl^-_{(aq)} + 2Fe^{2+}_{(aq)} = MnCl_{2(aq)} + 2H_2O_{(l)} + 2Fe^{3+}_{(aq)} \tag{6}$$

$$MnO_{2(s)} + 2H_2SO_{4(aq)} + 2NaCl_{(s)} + Fe^0_{(s)} = MnCl_{2(aq)} + 2H_2O_{(l)} + FeSO_{4(aq)} + Na_2SO_{4(aq)} \tag{7}$$

The reducing effect of Fe^0 is outlined in the reaction 5. This element provides better reduction capacities with respect to the use of ferrous sulfate (Fe^{2+}), because elemental iron can be oxidized in one step to Fe^{2+}, which is further oxidized to Fe^{3+}. This better-reducing effect can be explained chemically. The reaction 5 has a Gibbs free energy (ΔG^0) of -278 kJ, and a reaction rate coefficient K of 6.68×10^{48}, and reaction 2 has a ΔG^0 of -88 kJ and a K equal to 3.23×10^{15} (calculated by the HSC Chemistry 5.11 software, Chemistry Software Ltd, UK), which in general means that the reaction 5 is more spontaneous and rapid. It is due to the greater reducing effect of Fe^0, as explained above, accompanied with the contribution of sodium chloride [17]. In general, the reaction 7 explains the isolated behavior of manganese (IV) reduction from black copper. This reaction highlights stabilization of manganese (II), which is in the form of a chloride salt. On the other hand, the formation of ferrous sulfate ($FeSO_4$) contributes to continuing of the reduction of manganese still remaining in the mineral.

Pretreatment processes that involve agglomeration and curing stages have shown to be beneficial for optimization of extraction from copper minerals in subsequent leaching processes [17,29-31]. In our previous study [17] we have utilized addition of sodium chloride in the agglomeration and curing stages, varying its concentrations between 10 and 20 kg/t. It was demonstrated that sodium chloride can generate a reducing effect on MnO_2 upon being in contact for long periods of time (2 to 4 days). It was concluded that the resting time of the material (cured) increases dissolution of Cu and Mn, while the concentration of NaCl was less relevant. However, in that study, the optimal curing time in the process as well as the other variables such as acid concentration, particle size and temperature were not determined.

In the present manuscript, the use of iron scrap (Fe^0) for acid-reducing leaching of a black copper mineral was studied, with inclusion of a pre-treatment stage (agglomeration and curing) by adding NaCl, for dissolution of Mn. The obtained results are compared to the use of Fe^{2+} under the same conditions.

2. MATERIALS AND METHODS

2. 1. Black copper sample

In this research, we worked with the same mineral sample used in our previous study [17], which comes from a mining company in northern Chile. The sample was from a high-grade vein and was almost pure. The black oxide ores were ground in a porcelain mortar and sieved to sizes ranging from −173 to 147 µm. Chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) showing 22.01 wt.% Mn, 40.24 wt.% Cu and 7.92 wt.% Fe [17]. A QEMSCAN (Quantitative Evaluation of Minerals by SCANning) analysis was applied by a scanning electron microscope (FEI Company, Brisbane, Australia) that was modified, both in hardware and software as described previously [17]. By this analysis, inorganic solid phases are identified (minerals, alloys, slags, *etc.*) and auto-matically quantified. In brief, the identification, mapping of 2-D distribution, and quantification of inorganic phases, were 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) [17]. The obtained mineralogical composition of the black copper sample is presented in Table 1.

Table 1. Mineralogical composition of the black copper sample[17]

Mineral	Content, mass%
Native Cu/Cuprite/Tenorite	0.12
Cu-Mn 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. 2. Reagents

Iron scrap (Fe^0) was obtained from a steel sheet with a low carbon concentration (0.25 wt.% C) provided from the steel supplier Salomon Sack (Antofagasta, Chile). This sample was reduced in size with the use of a laboratory cone crusher followed by a pulverizer until reaching a size range -75 +53 µm. The salt $FeSO_4 \times 7H_2O$ (WINKLER, Santiago, Chile) was used as a source of ferrous ions. The reactant used in all experiments was sulfuric acid (please add the producer and the country of origin) at the concentration of 1 mol dm^{-3}. The sulfuric acid used for the leaching tests was of grade *p.a.* with 95-97 % purity, a density of 1.84 kg dm^{-3}, and a molecular weight of 98.80 g mol^{-1}. NaCl (CAS N° 7647 – 14 – 5) was obtained from Merck, Chile

2.3. Experimental design

For the leaching tests, experiments were performed under 4 different conditions: a) standard condition (without the addition of the reducing agent, only H_2SO_4), b) with the addition of the reducing agent (Fe), c) with the pre-treatment process and subsequent leaching by adding the reducing agent (Fe), d) with the pre-treatment process and subsequent

leaching by adding two reducing agents (Fe and NaCl). In addition, the effect of particle size was subsequently evaluated. Details for each procedure are presented below:

2. 3. 1. Pretreatment

For the pretreatment, we worked with 10 g of mineral, adding 0.1 cm³ of the concentrated H_2SO_4 solution (*i.e.* 20 kg of H_2SO_4/t) and 0.1 g of NaCl (*i.e.* 10 kg/t). The mineral sample and reactive agents were homogenized, followed by resting for 48 h in a Petri dish covered with plastic to avoid evaporation losses. The temperature during the resting time was controlled at 25 °C with the use of an air conditioner in the laboratory. At the end of the pretreatment, the mineral was washed with distilled water and then again homogenized.

2. 3. 2. Leaching tests

Next, leaching tests were carried out in a 100 cm³ glass reactor with a ratio of 0.01 S/L. Initial or pretreated black copper ore (10 g, particle size range of -75 + 53 µm) was added to the reactor with the use of an analytical spatula and then 1 kg of the 1 mol dm⁻³ H_2SO_4 solution was added. Stirring and suspension of the material was performed with the use of a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. For experimental conditions b, c and d iron scrap was added at the mass ratio Fe^0/black copper sample of 1/1, while at the condition d also 0.1 g of NaCl was added. The temperature was controlled using an oil heated circulator (Julabo, St. Louis, MO, USA). The tests had an operational time of 70 min.

The temperature in all experiments was maintained at 25 °C. Also, the tests were performed in duplicates, and 5 cm³ undiluted samples were analyzed by using atomic absorption spectrometry (Agilent 240FS, Agilent Technologies, USA) with a coefficient of variation ≤5 % and a relative error between 5 to 10 %.

The manganese extraction percentage is determined as the quotient between the amount of manganese measured in the leaching solution and the total manganese (22.01 wt.%) that is present in the initial sample as:

$$ME = \frac{MnPLS}{MnT} 100 \qquad (8)$$

where ME is manganese extraction in percentage, MnPLS is the manganese in leaching solution and MnT is total manganese in the initial sample before leaching.

2. 3. 3. Effect of particle size

The effects of particle size were investigated in experiments carried out under the conditions b and c (Section 2.3). Prior the experiments, the ore material was reduced in size by the use of a porcelain mortar, and then, it was passed through sieve meshes (Tyler)(Tyler soluciones, Monterrey, Mexico) until reaching two size ranges: a) -90 +75 µm and b) -173 +147 µm. These two sample sizes were compared in the experiments using two Fe reducing agents (Fe^0 and Fe^{2+}). The tests had an operational time of 30 min.

3. RESULTS AND DISCUSSION

3. 1. Effect of iron scrap in manganese extraction

Figure 1 shows the dissolution of Mn from the black copper sample under 4 conditions: 1) standard conditions (only H_2SO_4), 2) with the use of the reducing agent (Fe^0) without the agglomeration process (Fe), 3) with the agglomeration process (Fe + pretreatment NaCl) and 4) with the agglomeration process and subsequent NaCl addition (Fe + + pretreatment NaCl + NaCl). For comparison, Figure 2 shows the results obtained in our previous study with Fe^{2+} as a reducing agent and all other conditions identical [17]. It can be observed that higher Mn extraction percentages are obtained in general, when working with Fe^0 over Fe^{2+}, which agrees with our results reported previously [26] for dissolution of MnO_2 from manganese nodules with the use of Fe^0. The obtained findings are due to high activity provided by Fe^0, favoring regeneration of ferrous ions and also the acid-reducing leaching process [22,23,32]. On the other hand, it can be seen that, for both reducing agents, high Mn extractions are obtained in short periods of time, which is similar

to the results obtained in previous studies published in literature [16,18], for this type of minerals in stirred reactors under similar conditions. Also, a positive effect can be seen of the pretreatment as proposed by Wang and Zhou [33] and subsequently corroborated in our previous study [17], where higher Mn extractions were obtained due to the prolonged contact of NaCl with the mineral, generating a reducing effect on MnO_2. The results for conditions 3 and 4 are practically identical. This is beneficial from an industrial point of view, because Fe^0 is a low-cost input that can be obtained from industrial waste, while adding NaCl in the leaching process, would imply an additional cost to the process.
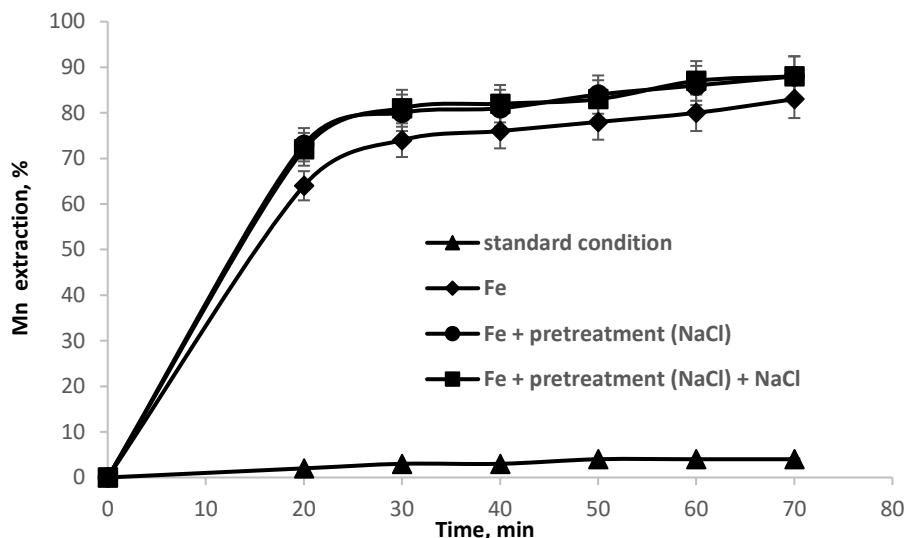

Figure 1. Dissolution of Mn from a black copper mineral with the use of Fe^0 in 4 experimental series: 1) standard conditions (only H_2SO_4), 2) with the use of the reducing agent (Fe^0) without prior agglomeration (Fe), 3) with prior agglomeration (Fe + pretreatment NaCl) and 4) with prior agglomeration with NaCl addition (Fe+ pretreatment NaCl+ NaCl) (data are average of n=2)
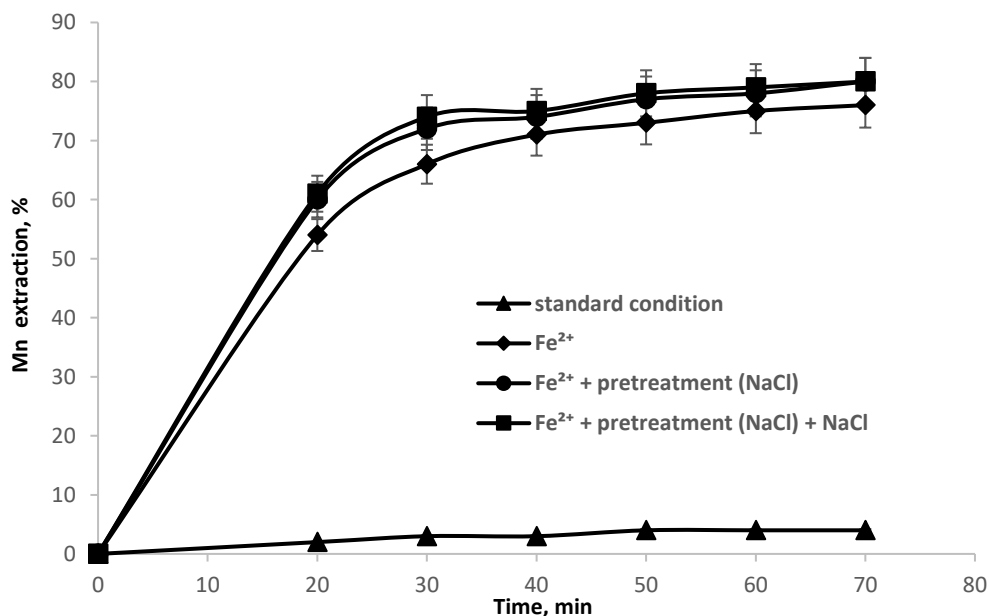

Figure 2. Dissolution of Mn from a black copper mineral with the use of Fe^{2+} in 4 experimental series: 1) standard conditions (only H_2SO_4), 2) with the use of the reducing agent (Fe^{2+}) without prior agglomeration (Fe^{2+}), 3) with prior agglomeration (Fe^{2+} + pretreatment NaCl) and 4) with prior agglomeration with NaCl addition (Fe^{2+}+ pretreatment NaCl+ NaCl) (data are average of n=2) (Figure modified from Torres et al.[17])

It should be added that by the use of Fe^0 as a reducing agent, high Mn concentrations were obtained in the leaching solutions of the order of 88 % which is beneficial from the practical point of view.

3. 2. Effect of the reducing agent particle size

Figure 3 shows the effects of particle size of reducing agents Fe^0 and Fe^{2+} on MnO_2 dissolution from the black copper ore sample. It can be seen that, using the smaller particle size, in general, results in higher extracted Mn amount for both reducing agents studied. It could be concluded that the particle size was not relevant to increase the dissolution rate of MnO_2 since high concentrations of reducing agents were used in the system. It is also important to note that a time of only 30 min was evaluated in order to better perceive potential effects of particle size due to the aggressive nature (rapid dissolution kinetics) of acid-reducing leaching.
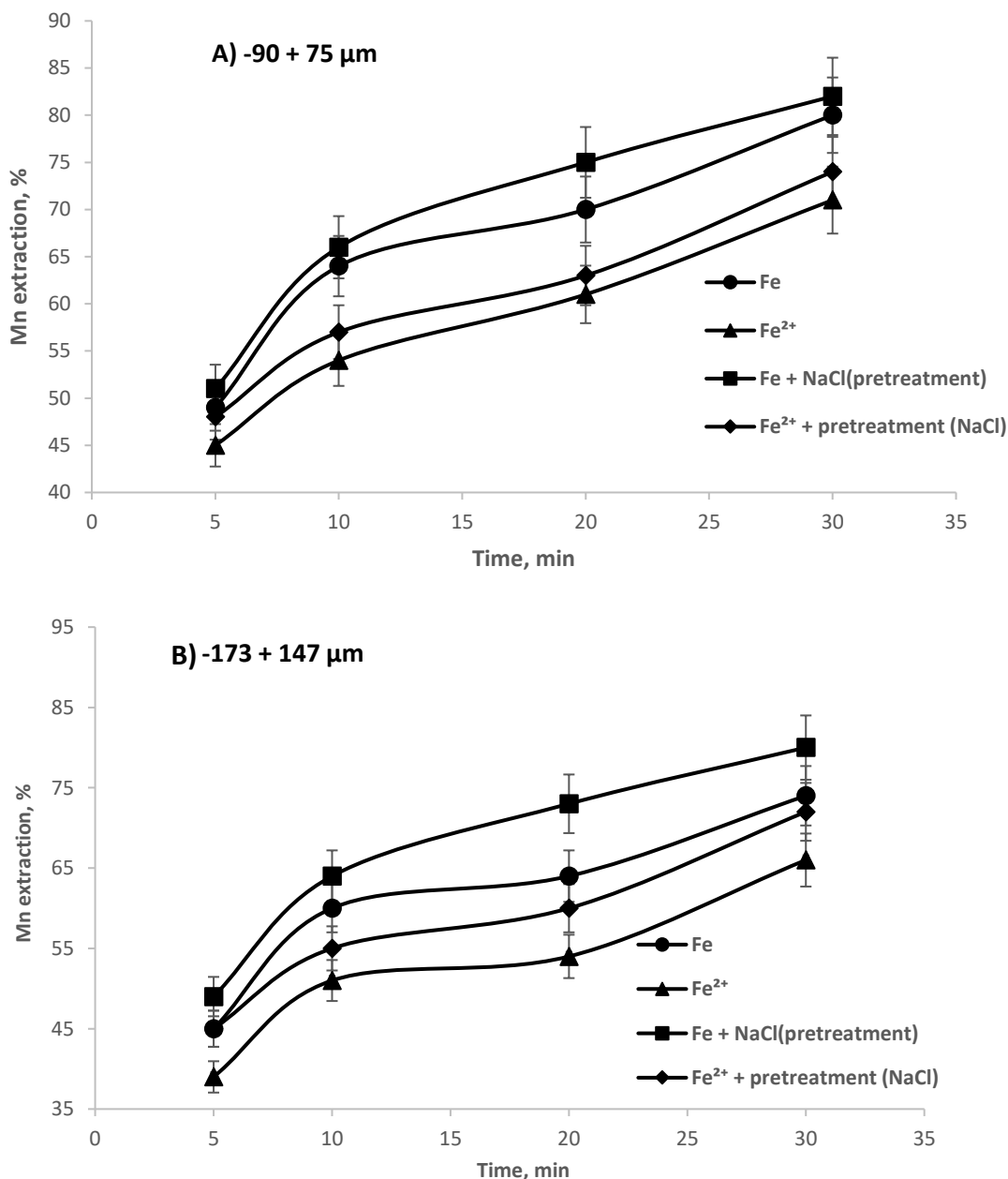

Figure 3. Effect of particle size on the Mn extraction from black copper with the use of two reducing agents without prior agglomeration (Fe⁰ and Fe²⁺) and with prior agglomeration (Fe⁰/Fe²⁺ + pretreatment NaCl) at two particle sizes range: A) -90 + 75 µm; B) -173 + 147 µm (data are average of n=2)

4. CONCLUSIONS

In the present manuscript, studies of Mn dissolution present in a black copper sample are performed with the use of iron scrap (Fe^0) as a reducing agent with and without pretreatment by addition of NaCl, followed by acid-reducing leaching. The results are also compared to the effects of Fe^{2+} as a reducing agent under the same conditions. The main discoveries are as follows.

1. In general, better results are obtained when working with Fe^0 as compared to Fe^{2+}, due to a high activity of the former reducing agent, favoring regeneration of ferrous ions.
2. There is a higher rate of dissolution of Mn when working with Fe^0 in short periods of time, although similar extraction percentages are obtained in prolonged times.
3. The pretreatment process by adding NaCl, resulted in the increase in Mn extraction in short periods of time (30 min).
4. By applying high concentrations of reducing agents, the effect of particle size on the dissolution rate of MnO_2 becomes negligible.

In future work, it would be attractive to evaluate the use of alternative water resources that contain chloride ions, such as, sea water (20 g dm^{-3} of Cl$^-$) or waste water from water desalination plants (40 g dm^{-3} of Cl$^-$ prox.). It is important, not only due to the shortage of fresh water worldwide and especially in arid areas, as a significant economic, environmental, and social problem, but also, due to the beneficial effect generated by chloride ions as a reducing agent for MnO_2, after long periods of contact with the mineral. This would allow us to propose a more efficient industrially pliable process, friendly to the environment, and promoting circular economy by taking advantage of industrial waste.

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SAŽETAK

Obrada crnog bakra upotrebom otpadnog gvožđa – Prvi deo

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(Stručni rad)

Trenutno postoji znatna količina sekundarnih sirovina koja se ne eksploatiše u velikim kopovima bakra, poput crnog bakra. Ovi resursi uglavnom nisu deo standardnih procesa ekstrakcije ili se ne tretiraju, bilo kao šljaka, otpad ili prašina. Iako ovi otpadni materijali sadrže znatne količine komercijalno vrednih metala, bakra i mangana, otporni su na uobičajene procese luženja. Iz tog razloga je upotreba redukujućih sredstava neophodna za tretiranje ovih sirovina kako bi se rastvorio prisutni MnO_2, što zauzvrat omogućava ekstrakciju Cu. U ovom istraživanju, otpadno gvožđe Fe^0 korišćeno je kao redukciono sredstvo za izluživanje Mn iz crnog bakra u kiselom medijumu i rezultati su upoređeni sa prethodnim studijama u kojima su korišćeni Fe^{2+} joni kao redukciono sredstvo pod istim uslovima. Pored toga, ispitani su efekti postupka prethodne obrade dodavanjem NaCl sa ciljem favorizovanja redukcije MnO_2. Pokazano je da se dobija brže rastvaranje Mn pri korišćenju Fe^0 u početnom vremenskom periodu, iako se posle dužeg vremena dobijaju slične efikasnosti ekstrakcije. Proces prethodne obrade dodavanjem NaCl doveo je do povećane ekstrakcije Mn u početnom vremenskom periodu (30 min). Pokazano je da veličina čestica nema značajan uticaj na brzinu rastvaranja MnO_2 pri primeni velike koncentracije redukujućeg agensa.

Ključne reči: MnO_2; redukujuće sredstvo, luženje; Fe^0