# Use of tailings in mn dissolution from marine nodule matrix

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**Abstract:** The nodules are spherical bodies that are scattered within the sedimentary zone of the seabed, and their growth is closely associated with the biogeochemical processes and water sediments. These nodules are mainly composed of Mn, Fe, $SiO_2$, Ca, Ni, Cu, Co and Al. Manganese nodules are an excellent source of base metals and sought-after and rare elements and the fact that they are used as a base elements matrix will be in high demand in industry. Previous studies have shown that primary concentrations of chemical such as Fe in the system are beneficial for increasing manganese extraction. However, it is necessary to optimize the operational parameters so as to maximise Mn recovery. This work investigates the effect of using of tailings, obtained after slag flotation ata foundry plant on the dissolution of Mn from marine nodules, where statistical analysis was distributed using factorial experimental design ontime, $MnO_2/Fe_2O_3$ ratio, and $H_2SO_4$ concentration.

## 1 Introduction

71percent of the total surface of the earth is covered by the oceans, where most of the seafloor reveals mineral deposits of economic interest, such as cobalt-rich crusts, polymetallic hydrometallurgical sulphides, and manganese nodules, reaching 1 to3 billion tonsof major-metal reserves can be found, such as Cu, Ni, Co, Fe and Mn, where the latter is most abundant, with an average content of around 24% [1]. [2]have installed pilot equipment that provides a realistic opportunity for marine nodules extraction, and previous studies,such as those carried out by [3]have already established that hydrometallurgical processes are a viablealternative for processing this mineral matrix, where manganese is obtained by selective precipitation after sulphating roasting.The use of iron as a reducing agent stands out by the abundance and positive results as shown by the authors over the past 20 years [4,5,6]. [7]investigated the effect of working with elemental Fe as a reducing agent at low $H_2SO_4$ rates. They concluded that the most randomvariables in the Mn extractions from the nodule were Fe concentration and nodule article size. Mn extraction increases at higher mixingrates[8,9]. [10] identified that the use of $SO_2$ as a reducing agent increases the leaching kinetics. [11] analysed the kinetic behaviour associated with the extraction of manganese and silver fromacidulated hydrometallurgical processes in the presence of $H_2O_2$, where they concluded that mixing rate was one of the critical variables that affect the extraction of these elements. In the countries of miners, it is necessary to find new applications for tailings with the useof more environmentally friendly hydrometallurgical technologies.This results in an attractive proposal given the quantities of waste generated in the country by flotation, providing an added value for this (CESCO, 2019).The objective of this studywasto evaluate the use of iron oxide present in tailings for reductive leaching of manganese nodules, which includes analysing the behaviourof parameters and their interaction during leaching of manganese nodules with the use of iron oxide ($Fe_2O_3$) and determiningwithin these limits the optimal ratio of iron and the manganese oxide, as well as the concentration of sulfuric acid in the system.

# 2 Methodology

## 2.1 Sample characterization

Marine nodules from the Blake plateau were used in this investigation; their chemical composition presented in Table 1is analysed with a Bruker® M4-Tornado µ-FRX benchtop device (Fremont, CA, USA). The (µ-XRF) X-ray fluorescence data shows that the nodules were composed of pre-existing nodule fragments that formed their core, with concentric layers that precipitated around the core in later stages.

**Table 1.** Chemical analysis (in the form of oxides) of manganese nodules.

| Component | MgO | $Al_2O_3$ | SiO2 | $P_2O_5$ | $SO_3$ | $K_2O$ | CaO | $TiO_2$ | $MnO_2$ | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Weight (%) | 3.54 | 3.69 | 2.97 | 7.20 | 1.17 | 0.33 | 22.48 | 1.07 | 29.85 | 26.02 |

The tailings sample used in this study was obtained after the slag was floated during the production of copper concentrate. Several phases containing iron were present in the tails, while the iron content was estimated at 41.9%, mainly in the form of magnetite.Mineralogical analysis of thetailings used as a reducing agent was carried out usingQEMSCAN analysis and is presented in Table 2.

**Table 2**. Mineralogical analysis of tailings (QUESCAM).

| Mineral | Mass (%) |
|---|---|
| Chalcopirite / Bornite ($CuFeS_2/Cu_5FeS_4$) | 0.47 |
| Tenantite / Tetrahedrite ($Cu_{12}As_4S_{13}/Cu_{12}Sb_4S_{13}$) | 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($FeTiO_3/CaTiSiO_5/TiO_2$) | 0.04 |
| Siderite ($FeCO_3$) | 0.22 |
| Jarosite ($KFe_3^{3+}(SO_4)_2(OH)_6$) | 0.00 |
| Tourmaline ($(Na)(Al)(Mg)_6(BO_3)_3(Si_6O_{18})(OH)_4$) | 0.00 |
| Chlorite / Biotite ($(Mg)_3(Si)_4O_{10}(OH)_2(Mg)_3(OH)_6/K(Mg)_3AlSi_3O_{10}(OH)_2$) | 3.13 |
| Other Phylosilicates | 11.61 |
| Others | 18.90 |
| Total | 100.00 |

## 2.2 Experimental design

The effect onthe Mn extraction rate of theindependent variables was studied using the surface response method to understand and optimize the response by refining the determinations of the relevant factors using amodel.Theexperiment was designed withthree factors that can affect the response variable and with three levels for each factor for a total of 27 experimental tests, where the goalwas to study the effects of particle size, time, and $H_2SO_4$concentrationon the dependent variable.

The leaching tests were carried out in a 50 mL glass reactor with a 0.01 solid/liquid ratioin the leaching solution.A total of 200 mg of previously homogenized nodules obtained from the original sample were kept in agitation and suspension with a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. The sulfuric acid used for the leaching tests is P.A grade, Merck brand with a molecular weight of 98.08 g / mol, 95-97% purity, and density of 1.84 kg / L. The tests were carried out at an ambient temperature of 25°C in duplicate. Measurements were carried out on 5 mL undiluted samples using atomic absorption spectrometry.

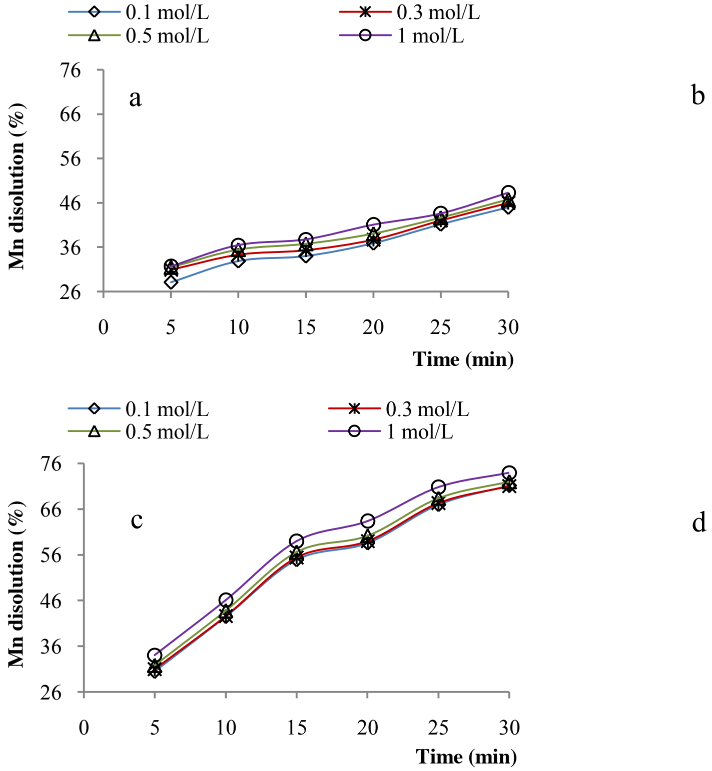
**Table 3**. Mn dissolution model experimental configuration.

| Test | Time (min) | Particle size (Tyler mesh) | Particle size (µm) | $H_2SO_4$ (mol/L) |
|---|---|---|---|---|
| **1** | 10 | [-320, +400] | [-47, +38] | 0.1 |
| **2** | 20 | [-100, +140] | [-150, +106] | 0.5 |
| **3** | 20 | [-320, +400] | [-47, +38] | 1.0 |
| **4** | 30 | [-320, +400] | [-47, +38] | 1.0 |
| **5** | 10 | [-200, +270] | [-75, +53] | 0.5 |
| **6** | 20 | [-100, +140] | [-150, +106] | 0.1 |
| **7** | 30 | [-100, +140] | [-150, +106] | 1.0 |
| **8** | 30 | [-200, +270] | [-75, +53] | 0.1 |
| **9** | 10 | [-100, +140] | [-150, +106] | 0.5 |
| **10** | 10 | [-100, +140] | [-150, +106] | 1.0 |
| **11** | 20 | [-320, +400] | [\|-47, +38] | 0.5 |
| **12** | 30 | [-100, +140] | [-150, +106] | 0.1 |
| **13** | 20 | [-320, +400] | [-47, +38] | 0.1 |
| **14** | 10 | [-100, +140] | [-150, +106] | 0.1 |
| **15** | 10 | [-320, +400] | [-47, +38] | 1.0 |
| **16** | 10 | [-200, +270] | [-75, +53] | 0.1 |
| **17** | 20 | [-200, +270] | [-75, +53] | 0.1 |
| **18** | 20 | [-200, +270] | [-75, +53] | 0.5 |
| **19** | 30 | [-320, +400] | [-47, +38] | 0.1 |
| **20** | 30 | [-320, +400] | [-47, +38] | 0.5 |
| **21** | 10 | [-200, +270] | [-75, +53] | 1.0 |
| **22** | 20 | [-200, +270] | [-75, +53] | 1.0 |
| **23** | 20 | [-100, +140] | [-150, +106] | 1.0 |
| **24** | 30 | [-200, +270] | [-75, +53] | 0.5 |
| **25** | 10 | [-320, +400] | [-47, +38] | 0.5 |
| **26** | 30 | [-200, +270] | [-75, +53] | 1.0 |
| **27** | 30 | [-100, +140] | [-150, +106] | 0.5 |

The proposed experiment involved three factors that could influence the response variable with three levels for each factor for a total of 27 experimental tests, using manganese iron oxide ratios of 0.25, 0.33; 1, and 2. Table 3 shows the ranges of the parameters used to design the validated model based on the results previously reported by [7] and [12]. The ratio levels were coded as (-1, 0, 1), where each number represents a particular value of the factor, with (-1) as the lowest value, (0) as the intermediate value, and (1) as the highest value (1).

## 3 Results

Figure 1 shows the manganese dissolution behaviour for the 4 $MnO_2/Fe_2O_3$ ratios (2:1 (a), 1:1 (b), 1:2 (c), 1:3 (d)) studied at different sulfuric acid concentrations for the medium particle size that obtained the best results. It is observed that the highest Manganese recoveriesare obtained when working at a raw iron oxide ratio below than 1:1, reaching 74%, which is consistent with previous works since thesm has more iron than manganese; manganese dissolution increasesin short intervals.If we increase the numberof tailings in the system,thus achieving ratios below1:1, and it is possible to obtain the best extraction results with low acid concentrations, benefiting the reuse of this waste and decreasing the use of acid in the system.



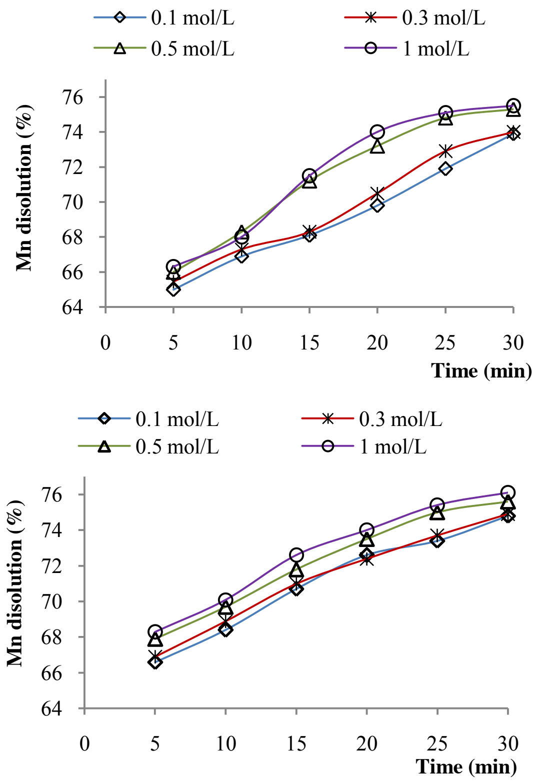


**Fig.1.** Effect ofacid concentration at a $MnO_2/Fe_2O_3$ 2:1 ratio (a), 1:1 ratio (b), 1:2 ratio (c), 1:3 ratio (d) (25°C, 600 rpm, −75 +53 µm).

To examinethe dissolution patternof these factors by ANOVA analysis, the interaction of the variables between them was analysed, where no significant levels of the interaction between them were observed ($p >> 0.05$). The curvature effects on the variables do not contribute to explaining the variability of the pattern. By analysing the linear effects present in the results, it was possible to identify that particle size, acid concentration, and time have a correspondingimpact on manganese dissolution, where the influenceof the factors corresponds to $F_{Regression}$ (98.07) $>F_{Table}$ with 95% confidence level of $F_{4.22}$ (2.8167) and a statistically significant p-level. In Figure 2, the normality test applied to the residuals from the regression isrelatively close to the fitted normal distribution line.

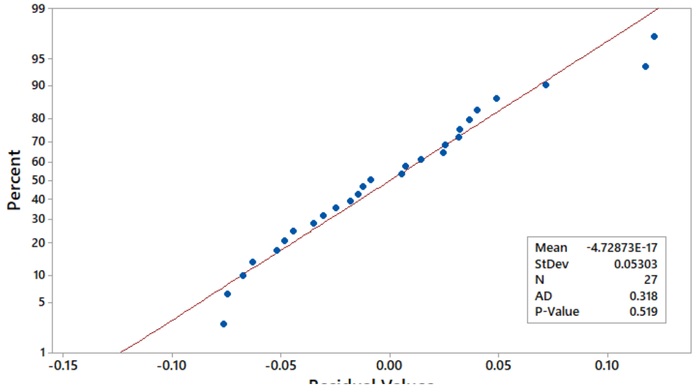


**Fig. 2.** Residual values probability diagram.

The results presented in Figure 3 show the benefit of operating at high concentrations of reducing agent (Fe). There is no significant difference in dissolution, modifying the ratio of manganese to iron oxide ratio from 0.33 (1:3) to 0.25 (1:4) for short periods, where is possible to achieve manganese dissolution close to 70%. However, up to 74% extraction can be achieved at 30 min with a ratio of 0.5. Figure 4 presents the potential and pH values obtained in the tests that correspond to ranges between -0.2 to 1.2 V for potential and -1.8 to 0.1 for pH.These results indicate a good generation of ferric and ferrous ions that are favoured by the high iron oxide concentration in the system which maintains the regeneration of ferrous ions. This results in high levels of ferrous ion concentration and activity, favouring the manganese dissolution and avoiding the formation of precipitates through oxidation-reduction.

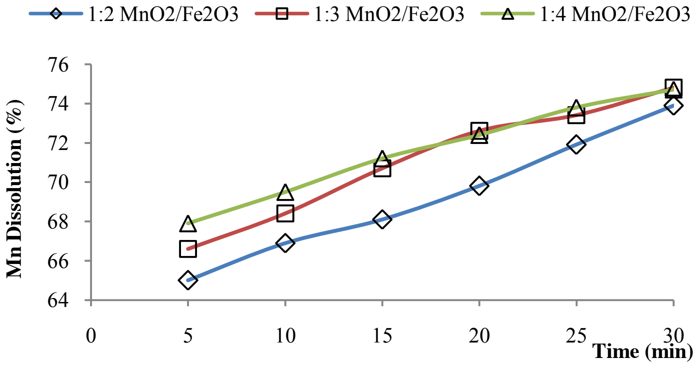


**Fig.3**. $MnO_2/Fe_2O_3$ ratio effect on the manganese extraction (25°C, -75 + 53 µm, 1 mol/L $H_2SO_4$).

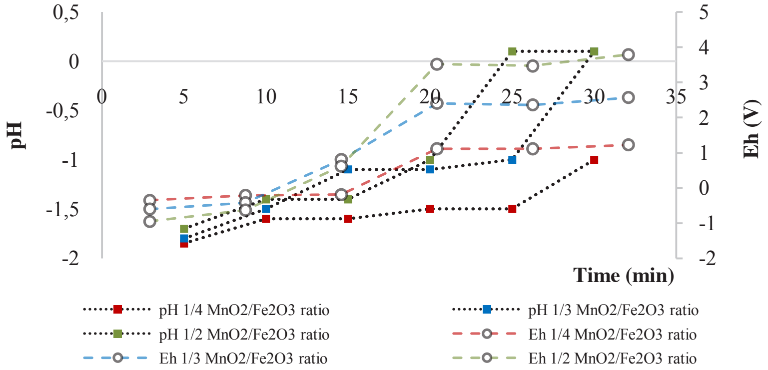


**Fig.4.** Potential effect and pH on Mn solution at different MnO2/$Fe_2O_3$ ratios (25°C, 600 rpm, −75 +53 µm, 0.1 mol/L acid concentration).

## 4 Conclusion

The dissolution rate of manganese is higher in the presence of tailings, being more reactive than other materials such as copper slags, which consume acidic protons due to the presence of elements such as copper. 74% dissolution of manganese can be achieved in 30 min with a manganese iron oxide rate of 0.5, a sulfuric acid concentration of 0.1 mol/L, and an average particle size of -75 + 53 µm. It is possible to reducethe leaching times by modifying the ratio to 0.33 (1:3), keeping the acid concentration at 0.1 and achieving manganese recoveryin the range of 68-73%. Alsooperatingat ratios below 0.5, the acid concentration in the system is not very relevant.

In future works, the leaching of marine nodules should be studied using different iron-reducing agents but under the same operational conditions. It is also necessary to determine the optimal ratio that improves the manganese dissolution.

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