**ABSTRACT**

The basis of the traditional technology of hydrometallurgical processing of manganese ore is the process of ore roasting. The results obtained in this article make it possible to exclude the roasting process and directly leach the crushed ore under the action of an electric current. The process of electrochemical leaching includes two simultaneous operations: reduction of hard-soluble higher manganese oxides (pyrolusite - MnO$_2$, vernadite - MnO$_2$·nH$_2$O) in an acid medium and transition of reduced manganese into an aqueous solution. The main part of the reduction process of higher manganese oxides proceeds in the Fe$^{2+}$ ↔ Fe$^{3+}$ catalytic system, the remaining part proceeds at the cathode under stirring. The degree of influence of iron (III) ions was determined. During studies on the transfer of manganese into solution from manganese ore by electrochemical leaching, the influence of L:S ratio, sulfuric acid concentration, and cathodic current density on the degree of manganese extraction were studied. As a result of electrochemical leaching studies in the presence of the catalyst system, Fe$^{2+}$ ↔ Fe$^{3+}$ under optimal electrolysis parameters the degree of manganese extraction was 99%.

**Keywords:** Manganese, Pyrolusite, Manganese Dioxide, Electrochemical Leaching, Catalytic System, Cathodic Reduction.

**INTRODUCTION**

Manganese is one of the widely used metals in the steel sector of ferrous metallurgy. Its alloys are used in electrical engineering, and in the production of food and chemical industry equipment. The content of manganese in alloyed steel ranges from 0.25% to 1.8%. They are used to make automobile parts, such as shafts and rebar items. Steel containing 12-13% of manganese (Hadfield) is used for making crushers, ball mills, and armor elements. Mirror iron contains up to 20% of manganese. High purity manganese is used to make high-strength steel. In this regard, the electrolysis method is one of the effective methods of obtaining high-purity manganese. The advantage of electrochemical methods over chemical methods is the comparative ease and cheapness of obtaining a number of metal products and their high-purity compounds.\cite{6-14} Due to the possibility of electrochemical methods, refractory, and other metals poorly soluble in aqueous media can be easily dissolved by chemical methods.\cite{15-18} Due to the fact that the solubility of higher manganese oxides (pyrolusite - MnO$_2$, vernadite - MnO$_2$·nH$_2$O) in acid medium is low, low-valent oxides are used in the processing of ore with acid. In this regard, the traditional technology of manganese production uses the roasting of higher manganese oxides in the presence of reducing agents.\cite{19,20} This traditional technology has the following disadvantages:

- The need to use a special complex drum-type unit to implement the roasting process in the presence of reducing agents;
- Power losses and the use of reducing agents lead to a decrease in the economic efficiency of the technology;
- The use of carbon-based reducing agents leads to environmental pollution.

This work is licensed under a CC BY 4.0 license.
The aim of the work is to develop a new method for hydrometallurgical technology of obtaining metallic manganese from manganese ore by direct transfer of manganese into an aqueous solution by electrochemical leaching in the presence of the catalytic system Fe$^{2+} \leftrightarrow$ Fe$^{3+}$. In this way, the traditional ore roasting process for hydrometallurgical processing technology can be eliminated, allowing manganese extraction from ore with greater efficiency and lower operating costs. This solution has the potential to increase the environmental and economic efficiency of traditional technological processes, as well as to expand the product range on the basis of new methods.

In the presented work it is shown that the manganese mineral MnO$_2$, which is hardly soluble in dilute acid medium, is actively dissolved as a result of contacting the cathode and using the catalytic system Fe$^{2+} \leftrightarrow$ Fe$^{3+}$.

The work is performed at room temperature, in a laboratory electrolyzer with a total volume of 1000 ml, where the anode and cathode spaces are separated by an MA-40 membrane, according to the cylindrical type design (Fig.-1). A plate of titanium or another metal resistant to the medium is used as the cathode material. The role of the anode is performed by the lead. An aqueous sulfuric acid solution containing crushed manganese ore and a small amount of iron (III) ions is used as a catholyte. An appropriate tank is filled with the necessary solution, electrodes are connected, and the titanium electrode is cathodically polarized in 100 g/l sulfuric acid solution with a concentration of 100-300 A/m$^2$ with mechanical stirring. During polarization the manganese mineral, MnO$_2$, interacts as a cathode and passes into the divalent state (MnO) well soluble in the indicated medium$^{21}$:

\[ \text{MnO}_2 + 4\text{H}^+ + 2e \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad E^0 = +1.23 \text{ B} \quad (1) \]

At the same time a small amount of trivalent iron ions is reduced at the cathode:

\[ \text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+} \quad E^0 = +0.77 \text{ B} \quad (2) \]

Reduced iron ions catalyze the reduction of higher manganese oxides and create conditions for further dissolution:

\[ \text{MnO}_2 + 2\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 \rightarrow \text{MnSO}_4^{+} \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \quad (3) \]

Reaction (3) is followed by the reaction of reverse regeneration of trivalent iron ions in the cathodic region, i.e., it converts to the divalent form at the cathode, thereby acting as a reverse reducing agent. Thus, reactions (2) and (3) repeat cyclically:

\[ \text{Fe}^{2+} + e \rightarrow \text{Fe}^{3+} \quad (4) \]

\[ \text{MnO}_2 + 2\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 \rightarrow \text{MnSO}_4^{+} \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \quad (5) \]

**EXPERIMENTAL**

Manganese ore was used as manganese raw material, lead, and titanium plates were used as electrodes, sulfuric acid (H$_2$SO$_4$), iron (III) sulfate Fe$_2$(SO$_4$)$_3$, and manganese dioxide (MnO$_2$) with the purity of HP were used as reagents. Bidistilled water was used to prepare the solutions.

Trial experiments were carried out to determine the effect of iron ions on manganese extraction from manganese ore. The titanium electrode is cathodically polarized in 100 g/l sulfuric acid solution containing crushed MnO$_2$ and 3 g/l trivalent iron ions under active stirring at a current density of 200 A/m$^2$. The anode space is filled with a sulfuric acid solution with a concentration of 100 g/l. A lead electrode is used as an anode.

The results of the analysis of manganese ore used for electrochemical leaching at the above parameters are shown in Table-1. Figure-2 shows the results of the X-ray spectroscopic analysis.
The process of leaching with manganese ore was carried out, and after the solution was filtered, the resulting cake was analyzed by elemental (Table-2) and X-ray spectral (Fig.-3) analyses. The obtained results of the analysis show that during electrochemical leaching of manganese ore in the presence of the Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ catalytic system, the process proceeds selectively. As can be seen from Table-2, mainly manganese takes part in the cathodic reduction process. Together with manganese, a small number of other elements (Mg, Cr, Ca, and Zn) passed into the solution. These results will undoubtedly give a positive effect on the technology of hydrometallurgical processing of manganese ore. Since the pulp after electrochemical leaching is filtered, the filtrate is sent for purification from metal ions having positive potential compared to manganese. The fact that there are few impurities in the solution reduces the consumption of reagents that are added to precipitate the metal ions negatively affecting the electrolysis in the cleaning process.

### RESULTS AND DISCUSSION

The influence of the concentration of iron ions (ILI) on the process of electrochemical reduction of higher manganese oxides in the composition of manganese ore was studied. Parameters of electrolysis are given...
EXTRACTION OF MANGANESE FROM MANGANESE ORES

T.E. Gaipov et al.

The concentration of sulfuric acid is 100 g/l, the temperature 25 °C, and the duration of electrolysis is 1 h.

As can be seen from the results obtained, the degree of manganese extraction increases with the increasing concentration of iron ions. However, concentrations of iron ions in larger amounts, contaminate the solution, making it difficult to purify. The gel-like iron hydroxide (III) formed during the hydrolytic purification process increases the duration of filtration and requires a lot of water and time for washing. In this regard, the concentration of iron ions (III) 3 g/l is sufficient for the process of manganese ore leaching. At this concentration, the degree of manganese extraction and WT of its dissolution was 61%, respectively. The effect of the L:S ratio on the degree of manganese extraction during electrochemical leaching was studied (Table-4). The ratio L:S is one of the parameters determining the activity of ore mixing with aqueous solution and collision of ore particles with the cathode.

The results show that increasing the volume of solvent in L: T has a positive effect on the dissolution of manganese. Due to the increase in contact of ore particles with the surface of the cathode, at the ratio L:S - 10:1, intensive mixing occurs. The influence of cathodic current density on the degree of manganese extraction was studied. At a cathodic current density of 100 A/m², the degree of manganese extraction is 46% (Table-5). With the increase of current density up to 200 A/m² the degree of manganese extraction increases up to 61%. Further increase of current density up to 300 A/m² results in an insignificant decrease of manganese extraction degree up to 58.7%. Increasing the current density above 200 A/m² leads to a decrease in overvoltage of hydrogen extraction, i.e., most of the current is spent on undesirable in this case process of hydrogen extraction.

The influence of pulp stirring speed on the degree of manganese extraction was investigated. Table-6 shows that as this parameter increases from 100 to 150 and 200 rpm, the degree of manganese extraction
increases from 34.8 to 61 and 98.9%, respectively. Consequently, during agitation, the manganese ore particles are closer to the cathode surface to a greater extent. A further increase in the stirring speed up to 250 rpm negatively affects the efficiency of the process, i.e. the degree of manganese extraction decreases to 81%.

Table 6: The Effect of the Electrolyte Mixing Rate on the Degree of Manganese Extraction

| No. | [Fe^{3+}], g/l | i_e, A/m^2 | L:S | Mixing speed, rpm | α, % |
|-----|----------------|------------|-----|-------------------|------|
| 1   | 3              | 200        | 10:1| 100               | 34.8 |
| 2   | 3              | 200        | 10:1| 150               | 61   |
| 3   | 3              | 200        | 10:1| 200               | 98.9 |
| 4   | 3              | 200        | 10:1| 250               | 81   |

CONCLUSION

According to the results of the studies, it was shown that the higher manganese oxides in the ore are actively dissolved in the dilute acid medium as a result of contact with the cathode and the use of the catalytic system Fe^{2+} ↔ Fe^{3+}. The degrees of influence of iron (III) ions, iron: T ratio, sulfuric acid concentration, and cathodic current density on the degree of manganese extraction were determined. As a result of the conducted studies at the optimal parameters of electrolysis the degree of extraction and calculated value of VT of manganese dissolution, which was 99 and 71.6%, respectively, were obtained.

ACKNOWLEDGEMENT

This research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08052565. “Development of the technology for producing metal manganese from manganese ores by electrochemical leaching”). The authors would like to place on record their sincere gratitude to the Ministry of Science and Education of the Republic of Kazakhstan for its financial support.

REFERENCES

1. S.M. Isabaev, H.M. Kuzgibekova, E.V. Zhinova, I.M. Zhilina, International Scientific Research Journal, 7(85), 19(2019), https://doi.org/10.23670/IJRJ.2019.85.7.003
2. L.A. Polulyakh, V.Ya. Dashevsky, Yu.S. Yusfin, News of Higher Educational Institutions, Ferrous Metallurgy, 9(57), 5(2014), https://doi.org/10.17073/0368-0797-2014-9-5-12
3. E.B. Godunov, A.D. Izotov, I.G. Gorichev, Inorganic materials, 54(1), 66(2018), https://doi.org/10.1134/S002016851801003X
4. R. Elliott, S.C. Kenneth, S. Mostaghel, M. Barati, The Journal of The Minerals, Metals & Materials Society, 70, 680(2018), https://doi.org/10.1007/s11837-018-2769-4
5. T. Jiang, Y. Yang, Z. Huang, B. Zhang, G. Qiu, Hydrometallurgy, 72(1-2), 129(2004), https://doi.org/10.1016/S0304-386X(03)00136-1
6. A.S. Kolesnikov, V.N. Naray, N. Natorhin, A.A. Saipov, O.G. Kolesnikova, Rasayan Journal of Chemistry, 13, 2420(2020), https://doi.org/10.31788/RJC.2020.1346102
7. A. Bayeshov, A.K. Bayeshova, U.A. Abduvaliyeva, D. Abizhanova, Oriental Journal of Chemistry, 35(2), 689(2019), https://doi.org/10.13005/ojc/350225
8. M. Hesari, D. Nematomallahi, L. Fotouhi, Journal of Coordination Chemistry, 61(11), 1744(2008), https://doi.org/10.1080/00958970701747012
9. T.E. Gaipov, A. Bayeshov, B.E. Myrzabekov, E.K. Abdulina, News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 3(441), 196(2020), https://doi.org/10.32014/2020.2518-170X.73
10. Y. Yamauchi, A. Tonegawa, M. Komatsu, H. Wang, L. Wang, Y. Nemoto, N. Suzuki, and K. Kuroda, Journal of the American Chemical Society, 134(11), 5100(2012), https://doi.org/10.1021/ja209044g
11. A.B. Bayeshov, B.E. Myrzabekov, A.V. Kolesnikov, News of the National Academy of Sciences of the Republic of Kazakhstan Series Chemistry and Technology, 6, 96(2018), https://doi.org/10.32014/2018.2518-1491.31
12. A. Makhanbetov, A. Zharmenov, A. Bayeshov, B. Mishra, O. Baigenzhenov, Russian Journal of Non-Ferrous Metals, 56(6), 606(2015), https://doi.org/10.3103/S1067821215060061
13. A. Mamyrbekova, A. Mamyrbekova, M.K. Kassymova, Zh. Aitbayeva, G.E. Shimirova, Zh. E. Daribayev and D. Tanatar, *Rasayan Journal of Chemistry*, **14**(3), 2040(2021), https://doi.org/10.31788/RJC.2021.1436384

14. A. B. Bayeshov, M. Zh. Zhurinov, U. A. Abduvaliyeva, A. A. Adaibekova, T. E. Gaipov, B.E. Myrzabekov, *News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences*, **6**(426), 178(2017).

15. K.G. Serrano, *Current Opinion in Electrochemistry*, **27**, 100679(2021), https://doi.org/10.1016/j.coelec.2020.100679

16. B.E. Myrzabekov, A.B. Bayeshov, A.B. Makhanbetov, B. Mishra, and O.S. Baigenzhenov, *Metallurgical and materials transactions B*, **49**(1), 23(2018), https://doi.org/10.1007/s11663-017-1139-x

17. A.B. Bayeshov, A.B. Makhanbetov, B.E. Myrzabekov, T.E. Gaipov, *Bulletin of the National Academy of Sciences of the Republic of Kazakhstan*, **3**, 87(2017).

18. B.E. Myrzabekov, A.B. Baeshov, B. Mishra, O. Baigenzhenov, V. Luganov, *International Journal of Nonferrous Metallurgy*, **6**, 17(2017), https://doi.org/10.4236/ijnm.2017.62002

19. A.A. Nayl, I.M. Ismail, H.F. Aly, *International Journal of Mineral Processing*, **100**(2), 116(2011), https://doi.org/10.1016/j.minpro.2011.05.003

20. A.B. Makhanbetov, A.B. Baeshov, B.E. Myrzabekov, A.N. Tabylganova, *International Journal of Chemical Sciences*, **13**(1), 115(2015).

21. A.B. Makhanbetov, B.E. Myrzabekov, T.E. Gaipov, A.Tazhibayev, U.A. Abduvaliyeva, *Rasayan Journal of Chemistry*, **14**(4), 2202(2021), https://doi.org/10.31788/RJC.2021.1446491 [RJC-6898/2021]