ELECTRO-REDUCTIVE LEACHING OF LOW-GRADE MANGANESE OXIDE RAW MATERIALS USING AN Fe3+/Fe2+ REDOX MEDIATOR

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Abstract: Electro-reductive leaching of 18.1% Mn residues (tailings) generated after enrichment of raw manganese oxide ore deposits from the Chiatura region in Georgia was conducted in a non-diaphragm electrolyzer using an Fe^{3+}/Fe^{2+} redox system as a mediator in a suspension with a limited concentration of Fe^{3+} (up to 3.5 $g·L^{-1}$). For regeneration of the Fe^{2+} reductant agent, the enhanced surface of an AISI 304 stainless steel mesh-cathode was chosen, which unlike the graphite felt electrodes (GFE-1) did not become clogged with solid silicates and sand particles. The apparatus, which was designed to ensure electro-leaching efficiency, consisted of a non-diaphragm electrolyzer with an intermediate tank, a peristaltic pump, and a compressor. The optimal conditions for the electro-reductive leaching process using a mesh cathode were as follows: i) a relatively low concentration of acid (16–20 $g·L^{-1}$ H_2SO_4 + 2.0 –2.5 $g·L^{-1}$ Fe^{3+}; pH of 1), a liquid/solid ratio in the suspension of 0.08 kg/L, ii) taking into account the overall surface of the cathode, the current density i_c=0.6A/dm2; $A·dm^{-2}$, and iii) intensive turbulence (boiling) of the suspension. Under these conditions, the Mn extraction rate was 96.0–98.1% and the current efficiency was 84.2–86.6%, while only 20–25% of the iron from raw material was transferred to the solution and its content did not exceed the limited concentration of 3.5 $g·L^{-1}$ Fe^{3+}. Large-scale laboratory testing of electro-reductive leaching showed that the total specific electricity consumption for raw material processing was 3760.8 $kWh·t^{-1}$, and for electro-reductive leaching, the value was 586.8 $kWh·t^{-1}$. After electro-leaching, filtration, and drying, light brown solid stuff was obtained, which could be used for cement production as an additive.

Keywords: low-grade manganese oxide raw materials; electro-reductive leaching; redox system Fe^{3+}/Fe^{2+}; leaching efficiency, current efficiency

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INTRODUCTION

Metallic manganese, its alloys (ferromanganese, silicomanganese), and various compounds (MnO_2, $MnSO_4·H_2O$, $KMnO_4$) have been widely used in metallurgy to produce different types of steel, in chemical energy sources, such as primary (non-rechargeable single use) and secondary (rechargeable) batteries, animal feed additives, dyes, pharmaceuticals, textiles, water purification, and in other industries. Owing to the increasing demand for manganese, which has caused the depletion of high-grade deposits, considerable attention has now been directed toward improving manganese extraction technologies from relatively low-grade ore deposits and secondary raw materials (for example, mining waste), and primarily for improving environmental conditions.

Several technologies for the extraction and leaching of manganese from oxide ores exist and have been thoroughly discussed in reviews (Zhang et al., 2007; Baba et al., 2014). In these technologies, soluble manganese (II) in the ore can be converted to its salt by acid leaching, mainly using sulfuric acid. For the conversion of insoluble Mn^{4+} to soluble Mn^{2+}, different reductants can be used, such as iron (II), methanol, oxalic acid, hydrogen peroxide, sawdust, cornstalk, biomass, sulfur dioxide, and various other reductants (Das at al., 1982; Tekin at al.,1993; Momade at al., 1999; Sahoo at al., 2001; Jiang at al., 2004; Senanayake, 2004; Hazek at al., 2006; Hariprasad at al., 2007; Cheng at al., 2008; Song at al., 2010; Sun at al., 2013; Liu at al., 2013).

Manganese oxide ores used as raw materials in industrial technology contain pyrolusite (MnO_2), which is insoluble in sulfuric acid. The ore is pre-dried, crushed, and then reduced at high temperatures using hydrogen, natural gas, and fuel oil. The manganese monoxide (MnO) product then leaches into sulfuric acid and the resulting manganese sulfate solution can be purified by hydrolytic and sulfide methods. Electrolytic manganese metal and electrolytic manganese dioxide can be obtained by electrolysis of the purified manganese sulfate solution, and manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$) is produced after autoclaving or heat treatment.

The high temperature reduction of manganese oxide ores can lead not only to large amounts of dust and high energy consumption, but also to significant greenhouse gas emissions (including CO_2), which often cause climate change. As a general motive for controlling greenhouse gas pollution, the UN Paris Agreement (2015) was accepted, calling on large industrial enterprises of leading developed countries to introduce new advanced technologies to prevent carbon dioxide pollution in the atmosphere.

Considering the methods of manganese extraction from manganese oxide ores and secondary raw materials, electro-reductive leaching is an area that needs special attention (Zhang et al., 2007). This method can be distinguished by its ability to simplify the control and purification of the solution from impurities, achieving high leaching efficiency, which ultimately benefits the production cost. The main advantage of electro-reductive leaching lies in its safety in terms of environmental pollution.

Historically, the study of electro-reductive leaching of oxide ores has been conducted mainly in combination with the electro-synthesis process of manganese dioxide (Dufour at al., 1957; Dim and Frazer, 1982; Agladze at al.,1984).

In the work by Dufour et al. (1982), the leaching of manganese oxide ore was conducted by adding Fe^{2+} ions from the reducing agent in the reactor:

$MnO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$ (1)

Following the filtration of the suspension, the filtrate containing 75–100 $g{\cdot}L^{-1}$ of $MnSO_4$ and 50–75 $g{\cdot}L^{-1}$ of $Fe_2(SO_4)_3$ was delivered to the anodic area of a diaphragm electrolyzer, where electrolytic manganese dioxide contaminated with iron (III) ions was obtained on the anode with a current efficiency of less than 30%. The Mn^{2+} depleted and Fe^{3+} containing-anolyte was transferred to the catholyte through the diaphragm, where Fe^{3+} was reduced to Fe^{2+} on a lead or graphite cathode:

$Fe^{3+} + \bar{e} \rightarrow Fe^{2+}.$ (2)

The catholyte (Fe^{2+} solution) leaving the electrolyzer was fed into the ore leaching reactor. Thus, the proposed technique (ex-cell method) envisioned the leaching of manganese oxide ore by indirect electrochemical reduction using an Fe^{3+}/Fe^{2+} redox mediator system, in which reactions (1) and (2) took place in different reactors. This method allowed the elimination of large amounts of greenhouse gas (CO_2) emissions into the atmosphere compared to the high-temperature reduction processes. However, it has no practical applications, because in the presence of Fe^{3+} in the anolyte, unconditioned electrolytic manganese dioxide will be released on the anode with low current efficiency (25–30%).A different approach was presented by Dim & Frazer (1982), who used the in-cell method to conduct electro-reductive leaching of manganese ore through an Fe^{3+}/Fe^{2+} redox mediator system in a diaphragm electrolyzer with graphite, titanium, or stainless steel cathodes, and titanium or graphite anodes. With the participation of the Fe^{2+} ions formed at the cathode as a result of reaction (2), reaction (1) took place in the anolyte leading to obtaining of the electrolytic manganese dioxide at the anode. In this case, it was also impossible to obtain a standard, high-quality electrolytic manganese dioxide, and the presence of a diaphragm made it difficult to operate the electrolyzer.

The Agladze at al. (1984) used similar approach; however, unlike the above-described process (Dufour et al., 1982), the suspension from the leached cathodic area was filtered, purified, and delivered to the anodic chamber of the diaphragm bath. In addition, electrolytic manganese dioxide was produced on the anode. In this method, the electro-reductive leaching of manganese oxide ore took place in the catholyte and Fe^{2+} was generated on the cathode. At the same time, direct partial reduction of the MnO_2 existing in the ore, took place at the cathode,

$MnO_2 + 4H^+ + 2\,\bar{e} \rightarrow Mn^2$ (3)

which accounted for 7% of the total manganese leaching process.

Based on the studies of electro-reductive leaching of ore using an Fe^{3+}/Fe^{2+} redox system and the simultaneous electrolysis of manganese dioxide, it has been determined that a low-quality electrolytic manganese dioxide with low current efficiency can be obtained on the anode. Furthermore, use of a diaphragm in the cell will have certain disadvantages, such as the clogging of pores with solid ore particles and insoluble salts ($BaSO_4$), which will form during the process, causing a decrease in the permeability of the diaphragm. Thus, the diffuse and convective transport of acid and Mn^{2+} ions will be inhibited, causing an increase in voltage on the electrolyzer.

An alternative method to the electro-reductive leaching of manganese oxide ores in a diaphragm electrolyzer through an Fe^{3+}/Fe^{2+} redox system involves the use of a non-diaphragm-type device. In this case, the production of manganese dioxide on the anode will be replaced by the oxygen generation process. In addition, the leaching process will be free from the restrictions dictated by the optimal conditions for the electrosynthesis of manganese dioxide. Specifically, it allows for the application of the electro-reductive leaching method for low-grade manganese ores. In addition, the characteristic side effects of processing low-grade ore, such as solid-liquid ratio in solution, and the increased concentration of impurities, will not result in additional technological complications in a non-diaphragm electrolyzer.

In patent (Shengelia at al., 2019), the electro-reductive leaching of high quality manganese oxide ore (51% Mn; 80.8% MnO_2) was conducted in a diaphragm electrochemical reactor with a carbon felt cathode and RuO_2/TiO_2 coated titanium (Ti) mesh anodes, where the concentration of iron ions in acid solution was 0.5–0.7 $g{\cdot}L^{-1}$, the leaching temperature was 20–40°C, and constant blowing air was used around the reactor. The porous carbon felt cathode achieved 92.3% current efficiency. In this case, the current efficiency of non-stoichiometric manganese oxide leaching was approximately twice as high as the process with stainless steel and titanium flat cathodes with a similar surface area. The method with 96% manganese leaching efficiency provided the obtained $MnSO_4$ solution, and its purification allowed for the production of high-quality metallic manganese, manganese dioxide, and other manganese compounds.

The electro-reductive leaching of a low-grade manganese oxide ore suspension in sulfuric acid solution was studied using cyclic voltammetry (Elsherief, 2000). This study determined that the manganese was reduced on the ore-containing carbon paste electrode, while the leaching rate reached a maximum at 0 mV vs. the $Hg/Hg_2SO_4/K_2SO_4$ reference electrode. The acid concentration, temperature, and potential influenced the reaction rate and the level of manganese extraction from the ore. The following reactions occurred in the electro-reduction process:

$MnO_2 + 4H^+ + 2\bar{e} \rightarrow Mn^{2+} + 2H_2O$ (4)

$MnO_2 + H^+ + \bar{e} \rightarrow MnOOH$ (5)

$MnOOH + 3H^+ + \bar{e} \rightarrow Mn^{2+} + 2H_2O$ (6)

The presence of Fe^{2+} ions in the solution significantly increased the reaction rate owing to their participation in MnO_2 reduction (reaction 1), and the amount of manganese extracted during electrolysis was five times greater than during chemical leaching.

A surface response methodology was used for the optimization of manganese electro-reductive leaching from low-grade (19.15% Mn) pyrolusite (Zhang at al., 2015). An $FeSO_4{\cdot}7H_2O$ solution was used as a reductant, and the following optimal leaching conditions were established: $m(FeSO_4{\cdot}7H_2O)/m(ore) = 10$; $m(H_2SO_4)/m(ore) = 0.9$, a liquid-to-solid ratio of 0.7, a current density of 947 $A{\cdot}m^{-2}$, a leaching time of 180 min, and a leaching temperature of 73°C. Modeling of these conditions showed a Mn leaching efficiency of 94.1% compared to the experimental value of 95.7%, which proved the acceptability of the selected model.

An increase in the efficiency of manganese leaching from low-grade oxide ore using an electric field for the intensification of hydrometallurgical leaching was shown in the work by Zhang at al. (2017). The experimental results showed that the efficiency of Mn leaching was 98.2% under the following optimal conditions: 0.65 M $FeSO_4$, 1.6 M H_2SO_4, liquid-solid ratio of 5.5 $ml{\cdot}g^{-1}$, a current density of 900 $A{\cdot}m^{-2}$, and a temperature of 80°C. The reaction rate was controlled by the diffusion of the reagent in the product layer. During the leaching process, the Fe^{3+} ions that were generated as a result of iron oxidation on the surface of manganese dioxide were reduced back to Fe^{2+} under the influence of the electric field. This process provided a large amount of Fe^{2+} in the solution for reaction (4). In addition, cycling between Fe^{3+} and Fe^{2+} provided highly efficient manganese leaching and this process did not require additional reductants.

Considering factors such as the low cost of iron salts, the presence of iron in almost all manganese ores, and the increased efficiency of manganese extraction, the method of electro-reductive leaching of low-grade manganese oxide raw materials using the Fe^{3+}/Fe^{2+} redox system as a reductant raises the prospect of introducing this method into practice. However, the use of iron salt as a reductant will be accompanied by a key problem related to its permissible concentration in solution, which should not exceed 3.0 $g{\cdot}L^{-1}$ Fe^{3+}. This is due to the technical complexity of purifying manganese sulfate solution from iron. Thus, the difficulty lies in removing gelatinous iron hydroxides using an economically viable hydrolytic method by filtration from a solution with a relatively high concentration, which is practically impossible.

In this work, a large-scale laboratory electro-reductive leaching of manganese from residues (tailings) generated after the enrichment of manganese oxide ore from deposits in the Chiatura region in Georgia was conducted using a Redox system Fe^{3+}/Fe^{2+} as a mediator. In contrast to works described in references (Zhang at al., 2015 & 2017), we focused on (i) conducting the electro-reductive leaching within the limited concentrations of iron ions (<3.5 $g{\cdot}L^{-1}$) in the suspension, (ii) the design of the electrochemical reactor and a common plant, and (iii) choosing the cathode and anode materials. We also investigated the impacts of certain factors (liquid-to-solid ratio, sulfuric acid concentration, and electro-reductive leaching time) on the degree of manganese extraction, current efficiency, and electricity consumption.

MATERIALS AND METHODS

Materials

The object of the study was the residue (tailing) that remained after the mechanical enrichment of raw manganese ore from the deposits in the Chiatura region (Republic of Georgia), whose granulometric composition is provided in Table 1. In the experiment, we used 0.15–0.2 mm fraction of manganese-containing secondary raw material obtained after drying, grinding, and sieving of the waste (the chemical and phase composition are presented in Table 2 and Fig. 1.

According to the X-ray diffraction pattern, the following main phases were observed in the manganese ore enrichment residue (secondary raw material): SiO_2, $(Ca, Mn)_3Si_3O_9$, and β-MnO_2. X-ray fluorescence (XRF) analysis showed that the content of total manganese in the raw material was 18.1 % Mn, and the content of Mn (IV), which was determined by the oxalate method (Glover at al., 1989), was 25.78% MnO_2.

All solutions were prepared with distilled water. Sulfuric acid of 95% analytical purity and $Fe_2(SO_4)_3{\cdot}9H_2O$ salt were used.

Table 1. Granulometric composition of the tailing.

Fraction (mm)	<10	10÷7.0	7.0÷4.0	4.0÷2.2	2.2÷0.9	0.9÷0.25	<0.25
Mass (%)	15.3	3.44	8.42	25.16	26.24	18.22	2.22

Table 2. Chemical composition of the tailing.

Component	MnO_2	Mn	Si	Mg	Ca	Al	Fe	K	P	Ni	Others
Mass (%)	25.78	18.1	22.7	4.8	4.5	2.7	2.2	1.8	0.67	0.04	42.49

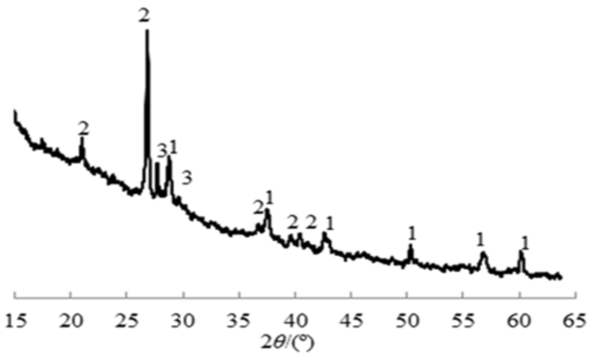


Figure 1. X-ray diffraction pattern of the manganese oxide raw material 1. β-MnO2 [ASTM-24-735]; 2. SiO2 [ASTM-5-490]; 3. (Ca, Mn)3 Si3O9 [ASTM-26-1066].

Electro-reductive leaching

The schematics of the electro-reductive leaching apparatus used for electro-reductive leaching of the residues generated during the enrichment of manganese oxide ores are shown in Fig. 2 (a, b).

The electro-reductive leaching apparatus consisted of three main interconnected units, namely, an electrochemical reactor, peristaltic pump, and a compressor. In the electrochemical reactors, an enhanced surface graphite felt electrode (GFE-1; PAN graphite felt), and thin wire (*d* = 0.35 mm) stainless steel mesh (AISI 304) were tested as the cathode, and the titanium plate mesh coated with titanium and ruthenium oxides as the anodes (ORTA). Electrolysis was conducted by the passage of direct current (DC) using a DC power supply-type rectifier (Power Station pe 1018; DC output: 15 V/200 A; plating electronic GmbH, Germany). A pH meter was used to conduct the leaching process at a constant pH value of 1, where the electrode was immersed in an intermediate tank outside the electrolyzer and 40% H_2SO_4 was added to maintain the pH value.

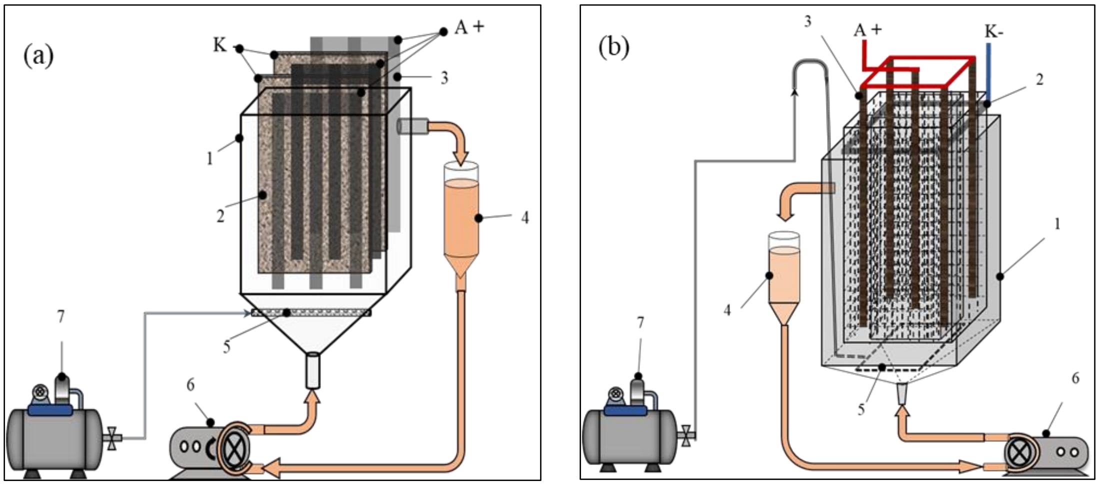


Figure. 2. Schematics of the electro-reductive leaching apparatus: 1. 5 L (a); 12.6 and 63 L (b) organic glass rectangular electrolyzer; 2. (a) – flat graphite felt cathodes; (b) – stainless steel mesh cathode; 3. titanium anodes, coated with titanium and ruthenium oxides; 4. intermediate tank; 5. compressed air supply pipe; 6. peristaltic pump; 7. compressor.

The electro-leaching process was monitored potentiometrically using a platinum electrode and saturated silver/silver chloride reference electrode, also in the intermediate tank. In a solution (pH = 1) with a limited concentration of Fe^{3+} ions (2.0–3.35 $g \cdot L^{-1}$), the platinum electrode potential varied within 0.66 ± 0.05 V (sat. Ag/AgCl). Towards the end of electro-reductive leaching, the platinum electrode potential shifted to a less positive value due to the practical depletion of manganese oxide in the raw material, and the increase in concentration of Fe^{2+} ions in the suspension as a result of electro-leaching. A shift in the platinum electrode potential to a less positive value indicated the end of the leaching, which was visually noticeable by the transition from the black color of the initial solution suspension to a light brown color.

To prepare the electrolyte, the required amounts of H_2SO_4 and $Fe_2(SO_4)_3 \cdot 9H_2O$ were added to the distilled water in the reactor equipped with a stirrer. The system was filled with the electrolyte, the peristaltic pump and compressor were simultaneously powered on, and compressed air was supplied to an air distributor, which was located horizontally at the bottom of the reactor. A pre-processed and weighed tailing sample (particle size of 0.15–0.20 mm) was supplied to the intermediate tank, while in hydrodynamic mode, the electrochemical reactor was connected to the direct-current circuit. After passing a certain quantity of electricity, the suspension was filtered using a vacuum filter, and the extracted manganese, iron, and sulfuric acid concentrations in the filtrate were determined by known chemical analysis methods.

Based on the analysis results, the percentage of manganese extraction (Q) was calculated according to the following formula:

$Q = m(\mathrm{Mn}^{2+})/m(\mathrm{Mn}_{(\mathrm{ore})} \cdot 100$ (%), (7)

where $m(\mathrm{Mn}^{2+})$ and $m(\mathrm{Mn}_{(\mathrm{ore})})$ denote the mass values of the manganese transferred to the solution and the manganese in the raw material sample, respectively (g).

As a rule, manganese-containing oxide raw materials, along with oxides of manganese (+4) oxidation, contain weakly oxidizable oxides. Therefore, to calculate the current efficiency of manganese according to the formula (Glover at al., 1989), we calculated the average oxidation number of manganese contained in the raw material ($\mathrm{MnO_n}$):

$$n = 1 + \frac{54.94}{86.94} \cdot \frac{Y}{X}\ , \quad (8)$$

where 54.94 and 86.94 denote the molar mass values of manganese and $\mathrm{MnO_2}$, respectively, Y is the $\mathrm{MnO_2}$ content determined by the oxalate method (%), and X is the total manganese content (%).

According to Formula (8) and based on the chemical composition of the raw materials (Y = 25,78%, X = 18.1%) used in the experiments, n = 1.9; i.e., the chemical formula of the non-stoichiometric oxide was $\mathrm{MnO_{1.9}}$ and the average oxidation state of manganese was 3.8. The reduction of non-stoichiometric oxide $\mathrm{MnO_{1.9}}$ to $\mathrm{Mn^{2+}}$ required 3.8–2 = 1.8 electrons.

Accordingly, the chemical equivalent of manganese was 54.94/1.8 = 30.52 g, while the electrochemical equivalent was k = 30.52/26.8 = 1.139 $\mathrm{g \cdot A^{-1} \cdot h^{-1}}$. According to Faraday's law, the current efficiency η of leached manganese can be calculated by

$$\eta = \frac{m}{k \cdot I \cdot \tau} \cdot 100\ (\%), \quad (9)$$

where m is the mass of manganese transferred to the solution during leaching (g), k is the electrochemical equivalent of 1.139 $\mathrm{g \cdot A^{-1} \cdot h^{-1}}$, I is amperes, (A), and τ is the leaching time (h). The specific energy consumption W ($\mathrm{W \cdot h \cdot g^{-1}}$), was calculated by the following formula:

$$W = \frac{V \cdot 100}{k \cdot \eta} \quad (10),$$

where V is the voltage across the electrolyzer (V).

Therefore, the cathodic current-voltage curves were recorded on these cathode materials in the aerated 50 $\mathrm{g \cdot L^{-1}}$ $\mathrm{H_2SO_4}$ solution with and without trivalent ferric ions in the stagnant and mobile solutions to determine the relationship between the electrochemical parameters (E-i_c) for the $\mathrm{Fe^{3+} + e \rightarrow Fe^{2+}}$ cathode reaction.

The cathodic current-voltage curves measured on the graphite felt cathode are shown in Fig. 3 (a, b). Fig. 3 (a), (curves 1 and 1') shows that the cathodic reduction process of hydrogen at the GFE in the background solution started at −0.5 V, and as expected due to the porosity of the GFE, the process proceeded with limited diffusion. In the unstirred background solution with trivalent ferric ions, a cathodic peak at +0.25 V was observed on the voltammograms (Fig. 3(b), curve 1), which shifted sharply in the cathodic direction in the stirred solution (Fig. 3(b), curve 1') and i_c (the cathodic current) increased significantly. Oscillation of the cathodic current was likely due to the limited diffusion of the ferric ions into the felt pores, which was affected by the rate of stirring. Notably, in the iron-containing solution, the hydrogen evolution potential at the felt changed in the cathodic direction and started at −0.8 V, in contrast to the background solution.

Volt-amperometric study

The electro-reductive leaching of the ore enrichment tailing through the $\mathrm{Fe^{3+}/Fe^{2+}}$ redox system as a mediator was studied according to the voltammetric technique using a Russian voltammeter. The complex equipment consisted of a potentiostat PI-50-1.1 and ПР-8 program support (Russia).

Voltametric measurements were conducted in a three-electrode glass cell with a GFE-1 (dimensional surface 1 $\mathrm{cm^2}$) and stainless steel (AISI 304) mesh (1 $\mathrm{cm^2}$) as the working electrodes, with a platinum plate (4 $\mathrm{cm^2}$) as the auxiliary electrode, and a saturated silver/silver chloride electrode as the reference electrode at room temperature.

Analytical methods

Folgard's method was used to determine the manganese ion concentration in the solution, and permanganate titration was used to determine the $\mathrm{Fe^{3+}}$ and $\mathrm{Fe^{2+}}$ ion concentrations (Kreshkov, 1976). XRF analysis of the manganese oxide raw material was performed using a Delta-Analyzer (Innov-X Systems, USA), and X-ray phase analysis was conducted using DRON-3 (Russia) with copper anode K_α emission, λ = 1.54184 Å.

RESULTS AND DISCUSSION

To ensure the high efficiency of electro-reductive leaching from low-grade manganese oxide raw materials using an $\mathrm{Fe^{3+}/Fe^{2+}}$ redox system, it is important to choose highly conductive cathode material with high mechanical and corrosion resistance on which the reductant $\mathrm{Fe^{2+}}$ is electrically generated at high speeds. Notably, it is important that the cathode occupy more space in the electrolyzer to increase the contact rate with the slurry, resulting in higher specific gravity and less movement restriction of the suspension.

According to the general kinetics of heterogeneous electrochemical reactions (Bard & Faulkner, 2001), the larger the cathode, the higher the current and the faster the rate of reaction. Therefore, to increase the reaction rate, cathodic materials should be used with a developed surface, i.e., graphite felt due to its high porosity, and stainless steel wire mesh.

In patent (Shengelia at al., 2019), a graphite felt cathode was used in the electro-reductive leaching of high-grade (48%–53% Mn) manganese oxide ore.

The graphite felt cathode was found to be approximately twice as effective in the leaching process due to its high porosity and low resistance to suspension, compared to the flat titanium and stainless steel cathodes.

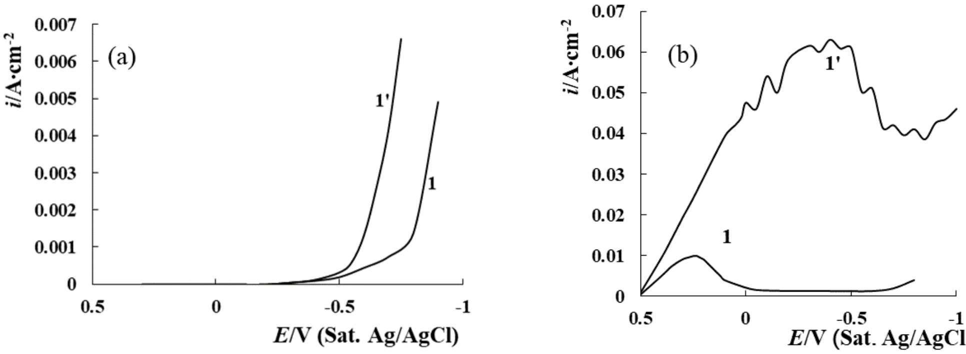


Figure. 3. Cathodic polarization curves (scan rate v=60 mV·min-1) taken on the GFE-1 electrode (dimensional surface 1 cm2) in the aerated solution: (a) background solution of 50 g·L−1 H2SO4; (b) solution of 50 g·L−1 H2SO4 + 2 g·L−1 Fe3+; Curve 1 – unstirred solution; Cuvre1' – stirred solution (magnetic stirrer)

Similar voltage–current curves were obtained for the stainless steel mesh cathode (Fig. 4, a and b).

Similar to the graphite felt cathode, the cathodic reduction of ferric ions occurred on the stainless steel mesh electrode in diffusion mode; however, the hydrogen evolution potential coincided with the potential obtained in the background solution and started at −0.43 V ÷ −0.45 V. Current oscillation was observed in the stirred solutions at high currents, which was most likely related to changes in solution hydrodynamics.

A comparison of the cathodic voltage-current curves showed that the rate of reduction of the ferric ions on the GFE was much higher than on the stainless steel mesh electrode, which was probably due to the felt structure and high porosity, owing to the increased surface area. Notably, no direct manganese dioxide reduction reaction (3) was observed in the voltage-current curves obtained using the stainless steel mesh electrode with the anodically electrodeposited manganese dioxide in the background solution of 50 $g \cdot L^{-1}$ H_2SO_4. Therefore, on both the graphite felt and stainless steel mesh cathodes, in a solution of 50 $g \cdot L^{-1}$ H_2SO_4 + 2 $g \cdot L^{-1}$ Fe^{3+}, cathodic reduction of trivalent ferric ions occurred in the diffusion regime (under limited concentrations of Fe^{3+}) and the rate of generation of the Fe^{2+} reducing agent was dependent on the solution stirring rate.

The requirement for a limited concentration of Fe^{3+} in the leaching solution and the voltammetry results showed that for the intensification of the electro-reductive leaching of the raw material using the Fe^{3+}/Fe^{2+} redox system, it was necessary to ensure a high stirring rate of the solution and the use of high surface area cathodes.

To ensure the electro-leaching efficiency of the Fe^{3+}/Fe^{2+} redox system, the following technical solutions should be implemented, namely, a) the use of a peristaltic pump and a compressor for the circulation of the electrolyte-suspension in the electrochemical reactor, and strong turbulence, b) equipping the electrochemical reactor with high surface graphite felt electrode, or high surface stainless steel mesh cathode, and c) outflowing the suspension from the electrochemical reactor through the porous graphite felt cathode or stainless steel mesh cathode into the intermediate tank.

Based on the preliminary experiments, we established that under a solid-to-liquid ratio of 0.08 $kg \cdot L^{-1}$, intensive turbulence (boiling) of the suspension in the electrolyzer was achieved through the air inflow from the compressor. With this in mind, volumes of circulating electrolytes in the electro-recovery reactors in large-scale laboratory experiments have been selected.

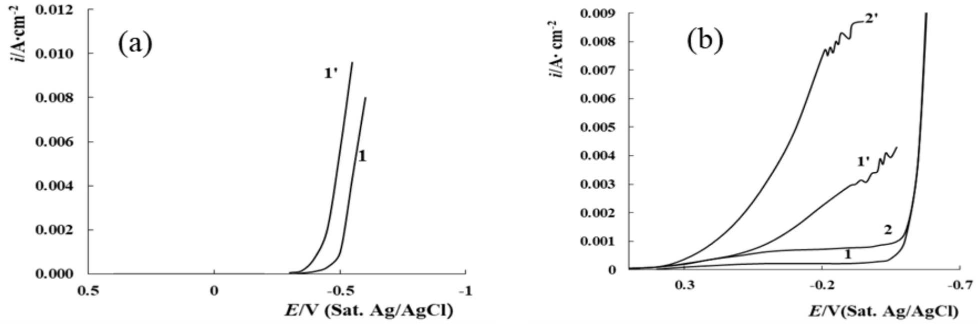


Figure. 4. Cathodic volt-ampere curves (v=60 mV·min-1) taken on the stainless steel AISI 304 mesh electrode (dimensional surface 1 cm2) in the aerated solution: (a) background solution of 50 g·L−1 H2SO4; (b) solution of 50 g·L−1 H2SO4 + 1 g·L−1 Fe3+ (Curve 1, 1'), and solution of 50 g·L−1 H2SO4 + 2 g·L−1 Fe3+ (Curve 2, 2'); Curves 1, 2- unstirred solution; Curves 1', 2'- stirred solution (magnetic stirrer).

Electro-reductive leaching using the GFE-1 cathode

Electro-reductive leaching of the low-grade manganese oxide raw materials (manganese ore enrichment tailing) mediated by the Fe^{3+}/Fe^{2+} redox system was conducted in the electrolyzer, as shown in Fig. 2 (a). The GFE-1 attached to an organic glass frame was used as the cathode with a total dimensional surface of 5 dm^2, and the pH level in the sulfuric acid solution was maintained within 1 by adding acid (*t* = 25°C).

The pre-processed and weighed raw material sample was supplied to the intermediate tank, through a peristaltic pump and compressed air, and powerful turbulence and circulation of the suspension were achieved in the electrolyzer. The solid/liquid ratio in the suspension varied between 0.08 kg·L^{-1} and 0.12 kg·L^{-1}. When the power was turned on (I = 3A,), the potential of the graphite cathode in galvanostatic mode initially changed within −700 ± 50 mV with respect to the saturated Ag/AgCl and changed over time in the negative direction −1.1 ÷ −1.3 V, Ag/AgCl.

The experimental data are provided in Table 3, and new, unused graphite felt electrodes were used in each experiment.

The data (experiments 1, 2) in Table 3 showed that electro-reductive leaching occurred at a constant current of 3.0 A, Therefore, during electro-reductive leaching, the reduction of the active surface for Fe^{2+} electro-generation, the shift in the cathode potential in the negative direction, and the increase in where leaching initially proceeded under a low voltage (2.45 ÷ 2.5 V). The manganese extraction rate was 94.6 ÷ 93.6%, while the current efficiency was 80.2 ÷ 79.3%, and the electricity consumption 3.1–3.2 W·h·g^{-1}. In a relatively high solid/liquid ratio suspension, the bath voltage was high and the power consumption significantly increased to 6.2 W·h·g^{-1} (Table 3, experiment 3). Re-use of the graphite felt cathodes in the electro-leaching processes was virtually impossible, because the felt pores were sealed with the solid extruded particles that could not be completely washed off with water, causing the voltage on the electrolyzer to increase to 10 V after 3 to 4 experiments.

voltage over time (≥ 4.92 V) made it unreasonable to use the graphite felt in the low- quality ore suspension.

Table 3. Average data from the 3 electro-reductive leaching experiments of the tailing using the GFE-1 cathode. The electrolysis conditions were as follows: a solution volume of 5 L, pH of 1, I=3A, ic=0.6 A·dm−2, ia=0.8 A·dm−2, and t=25°C.

Exp. number	Solution composition / g·L^{-1}	Solution composition at the end of experiment/ g·L^{-1}	$m_{(sample)}$/g	m_{Mn}/g	q/A·h	V/ V	Q_{Mn}/%	η_{Mn}/%	W/ W·h·g^{-1}
1	Fe^{3+} – 2.7 H_2SO_4 – 18.2	Fe^{3+} – 3.05 H_2SO_4 – 16.8 Mn^{2+} – 3.7	400	68.5	75	2.45	94.6	80.2	3.1
2	Fe^{3+} – 2.7 H_2SO_4 – 20.2 Mn^{2+} – 6.44	Fe^{3+} – 2.83 H_2SO_4 – 18.3 Mn^{2+} – 20.0	400	67.8	75	2.5	93.6	79.3	3.2
3	Fe^{3+} – 2.7 H_2SO_4 – 20.2 Mn^{2+} – 6.44	Fe^{3+} – 2.94 H_2SO_4 – 17.6 Mn^{2+} – 20.6	600	80.8	105	4.2	74.4	67.5	6.2

Electro-reductive leaching using the AISI 304 stainless steel mesh cathode

Electro-reductive leaching of the manganese oxide raw material using the AISI 304 stainless steel mesh cathode was conducted according to a large-scale laboratory testing method, where the working volumes of the electro-leaching devices were 12.6 L and 63 L (Fig. 2, b).

AISI 304 stainless steel was selected as the cathode material due to its corrosion resistance (25.83 g·L−1 Mn2++ 3.0 g·L−1 Fe3++ 20.28 g·L−1 H2SO4). No change in the mass of the stainless steel mesh was observed for 1 month.

The value of the current was chosen as an effective load for the electrolyzers in a circulated solution of 2.5 g·L−1 Fe3++20 g·L−1 H2SO4 (without the solid phase of the leaching raw material) and air inflow from the compressor, during which gaseous hydrogen did not form at the mesh cathode, because the current was practically spent on Fe3+ reduction. Considering the dimensional surface of the cathode, the current density was 0.6 A·dm−2.

Titanium plate mesh was used as the anodes, with a surface that was modified with titanium and

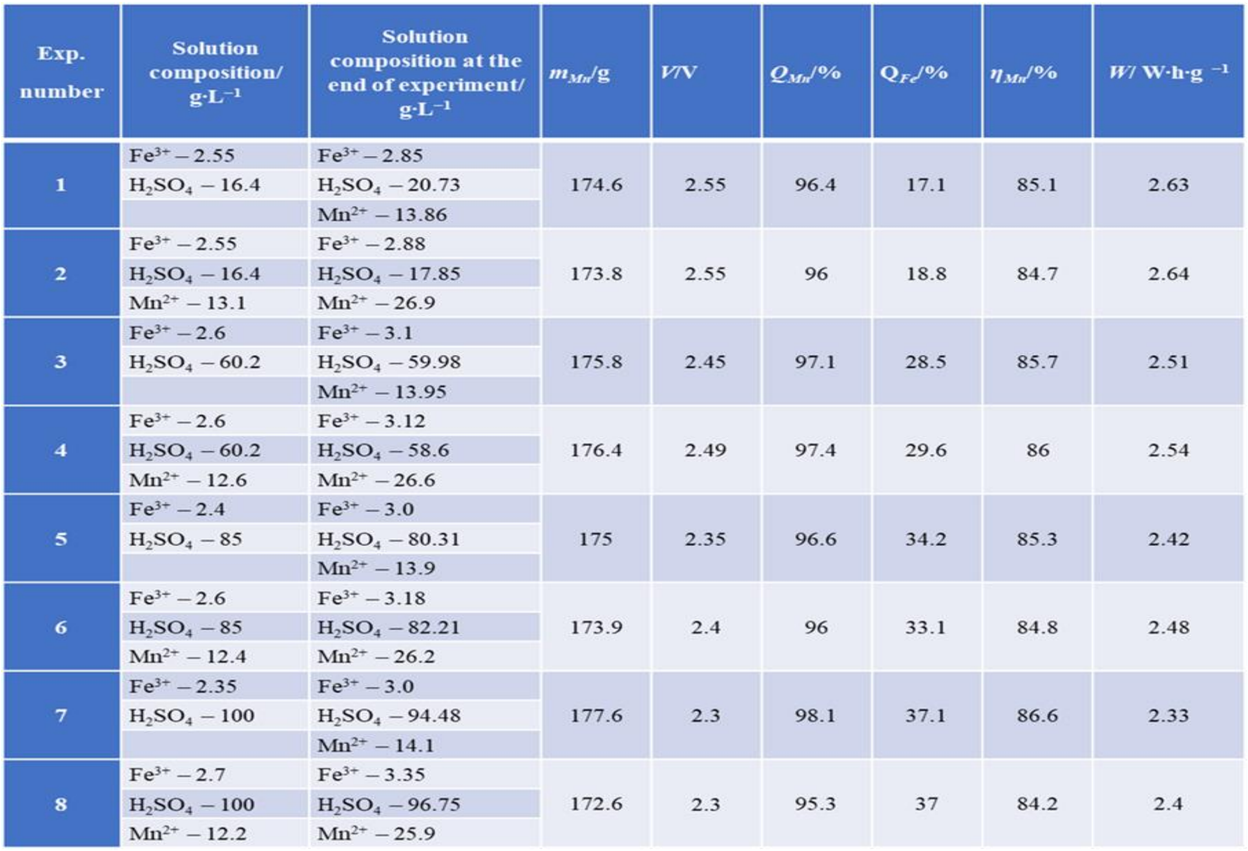
ruthenium oxides. The anodes, unlike the lead anodes, which have been widely used in hydrometallurgy, did not contaminate the suspension with lead ions and had a lower overpotential of oxygen evolution. Hence, they practically did not affect the voltage. There was only the threat of electrogenerated Fe2+ ions appearing at the anodes through convection causing oxidation. However, the presence of the ore suspension in the entire reactor minimized this effect, which was confirmed by the experimental data presented in Table 4 below.

Table 4 shows that the use of the stainless steel mesh cathode provided a high manganese extraction rate (96.0–98.1%) and relatively lower current efficiency (84.2–86.6%). Voltage in the electrolyzer was affected by the concentration of sulfuric acid in the solution (Table 4, experiments 1–8). The initial concentration of acid in the solution was maintained during the leaching process, either by pH control, or through analysis of the acid content in the solution.

Table 4 shows that although in the suspension containing a relatively higher concentration of acid (85–100 g·L−1 of H2SO4) the electro-reductive leaching of the raw material took place at a low voltage 2.3÷2.4 V and consequently at a low power consumption 2.33 ÷ 2.48 W·h·g−1, filtration of the viscous suspension containing manganese sulfate was virtually impossible due to the large amount of less soluble calcium sulfate that was produced in the suspension by the dissolution of ore in the acid. In solutions with a lower concentration of acid (< 60.2 g·L−1 of H2SO4), the manganese extraction rate was 96%, current efficiency was 84.7%, and the electricity consumption was 2.64 W·h·g−1 (Table 4, experiment 2). Under these conditions, the suspension obtained after leaching could be easily filtered, in contrast to the suspension that contained high concentrations of sulfuric acid. The effect of solid/liquid ratio in the leaching suspension on the electrochemical reactor voltage was clearly indicated by the data in Table 5, which showed that despite the increase in acid concentration, the voltage in the high-density suspension (solid /liquid ratio 0.16 kg·L^{-1}) with the same quantity of electricity (180 A·h) was higher, similar to the low-density suspension (Table 4). Consequently, the electricity consumption was higher compared to the results obtained in the lower density suspension (Table 5, experiments 1–4). Passage of twice as much electricity in the high-density suspension led to an increase in the manganese extraction rate of up to 95.3%; however, owing to the high voltage, the electricity consumption increased to 4.4 W·h·g^{-1} (Table 5, experiment 5).

The experimental results showed that increasing solid/liquid ratio in the suspension led to an increase in the voltage on the electrolyzer; thus, increasing the power consumption and complicating the filtration process of the suspension due to the high rate of manganese extraction. Therefore, for electro-reduction leaching of low-quality manganese raw materials, it would be advisable that the solid/liquid ratio in the suspension was 0.08 kg· L^{-1}; i.e., with intensive turbulence of the suspension, there was so-called boiling in the electrolyzer and relatively low acid concentrations, of approximately 15–20 g·L^{-1} H_2SO_4 (pH of 1).

Table 4. Results of electro-reductive leaching of the tailing using the AISI 304 stainless steel mesh cathode in a suspension containing sulfuric acid with various concentrations, where the electrolysis conditions were as follows: raw material mass of 1000 g, a solution volume of 12.6 L, solid/liquid ratio = 0.08 kg·L−1, I=20A, ic=0.6 A·dm−2, ia=0.8 A·dm−2, q=180 A· h, and t=25°C.



Exp. number	Solution composition/ g·L^{-1}	Solution composition at the end of experiment/ g·L^{-1}	m_{Mn}/g	V/V	Q_{Mn}/%	Q_{Fe}/%	η_{Mn}/%	W/ W·h·g $^{-1}$
1	Fe^{3+} – 2.55 H_2SO_4 – 16.4	Fe^{3+} – 2.85 H_2SO_4 – 20.73 Mn^{2+} – 13.86	174.6	2.55	96.4	17.1	85.1	2.63
2	Fe^{3+} – 2.55 H_2SO_4 – 16.4 Mn^{2+} – 13.1	Fe^{3+} – 2.88 H_2SO_4 – 17.85 Mn^{2+} – 26.9	173.8	2.55	96	18.8	84.7	2.64
3	Fe^{3+} – 2.6 H_2SO_4 – 60.2	Fe^{3+} – 3.1 H_2SO_4 – 59.98 Mn^{2+} – 13.95	175.8	2.45	97.1	28.5	85.7	2.51
4	Fe^{3+} – 2.6 H_2SO_4 – 60.2 Mn^{2+} – 12.6	Fe^{3+} – 3.12 H_2SO_4 – 58.6 Mn^{2+} – 26.6	176.4	2.49	97.4	29.6	86	2.54
5	Fe^{3+} – 2.4 H_2SO_4 – 85	Fe^{3+} – 3.0 H_2SO_4 – 80.31 Mn^{2+} – 13.9	175	2.35	96.6	34.2	85.3	2.42
6	Fe^{3+} – 2.6 H_2SO_4 – 85 Mn^{2+} – 12.4	Fe^{3+} – 3.18 H_2SO_4 – 82.21 Mn^{2+} – 26.2	173.9	2.4	96	33.1	84.8	2.48
7	Fe^{3+} – 2.35 H_2SO_4 – 100	Fe^{3+} – 3.0 H_2SO_4 – 94.48 Mn^{2+} – 14.1	177.6	2.3	98.1	37.1	86.6	2.33
8	Fe^{3+} – 2.7 H_2SO_4 – 100 Mn^{2+} – 12.2	Fe^{3+} – 3.35 H_2SO_4 – 96.75 Mn^{2+} – 25.9	172.6	2.3	95.3	37	84.2	2.4

Table 5. Results of electro-reductive leaching of the tailing using the AISI 304 stainless steel mesh cathode in a suspension containing sulfuric acid with various concentrations, where the electrolysis conditions were as follows: raw material mass of 2000 g, a solution volume of 12.6 L, solid/liquid ratio = 0.16 kg·L−1, I=20A, ic=0.6 A·dm−2, ia=0.8 A·dm−2, and t=25°C.

Exp. number	Solution composition/ g·L^{-1}	Solution composition at the end of experiment/ g·L^{-1}	*q*/A·h	m_{Mn}/ g	*V*/V	Q_{Mn}/%	Q_{Fe}/%	η_{Mn}/%	*W*/ W·h·g $^{-1}$
1	Fe^{3+} – 2.55	Fe^{3+} – 2.95	180	176.4	3.95	48.7	11.4	86	4.03
	H_2SO_4 – 16.4	H_2SO_4 – 18.46							
	Mn^{2+} – 13.1	Mn^{2+} – 27.1							
2	Fe^{3+} – 2.6	Fe^{3+} – 3.18	180	177.6	3.85	49	16.5	86.6	3.9
	H_2SO_4 – 60.2	H_2SO_4 – 58.67							
	Mn^{2+} – 12.6	Mn^{2+} – 26.7							
3	Fe^{3+} – 2.6	Fe^{3+} – 3.22	180	177.7	3.8	49.1	17.7	86.6	3.85
	H_2SO_4 – 85	H_2SO_4 – 78.37							
	Mn^{2+} – 12.4	Mn^{2+} – 26.5							
4	Fe^{3+} – 2.7	Fe^{3+} – 3.44	180	178.9	3.9	49.4	21.1	87.2	3.92
	H_2SO_4 – 100	H_2SO_4 – 96.23							
	Mn^{2+} – 12.2	Mn^{2+} – 26.4							
5	Fe^{3+} – 2.55	Fe^{3+} – 3.43	360	345.2	4	95.3	25.1	84.2	4.4
	H_2SO_4 – 16.4	H_2SO_4 – 17.6							
	Mn^{2+} – 13.1	Mn^{2+} – 40.5							

Tables 4 and 5 show that the concentration of acid increased to 20–100 g·L^{-1} at a constant pH, which resulted in 95–98% manganese extraction from the raw material, while only 20–42% of iron was transferred to the solution from the raw material, and its content did not exceed the allowable concentration of iron (3.5 g·L^{-1} Fe^{2+}). This was probably due to the low iron content in Georgian ores.

Based on the obtained data, the main reactions of electro-reduction discharge of the manganese oxide raw material suspension in the reactor using the Fe^{3+}/Fe^{2+} system as a mediator could be expressed as follows:

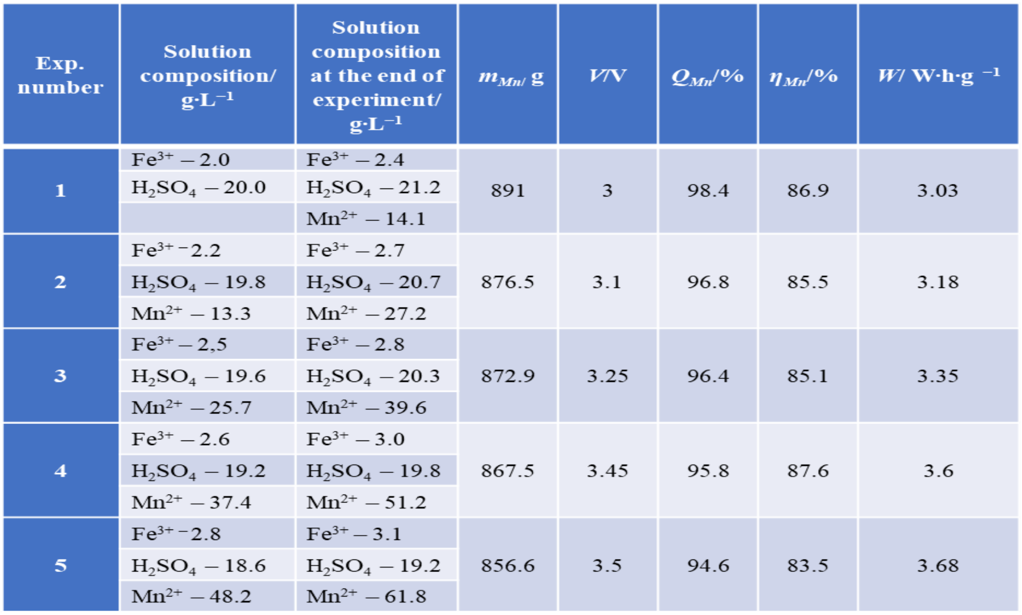
cathode: $4Fe^{3+} + 4\,\bar{e} \rightarrow 4Fe^{2}$, (6)
anode: $2H_2O - 4\,\bar{e} \rightarrow 4H^{+} + O_2$, (7)
total reactions: $4Fe^{3+} + 2H_2O \rightarrow 4Fe^{2+} + O_2$, (8)
$2Fe_2(SO_4)_3 + 2H_2O \rightarrow 4FeSO_4 + 2H_2SO_4 + O_2$, (9)
and in the suspension:
$MnO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$. (10)

A certain amount of H_2SO_4 was spent on the dissolution of the carbonates and some silicates were present in the raw material. Based on the data (Table 4) obtained by the electro-reduction leaching the manganese oxide raw material (18.1% Mn), a series of experiments was conducted to prepare a solution of 50–60 g·L^{-1} of Mn^{2+} using a larger (63 L) electrolyzer, where current was tripled (60 A) under similar leaching conditions: solid/ liquid ratio of 0.08 kg·L^{-1}, i_c = 0.6 A·dm^{-2}, i_a = 0.8 A·dm^{-2}, pH of 1, and t = 25°C. Initially, the suspension for electro-reductive leaching contained 63 L of electrolyte (20 g·L^{-1} H_2SO_4 + 2.0 g·L^{-1} Fe^{3+}) and 5 kg of raw material. The process took about 15 h.

The experiments were conducted in a device (Fig. 2 (b)) under intense circulation (boiling) of the suspension, which was provided by a 0.05 kW peristaltic pump (VANTAGE 3000, VENDER LIMITEX, UK) and 2.2 kW compressor (REM POWER E 401/9/100, Germany).

To prepare the 50–60 g·L^{-1} solution, it was necessary to carry out 5 consecutive electro-reductive processes. In each experiment, the suspension obtained after processing of the three portions of a five-kilogram raw materials was filtered through a Nutsche filter. The filtrate was adjusted with wash water from the accumulated sludge and used in subsequent experiments to obtain a concentrated solution. Similar procedures were performed sequentially in all subsequent experiments. The results for the series of experiments to obtain concentrated manganese solution are provided in Table 6.

Table 6. Data of series of experiments to obtain a concentrated solution of manganese through electro-reductive leaching of the tailing where the electrolysis conditions were as follows: raw material mass of 5000 g, a solution volume of 63 L, solid/liquid ratio = 0.08 kg·L−1, I=60A, ic=0.6 A·dm−2, ia=0.8 A·dm−2, q=900 A·h and t=25°C.



Exp. number	Solution composition/ g·L^{-1}	Solution composition at the end of experiment/ g·L^{-1}	m_{Mn}/ g	V/V	Q_{Mn}/%	η_{Mn}/%	W/ W·h·g $^{-1}$
1	Fe^{3+} – 2.0 H_2SO_4 – 20.0	Fe^{3+} – 2.4 H_2SO_4 – 21.2 Mn^{2+} – 14.1	891	3	98.4	86.9	3.03
2	Fe^{3+} –2.2 H_2SO_4 – 19.8 Mn^{2+} – 13.3	Fe^{3+} – 2.7 H_2SO_4 – 20.7 Mn^{2+} – 27.2	876.5	3.1	96.8	85.5	3.18
3	Fe^{3+} – 2,5 H_2SO_4 – 19.6 Mn^{2+} – 25.7	Fe^{3+} – 2.8 H_2SO_4 – 20.3 Mn^{2+} – 39.6	872.9	3.25	96.4	85.1	3.35
4	Fe^{3+} – 2.6 H_2SO_4 – 19.2 Mn^{2+} – 37.4	Fe^{3+} – 3.0 H_2SO_4 – 19.8 Mn^{2+} – 51.2	867.5	3.45	95.8	87.6	3.6
5	Fe^{3+} –2.8 H_2SO_4 – 18.6 Mn^{2+} – 48.2	Fe^{3+} – 3.1 H_2SO_4 – 19.2 Mn^{2+} – 61.8	856.6	3.5	94.6	83.5	3.68

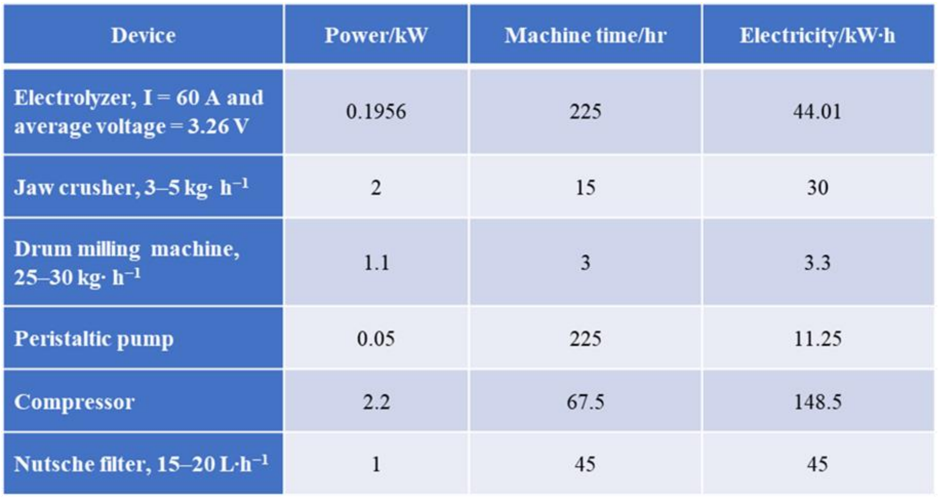
In each experiment, the suspension obtained after processing three portions of a five-kilogram raw material was filtered through a suction filter.

As a result of serial tests, 180 L of a solution containing 61 g·L^{-1} Mn^{2+} was obtained. 75 kg of raw material (18.11% Mn) was processed during 225 h, 54.1 L of 40% H_2SO_4 was used to maintain the pH of 1 in the suspension during the leaching process. Through extraction of manganese from raw materials amounted to 81.3%, while the acid extraction in the form of manganese sulphate was 69.1%. The total amount of electricity consumed was 282.06 kW h, including 44.01 kW·h spent on the electro-reductive leaching process (Table 7).

According to the data from the large-scale laboratory experiment, the total specific electricity consumption for processing the raw materials containing 18.1% Mn was 282.06/75x1000 = 3760.8 kW·h·t^{-1}, of which 15.6% (586.8 kW·h·t^{-1}) was spent on the electro-reductive leaching process.

After electro-reductive leaching, the filtration and drying of the light-yellow sludge remained (mass percent values: SiO_2: 46.2; BaO: 11.4; SO_3: 8.1; Fe_2O_3: 3.6; Al_2O_3: 3.4; CaO: 2.7; MnO_2: 2.5; K_2O: 2.0; others: 20.1), which has been tested in a laboratory for use as an additive for cement. Assessments of the physical and mechanical properties of the cement samples, namely, the grinding size, hardening time, and strength, were conducted according to the European standard EN 197-1: 2017. Testing showed that the optimal additive of the leached waste in the cement was within the range of 10–20%.

Table 7. Consumption of electricity in the series of experiments.



Device	Power/kW	Machine time/hr	Electricity/kW·h
Electrolyzer, I = 60 A and average voltage = 3.26 V	0.1956	225	44.01
Jaw crusher, 3–5 kg· h^{-1}	2	15	30
Drum milling machine, 25–30 kg· h^{-1}	1.1	3	3.3
Peristaltic pump	0.05	225	11.25
Compressor	2.2	67.5	148.5
Nutsche filter, 15–20 L·h^{-1}	1	45	45

CONCLUSIONS

The graphite felt (GFE-1) and AISI 304 stainless steel mesh were tested as the cathode material in the electro-reductive leaching process of the 18.1% Mn residues (Chiatura, Georgia) using an Fe^{3+}/Fe^{2+} redox system. The volt-ampere method showed that the electrogeneration of Fe^{2+} on the graphite felt cathode occurred at a higher rate compared to the stainless steel mesh cathode. However, it was virtually impossible to use the GFE-1 cathode in electro-reductive leaching of the suspension consisting of the low-grade manganese raw material, since the felt pores were clogged with insoluble silicates and sand particles. Under optimal conditions for electro-leaching of the low-grade manganese raw material using the stainless steel mesh cathode, a high manganese extraction rate (96.0–98.1%) and current efficiency as 84.2–86.6% were achieved, while only 20–42% of iron was transferred to the solution from the raw material and its content did not exceed the allowable concentration of iron (3.5 $g\cdot L^{-1}$ Fe^{3+}). During large-scale laboratory testing of electro-reductive leaching, processing of 75 kg (18.1% Mn) of oxide raw material produced 180 L of solution containing 61 $g\cdot L^{-1}$ Mn^{2+}. The total electricity consumption was 282.06 kW·h, of which 15.6% (44.01 kW·h) was spent on electro-reductive leaching.

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COMPLIANCE WITH ETHICAL STANDARDS STATEMENTS

Ethical Approval: The authors are responsible for the novelty and reliability of the research results presented in the manuscript. Similar works in the scientific literature are thoroughly discussed and cited, and no copyrights are violated.
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AUTHORSHIP: We attest that all authors contributed significantly to performing of research works and to preparing the manuscript.

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