

Electrolytic manganese obtaining from product solution of manganiferous ore of deposit “Karamola”

Makhanbetov A. B., Zharmenov A.A., Baeshov A. B.

*Laboratory of Electrochemical Production Technology,
RSE National Center on Complex Processing of Mineral Raw Materials of the Republic of
Kazakhstan,
Almaty, Republic of Kazakhstan
Email: armanmab@mail.ru*

Abstract

The electrolysis bath for manganese electrolysis was made. The influence of electrolysis parameters on cathodic reduction of metal was investigated in this bath. The optimum on composition and structure diaphragm material, which allowed regulating of ions exchange in electrolytic solution, was selected for an electrolysis bath in order to normalize pH media of a catholyte and, therefore, to electrolyze for longer time.

As a result of the conducted researches, data on cathodic current density, electrolyte temperature and electrolysis duration influence on current output were obtained.

The electrolytic manganese was obtained from manganiferous ore of Kazakhstan deposit “Karamola” consisting of impurity and with the following composition: Mn 15.18; CaO 1.38; Ni 0.007; SiO₂ 64.72; Al₂O₃ 2.37; Fe 1.24; Co 0.004; P 0.051; Zn 0.011; As <0.002; MgO 0.50. Quality of obtained manganese was evaluated by means of scanning electron microscopy (SEM) and element analysis.

Key words: MANGANESE, ELECTROLYSIS, MANGANIFEROUS ORE, CATHODIC REDUCTION, ELECTROLYTIC MANGANESE

Introduction

Special properties of each metal depend directly on its purity. In this regard, the properties of some metals came to be known only after obtaining of them in especially pure form. Development of electrochemical methods gave opportunities for solution of such problems from technical, theoretical and ecological standpoint. It is also known [1] that some especially pure metals are obtained by this method only. Manganese also belongs to such metals. The superpurity metal manganese is obtained by electrolysis in aqueous media only; and it is seen from literary data [2, 3, 4] that none of other known methods is capable to compete with this method.

The application area of manganese is very wide.

It is known that the main consumer of manganese ores is ferrous metallurgy, where about 90% of the produced commercial manganese is used. At the same time, consumption of this metal grows in other spheres of its application.

Metal manganese possesses the excessive hardness and brittleness; therefore, it is not used in pure form. Pure manganese is added to alloys composition as the alloying element. Depending on the quantity of added manganese, it is possible to obtain up to 200 types of stainless steel. Therefore, the suggested work gives opportunities to find the solution of relevant problems.

Electrolysis of manganese and its researches were conducted with use of sulphate solution of ore of the

Karamola deposit near to the city Alakol of Almaty Region of the Republic of Kazakhstan. This ore differs by composition, %: Mn 15.18; CaO 1.38; Ni 0.007; SiO₂ 64.72; Al₂O₃ 2.37; Fe 1.24; Co 0.004; P 0.051; Zn 0.011; As <0.002; MgO 0.50.

The analysis of literary data showed that the content of such elements as iron and phosphorus as a part of this ore is less in comparison with other manganese ores of Kazakhstan [5]. This difference gives the chance to reduce a stage of special removal of the specified impurities in process of hydrometallurgical ore processing.

Experimental

The researches on manganese electrolysis in sulphate solution were carried out in the laboratory electrolysis bath (Fig. 1), which was made of organic glass, with the general operating volume of 8.97 ~ 9 dm³ (1). 4.61 dm³ of volume belong to anode area, 4.36 dm³ of volume - to cathodic area, i.e. C:A ratio = 1:1.06.

The top layer of an electrolysis bath consists of a rectangular prismoidal knock-down box (2), where

cathodic and anodic cells are connected by special screws. The lower part consists of false bottom (3) for introduction of solution or residual matter and their easy underflow.

Anode and cathode spaces are divided by flowing diaphragm (4).

Stability of operating volume of bath electrolysis is carried out via the crane (5) providing continuous underflow of utilized solution.

The cathode (6) consists of 2 mm in thickness titanium plate located in cathodic cell. Perforated plates from rolled lead containing 1% of Ag were used as the insoluble anode (7). Perforation was stenciled by Ø5 mm drill in such a way that the active area of the anode was 70% from the cathode active area. Anodes were installed on both sides from diaphragm at equidistance from the cathode. The current supply to the cathode and anodes was carried out by means of terminals with screw clamps. The anode current density could be controlled by anodes movement at one or another depth of steeping into solution.

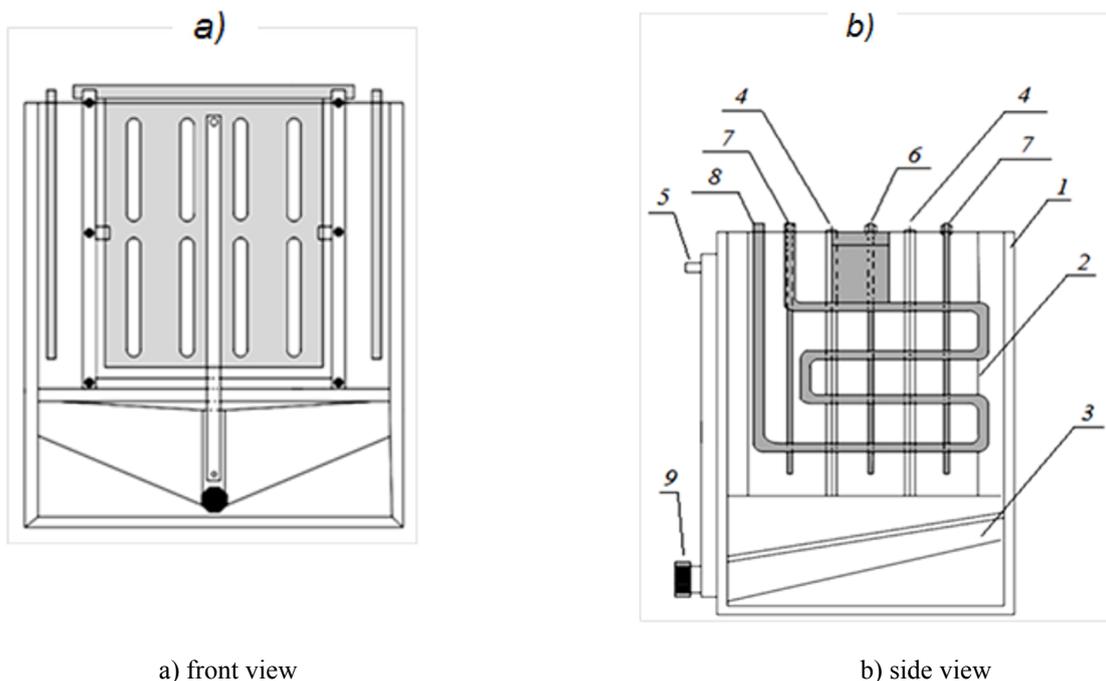


Figure 1. Electrolysis bath for manganese electrolysis

The plate coils, which were placed lengthwise of the bath (perpendicular to the plane of electrodes), were made from the quartz tube of Ø8 mm in order to maintain the temperature of solution. The flowing water was pumped through these coils.

At the end of electrolysis, electrolyte and residual matter are removed by the special crane (9).

Results and discussion

Electrolysis of manganese is carried out under fol-

lowing conditions:

- composition of an electrolyte, g/dm³: [(NH₄)₂SO₄] – 160, [Mn²⁺] – 35;

- impurities as a part of an electrolyte, g/dm³: Sb, Fe, Co < 0,001; As 0.0013; Zn 0.0014; Cu 0.0034; Ni 0.0062;

- pH of electrolyte: 7;

- volume rate of solution feeding, ml/(A·h): 44;

One of the main factors influencing the system sta-

bility is diaphragm role during manganese electrolysis. Material of a diaphragm controls the exchange of ions as a part of electrolyte and gives opportunities to electrolyze for a long time. Therefore, in case of the specified electrolysis parameters maintaining, influence of diaphragm materials on the cathode reduction

of manganese and on experiment duration was investigated.

Before and after each experiment in certain sequence, the value pH of solutions under investigation is measured by iontometer I 500 of Akvilon.

Table 1. Influence of diaphragms on manganese electrolysis

| Experiment No | Diaphragm type | Experiment time, h. | Initial pH of electrolyte | | Final pH of electrolyte | | Current Output, % |
|---------------|----------------|---------------------|---------------------------|-----------------|-------------------------|-----------------|-------------------|
| | | | pH _c | pH _a | pH _c | pH _a | |
| 1 | TFP-92 | 6 | 6,71 | 6,74 | 8,67 | 1,41 | 60,75 |
| 2 | Item 0498 | 6 | 6,74 | 6,83 | 8,67 | 1,52 | 72,25 |
| 3 | PVC | 6 | 6,83 | 6,90 | 8,23 | 1,84 | 63,26 |
| 4 | KS-34 | 6 | 6,92 | 6,94 | 7,97 | 1,67 | 68,41 |
| 5 | TLF-5 | 6 | 6,89 | 6,91 | 8,92 | 1,46 | 72,98 |

As is seen from Table 1, the environment hydrogen value is less than 8.4 in two types of the filtering material among diaphragms. They are No3 polyvinylchloride (PVC) and No4 polypropylene (KS-34).

PVC – the filtering material, which is 1.0 mm in thickness; the density of the surface area is 350 ± 20 g/m², air permeability at pressure of 50 Pa is 20-42 dm³ (m²·c).

KS-34 – the filtering material which is 1.1 mm in thickness, the density of the surface area is 437 ± 20 g/m², air permeability at pressure of 50 Pa is 30-60 dm³ (m²·c).

Other materials of a diaphragm in manganese electrolysis do not give the chance to conduct long experiments; that we can observe from data of Table 1. As it is known, manganese ions (II) in water solutions at pH 8.4 begin to deposit in the form of Mn(OH)₂; consequently, cathodic process can be failed. Therefore, the adequate choice of diaphragm material is of great importance for manganese electrolysis.

In water solutions of manganese and ammonium sulphate, the current output of cathodic reduction of manganese ions is influenced also by other many factors as well as diaphragm material. They are the following: density of cathodic current, electrolyte temperature and electrolysis duration.

Influence of cathodic current density on current output (CO) is considered in the range of 300-600 A/m². With growth of cathodic current density, CO is increased (Fig. 2).

It has been established that CO increases from 57% to 60% at the current density of 300-500 A/m², and decreases to 50% at 600 A/m². With increase in cathodic current density, the growth of electrolysis bath tension from 5 to 5.5 V and electrolyte tempe-

perature from 25 to 30°C was observed. Therefore, the following experiment is focused on determination of environment temperature influence on CO.

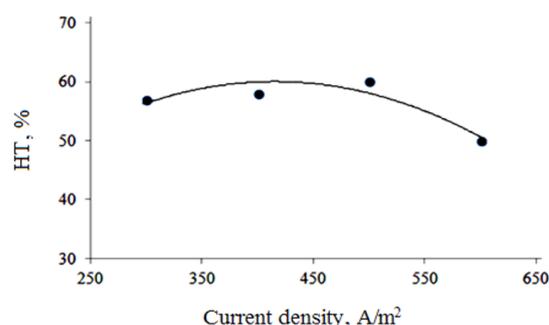


Figure 2. Influence of current density at cathodic manganese CO

In experiment, the influence of electrolyte temperature on CO in the range of 15-30 °C (Fig. 3) was considered. It is shown that the current output reaches the maximum value at 20°C and is 63%. The further increase in the environment temperature from 20 to 30°C causes the decrease in CO to 34%.

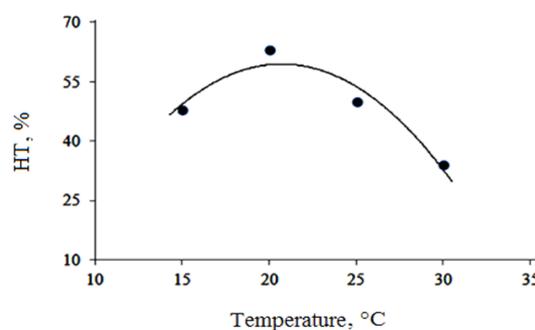


Figure 3. Influence of electrolyte temperature at cathodic manganese CO

The voltammetric studies of electrolyte media for potentiostat P8 were conducted for establishment of the obtained values certainty concerning temperature. Polarization curves were removed from titanic electrode (Fig. 4).

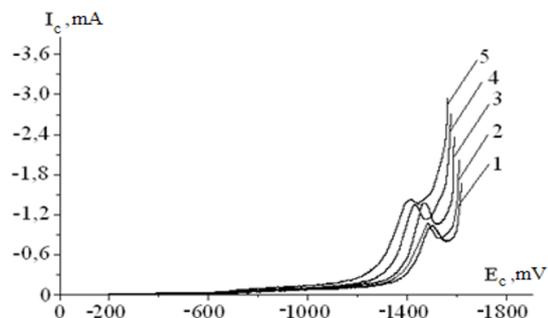


Figure 4. The cathodic polarization curves removed from titanic electrode at different temperatures: $(\text{NH}_4)_2\text{SO}_4$ 160 g/dm³; Mn 36 g/dm³; V=100 mV/c; t, °C: 1 – 15; 2 – 30; 3 – 45; 4 – 60; 5 – 75

As is seen from the Fig. 4, there are no significant changes at a temperature of electrolyte of 15 and 30°C. At a temperature of 45 °C, the value of potential of manganese ions (II) reduction becomes positive-going with increase in a maximum of current.

These data show that, in its turn, temperature increase gives opportunities to cathodic reaction with a low overstrain. The rate of electrochemical reactions increases at electrolyte temperature above 45 °C; therefore, the overstrain decrease of hydrogen release is observed.

On the basis of obtained data, it is recommended to conduct the following researches at electrolyte temperature not exceeding 25 °C and cathodic current density of 500 A/m².

Electrolysis was carried out during the time period from 5 hours to 1 day (Fig. 5).

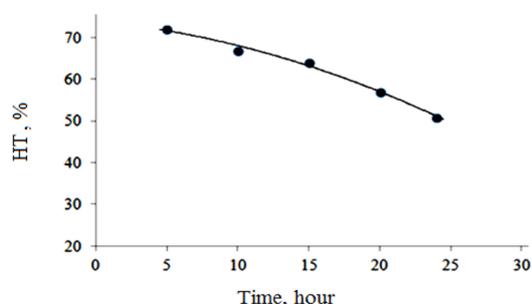


Figure 5. Influence of experiment duration at CO of cathodic manganese

Time of each experiment was renewed for 5 hours and values of CO for the manganese weight reduced

on the cathode were calculated. CO showed the maximum value (72%) at the beginning of electrolysis during the first 5 hours. When further prolonging of time, the value of CO decreased approximately by 5-7%. After 1 day (24 hours) of electrolysis, according to calculations for obtained manganese, value of CO is 51%.

Considering the fact that overstrains of hydrogen release are different on surfaces of the electrode materials used as cathode, decrease of CO during electrolysis can be explained as follows. In course of time, manganese crystals cover the titan surface almost completely; consequently, the titanic electrode passes into manganese [6].

As uniformity and purity of obtained metal of manganese are one of the main problems of electrowinning, the obtained metal underwent the analysis. The analysis was carried out by device JSM-5300LV of JEOL suitable for determination of elemental composition of sample with accuracy of $\pm 1\%$.

The results are presented in Fig. 6.

The chemical analysis showed that 99.7% of cathodic metal is the part of manganese. These data prove the high purity of cathodic manganese obtained from product solution.

The achieved researches results are of great practical importance for technology development of high pure manganese obtaining from manganiferous ore of deposit Karamola as an additional source of raw materials of “Kazakhstan”. Further work gives the opportunity to find effective ways of manganese electrolysis and development of cheap and easy technology.

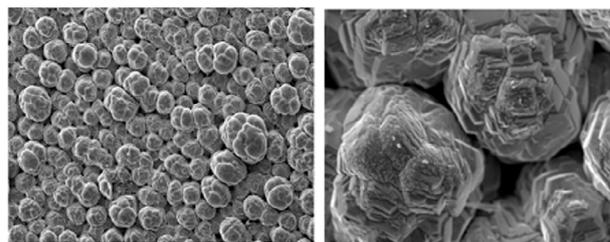


Figure 6. The microscopic picture of cathodic manganese increased to the size of 10-100 μm

References

- Stepin D.B. et al. *Metody polucheniya osobochistykh neorganicheskikh veshchestv*. [The methods of obtaining of especially pure inorganic substances]. Moscow, Khimiya, 1969. 480 p.
- Kozin A.F. *Fizicheskaya khimiya i osnovy amal'gannoy metallurgii*. [Physical chemistry

- and fundamentals of amalgamate metallurgy]. Almaty, Nauka, 1964. 316 p.
3. Tikhonov K.I., Agafonova N.I. *Elektroosazhdenie metallov iz organicheskikh rastvoriteley*. [metals electroplating from organic solvents]. Leningrad, 1979. 83 p.
 4. Tomilova A.P. *Prikladnaya elektrokimiya*. [Applied electrochemistry]. M.oscow, Khimiya, 1984. 520 p.
 5. Uzhkenov B.S., Mazurov A.K., Selifonov E.M. (2003) Condition of raw materials source of iron, manganese and chromite ores of Kazakhstan and prospect of ferrous metallurgy development for the period till 2030. *Industriya Kazakhstana*. No 10 (18), p. 23.
 6. A.B. Makhanbetov, A.B. Baeshov, B.E. Myrzabekov, A.N. Tabylganova (2015) Studying the effect of compounds in the manganese electrolysis by voltmeter-ammeter method. *Int. J. Chem. Sci.* No 13(1), p.p. 115-122.

The logo for 'METAL JOURNAL' is displayed in a large, bold, red, 3D-style font. The letters are thick and have a slight shadow, giving them a metallic appearance. The background behind the text is a gradient of yellow and orange, with a bright light effect in the top-left corner that fades into the background.

www.metaljournal.com.ua