Study of Manganese Removal in the Process of Mine Water Remediation

Eva MAČINGOVÁ[1], Stefano UBALDINI[2], Alena LUPTÁKOVÁ[3]

[1] Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovak Republic; email: macingova@saske.sk
[2] Institute of Environmental Geology and Geoengineering, CNR, Area della Ricerca di Roma RM 1 – Montelibretti, Via Salaria Km 29,300, 00015, Monterotondo Stazione, Roma, Italy; email: stefano.ubaldini@igag.cnr.it
[3] Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovak Republic; email: luptakal@saske.sk

DOI: 10.29227/IM-2016-01-19

Abstract

In this work a comparative study of manganese removal from pre-treated acid mine drainage is described. Manganese removal by three ways was realized. At the first method sodium hydroxide was added to raise pH of processed AMD to the 9.5 to promote the abiotic oxidation of soluble divalent species to insoluble form of manganese. Potassium permanganate was used at pH near neutrality for elimination of manganese from AMD by oxidative precipitation in the second process. A third method, as electrowinning, was applied, finalized to the anodic Mn recovery under MnO_2 form.

The results showed that the three methods are effective and manganese were removed from acid mine drainage for values that comply with environmental requirements. However, when sodium hydroxide was used as reagent, coprecipitation of manganese and magnesium present in AMD was observed. In the second experiment enhanced selectivity of the process and purity of obtained precipitates were achieved. In the process of electrowinning – over 95% of Mn removal under MnO_2 form, with a high degree of purity (about 99%) was attained.

Keywords: acid mine drainage, manganese removal, oxidative precipitation, electrowinning

Introduction

Acid mine drainage (AMD), acidic waste water with elevated contents of metals and sulphates is produced by oxidation of sulphide-bearing minerals exposed to both oxygen and water during the mining and mineral processing. The oxidative dissolution process is accelerated by autochthon acidophilic microbial communities (Baker and Banfield, 2003). Manganese is a common contaminant found in mine impacted water derived from coal and metal mining. Along with iron and aluminium, manganese hydrolysis contributes to the total mineral acidity of mine waters (Halberg and Johnson, 2005).

Manganese exists in the aquatic environment in its dissolved and undissolved form in oxidation states of +2, +3 and +4 governed by pH and redox conditions. Transition between these forms occurs via oxidation and reduction reactions that may be abiotic or microbial mediated. In acid mine drainage the soluble divalent species are predominant. In a stream receiving manganese-rich inflows caused by AMD, there occur oxidation and precipitation of manganese oxides. The sequence of reactions involving the oxidation of Mn^{2+} and subsequent precipitation as manganese dioxide includes simultaneous occurrence of several manganese forms (i.e. dissolved Mn^{2+}, hydrous oxides of Mn^{3+}, Mn^{2+}adsorbed to particulates and Mn^{2+} ligand complexes) (Howe et al., 2004).

Manganese present in mining water negatively affects the appearance, taste and odour of water. Exposure to high concentration of manganese can be detrimental to health, although it is consider as lover toxic than most of other metal co-contaminants. Several of agencies prepared risk assessment and developed different recommended reference concentrations or regulations for chronic oral or inhalation exposure levels for Mn in the environment. There are significant differences between the suggested values due to the potential for greater absorption of Mn through the respiratory tract than the gastrointestinal tract (Santamaria, 2008). Manganese toxicity is evidenced primarily in the central nervous system, moreover lung, cardiac, liver, reproductive and fetal toxicity have been noted. Its neurotoxicity arising from an accumulation of the metal in brain tissue and results in a progressive disorder similar to Parkinson`s disease. Children are potentially more sensitive to manganese toxicity than adults. (Crossgrove and Zheng, 2004). Acute toxicity in aquatic invertebrates and fish decreased with increasing water hardness (Howe et al., 2004). Doyle et al. (2003) have shown that elevated concentrations of manganese are highly correlated to the toxicity of sediments pore water. In view of these facts, manganese removal from mine water before release to surface water is desirable.

Numerous studies have reported promising techniques of manganese removal from mine waters. The different methods are based on the transformation of the dissolved forms by oxidation into precipitates. Manganese is soluble over a wide pH

Tab. 1. MnO_2 anodic electrodeposition: experimental conditions

Tab. 1. Elektrolityczny anodowy odzysk MnO_2: warunki eksperymentalne

Parameter	Value
Anode vs. SCE (V)	1.3–1.9
Cell voltage (V)	2.3–2.9
Current intensity (mA)	1000–1600
Current density (mA.cm^{-2})	10–16
pH	0.5–1.0
Bath temperature (°C)	90
Electrolysis time (h)	3
Stirring conditions (rpm)	250

range. Uncatalysed oxidation to insoluble Mn4+ does not proceed below pH 9. Active systems of treatment often involve the addition of large quantities of oxidant or the addition of chemicals to raise the pH and encourage abiotic oxidation of Mn^{2+} to Mn^{3+}/ Mn^{4+} (oxyhydr)oxides (Tan et al. 2010). Such processes are often expensive and can produce huge amount of undesirable products. Balintova and Petrilakova (2011) reported a manganese recovery using sodium hydroxide in the process of selective precipitation of metals from AMD. Study of Aguiar et al, (2013) confirm than effective manganese removal is possible at near-neutral pH with the use of MnO_2 owing to its catalytic/sorption properties. Oxidative precipitation by potassium permanganate is a widely applied method for manganese removal from drinking water supplies. Some authors performed the same process with highly contaminated AMD (Freitas et al., 2013; Heviankova and Bestova, 2007). Hallberg and Johnson (2005) referred the wetland-based treatment system, where the manganese-oxidizing microbes catalysed the removal of soluble manganese using fixed bed bioreactors. Mariner et al. (2008) described the development of self-sustaining bioreactors that can be used

in-situ for passive removal of manganese from contaminated water courses. Manganese-oxidising microorganisms used in this process included two species of fungi and one bacterial species. Several different strains of Mn-oxidizing bacteria have been used in the "Pyrolusite Process", a patented passive bioremediation method for treating manganiferous mine waters (Hiremath et al., 2013).

This paper describes three methods for the removal of manganese from pre-treated AMD at laboratory condition with aim reach required limits for waste water discharge and recover purified value-added products.

Materials and methods

Mine water

The mine water was sampled in the shaft Pech, which receives waters draining the abandoned Smolnik sulphidic deposit (Slovakia). The historical Smolnik mine was exploited for Au, Ag, Cu and Fe from the 14th century to 1990. The flooding in the period 1990–1994 led to generation of acidic water with high content of heavy metals and sulphates, which far exceed allowable pollution levels. The flow from eight to twenty five litres per second results a daily loading of dissolved metals about 500 kg (Kupka et al., 2012). The pH of drained water is about 3.5–3.9, the concentration of manganese is in the range 18–35 mg/L and concentration of magnesium is in the interval 250–450 mg/L depending on season and rainfall.

The mine water with pH 3.75 and 3.71, with concentration of manganese 24.38 mg/L and 18.28 mg/L and with concentration of magnesium 328.00 mg/L and 191.25 mg/L was used in the first and second procedure respectively. The differences were caused by sampling at various dates.

Synthetic solution of AMD with similar composition was prepared for electrowinning tests with concentration of manganese 21.33 mg/L and pH 3.8. The corresponding salts of metals (RPE Carlo Erba) were dissolved in deionised water.

Removal of manganese from AMD

At first and second experiment manganese was removed from AMD as the last step of selective sequential precipitation process (SSP). By SSP selective recovery of metals (Fe, Cu, Al, and Zn) was achieved using discrete chemical and biological stages (Macingova and Luptakova, 2012). During this procedure increasing of pH from 3.75 and 3.71 to 5.0 and mild decreasing of manganese concentration from 24.38 mg/L to 23.63 mg/L and from 18.28 mg/L to 16.75 at two samples of AMD occurred respectively. Contents of magnesium did not change. The concentration of metals in the samples was determined by atomic absorption spectrometry using Spectrometer Varian 240FS/240Z.

Tab. 2. Results of manganese oxidative precipitation process

Tab. 2. Wyniki strącania tlenowego manganu

Multiple of $KMnO_4$ dose	Mn [mg/L] in filtrate
0.6	4.75
0.8	1.25
1.0	< 0.03
1.2	1.50
1.4	3.25

The manganese removing by following different manners was performed:

(1) Alkalization

Experiment was carried out in glass beaker with 500 ml of pre-treated AMD. Under stirring the pH of processed water was adjusted by sodium hydroxide (5 M solution) from 5.0 to 9.5. The resulting precipitate (sample 1) was filtered through a 0.40 µm membrane filter Pragopor. The filtrate was used for determination of manganese and magnesium concentration.

(2) Oxidative-precipitation

In this process as first the pH of pre-treated AMD was adjusted to 7.0 using NaOH. In the five glass beaker 200 ml of processed AMD was supplied with different volume of potassium permanganate (1% solution) under stirring. The obtained solids were separated by filtration (samples 2, 3, 4, 5, 6). The filtrates were used for determination of manganese and magnesium concentration.

The solid samples 1 and 4 were dried at room temperature and examined by energy dispersive spectrometry (EDX) using microanalyser MIRA3 FE-SEM (TESCAN, Czech Republic).

(3) Electrowinning

This experiment was realized with synthetic AMD after chemical iron/aluminium precipitation. Fe present in the solution interferes negatively with the electrolytic process, masks the electrodes surface and decreases the current efficiency (Ubaldini et al., 2008). Nitric acid was added to the synthetic solution with aim to oxidize ferrous iron to ferric iron. In the next step the pH was adjusted to 4.0 using sodium hydroxide. Together with iron precipitation (approx. 99%) aluminium precipitation also occurred (approx. 94%). The precipitates were separated by filtration.

Electrowinning test was performed in a cylindrical glass laboratory cell of 200 cm³ volume. The cell was equipped by a thermostatic water jacket connected with thermostatic bath, magnetic stirrer and three electrodes: as cathode or working electrode, a platinum mesh; as anode or counter electrode, a platinum wire; as reference, a saturated calomel electrode (SCE). Tests were conducted by the main experimental conditions reported in Table 1 (Abbruzzese et al., 1994; Luptakova et al., 2012).

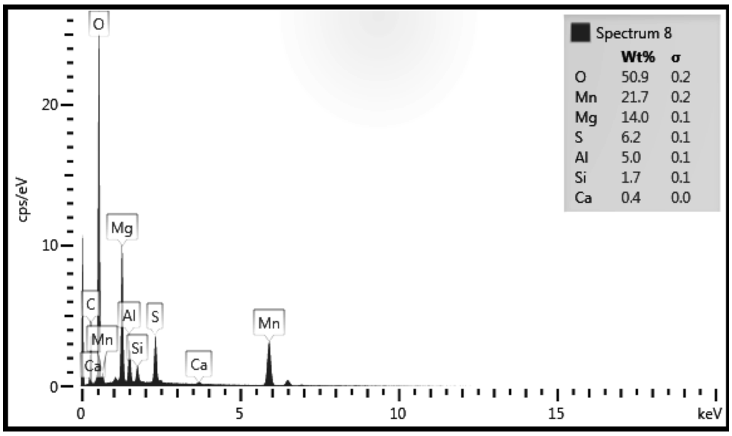
The cell was connected to a potentiostat-galvanostat (AMEL, mod. 555B), equipped with an instrument system to automatically control the process parameters, at constant anodic potential and stirring conditions during the same test (Table 1). Selected voltages studied the kinetic of metals deposition. By this way, the voltage between working and reference electrodes was automatically monitored.

With the scope to study the electrodeposition kinetic, liquid samples for chemical analysis have been withdrawn. The aqueous phase was analyzed for concentration of metals by inductively coupled plasma mass spectrometry (ICP-MS) using Perkin Elmer, mod. Elan 6000 equipment. The purity of the metallic deposit was detected by X-ray diffraction (XRD) using Bruker mod. AXS D8 Advance diffractometer.

Results and discussion

In the first procedure controlled addition of sodium hydroxide raise pH of pre-treated AMD from 5.0 to 9.5 to promote the oxidation of soluble manganese connected with precipitation. At the pH 9.5 removing of manganese to concentration lower than 0.03 mg/L was watched, but also decreasing of magnesium concentration from 328.00 mg/L to 304.07 mg/L was observed. EDX study of acquired amorphous precipitates confirmed the coprecipitation of manganese and magnesium (Figure 1) in this process.

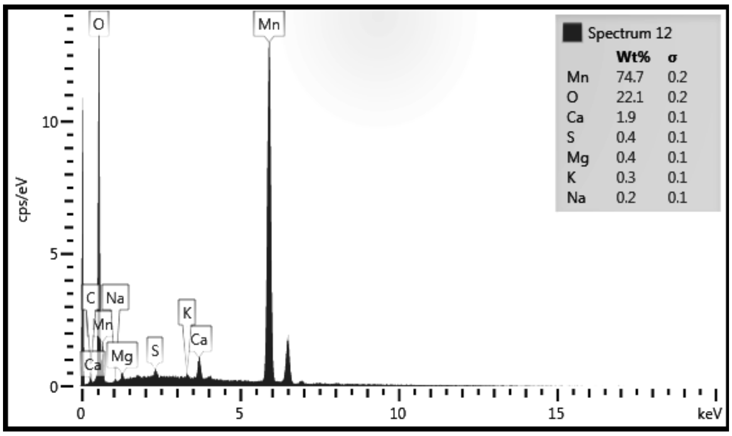
Van Benschoten et al. (1992) investigated, that oxidative precipitation of manganese by potassium permanganate takes place preferably at neutral pH. Accordingly the pH of treated AMD from 5.0 to 7.0 was adjusted at the second experiment of manganese removal. In this step modest decreasing of manganese concentration from 16.75 mg/L to 16.50 mg/L was observed. Concentration of magnesium did not change.



	Wt%	σ
O	50.9	0.2
Mn	21.7	0.2
Mg	14.0	0.1
S	6.2	0.1
Al	5.0	0.1
Si	1.7	0.1
Ca	0.4	0.0

Fig. 1. EDX analysis of sample 1

Rys. 1. Analiza EDX próbki 1



	Wt%	σ
Mn	74.7	0.2
O	22.1	0.2
Ca	1.9	0.1
S	0.4	0.1
Mg	0.4	0.1
K	0.3	0.1
Na	0.2	0.1

Fig. 2. EDX analysis of sample 4

Rys. 2. Analiza EDX próbki 4

In theory 1.92 mg/L of potassium permanganate is required to oxidize 1 mg/L of soluble manganese:

$$3Mn^{2+} + 2MNO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

According to literature (Van Benschoten et al., 1992; WWW) secondary oxidation reaction, adsorption and the autocatalytic effect of precipitates occur to affect the process and due to lower $KMnO_4$ dosage is needed than the theoretical value. By contrast, Heviankova and Bestova (2007) referred the best results of manganese removing from AMD at 1.2-fold of basic dose of $KMnO_4$. In our study different multiples of the basic doses of potassium permanganate were tested. The results are given in Table 2. The basic dose of KMnO4 was calculated as 3.17 ml of 1% solution to one litre of mine water.

The obtained solids after filtration were marked as sample 2–6. As can be considered, an optimum result was achieved with basic dose of potassium permanganate application in our experiment. Concentration of magnesium was in all cases without change and coprecipitation of manganese and magnesium did not observed. It was verified also by EDX analysis of the sample 4 (Figure 2).

The differences in results of various authors are probably caused by presence of different co-contaminants in the treated waters. Mechanisms by which other elements interfere in the oxidative precipitation by $KMnO_4$ are not clear and require further investigation (Freitas et al., 2013).

In the course of electrowinning process, the following reactions occur to the electrodes during Mn deposition (Veglio et al., 2003):

cathodic reaction:

$$Mn^{2+} + 2e^- \rightarrow Mn^0 \qquad E^0 = -1.18\ V$$

anodic rection:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \qquad E^0 = 1.23\ V$$

As far as electrowinning process, manganese was deposited on the anode as MnO_2, while only

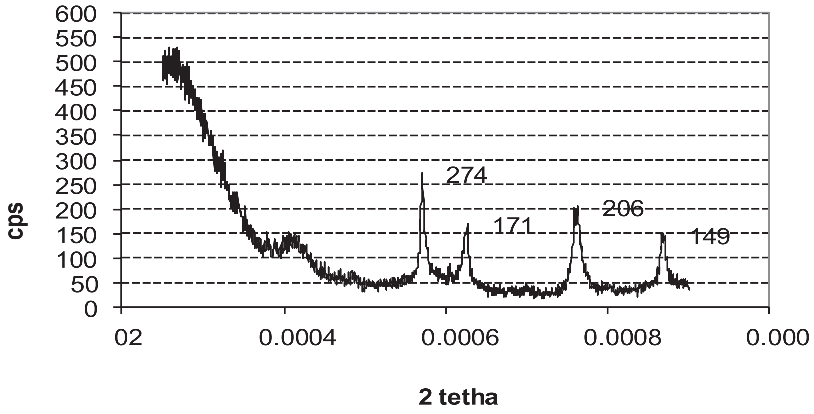


Fig. 3. XRD spectrum. Main peaks of MnO2 identified as 274, 171, 206 and 149 cps

Rys. 3. Spektrum XRD. Główne piki Mno2 zidentyfikowano jako 274, 171, 206 oraz 149 cps

a small amount was deposited on the cathode as Mn0. The analysis of the results, achieved using statistical methods (Ubaldini et al., 1995) demonstrates that, after 3 h, over 95% Mn was removed. A high-grade purity deposit was achieved (about 99% MnO_2), as proved from the results of the quantitative chemical analysis by ICP-MS. Main peaks of the X-ray diffraction spectrum reported in Figure 3, demonstrate the presence of manganese mainly in the form of MnO_2.

Conclusions

Summarize, manganese present in highly contaminated AMD was rapidly and effectively removed in aforementioned processes, meeting the limit established by Slovak legislation of 1 mg/L for industrial waste waters discharge into surface waters. However, the alkalization did not show sufficient selectivity due to observed coprecipitation of manganese and magnesium at the first method. Oxidative precipitation by potassium permanganate results in an enhanced selectivity of the process and purity of acquired manganese-solids in second experiment. Further investigation remains necessary to clarify the chemical and mineralogical profiles of Mn-product obtained in the second procedure sake its potential reuse. By the electrowinning process, a high recovery of Mn (over 95% in MnO_2 form) was achieved, with a degree of purity of about 99%.

Acknowledgements

The work has been supported by Slovak Research and Development Agency within the project APVV-0252-10/WATRIP, by the Scientific Grant Agency under the contract 2/0166/11 and by Joint Project CNR/SAV (2013/2015).

Received 10 April 2015, accepted 10 May 2015.

Literatura – References

1. ABBRUZZESE C., UBALDINI S., VEGLIO' F., TORO L. "Preparatory Bioleaching to the Conventional Cyanidation of Arsenical Gold Ores." *Minerals Engineering* 7/1(1994): 49–60, doi: 10.1016/0892-6875(94)90146-5.
2. AGUIAR A.O., DUARTE R.A., LADEIRA A.C. "The application of MnO_2 in the Removal of Manganese from Acid Mine Water." *Water Air Soil Pollut* 224:1690, 2013.
3. BAKER B.J., BANFIELD J.F. "Microbial communities in acid mine drainage." *FEMS Microbiology Ecology* 44(2003): 139–152, doi: 10.1016/S0168-6496(03)00028-X.
4. BALINTOVA M., PETRILAKOVA A. "Study of pH Influence of Selective Precipitation of Heavy metals from Acid Mine Drainage." *Chemical Engineering Transaction* 25(2011): 345–350.
5. CROSSGROVE J., ZHENG W. "Manganese toxicity upon overexposure." *NMR Biomed.*, 17(2004): 544–553, doi: 10.1002/nbm.931.
6. DOYLE C.J., PABLO F., LIM R.P., HYNE R.V. "Assesment of metal toxicity in sediment pore water from lake Macquarie, Australia." *Arch. Environ Contam. Toxicol.* 44(2003): 343–350, doi: 10.1007/s00244-002-2003-8.
7. FREITAS R.M., PERILLI T.A.G., LADEIRA A.C. "Oxidative Precipitation of Manganese from Acid Mine Drainage by Potassium Permanganate." *Journal of Chemistry* Article ID 287257, 2013.
8. HALLBERG K.B., JOHNSON D.B. "Biological manganese removal from acid mine drainage in constructed wetlands and prototype bioreactors." *Science of the Total Environment* 338(2005): 115–124, doi:10.1016/j.scitotenv.2004.09.011.
9. HEVIANKOVA S., BESTOVA I. "Removal of Manganese from Acid Mine Water." *Journal of Mining and Metallurgy* 43A(2007): 43–52.
10. HIREMATH S., LEHTOMA K., NICKLOW M., WILLISON G. *Pyrolusite Process to Remove Acid Mine Drainage Contaminants from Kimble Creek in Ohio: A Pilot Study*. Research Note NRS-194, U.S. Department of Agriculture, November 2013.
11. HOWE P.D., MALCOLM H.M., DOBSON S. "Manganese and its compounds: Environmental aspects." Concise International Chemical Assesment Document 63, World Health Organization, 2004.
12. KUPKA D., PALLOVA Z., HORNAKOVA A., ACHIMOVICOVA M., KAVECANSKY V. "Effluent water quality and the ochre deposit characteristics of the abandoned Smolnik mine, East Slovakia." *Acta Montanistica Slovaca* 17(2012): 56–64.
13. LUPTAKOVA A., UBALDINI S., MACINGOVA E., FORNARI P., GIULIANO V. "Application of Physical-chemical and Biological-chemical Methods for Heavy Metals Removal from Acid Mine Drainage." *Process Biochemistry* 47(2012): 1633–1639, doi: 10.1016/j.procbio.2012.02.025.
14. MACINGOVA E., LUPTAKOVA A. "Recovery of Metals from Acid Mine Drainage." *Chemical Engineering Transaction* 28(2012): 109–114.
15. MARINER R., JOHNSON D.B., HALLBERG K.B. "Characterisation of an attenuation system for the remediation of Mn(II) contaminated water." *Hydrometallurgy* 94(2008): 100–104, doi:10.1016/j.hydromet.2008.05.024.
16. SANTAMARIA, A.B. "Manganese exposure, essentiality & toxicity." *Indian J. Med. Res.* 128(2008): 484–500.
17. TAN H., ZHANG G., HEANEY P.J., WEBB S.M., BURGOS W.D. "Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems." *Applied Geochemistry* 25(2010): 389–399, doi: 10.1016/j.apgeochem.2009.12.006.

18. UBALDINI S., VEGLIO' F., TORO L., ABBRUZZESE C. "Gold recovery from Pyrrhotite by Bioleaching and Cyanidation: a preliminary study using statistical methods." *JOM-Journal of The Minerals, Metals & Materials Society, Mineral bioprocessing II* 1995: 145–155.
19. UBALDINI S., ABBRUZZESE C., FORNARI P., LUPTAKOVA A., MASSIDDA R., VEGLIO' F. "Electro-hydrometallurgical recovery of zinc and manganese from spent batteries." *Acta Metallurgica Slovaca*, 14(2008): 262–267.
20. VAN BENSCHOTEN J.E., LIN W., KNOCKE W.R. "Kinetic modeling of manganese (II) oxidation by chlorine dioxide and potassium permanganate." *Environmental Science and Technology* 26/7(1992): 1327–1333.
21. VEGLIO' F., QUARESIMA R., FORNARI P., UBALDINI S. "Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning.", *Waste Management* 23(2003): 245–252.
22. Iron and Manganese Removal [online]. [cited 2014-08-10], http://www.khoamoitruonghue.edu.vn/courses/EnvTech/Fe_and_Mn_removal.pdf

Badanie usuwania manganu w procesie rekultywacji wód kopalnianych

W pracy tej opisano porównawcze badanie usuwania manganu z przygotowanego drenażu kwaśnych wód kopalnianych. Usuwanie manganu odbyło się na trzy sposoby. Po pierwsze, dodano wodorotlenek sodu aby podnieść pH przerabianego AMD do 9.5 aby spowodować abiotyczne utlenianie rozpuszczalnych dwuwartościowych gatunków do nierozpuszczalnej formy manganu. Nadmanganian potasu zastosowano przy pH bliskim poziomu neutralnego aby wyeliminować mangan z kwaśnych wód kopalnianych poprzez tlenowe strącanie w drugiej metodzie. Trzecia metoda, jako elektrolityczna, została zastosowana do anodowego odzysku Mn w formie MnO_2.

Wyniki wskazały, że trzy metody są efektywne i mangan został usunięty z drenażu kwaśnych wód kopalnianych w ilościach porównywalnych z wymaganiami środowiskowymi. Jednakże, przy zastosowaniu wodorotlenku sodu zaobserwowano wzajemne strącanie manganu i magnezu obecnego w kwaśnych wodach kopalnianych. W drugim eksperymencie zwiększona została selektywność procesu i czystość otrzymanych substancji. W procesie elektrolitycznym – ponad 95% Mn zostało usuniętych w postaci MnO_2, przy dużym stopniu czystości (około 99%).

Słowa klucze: drenaż kwaśnych wód kopalnianych, usuwanie manganu, strącanie tlenowe, elektroliza