



Recovery of Iron from Acid Mine Drainage in the Form of Oxides

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Summary

Acid mine drainage (AMD) typical by low pH, high concentration of sulphates and different heavy metals is one of the major sources of environmental damage in mining industry. Treatment methods to address AMD are focused on neutralizing, stabilizing and removing pollutants through various physical, chemical and biological processes. However this type of mining influenced water should be considered not only as serious environmental problem, but also as an important resource due to the universal high metal demand and ambition of potential reuse of metals recovered from AMD.

The aim of this work was to recovery of iron in the form of oxides from AMD drained from enclosed and flooded Smolnik sulphidic deposit (Slovakia). The iron was removed from AMD in two steps to very low levels that meet required water quality criteria. The ferrous iron present in AMD was oxidized using hydrogen peroxide. In this stage decreasing of pH value and partial iron precipitation were observed. The follow neutralization using sodium hydroxide resulted in total iron removing by precipitation. The obtained solids were identified as a schwetmannite. The iron oxides were produced by thermal decomposition of precipitates. The morphology of acquired intermediates was studied by cryo-scanning electron microscopy (cryo-SEM) and the Fourier transform infrared spectroscopy (FTIR) was applied to characterization of their composition. Energy dispersive X-ray spectroscopy (EDX) was used for qualitative and quantitative analysis of intermediates and products. The X-ray powder diffraction (XRPD) was performed for the mineralogical analysis of the iron precipitates before and after the differential (DTA) and thermogravimetric (DTG) experiment.

Keywords: acid mine drainage, iron oxide recovery, structural and mineralogical analysis

Introduction

Acid mine drainage (AMD) is produced at mine sites when geologic materials containing metal sulphides are exposed to oxidizing condition and water. The process of oxidative dissolution is catalyzed by acidophilic microbial communities (Baker and Banfield, 2003). The quality of drainage is different from site to site in depend on the complex of mineralogical, hydrological, microbiological and geochemical post-depositional processes and their coupled interactions in mine waste environment (Nordstrom, 2011). AMD negatively affects the aquatic and terrestrial surroundings. The dissolution and subsequent mobilization of toxic metals into surface and groundwater is one of the significant environmental impact associated with AMD generation.

Alkaline reagents are widely used to remove metals from AMD, however by this technique large volume of metal-laden sludge is produced without possibility of following processing and requires ongoing storage and management. Recent developments in mine waste rehabilitation have led to more sophisticated reclamation approach and solutions. The concept of sustainable growth includes the effective reuse and recycling of waste streams.

AMD abundant in iron has been considered for the potential recovery of iron-products in different form and by different way. Silva et al. (2012) referred the production of magnetite from AMD using selective precipitation and photoreduction combined process. The magnetite particles were applied for paint production. The same group of researchers (2011) reported a method for the generation of goethite and hematite from AMD, tested for paint pro-

duction and colored concrete. In other method Flores et al. (2012) recovered mix of iron oxides in four-step process for adsorption and catalyst experiments to remove azo-dyes from an aqueous solution. In the processes described by Michalkova et al. (2013) inter alia hematite and zinc ferrite were obtained from AMD. In the work of Cernotova et al. (2012) the waste pigment samples were compared to standard pigments.

Our research was focused on the recovery of hematite from raw AMD at laboratory condition. The physico-chemical properties of obtained intermediates and final products were examined.

Materials and methods

Acid mine drainage

In this experiment raw AMD was used, discharged from 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 (Aquipur, 2000; Kupka et al., 2012). The pH of drained water is about 3.5–3.9, the concentration of sulphates is in the interval 2,500 – 2,900 mg/L and concentration of iron is in the range 200 – 400 mg/L depending on season and rainfall. Several groups of researchers reported the results of the monitoring and treatment of mentioned mine water (Jencarova et al., 2013; Singovska et al., 2013,

Spaldon et al., 2012). In our work AMD with pH 3.68 and concentration of iron 378 mg/L was used.

Analytical procedures

The concentration of iron in the samples was determined by atomic absorption spectrometry (AAS) using Spectrometer Varian 240FS/240Z. The precipitates were filtered using 0.40 μm membrane filters Pragopor. The X-ray powder diffraction was used for the analysis of crushed samples before and after thermal decomposition. The XRPD data of intermediate and end product were collected over an angular range $10 < 2\theta < 80^\circ$ with step 0.08° and $20 < 2\theta < 90^\circ$ with step 0.03° , respectively, using Bruker D8 Advance diffractometer, working with the $\text{Cu K}\alpha$ radiation and equipped with a secondary graphite monochromator. Diffraction patterns were processed with the Diffracplus Basic analysis program with PDF-2 Database. The qualitative analysis of samples was done by energy dispersive spectrometry (EDX) using microanalyser MIRA3 FE-SEM

(TESCAN, Czech Republic). FTIR absorption spectra were recorded with a Bruker Tensor 27 spectrometer from 4000 to 400cm^{-1} using KBr pellets method. The samples prepared for observation in a cryofield-emission were frozen by plunging in to liquid nitrogen, then broken and immediately transferred under vacuum into the chamber of the cryo-attachment CryoALTO 2500 (Gatan). At the temperature -90°C the sublimation was performed to cleanup the contamination from the surface of the specimen and finally was coated by platinum at -140°C . The frozen specimens were moved to the microscope cryo-stages and it was observed in FE SEM JSM-7401F (JEOL Ltd., Tokyo, Japan) operated with 2 kV accelerating voltage at -130°C . Simultaneous thermal gravimetric (TG) and differential thermal analysis (DTA) were conducted on a NETZSCH STA 449 F3 thermal analyzer. A dry sample, weighing 50 mg, were placed in aluminium crucible and heated under argon flux of 50ml/min, from room temperature up to 800°C at a linear heating rate $10^\circ\text{C}/\text{min}$.

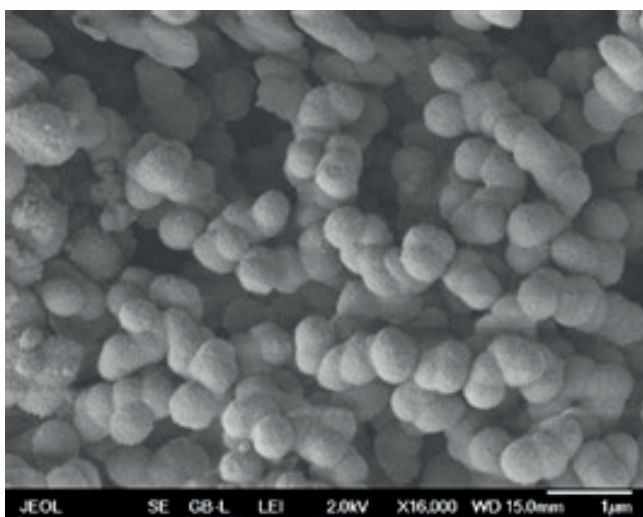


Fig. 1 Cryo-SEM micrograph of sample 1
Rys. 1 Mikrograf Cryo-SEM próbki 1

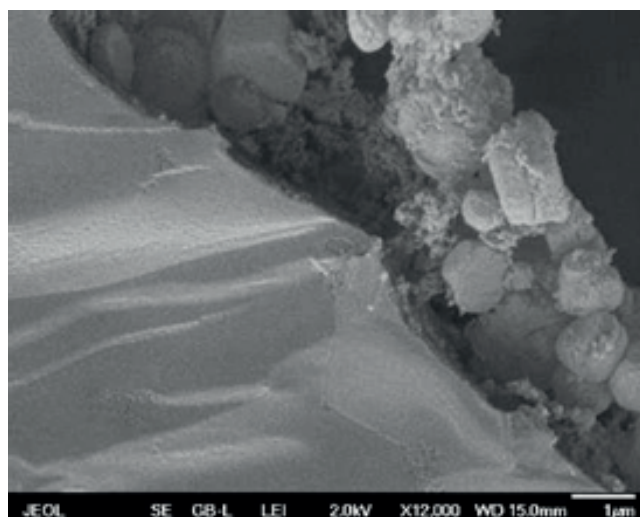


Fig. 2 Cryo-SEM micrograph of fractured sample 2
Rys. 2 Mikrograf Cryo-SEM podzielonej próbki 2

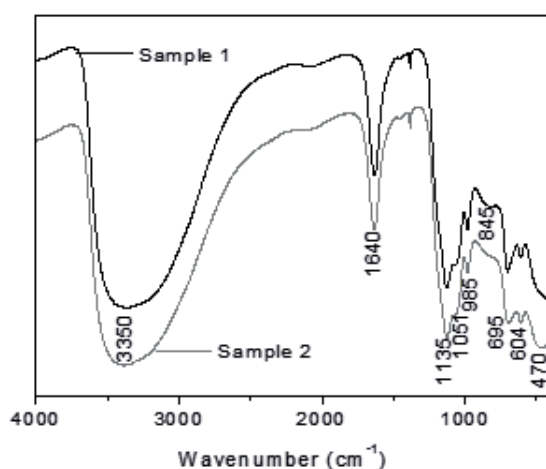


Fig. 3 Infrared spectra of intermediate products
Rys. 3 Widmo podczerwieni produktów pośrednich

Preparation of iron oxide

The procedure of iron oxides recovery from the acid mine drainage involves several steps.

- 1) The ferrous iron present in AMD was oxidized using 31% H₂O₂ in the continuously stirred beaker. The required amount of hydrogen peroxide was determined in our previous experiment (Macingova, 2010). In this process decreasing of pH value and partial iron precipitation were observed. The solid phase (sample 1) was separated by filtration. Rusty precipitates were air dried at room temperature.
- 2) In the next step the neutralization of filtrate using 5 M NaOH resulted in total iron removing by precipitation. After filtration the solids (sample 2) was air dried at room temperature.
- 3) The mineralogical (XRPD, FTIR), elementary (EDX) and morphological profile (cryo-SEM) of the samples has been examined.
- 4) The thermal decomposition was carried out on the samples.
- 5) In fine the structural properties (XRPD) of final product have been investigated.

Results and discussion

Iron is present in AMD in both, ferrous and ferric forms. Ferric iron precipitates at pH 3-4 while ferrous iron not precipitates at pH lower than 6. In this reason removal of iron from AMD at low pH requires oxidation of ferrous to ferric form in the first step of the process. After oxidation process hydrolysis of a part of generated ferric iron was recognised in a proton-generating reaction (Eq. 1), where the solid phase shown is a schwertmannite (Hedrich and Johnson, 2012).



In the processed water the value of pH decreased from 3.68 to 2.64 and the concentration of iron declined from 378 mg/L to 145 mg/L in this stage.

In the next step the controlled addition of sodium hydroxide in the water caused pH increasing to 3.75 and lowering of iron concentration to < 0.05 mg/L. No adjustment to higher pH values were made, in order to avoid co-precipitation of other metal hydroxides. Precipitation of ferric iron in the form of schwertmannite has been observed.

Identification of schwertmannite as product of oxidation, hydrolysis and neutralisation of real AMD sample are consistent with results of Bigham et al. (1994, 2000) who refers that schwertmannite is the dominant Fe-phase precipitated over the pH range 2.5 - 4.5 and sulphate levels 1,000 – 3,000 mg/L. Bigham et al. (1994) suggested the chemical formula of natural samples of schwertmannite as Fe₈O₈(OH)_{8-2x}(SO₄)_x · nH₂O where 1 ≤ x ≤ 1.75 and Fe/S molar ratio is in the interval 8 – 4.57. Bigham et al. (1996) pointed out that sulphate content is variable and some of the sulphates analyzed may be present not as the structural but as the adsorbed form. Later Yu et al. (1999) reported the occurrence of natural schwertmannite having 1.74 ≤ x ≤ 1.86 and Fe/S molar ratio in the interval 4.59 – 4.30. In our experiment from the results of elementary analysis (EDX) the calculated molar ratio Fe/S was 4.45 and 4.57 for sample 1 and sample 2 respectively.

The cryo-SEM study of precipitates indicated the schwertmannite formation. There are distinct morphologic differences resulting from different pathways of the schwertmannite synthesis. Samples synthesized by fast oxidation consist of round spheres whereas samples produced by slower oxidation processes showed the characteristics

Tab. 1 Position of absorption band in the FTIR spectra and interpretation according to literature data

Tab. 1 Pozycja widma absorpcji w widmie FTIR i ich interpretacja według danych literaturowych

Position (cm ⁻¹)	470	604	695	845	985	1051	1640	3350
						1135		
Interpretation	νFeO/ν ₂ SO ₄	ν ₄ SO ₄	ν FeO	δ OH	ν ₁ SO ₄	ν ₃ SO ₄	H ₂ O	ν OH

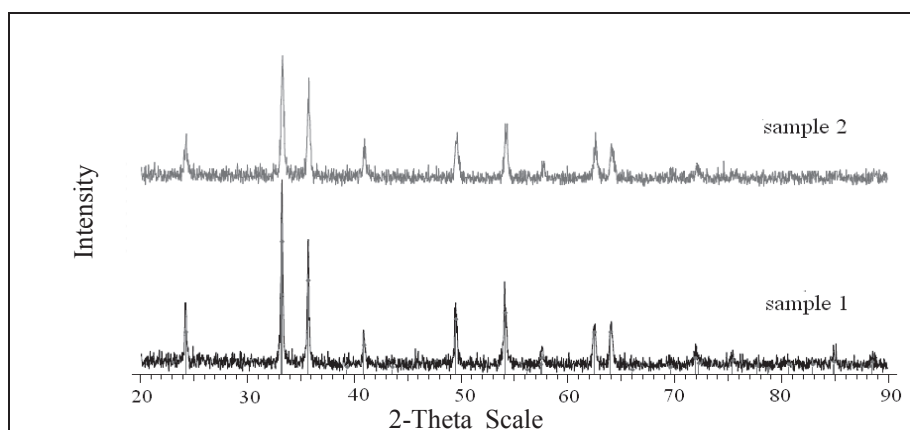


Fig. 4 XRD pattern of products of thermal decomposition

Rys. 4 Schemat XRD produktów rozkładu termicznego

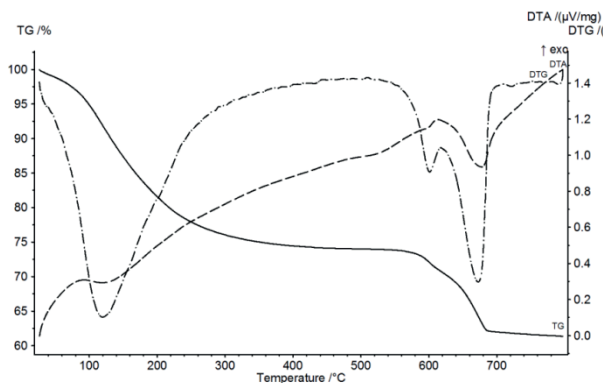


Fig. 5 TG/DTG and DTA curves of sample 1
Rys. 5 Krzywe TG/DTG i DTA próbki 1

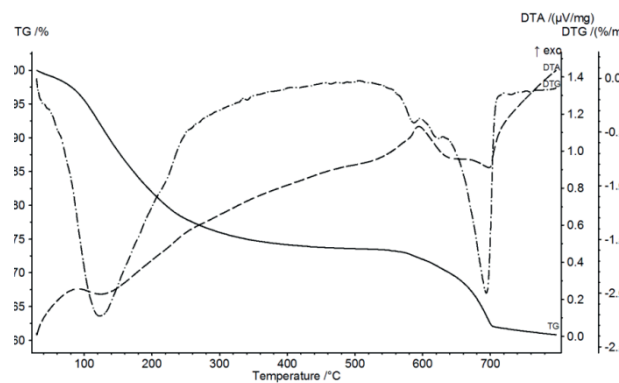


Fig. 6 TG/DTG and DTA curves of sample 2
Rys. 6 Krzywe TG/DTG i DTA próbki 2

hedge-hog form (Peiffer et al., 2010). SEM micrographs of sample 1 and sample 2 (Figure 1 and Figure 2) showing globular spheres with a drab whiskers verifies the rapid process of schwertmannite formation.

The FTIR spectrum of sample 1 and sample 2 is shown in Figure 3. The comparison of absorption bands for solids obtained in the experiment and literature data (Bigham and Nordstrom, 2000; Parafiniuk and Siuda, 2006) showed in the Table 1 reflects the composition of schwertmannite.

The mineralogical composition of intermediates and their final products of thermal decomposition were studied by X-ray powder diffractometry. The poor crystallinity of schwertmannite places limitations on the utility of this analysis, but the mineral has a unique XRPD profile. The comparison of the sample 1 and sample 2 diffractograms (data not shown) with the schwertmannite patterns from literature data shows some differences. This does not only indicated that the obtained samples are not the same phase but also may results from characterization of schwertmannite structure as compromise of the poor crystallinity, nanoscale size, metastability and co-precipitation with other nanoscale iron minerals with different crystallinity (Bigham et al, 1994; Bigham and Nordstrom, 2000). Properties of schwertmannite are affected also by the way of the preparation.

In line with the literature, heating to 800°C caused complete transformation of schwertmannite to hematite. X-ray powder diffraction patterns of the final products of thermal decomposition of sample 1 and sample 2 projected in Figure 4 verifies the recovery of iron from AMD in the

form of hematite.

TG/DTG and DTA curves of sample 1 and sample 2 displayed in the Figure 5 and Figure 6 are consistent with those from other studies. As samples were heated, adsorbed and structural water was lost above 100°C. At about 580°C $\text{Fe}_2(\text{SO}_4)_3$ is formed by an exothermic reaction and transformation to hematite occurs via an endothermic reaction at cca 680°C with release of gaseous SO_3 (Bigham and Nordstrom, 2000). Mazzetti and Thistlethwaite, (2002) incline to the view that the crystal structure of schwertmannite favoured only the loss of SO_3 and $\text{Fe}_2(\text{SO}_4)_3$ was not formed.

Hematite obtained from acid mine drainage in our experiment can find potential application as pigments, coatings, catalysts, photoelectrochemical electrode materials or the raw materials for the iron and steel industry.

Conclusion

This study showed the possibility of iron recovery from acid mine drainage in the form of hematite. At first the iron was highly effective and selectively removed from AMD in two steps. The thermal decomposition of obtained precipitates leads to formation of hematite.

These results confirm the utility of the new process in treatment of acid impacted water.

Acknowledgements

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Literatura - References

1. AQUIPUR a. s., Knight Piesold Consulting. *Project Summary: Feasibility test for water quality improvement using passive treatment system on effluent waters from the Smolnik mine in Slovakia*. 2000, 7 p
2. Baker B.J., Banfield J.F.: *Microbial communities in acid mine drainage*. *FEMS Microbiology Ecology*, 44, 2003, p. 139-152, doi: 10.1016/S0168-6496(03)00028-X
3. Bigham J.M., Carlson L., Murad E.: *Schwertmannite, a new iron oxyhydroxysulfate from Pyhäsalmi, Finland, and other localities*. *Mineralogical Magazine*, 58, 1994, p. 641-648
4. Bigham J.M., Nordstrom D.K.: *Iron and aluminium hydroxysulfates from acid sulfate waters*. Alpers C.N., Jambor J.L., Nordstrom D.K. (eds.), *Sulfate Minerals: Crystallography, Geochemistry and Environmental Significance, Mineralogy and Geochemistry* 40, Chapter 7, 2000, p. 351-403, doi: 10.2138/rmg.2000.40.7
5. Bigham J.M., Schwertmann U., Traina S.J., Winland R.L., Wolf M.: *Schwertmannite and the chemical modelling of iron in acid sulphate waters*. *Geochimica and Cosmochimica Acta*, 60, 1996, p. 2111-2121
6. Cernotova L., Tora B., Cablik V., Cablikova L. *Comparison of pigments and waste industrial pigments*. *Inżynieria Mineralna*, 2012, No 2(30), p. 65-72, ISSN 1640-4920
7. Flores R.G., Andersen S.L.F., Maia L.K.K., Jose H.J., Moreira R.F.P.M.: *Recovery of iron oxides from acid mine drainage and their application as sorbent or catalyst*. *Journal of Environmental management*, 111, 2012, p.53-60
8. Hedrich S., Johnson D.B.: *A modular continuous flow reactor system for the selective bio-oxidation of iron and precipitation of schwertmannite from mine-impacted water*. *Bioresource technology*, 106, 2012, p. 44-49
9. Jencarova J., Luptakova A., Kupka D.: *The possibilities of sulphate-reducing bacteria use in mine drainage waters remediation*. *Inżynieria Mineralna*, 2(32), 2013, p. 47-51, ISSN 1640-4920
10. 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, p. 56-64, ISSN 1335-1788
11. Macingova E.: *Application possibilities of the bioremediation methods for the elimination of the environmental and industrial loads*. PhD dissertation, The Technical University of Kosice, Slovak Republic, 2010 (in Slovak)
12. Mazzetti L., Thistlethwaite P.J.: *Raman spectra and thermal transformations of ferrihydrite and schwertmannite*. *Journal of Raman Spectroscopy*, 33, 2002, p. 104-111
13. Michalkova E., Schwarz M., Pulisova P., Masa B., Sudovsky P.: *Metals recovery from acid mine drainage and possibilities for their utilization*. *Pol. J. Environ. Stud.*, 4, 2013, p. 1111-1118
14. Nordstrom D.K.: *Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters*. *Applied Geochemistry*, 26, 2011, p. 1777-1791, doi: 10.1016/j.apgeochem.2011.06.002
15. Parafiniuk J., Siuda R.: *Schwertmannite precipitated from acid mine drainage in the Western Sudetes (SW Poland) and its arsenate sorption capacity*. *Geological Quarterly*, 50, 2006, p. 475-486
16. Peiffer S., Paikaray S., Damian C. et al.: *SURFTRAP – Development and optimisation of a process to biosynthesize reactive iron mineral surfaces for water treatment purposes*, *Geotechnologien Science Report* 16, 2010, p.154-169, doi: 10.2312/GFZ.gt.16.11
17. Silva R. de A., Castro C.D., Petter C.O., Schneider I.A.H.: *Production of iron pigments (goethite and hematite) from acid mine drainage*. Rüde, Freund, Wolkersdorfer (eds.), *IMWA 2011, Mine Water – Managing the Challenges*, Aachen, Germany, p. 469-473

18. Silva R. de A., Castro C.D., Viganico E.M., Petter C.O., Schneider I.A.H.: Selective precipitation/UV production of magnetite particles obtained from the iron recovered from acid mine drainage. *Mineral Engineering*, 29, 2012, p. 22-27, doi:10.1016/j.mineng.2011.12.013
19. Singovska E., Balintova M., Junakova N.: Evaluation of surface water pollution in the Smolnik creek. In *13th International Multidisciplinary Scientific Geoconference SGEM 2013, 16-22 June 2013, Albena, Bulgaria, Conference Proceedings, Volume I*, p. 445-450, ISBN 978-619-7105-04-9, doi: 10.5593/sgem2013
20. Spaldon T., Hanculak J., Sestinova O., Findorakova L., Kurbel T.: Methods of sulphates and heavy metals removal from acid mine drainage. *Waste Forum*, 3, 2012, p. 126-131, ISSN 1804-0195
21. Yu J.Y., Heo B., Choi I.K., Cho J.P., Chang H.W.: Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. *Geochimica and Cosmochimica Acta*, 63, 1999, p. 3407-3414

Odzyskiwanie żelaza w formie tlenków z kwaśnego drenowania kopalni

Kwaśne drenowanie kopalni (AMD – Acid Mine Drainage) typowe dla niskiego pH, wysokiego stężenia siarczanów i innych metali ciężkich jest jednym z głównych źródeł szkód środowiskowych w przemyśle wydobywczym. Metody obróbki adresowane dla AMD są skupione na neutralizowaniu, stabilizacji i usuwaniu zanieczyszczeń za pomocą różnych procesów fizycznych, chemicznych i biologicznych. Jednakże ten typ wydobywania, który wpływa niekorzystnie na wodę powinien być uważany nie tylko za poważny problem środowiskowy, a także za ważne źródło zasobów, w związku z powszechnym zapotrzebowaniem na metale i ambicją do potencjalnego powtórnego użycia metali odzyskanych z AMD.

Celem tej pracy jest odzysk żelaza w formie tlenków z AMD z zamkniętego i zalanego depozytu Smolniksulphidic (Słowacja). Żelazo zostało usunięte z AMD w dwóch krokach, aż do uzyskania bardzo niskiego poziomu aby zaspokoić kryteria jakości wody. Żelazo (II) obecne w AMD zostało utlenione z użyciem nadtlenu wodoru. Na tym etapie zaobserwowano malejącą wartość pH i częściowe wytrącanie się żelaza. Następująca później neutralizacja z użyciem wodorotlenku sodu skutkowałą całkowitym usunięciem żelaza w skutek wytrącania. Uzyskane ciała stałe zostały zidentyfikowane jako schwetmannit. Tlenki żelaza zostały wytworzone w procesie rozkładu termicznego wytrąconego osadu. Morfologia uzyskanych półproduktów została zbadana za pomocą krio-skaningowego mikroskopu elektronowego (krio-SEM) oraz w celu zbadania ich składu zastosowana została spektroskopia w podczwernieni z transformatą Fouriera (FTIR). Spektroskopia z dyspersją energii promieniowania rentgenowskiego (EDX) została zastosowana w analizie jakościowej i ilościowej półproduktów i produktów. Dyfrakcja proszkowa promieniowania rentgenowskiego została użyta do analizy mineralogicznej osadów żelaza przed i po eksperymentach różnicowych (DTA) i termo grawimetrycznych (DTG).

Słowa kluczowe: kwaśny odciek kopalniany, odzysk tlenku żelaza, analizy strukturalne i mineralogiczne