Wolkersdorfer, C., Lopes, D. V. & Nariyan, E. (2015): Intelligent Mine Water Treatment – Recent International Developments. – In: Paul, M. (ed) Sanierte Bergbaustandorte im Spannungsfeld zwischen Nachsorge und Nachnutzung – WISSYM 2015. – p. 63-68; Chemnitz (Wismut GmbH).

INTELLIGENT MINE WATER TREATMENT – RECENT INTERNATIONAL DEVELOPMENTS

Christian Wolkersdorfer[1,2], Daniela V. Lopes[2], Elham Nariyan[2]

Abstract: Several technologies that are currently in development or are already used in mine water treatment are described and challenges for future research and development is outlined.

Kurzfassung: Der Beitrag beschreibt die verschiedenen in Nutzung bzw. in Entwicklung befindlichen Technologien zur Behandlung bergbaulicher Wässer. Daneben werden diesbezüglich aktuelle Forschungsrichtungen umrissen.

Introduction and Outlook

Technology is constantly improving, especially in the emerging and innovative technologies such as the automotive industry, computer sciences, biosciences or the disruptive civil technologies (S. R. I. Consulting Business Intelligence 2008), where innovations are generally occurring in a five years cycle. Though the equipment and the monitoring within mine water treatment plants is keeping up with those technological improvements, the techniques itself date mostly back to developments in the last century. One of those examples is the high density sludge process (HDS) that was first published in 1970 by Kostenbader and Haines (1970). Besides small improvements and modifications, this is still the most commonly used treatment process in mine water purification (Blowes et al. 2014; Pouw et al. 2015), and currently no other evolving and widely used technology seems to be available to treat large quantities of polluted mine water – at least there is nothing in the most current "Reference guide to treatment technologies for mining-influenced water" from the US EPA (EPA 2014) or in publications of the International Mine Water Association. Having said this, there are many locations with treatment technologies other than the HDS process, such as ion exchange or reverse osmosis (e.g. eMalahleni, South Africa; Fig. 1), but their application is restricted to localised cases (Hutton et al. 2009).

This observation does not imply that there is no research into novel technologies (on the contrary) – yet, they are either repetitive or they are not at a development stage, where they could be widely used for industrial scale applications – one example being freeze crystallization (Fig. 2). In the view of the valorisation of mine water, there is need for evolving treatment options that are able to recover valuables, such as metals, fertilizers or sulphur. A long-term vision from mining companies, researchers and consulting companies and the willingness to do research on one or several technologies over a longer period of time to bring it to the "market" is essential for novel applications. Yet, researchers need to publish new results every couple of months which forces them to use methods that produce "results" (or they don't have enough time to think about completely new technologies), consulting companies often lack the financial sources for research and mining companies prefer "established" technologies. What is needed is a combined approach to "intelligent" solutions for mine water treatment – but that would require approximately a decade of trial-and-error

1 Tshwane University of Technology (TUT), Faculty of Science, Department of Environmental Water and Earth Science, Private Bag X680, Pretoria 0001, South Africa, christian@wolkersdorfer.info;

2 Lappeenranta University of Technology, Laboratory of Green Chemistry, Sammonkatu 12, 50130 Mikkeli, Finland

before applicable solutions are available; at the current economic and academic situation just a wishful thinking.

Under the auspices of MEND Canada, Hatch performed an extensive study of 'best available technologies economically achievable' (BATEA) and they came up with the following list (taken from Hatch 2014):

- Neutralization and Hydroxide Precipitation
- Sulfide Precipitation
- Ferric Iron or Aluminum Salt Co-Precipitation
- Barium Chloride Co-Precipitation
- Metal Oxidation
- Reacidification
- Solid/Liquid Separation
- Enhanced Coagulation and Settling
- Cyanide Destruction
- Air Stripping
- Ion Exchange
- Adsorption
- Active Aerobic Biological Oxidation
- Active Anoxic/Anaerobic Biological Reduction
- Membrane Size/Charge Exclusion
- Passive Treatment

This list is based on an extensive study within the Canadian mining industry. Besides some country specific details, resulting from the commodities mined in Canada, their findings are similar for other countries in the world.

The following chapters present a small selection of methods that are either in use in the mining industry or developed and might become available in the future. They are partly based on research within the Finnish iMineWa ("Intelligent Mine Water Management") project, hosted by Lappeenranta University of Technology in Mikkeli/Finland.

Fig. 1. Membrane (nano filtration, reverse osmosis) treatment of mine water at the eMalahleni mine water treatment plant (Mpumalanga, South Africa).

Nitrate Removal from Mine Water

Nitrate might have severe impacts on the environment and public health (Hem 1985) and consequently needs to be addressed by water treatment technologies. While the legislation is becoming stricter, the treatment for nitrate removal from water rarely becomes more specialized. The most used treatment for nitrate removal from mine water is the biological, where nitrate is converted to nitrogenous gas without ammonia or nitrite formation. However, the high production of biomass is one of the problems associated with biological approaches (Koren et al. 2000). Biofilms attached to granular activated carbon were used in anaerobic bioreactors at a full scale by Kennecott Utah Copper Corporation for selenium, nitrate and metals removal, where 10–25 mg/L of nitrate were completely removed (EPA 2014). Ion exchange (Song et al. 2012) and reverse osmosis (Häyrynen et al. 2008) have been applied for nitrate contaminated waters, but high costs and membrane regeneration problems are commonly associated with these technologies. Chemical reduction has been applied as well, where zero-valent iron (ZVI) is one of the most used materials for reducing nitrate to ammonium (Rodríguez-Maroto et al. 2009). An *in situ* treatment for removing nitrate from groundwater due to the leaching of a uranium mine was studied with the use of ZVI powder and with the help of denitrifying bacteria allowed the reduction to nitrogenous gas, where removal rates higher than 90% were obtained (Hu et al. 2011). At an industrial scale, biological processes are still the most common used but they have been combined with physico-chemical processes to increase the nitrate removal efficiencies and to avoid high flow of water in the biological reactors.

Reverse osmosis is applied as a pre-treatment and then combined with a biological treatment based on biofilm reactors using methanol as a carbon source for the nitrification and denitrification of ammonium to nitrate and subsequently nitrate to nitrogenous gas. Ammonium and nitrate removal achieved efficiencies higher than 90% in Finnish mines, with 10 °C water temperatures (Mattila et al. 2007). Electrochemical removal technologies are being used for nitrate removal, but since nitrite and ammonia are two of the main products, these methods are still being improved (Govindan et al. 2015) and not readily available.

Sulphate Removal

Many technologies were introduced and are available for removing sulphate from mine water (Bowell 2004; Bratty et al. 2015; Lorax 2003). Nevertheless, amongst them, the-state-of-the-art methods might show to be more promising in future “intelligent” mine water applications.

Electrocoagulation, though it has first been used in mine water treatment more than 4 decades ago (Jasinski and Gaines 1972), is one of those evolving applications, in which Fe and Al electrodes are extensively used. It was found that sulphate can be better removed with Al electrodes (Yadav et al. 2012). One of the most problematic issues relating to electrocoagulation is producing a passive layer on the electrodes’ surface, which avoids more dissolution of the electrodes. However, it has been shown that chloride ions in the range of 60 mg/L can break down the passive layer remarkably and as a result reduce the cell voltage during electrocoagulation (Mouedhen et al. 2008).

The potential-pH diagram of the Al-H_2O shows that aluminium reacts to passive species above a potential of $E_{Al/Al(OH)_3}$ (SHE) = –1.9 V at pH of ≈ 7. Thus, in principle the dissolution can occur only through defects in the passive film at high electrode potentials by lowering the pH near the electrodes. Rough electrodes showed better performance in avoiding passivation compared to smooth ones. pH 5 for the anode and pH 12 for the cathode showed that this set-up will avoid passivation and the metals' dissolution will continue (Mechelhoff et al. 2013).

Capacitive deionization (CDI) is one of the recent alternative methods in which anions and cations can be removed by electrostatic attractive forces between the charged electrodes and the ions in the solute. Positively charged ions such as calcium and magnesium move to the negatively charged electrodes. On the other hand, negatively charged ions such as chloride, nitrate and sulphate move to the positively charged electrodes, ultimately producing deionized water. Various materials have been used for CDI as electrodes including aerogel carbon, nanoporous activated carbon cloth, titania incorporated activated carbon cloth, carbon aerogel–silica gel composite electrodes, graphitized-carbon monolithic column and multiwall carbon nanotubes (Xu et al. 2008).

Electroreduction was utilized for converting sulphate to sulphide. In this mine water treatment, stainless steel plates are used as cathode and a titanium mesh as anode. The mine water's composition was 1979 mg/L of As, 164 mg/L Cu, 76 mg/L Cd and 4565 mg/L Zn. In the experiments, metal sulphides precipitated and caused the effluent turn black while the anode reduced the sulphate to sulfide (Ahmed Basha et al. 2008).

One of the potentials of sulphate is producing sulphuric acid instead of removing it, which might be more beneficial, economically. For this approach electro dialysis can be used. This is a membrane assisted electro-remediation process. By using this method, anions could be recovered to their acidic forms. To improve the exclusion of hydrogen ions by the anion exchange membranes under very acidic conditions, Rajeshwar and Ibanez (1997) recommended that water neutralisation to be applied before the electro dialysis step.

Electricity harvesting from sulphate laden wastewaters is achievable by microbial fuel cells (MFC). In this treatment, anode respiring bacteria (ARB) are used as electron donors for the production of electricity. The generated power density currently reaches 0.68 W m^{-2} and a current density of 3.2 A m^{-2} at an electrode resistivity of 150 Ω (Angelov et al. 2013; Lee et al. 2012).

Fig. 2. Tshwane University of Technology's (TUT) HybridICE freeze crystallisation pilot plant (Soshanguve, Gauteng, South Africa).

Most promising Technologies – Where Research is needed

As described in the first section, there seems to be no ground-breaking technology available that could be described as the silver bullet for mine water treatment – not only because each mine water is unique. Yet, several technologies, once developed further, have the capabilities of becoming leading in active mine water treatment.

Adsorption, though many research papers are available, is currently not in a state to replace chemical treatment of mine effluents. As soon as it is able to recover the valuables from the (ad)sorbents and reuse them on a large scale, it will become a promising technology. Presently, no full scale operating mine water treatment plant with sorbents is in operation.

Out of the technologies studied, the most promising active treatment options for the future are – without a specific order – ion exchange, electrochemical methods (with and without membrane support), membrane technologies and all of them potentially assisted by biological approaches. Yet, a lot of research is still needed to bring them together in an intelligent integrated approach and to bring them to the size of full scale plants.

Conclusions

Out of the many methods available, the most promising ones for future development seem to be integrative methods that combine already existing technologies into a new mine water treatment potpourri. eMalahleni in Mpumalanga/South Africa is such an example, where three existing technologies work together to form a new way of mine water treatment: integrated limestone method, lime neutralization, nano filtration and reverse osmosis. Promising – at the current stage – are combinations of electrochemical methods with neutralisation, ion exchange or membrane technologies. Yet, it needs a combined approach of various stakeholders and a lot of staying power to develop something novel and “intelligent” with the option of valorising mine water.

Acknowledgements

This work was financed by the South African SARChI Chair programme of the NRF (National Research Foundation) and by the FiDiPro programme of Tekes in Finland. The authors thank their respective institutions for their financial support. CW also thanks Wismut GmbH for considering this paper for WISSYM2015.

References

Ahmed Basha, C., Bhadrinarayana, N. S., Anantharaman, N. & Meera Sheriffa Begum, K. M. (2008): Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor. – J. Hazard. Mater., 152(1):71-78; doi:10.1016/j.jhazmat.2007.06.069.

Angelov, A., Bratkova, S. & Loukanov, A. (2013): Microbial fuel cell based on electroactive sulfate-reducing biofilm. – Energy Convers. Manage., 67:283-286; doi:10.1016/j.enconman.2012.11.024.

Blowes, D. W., Ptacek, C. J., Jambor, J. L., Weisener, C. G., Paktunc, D., Gould, W. D. & Johnson, D. B. (2014): The Geochemistry of Acid Mine Drainage. – In: Turekian, H. D. & Holland, K. K. (eds): Treatise on Geochemistry, 2 edn. – p. 131-190; Oxford (Elsevier).

Bowell, R. J. (2004): A review of sulphate removal options for mine waters: mine water 2004 – Proceedings International Mine Water Association Symposium 2. – 75-91 p.; Newcastle upon Tyne (University of Newcastle).

Bratty, M., Rutkowski, T., Blumenstein, E., Conroy, K. & Niekerk, A. V. (2015): Established and Emerging Passive and Hybrid Biological Sulphate Removal from Mining Effluents. – In: Brown, A., et al. (eds): Agreeing on solutions for more sustainable mine water management. – p. 1-11 [electronic document]; Santiago/Chile (Gecamin).

EPA (2014): Reference guide to treatment technologies for mining-influenced water. U. S. Environmental Protection Agency, 94.

Govindan, K., Noel, M. & Mohan, R. (2015): Removal of nitrate ion from water by electrochemical approaches. – J. Water Pro. Eng., 6:58-63; doi:10.1016/j.jwpe.2015.02.008.

Hatch (2014): Study to Identify BATEA for the Management and Control of Effluent Quality from Mines: MEND Report 3.50.1. – 527 p.; Ottawa (The Mine Environment Neutral Drainage [MEND] Program).

Häyrynen, K., Langwaldt, J., Pongrácz, E., Väisänen, V., Mänttäri, M. & Keiski, R. L. (2008): Separation of nutrients from mine water by reverse osmosis for subsequent biological treatment. – Miner. Eng., 21(1):2-9; doi:10.1016/j.mineng.2007.06.003.

Hem, J. D. (1985): Study and interpretation of the chemical characteristics of natural water. – US Geological Survey Water Supply Paper, 2254:263.

Hu, E., Wang, Q., Zhang, G., Wu, W. & Ding, D. (2011): Comparison of Removing NO3- in the Polluted Groundwater of In-Situ Leaching of Uranium Mine with DNB and Fe0. – IEEE:3014-3017.

Hutton, B., Kahan, I., Naidu, T. & Gunther, P. (2009): Operating and Maintenance Experience at the Emalahleni Water Reclamation Plant: Proceedings, International Mine Water Conference. – 415-430 p.; Pretoria (Document Transformation Technologies).

Jasinski, R. & Gaines, L. (1972): Electrochemical treatment of acid mine wastes. – Wat. Poll. Contr. Res. Ser., 14010 FNQ 02-72:81.

Koren, D. W., Gould, W. D. & Bédard, P. (2000): Biological removal of ammonia and nitrate from simulated mine and mill effluents. – Hydrometallurgy, 56:127-144; doi:10.1016/S0304-386X(99)00088-2.

Kostenbader, P. D. & Haines, G. F. (1970): High-density sludge treats acid mine water. – Coal Age, 75(September):90-97.

Lee, D. J., Lee, C. Y. & Chang, J. S. (2012): Treatment and electricity harvesting from sulfate/sulfide-containing wastewaters using microbial fuel cell with enriched sulfate-reducing mixed culture. – J. Hazard. Mater., 243:67-72; doi:10.1016/j.jhazmat.2012.09.071.

Lorax, E. (2003): Treatment of Sulphate in Mine Effluents. – 129 p.; London (INAP – International Network of Acid Prevention).

Mattila, K., Zaitsev, G. & Langwaldt, J. (2007): Biological removal of nutrients from mine waters Finnish Forest Research Institute, Rovaniemi.

Mechelhoff, M., Kelsall, G. H. & Graham, N. J. D. (2013): Electrochemical behaviour of aluminium in electrocoagulation processes. – Chem. Eng. Sci., 95:301-312; doi:10.1016/j.ces.2013.03.010.

Mouedhen, G., Feki, M., Wery Mde, P. & Ayedi, H. F. (2008): Behavior of aluminum electrodes in electrocoagulation process. – J. Hazard. Mater., 150(1):124-35; doi:10.1016/j.jhazmat.2007.04.090.

Pouw, K., Campbell, K. & Babel, L. (2015): Best Available Technologies Economically Achievable (BATEA) to Manage Effluent from Mines in Canada. – In: Brown, A., et al. (eds): Agreeing on solutions for more sustainable mine water management. – p. 1-11 [electronic document]; Santiago/Chile (Gecamin).

Rajeshwar, K. & Ibanez, J. (1997): Environmental Electrochemistry – Fundamentals and Applications in Pollution Sensors and Abatement. – 776 p.; Amsterdam (Academic Press).

Rodríguez-Maroto, J. M., García-Herruzo, F., García-Rubio, A., Gómez-Lahoz, C. & Vereda-Alonso, C. (2009): Kinetics of the chemical reduction of nitrate by zero-valent iron. – Chemosphere, 74:804-809; doi:10.1016/j.chemosphere.2008.10.020.

S. R. I. Consulting Business Intelligence (2008): Disruptive Civil Technologies – Six Technologies with Potential Impacts on US Interests out to 2025: CR 2008-07. – 34 p.; Washington (National Intelligence Council).

Song, H., Zhou, Y., Li, A. & Mueller, S. (2012): Selective removal of nitrate from water by a macroporous strong basic anion exchange resin. – Desalination, 296:53-60; doi:10.1016/j.desal.2012.04.003.

Xu, P., Drewes, J. E., Heil, D. & Wang, G. (2008): Treatment of brackish produced water using carbon aerogel-based capacitive deionization technology. – Water research, 42(10–11):2605-2617; doi:10.1016/j.watres.2008.01.011.

Yadav, A. K., Singh, L., Mohanty, A., Satya, S. & Sreekrishnan, T. R. (2012): Removal of various pollutants from wastewater by electrocoagulation using iron and aluminium electrode. – Desalin. Water. Treat., 46(1-3):352-358; doi:10.1080/19443994.2012.677560.