Application of Membrane Processes for Mine Water Treatment

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Summary

In this study, the possibility of using electrodialysis for the treatment of mine water from coal mining is investigated. The research is focused on mine water in the coal mine Československá armáda (ČSA) and Jan Šverma (JŠ). The main contaminants of mine water are sulphates, iron and manganese. Treatment process of this mine water consists of neutralization, oxidation, precipitation of iron and manganese, thickening of the mine water sludge, its flocculation and drainage using the pressure filtration. When compared to conventional technologies of water treatment, membrane technology has a number of advantages (high quality treated water at lower quantities of chemical agents, high selectivity and low energy demands). When considering an application of this technology, it is important to primarily reduce the negative impacts of the raw mine water chemism on the used semipermeable membranes. In particular, it is important to prevent the formation of low soluble (insoluble) salts which would otherwise negatively influence the mine desalination process by electrodialysis. The electrodialysis tests were carried out on the lab-scale units EDR-Z/10-0.8 (Mega a.s., Stráž pod Ralskem). The first part of the research was focused on the determination of specifications and operating parameters for the maximum of desalination rate. The laboratory tests were operated in batch mode and feed and bleed mode. The results show that electrodialysis is suitable for treatment of mine water, with contaminant removal efficiencies 90 %. The second part of the research was focused on the reducing of waste products of electrodialysis (concentrate). In the present work was achieved a reduction of concentrate stream from 50 % to 1 % of the total volume of feed water.

Keywords: mine water, electrodialysis, concentrate, diluate, feed water

Introduction

Mine water and its potential impact on groundwater isone of the most serious environmental concern associated with coal mining. During mine water drainage a number of hydrochemical processes can occur as the mine water evolves through varied stages towards a particular hydrochemical type and quality.

The different technologies could be used to minimize the impact of mine water and make the water reuse in other activities possible. Mine water treatment plant mainly use lime for neutralization, resulting in the concomitant precipitation of iron. The treatment with lime requires a short reaction period because of its high solubility. The maximum removal efficiency of soluble metals cannot be achieved through precipitation at a single pH level. Therefore, other technologies for the treatment of mine water are being investigated to replace the conventional treatment systems (Ali, 2011).Very few studies have focused on chemical free treatment technologies. One of these technologies are membrane processes.

The aim of this study is to investigate the possibility of using the electrodialysis to treat the mine water. The heart of the electrodialysis system is the membrane stack which consists of many cell pairs. The basic requirements of a system are membrane stack, power supply and pumps for feed, diluate and concentrate (Mulder, 2003). Electrodialysis is a clean technology entailing several advantages. It does not imply addition of chemicals and it can be operated in various modes.

Materials and methods

Mine water samples were collected from the inlet to the effluent treatment plant Československé armády (ČSA) and Jana Švermy (JŠ). Seven samples were collected into clean 50 litters tanks. The mine water was characterised by analyzing the following parameters: temperature, pH, conductivity, hardness, Cl^-, SO_4^{2-}, Fe, Mn, TDS and carbon dioxide forms. Another important characterization is the calcium carbonate stability of mine water - Langelier saturation index (LSI). It indicates whether the water will precipitate, dissolve or be in equilibrium with calcium carbonate.

The main contaminants of concern in this mine water are sulphates, iron and manganese. The rest of the detected metals are generally in low concentrations. The pH measured in the mine water samples ranges 7.43 to 8.45. According to Langelier saturation index the mine water is supersaturated with respect to calcium carbonate and scale forming may occur. Concentrations of select contaminants are presented in Table 1.

Membrane fouling. Feed water should be treated to prevent fouling of the electrodialysis system. The types

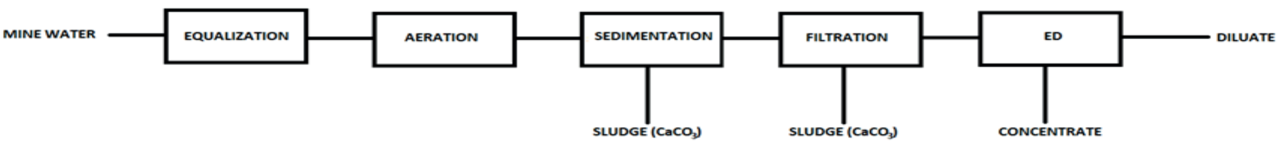
Tab. 1 Specific concentration detected in the 7 samples of mine water

Tab. 1 Stężenie stwierdzone w 7 próbkach wody kopalnianej

	pH	Condutivity	HCO_3^-	Hardness	Ca^{2+}	Mg^{2+}
	(_)	($mS.cm^{-1}$)	($mg.l^{-1}$)	($mmol.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
Arithmetic Mean	7.43	2.73	257.57	7.72	156.55	61.42
Maximum	8.45	3.13	890.60	8.61	387.17	91.16
Minimum	6.77	2.25	114.68	3.25	29.66	32.70
	COD	SO_4^{2-}	Cl^-	TDS	Fe	Mn
	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
Arithmetic Mean	2.03	1 071	38.15	2 011	0.6	1.0
Maximum	3.00	1 789	51.41	2 552	1.2	1.1
Minimum	1.43	684	30.29	1 474	0.2	0.4

Fig. 1 Scheme of mine water treatment

Rys. 1 Schemat przeróbki wód kopalnianych



of pretreatement are determined by the chemical nature of the water as well as the system configuration. Colloidal particles are the major foulants in all kinds of membrane processes. These colloidal particles will accumulate on the membrane surface to form a cake layer. It adds on an additional resistance to the membrane resistance. This type of fouling is known as colloidal fouling. Organic fouling is another problem in water treatment with application of membrane processes. A common organic foulant is the natural organic matter, which is a complex heterogeneous mixture of different organic macromolecules from degradation and decomposition of living organisms. Organic matters are adsorbed onto the membrane surface. Biological fouling (biofouling) occurs when living microorganisms in the water are transported onto the membrane surface where they absorb or adhere, forming a thin fouling layer. Biofouling not only increase the membrane resistance, but also biodegrades the membranes.

The precipitation of sparingly insoluble minerals to form and impermeable layer on the membrane surface is commonly known as scaling (Lawrence K. Wang et al., 2010; Mulder, 2003).

In our case the problem of scaling may occur. Calcium carbonate scaling is most common. Mine water may require addition of antiscalant. It interferes with the precipitation of the salt and maintains the salt in solution even when the solubility limit is exceeded. To prevent scaling the lime softening (with lime or soda ash) can be used. Another way to prevent scaling is application of electrodialysis reversal (EDR).

Another problem is focused on high concentrations of manganese and iron. In our application are critical concentrations around 1mg.$l^{-1}$of manganese and 3 mg.l^{-1} of iron. There are many studies on the issue of removal of manganese and iron from waste water. The most widely used method is application of lime. Manganese is soluble over a wide pH range and very difficult to remove from contaminated water, requiring pH above 11 for an effective removal as hydroxide (Ellis et al). Another method is oxidation performed by aeration or applying strong oxidizing agents. The presence of iron increases oxidant consumption so that iron removal is required prior to manganese oxidation (Silva et al., 2010; Ghaly et al., 2007). Limestone is the common neutralizing agent for acid waters due to its availability and low-cost and it is first option for metal removal from many wastewaters (Douglas and Degens, 2005; Hammarstorm et al., 2003).

During electrodialysis experiments with row mine water calcium carbonate was precipitated in the concentrate stream. The negative effect of iron and manganese was not proved. For the pretreatment of this water was chosen intensive aeration (Figure 1.).

Electrodialysis experiments. The electrodialysis stack comprised ten repeating cells, each consisting of a cation and anion exchange membrane. The membranes that was used throughout the experiment were AM-PES (anion and cation exchange membranes RALEX®, MemBrain, Stráž pod Ralskem). These membranes are separated by gaskets that form flow channels for alternating the concentrate and diluate. ED stack with effective area of 1 344 cm^2 was used to investigated desalination efficiency.

Electrodialysis experiments were operated as batch and feed-and-bleed mode. The aim of batch mode was to determine the maximum desalination degree of mine water.

Another aim was to reduce the volume of waste generated and determine the maximum degree of concentration of concentrate stream. Therefore, different volume ratios of feed water were tested:

- sample No.1 – No.5 at ratio 2:2 (diluate/concentrate);
- sample No.6 at ratio 2:0.5 (diluate/concentrate);
- sample No.7 at ratio10:0.5 (diluate/concentrate).

In batch mode the flow rates were equal in the concentrate and diluate channels and were set to 70 l/h. 2% Na_2SO_4 solution was used as electrode rinse fluid (electrolyte). The electrodialysis experiments were operated at constant voltage condition (14V). All presented experiments in batch mode were repeatable and performed at least three times. The actual values of potential, conductivity, pH, temperature and current were logged every five minutes. Samples of the experiments were collected at the end of each experiment and analyzed.

The aim of feed-and-bleed mode was to verify the results of experiments in batch mode especially to verify the possibility the operation of electrodialysis process in the longer period of time. In the first part of experiments the feed water was added continuously to the diluate and concentrate circuit from a storage tank. Flow rates were set according to the diluate quality. In the second part of experiments the concentrate circuit was run in batch mode (waste reduction).

Concentration of total dissolved salt is determined by the conductivity of solution. The desalination degree of treated water was calculated (Mulder, 2003):

$$R=\frac{\delta_0-\delta_t}{\delta_0} \tag{1}$$

R is desalination rate; δ_0 and δ_t (μS/cm) is time of 0 min and t mine diluate compartment solution conductivity respectively. The water efficiency of the desalination technique is expressed by the water recovery factor (Mulder, 2003):

$$r=\frac{V_D}{V_F} \tag{2}$$

V_D is volume of diluate and VF is volume of concentrate.

Results and discussion

Batch mode. Experiments were first carried out using saline solutions that were made by combining Na_2SO_4 with distilled water. In batch mode were performed seven samples of real mine water.

All experiments were performed at least three times. The removal efficiency of major ions was investigated by measuring the concentration in feed water and permeates samples (diluate).

The process time was around 40 minutes (Figure 3). The desalination degree of treated water was about 89 – 98 % and almost constant for all batch modes (Figure 2). One of the aims was to reduce the volume of waste generated and determine the maximum degree of concentration of concentrate stream. Therefore, different ratios of feed water were tested.

The best results were achieved with 0.5 litters initial volume of feed water (sample No.7). The process time was 240 minutes with maximum desalination degree 95% and water recovery rate of 94% (Figure 2 and Figure 4). In this experiment was achieved the maximum degree of concentration of concentrate stream (respect to the quality of diluate) around 30 $mS.cm^{-1}$. Operation at maximum concentrate degree may represent many operation problems.

The experiments also confirmed high efficiency of reducing the concentration of examined indicators (Table 2).

Feed-and-bleed mode. In this case were carried out several experiments. The first experiments were focused on the maximum desalination degree in terms of dissolved solids. To achieve the maximum desalination degree was necessary to reduce the residence time in the diluate stream. This means that efficiency of the process was about 2.2$lm^2.h^{-1}$ (Table 3). Two tests were conducted with a sample No.4 and sample No.5. The first one was conducted for 21 hours with constant desalination degree around 92%. The second

Tab. 2 Specific concentration detected in the treated mine water

Tab. 2 Specyficzne stężenie wykryte w wodach kopalnianych poddanych przeróbce

	pH	Conductivity	Hardness	Ca^{2+}	Mg^{2+}
	(_)	($mS.cm^{-1}$)	($mmol.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
Arithmetic Mean	6.82	0.167	0.693	9.76	5.79
Maximum	7.72	0.200	1.430	20.44	11.54
Minimum	5.62	0.079	0.305	4.61	1.31
$Removal_{max}$ (%)	_	94.60	97.08	94.60	99.84
$Removal_{min}$ (%)	_	90.60	81.37	90.57	81.37
	SO_4^{2-}	Cl^-	TDS	Fe	Mn
	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
Arithmetic Mean	46.42	1.69	104.67	_	_
Maximum	54.00	2.66	160.00	<0.1	<0.3
Minimum	21.74	0.35	42.00	<0.1	<0.3
$Removal_{max}$ (%)	95.86	95.90	97.36	_	_
$Removal_{min}$ (%)	93.45	84.76	78.06	_	_

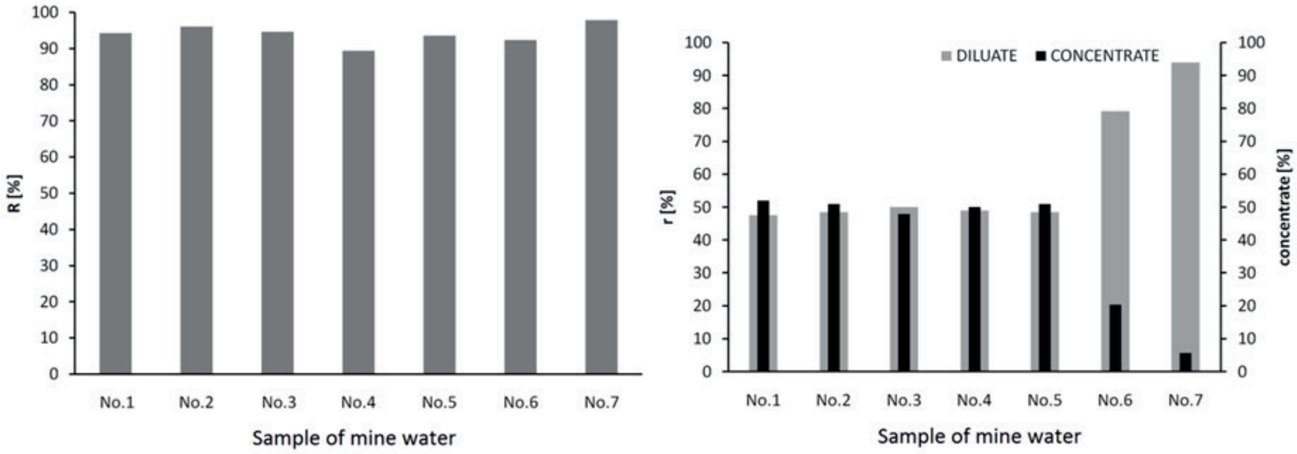


Fig. 2 Desalination rate of treated water and water recovery with different volume ratio of feed water

Rys. 2 Stopień odsalania wody poddanej przeróbce i odzysku wody z różnym stosunkiem objętościowym wody zasilającej

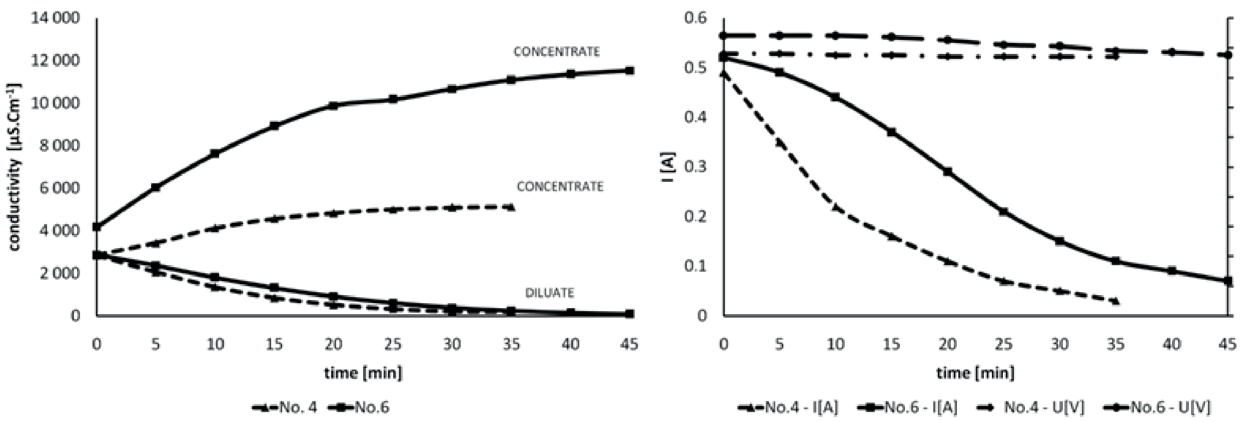


Fig. 3 Electrodialysis process: Sample No.4 -volume ratio of feed water 2:2, Sample No.6 - volume ratio of feed water 2:0.5

Rys. 3 Proces elektrodializy: próbka nr 4 – stosunek objętościowy wody zasilającej 2:2, próbka nr 6 - stosunek objętościowy wody zasilającej 2:0,5

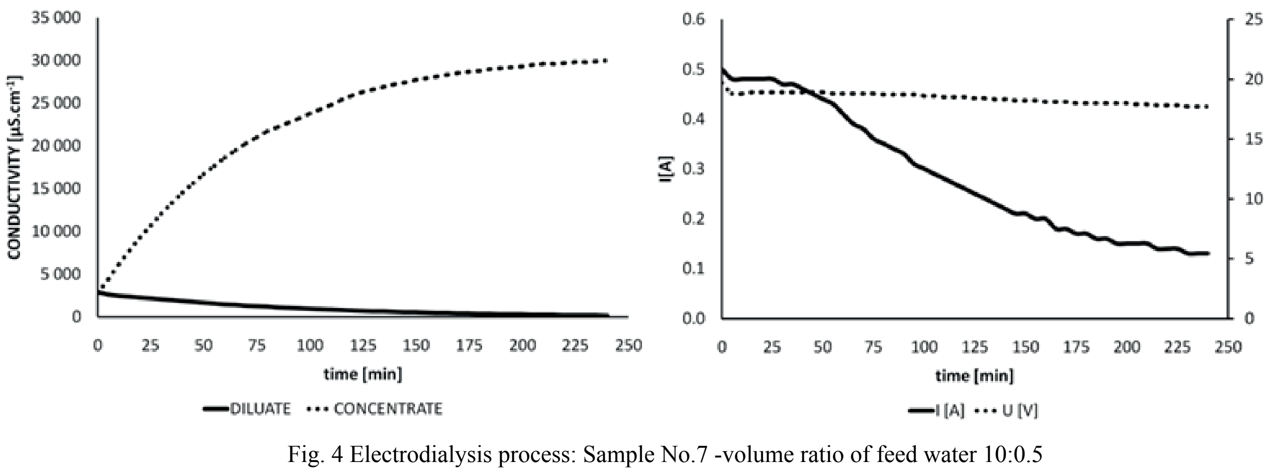


Fig. 4 Electrodialysis process: Sample No.7 -volume ratio of feed water 10:0.5

Rys. 4 Proces elektrodializy: próbka nr 7 – stosunek objętościowy wody zasilającej 10:0,5

Tab. 3 Tests results for feed-and-bleed-mode

Tab. 3 Wyniki testu w trybie podaj i zmierz

	Process time	Process efficiency	R	r	Water quality						
	(h)	($l/m^2.h^{-1}$)	(%)	(%)	pH	Ca^{2+}	Mg^{2+}	COD	SO_4^{2-}	Cl^-	TDS
					(_)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)	($mg.l^{-1}$)
No.4	21	2.2	92	50	5.65	24.05	4.86	0.04	429.5	1.06	96
No.5	48	2.2	80	50	6.50	29.06	10.94	0.26	207.4	4.25	436
No.7	6	70	50	99	7.25	25.0	32.25	0.72	482.3	10.85	983

one was conducted for 48 hours with constant desalination degree around 80%.

Further experiments were focused on the quality of treated water and on reducing the volume of concentrate stream. Therefore the concentrate circuit was run in batch mode (one circulation volume during the entire test). Maximum concentration degree of concentrate stream was determined by 30 $mS.cm^{-1}$.

The criterion for the quality of the treated water was concentration of dissolved solids below 1 $g.l^{-1}$ corresponding to 50% desalination degree. This means that efficiency of the process was about 70 $l/m^2.h^{-1}$. The quality of the treated water was constant throughout the test.

The most important results of these experiments are shown in Table 3.

Conclusion

This study was focused on application of membrane process (electrodialysis) for the treatment of mine water. It was shown that this technology is capable of successfully desalinating with salinity removal more than 90%. One of the advantages of this technology is high water recovery rates. In our case the water recovery was from 50% to 99%. One aim of the experiments was to reduce the volume of concentrate stream (waste product). In the present work was achieved a reduction of concentrate stream from 50% to 1% of the total volume of feed water.

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Zastosowanie procesów membranowych w oczyszczaniu wody kopalnianej

W pracy tej zbadano możliwość zastosowania elektrodializy w obróbce wody kopalnianej z wydobycia węgla. Badania skupiają się na wodzie kopalnianej z kopalni węgla Československáarmáda (ČSA) i Jan Šverma (JŠ). Głównymi zanieczyszczeniami wód kopalnianych są siarczany, żelazo i mangan. Proces oczyszczania wód kopalnianych składa się z neutralizacji, utleniania, wytrącania żelaza i manganu, zagęszczaniu zawiesiny z wód kopalnianych, ich strącaniu w postaci kłaczków i odwadnianiu z użyciem filtracji pod ciśnieniem. W porównaniu z konwencjonalnymi technologiami oczyszczania wody, metoda membranowa ma wiele zalet (wysoka jakość oczyszczonej wody przy mniejszej ilości środków chemicznych, wysoka selektywność i niskie zapotrzebowanie na energię). Biorąc pod uwagę zastosowanie tej technologii, ważnym jest aby najpierw zredukować negatywny wpływ chemizmu nieprzerobionej wody kopalnianej na używanych membranach półprzepuszczalnych. W szczególności ważne jest zapobieganie tworzenia się słabo rozpuszczalnych (nierozpuszczalnych) soli, które mogły by w przeciwnym razie negatywnie wpłynąć na kopalniany proces odsalania z udziałem elektrodializy. Testy elektrodializy przeprowadzane były na skalę laboratoryjną z użyciem urządzenia EDR-Z/10-0.8 (Mega a. s., Stráž pod Ralskem). Pierwsza część badań skupiała się na określeniu specyfikacji i parametrów operacyjnych w celu uzyskania maksymalnego stopnia odsalania. Testy laboratoryjne operowane były w trybie okresowym i w trybie zasilania i upuszczania. Wyniki pokazują, że elektrodializa jest odpowiednim procesem do oczyszczania wody kopalnianej, z wydajnością usuwania zanieczyszczeń na poziomie 90%. Druga część badań skupiała się na zredukowaniu produktów odpadowych z elektrodializy (koncentratu). W pracy uzyskano redukcję strumienia koncentratu z 50% do 1% objętości całkowitej wody zasilającej.

Słowa kluczowe: wody kopalniane, elektrodializa, koncentrat, rozcieńczalnik, woda zasilająca