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Mine water treatment by membrane filtration processes – Experimental investigations on applicability

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ABSTRACT

Mine waters, rich in sulphate, acid and different metal species, are an environmental risk of great importance. Untreated mine waters released into the environment influence complete ecosystems and can reduce species of plant and animal life drastically from thousands to some microbial and algae species. Hence, mine waters are treated before released into the environment by state-of-the-art procedures such as lime treatment or constructed wetlands which focusing on future legislation will not meet discharge criteria especially for sulphate.

Therefore the Department for Thermal, Environmental and Natural Products Process Engineering of TU Bergakademie Freiberg investigated the applicability of membrane filtration using nanofiltration (Alfalaval NF99) and reverse osmosis (Alfalaval RO 98pHt) membranes. Experiments covered parameter and long-term studies to determine applicability of membrane filtration theory and appearance of scaling (precipitation of inorganic solutes). Results suggest applicability of desalination by membrane filtration as well as the occurrence of scaling due to strong flux decline during long-term studies for some experimental conditions.

Keywords: Nanofiltration; Reverse osmosis; Mine water Scaling

1. Introduction

Mining causes several process waters such as mill, flotation and refining waters from conditioning processes. Next to these process waters wastewaters from active and abandoned underground and open pit mines form a wastewater stream and leachates from large tailings, overburden and other mineral waste piles characterized by low pH, high content in sulphate and different dissolved metal species [1–3]. These waters referred to as acid mine drainage (AMD) or acid rock drainage (ARD) evolve from the oxidation of sulphidic minerals caused by infiltrating surface water, groundwater and air oxygen as well as the activity of sulphide oxidizing bacteria such as *Acidothiobacillus ferrooxidans* and *Acidothiobacillus thiooxidans* [2,3]. Detailed information on mine water formation and chemistry can be found in [2–4].

Although several active and passive technologies to treat mine waters exist, mainly two became the favorite treatment concepts due to low energy, personnel and maintenance costs. Aeration followed by addition of an alkaline agent (lime, limestone, caustic soda, fly ash) causes precipitation of metal hydroxides and mineral phases such as gypsum and is considered state-of-the-art treatment technology [5] and the first of the

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Table 1
Composition of investigated mine water and EPA [13], EU [14] and WHO [15] water quality criteria

Parameter	Unit	Concentration	EPA	EU	WHO
Al^{3+}	mg/L	1139.0	0.05–0.2	0.2	0.1–0.2
Ca^{2+}	mg/L	325.9	–	50	[a]
Cu_{total}	mg/L	2298.0	1.0	50	2
Fe_{total}	mg/L	627.5	0.3	0.2	n.p.[b]
Mg^{2+}	mg/L	630.6	–	50	[a]
Mn_{total}	mg/L	224.5	0.005	0.5	0.4
SO_4^{2-}	mg/L	14337	250	250	250
pH	–	2.7	6.5–8.5	6.0–8.5	n.p.[b]
Conductivity	mS/cm	11,100	–	–	–

[a] 500 mg/L total hardness calculated as $CaCO_3$ based on taste and household use consideration, 200 mg/L total hardness calculated as $CaCO_3$ for prevention of scale deposition [15].

[b] Not proposed as health-based guideline [15].

favored concepts. Since precipitation of dissolved salts strongly depends on water composition, solubility and pH these parameters strongly determine discharge quality. Optimization of precipitation procedures investigated in different studies led to multi-step treatment e.g. stepwise increase of pH, higher final pH or use of different alkaline agents [3,5] and decreased residual content to some mg/L of metals and some 100 mg/L for sulphate. The second favored treatment option is biological processes such as aerobic and anaerobic wetlands or anaerobic sulphate reduction by sulphate reducing bacteria (SRB) [3]. Natural or constructed wetlands dominate the biological treatment systems due to low energy and maintenance costs and are used in the treatment of mine waters for decades [5]. They involve a complex system of biological and physico-chemical processes such as adsorption, ion exchange, biosorption and bioaccumulation, biotic and abiotic oxidation as well as reduction of sulphate, sedimentation and neutralization in anaerobic regimes. The most important processes to remove dissolved metals are biologically catalyzed oxidation of dissolved metals followed by hydrolysis and hydroxide precipitation and precipitation of dissolved metals as sulphides, that are formed during biological sulphate reduction [3]. Detailed information on chemical and biological mine water treatment methods will not be discussed here in detail, but can be found in [3,5].

Due to new environmental legislation fresh water costs are increasing constantly and therefore treatment of such process and wastewaters gain more and more importance in the mining and metals industry focusing on water reuse. Next to this, mine waters pose a serious thread to the environment by contamination of surface and groundwater as well as soils causing damage to flora and fauna at innumerable mining sites all over the world [1]. Therefore legislation will define stricter quality criteria for mine water discharge in the near future. Considerable criteria will be in the range of drinking water quality (see Table 1) standards for pH, sulphate and metals as mentioned in [6].

Concerning separation of salts and handling of large water streams another treatment concept comes into ones mind. Membrane filtration processes, namely nanofiltration and reverse osmosis, known from water softening and sea and brackish water desalination are pressure driven filtration processes, that separate a feed stream into two streams by forcing the solvent (water) through a semipermeable membrane [1,7–9]. Detailed information on basics of desalination by membrane filtration can be found in [7–9].

Scaling, namely the precipitation of inorganic compounds, on the membrane surface, caused by elevated concentrations of dissolved salts near the membrane surface will also be an efficiency determining factor in mine water filtration. Hard mine waters often occur due to composition of ambient rock and contain Mg^{2+} and Ca^{2+} ions, which form insoluble sulphate minerals such as gypsum, when their solubility is exceeded. Next to this the pH-dependent formation of colloidal metal hydroxides referred to as colloidal fouling, can appear in the treatment of mine waters by membrane filtration as well [10–12]. Le Gouellec and Elimelech [10] and Lee et al. [11,12] and many other authors investigated scaling and concentration polarization effects in nanofiltration and reverse osmosis and suggested transmembrane pressure, pH and composition as well as water recovery as important factors influencing scaling.

2. Material and methods

2.1. Membranes

The separation behaviour of two commercially available membranes (1 NF: AlfaLaval NF99, 1 RO:

AlfaLaval RO 98Ht) was investigated in this study. The investigated membranes are thin-film composite membranes with an active polyamide separation layer. All membranes were punched to circular pieces of 90 mm diameter resulting in about 63 cm^2; of filtration area and were immersed at least for 60 min in deionized water (15–25 μS/cm).

2.2. Mine water composition

A mine water from a chilenean copper mine, that has been kindly provided by SIEMENS AG Germany, was used in the applicability investigations of mine water membrane filtration. The original sample was coloured red to brown due to high content in ferric iron that precipitates as ferric iron hydroxide. To remove precipitated particles from solution the sample was filtered through a paper filter (Filtrak 388, Spezialpapierfabrik, Niederschlag, Germany). The ion composition of the water is shown in Table 1. The water shows high content of metals (especially Cu, Fe, Al) and sulphate. Besides, the sample also shows elevated concentrations of magnesium and calcium causing a high hardness of the water, possibly causing scaling of Mg-Ca-SO_4-compounds during membrane filtration. Next to the concentrations of ion species water quality criteria are listed as well. As can be seen in Table 1 all parameters exceed the chosen quality criteria.

2.3. Experimental set-up

All permeation experiments were conducted with a lab scale membrane filtration device, that mainly consists of a 30 L feed tank, two membrane test cells, a Cat-Pumps 1051 plunger pump, a control unit with integrated pressure, temperature and flow indicators and a thermostat. The circular membrane test cells are equipped with a sinter plate of 90 mm in diameter to support the membrane sheet. The feed liquid is pumped through a port in the test cells top into the module, where it is separated into a concentrate and a filtered permeate stream. First the concentrate stream, that is directed in a tangential radial flow to the test cells circumference, exits the cell through an annular gap, while the permeate stream exits the cell through the sinter plate. Both streams are recycled into the feed tank. Each module has been equipped with either a nanofiltration or a reverse osmosis membrane. The experiments were conducted at different transmembrane pressures, feed flow rate, concentration of feed and different experiment duration at a temperature of (25 ± 1) °C. Permeate flux has been calculated by time necessary to collect a permeate sample of 10 mL volume. Rejections for selectivity investigations were calculated using the following equation:

$$R = 1 - \left(\frac{c_i^p}{c_i^f}\right),$$

while for all the other investigations rejection has been calculated by using conductivity ratios as suggested in the following equation:

$$R = 1 - \left(\frac{\kappa_{25}^p}{\kappa_{25}^f}\right),$$

where c_i^p and c_i^f are the permeate and the feed concentration of the solute i and κ_{25}^p and κ_{25}^f the permeate and feed conductivity at 25 C, respectively.

2.4. Sampling and analytical methods

Each sampling covered a permeate sample and a feed sample directly taken from the feed tank. Pressure, feed flow rate, permeate flow rate (permeate flux) were noted from the control unit. Conductivity and sample temperature were determined with a WTW Cond 340i conductivity meter and a WTW pH340 pH meter, respectively. Samples were analyzed for cations by a Perkin-Elmer (USA) OPTIMA 3000 ICP-OES, while sulphate concentration was analyzed photometrically using HACH Lange (Germany) LCK 153 or LCK 154 test kits.

3. Results and discussion

3.1. Flux and rejection dependence on pressure and flow rate

Initial experiments concerning the applicability of membrane filtration processes in mine water treatment showed typical experimental results as well known from groundwater, surface water treatment and desalination of brackish and seawater. Fig. 1a shows permeate and pure water flux, calculated from pure water permeability of 6.30 L/(bar m^2; h) for NF99 and 2.92 L/(bar m^2; h) for RO 98pHt membrane, for different feed pressures and transmembrane pressures accordingly. As can be clearly seen permeate flux shows the well known linear relationship to transmembrane pressure. Next to this it seems obvious that in case of NF99 nanofiltration membrane pure water flux and permeate flux show different permeabilities, namely a lower permeability for the investigated mine water. Therefore osmotic pressure seems to influence the permeability for NF99, while in case of RO 98pHt membrane pure water and permeate flux appear to be comparably. Fig. 1b illustrates rejection of total

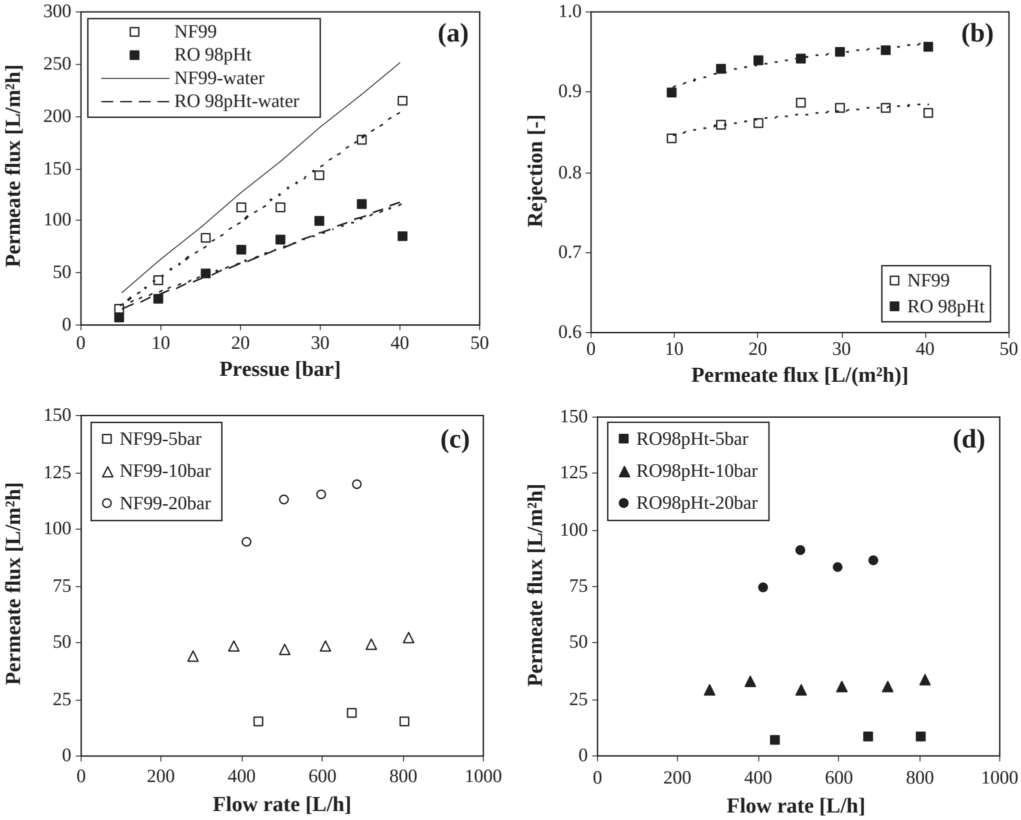

Fig. 1. Pure water flux, permeate flux as function of feed pressure (a) and rejection as function of feed pressure (b) for NF99 nanofiltration and RO 98pHt reverse osmosis membrane at (25 ± 1) °C and 490 L/h feed flow rate. Permeate flux as function of feed flow rate for NF99 nanofiltration membrane (c) and RO 98pHt reverse osmosis membrane (d) at (25 ± 1) °C and for three different feed pressures: 5, 10, 20 bar.

Table 2
Average rejections (standard deviation) for feed flow rate variation at three different pressures: 5, 10, 20 bar.

	5 bar	10 bar	20 bar
NF99	72.0% (3.7%)	80.3% (0.8%)	83.8% (0.8%)
RO 98pHt	78.7% (8.5%)	91.1% (0.4%)	93.9% (0.1%)

dissolved solids content determined by conductivity ratio for feed and permeate sample as a function of pressure and shows the typical behaviour of logistic increase to a constant rejection of about 87% for NF99 and 95% for RO 98pHt membrane.

Fig. 1c and d shows the dependence of flux on feed flow rate. As can be seen significant increases can be found for 20 bar experimental condition for NF99 and RO 98pHt membrane, respectively. This increase can be explained by a decrease of boundary layer resistance that is, due to film theory, directly influenced by the feed cross-flow velocity and therefore the feed flow rate accordingly. Table 2 summarizes average rejections over feed flow rate and indicate, based on standard deviation of rejection, no correlation with feed flow rate concerning this experimental set-up. Higher flux results from transmembrane pressure increase.

3.2. Flux and rejection dependence on total dissolved solids concentration

As expected, Fig. 2a shows a linear decrease of permeate flux with increasing concentration in total dissolved solids, resulting from higher osmotic pressure. Due to increase of osmotic pressure and permeate flux decrease accordingly, rejection should decrease as well [16]. Experimental results as shown in Fig. 2b illustrates opposite behaviour and may indicate the appearance of scaling, causing a rejection of inorganic solutes by filtration and precipitation (scaling).

3.3. Selectivity

Fig. 3 illustrates rejections for different ions for NF99 and RO 98pHt membrane. Results from nanofiltration and reverse osmosis treatment show promising

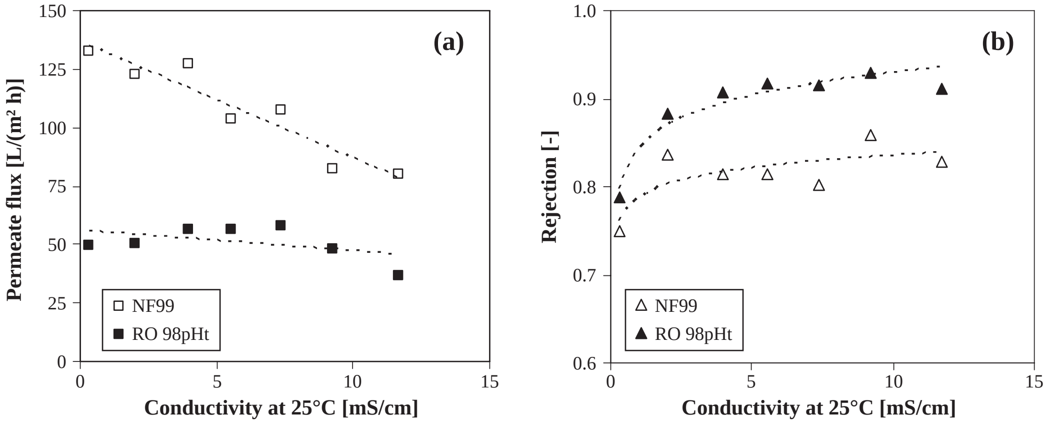

Fig. 2. Permeate flux (a) and rejection (b) as function of conductivity (25 °C) as a measure for total dissolved solids content for NF99 nanofiltration and RO 98pHt reverse osmosis membrane at (25 ± 1) °C process temperature, 15 bar feed pressure and 500 L/h feed flow rate.

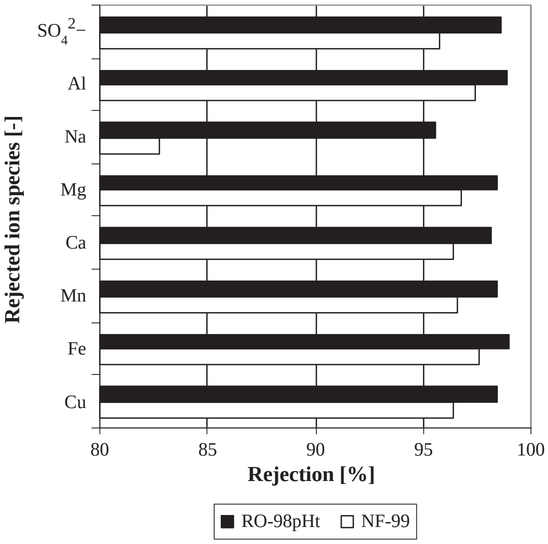

Fig. 3. Selectivity of NF99 nanofiltration and RO 98pHt reverse osmosis membrane at (25 ± 1) °C process temperature,15 bar feed pressure and about 500 L/h feed flow rate for dissolved sulphate, Al^{3+}, Na^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Cu^{2+}.

rejections higher than 95% for polyvalent ions such as dissolved metals but also sulphate. Besides, sodium rejection by NF99 shows typical behaviour of nanofiltration membranes, namely the lower rejection of monovalent ions. This can also be understood as a reason for lower total dissolved solids (TDS) rejection. Since rejection of TDS has been determined by conductivity ratio between feed and permeate sample, nanofiltration shows lower rejections due to permeation of monovalent ions, while multivalent ion rejections for NF99 are comparable to RO 98pHt membrane.

3.4. Permeate flux as function of experiment duration at different conditions

Fig. 4a–d illustrates relative flux decline for long-term permeation tests with NF99 and RO 98pHt membranes at four different experimental conditions: 20 and 30 bar experiments have been conducted for either original mine water as stated in Table 1 and an about twofold concentrated mine water compared to mine water composition. Concentration of the mine water was reached by permeate removal during reverse osmosis filtration with RO 98pHt membrane. Time dependent flux decline can be divided into two phases: (I) an exponential decline in the beginning followed by (II) a linear decrease of flux after the exponential phase. Exponential decline occurs due to membrane compaction and concentration polarization effects in the beginning of the permeation experiments. Linear decline occurs after membrane compaction and concentration polarization reached an equilibrium state until flux finally reaches either a minimum constant level or decline proceeds until membrane is totally blocked due to scaling effects. Exponential decline has been observed for all investigated experimental conditions, while linear decline or constant flux has only been observed for 20 bar conditions for both membranes and for NF99 membrane at 30 bar experiments, respectively. A slight linear decline or constant minimum flux indicate no scaling over experiment duration for NF99 and RO 98pHt membranes at 20 bar experiments with original and twofold concentrated mine water, respectively. Surprisingly flux decline and final flux for nanofiltration membrane NF99 is lower than final flux for RO 98pHt membrane. This can be explained by higher solvent permeability of nanofiltration membrane NF99 compared to RO 98pHt membrane, causing higher

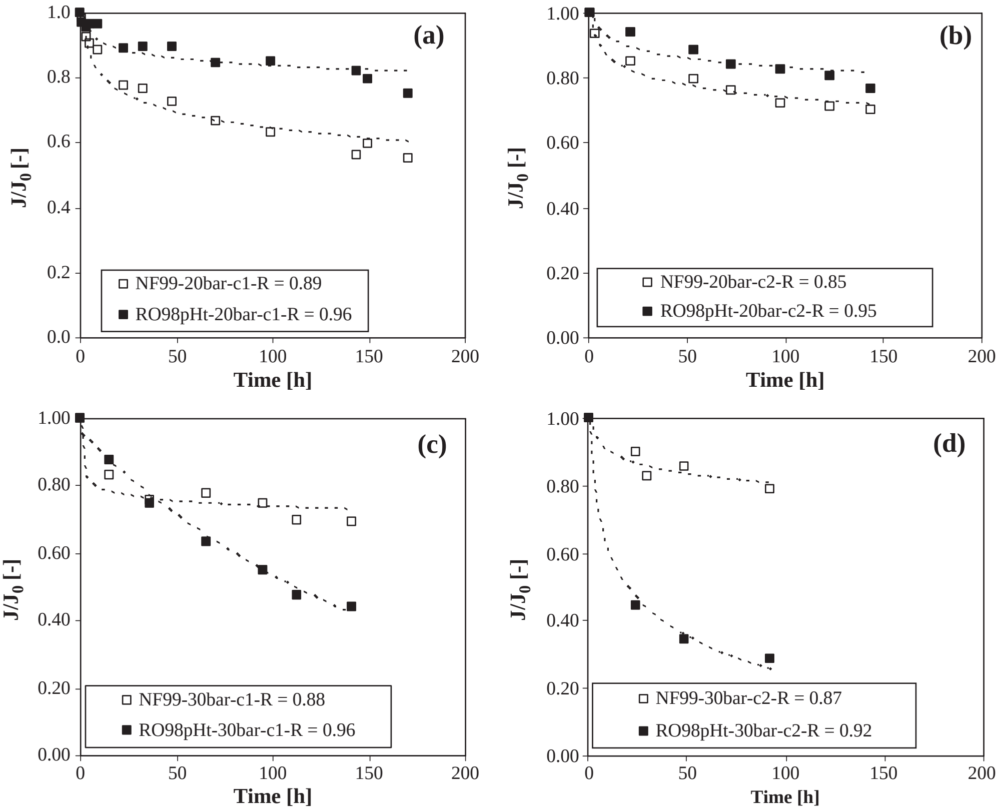

Fig. 4. Relative flux decline compared to initial permeate flux for four different experimental conditions at (25 ± 1) °C. Codes: NF99, RO 98pHt – nanofiltration and reverse osmosis membrane, c1 – original mine water, c2 – twofold concentrated mine water, R – rejection.

concentration polarization and therefore a higher total membrane resistance leading to a stronger relative flux decline. Next to the described observations flux decline for RO 98pHt membrane at 30 bar and for both mine water concentrations (original and twofold) show a different behaviour namely a strong linear to exponential decline over the complete experiment duration. This observation indicates the appearance of scaling for these experiments, causing a blockage of the membrane and therefore a reduction of active filtration area.

To confirm appearance of scaling, the used membrane sheets have been examined after the filtration experiment. All membranes from experimental conditions using twofold concentrated mine water showed a crystalline white precipitate on the membranes surface identified as gypsum. Next to this an accumulation of gypsum has been observed at the membranes circumference for reverse osmosis experiments using twofold concentrated mine water, caused by convective transport of in-bulk crystallized gypsum. Additionally a colloidal brownish precipitate has been found on membranes using original mine water, representing metal hydroxides, that can be easily swept away. Rejections, determined by permeate-feed conductivity ratio, were comparable to the previously presented results and constant according to negligible standard deviations <2% for all conditions.

4. Conclusion

Chemical mine water treatment by the addition of alkaline agents leads to precipitation of insoluble metal hydroxides and sulphate containing mineral compounds resulting in product water poor in metals but high in sulphate according to future water quality criteria considerations. The use of constructed wetlands bypass solubility limitations of sulphate by microbial sulphate reduction leading to waters low in metals and sulphate. Although mine waters treated by microbial methods show good results, treatment capacity of large water streams is, due to comparably low degradation rates and therefore necessarily high residence times, only given for huge wetlands.

Therefore experimental investigations of mine water membrane filtration treatment at different experimental conditions has been conducted and support the applicability of nanofiltration and reverse osmosis to treat mine waters. Next to this it has been shown that scaling due to in-bulk and on-membrane precipitation of solutes occurs and has a significant effect on process efficiency. Rejection results indicate comparable separation efficiency for nanofiltration and reverse osmosis membranes concerning polyvalent ions such as metals and sulphate. Therefore it can be concluded that nanofiltration of the investigated mine water at 20 bar feed pressure is the most promising treatment option, since it provides a clean almost directly dischargeable permeate with high rejection of toxic metals and sulphate. Besides, lower scaling potential and energy consumed for fluxes comparable to RO favor NF as well. Future plans involve investigations concerning the applicability of commercially available membrane modules and turn-key-solutions, scaling a fouling countermeasures and considerations concerning hybrid processes (e.g. recycling of nanofiltration concentrate streams into a precipitation–sedimentation treatment).

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