

Reduction of Sulphate Load by Nanofiltration – Process Development in Bench Scale

Volker PREUSS¹, Ralph SCHOEPEKE¹, Thomas KOCH²

¹Brandenburg University of Technology Cottbus, Chair of Water Technology and Urban Hydraulic Engineering, PO Box 101344, 03013 Cottbus, Germany, preuss@tu-cottbus.de, schoepke@tu-cottbus.de

²Vattenfall Europe Mining AG, Vom-Stein-Strasse 39, 03050 Cottbus, Germany, thomas2.koch@vattenfall.de

Abstract Mine water typically contains a high concentration of sulphate ions. Traditional mine water treatment by liming operates without a significant deviation of this parameter. The discharge of treated mine water into rivers raises their sulphate load. In connection with the use of these water bodies, e.g. for drinking water production by bank filtration, a reduction of the sulphate load is of particular interest. Nanofiltration, as an applicable technology, is characterised by nearly complete sulphate retention (Bertrand et al. 1997). However, typical mine water quality implies a serious problem by scaling (Melin 2004). Therefore a research project was started to develop an additional membrane filtration process to improve the traditional mine water treatment. In this paper the results of the process development are shown.

Key Words mine water, sulphate, membrane filtration, nanofiltration

Introduction

In the eastern part of Germany in the Lusatian lignite mining district coal exploitation has taken place for more than 100 years. In several mine water treatment plants the pH values are increased by liming and dissolved iron and other heavy metals are removed but there is no significant deviation of the sulphate content. A large part of this treated mine water is discharged into the river Spree. Within the next years an increase of the river water sulphate concentration is forecast (G.E.O.S. 2009). If river water is used for drinking water production, e.g. by bank filtration, the sulphate concentration in the clean water could exceed the drinking water limit in the future.

Typically nanofiltration is used for the retention of multivalent ions. However, high amounts of calcium, sulphate and carbonate in mine water cause scaling problems. To inhibit scaling measures in addition to the membrane filtration process are needed. An external seeding (Kuemmel et al. 1999) was intended for that purpose. With a regular membrane filtration process salt-rich water (retentate) is produced and discharged. To avoid a discharge of sulphate-rich water a treatment process is required which concentrates the multivalent ions by nanofiltration and separates the accumulated salts by precipitation.

Materials and Methods

Filtration unit and membranes

The laboratory-scale membrane filtration unit LSta-80 by SIMA-tec GmbH was used in this study. Two cross-flow flat-sheet membrane modules were run in series. The membrane area and the channel height in each module were 84 cm² and 1.1 mm, respectively.

The membranes used in the mine water treatment process were SR 2 by Koch Membrane Systems, Inc. and Filmtec™ NF270 by Dow Chemical Company. Both membranes achieved the best performance in membrane screening made in former times. The membrane sheets were cut into suitable pieces for the module and the pieces were pre-treated by soaking them for an hour in pure water. For the purpose of external seeding a fixed bed reactor filled with 9.4 kg gypsum particles was used. The grain size of the particles was between 500 and 2,000 µm. Different casks with stirring units were used for the desalting procedure by multistage precipitation.

Water quality

The mine water used in these tests was conventionally treated by liming. It was taken from the outlet of a mine water treatment plant of the Vattenfall Europe Mining AG and stored in the laboratory at room temperature. The results of the water analysis are presented in Table 1. The used mine water was saturated with gypsum and over-saturated with respect to calcite.

Table 1 Quality of mine water used

Parameter	Sample value	Parameter	Sample value
pH	7.67	Sodium, mg/l	15.2
Electrical conductivity, $\mu\text{S/cm}$	2,760	Potassium, mg/l	8.9
Temperature, $^{\circ}\text{C}$	21	Magnesium, mg/l	97
Alkalinity, mmol/l	2.57	Calcium, mg/l	605
Silicate, mg/l	6.3	Iron, mg/l	0.3
Chloride, mg/l	10.4	Manganese, mg/l	1.4
Sulphate, mg/l	1,850	TOC, mg/l	6.8

Operation

The membrane filtration unit was operated in a feed & bleed scheme with two membrane modules in series. Permeate flows were discharged and the feed water level was kept on a constant level by adding mine water.

Feed water pH was lowered to a value of 6.5 by adding carbon dioxide to prevent scaling by carbonates. Retentate flow was circulated back to the feed water container after a depletion of the over-saturation by gypsum in the fixed bed reactor.

The operating conditions of the membrane filtration unit were a constant cross flow velocity and a constant permeate flow rate for the first membrane module at 20°C (Fig. 1).

Results and discussion

Membrane characteristics

Seeing that pressure is the driving force for water permeation, flux increases linearly with increasing pressure (Fig. 2). The flux of the SR2 membrane is higher than that of the NF270 membrane. The sulphate retention of the NF270 membrane is larger than 96 % and is nearly constant in the tested pressure range. The sulphate retention of the SR2 membrane is less than that of the NF 270 membrane and increases with pressure in the range below 5 bar (Fig. 2). This behaviour can be explained with reduced diffusion as flux increases. Under conditions of the flat-sheet membrane module the higher flux of the SR2 membrane seems advantageous. However, with respect to the element recovery of a spiral wound membrane module the use of the NF270 membrane with high retention in the range of lower fluxes is more profitable.

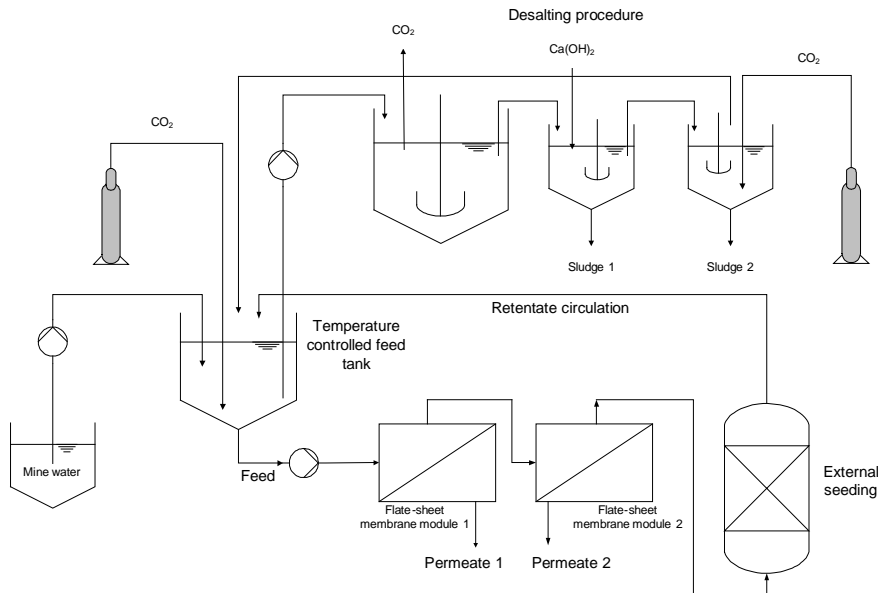


Figure 1 Schematic of the laboratory scale treatment process

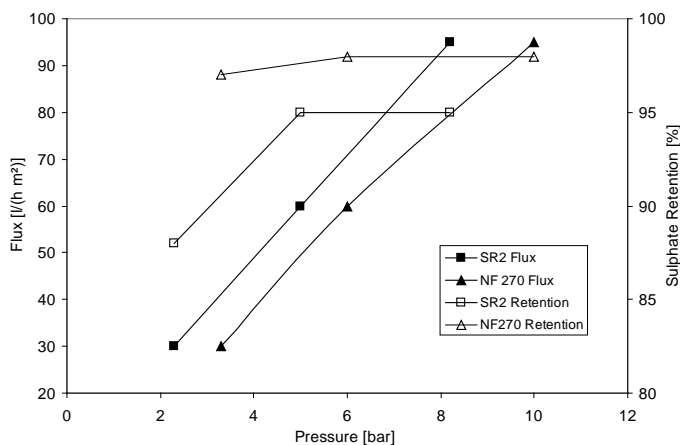


Figure 2 Flux and sulphate retention as a function of pressure for SR2 and NF270 membranes

The retention of the bivalent ions was in the sequence sulphate > magnesium > calcium. Thus the precipitation of gypsum is not sufficient to keep the salinity of the process water on a constant level. A branch current was withdrawn from the feed water container and collected for the discontinuous desalting procedure. In the first step the pH was increased by stripping carbon dioxide. In a second step lime hydrate was added and the pH value rose to 12.0. In particular, magnesium oxide and calcium sulphate were precipitated. After solid-liquid-separation in the third step the pH of the supernatant was lowered by adding carbon dioxide to a value of 9.0. After precipitation of carbonates the supernatant was circulated back to the feed water.

Feed flow variation

For economic reasons it is of interest to reduce the circulation flow. With decreasing feed flows at constant permeate flow the element recovery increases. But with a higher repletion of the retentate scaling problems occur. Element recovery was varied between 2 % and 5,3 %. A critical value was achieved with an element recovery of 4 %. This result directly depends on the performance of the external seeding.

External seeding

Samples were taken from the inlet and the outlet of the crystallisation reactor. With PhreeqC the gypsum precipitation capacities of these waters were calculated. On average, the inlet and outlet gypsum precipitation capacity was 4,5 mmol/L and 1,34 mmol/L, respectively. The needed effectiveness of this treatment step was not achieved. Based on gypsum crystallisation kinetics by Niemann (2004) an outlet value of 0,27 mmol/L was expected. As a consequence, the reactor design was changed into a fluidised bed reactor. In separate tests (data are not shown) the needed seed crystal concentration and contact time were ascertained.

Quality of clear water and precipitates

Although the seeding performance was not in the rated range the overall process was carried on in a period between 100 and 200 hours. Table 2 shows the average permeate characteristics. The clear water sulphate concentration was significantly lowered. So it would be possible to discharge a mixed water (permeate and conventionally treated mine water).

In the overall process accumulated salts were precipitated in three different qualities. The precipitation product of external seeding is gypsum. The first and the second sludge of the desalting procedure consist of brucite, calcite, gypsum and calcite, gypsum, magnesite respectively.

The process recovery is larger than 80 % and depends on the water content of the precipitates only.

Table 2 Quality of clear water

Parameter	Sample value	Parameter	Sample value
pH	6.80	Sodium, mg/l	29.5
Electrical conductivity, $\mu\text{S}/\text{cm}$	350	Potassium, mg/l	12.0
Temperature, $^{\circ}\text{C}$	23.5	Magnesium, mg/l	13.0
Alkalinity, mmol/l	1.5	Calcium, mg/l	95.0
Silicate, mg/l	6.2	Iron, mg/l	<0.1
Chloride, mg/l	26.0	Manganese, mg/l	<0.05
Sulphate, mg/l	65	TOC, mg/l	6.1

Conclusions

Nanofiltration could be an appropriate technology for lowering the mine water sulphate concentration. In bench scale, a combination process was developed to handle conventionally pre-treated mine water. To control scaling problems pH adjustment and external seeding were used. With a three-step desalting procedure all accumulated salts were precipitated. Due to the high sulphate retention by nanofiltration the additional treatment of a branch current is required. Overall process recovery reaches usual values of nanofiltration applications and depends on the water content of the precipitates only.

Acknowledgements

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