

## NANOFILTRATION AS AN EFFECTIVE TOOL OF REDUCING SULPHATE CONCENTRATION IN MINE WATER

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### Abstract

Mine water typically contains a high concentration of sulphate ions. Conventional mine water treatment by liming operates without a significant decline of this parameter. A discharge of treated mine water into rivers raises their sulphate load. The reduction of sulphate level in the river waters is of particular interest, especially if such waters are to be used for drinking purposes. Nanofiltration, as an applicable technology, is characterized by nearly complete sulphate retention. However, typical mine water quality implies a serious problem by scaling. Therefore, an additional membrane filtration process was developed to improve the conventional mine water treatment. This paper shows the results of process development towards removing sulphate as well as minimizing waste and indicates nanofiltration as an appropriate technology for lowering mine water sulphate concentration.

### Streszczenie

Wody kopalniane charakteryzują się wysokim stężeniem jonów siarczanowych. Tradycyjne techniki oczyszczania wód kopalnianych przy użyciu wapna nie wpływają znacząco na obniżenie wartości tego parametru. Odprowadzenie tak oczyszczonych wód kopalnianych do rzek zwiększa ładunek siarczanów w ciekach. W związku z tym bardzo ważna jest redukcja poziomu siarczanów w ciekach szczególnie w przypadku stosowania tych wód do produkcji wody pitnej. Zastosowanie procesu nanofiltracji pozwala na niemal całkowite zatrzymanie siarczanów. Jednak typowa jakość wód kopalnianych powoduje w procesie ich oczyszczania poważny problem związany z osadzaniem się nierozpuszczalnych soli na powierzchni membran. W celu usprawnienia tradycyjnej metody oczyszczania wód kopalnianych zastosowano dodatkowy proces filtracji membranowej. W publikacji przedstawiono wyniki udoskonalania procesu oczyszczania wód kopalnianych w kierunku redukcji wysokich stężeń siarczanów oraz ograniczania odpadów, wskazując jednocześnie na efektywność nanofiltracji.

**Keywords:** Mine water; Sulphate; Membrane filtration; Nanofiltration.

## 1. INTRODUCTION

In the eastern part of Germany in the Lusatian lignite mining district coal exploitation has taken place for more than 100 years. Mine dewatering is an inherent part of mining operations. Typical mine water quality

is characterized by low pH values and high amounts of iron and sulphate. In several mine water treatment plants the pH values are increased by liming and dissolved iron and other heavy metals are removed. However, there is no significant decline of the sulphate content.

A large part of this treated mine water is discharged directly into the Spree river. Within the next years an increase of the river water sulphate concentration is forecast [1]. If river water is used for drinking water production, e.g. by the use of riverbank filtration, the sulphate concentration in the clean water could exceed the drinking water limit in the future. Therefore, a better mine water treatment is required which also lowers the sulphate content. The Brandenburg University of Technology in cooperation with the Institute for Water Management, Urban Water Engineering and Ecology is developing a new mine water treatment technology on behalf of the Vattenfall Europe Mining AG.

Due to the growing demand for a high water quality it is necessary to continuously improve existing and new water treatment technologies. All the disadvantages associated with traditional water treatment technologies open the way to the application of new separation techniques among which membrane techniques are the most advantageous. Pressure driven membrane processes guarantee the constant quality of water production, small quantities of reagents and a little amount of wastes, requiring additional management.

Water Treatment Plant KWK "Pokój" in Ruda Śląska (Poland) is the one of many examples of purification mine water with high sulphate content (about  $2000 \text{ mg} \cdot \text{dm}^{-3}$ ) with using membranes for drinking water purpose. At the station pretreatment process consists of pH correction, coagulation and pressure filtration. Next, the water is directed to a two-step process of reverse osmosis. After that, purified water is mixing with approximately 10% of the raw water. Similarly, the station "Rudultowy" (Poland) uses reverse osmosis for the purification of mine water with satisfactory results [2]. Several authors also confirm the effectiveness of nanofiltration in removing sulfates from wastewater [3] and from water [4, 5] even if concentration reaches nearly  $3000 \text{ mg} \cdot \text{dm}^{-3}$  [6]. Unfortunately, all retentate is accumulated at the stations as waste.

Although manufacturers constantly produce better solutions of membrane modules, the present problems concern not only the removal of impurities from water but also management of waste. For instance the technology from Poland based on recovery NaCl or  $\text{CaSO}_4$  from retentate [7] and similar technology from South Africa are good examples of minimizing waste production [8]. Nevertheless, methods based on minimizing waste production are relatively new and need to be developed especially to protect the environment.

Recent requirements for mine water purification did not include the minimization of neutral salts. Therefore, purified mine water is characterized by high salt concentrations such as sulphate. In particular, purified mine water with sulphate concentration cause increased sulphate loads in river streams. For that reason more emphasis has to be placed upon optimizing sulphate reduction. Conventional treatment with lime may not be sufficient.

Nanofiltration (NF) is an innovative membrane water treatment technique. NF process involves separation of substances with a range of sizes between 1-5 nm and provides efficient removal of organic and inorganic compounds that ensures water quality sufficient to reuse for different purposes. Method of separation of the components in the NF is a combination of molecular sieving mechanism characteristic of microfiltration and ultrafiltration and dissolve-diffusion mechanism characteristic of reverse osmosis (RO) [8]. Rejection of charged solutes by nanofiltration membranes is complicated. The process consists of different mechanisms such as electrostatic interactions between the membrane and the charged species, sieving or size effect, differences in diffusivity and solubility, dielectric repulsion, etc. [9] The characteristic feature of NF membranes is selectivity of ions with different valence. Ion selectivity of nanofiltration for the most commonly used negatively charged membranes depends on the presence on the membrane surface or in the pores groups with a negative charge, such as carboxyl ( $-\text{OOC}^-$ ) or sulfo ( $-\text{SO}_3^-$ ) groups. Negative charge of the membrane causes repulsion of multivalent anions ( $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ) and retention of salts containing divalent anions and monovalent cations is close to 100%. Only at very high salt concentrations the multivalent anions can permeate through the membrane because of their weak electric charge [10].

The results of the nanofiltration experiments have shown very high retentions of sulfates by the examined nanofiltration membranes [3-6, 9]. Therefore, nanofiltration process is attractive to be applied in advanced mine water treatment. The paper describes nanofiltration as an appropriate technology for lowering mine water sulphate concentration and present the solution for managing retentate at the station.

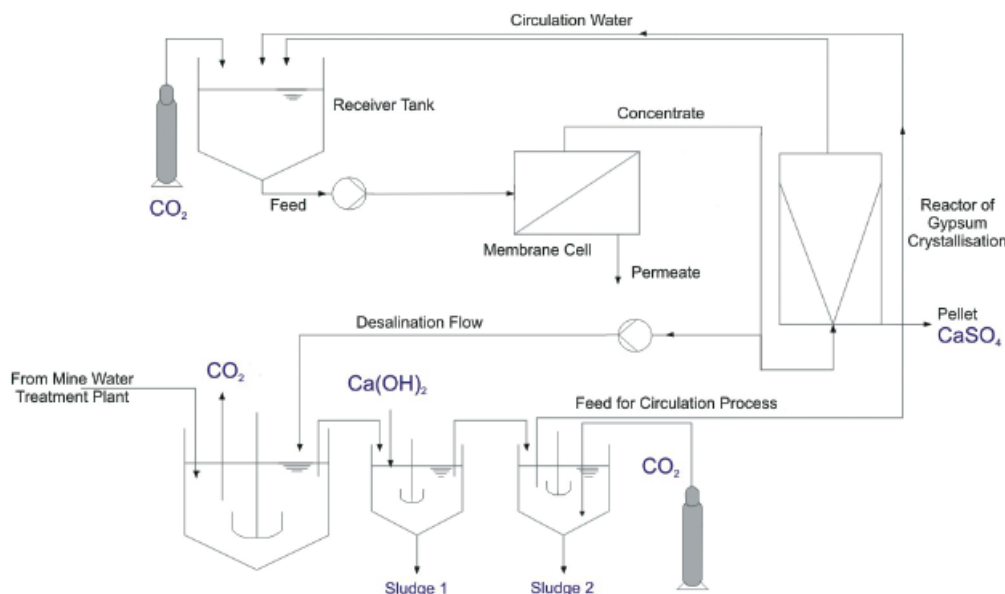


Figure 1. Overall process including nanofiltration, gypsum crystallization and process water pretreatment

## 2. MATERIALS AND METHODS

### 2.1. Quality of water

The mine water used in this research was conventionally treated by liming. It was taken from outlet of a mine water treatment plant of the Vattenfall Europe Mining AG. The results of water analysis presented in Table 1 indicate the high concentration of sulphate and show the need to improve mine water quality. The mine water was saturated with gypsum and over-saturated with respect to calcite.

### 2.2. Process development

Nanofiltration is well known for its removal capability especially for multivalent ions. The sulphate rejection reaches typically more than 90%. To avoid a discharge of sulphate rich water cross-flow membrane filtration technology must be improved. A treatment process is required which concentrates multivalent ions by nanofiltration and separates accumulated salts by precipitation. In this way permeate can be discharged only. However, high amounts of calcium, sulphate and carbonate in mine water cause scaling problems. Therefore feed water pH is lowered to a value of 6.5 by adding carbon dioxide to prevent scaling by carbonates. While membrane filtration gypsum-saturated feed is transformed into an over-saturated concentrate. Over-saturation is depleted in a moving bed gypsum crystallization reactor (external seeding [12, 13]). Subsequent concentrate flow is cir-

culated back to the feed water container (Fig. 1). In this process Filmtec TM membrane NF270 by Dow Chemical Company achieves best performance [14]. Furthermore it is necessary to limit the magnesium concentration in the treated feed. Magnesium would be concentrated by NF and would interfere with gypsum crystallization. Moreover, high amounts of magnesium in feed cause a higher gypsum saturation limit and consequently a higher sulphate content in permeate. Thus a pretreatment of rough water together with a small amount of concentrate (desalting flow in the order of 10% of permeate flow) by a multistage precipitation is proposed. This treatment is realized as three step desalting procedure. At first carbon dioxide degases. This reduces lime consumption in the next step. By adding lime hydrate pH value of 11.8 is achieved and magnesium hydroxide precipitates. Finally pH is lowered by adding carbon dioxide. In this step mostly calcium carbonate precipitates. By simultaneous removal of iron, manganese and organic matter fouling potential of this pretreated water is significantly lowered. Overall water recovery reaches typical values for NF process (> 75%) and is limited by water content of sludge.

### 2.3. Quality of permeate and precipitates

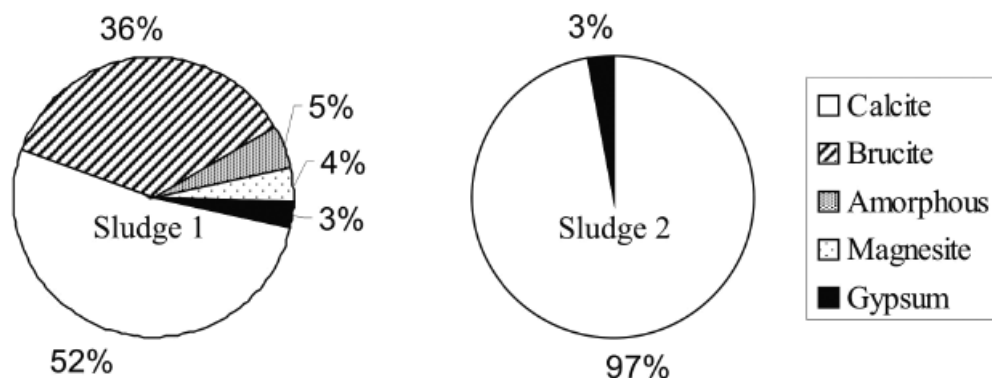
Table 2 shows the average permeate characteristics. Sulphate concentration is significantly lowered. Water quality meets the requirements of drinking water.

**Table 1.**  
Quality of mine water after conventional lime treatment

| Parameter                                                 | Sample value |
|-----------------------------------------------------------|--------------|
| pH                                                        | 7.67         |
| Electrical conductivity, $\mu\text{S}\cdot\text{cm}^{-1}$ | 2,760        |
| Temperature, $^{\circ}\text{C}$                           | 21           |
| Alkalinity, $\text{mmol}\cdot\text{dm}^{-3}$              | 2.57         |
| Silicate, $\text{mg}\cdot\text{dm}^{-3}$                  | 6.3          |
| Chloride, $\text{mg}\cdot\text{dm}^{-3}$                  | 10.4         |
| Sulfate, $\text{mg}\cdot\text{dm}^{-3}$                   | 1,850        |
| Sodium, $\text{mg}\cdot\text{dm}^{-3}$                    | 15.2         |
| Potassium, $\text{mg}\cdot\text{dm}^{-3}$                 | 8.9          |
| Magnesium, $\text{mg}\cdot\text{dm}^{-3}$                 | 97           |
| Calcium, $\text{mg}\cdot\text{dm}^{-3}$                   | 605          |
| Iron, $\text{mg}\cdot\text{dm}^{-3}$                      | 0.3          |
| Manganese, $\text{mg}\cdot\text{dm}^{-3}$                 | 1.4          |
| TOC, $\text{mg}\cdot\text{dm}^{-3}$                       | 6.8          |

**Table 2.**  
Quality of mine water after nanofiltration process

| Parameter                                                 | Sample value |
|-----------------------------------------------------------|--------------|
| pH                                                        | 6.80         |
| Electrical conductivity, $\mu\text{S}\cdot\text{cm}^{-1}$ | 350          |
| Temperature, $^{\circ}\text{C}$                           | 23           |
| Alkalinity, $\text{mmol}\cdot\text{dm}^{-3}$              | 1.5          |
| Silicate, $\text{mg}\cdot\text{dm}^{-3}$                  | 6.2          |
| Chloride, $\text{mg}\cdot\text{dm}^{-3}$                  | 26.0         |
| Sulfate, $\text{mg}\cdot\text{dm}^{-3}$                   | 65           |
| Sodium, $\text{mg}\cdot\text{dm}^{-3}$                    | 29.5         |
| Potassium, $\text{mg}\cdot\text{dm}^{-3}$                 | 12.0         |
| Magnesium, $\text{mg}\cdot\text{dm}^{-3}$                 | 13.0         |
| Calcium, $\text{mg}\cdot\text{dm}^{-3}$                   | 95           |
| Iron, $\text{mg}\cdot\text{dm}^{-3}$                      | <0.1         |
| Manganese, $\text{mg}\cdot\text{dm}^{-3}$                 | <0.05        |
| TOC, $\text{mg}\cdot\text{dm}^{-3}$                       | 6.1          |

**Figure 2.**  
Composition of resulting sludge from process water pretreatment

In the overall process accumulated solids are precipitated in three different forms. First sludge of the desalting process consist of calcite (52%), brucite (36%), amorphous (5%), magnesite (4%) and gypsum (3%), whereas the second sludge contains 97% of calcite and a small amount of gypsum (3%) (Fig. 2). The results achieved show that the alkaline sludge can be used instead of lime. The water quality after liming coagulation was similar to the water treating with the use of alkaline sludge except for the higher value of magnesium ( $170.9 \text{ mg}\cdot\text{dm}^{-3}$ ) and manganese ( $3.48 \text{ mg}\cdot\text{dm}^{-3}$ ). The third product is gypsum from the crystallization reactor. In the future gypsum, in the form of pellet can be used for example as a building material.

#### 2.4. Advanced mine water treatment

Due to the high sulphate retention by nanofiltration advanced treatment of a side stream is sufficient. According to the ratio of the partial flows a purification aim for the complete treatment process can be defined. Furthermore, the sludge of the desalting procedure can be reused in conventional mine water treatment. In this way cost effectiveness is increased. A mine water treatment in two lanes, as shown in Fig. 3, is sufficient.

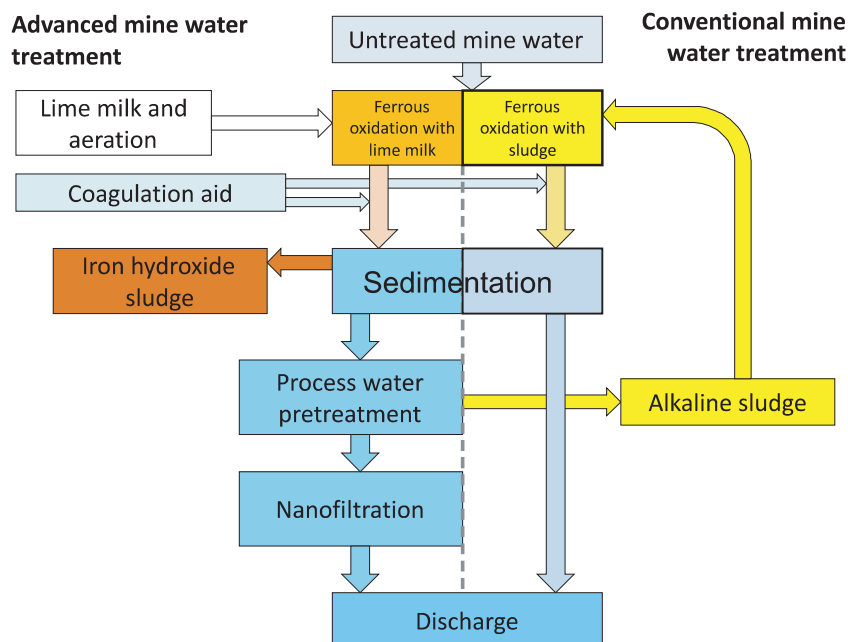


Figure 3.  
Proposed combination of conventional and advanced mine water treatment

### 3. CONCLUSION

In bench scale and pilot scale a combination process was developed to handle conventionally 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, additional treatment of a side stream is required. Overall process recovery reaches usual values of nanofiltration applications and depends on the water content of sludge only. It is worth emphasizing that the alkaline sludge of the desalting procedure can be reused in conventionally mine water treatment in order to minimize waste. The results of these experiments clearly show that nanofiltration is suitable technique for water with high concentration of sulphate but to understand the phenomenon of the process detected in the experiment further investigations are required.

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