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Membrane concept for valorization of bicarbonate in sulfate-reduced effluent

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ABSTRACT

Bicarbonate and toxic hydrogen sulfide are generated in sulfate-reducing bacterial processes in the presence of suitable bacteria and conditions. They are often preferably eliminated from the solutions rather than utilized. However, hydrogen sulfide could be utilized for precipitation of metal products, whereas bicarbonate could be considered as a precursor for a calcium precipitation chemical. This study focused on the valorization of bicarbonate-containing mine water effluent from a sulfate-reducing bacterial process, called biosolution, using membrane concentration as the main technology in the concept. Concentration was found to be an essential step for the utilization of biosolution in calcium precipitation. Good quality water was produced at the same time, for reuse or safe discharge. Biosolutions contained residual concentrations of sparingly soluble sulfides, which caused problems for membrane filtration performance. This study revealed that microfiltration to stop the biological sulfate-reducing process by removing bacteria, aeration to oxidize residual sulfides, and microfiltration to remove suspended solids were needed for sufficient pre-treatment prior to membrane concentration. Both nanofiltration and reverse osmosis worked well as a bicarbonate concentration technology. Concentrated bicarbonate solution was then converted to effective calcium precipitation chemical by adjusting the pH, as a result of which the chemical balance favored the effective carbonate instead of the ineffective bicarbonate. This membrane concept is a step towards the closed-loop processes of the circular economy.

Keywords: Membrane concept; Nanofiltration; Mine water; Bicarbonate; Sulfide; Calcium precipitation; Wastewater; Sulfate removal; Circular economy

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1. Introduction

Mineral processing requires large quantities of good quality water but also produces water effluents containing large quantities of impurities, such as metal sulfates. The composition of effluent waters is different depending on the minerals to be mined and on the mining process itself [1]. For this reason, suitable water treatment technologies must be evaluated case by case. Several methods, such as chemical treatments, membrane filtration, ion exchange, and biological treatments have been suggested for purification of mine waters [2–4].

Of the biological treatments, the utilization of sulfate-reducing bacteria (SRB) has gained attention due to the possibilities for performing the sulfate removal with a low-cost process. It can facilitate the recovery of valuable metals as stable sulfide precipitates and simultaneous reduction of metal and sulfate concentrations in the mining effluents [5–7]. Compared to conventional chemical wastewater treatment alternatives usually performed with lime and hydroxides, lower sulfate and metal concentrations of the wastewaters can be achieved with biological SRB-treatment [2,8]. SRBs are anaerobic microorganisms, which in suitable conditions can utilize sulfate ions (SO_4^{2-}) as the

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terminal electron acceptor for the metabolism of organic substrates. Most of the process sulfur is released as sulfide ions (S^{2-}), usually as free hydrogen sulfide (H_2S). SRB can utilize a wide range of low molecular weight substrates such as ethanol, methanol and acetate. Although some SRB can oxidize organic substrates down to acetate, some can mineralize them to alkaline carbon compounds (Eq. (1)). When hydrogen is used, instead of the above-mentioned substrates, as an electron donor for sulfate reduction, the reaction yields hydroxide ions.

$$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^- \tag{1}$$

H_2S is extremely toxic to human and animal life. It is corrosive to most metals and can cause cracking of drill pipes and tubular goods, as well as the destruction of testing tools and wire lines [6,9]. If sulfate removal is carried out from mine waters by SRB, the produced compounds, especially H_2S but also bicarbonate (HCO_3^-), need to be handled safely, without contaminating the environment. However, rather than removing them, the compounds can be considered as utilizable chemicals. Sulfide forms typically very sparingly soluble metal salts. The precipitation can be made using either solid (iron(II) sulfide (FeS), calcium sulfide (CaS)), aqueous (sodium sulfide (Na_2S), sodium bisulfide (NaHS), ammonium sulfide (NH_4S)), or gaseous sulfide sources (H_2S) [10]. Sulfide precipitation is dependent on the availability of bisulfide ions (HS^-) in solution, which in turn is dependent on pH [10,11]. Sulfide precipitation of metals has been demonstrated to have several benefits over hydroxide precipitation, such as lower effluent metal concentrations and the possibility to recover valuable metals. Compared to lime treatment, it occurs in lower pH, and selective metal recovery is possible [12,13].

Alkaline bicarbonate, such as sodium bicarbonate ($NaHCO_3$), shows the potential for neutralizing acidic process effluents. Bicarbonate does not easily produce sparingly soluble salts, but sodium carbonate (soda, Na_2CO_3) does and can be used as a precipitation chemical, for example, in calcium (Ca) removal [14]. The solubility of calcium bicarbonate ($Ca(HCO_3)_2$) in water is 166 g/L (20°C), whereas solubility of calcium carbonate ($CaCO_3$) is 0.013 g/L (25°C). $NaHCO_3$ can be converted to Na_2CO_3, for example, by reaction with sodium hydroxide (NaOH) to produce Na_2CO_3 and water:

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \tag{2}$$

Thermal decomposition of $NaHCO_3$, starting at a temperature of 50°C, also produces Na_2CO_3:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \tag{3}$$

This study focuses on the utilization of bicarbonate of the SRB process effluent, called biosolution. Since water circulation with reused biosolution causing dilution of process solutions is not desired, the potential chemical is recovered by membrane concentration, either by nanofiltration (NF) or reverse osmosis (RO). When concentrating by either of these technologies it is not only bicarbonate which is concentrated, but all the other compounds in biosolution, such as sulfide, sulfate and calcium, will be concentrated as well. Sulfide forms sparingly soluble metal salts with many metal ions already at very low concentrations, as described above. Calcium sulfate ($CaSO_4$), that is, gypsum, has a tendency to bring on scaling, which is caused by the supersaturation of inorganic compounds concentrated on the feed side of the membrane. Supersaturated salts can precipitate on the membrane surface, building a layer of deposit which hinders mass transfer through the membrane [15,16]. This can be avoided by keeping concentrations low enough using low water recovery (WR). However, low WR is not the aim of desalination processes, not today and even less in the future because of productivity and energy savings [17]. Thus, scaling control is needed when aiming at high WR with waters containing inorganic salts, as was the case in this study. Control of pH can be used successfully in scaling control, for example, in the case of carbonate (CO_3^{2-}). However, pH control has not been effective for the control of gypsum scaling, since the solubility of the salt has weak pH dependence [15,18]. Scale inhibitors, that is, antiscalants, can be used in scaling control. It is also possible to control scaling by removal of scalant-forming ions, such as calcium, by precipitation [18–20] or by ion exchange [18,21,22].

Apart from scaling, fouling needs to be taken into account when biosolution is concentrated by membranes. Little research can be found relating to fouling and SRB. Sahinkay et al. [23] studied fouling in AnMBR for sulfate reduction and sulfide generation together with investigating the filtration performance and characterizing the membrane foulants when the reactor was fed with synthetic sulfate-rich wastewater. High molecular weight soluble organics and accumulation of extracellular polymeric substances, as well as deposition of inorganic substances, such as sulfur (S), silicon (Si), iron (Fe), sodium (Na), and magnesium (Mg), on the cake layer, may have contributed to membrane fouling. Irreversible fouling is often due to the complexation of calcium with organic foulants. Ca complexes form a highly compactable floc-like structure, which also causes the highest flux decline compared to other chelates [16]. According to Zhou et al. [24], inorganics play a significant role in the fouling by precipitating on or into the membrane, or by bridging organic molecules on the membrane surface as described in a variety of studies. The important inorganic foulants can be calcium phosphate ($Ca_3(PO_4)_2$), calcium hydrogenphosphate ($CaHPO_4$), silica (SiO_2), and aluminum oxide (Al_2O_3).

Herein, a membrane method for biosolution concentration is presented, targeting precipitation chemicals and good quality water as final products. Moreover, utilization of the produced chemical in calcium precipitation is demonstrated.

2. Materials and methods

2.1. Studied concept

In this study, biosolution from an SRB-process was pre-treated in order to separate residual toxic H_2S gas and formed precipitates before concentrating alkali, that is, $NaHCO_3$, by membranes. The concentrated biosolution was studied as a calcium precipitation chemical using neutralizing pond (NP) water from the mining industry as a Ca source. The simplified concept consisting of pre-treatment and concentration is shown in Fig. 1.

2.2. Feed solution and composition analysis

Three authentic biosolutions (Table 1) were collected from operational SRB processes for the membrane filtration experiments. Biosolution 1 was collected from the process while microbes were still adapting to new conditions. At this point, the reactor tank was filled with a total volume of 1,200 L of biosolution. Conditions in the reactor were average: pH 7.6, ORP –440 mV, temperature 31°C, sulfate 4,400 mg/L and sulfide 240 mg/L. Biosolution 2 was collected when the total volume of biosolution in the process tanks was 2,000 L. This was achieved by also filling the stripper tank, which is connected via piping with the reactor tank. Process conditions were otherwise the same as in the previous biosolution 1, but microbes had already decreased sulfate to 3,800 mg/L and sulfide had also decreased to 120 mg/L. Biosolution 3 was collected during the ramp-up phase. The daily flow was 300 L/d and sulfate loading was about 2,800 g/d, that is, 9,300 mg/L. Process pH had been increased to 8, ORP was about –460 mV and temperature about 28°C. Sulfate concentration in the biosolution was about 2,400 mg/L and sulfide was about 460 mg/L at this stage. Nutrients and trace elements were added to the process in proportion to the amount of feed. The same nutrients and trace elements were used throughout the process, with the exception of the carbon source. For biosolutions 1 and 2, the carbon source was sodium acetate (CH_3COONa) and for biosolution 3 the source was acetic acid (CH_3COOH). Other nutrients were ammonium sulfate ($(NH_4)_2SO_4$) and potassium dihydrogen phosphate (KH_2PO_4). Trace elements used were calcium (Ca), magnesium (Mg), aluminum (Al),

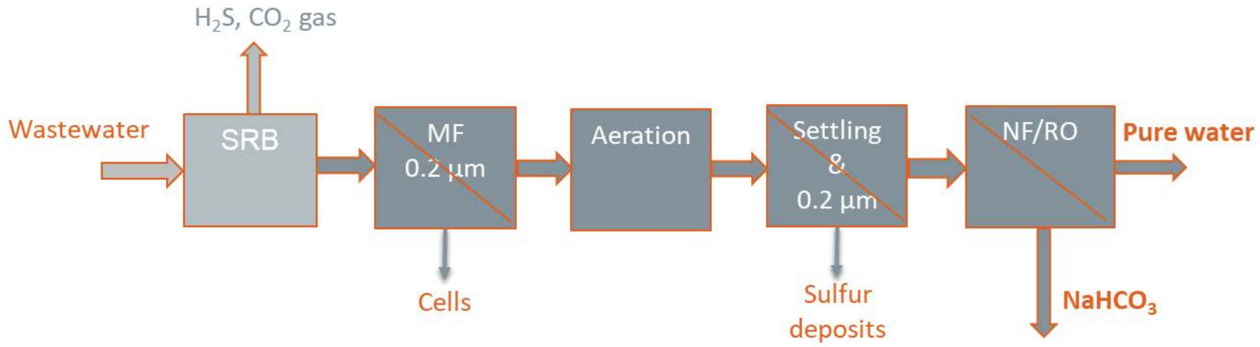

Fig. 1. The simplified concept for SRB biosolution concentration.

Table 1
Composition of the NP water and the used biosolutions (contents as mg/L unless stated otherwise)

Component	Biosolution 1	Biosolution 2	Biosolution 3	NP water in chemical testing
Ca	390	120	11	410
Mg	54	49	38	7.5
Na	3,100	2,600	3,400	2,200
K	42	47	55	52
P	9.9	9.0	12	<0.1
S	1,700	1,900	1,400	1,800
S^{2-}–S	380	344	310	N.A.
Cu	<0.05	<0.05	<0.05	<0.05
Mn	0.53	0.14	<0.05	<0.05
Zn	<0.05	<0.05	<0.05	<0.05
Fe	<0.05	<0.05	<0.05	<0.05
Al	<0.1	<0.1	<0.1	<0.1
Ni	<0.05	<0.05	<0.05	<0.05
Si	6.1	8.0	6.5	0.23
Co	<0.05	<0.05	<0.05	<0.05
Total alkalinity[a]	60[a]	63[a]	63[a]	N.A.
COD	3,698	1,215	1,400	N.A.

[a] mmol/L, measured within one day of sample collection/storing.

copper (Cu), cobalt (Co), manganese (Mn), iron (Fe), nickel (Ni) and zinc (Zn).

The biosolutions and the filtrates were analyzed in terms of elemental composition, concentrations of sulfate, sulfide, chemical oxygen demand (COD), total alkalinity, pH, conductivity, and turbidity. The elemental composition of the solutions was analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-OES) using SFS-EN ISO 11885. Prior to ICP-OES analysis, sample solutions were diluted and acidified and precipitated samples were dissolved according to standards SFS-EN 13656 and SFS-EN 15410. A Hach DR3900 laboratory spectrophotometer (Hach, USA) was used for the analysis of sulfate using the method of LCK 153, sulfide was analyzed by the LCK 653 method, and COD was analyzed by LCK methods 314, 114 or 014 depending on the COD concentration. The total alkalinity of the solutions was determined using titration method SFS-EN ISO 9963-1 or a Hach DR3900 spectrophotometer using method 10239. Turbidity was measured using a HACH 2100AN IS Turbidimeter (Hach, USA) and ISO method 7027. Conductivity was measured using a VWR Conductivity meter CO 3000 H (VWR, Germany), and pH using a VWR pH 1000 H meter (VWR, Germany).

The biosolutions were rather similar in consistency, except for their Ca content and COD. The proportional variation was also high for Mg, although the contents were low.

2.3. Pretreatment

The biosolutions were pre-treated prior to membrane concentration in order to remove possible foulants and scalants. The pre-treatment concept also targeted low sulfide and high alkali content, which could stabilize the sample during storage and filtering. As the first step of pre-treatment, biosolution was filtered by microfiltration (MF) for the removal of microbes, thus eliminating sulfate-reducing microbial activity. A cartridge filter WatMan PX01-9 ¾″ (WatMan, Finland) with a nominal pore size of 1 μm and an absolute PTFE cartridge filter Fluorogard® with a pore size of 0.2 μm (VWR International Oy, Belgium) were tested for the selection of an appropriate filter. Sulfide oxidation and removal of precipitated deposits by settling and MF were then carried out. Sulfide oxidation was accomplished by aeration performed with pressurized air (1.5 bar), feeding air to the biosolution through a ceramic filter with a pore size of 1–2 μm. Another aeration method tested was propeller mixing using a rotor speed of 400 rpm. Both aeration methods were tested for achieving the low level of sulfide in the solution, but they were not optimized regarding, for example, energy use or end products. Suspended solids removal was carried out using the absolute PTFE cartridge filter Fluorogard® with a pore size of 0.2 μm.

2.4. Concentration

Pre-treated biosolution, biosolution 1, was concentrated in order to select a suitable NF or RO membrane for longer filtration tests with a commercial spiral wound element. The tested membranes were NF270, NF90, and BW30LE (Dow, USA). 42 cm^2 membrane coupons were used in a CF042-PTFE cell installed in the filtration unit and equipped with on-line feed flow, pressure, and temperature control and measurement. Permeate flow was also measured on-line. Pressure in the membrane characterization using sodium chloride (NaCl) in rejection tests and membrane selection filtrations was 15 bar, temperature 25°C, and crossflow velocity 1.3 m/s.

Of these membranes, the NF90 membrane was eventually selected for longer concentration filtrations. In concentration filtration using a spiral wound element, NF90-2540 with a 2.6 m^2 membrane area was used. The membrane was characterized by NaCl (VWR International Oy, Belgium) rejection using a normal characterization protocol, that is, 2 g/L NaCl as feed, pressure 4.8 bar, temperature 25°C, and rejection measured at WR 15%. When biosolution was concentrated, that is, biosolution 2 in this case, the osmotic pressure of the feed solution increased when salts in the biosolution concentrated. Hence, the pressure was increased step by step from 15 to 30 bar in order to achieve reasonable operation pressure for concentration.

Flux decline of NF90-2540 due to fouling was studied when biosolution 3 was filtered using feed with a constant biosolution concentration. Pre-treated biosolution was first concentrated to WR 70%. After concentration, the permeate was recycled back to the feed tank in order to maintain a constant concentration of the feed for 28 d. The feed had 3.3 times higher concentration compared to the initial feed concentration. The conductivity of the feed was measured to control concentration. If conductivity increased, some evaporation had occurred, and deionized water was added to the feed tank to dilute the feed to a conductivity level of WR 70%. After 28 d, the feed was diluted back to the initial concentration using the permeate, and the fouling test could be continued 19 d more at WR 0%. After the entire fouling study, the membrane element was flushed with deionized water and cleaned with acid and base to restore the flux and rejection of the original value.

For testing the prepared solution in Ca removal, the biosolution was mixed together with neutralizing pond (NP) water (Table 1). Dissolved Ca reacted with sodium carbonate according to Eq. (4). After the precipitation, the composition of the supernatant was analyzed.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 \quad (4)$$

3. Results and discussion

3.1. Pretreatment

In pre-treatment, microbial cells were filtered from the biosolution by MF before sulfide removal using aeration and suspended solids filtration. If too large MF pores, that is, 1 μm, were used for cell removal, sulfide content could not be stabilized but was first somewhat lowered and then increased back to the original level during aeration. When using a tighter 0.2 μm filter, the sulfide content decreased to zero and was at a low level during the subsequent procedure to prepare calcium precipitation chemical. Thus, a 1 μm nominal filter was not sufficient for eliminating microbial activity, but a 0.2 μm absolute filter rejected microbes and produced a stable biosolution with a low sulfide content (Fig. 2a). When the biosolution was prepretreated using the 0.2 µm filter both aeration methods, that is, propeller mixing and pressing air through a ceramic filter, produced similar sulfide removal from the biosolution (Fig. 2b).

The alkalinity of biosolution, which was taken straight from the bioreactor, was 120 mmol/L. During sample collection, the alkalinity decreased to half the initial value. A part of the alkali could have been released from biosolution as CO_2 gas since pH was 7.7 in the bioreactor. At this pH, both CO_2 gas and bicarbonate ions exist in the solution. During aeration, acid gases were also partly stripped out from the biosolution, and the pH of the solution increased almost to 9. The dominant form of carbonate at this pH is bicarbonate ion, which could not vaporize out of the solution.

Alkalinity of biosolution stabilized in pre-treatment to the level of 60–75 mmol/L (Fig. 3 and Table 1). pH of the pre-treated biosolutions was similar, 8.9. The highest alkalinity after pre-treatment was measured in biosolution 3, which contained originally the lowest Ca content, and the lowest alkalinity in biosolution 1, which contained originally the highest Ca content. However, the differences were not great. Since the alkalinity was similar or higher after pre-treatment than before pre-treatment, it is possible that CO_2 was dissolved into the biosolution during aeration and converted to bicarbonate. Increased bicarbonate concentration elevated the alkalinity of the biosolution.

After aeration, the formed particles were removed from the solution by settling and repeating 0.2 µm MF before concentration by spiral-wound filtration. Due to the high Ca content of biosolution 2 compared to other multivalent cations, the main constituent of the removed deposit was Ca, 39 w-%, probably appearing as sulfate and as carbonate form (Table 2). During pre-treatment, the osmotic pressure of the solution decreased from 6.4 bar down to 4.5 bar.

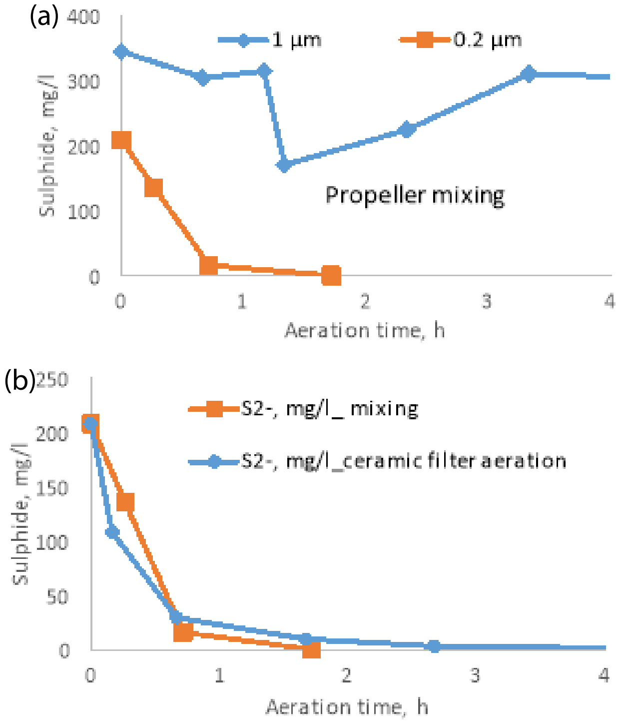

Fig. 2. Sulfide contents during aeration with propeller mixing when microbe removal was carried out using either 1 or 0.2 µm filters (a) and Sulfide content when aeration was carried out either by pressing air through a ceramic filter or using propeller mixing (b).

Turbidity measurement of MF filtrate was used to follow the presence of suspended solids in the feed to concentration. The initial turbidity of the biosolution was 110 NTU. After cell removal the turbidity was 20 NTU, and after the entire pre-treatment turbidity was only 0.2 NTU, corresponding to ≥99% reduction of the suspended solids. However, it was observed that several days of storage caused a turbidity increase of pre-treated biosolution due to $CaCO_3$ precipitation over time. This necessitated a repetition of 0.2 µm MF before membrane concentration using the spiral wound element.

3.2. Concentration

Membrane characterization using 2 g/L NaCl at 15 bar pressure produced higher rejections for the NF90 membrane than informed by the membrane manufacturer. However, the pressure was much higher in the characterization than that used by the manufacturer. The used pressure was selected due to the high initial osmotic pressure of the biosolution, 4.5 bar, which also caused the relatively high hydraulic pressure needed in the concentration filtration of biosolution. The rejection of BW30LE was rather lower measured in the CF042-PTFE cell than informed by the manufacturer for the 2540 spiral wound element (Table 3). Considerable variation between membrane coupons was observed during the study.

A membrane study using biosolution 1 produced good rejections of alkalinity for both NF90 and BW30LE membrane, 94% and 96% respectively (Table 4). NF270 rejection, 84%, was estimated as too low for later concentration filtrations. Conductivity rejections were also clearly higher for NF90 and BW30LE than for NF270, which was an expected result. A similar trend was observed in permeate qualities, especially in sodium concentration (Table 5). Both NF90 and BW30LE produced very good quality water for reuse or safe discharge.

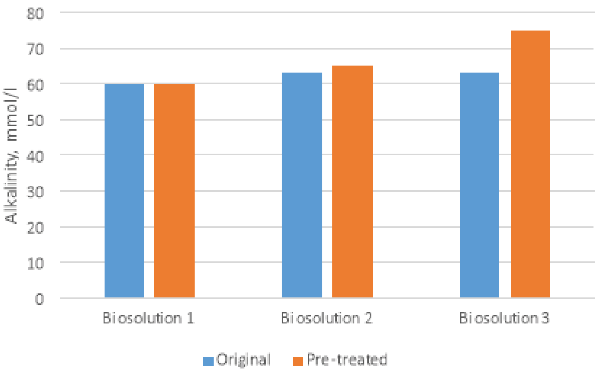

Fig. 3. The alkalinity of biosolutions studied before and after pre-treatment.

Table 2
Composition of the produced precipitate and filtrate at the beginning of pre-treatment using Biosolution 2

	Ca	Mg	Na	K	P	S	Mn	Fe	Al	Si	Zn
Biosolution 2, mg/L	110	47	2,500	47	7.5	1,800	0.089	<0.05	<0.1	8.7	<0.05
Precipitate, mg/kg	393,000	330	2,000	70	120	1,900	63	78	<10	130	14
Filtrate, mg/L	39	45	2,300	54	9.8	1,200	0.2	<0.05	0.12	6.2	<0.05

Table 3
Characterization of membranes using 2 g/L NaCl

	Rejection, % measured	Rejection, % informed	Permeability, LMH/bar measured	Permeability, LMH/bar informed
NF270	78 (NaCl)	>97 ($MgSO_4$)	16 (NaCl)	11% ± 15% ($MgSO_4$)
NF90	97	90	11	7
BW30LE	95	99	7	5

Rejection and permeability were measured at 15 bar pressure (measured), or the values were informed by the manufacturer, measured either at 4.8 bar (NF) or 10 bar (RO) pressure (informed). NF270 is characterized by the manufacturer using 2 g/L $MgSO_4$ salt.

Table 4
Alkalinity and conductivity rejections of the studied membranes

	Rejection, % alkanility	Rejection, % conductivity
NF270	84	90
NF90	94	98
BW30LE	96	97

The fluxes in the biosolution filtration were 60%–70% of the fluxes during characterization with 2 g/L NaCl. 2 g/L NaCl produces lower osmotic pressure, 1.4 bar, than the osmotic pressure of the biosolution. Hence, the fluxes were good and stable in short biosolution filtrations. The flux of NF270 was the best of the three studied membranes, as expected. NF90 produced slightly higher flux than BW30LE (Fig. 4). However, the two membranes were very similar with regard to flux, alkalinity rejection, and permeate qualities. Thus, either of them could have been selected for the concentration filtration, but NF90 was selected.

Concentration filtration of pre-treated biosolution 2 using the NF90-2540 spiral wound membrane element performed rather well (Fig. 5). Good quality water was produced, as expected (Table 6). The flux decline during the filtration was mainly caused by the osmotic pressure increase from 4.5 bar up to 21 bar (Table 6). However, the final WR was high, 86%, and the concentration factor was 7.1, which should have produced even higher final osmotic pressure. It was observed that some of the salts, that is, calcium, phosphate, manganese, and aluminum, precipitated in the concentrate (Table 6). Hence, the amount of dissolved ions in the concentrate was lower than would have been calculated using the achieved concentration factor.

As seen in the quality of NF90-2540 concentrate, a part of the sparingly soluble salts precipitated when high WR in the concentration was achieved. Although the filtration went well, WR was probably too high, and the flux of the spiral wound element could not be restored by flushing with water after concentration filtration. The flux after biosolution filtration decreased from 30 LMH to 14 in the characterization filtration using 2 g/L NaCl solution with a pressure of 4.8 bar and a temperature of 25°C. However, the fouling was not observed in the NaCl rejection, which was 89% in both cases.

Fouling in long-term filtration was carried out first at WR 70% and then at WR 0% using the NF90-2540 membrane element. The flux decreased clearly during the first day of filtration at WR 70%, indicating fouling at the beginning of the filtration. After that, the flux stabilized to a level of 15 LMH. The fouling was also observed when the biosolution was diluted to the original conductivity level using the permeate, while the flux did not increase to the theoretical value of 3.3 × 15 LMH. It was stabilized to a flux of 22 LMH (Fig. 6). After concentration filtration up to WR 70%, 28 d filtration at WR 70%, dilution back to WR 0%, and 19 d filtration at WR 0%, the flux of the membrane was difficult to restore by flushing with deionized water or with any of the tested chemical cleaning agents.

3.3. Biosolution as a precipitation chemical

The concentrated biosolution 1 with an alkalinity of 140 mmol/L was tested as a calcium precipitation chemical. When the concentrate was used as a precipitation chemical with no pH adjustment, 27% of dissolved Ca precipitated. The time to carry out complete precipitation was long, 24 h. However, Ca precipitated clearly more than when biosolution was used as such, when only 2% of the Ca precipitated. When the pH of the concentrated biosolution was adjusted to 9.1 with NaOH, over 80% of the dissolved Ca was precipitated in 2.2 h. After 24 h, the precipitated fraction corresponded to 95% of the original Ca. The amount of NaOH needed for increasing the pH of the water sample to 9.1 was 0.5 kg/t in these preliminary tests. Since the solubility of $Ca(HCO_3)_2$ is much higher than that of $CaCO_3$, pH adjustment is needed to keep carbonate

Table 5
Permeated qualities produced by the studied membranes

Feed and the permeates	Ca, mg/L	Mg, mg/L	Na, mg/L	K, mg/L	P, mg/L	S, mg/L	Si, mg/L	Alkalinity, mmol/L
Feed	68	58	3,500	43	6.7	1,900	6.4	64
NF270	1.1	0.55	210	2.2	0.1	17	3.5	8
NF90	<0.5	<0.5	36	<1.0	<0.1	3.2	<0.1	3
BW30LE	<0.5	<0.5	53	1.2	0.1	15	0.47	2

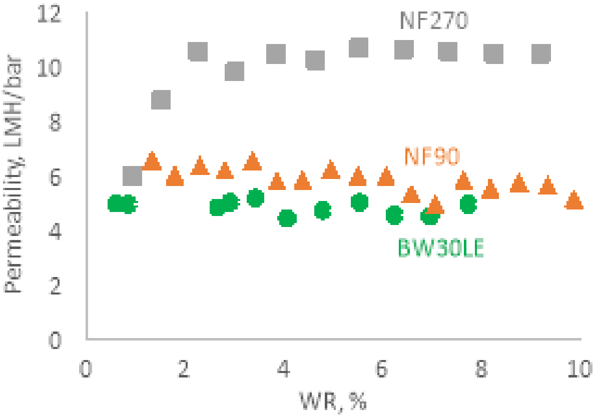

Fig. 4. Fluxes during biosolution 1 filtration at 25°C and 15 bar.

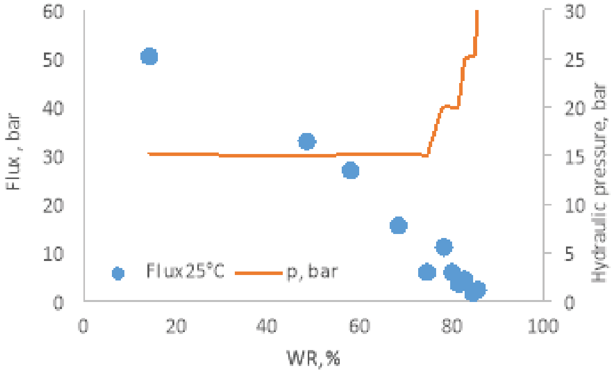

Fig. 5. The concentration of the pre-treated biosolution 2 using NF90-2540.

Table 6
Quality of feed, permeate and concentrate of biosolution 2 filtered by NF90-2540

Component	Feed	Permeate	Concentrate
Ca, mg/L	39	0.6	120
Mg, mg/L	45	<0.5	250
Na, mg/L	2,300	140	13,400
K, mg/L	54	3.9	270
P, mg/L	9.8	<0.1	25
S, mg/L	1,200	10	8,000
Cu, mg/L	<0.05	<0.05	0.2
Mn, mg/L	0.2	<0.05	0.06
Zn, mg/L	<0.05	<0.05	<0.05
Fe, mg/L	<0.05	<0.05	<0.05
Al, mg/L	0.1	<0.1	<0.1
Ni, mg/L	<0.05	<0.05	<0.05
Si, mg/L	6.2	0.9	34
Co, mg/L	<0.05	<0.05	0.1
Alkalinity, mmol/L	65	1.3	350
Turbidity, NTU	15	0.3	21
COD, mg/L	45	15	650
Osmotic pressure, bar	4.5	0.3	21
pH	9.1	10.1	8.9

ions in solution instead of bicarbonate counterparts. After precipitation, dissolved Ca content was less than 50 mg/L.

It is also noteworthy that when Ca of the NP water (composition in Table 1) was precipitated using the concentrate from NF90-2540, the alkalinity of the biosolution concentrate decreased to 140 mmol/L instead of being 210 mmol/L at WR 72%. Thus, part of the carbonate was precipitated before using it as a precipitation chemical.

4. Conclusions

This study showed that biosolution from a sulfate-reducing bacterial process can be processed into a usable calcium precipitation chemical and good quality water using a membrane concept. The interesting compound in the biosolution is bicarbonate, that is, alkali, which was a starting material for the valorization. Since membrane technology is very sensitive to fouling and scaling, the feed to the membrane concentration had to be pre-treated. It was found that pre-treatment needed to include microbe removal, sulfide oxidation, and suspended solids removal sufficiently effective for subsequent alkali concentration. Tight NF and brackish water RO had equal performance in alkali recovery. NF was used in a spiral wound element in order to study the concentration on a larger scale and for long-lasting filtration. Some fouling in the NF spiral wound element was seen at the beginning of concentration. When stabilized, NF performed well for 47 d until the filtration study was stopped. Concentrated biosolution worked well as a precipitation chemical when the pH was adjusted above 9 in order to convert bicarbonate to carbonate form. Calcium concentration in the NP water could be lowered by precipitation with the produced biosolution from hundreds of mg/L down to less than 50 mg/L. The developed membrane concept to produce pure water

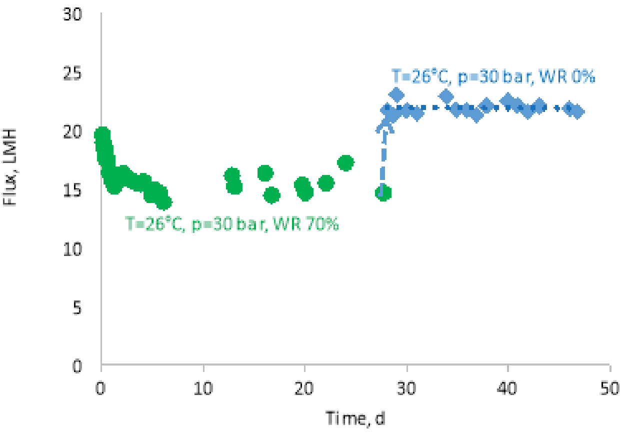

Fig. 6. Prolonged filtration using NF90 2540 first at WR 70% and then at WR 0%.

and a usable chemical from the waste stream is a step towards closed-loop processes and near-zero discharge in the mining industry, and generally in the circular economy.

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