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Sulphate removal from mine water with chemical, biological and membrane technologies

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Abstract

Chemical, physical and biological technologies for removal of sulphate from mine tailings pond water (8 g SO_4^{2-}/L) were investigated. Sulphate concentrations of approximately 1400, 700, 350 and 20 mg/L were obtained using gypsum precipitation, and ettringite precipitation, biological sulphate reduction or reverse osmosis after gypsum pretreatment, respectively. Gypsum precipitation can be widely utilized as a pretreatment method, as was shown in this study. Clearly the lowest sulphate concentrations were obtained using reverse osmosis. However, reverse osmosis cannot be the only water purification technology, because the concentrate needs to be treated. There would be advantages using biological sulphate reduction, when elemental sulphur could be produced as a sellable end product. Reagent and energy costs for 200 m^3/h tailings pond water feed based on laboratory studies and process modelling were 1.1, 3.1, 1.2 and 2.7 MEur/year for gypsum

precipitation, ettringite precipitation, reverse osmosis and biological treatment after gypsum precipitation, respectively. The most appropriate technology or combination of technologies should be selected for every industrial site case-by-case.

Keywords: sulphate, gypsum, ettringite, membrane, biological sulphate reduction

Introduction

Sulphate (SO_4^{2-}) has been traditionally considered as a relatively harmless substance in the environment. Sulphates are discharged into the aquatic environment from industrial operations such as mining and smelting, steel manufacturing, kraft pulp and paper mills and flue gas desulphurization circuits. In addition, sulphate is released to waters from natural sources through mineral weathering, volcanoes, decomposition, combustion of organic matter, and sea salt. (International Mining 2013; Meays and Nordin 2013)

Most metals are won from ore bodies containing sulphidic minerals that oxidize to sulphate during the metal extraction process. Therefore, sulphate is a common impurity in mining waters and wastewaters of hydrometallurgical processing. Same oxidation of sulphide occurs naturally in mines through the activity of sulphur and iron oxidizing bacteria producing acid mine drainage (AMD) (Johnson & Hallberg 2005). Furthermore, sulphur-containing reagents are common in hydrometallurgy and a huge amount of sulphuric acid is used to dissolve metals from metal concentrates (Bar & Barkat 2016).

The focus on the treatment of AMD and mine effluents has been on acidity and dissolved metals, whereas less attention has been paid to sulphate. Nowadays concerns against sulphate discharge have increased and resulted in guidelines and regulations that limit the discharge into the receiving waters. Global sulphate limits range from 2000 mg/L for surface water discharge in Chile to 10 mg/L in the US state of Minnesota (International Mining 2013; Minnesota Pollution Control Agency 2014) and typically vary between 250 and 1000 mg/L (Liang 2014).

The fundamental requirement of all sulphate removal technologies in industrial processes is the capability to meet the regulatory limits. Sulphate removal may also be necessary for reuse of water in mine operations. The suitable water treatment technology needs to be evaluated case by case, since site-specific conditions will control the most suitable option for a particular mining operation.

Alternative treatment processes for the removal of sulphate from mining effluents are chemical treatment, membrane filtration, ion exchange and biological sulphate removal. Chemical precipitation of sulphate with lime or limestone to gypsum (Eq.1) is the most common way for sulphate removal from mine water, which can reduce sulphate concentrations to generally 1500–2000 mg/L, and even to below 1200 mg/L depending on the composition and ionic strength of the solution (INAP 2003; Liang 2014).

$$2Ca(OH)_2(s) + 2MeSO_4(aq) + 4H_2O(l) \rightarrow 2Me(OH)_2(s) + 2[CaSO_4 \cdot 2H_2O](s) \qquad \text{(Eq.1)}$$

When more advanced technologies are required for lower sulphate limits, gypsum precipitation can be used as a pre-treatment step. Ettringite precipitation (Eq.2) has been shown to be an effective method for sulphate removal, as it can reduce sulphate concentration to 200 mg/L (Madzivire et al. 2010). Ettringite is also considered to be stable waste for long term disposal. The main disadvantage of the process is high aluminium consumption and thus high operational cost.

$$3CaO + 3Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3(s) + 28H_2O \rightarrow [3CaO \cdot 3CaSO_4 \cdot Al_2O_3(s) \cdot 31H_2O] \text{ (Eq.2)}$$

In biological sulphate reduction micro-organisms use sulphate as an electron acceptor and reduce it to hydrogen sulphide (Eq.3), which can be further oxidized to elemental sulphur (Eq.4).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad (CH_2O\text{=electron donor}) \qquad \text{(Eq.3)}$$

$$H_2S + 2O_2 \rightarrow S + H_2O \qquad \text{(Eq.4)}$$

The best known possible membrane technologies for metals and sulphate rejection are conventional nanofiltration (NF) and reverse osmosis (RO). When multivalent ions dominate in the water, NF membrane is sufficient. If good rejection of monovalents needs to be achieved, RO membrane is required. Sulphate rejections have varied from 93% to 98% for mine waters using different NF membranes, as high as 99% for RO membrane. Depending on the feed water quality, sulphate content 10 mg/L is achievable by membrane technology, either by single or two stage filtration.

(Laskowska et al. 2014; Banerjee 2015). Despite its potential to produce pure water, certain limitations can hinder membrane processes from large-scale operation. When aiming to low concentrate volumes and subsequently high water recoveries, dissolved salts are concentrated at the membrane surface causing precipitation when exceeding the solubility. Since cleaning sulphate scale is relatively difficult for alkaline scales in water treatment plants, the best practice for managing calcium sulphate scale can be to operate the RO system below the saturation level (Antony et al. 2011). Concentrate treatment is an essential issue when considering the feasibility of membrane filtration, since water recoveries in mine water treatment can remain as low as 60% (Banerjee 2015) leaving 40% to concentrate stream.

In this study i) Sulphate precipitation as gypsum, ii) ettringite precipitation after gypsum precipitation, iii) biological sulphate reduction after gypsum precipitation and iv) membrane treatment after gypsum precipitation were studied as alternatives for sulphate removal from mine waters from both technological as well as from economical points of view.

Materials and methods

Tailings pond solution from the Agnico Eagle gold mine in Finland with long-term average sulphate concentration of 8 g/L was utilized in the experiments. The temperature of the water varies between 4-20°C depending on the season.

All sulphate removal experiments were conducted at the room temperature (20-25ºC) with the upper pH limit of 10 based on typical environmental permit limits. In the gypsum precipitation tests in batch reactors, 3 L of mine water (Batch 1) was maintained at the pH of approximately 10.5 or 12 with ~10% lime solution. Samples (150 mL) were filtered (0.45 µm) and purged with CO_2 to lower the pH <10 before refiltering and analysis.

In ettringite precipitation tests, the lime treated mine water (1700 mg/L SO_4^{2-}, pH 12.3) without CO_2 bubbling was further processed by reactive aluminium. $AlNaO_2$ (26-30% Al technical grade powder) was used (Janneck et al. 2012). To optimize the dose of $AlNaO_2$, 200 mL of lime-treated mine water was mixed with $AlNaO_2$ for two hours at the Al/SO_4^{2-} molar ratios of 1, 1.5, 3, 7.5 and 15 at pH 11.5–12. Based on the preliminary ettringite precipitation tests a larger scale test was performed in a 3 L reactor. $AlNaO_2$ was added as one time dosage in the beginning of the 6-hour test and pH was maintained at 11.5–12. Samples (150 mL) were filtered (0.45 µm) and purged with CO_2 to lower the pH <10 before refiltering and analysis.

Biological sulphate removal after gypsum precipitation was studied in two 700 mL reactors with reactor 1 operated first as a fluidized-bed reactor (FBR) and later as an upflow anaerobic sludge blanket reactor (UASB), and reactor 2 as a FBR throughout the study with the aim to further decrease the sulphate concentration. The FBRs contained 385 mL of biobased granular activated carbon as carrier material. They were inoculated with anaerobic granular sludge from an operating wastewater treatment plant in Finland and with sulphate reducing bacteria (SRB) enrichment cultures from that same sludge. Ethanol was used as electron donor (1.5x stoichiometric concentration), since ethanol is utilized in commercial scale applications and the microbial culture utilized as inoculum was originally treating wastewaters from the ethanol plant. The feed solution contained also added nutrients, 56 mg/L KH_2PO_4, 137 mg/L $(NH_4)_2HPO_4$, 11 mg/L ascorbic acid and 11 mg/L yeast extract. Both reactors 1 and 2 were started batch wise for the first 17 days to ensure microbial growth on carrier material after inoculation. Thereafter, the reactors were operated in the continuous mode with the hydraulic retention time of 24–96 hours. Ethanol was added in double concentration after 33 and 43 days to reactors 1 and 2, respectively, to verify that the operation was not limited by the availability of electron donor. After 50 days, reactor 1 was switched to operate as UASB. Tailings pond water from batch 1 was used in the experiments during the first 26 days, and from batch 2 day 27 onwards.

Membrane experiments were conducted in a plate-and-frame laboratory filtration unit. The feed solution was pumped from the feed tank to the cross-flow membrane cell, SEPA CF with a membrane area of 140 cm^2. Nanofiltration NF270 (Filmtec, USA) membrane (NF) and reverse osmosis BW30LE (Filmtec, USA) membrane (RO) were used in the tests. The membrane flat sheets were rinsed before filtrations with de-ionized water and stored overnight at 5°C in a glass bottle filled with de-ionized water. Salt rejections at 2000 ppm were determined based on conductivity measurements of permeate at pH 8 and with 15% recovery using magnesium sulphate ($MgSO_4$) and 5 bar pressure for the NF membrane, and sodium chloride (NaCl) and 10 bar pressure for the RO membrane. All filtrations were carried out at 25±1°C and feed flow of 6.5±0.1 L/min, which generated a cross flow velocity of 0.6 m/s. Feed solution (Batch 3) was filtered as such or after pre-treatment using microfiltration (MF) or chemical gypsum precipitation continued by MF. MF was carried out using 0.2 µm filter element (Sofi Filtration, Finland) using the normalized pressure of 1.0 bar and the feed flow of 1.5±0.1 L/s.

The pH was measured with the Radiometer PHM240 analyser equipped with a Radiometer pHC2011-8 electrode in chemical and biological experiments, and with VWR 1000H equipped with pHenomena111 in membrane filtration tests. Oxidation-reduction-potential (ORP) was analysed with SCHOTT CG840 analyser equipped with the SCHOTT Blue Line 31 RX electrode (Ag/AgCl 3M KCl). Conductivity was measured using VWR CO3000H equipped with the CO11 sensor. Total dissolved solids (TDS) was determined using a standard method SFS-EN 15216. SO_4^{2-} and Cl^- concentrations were analysed with a spectrophotometrical method at Metropolilab Oy for chemical and biological experiments, and with a liquid chromatography standard SFS-EN ISO 10304-1 at Labtium Oy for membrane experiments. For process control purposes, SO_4^{2-} and S^{2-} were determined with Hach Lange DR3900 spectrophotometer and LCK 353 and LCK 653 kits, respectively. Ca, Na, K, Mg and Mn were analysed by ICP-OES using a standard SFS-EN ISO 11885 and Thermo Scientific iCAP 7600 Duo at Labtium Oy. In addition, Sb, As and Ni were

analyzed either by ICP-MS at Metropolilab Oy or by ICP-OES at Labtium Oy. Bromide, fluoride and nitrate were analysed using a standard SFS-EN ISO 10304-1and Dionex ICS-3000 at Labtium Oy. Determination of ammonium was carried out by distillation and titration method ISO 5664 and Büchi Distillation Unit B-324 at Labtium Oy. NO_2-N, NO_3-N and NH_4-N were analysed during membrane experiments with Hach Lange DR3900 spectrophotometer and LCK 339, LCK 341 and LCK 363 analyse kits, respectively, or alternatively with AQUAKEM photometric analyser at Metropolilab Oy.

Process models were made using the HSC-Sim process modelling software based on the test results for 200 m^3/h tailings pond water feed. Reagent and energy consumptions of each process were calculated using information from the process models. Energy consumption was calculated from the energy need of main equipments such as reactors and pumps. Investment cost and some minor operational costs like RO washing reagent or flocculant costs have not been included into the calculations. Long-term pilot tests would be needed for more accurate cost calculations.

Results and Discussion

Characteristics of mine water

Chemical characteristics of the mine water were as shown in Table 1. Together with sulphate, some major components of the mine water are presented, and also components that may be critical for environmental reasons. Water batches 1 to 3 were received for the studies in different batches, as different unit operations were studied at different times and partly also in different locations. Generally the concentrations in studied components were on quite steady level from batch to batch with some variations observed for sulphate, which was most likely due to both variations in mine processes and storage time before analysis.

Table 1. Chemical characteristics of different mine water batches used in the experiments. n.a. = not analysed.

Component	**Batch 1 (analysed 7/2014)**	**Batch 1 (analysed 9/2014)**	**Batch 2 (analysed 9/2014)**	**Batch 3 (analysed 8/2014)**	**long term average (for modelling)**
pH	7.8	8.0	8.0	7.9	8.2
Sulphate, mg/L	8 900	7 600	9 400	9 790	8 140
Calcium, mg/L	430	480	n.a.	460	430
Sodium, mg/L	165	170	n.a.	170	143
Potassium, mg/L	132	120	n.a.	130	132
Chloride, mg/L	26	25	21	27	23
Magnesium, mg/L	1 890	2 000	n.a.	1 930	1 610
Manganese, mg/L	0.924	0.860	n.a.	1	n.a.
Arsenic, mg/L	0.15	0.14	0.16	0.16	n.a.
Nickel, mg/L	0.015	0.016	0.035	<100	n.a.
Antimony, mg/L	0.058	0.067	0.082	0.07	n.a.

Removal of sulphate by chemical precipitation

Most precipitation of sulphate took place during the first 10–20 minutes in gypsum precipitation (Figure 1a). Sulphate removal kinetics were similar at pH of 10.5 and 12, but the treatment at pH of 12 resulted in slightly lower residual sulphate concentrations quite similar to the solubility of gypsum. In ettringite precipitation the selected aluminium to sulphate molar ratio was 1.5 showing lowest residual sulphate concentrations. Most precipitation of sulphate occurred during the first 10 minutes of mixing after the aluminium addition (Figure 1b).

Sulphate concentration of approximately 1400 mg/L was achieved using gypsum precipitation (Table 2). In addition, arsenic, antimony and nickel concentrations were reduced to very low levels complying clearly with the mine's environmental limit values 0.5 mg/L, 0.5 mg/L and 0.3 mg/L respectively, and even with drinking water guidelines (WHO 2011). Chloride concentrations in mine water were not affected by gypsum precipitation. Sodium and potassium sulphates do not precipitate with lime and the increase in these elements can lead to exceeding of the often imposed

2000 mg/L sulphate discharge limits. With ettringite precipitation, sulphate concentration of 700 mg/L was achieved.

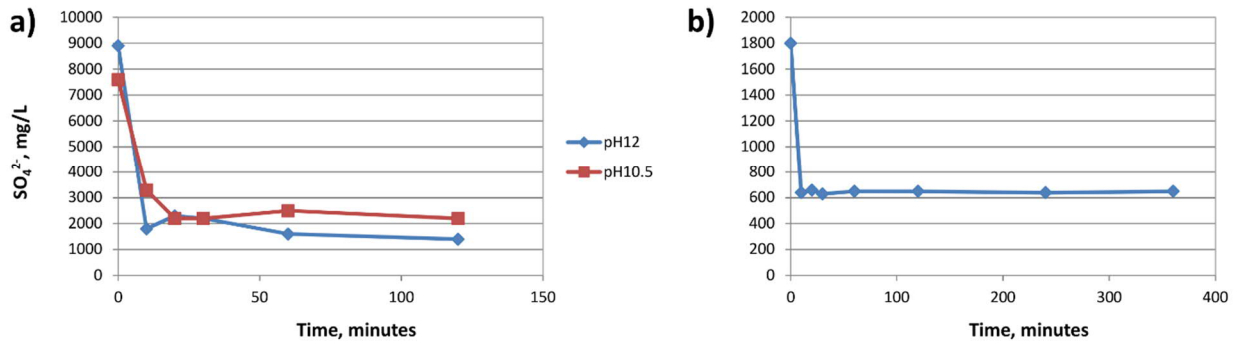


Figure 1. Sulphate removal in a) gypsum precipitation and b) ettringite precipitation.

Table 2. Mine water characteristics after chemical precipitation.

	Gypsum precipitation tests		**Ettringite precipitation tests**	
Component	**120 min lime, pH12**	**120 min lime, pH10.5**	**60 min lime, pH12 (feed to ettringite precipitation)**	**60 min lime, pH12 + 360 min $AlNaO_2$, pH 11.5-12**
pH	7.1*	7.4*	12.1	7.5*
Sulphate (mg/L)	1 400	2 200	1 800	650
Calcium (mg/L)	n.a.	n.a.	910	20
Arsenic (mg/L)	0.0038	0.0021	0.0022	0.0019
Nickel (mg/L)	0.0012	0.0021	0.001	0.0017
Antimony (mg/L)	0.005	0.006	0.008	<0.001

* pH after filtration (0.45 µm), subsequent purging with CO_2 and second filtration (0.45 µm)

Gypsum precipitation (pH 12) consumed approximately 7.3 g of >96% $Ca(OH)_2$ and produced 17 g dry sludge (105°C) per litre of mine water. Same parameters at the pH of 10.5 were 5.3 g of $Ca(OH)_2$ and 14 g of dry sludge per litre. Sodium aluminate consumption in the ettringite

precipitation was 0.97 g per litre of lime treated water producing 3.9 g of dry sludge per litre of water. In the filtrations following CO_2 bubbling, the amounts of sludge were negligible.

Removal of sulphate by biological sulphate reduction

After the start-up operated batch wise after inoculation, the ORP gradually decreased to the level of -300 mV (Ag/AgCl, 3M KCl) in both reactors 1 and 2 (Figure 2). Also the pH decreased and was mainly at the level of 6<pH<7. Biological sulphate reduction rates of maximum 1250 $gm^{-3}d^{-1}$ and 1450 $gm^{-3}d^{-1}$ were obtained in reactors 1 and 2, respectively. The obtained rates were at the similar level as in several previous biological sulphate reduction studies, but also higher sulphate reduction rates have been obtained in longer experiments and at higher temperatures (Kaksonen 2004; Liamleam & Annachhatre 2007). It would likely be possible to enrich more SRB into the reactors with simultaneous increase in the sulphate reduction rate during a longer operation time. The lowest sulphate concentration obtained was approximately 350 mg/L.

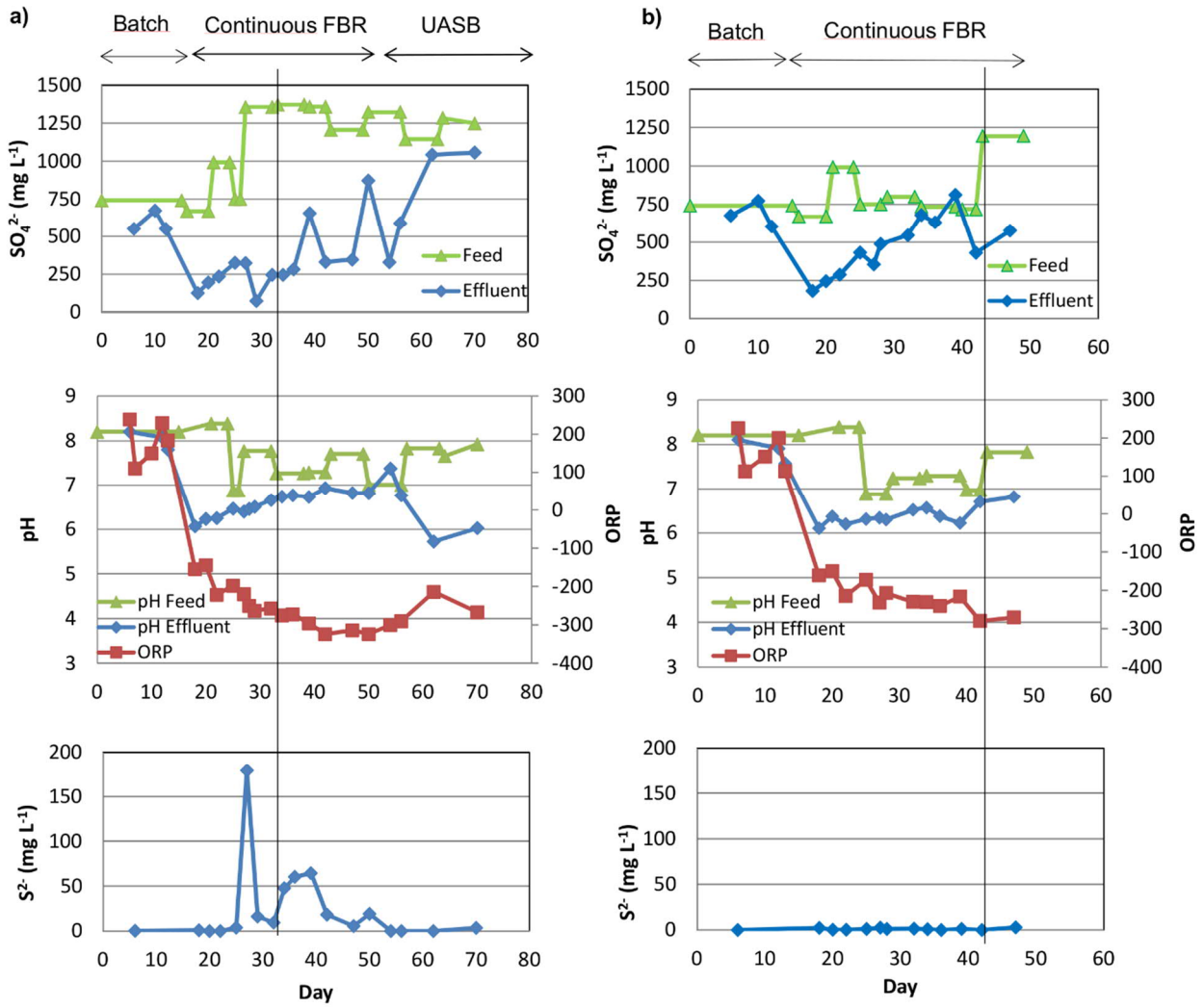


Figure 2. Feed water sulphate concentration and pH, and effluent sulphate concentration, pH, ORP and dissolved sulphide concentration after the biological sulphate reduction in a) reactor 1 operated for 70 days and in b) reactor 2 operated for 47 days. The vertical line shows the start of the double ethanol dosage until the end of the experiment.

Excess ethanol addition did not have a significant effect on reactor performance. Although ethanol is considered as an attractive electron donor for SRB applications also in commercial applications, the drawback is a rather low growth rate of SRB on ethanol. The main consumable in the SRB operation is electron donor, such as ethanol, lactate, acetate and hydrogen gas, and the cost of electron donor has a significant effect on total operational costs.

When there are no metals present in the waste-water to precipitate as sulphides, as in this study, sulphide can accumulate and result in severe inhibition of the biological sulphate reduction process. Most of hydrogen sulphide is in the form of molecular H_2S at the pH of 6, whereas at the pH of 8 most of the total sulphide is in the less toxic HS^- form. Studies have shown sulphate reduction inhibition by sulphide concentrations above 500 mg/L at the pH of 6.5-7, and tolerance to higher sulphide concentrations of 700–1400 mg/L at the pH of 7.5 (Greben et al. 2004). In this study, the pH in the reactors was most of the time between 6–7 and thus in the range that could have H_2S toxicity effect on biological operations. However, no or very limited amount of dissolved sulphide was detected in the effluent of anaerobic reactors. No H_2S gas was collected into the gas collection bags and no H_2S leakages were detected neither. Despite the fact that activated carbon has been successfully utilized as a biomass carrier material in the fluidized bed reactors treating sulphate containing wastewaters with SRB (Sahinkaya et al. 2011), activated carbon can also adsorb formed H_2S to a certain extent before saturation. Therefore, the carrier material was removed from the reactor and the reactor was started again in the UASB mode without any added carrier material to confirm the fate of sulphur. Even with no carrier material, the dissolved sulphide level remained at a very low level and sulphur oxidation experiments for the production of elemental sulphur were not possible. There would be significant advantages of the SRB operation, if elemental sulphur could be produced by oxidizing the H_2S biologically (e.g. Maree et al. 2004) or chemically (e.g. Chen & Morris 1972) to S^0. The elemental sulphur product could be sold and waste amount would be lower compared to chemical precipitation and physical sulphate removal. Further investigation on possible reaction conditions for elemental sulphur production would be needed.

Removal of sulphate by membrane filtration

The membranes used in this study had water fluxes similar to those reported by the membrane manufacturer during salt filtration and salt rejections (results not shown). The pH, conductivity and TDS values for permeates and concentrates were logical compared to the values of feed mine water

(Tables 1 and 3). Suspended solids concentration of mine water was 7.1 mg/L and of MF pre-treated water <1 mg/L. The concentrates started to precipitate due to high ion concentrations. TDS determined by drying gave similar, slightly larger, values than calculated as a sum from elementary analysis (Table 3). Therefore, the main compounds in mine water were those analysed, i.e. metal sulphates, halogens, and inorganic nitrogen. Nickel, iron, copper and aluminium were <0.1 mg/L in all measured samples. Also zinc concentration was <0.1 mg/L for feeds and permeates. MF membrane did not remove much dissolved solids. Rejections of metals and sulphates were good for both NF membrane and RO membrane (Figure 3a). Sulphate concentration in the permeate after NF membrane was at the maximum 690 mg/L and only at the highest 23 mg/L after RO membrane. Rejections of sodium and potassium were ≥65% for NF membrane and 97% for RO membrane. Chloride was not removed by NF membrane, whereas RO membrane removed chloride (Figure 3a).

Table 3. Membrane filtration efficiency with or without pre-treatment for Batch 3 mine water.

	pH	λ mS/cm	TDS g/L
Feed NF/RO	7.9	9.5	13.5
NF-permeate	8.3	1.4	1.0
RO-permeate	8.1	0.1	0.0
Feed MF+NF/RO	8.1	8.8	12.3
MF+NF -permeate	8.3	1.0	0.7
MF+RO -permeate	8.4	0.1	0.0
Feed PREC.+MF+NF/RO	9.8	3.2	3.2
PREC.+MF+NF -permeate	9.4	0.3	0.2
PREC.+MF+RO -permeate	9.1	0.1	0.0

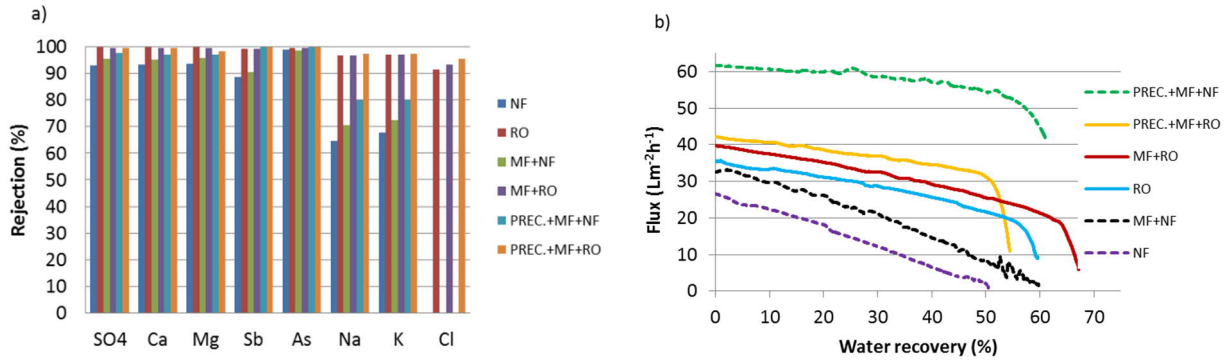


Figure 3. a) Rejections and b) Flux versus water recovery achieved in nanofiltration (NF) and reverse osmosis (RO) with no pre-treatment and with pre-treatment.

The NF fluxes for original mine water and MF pre-treated water were lower than RO fluxes (Figure 3b). NF membrane with no chemical pre-treatment for the feed fouled by elements of mine water. The best RO flux was obtained for $Ca(OH)_2$ precipitated and MF pre-treated mine water, although the fluxes with no chemical pre-treatment were also good. Attainable water recovery just before the flux dramatically decreases due to scaling remained lower for lime precipitated feed than for feeds with no chemical pre-treatment, due to added Ca in lime precipitation. RO fluxes were close to the flux obtained during salt rejection characterisation (33-41 $Lm^{-2}h^{-1}$ compared to 45 $Lm^{-2}h^{-1}$ at the water recovery of 15%). The best water recovery of all the filtrations, 63%, was obtained for the MF pre-treated mine water. Although the best flux of all the filtrations were obtained using NF membrane for $Ca(OH)_2$ precipitated and MF pre-treated mine water, water recovery remained lower (55%) than in RO membrane filtration using only MF pre-treatment. In this best flux case, the flux was close to the flux obtained with salt rejection test (68 $Lm^{-2}h^{-1}$). On the other hand, chlorides were not removed by nanofiltration which makes the reuse of permeate for the leaching process more difficult.

Water recovery of the RO process was approximately 60% and flux approximately 30 $Lm^{-2}h^{-1}$, which are relatively good values for RO operations. Very pure solution of 20 mg/L sulphate concentration in the permeate was produced using RO membrane after the gypsum precipitation

pre-treatment. In addition, the chloride concentration was around 2 mg/L and concentrations of other halides and nitrogen were also very low in the permeate. This kind of solution is suitable for water discharge, but it can also be recycled back to the processes in the plant. The disadvantage of the RO treatment is the production of concentrate containing high levels of sulphate, chloride, sodium, magnesium and nitrogen in addition to the very pure permeate. RO cannot be the only water purification technology, because the concentrate needs to be treated. The concentrate, which has high calcium sulphate content, could be potentially lead to the gypsum or ettringite precipitation, recycled back to the existing neutralization process or used in the pasta cementation.

It should be notified that temperature has a high impact on various sulphate treatment technologies and all experiments in this study were done at room temperature. The temperature limitations of technologies should be taken into account, when sulphate removal technologies will be operated in arctic conditions, such as in the mine in Finland where the mine water originated from. In the studies of Isaksen and Jorgensen (1996), the biological sulphate reduction activities were 4-10% of maximal activity at 0°C, and 10-29% of maximal activity at 5°C. Temperature has also an effect on the membrane operation, because increasing temperature decreases viscosity of the feed solution. Thus, the increase of temperature increases reverse osmosis efficiency and decreases pumping costs. Temperature affects also gypsum solubility, which increases until 40°C and decreases thereafter.

Conceptual study

Gypsum precipitation (Figure 4a) is carried out at the pH of 11 using milk of lime. The main reaction is the precipitation of magnesium sulphate as gypsum and magnesium hydroxide. All magnesium is removed and sulphate concentration will be 1.8 g/L after the precipitation with 2 hours retention time. Part of the slurry is circulated back to the process in order to increase reaction

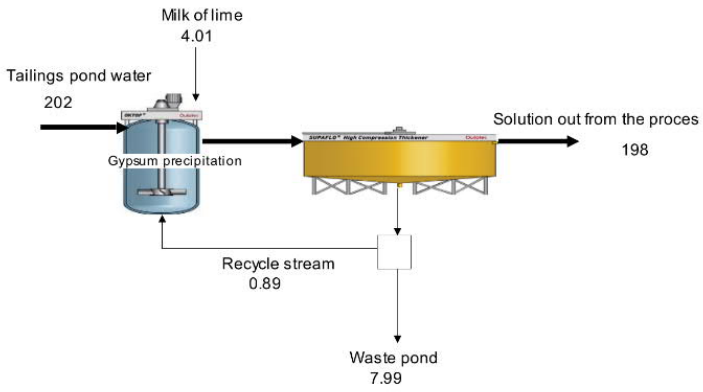
kinetics and to improve thickening properties of the slurry. The pH is adjusted using carbon dioxide from 12 to 8.5 in the neutralization reactor for discharge.

If sulphate concentration of feed solution is high, as in this study, gypsum precipitation should be carried out before ettringite precipitation in order to decrease operational costs of the process. The first step of the ettringite precipitation process (Figure 4b) is gypsum precipitation. Solution containing 1.8 g/L sulphate is further precipitated using lime and sodium alunate at pH 12 as ettringite. Sulphate concentration after the ettringite precipitation is 0.8 g/L. The pH of the solution is too high for discharge and pH is adjusted using carbon dioxide from 12 to 8.5.

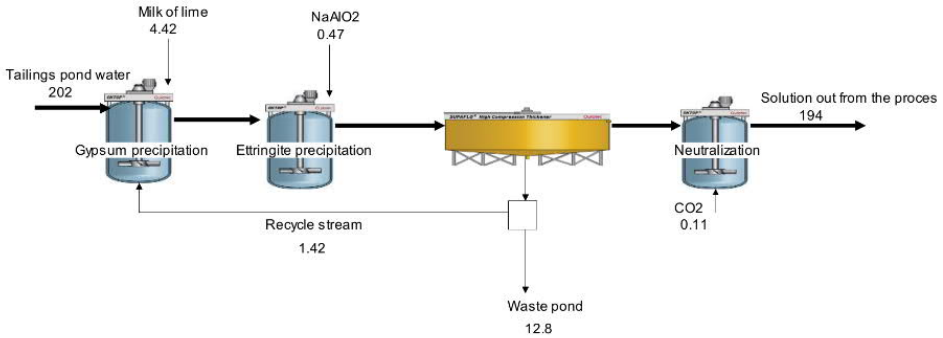
In membrane filtration process (Figure 4c), filtration of fine particles is needed before reverse osmosis to prevent membrane fouling. Filtrate from the filter is pumped with high pressure pump (10 bar) to RO system. It was approximated that 60% of water goes to permeate and 40% to concentrate. Flux through the membrane was 30 $Lm^{-2}h^{-1}$. Almost all anions and cations end to the concentrate. Sulphate concentration of the permeate is only 20 mg/L. Concentrate from the RO system and part of the tailings pond solution goes to gypsum precipitation process. Sodium and potassium concentrations increase in RO and because of these elements, sulphate concentration achieved in gypsum precipitation is around 1900 mg/L.

The first step of the biological sulphate removal process (Figure 4d) is gypsum precipitation resulting in sulphate concentration of 1.8 g/L and further to 800 mg/L using the biological process. Retention time in the test work was 24 hours. Ethanol is used as an electron donor. Hydrogen sulphide gas produced in the reactions is oxidized to elemental sulphur using oxygen. The efficiency of the oxygen usage is estimated to be 90%. Elemental sulphur is filtrated out from the process.

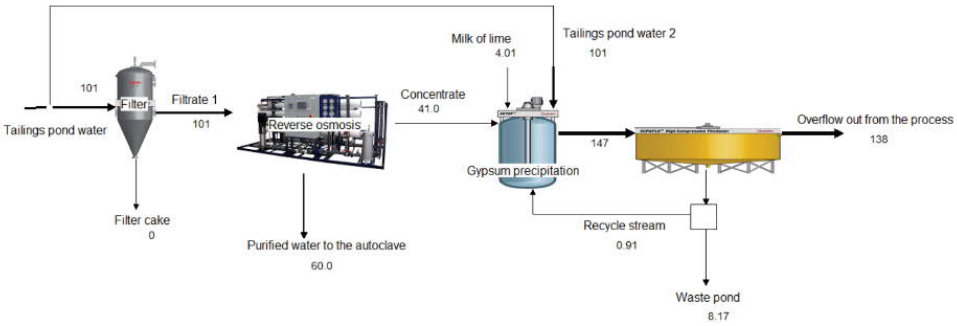
a)


Milk of lime
4.01
Tailings pond water
202
Gypsum precipitation
Solution out from the proces
198
Recycle stream
0.89
Waste pond
7.99

b)


Milk of lime
4.42
NaAlO2
0.47
Tailings pond water
202
Gypsum precipitation
Ettringite precipitation
Neutralization
Solution out from the proces
194
CO2
0.11
Recycle stream
1.42
Waste pond
12.8

c)


Milk of lime
4.01
Tailings pond water 2
101
101
Filter
Filtrate 1
101
Tailings pond water
Reverse osmosis
Concentrate
41.0
Gypsum precipitation
147
Overflow out from the process
138
Filter cake
0
Purified water to the autoclave
60.0
Recycle stream
0.91
Waste pond
8.17

d)

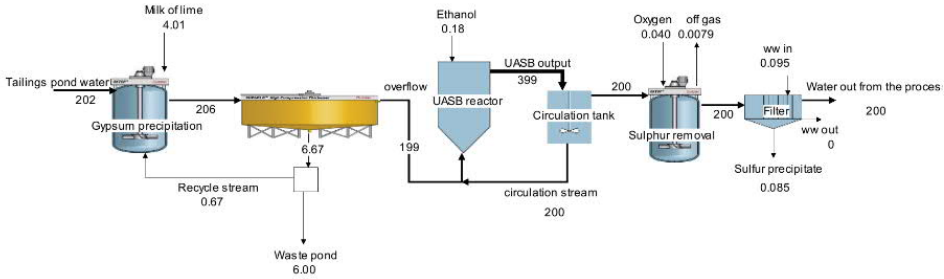

Milk of lime
4.01
Tailings pond water
202
Gypsum precipitation
206
6.67
Recycle stream
0.67
Waste pond
6.00
overflow
199
Ethanol
0.18
UASB reactor
UASB output
399
Circulation tank
circulation stream
200
200
Oxygen
0.040
off gas
0.0079
Sulphur removal
200
ww in
0.095
Filter
Water out from the proces
200
ww out
0
Sulfur precipitate
0.085

Figure 4. Process model for a) gypsum precipitation process, b) ettringite precipitation process, c) reverse osmosis process and d) biological sulphate reducing process. Process streams are presented as tons/h with the total tailings pond water feed of 202 tons/h for all processes.

Preliminary costs related to reagent and energy consumptions of process options were calculated based on process calculations (Table 4). The direct gypsum precipitation of sulphate was the most inexpesive process option. However, after gypsum precipitation the sulphate concentration is still around 1.8 g/L. The increase of sodium and potassium also increase the solubility of sulphate in the gypsum precipitation process.

Reverse osmosis system was slightly more expensive than gypsum precipitation. The advantage of reverse osmosis is the production of very pure permeate, which is suitable for water discharge or recycling back to the process. The disadvantage of the RO is the production of concentrate with high levels of sulphate, chloride, sodium, magnesium, nitrogen and other metals. Further treatment of the concentrate should be carefully designed or otherwise the concentrate might cause problems with discharge limits.

The costs calculated for the biological sulphate reduction process were significantly higher than the costs of gypsum precipitation and RO. The SRB process would show significant advantages, if elemental sulphur could be produced as an end sulphur product, which was not taken into calculations in this study. Elemental sulphur could be sold and waste amount would be lower than in other process options. Ethanol was used as the electron donor in process calculations and there could be cheaper alternatives, such as manure. The main concern of the SRB is the reliability of the process in colder climates. Re-start of the operation might be very slow, if there are problems in the process feed or in the SRB process leading to the inhibition of microorganisms. The retention time

of SRB process based on laboratory tests was long and around 5000 m^3 reactor volume would be needed. Cost of the reactors was not calculated in this study.

Low sulphate concentration can be achieved using ettringite precipitation, but calculated operational energy and chemical costs were very high. The annual costs for the decrease of sulphate concentration from 8 to 1.8 g/L for 200 m^3/h feed using gypsum precipitation were around 1 MEUR/a. Further decrease of sulphate concentration from 1.8 to 0.8 g/L in ettringite precipitation would cost around 2 MEUR/a. The costs of ettringite precipitation depend significantly on the costs of aluminium source. If aluminium waste would be available, the ettringite process could be economically much more feasible.

Table 4. The consumption of reagents and energy in selected process alternatives for 200 m^3/h feed.

	consumption t/year	consumption MW/year	cost/year MEUR
Gypsum precipitation			
CaO	6255		0.94
Energy		2400	0.156
Total			1.09
Ettringite precipitation			
CaO	7024		1.054
NaAlO2	3680		1.840
CO2	640		0.005
Energy		3600	0.234
Total			3.133
Membrane filtration			
CaO	6255		0.94
Energy		6896	0.45
Total			1.18
SRB			
CaO	6255		0.94
O_2	321		0.02
Ethanol	2848		1.60
Energy		2624	0.17
Total			2.73

The main equipment lists of the process options have been presented in the Table 5.

Table 5. The main equipment lists of the process options.

Gypsum precipitation	Feed m^3/h	retention time h	total volume m^3	units	Size of reactor m^3	Power kW
Precipitation reactors	200	2	400	3	133	300
Other equipment						
$Ca(OH)_2$ preparation tank						
$Ca(OH)_2$ feed tank						
Thickener						
Ettringite precipitation	Feed m^3/h	retention time h	total volume m^3	units	Size of reactor m^3	Power kW
Precipitation reactors	200	3	600	3	200	450
Other equipment						
Thickener/Filter						
$Ca(OH)_2$ preparation tank						
$Ca(OH)_2$ feed tank						
$NaAlO_2$ feed tank						
CO_2 neutralization reactor						
CO_2 feed						
Biolocical sulfate removal	Feed m^3/h	retention time h	total volume m^3	units	Size of reactor m^3	Power kW
Precipitation reactors	200	2	400	3	133	300
UASB reactor	200	4	800	1	800	5
Other equipment						
Oxidizing reactors						
Thickener/Filter						
$Ca(OH)_2$ preparation tank						
$Ca(OH)_2$ feed tank						
Ethanol feeding tank						
Sulphur filter						
Membrane filtration	Feed m^3/h	Flux $Lm^{-2}h^{-1}$	Permeate flow m^3	Area of membrane m^2	Mebrane units pcs	Power kW
RO equipment	200	30	60	2000	49	151
	Precip. feed m3/h	retention time h	total volume m^3	units	Size of reactor m3	Power kW
Precipitation reactors	140	3	420	3	140	315
Other equipment						
Fine filter						
$Ca(OH)_2$ preparation tank						
$Ca(OH)_2$ feed tank						
Thickener						

Conclusions

Chemical, physical and biological processes can be successfully utilized for sulphate removal from mine wastewaters. Sulphate concentrations of approximately 1400 mg/L, 700 mg/L, 350 mg/L and 20 mg/L were obtained using gypsum precipitation, and ettringite precipitation, biological sulphate treatment and reverse osmosis after gypsum pretreatment for the treatment of sulphate rich (8 g/L SO_4^{2-}) mine wastewater, respectively.

Chemical, physical and biological sulphate removal technologies have different advantages, challenges and limitations related to e.g. the obtained sulphate concentrations and removal efficiencies, halide removal, retention time, operating costs and generated waste. Chloride or other halides were not removed from the water during the gypsum precipitation, ettringite precipitation nor biological sulphate reduction meaning that purified water from these treatment processes is not suitable for recycling back to the hydrometallurgical processes at the mine site. The selection of the most appropriate technology or combination of technologies should be selected for every industrial site case-by-case. The capability to meet the regulatory limits is the first priority. Since the global sulphate limits range between 10 mg/L and 2000 mg/L, the technology requirements vary. The lowest sulphate levels, 20 mg/L in this study, were achieved using reverse osmosis membranes. Lower limits of 10 mg/L used in Minnesota could likely be achieved by the two stage filtration. However, two stage filtration was not tested in this study, since the mine site is located in Finland and has 2000 mg/L sulphate limits for the effluent. All tested technologies achieved sulphate levels below the 2000 mg/L limits. In the areas of 1000 mg/L sulphate limits, gypsum precipitation does not suffice as the sole treatment method. Sometimes the mine sites have also total mass limits in addition to the sulphate concentration limits, which can influence the technology selection.

Calculated reagent and energy costs were in the order from the lowest to the highest: gypsum precipitation, reverse osmosis, biological sulphate reduction and ettringite precipitation. Investment

costs were not included into the calculations. Gypsum precipitation can be used as the pretreatment method in combination with other sulphate removal technologies. The possibility to utilize cheaper electron donors in biological processes and aluminium from secondary sources in ettringite precipitation would significantly affect the costs for these technologies. In addition, the waste disposal costs or alternatively the possibility to produce a sellable end product have a significant effect on the total costs of the selected process.

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