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

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11

12 Abstract

13 Chemical, physical and biological technologies for removal of sulphate from mine tailings pond
14 water (8 g SO₄²⁻/L) were investigated. Sulphate concentrations of approximately 1400, 700, 350 and
15 20 mg/L were obtained using gypsum precipitation, and ettringite precipitation, biological sulphate
16 reduction or reverse osmosis after gypsum pretreatment, respectively. Gypsum precipitation can be
17 widely utilized as a pretreatment method, as was shown in this study. Clearly the lowest sulphate
18 concentrations were obtained using reverse osmosis. However, reverse osmosis cannot be the only
19 water purification technology, because the concentrate needs to be treated. There would be
20 advantages using biological sulphate reduction, when elemental sulphur could be produced as a
21 sellable end product. Reagent and energy costs for 200 m³/h tailings pond water feed based on
22 laboratory studies and process modelling were 1.1, 3.1, 1.2 and 2.7 MEur/year for gypsum

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

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

27

28 **Introduction**

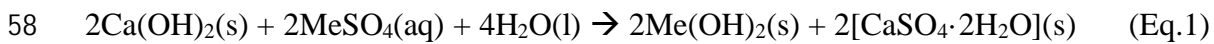
29 Sulphate (SO_4^{2-}) has been traditionally considered as a relatively harmless substance in the
30 environment. Sulphates are discharged into the aquatic environment from industrial operations such
31 as mining and smelting, steel manufacturing, kraft pulp and paper mills and flue gas
32 desulphurization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

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

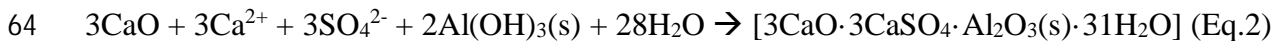
42 The focus on the treatment of AMD and mine effluents has been on acidity and dissolved metals,
43 whereas less attention has been paid to sulphate. Nowadays concerns against sulphate discharge
44 have increased and resulted in guidelines and regulations that limit the discharge into the receiving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

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

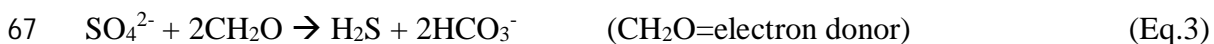
52 Alternative treatment processes for the removal of sulphate from mining effluents are chemical
 53 treatment, membrane filtration, ion exchange and biological sulphate removal. Chemical
 54 precipitation of sulphate with lime or limestone to gypsum (Eq.1) is the most common way for
 55 sulphate removal from mine water, which can reduce sulphate concentrations to generally 1500–
 56 2000 mg/L, and even to below 1200 mg/L depending on the composition and ionic strength of the
 57 solution (INAP 2003; Liang 2014).



59 When more advanced technologies are required for lower sulphate limits, gypsum precipitation can
 60 be used as a pre-treatment step. Ettringite precipitation (Eq.2) has been shown to be an effective
 61 method for sulphate removal, as it can reduce sulphate concentration to 200 mg/L (Madzivire et al.
 62 2010). Ettringite is also considered to be stable waste for long term disposal. The main disadvantage
 63 of the process is high aluminium consumption and thus high operational cost.



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



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

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

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

88

89 **Materials and methods**

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

93 All sulphate removal experiments were conducted at the room temperature (20-25°C) with the upper
94 pH limit of 10 based on typical environmental permit limits. In the gypsum precipitation tests in
95 batch reactors, 3 L of mine water (Batch 1) was maintained at the pH of approximately 10.5 or 12
96 with ~10% lime solution. Samples (150 mL) were filtered (0.45 µm) and purged with CO₂ to lower
97 the pH <10 before refiltering and analysis.

98 In ettringite precipitation tests, the lime treated mine water (1700 mg/L SO_4^{2-} , pH 12.3) without
99 CO_2 bubbling was further processed by reactive aluminium. AlNaO_2 (26-30% Al technical grade
100 powder) was used (Janneck et al. 2012). To optimize the dose of AlNaO_2 , 200 mL of lime-treated
101 mine water was mixed with AlNaO_2 for two hours at the $\text{Al}/\text{SO}_4^{2-}$ molar ratios of 1, 1.5, 3, 7.5 and
102 15 at pH 11.5–12. Based on the preliminary ettringite precipitation tests a larger scale test was
103 performed in a 3 L reactor. AlNaO_2 was added as one time dosage in the beginning of the 6-hour
104 test and pH was maintained at 11.5–12. Samples (150 mL) were filtered (0.45 μm) and purged with
105 CO_2 to lower the pH <10 before refiltering and analysis.

106 Biological sulphate removal after gypsum precipitation was studied in two 700 mL reactors with
107 reactor 1 operated first as a fluidized-bed reactor (FBR) and later as an upflow anaerobic sludge
108 blanket reactor (UASB), and reactor 2 as a FBR throughout the study with the aim to further
109 decrease the sulphate concentration. The FBRs contained 385 mL of biobased granular activated
110 carbon as carrier material. They were inoculated with anaerobic granular sludge from an operating
111 wastewater treatment plant in Finland and with sulphate reducing bacteria (SRB) enrichment
112 cultures from that same sludge. Ethanol was used as electron donor (1.5x stoichiometric
113 concentration), since ethanol is utilized in commercial scale applications and the microbial culture
114 utilized as inoculum was originally treating wastewaters from the ethanol plant. The feed solution
115 contained also added nutrients, 56 mg/L KH_2PO_4 , 137 mg/L $(\text{NH}_4)_2\text{HPO}_4$, 11 mg/L ascorbic acid
116 and 11 mg/L yeast extract. Both reactors 1 and 2 were started batch wise for the first 17 days to
117 ensure microbial growth on carrier material after inoculation. Thereafter, the reactors were operated
118 in the continuous mode with the hydraulic retention time of 24–96 hours. Ethanol was added in
119 double concentration after 33 and 43 days to reactors 1 and 2, respectively, to verify that the
120 operation was not limited by the availability of electron donor. After 50 days, reactor 1 was
121 switched to operate as UASB. Tailings pond water from batch 1 was used in the experiments during
122 the first 26 days, and from batch 2 day 27 onwards.

123 Membrane experiments were conducted in a plate-and-frame laboratory filtration unit. The feed
124 solution was pumped from the feed tank to the cross-flow membrane cell, SEPA CF with a
125 membrane area of 140 cm². Nanofiltration NF270 (Filmtec, USA) membrane (NF) and reverse
126 osmosis BW30LE (Filmtec, USA) membrane (RO) were used in the tests. The membrane flat sheets
127 were rinsed before filtrations with de-ionized water and stored overnight at 5°C in a glass bottle
128 filled with de-ionized water. Salt rejections at 2000 ppm were determined based on conductivity
129 measurements of permeate at pH 8 and with 15% recovery using magnesium sulphate (MgSO₄) and
130 5 bar pressure for the NF membrane, and sodium chloride (NaCl) and 10 bar pressure for the RO
131 membrane. All filtrations were carried out at 25±1°C and feed flow of 6.5±0.1 L/min, which
132 generated a cross flow velocity of 0.6 m/s. Feed solution (Batch 3) was filtered as such or after pre-
133 treatment using microfiltration (MF) or chemical gypsum precipitation continued by MF. MF was
134 carried out using 0.2 µm filter element (Sofi Filtration, Finland) using the normalized pressure of
135 1.0 bar and the feed flow of 1.5±0.1 L/s.

136 The pH was measured with the Radiometer PHM240 analyser equipped with a Radiometer
137 pHC2011-8 electrode in chemical and biological experiments, and with VWR 1000H equipped with
138 pHenomena111 in membrane filtration tests. Oxidation-reduction-potential (ORP) was analysed
139 with SCHOTT CG840 analyser equipped with the SCHOTT Blue Line 31 RX electrode (Ag/AgCl
140 3M KCl). Conductivity was measured using VWR CO3000H equipped with the CO11 sensor. Total
141 dissolved solids (TDS) was determined using a standard method SFS-EN 15216. SO₄²⁻ and Cl⁻
142 concentrations were analysed with a spectrophotometrical method at Metropolilab Oy for chemical
143 and biological experiments, and with a liquid chromatography standard SFS-EN ISO 10304-1 at
144 Labtium Oy for membrane experiments. For process control purposes, SO₄²⁻ and S²⁻ were
145 determined with Hach Lange DR3900 spectrophotometer and LCK 353 and LCK 653 kits,
146 respectively. Ca, Na, K, Mg and Mn were analysed by ICP-OES using a standard SFS-EN ISO
147 11885 and Thermo Scientific iCAP 7600 Duo at Labtium Oy. In addition, Sb, As and Ni were

148 analyzed either by ICP-MS at Metropolilab Oy or by ICP-OES at Labtium Oy. Bromide, fluoride
149 and nitrate were analysed using a standard SFS-EN ISO 10304-1 and Dionex ICS-3000 at Labtium
150 Oy. Determination of ammonium was carried out by distillation and titration method ISO 5664 and
151 Büchi Distillation Unit B-324 at Labtium Oy. NO₂-N, NO₃-N and NH₄-N were analysed during
152 membrane experiments with Hach Lange DR3900 spectrophotometer and LCK 339, LCK 341 and
153 LCK 363 analyse kits, respectively, or alternatively with AQUAKEM photometric analyser at
154 Metropolilab Oy.

155 Process models were made using the HSC-Sim process modelling software based on the test results
156 for 200 m³/h tailings pond water feed. Reagent and energy consumptions of each process were
157 calculated using information from the process models. Energy consumption was calculated from the
158 energy need of main equipments such as reactors and pumps. Investment cost and some minor
159 operational costs like RO washing reagent or flocculant costs have not been included into the
160 calculations. Long-term pilot tests would be needed for more accurate cost calculations.

161

162 **Results and Discussion**

163 *Characteristics of mine water*

164 Chemical characteristics of the mine water were as shown in Table 1. Together with sulphate, some
165 major components of the mine water are presented, and also components that may be critical for
166 environmental reasons. Water batches 1 to 3 were received for the studies in different batches, as
167 different unit operations were studied at different times and partly also in different locations.

168 Generally the concentrations in studied components were on quite steady level from batch to batch
169 with some variations observed for sulphate, which was most likely due to both variations in mine
170 processes and storage time before analysis.

171 Table 1. Chemical characteristics of different mine water batches used in the experiments. n.a. = not
172 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.

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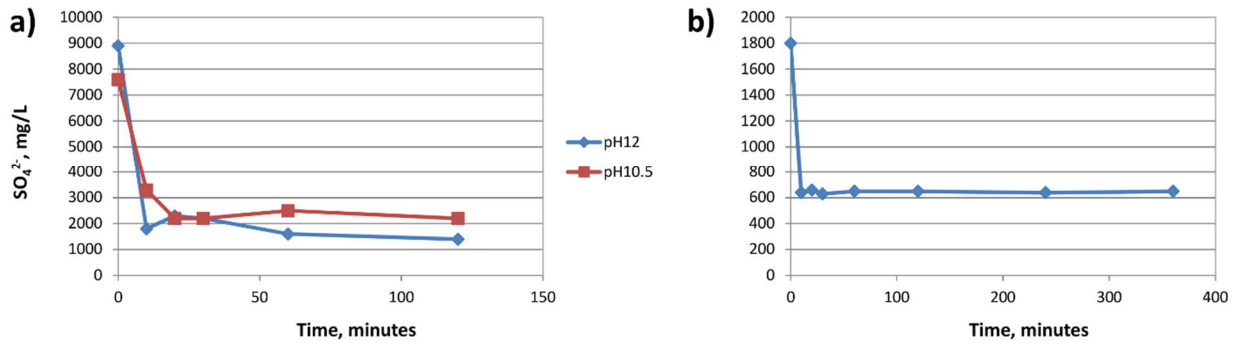
175 *Removal of sulphate by chemical precipitation*

176 Most precipitation of sulphate took place during the first 10–20 minutes in gypsum precipitation
177 (Figure 1a). Sulphate removal kinetics were similar at pH of 10.5 and 12, but the treatment at pH of
178 12 resulted in slightly lower residual sulphate concentrations quite similar to the solubility of
179 gypsum. In ettringite precipitation the selected aluminium to sulphate molar ratio was 1.5 showing
180 lowest residual sulphate concentrations. Most precipitation of sulphate occurred during the first 10
181 minutes of mixing after the aluminium addition (Figure 1b).

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

188 2000 mg/L sulphate discharge limits. With ettringite precipitation, sulphate concentration of 700
 189 mg/L was achieved.

190



191

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

193

194 Table 2. Mine water characteristics after chemical precipitation.

Component	Gypsum precipitation tests		Ettringite precipitation tests	
	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

195 * pH after filtration (0.45 μm), subsequent purging with CO₂ and second filtration (0.45 μm)

196

197 Gypsum precipitation (pH 12) consumed approximately 7.3 g of >96% Ca(OH)₂ and produced 17 g
 198 dry sludge (105°C) per litre of mine water. Same parameters at the pH of 10.5 were 5.3 g of
 199 Ca(OH)₂ and 14 g of dry sludge per litre. Sodium aluminate consumption in the ettringite

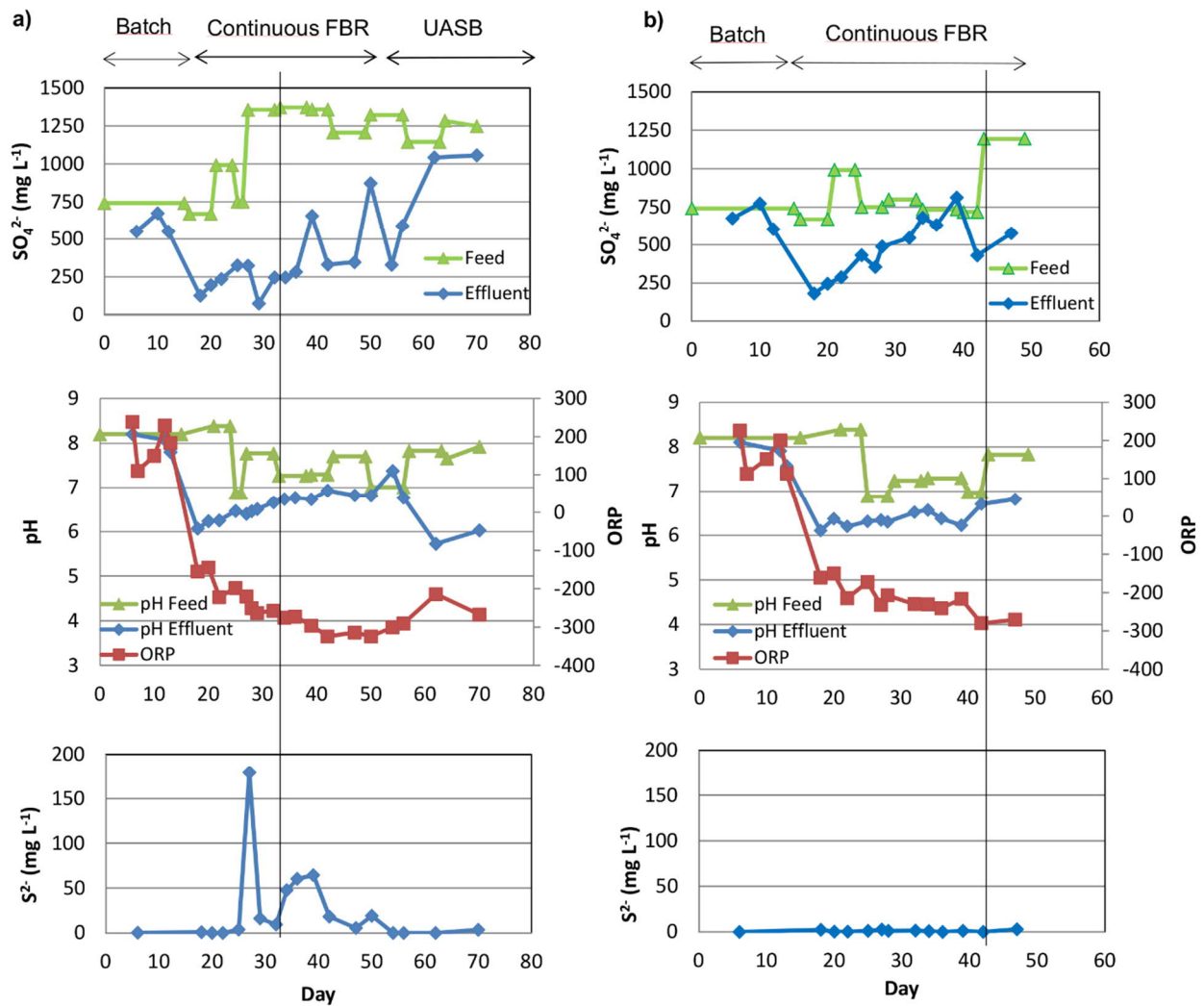
200 precipitation was 0.97 g per litre of lime treated water producing 3.9 g of dry sludge per litre of
201 water. In the filtrations following CO₂ bubbling, the amounts of sludge were negligible.

202

203 *Removal of sulphate by biological sulphate reduction*

204 After the start-up operated batch wise after inoculation, the ORP gradually decreased to the level of
205 -300 mV (Ag/AgCl, 3M KCl) in both reactors 1 and 2 (Figure 2). Also the pH decreased and was
206 mainly at the level of 6<pH<7. Biological sulphate reduction rates of maximum 1250 gm⁻³d⁻¹ and
207 1450 gm⁻³d⁻¹ were obtained in reactors 1 and 2, respectively. The obtained rates were at the similar
208 level as in several previous biological sulphate reduction studies, but also higher sulphate reduction
209 rates have been obtained in longer experiments and at higher temperatures (Kaksonen 2004;
210 Liamleam & Annachhatre 2007). It would likely be possible to enrich more SRB into the reactors
211 with simultaneous increase in the sulphate reduction rate during a longer operation time. The lowest
212 sulphate concentration obtained was approximately 350 mg/L.

213



214

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

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

224 When there are no metals present in the waste-water to precipitate as sulphides, as in this study,
225 sulphide can accumulate and result in severe inhibition of the biological sulphate reduction process.
226 Most of hydrogen sulphide is in the form of molecular H₂S at the pH of 6, whereas at the pH of 8
227 most of the total sulphide is in the less toxic HS⁻ form. Studies have shown sulphate reduction
228 inhibition by sulphide concentrations above 500 mg/L at the pH of 6.5-7, and tolerance to higher
229 sulphide concentrations of 700–1400 mg/L at the pH of 7.5 (Greben et al. 2004). In this study, the
230 pH in the reactors was most of the time between 6–7 and thus in the range that could have H₂S
231 toxicity effect on biological operations. However, no or very limited amount of dissolved sulphide
232 was detected in the effluent of anaerobic reactors. No H₂S gas was collected into the gas collection
233 bags and no H₂S leakages were detected neither. Despite the fact that activated carbon has been
234 successfully utilized as a biomass carrier material in the fluidized bed reactors treating sulphate
235 containing wastewaters with SRB (Sahinkaya et al. 2011), activated carbon can also adsorb formed
236 H₂S to a certain extent before saturation. Therefore, the carrier material was removed from the
237 reactor and the reactor was started again in the UASB mode without any added carrier material to
238 confirm the fate of sulphur. Even with no carrier material, the dissolved sulphide level remained at a
239 very low level and sulphur oxidation experiments for the production of elemental sulphur were not
240 possible. There would be significant advantages of the SRB operation, if elemental sulphur could be
241 produced by oxidizing the H₂S biologically (e.g. Maree et al. 2004) or chemically (e.g. Chen &
242 Morris 1972) to S⁰. The elemental sulphur product could be sold and waste amount would be lower
243 compared to chemical precipitation and physical sulphate removal. Further investigation on possible
244 reaction conditions for elemental sulphur production would be needed.

245 *Removal of sulphate by membrane filtration*

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

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

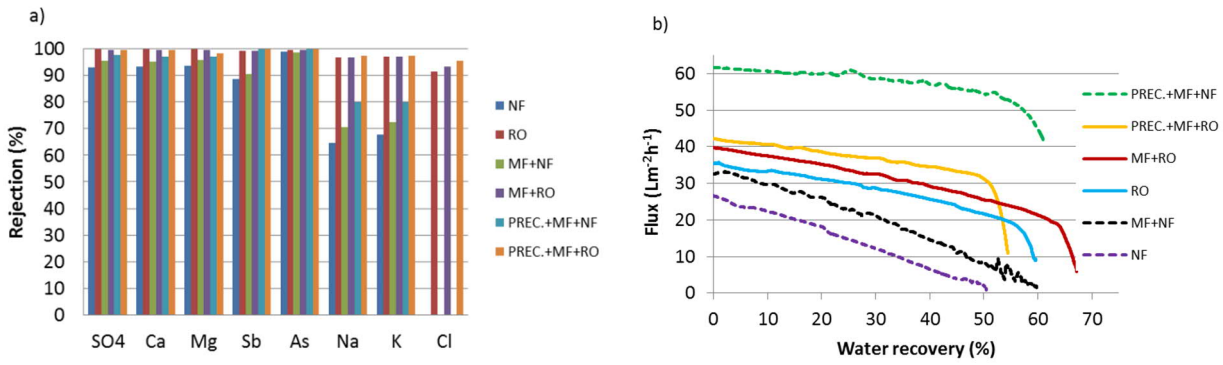
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261 Table 3. Membrane filtration efficiency with or without pre-treatment for Batch 3 mine water.

	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

262

263



264

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

267 The NF fluxes for original mine water and MF pre-treated water were lower than RO fluxes (Figure
 268 3b). NF membrane with no chemical pre-treatment for the feed fouled by elements of mine water.
 269 The best RO flux was obtained for Ca(OH)₂ precipitated and MF pre-treated mine water, although
 270 the fluxes with no chemical pre-treatment were also good. Attainable water recovery just before the
 271 flux dramatically decreases due to scaling remained lower for lime precipitated feed than for feeds
 272 with no chemical pre-treatment, due to added Ca in lime precipitation. RO fluxes were close to the
 273 flux obtained during salt rejection characterisation (33-41 Lm²h⁻¹ compared to 45 Lm²h⁻¹ at the
 274 water recovery of 15%). The best water recovery of all the filtrations, 63%, was obtained for the
 275 MF pre-treated mine water. Although the best flux of all the filtrations were obtained using NF
 276 membrane for Ca(OH)₂ precipitated and MF pre-treated mine water, water recovery remained lower
 277 (55%) than in RO membrane filtration using only MF pre-treatment. In this best flux case, the flux
 278 was close to the flux obtained with salt rejection test (68 Lm²h⁻¹). On the other hand, chlorides
 279 were not removed by nanofiltration which makes the reuse of permeate for the leaching process
 280 more difficult.

281 Water recovery of the RO process was approximately 60% and flux approximately 30 Lm²h⁻¹,
 282 which are relatively good values for RO operations. Very pure solution of 20 mg/L sulphate
 283 concentration in the permeate was produced using RO membrane after the gypsum precipitation

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

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

302 *Conceptual study*

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

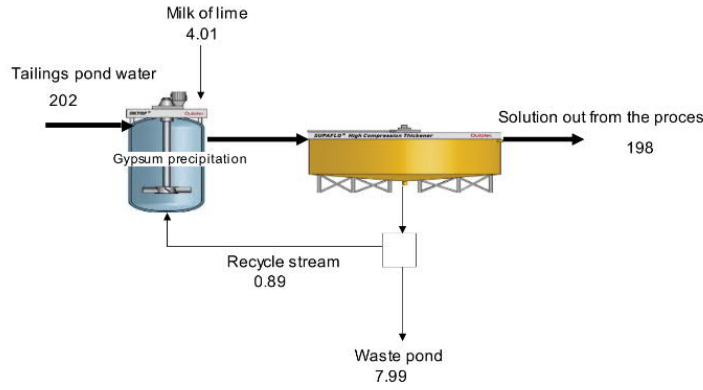
307 kinetics and to improve thickening properties of the slurry. The pH is adjusted using carbon dioxide
308 from 12 to 8.5 in the neutralization reactor for discharge.

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

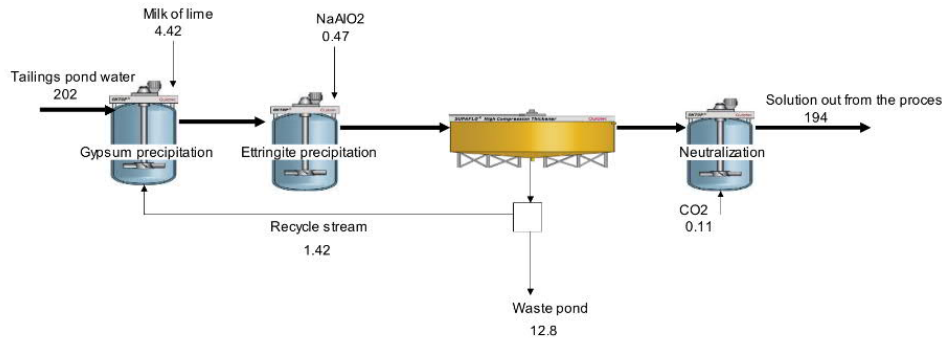
315 In membrane filtration process (Figure 4c), filtration of fine particles is needed before reverse
316 osmosis to prevent membrane fouling. Filtrate from the filter is pumped with high pressure pump
317 (10 bar) to RO system. It was approximated that 60% of water goes to permeate and 40% to
318 concentrate. Flux through the membrane was $30 \text{ Lm}^{-2}\text{h}^{-1}$. Almost all anions and cations end to the
319 concentrate. Sulphate concentration of the permeate is only 20 mg/L. Concentrate from the RO
320 system and part of the tailings pond solution goes to gypsum precipitation process. Sodium and
321 potassium concentrations increase in RO and because of these elements, sulphate concentration
322 achieved in gypsum precipitation is around 1900 mg/L.

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

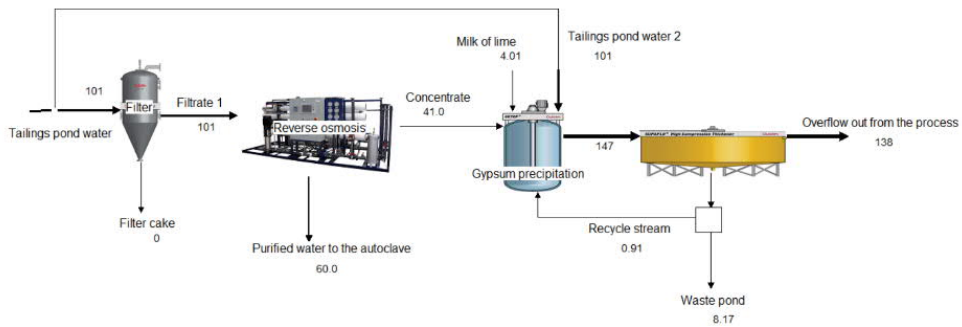
a)



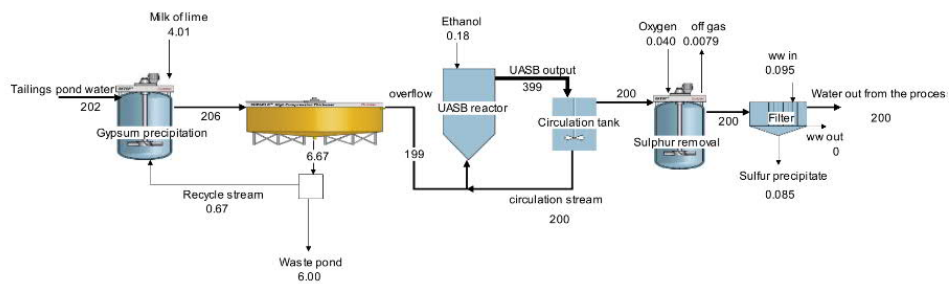
b)



c)



d)



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

333

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

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

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

353 of SRB process based on laboratory tests was long and around 5000 m³ reactor volume would be
 354 needed. Cost of the reactors was not calculated in this study.

355 Low sulphate concentration can be achieved using ettringite precipitation, but calculated operational
 356 energy and chemical costs were very high. The annual costs for the decrease of sulphate
 357 concentration from 8 to 1.8 g/L for 200 m³/h feed using gypsum precipitation were around 1
 358 MEUR/a. Further decrease of sulphate concentration from 1.8 to 0.8 g/L in ettringite precipitation
 359 would cost around 2 MEUR/a. The costs of ettringite precipitation depend significantly on the costs
 360 of aluminium source. If aluminium waste would be available, the ettringite process could be
 361 economically much more feasible.

362

363 Table 4. The consumption of reagents and energy in selected process alternatives for 200 m³/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
NaAlO ₂	3680		1.840
CO ₂	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

364

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

366 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 <u>Other equipment</u> Ca(OH) ₂ preparation tank Ca(OH) ₂ feed tank Thickener	200	2	400	3	133	300
Ettringite precipitation	Feed m ³ /h	retention time h	total volume m ³	units	Size of reactor m ³	Power kW
Precipitation reactors <u>Other equipment</u> Thickener/Filter Ca(OH) ₂ preparation tank Ca(OH) ₂ feed tank NaAlO ₂ feed tank CO ₂ neutralization reactor CO ₂ feed	200	3	600	3	200	450
Biological 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
<u>Other equipment</u> 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 m ³ /h	retention time h	total volume m ³	units	Size of reactor m ³	Power kW
Precipitation reactors <u>Other equipment</u> Fine filter Ca(OH) ₂ preparation tank Ca(OH) ₂ feed tank Thickener	140	3	420	3	140	315

367

368

369 **Conclusions**

370 Chemical, physical and biological processes can be successfully utilized for sulphate removal from
371 mine wastewaters. Sulphate concentrations of approximately 1400 mg/L, 700 mg/L, 350 mg/L and
372 20 mg/L were obtained using gypsum precipitation, and ettringite precipitation, biological sulphate
373 treatment and reverse osmosis after gypsum pretreatment for the treatment of sulphate rich (8 g/L
374 SO_4^{2-}) mine wastewater, respectively.

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

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

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

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