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# Valorisation of Separated Solids from Mine Water Treatment

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**Abstract** This paper describes two concepts for simultaneous recovery of magnesium and removal of sulphate from mine effluent. Treatment of mixed gypsum sludge generated in sulphate removal by lime precipitation containing roughly 2/3 of gypsum and 1/3 of magnesium hydroxide was treated with CO<sub>2</sub> to separate Mg from Ca. Another concept utilizes selective precipitation of Mg before any sulphate removal measures to recover as pure magnesium hydroxide as possible. In terms of Mg recovery, the latter concepts seems more promising, but it has impacts on sulphate removal with regards to increased chemical consumption.

**Key words** sulphate removal, magnesium, valorisation, recovery

## Introduction

Solid residues generated in the treatment of mine process waters reflect the quality of the feed to the water treatment as well as chemicals used in the treatment. The most common treatment for sulphate laden water is precipitation with lime. In such case the solids often contain high concentrations of gypsum, but also other minerals that have dissolved in mine processes and precipitate together with gypsum. For instance magnesium, which is present in many metal ores, dissolves into the process water and often precipitates as magnesium hydroxide in the same pH-window with gypsum. Sustainable mining calls for maximal recycling of water and solid materials to be used again in the mine processes. Therefore, it is necessary to search for cost-efficient methodologies to separate solid and liquid streams with different properties from each other to best utilize each of these secondary resources. Moreover, the amount of wet gypsum residuals generated can be substantial and challenging from a disposal point of view. This paper concentrates on magnesium recovery from mine effluent and a mixed sludge of gypsum and magnesium hydroxide. The global market of magnesium has recently seen a rapid increase in demand and production, whereas the production is very heterogeneously distributed (Cipollina et al. 2014). EU has classified Mg among the 14 most critical raw materials.

Recovery of magnesium from mixed gypsum sludge by bubbling with carbon dioxide is described in the literature (Rukuni et al. 2015). Similar technology is also proposed earlier (Bologo et al. 2009). However, these papers do not give clear description whether magnesium is dissolved from gypsum as carbonate or sulphate. If Mg was dissolved as sulphate, it could be crystallized by evaporation and further roasted to form MgO and sulphurous acid gas that could be used in sulphuric acid production (Ozaki et al 2014) Another concept for recovery of magnesium would be selective precipitation of magnesium hydroxide before a mixed gypsum sludge is formed. Cipollina et al. (2014) proposed a reactive crystallization process for concentrated brines, in which magnesium is precipitated with sodium hydroxide to form magnesium hydroxide. They suggested, that the process could be economically viable, if magnesium sulphate with high purity was generated. A drawback in sulphate bearing

water would be the generation of very soluble sodium sulphate, which would not be removable through lime treatment.

This paper describes laboratory scale experimental efforts coupled with thermodynamic multi-phase modelling for recovery of magnesium and removal of sulphate from mine effluent. Two concepts for magnesium recovery are assessed, and a qualitative comparison is made between these concepts together with their possible impacts on sulphate removal, an angle from which the proposed magnesium recovery concepts have not been looked before. The ettringite process, consisting of chemical sulphate precipitation as low-soluble mineral ettringite with the use of lime and aluminium salt, was chosen as the sulphate removal technique in combination with Mg recovery. With the ettringite process very low residual sulphate concentrations are possible to reach, and the process has also been applied in industrial scale (Tolonen et al. 2016).

## Materials and methods

### Mine effluent

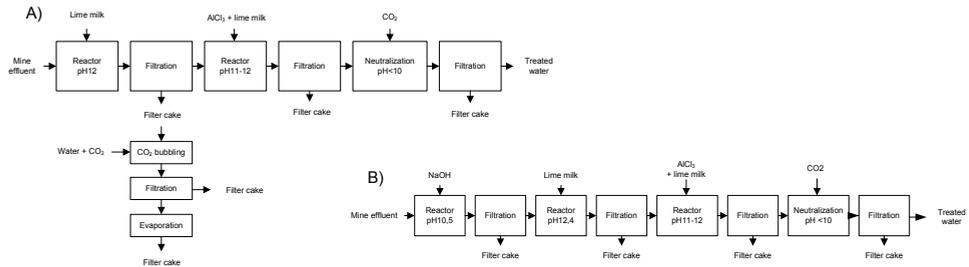
Mine waste water with main characteristics shown in Table 1 was used for the experiments.

*Table 1. Major substances in mine effluent*

Parameter	Mine effluent
pH	7.0 – 7.5
Sulphate $\text{SO}_4^{2-}$ , mg/L	9 200
Calcium Ca, mg/L	450
Magnesium Mg, mg/L	1 900
Potassium K, mg/L	120
Sodium Na, mg/L	220

### Studied concepts for magnesium recovery and sulphate removal

Figure 1 shows the flow-sheets of the compared concepts in the study. In concept A a mixed gypsum sludge is formed in the first reactor to remove most of the sulphate. The sludge is then treated with  $\text{CO}_2$  for the separation of Ca and Mg. Dissolved Mg is then crystallized by evaporation. In concept B the first step is precipitation of  $\text{Mg}(\text{OH})_2$  with NaOH followed by gypsum precipitation in the next phase. Both concepts include the ettringite precipitation (addition of Al-salt and lime) as the last sulphate removal step, after which neutralization of the treated effluent takes place to meet effluent discharge pH-criteria (often pH10 at Finnish mines).



**Figure 1.** Studied concepts for Mg recovery and sulphate removal.

## Computational assessment

Opportunities of recovering magnesium and removing sulphate from mine waters were assessed using thermodynamic multi-phase modelling (Pajarre et al. 2016b) where Pitzer formalisms (Harvie et al. 1984; Holmes and Mesmer 1986) were applied for describing the activities of solute species in the aqueous media. More details of applied database and models are given in the literature where mine water and hydrometallurgical processes are studied (Pajarre et al. 2016a, c; Koukkari et al. 2017).

Multiphase chemical system of Na-K-Ca-Mg-Al-SO<sub>4</sub>-CO<sub>3</sub> was utilised for modelling the mine water chemistry. Here ideal mixed gaseous phase, aqueous phase based on Pitzer formalism and pure precipitated phases were included. This thermodynamic database is applicable for elevated temperatures up to 90 °C and up to molality ≈ 10 mol/kg. For modelling purposes following compositions of mine waters and gypsum were applied, Table 2.

**Table 2** Composition of treated stream and mixed gypsum sludge (ppm) used for thermodynamic modelling. The elements are converted to respective salts for the thermodynamic multi-phase model (e.g. Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>·2H<sub>2</sub>O, MgSO<sub>4</sub> and Mg(OH)<sub>2</sub>). Note. Slight differences in water composition in comparison to Table 1, because data from different batch of water was used as starting point for modelling.

	Na	K	Ca	Mg	SO <sub>4</sub>
Water before gypsum precipitation	240	130	470	1900	9200
Mixed gypsum sludge	400	200	190000	120000	450000
Water after gypsum precipitation	210	120	850	1,0	1700

## Experimental work

All the reactor tests (Figure 1) were performed as batch tests in room temperature in continuously stirred reactors, in which the volume of mine effluent was 10 litres when entering the first stage. In all precipitation steps, water was first added to the reactor, mixing was started,

and the reagents were added as one-time dose into the reactors. In all precipitation tests the duration of experiment was 30 minutes, after which the stirring was ceased and the mixture was filtrated through 0,45  $\mu\text{m}$  membrane filter.  $\text{CO}_2$ -bubbling of filter cake from lime precipitation step in concept A was performed in 1 litre reactor for 60 minutes, after which the mixture was also filtrated (0,45  $\mu\text{m}$ ). The final  $\text{CO}_2$  neutralization of ettringite precipitation effluents was monitored with pH meter and ceased when pH was below 10.

Lime was added as 10 % solution (100 g analytical grade  $\text{Ca}(\text{OH})_2$  (>96 %) in 1000 mL). Lime dosing was based on pH in steps were only lime was used, and on pH and stoichiometry in ettringite precipitation steps. Extra-pure anhydrous  $\text{AlCl}_3$  (>99%) was used as the aluminium source in ettringite precipitation.  $\text{AlCl}_3$  was first solubilized, and added as a solution of 25% (25 g in 100 ml).  $\text{AlCl}_3$  dosing was based on stoichiometry (molar ratio of sulphate and Al). NaOH was added as 4 M solution, and the dosing was based on pH shown by modelling.  $\text{CO}_2$  was added to the treatment step of mixed gypsum sludge as pure  $\text{CO}_2$  through a glass sinter, and the dosing was adjusted with a rotameter to 1 litre per minute.

All the filter cakes except for the  $\text{CO}_2$ -neutralized effluents from ettringite precipitation (small amounts) were characterised for inorganic elemental composition by X-ray fluorescence (XRF). All water samples (mine effluent + samples after filtration) were analysed for sulphate by ion chromatography (IC) and Ca, Mg, K and Na by inductively coupled plasma optical emission spectrometry (ICP-OES). Additionally, for process control purposes sulphate was analysed with Hach Lange DR3900 spectrophotometer and LCK 353 kits. Also pH, conductivity and redox values of all water samples were determined.

Filter cakes from  $\text{CO}_2$  treatment of mixed gypsum sludge and NaOH precipitation were washed on the filters in liquid to solid ratio of 5 after collecting the first filtrate. Washing was done to remove dissolved substances from the filter cakes and thus 1) increase the recovery of dissolved Mg in the  $\text{CO}_2$  treatment and to 2) purify the  $\text{Mg}(\text{OH})_2$  recovered in the selective precipitation. The filtrates from filter cake washing were also analysed for same substances than other water samples.

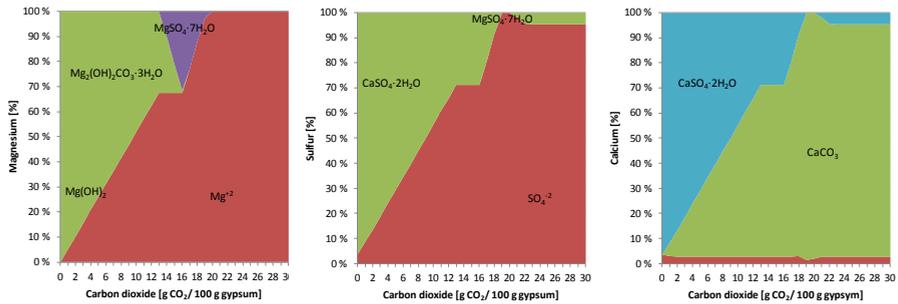
Effluent from  $\text{CO}_2$  treatment from mixed gypsum sludge in concept A was dried overnight at 105 °C in order to evaporate water and crystallize magnesium sulphate. The formed solid was also characterised by XRF.

## Results

### Computational assessment

Figure 2 shows the results from computational assessment performed in order to suggest the dissolving species of magnesium in  $\text{CO}_2$  treatment of mixed gypsum sludge (concept A). The composition of mixed gypsum sludge is given in Table 2 and the amount of gypsum is 100 g per 1000 g of water. Applied temperature is 25 °C and pressure is 1 bar.

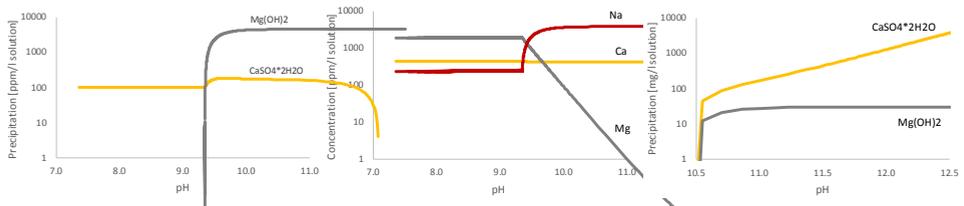
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**Figure 2** Appearance of magnesium (left), sulphur (centre) and calcium (right) species within the chemical system during the carbon dioxide treatment of mixed gypsum sludge. Here the composition of raw material is 25% of  $Mg(OH)_2$  and 75% of gypsum. Amount of water is 1000 g per 100 g of solids.

Based on the thermodynamic analysis, the magnesium is dissolving from the gypsum due to the reaction with carbon dioxide. However, the sulphate ion is dissolving respectively. Thus, the gypsum is transforming to the calcium carbonate and dissolved species is magnesium sulphate. The optimal charge of carbon dioxide is 20 g per 100 gram of treated solids.

Figure 3 shows the results from computational assessment for concept B, where NaOH is used in the first stage to selectively precipitate  $Mg(OH)_2$ . The composition of treated mine water before precipitation with NaOH is given in Table 2.



**Figure 3** The precipitated phases (left) and dissolved metals (centre) during the neutralisation of mine water by caustic soda. The precipitated phases (right) during the neutralisation of remaining water by lime milk.

Computational assessment, Figure 3, illustrates that  $Mg(OH)_2$  could be selectively precipitated at pH level 9.3 – 10.0. Some gypsum precipitates simultaneously. However, the drawback here is the extensive usage of caustic soda resulting in high level of soluble sodium sulphate in treated water. According to the computational assessment, the sulphate level will remain > 6000 ppm even after lime treatment if magnesium is selectively precipitated with caustic soda.

## Experimental work

### Concept A

Table 3 shows the concentrations of studied substances in liquid fractions collected at different stages of the process in concept A. Table 4 shows the concentrations of same elements

in solid matrices generated in this concept. Sulphate concentrations in lime treatment decreased to below 2 000 mg/L like expected. Subsequent ettringite precipitation further decreased sulphate concentrations to 3.9 mg/L. In CO<sub>2</sub> treatment of mixed gypsum sludge, plenty of sulphate was released to water phase being in accordance with predictions from the modelling work. Magnesium concentrations in the filtrate of CO<sub>2</sub> bubbled sludge were roughly 4.5 times the concentrations in the mine effluent giving justification to this concentration stage. Not much Mg was left in the sludge after CO<sub>2</sub> treatment, whereas Ca retained in solid form in the CO<sub>2</sub> treatment also being in accordance with model prediction. Sulphate ends up mainly in 1) washed sludge after CO<sub>2</sub> bubbling 2) Evaporation residue and 3) ettringite sludge. Some sulphate is also released to the wash water of the CO<sub>2</sub> treated sludge, which would still have to be treated.

Based on Mg concentrations in the mine effluent, amounts of generated solids and Mg concentrations in the solid, some 55 % (w/w) of input Mg was found in crystallized evaporation residue from CO<sub>2</sub> bubbled sludge – filtrate. 9.5 % was retained in the solid form in the CO<sub>2</sub> bubbling, and some Mg (<10 %) was also lost in the washing water of the CO<sub>2</sub> treated sludge. However, mass balance calculations do not reach even close to 100 % in the case of Mg, which most likely is a consequence of the different analytical techniques used for liquid and solid phases and the semi-quantitative nature of the XRF analysis. Based on the concentration of Mg in the evaporation residue from CO<sub>2</sub> bubbled sludge – filtrate, the highest possible purity of the Mg product from concept A, magnesium sulphate, is 84 %.

Overall chemical consumptions for concept A were 10 g Ca(OH)<sub>2</sub> (pure) and 2.7 g AlCl<sub>3</sub> (pure) per litre treated water. CO<sub>2</sub> was dosed in surplus, but modelling work proposed a dose equivalent to 3.4 g CO<sub>2</sub> of one litre treated water. Additional lime and possibly Al-salt would be needed to precipitate sulphate from the filter cake wash water.

**Table 3.** Water quality in different stages of the concept A.

Parameter	Mine effluent	After lime treatment	Treated water (ettringite precip. + neutralization)	CO <sub>2</sub> bubbled sludge – filtrate	CO <sub>2</sub> bubbled sludge – filter cake wash water
pH	7,0	12,2	7,2	7,7	7,8
Sulphate, mg/L	9 200	1 700	3,9	19 000	10 000
Ca, mg/L	450	850	980	83	500
Mg, mg/L	1 900	1,3	0,16	8 900	2 800

**Table 4.** Characteristics of solids formed in different stages of concept A.

Parameter	Mixed gypsum sludge	Washed sludge after CO <sub>2</sub> bubbling	Crystallized evaporation residue from CO <sub>2</sub> bubbled sludge – filtrate	Ettringite sludge
Amount generated (dry), grams per litre treated water	17	9.0	6.2	8.6
S, %	15	11	13	6,9
Ca, %	19	31	2,0	21
Mg, %	13	2.0	17	0.17

**Concept B**

Table 5 shows the concentrations of studied substances in liquid fractions collected at different stages of the process in concept B. Table 6 shows the concentrations of same elements in solid matrices generated in this concept.

As predicted by modelling, NaOH precipitation removes most of Mg while other major components are passed on to next phases. Lime treatment of NaOH treated water results in slight decrease in sulphate concentrations also in accordance with the model, and ettringite precipitation takes care of the rest of sulphate.

From the input Mg, some 72 % was found in washed precipitate from NaOH precipitation. Sulphate ends up mainly in ettringite sludge. Based on the concentration of Mg in the washed NaOH precipitated sludge, the highest possible purity of the Mg product from concept B, magnesium hydroxide, is 94 %.

Overall chemical consumptions for concept B were 5.3 g NaOH (pure), 20 g Ca(OH)<sub>2</sub> (pure) and 4.5 g AlCl<sub>3</sub> (pure) per litre treated water. Additional lime and possibly Al-salt would be needed to precipitate sulphate from the filter cake wash water.

**Table 5.** Water quality in different stages of the concept B.

Parameter	Mine effluent	After NaOH treatment	After lime treatment	Treated water (ettringite precip. + neutralization)	NaOH-precipitated sludge, wash water
pH	7.0	10.2	12.6	6.8	8.0
Sulphate, mg/L	9 200	8 200	5 600	4,8	5 600
Ca, mg/L	450	450	630	740	260
Mg, mg/L	1 900	100	<0.15	<0.15	210

**Table 6.** Characteristics of solids formed in different stages of concept B.

Parameter	Washed NaOH-precipitated sludge	Ca(OH) <sub>2</sub> precipitated sludge	Ettringite sludge
Amount generated (dry), grams per litre treated water	3,5	11	12
S, %	1,0	0.86	8,4
Ca, %	0,14	47	26
Mg, %	39	1.2	0.16

## Conclusions

Based on the computational assessment, it can be concluded that i) magnesium sulphate is dissolved from mixed gypsum waste by carbon dioxide treatment, ii) magnesium can be selectively precipitated by caustic soda but simultaneously the residual sulphate in effluent does not obey lime treatment.

Laboratory scale experimental work was done to validate the findings from computational assessment. The overall conclusion is that modelling and experimental results were in good agreement in this study. Selective precipitation of magnesium with NaOH before any sulphate removal measures led to recovery of quite pure (94 %) magnesium hydroxide and also giving better recovery of Mg (72 %) making this concept more promising for Mg recovery. However, this led to increased chemical consumption in subsequent sulphate removal steps that possibly worsens the economic feasibility of the concept.

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