

# Valorisation of effluent from metal recovery plant

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## Abstract

Resource efficiency in a mine was assessed in this study. Two new process concepts were screened; (i) valorising metals from mine raffinate with selective precipitation with different alkalis and with possible CO<sub>2</sub> treatment and (ii) calcium removal through precipitation from neutralising pond water for improved performance of reverse osmosis. Both new concepts were evaluated with several alkalis. Concept screening was based on computational assessment and results were verified by experiments. Experiments showed qualitative agreement with findings from computational assessment and simultaneously promoted this computer-aided methodology for rapid screening of new processes.

**Keywords:** metal recovery, mine water, precipitation, concept development, process simulation; thermodynamic equilibrium

## Introduction

There is a clear trend towards material efficiency and tightening environmental regulations, which has generated needs for valorising previously unutilized metals within mine waters. In addition, the limited availability of water in many regions has increased the reuse of water in the mining industry.

The case process in this study is a mining process based on bioheap leaching method to recover copper, zinc, nickel and cobalt present in the ore by first dissolving them into pregnant leach solution (PLS) as sulphates. The sulphates in the PLS are then stage wise recovered as sulphides through hydrogen sulphide precipitation. In addition to the aforementioned valuable metals, components with lower value are present in the PLS. The PLS containing these components is recirculated back to the heaps to maintain the water balance in the process. Rest of the remaining PLS needs to be neutralised before discharge. This is carried out through lime precipitation, which is the current BAT solution (see details in Geldenhuys et al., 2003). First step is to precipitate aluminium using limestone. Secondly, lime milk is used to precipitate iron, manganese and magnesium from the solution. With both of these steps, gypsum is formed and the sulphate

level decreases. The precipitates from these stages are settled and the neutralizing pond (NP) overflow is further treated with reverse osmosis (RO).

According to current practice, the excess metals are precipitated simultaneously with gypsum, which is decreasing the possibilities of valorising these metals. In addition, the water recovery in the RO units can be quite low, i.e. 50–60%, due to scaling tendency (Kyllönen et al., 2016). When mine water contains a lot of sulphate and is treated with lime there is a great risk of gypsum scaling on the membrane (Kyllönen et al., 2017).

The aim of the present work was to study possibilities, using simulation as a method, to fractionate dissolved metals; magnesium (10000 mg/L), manganese (5000 mg/L), aluminium (4000 mg/L) and iron (20000 mg/L) from the residual raffinate of a metal recovery plant instead of precipitating these metals together with gypsum. Similar study has been previously conducted by (Kaartinen et al., 2017) for magnesium recovery from mine water. Besides valorisation of metals, the other target was to increase the amount of purified water and concentration of metal sulphates by reducing the scaling tendency in the RO plant occurring due to the calcium content of water (500 mg/L).

## Methods

The screening and development of new process concepts was conducted based on process simulation. A thermodynamic multi-phase model describing the aqueous effluents and precipitated phases was developed. Thermodynamic simulations were applied to obtain the chemical equilibrium in the studied multiphase and multicomponent systems in this study. The chemical reactions taking place in multiphase systems were calculated with the Gibbs energy minimization method assuming that the reactions are fast and equilibrium assumption is valid in the aqueous solutions. The Gibbs energy minimization method does not entail assumptions of exact reaction paths between the chemical species but the equilibrium concentrations are obtained as the composition that gives the minimum Gibbs energy without violating the elementary mass balances. The aqueous phase describing mine water was based on the Pitzer formalism for solute interactions. (Pajarre et al., 2018) give detailed description of modelling aqueous solutions. The thermodynamic models have been applied using the VTT's Chemsheet program (Koukkari et al., 2000), which can be used in Microsoft's Excel. Key ions in the applied thermodynamic model were  $\text{Na}^+$ / $\text{K}^+$ / $\text{H}^+$ / $\text{Ca}^{+2}$ / $\text{Mg}^{+2}$ / $\text{Mn}^{+2}$ / $\text{Fe}^{+2}$ / $\text{Fe}^{+3}$ / $\text{Al}^{+3}$ / $\text{Ni}^{+2}$ / $\text{Zn}^{+2}$ / $\text{Cu}^{+2}$  and  $\text{Cl}^-$ / $\text{OH}^-$ / $\text{CO}_3^{2-}$ / $\text{SO}_4^{2-}$ . Similarly gaseous phase and tens of solid phases describing the precipitation were incorporated into the model, which can be used for modelling aqueous electrolyte solutions between temperatures 25–95 °C and ionic concentrations up to 6 mol/kg. The gaseous and aqueous phases include several compounds and ions. The solid phases were assumed to be pure stoichiometric

phases comprising single precipitate. Examples of typical speciation of mine water are presented in (Pajarre et al., 2018).

The screening considered two mine water flows; raffinate and NP-water. The evaluated waters were obtained from Sotkamo mine, Finland and are described in Table 1. In the computational assessment, the anions were considered as sulphates and the pH of each solutions were adjusted by sodium hydroxide or sulphuric acid. Moreover, alkalis and acids were considered as pure components.

Figure 1 shows the flowsheets of screened concepts. In both concepts the solutions were treated with various alkalis and/or acids including sodium hydroxide, sodium carbonate, lime milk ( $\text{Ca}(\text{OH})_2$ ), limestone ( $\text{CaCO}_3$ ) and carbon dioxide in the consecutive steps. The chemicals were dosed in such way that desired pH levels were achieved. Between steps, precipitates were removed. In the experimental work the most promising treatments, based on computational assessment were selected to be studied in laboratory scale. The experimental methods are not described here in detail but results are compared to the results of the computational assessment.

## Results and discussion

### *Computational assessment - raffinate treatments*

The screening of possible process concepts for recovering aluminium, manganese, iron and magnesium from raffinate solution was conducted. A list of screened chemicals is shown in Table 2, used raffinate (raffinate 1) composition is shown in Table 1. The study included tens of simulations with various combinations of chemicals.

**Table 1.** Mine water compositions, mg/L, pH, and pH adjusting chemicals in computational assessment.

Description	$\text{Al}^{+3}$	$\text{Ca}^{+2}$	$\text{Fe}^{+2}$	$\text{Fe}^{+3}$	$\text{Mg}^{+2}$	$\text{Mn}^{+2}$	$\text{Na}^+$	$\text{Ni}^{+2}$	$\text{Zn}^{+2}$	$\text{K}^+$
Raffinate 1	4411	637	19495	-	9665	5585	2415	76	1	-
Raffinate 2	4100	510	22000	-	12000	6300	2900	2800	54	-
NP-water	0.4	470	-	0.9	18	-	1300	-	-	41
Description		pH				$\text{H}_2\text{SO}_4$ , mg/L			NaOH, mg/L	
Raffinate 1/2		2.7/3				1913/1225			-	
NP-water		10.4 / 9				-			42 / 6	



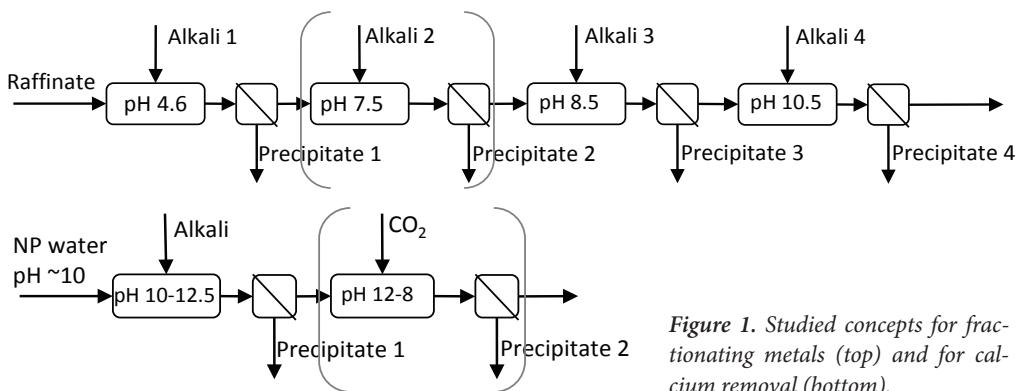


Figure 1. Studied concepts for fractionating metals (top) and for calcium removal (bottom).

Table 2. Screened chemicals for metal fractionating concepts.

Alkali 1 (pH 4.6)	Alkali 2 (pH 7.5)	Alkali 3 (pH 8.5)	Alkali 4 (pH 10.5)
CaCO <sub>3</sub>	CaCO <sub>3</sub>	NaOH	NaOH
Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub>
NaOH	-	-	-

Based on analysis similar amounts of precipitates seemed to be formed in certain pH independently of previous steps, except gypsum in the last precipitate step. The precipitated phases and chemical consumption after treatments are illustrated in Figure 2. Based on analysis Na<sub>2</sub>CO<sub>3</sub> and NaOH can be used in first step to selectively precipitate Al(OH)<sub>3</sub>. Na<sub>2</sub>CO<sub>3</sub> selectively precipitated MnCO<sub>3</sub> in second step. Further, NaOH can be used to

precipitate Fe(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> without simultaneous gypsum precipitation. The usage of lime and/or limestone as alkali caused simultaneous gypsum precipitation, always. However, the utilization of alternative alkalis (Na<sub>2</sub>CO<sub>3</sub>, NaOH) for recovering the metals may decrease the economic feasibility compared to the treatment with traditional alkalis, limestone and lime.

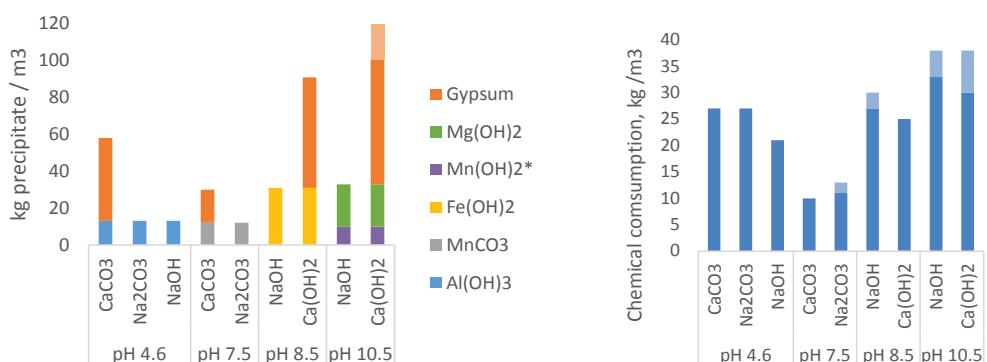


Figure 2. Summary of screened concepts for metal recovery. Precipitates after each treatment, kg/m<sup>3</sup> (left). \* Mn(OH)<sub>2</sub> precipitates only if it is not precipitated as carbonate at pH 7.5. Chemical consumption in each treatment, kg/m<sup>3</sup> (right). Light orange and light blue indicates range of gypsum precipitate and the range of chemical usage. Previous steps affect slightly on amounts of used chemicals.



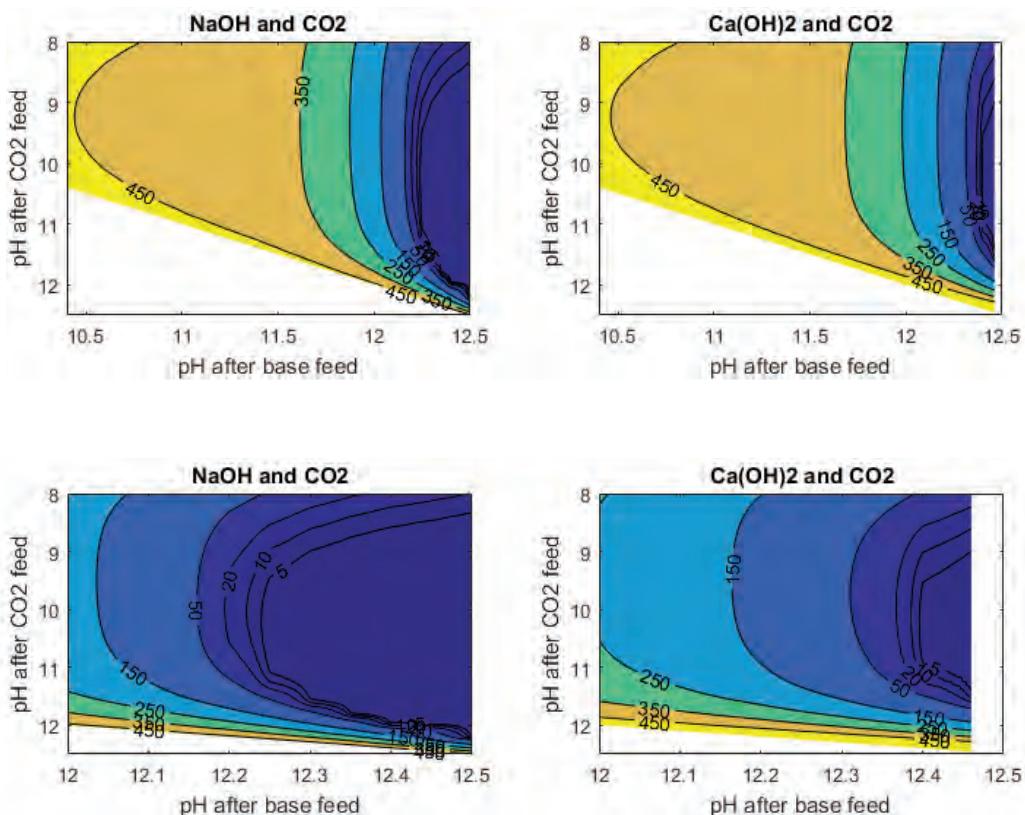
### Computational assessment – NP water treatments

Similarly, the sequential treatments to minimize calcium concentration in NP water were screened. The pH of NP water was first raised with different alkalis;  $\text{Ca}(\text{OH})_2$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  and the precipitate was removed. Next, carbon dioxide was fed to the solute aiming to precipitate calcium as  $\text{CaCO}_3$ . The  $\text{CO}_2$  treatment simultaneously lowered the pH.

If  $\text{Ca}(\text{OH})_2$  was used (see Figure 3), the additional gypsum precipitate formed during pH rise, however dissolved Ca concentration started to rise near pH 12. During  $\text{CO}_2$  dosing, Ca first precipitated as  $\text{CaCO}_3$ , and next dissolved again when the decrease in the pH continued. If  $\text{NaOH}$  was used (Figure 3), no gypsum formed during pH rise. During  $\text{CO}_2$

dosing, Ca first precipitated as  $\text{CaCO}_3$ , and next dissolved again when the decrease in the pH continued, similar to  $\text{Ca}(\text{OH})_2 + \text{CO}_2$  treatment. However, when  $\text{NaOH} + \text{CO}_2$  was applied, the possible pH ranges were larger than when  $\text{Ca}(\text{OH})_2 + \text{CO}_2$  was applied. This may affect the applicability of the method in the experimental work. With both alkalis, Mg precipitated as  $\text{MgOH}$  and Fe precipitated as  $\text{Fe}(\text{OH})_3$  during  $\text{CO}_2$  dosing (Figure 4).

If  $\text{Na}_2\text{CO}_3$  was applied (Figure 5), Ca precipitated as  $\text{CaCO}_3$  with the alkali addition only and  $\text{CO}_2$  treatment was not needed. Simulation was carried out with two initial pH levels (9 and 10.4) as the pH of water sample were lowered during storage. Very low calcium content ( $\text{Ca} < 10 \text{ mg/L}$ ) was reached before pH 10.1 or 10.5 depending on starting pH of solute.



**Figure 3.** Treatment of NP overflow with base (NaOH left and  $\text{Ca}(\text{OH})_2$  right) and  $\text{CO}_2$ . Calcium ion concentrations in solute as function of pH after base feed and pH after  $\text{CO}_2$  feed, mg/L. Bottom figures are enlargements of pH range 12-12.5.



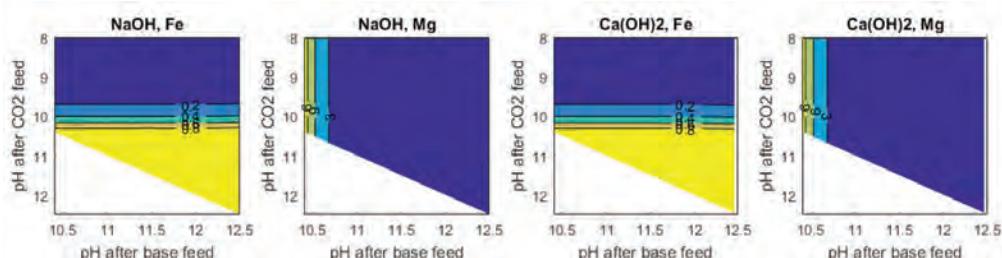


Figure 4. Treatment of NP overflow with base (NaOH left and Ca(OH)<sub>2</sub> right) and CO<sub>2</sub>. Magnesium and iron ion concentrations in solute as function of pH after base feed and pH after CO<sub>2</sub> feed, mg/L.

Based on simulation results Ca concentration in NP water can be decreased below 10 mg/L, with all studied options.

NaOH treatment, up to pH 5, of metal recovery treatments was performed experimentally. Composition of used water, raffinate 2, differed somewhat from the one used in simulation (see Table 1). NaOH treatment of raffinate 2 was also simulated to obtain comparable data. Figure 6 shows the results of the prediction and the experiment. Based on the results similar amount of NaOH was needed to reach pH 5, however the more rapid consumption of NaOH was predicted than what was obtained in the experiments. Moreover, computational assessment predicted that Al(OH)<sub>3</sub> precipitates selectively in the applied pH range, but in experiments precipitate seemed to contain also other phases and the amount of precipitate is significantly larger than predicted.

### Experimental – NP water treatments

All three NP water treatments were carried out in experimental research. Figure 7 (left) shows the results of NaOH and Ca(OH)<sub>2</sub> treatments with CO<sub>2</sub> treatment. Alkali was first added to reach pH 12.2, and next CO<sub>2</sub> addition was carried out. Based on the experiments, dissolved Ca content first decreases during CO<sub>2</sub> dosing, and while continuing CO<sub>2</sub> dosing Ca dissolves again. When NaOH was used as alkali low (<10 mg/L) Ca content was achieved. When Ca(OH)<sub>2</sub> was applied, low Ca content was not achieved, but qualitatively similar phenomena occurred. The reason for this behaviour may be, that the pH was not raised high enough in the experiments, because based on computational assessment CO<sub>2</sub> dosing should be started after reaching pH of 12.4. Figure 7 (right) shows the results of Na<sub>2</sub>CO<sub>3</sub> treatment. As predicted by modelling, Na<sub>2</sub>CO<sub>3</sub> precipitation re-

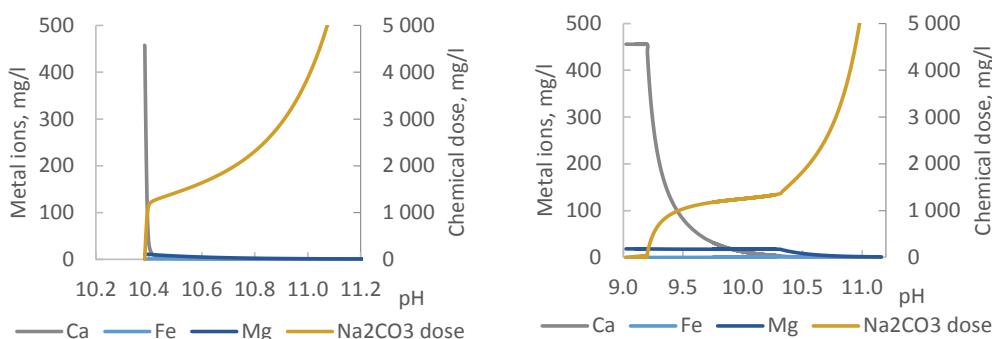
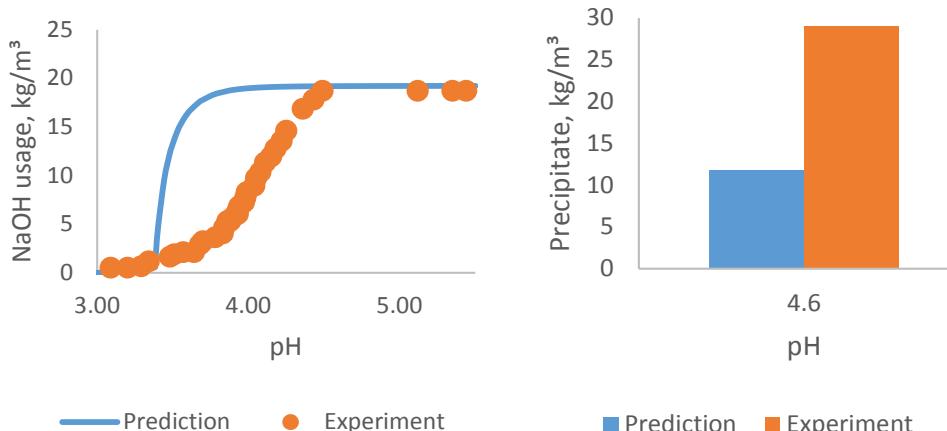


Figure 5. Treatment of NP water with Na<sub>2</sub>CO<sub>3</sub>. Metal ion concentrations and sodium carbonate feed as a function of pH, mg/L. Initial pH of NP water 10.4 (left) and 9.0 (right).





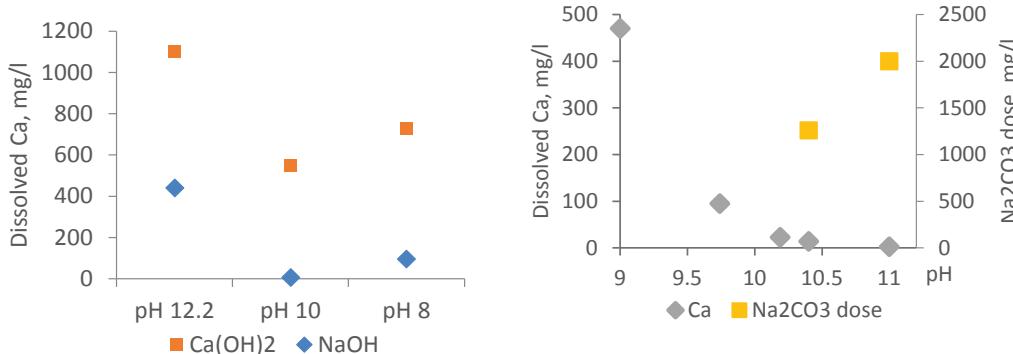
**Figure 6.** Treatment of raffinate 2 with NaOH. Alkali usage as a function of pH (left), and precipitate after treatment (right).

moves almost all dissolved calcium from water before pH reaches value 10.5.

## Conclusions

From the results gained within this study, it can be deduced that computational methods can be utilized when surveying for new process concepts. They are useful tools especially in early stage evaluation of the feasibility of a new solution and in screening the most potential process options among several possibilities. However, the process options with the most potential still need validation with experimental studies. The simulations help guide also the experimental studies and reduce the amount of work needed.

NaOH and Na<sub>2</sub>CO<sub>3</sub> can be used for fractionating metals from raffinate without simultaneous gypsum precipitation based on the computational assessment. However, the experimental validation of this concept was vague, and the topic is suggested to be studied in more detail. The other concept, the possibilities of calcium removal were assessed by simulation and later successfully confirmed with experimental results. Based on results NaOH + CO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>, can be used for calcium removal. Calcium removal with Ca(OH)<sub>2</sub> + CO<sub>2</sub> succeeded only in simulations. The process kinetics and super-saturations might result in variations between the predicted and validated results.



**Figure 7.** Dissolved calcium content after different experimental treatments. Sequential treatment with NaOH or lime up to pH 12.2 continued with acidification (left), Na<sub>2</sub>CO<sub>3</sub>, as treatment chemical (right).



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