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High Purity Recovery of Magnesium and Calcium Hydroxides from Waste Brines

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Direct disposal of concentrate brines, generated by many industrial sectors, causes serious environmental concerns. An industrial sector that produces high concentrate brines is softening water industry, in particular during the regeneration of ion exchange resins. These brines are mainly rich in sodium, magnesium and calcium chlorides, thus, their regeneration, by removal/recovery of magnesium and calcium, can be a valuable option to turn the brine into a source of minerals and reduce disposal costs and environmental concerns. In this regards, one of the goals of EU-funded ZERO BRINE project is to develop a treatment chain for the valorization and regeneration of spent brines from water softening plants. The treatment chain consists of Nanofiltration, crystalization and evaporation to regenerate spent brines and recover high purity magnesium and calcium hydroxides. In this work, a wide experimental campaign was carried out to recover high purity magnesium and calcium via selective chemical precipitation of relevant hydroxides adding by injection of an alkaline solution in two consecutive steps at controlled pH. Precipitations were performed using synthetic brine solution, mimicking the retentate produced by nanofiltration, some of them were carried out considering a pre-treatment step to remove bicarbonate ions.

1. Introduction

Freshwater scarcity coupled with a rising demand for water, along with the research of novel and more sustainable sources of raw materials, pushes researchers to implement circular approaches within any industrial sector in order to valorise effluent streams recovering water and minerals. In this regard, many industrial sectors, such as (i) mining, (ii) desalination, and (iii) water softening, produce a high amount of brines, which are disposed in water body causing several environmental issues due to content of dissolved minerals (i.e. sodium (Na), calcium (Ca), magnesium (Mg) potassium (k) and chloride (Cl)) (Cipollina et al, 2009). Consequently, a rising interest towards these effluents is shown due to the high potential for recovery of minerals, such as Magnesium, and to minimize/avoid any release into the water bodies (Sars et al, 2014). In particular, magnesium has been defined by European Commission as one of thirty Critical Raw Material (CRM) (European commission, 2020), because more than 96% of magnesium used in Europe is imported causing a high risk to supply interruption (Cipollina, 2015).

As regards the brine produced during the mining activities (i), this brine contains about 0.3-0.5 g/l of magnesium (Turek et al, 2004), which are typically disposed of in rivers or seas. Thus, many efforts have been carried out to minimize the disposal and valorise these effluent brines. Turek and Gnot (Turek and Gnot, 1995) carried out an experimental campaign to recover magnesium as magnesium hydroxide (used for the refractories industries) adding sodium hydroxide as an alkaline solution. In 2020, La Corte et al (La Corte, 2020) performed an extensive experimental campaign recovering magnesium hydroxide at high purity using calcium hydroxide solution as an alkaline reactant, through an innovative membrane reactor called Crystallizer with Ionic Exchange Membrane (CrIEM). In the same year, Micari et al (Micari et al, 2020 (a)) performed a theoretical techno-economic analysis of an integrated treatment chain demonstrating the possibility to recover minerals and salts, such as $Mg(OH)_2$, $CaCO_3$, NaCl, and freshwater.

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Seawater desalination (ii) is the industrial sector producing the largest volume of waste brines and their disposal causes serious environmental concerns (Jones et al, 2019). Normally, desalination brines have a magnesium content 1.5-2 times higher than seawater. Commonly, desalination plants are located near water bodies (such as seas or oceans), so direct disposal has been the most commonly adopted strategy. However, this disposal strategy, beside causing a high environmental impact, has a high cost, ranging from 5% up to 33% of the total desalination cost (Pramanik et al, 2017). Therefore, in the last two decades, minimization of brine volume is emerging as a new alternative to direct disposal. This new strategy can be carried out exploiting membrane-based technologies (e.g. forward osmosis (Subramani and Jacangelo, 2014)), or thermal-based technologies (e.g. multi-effect distillation (Bamufleh et al, 2017)). Thus, minimization techniques can allow reducing/avoiding direct disposal and recovering useful salts, meeting the concept of Zero Liquid Discharge (Al Mutaz and Wagialia, 1990).

The last industrial sector analysed is the water softening sector (iii), producing a highly concentrated waste brine. Generally, NaCl solutions are used for the regeneration of ionic exchange resins. Afterwards, these spent solutions, rich in sodium, magnesium and calcium chlorides, are directly disposed of in water bodies causing serious environmental concerns. Thus, their regeneration is a useful strategy to avoid/reduce their disposal. In this regard, Flodman and Dvorak (Flodman and Dvorak, 2012) suggested two strategies to reduce the NaCl consumption during the regeneration process. These two strategies consisted of mixing a portion of spent NaCl-solution with a fresh one. However, even if the NaCl consumption was reduced, the regeneration frequency increased. Recently, Micari et al (Micari et al, 2020 (b)) performed a techno-economic analysis of a treatment chain for the regeneration of spent NaCl solutions, producing freshwater and marketable minerals, such as magnesium and calcium hydroxides.

The present work focuses on the recovery of magnesium and calcium hydroxide at high purity via a selective precipitation. In particular, this work was developed within the framework of the EU-founded project “ZERO BRINE” (www.zerobrine.eu). The crystallizer is interposed within the above-mentioned treatment chain for the valorisation and regeneration of a spent NaCl solutions from the regeneration of ionic exchange resins produced at Evides Industriewater B.V., in Rotterdam. The treatment chain consists of: (i) Nanofiltration (NF), (ii) magnesium and calcium crystallization and (iii) multi-effect distillation (MED). Spent NaCl solution is fed to NF unit, which produces a retentate enriched in bivalent ions, such as magnesium and calcium, and a permeate rich in monovalent ions, i.e. sodium chloride. The retentate is fed to crystallization for the recovery of magnesium and calcium by chemical precipitation using sodium hydroxide solutions. After the separation and recovery of the two solid products, the clarified brine, together with the permeate of NF, is fed to a MED unit to further concentrate the solution in sodium chloride, reaching the target value for the reuse in the IX resins regeneration step.

This paper presents an experimental campaign aiming at producing magnesium and calcium as hydroxide at high purity using ad-hoc synthetic brines, which were made mimicking the average compositions of the retentates produced by Nanofiltration. In particular, the effect of a decarbonisation step, useful to reduce the co-precipitation of $CaCO_3$ with $Mg(OH)_2$ is analysed. The performance of the operation were assessed in terms of bivalent cations recovery and producted solids purity.

2. Experimental

2.1 Materials and methods

Experiments were carried out using three different synthetic solutions brines, prepared in order to simulate the retentate produced by NF. The feed solutions were made dissolving in deionised water the following salts: sodium bicarbonate ($NaHCO_3$) (Natural products, purity >99%), calcium chloride bi-hydrate ($CaCl_2 \cdot 2(H_2O)$) (Ciech, purity >99%), sodium sulphate (Na_2SO_4) (Fluka, purity >99%), magnesium chloride hexahydrate ($MgCl_2 \cdot 6(H2O)$) (purity >99%) and potassium chloride (KCl) (Honeywell, purity >99%). The alkaline solution was prepared dissolving micro-pellet of NaOH (Inovyn, purity 99%) into deionised water.

In Table 1, the average composition of the three different tested brines is reported.

Table 1: Composition and volume of the adopted synthetic brine and alkaline solution.

Test	Inlet Brine								NaOH solution	
	Composition[g/L]							Volume [L]	Composition [mol/L]	
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-		Mg Step	Ca Step
A & D	9.67	0.55	1.87	14.77	46.75	0.16	0.43	200	0.5	2
B & E	8.96	0.54	1.74	13.39	42.71	0.43	0.11			
C & G	10.74	0.73	2.44	16.84	53.70	0.65	0.17			

2.2 Experimental set-up and procedure

The experiments were carried out in an experimental set-up (Figure 1) consisting of: (a) brine storage tank, (b) precipitation reactor, where magnesium, first, and calcium, after, are precipitated from the brine with sodium hydroxide solution (the two steps are illustrated as two separate units although being the same unit used in subsequent steps), (c) magnesium and calcium settling tanks, which collect the produced slurry and allow the settling of produced solids from the brine, (d) intermediate storage tank, where the first clarified brine is stored before the precipitation of calcium.

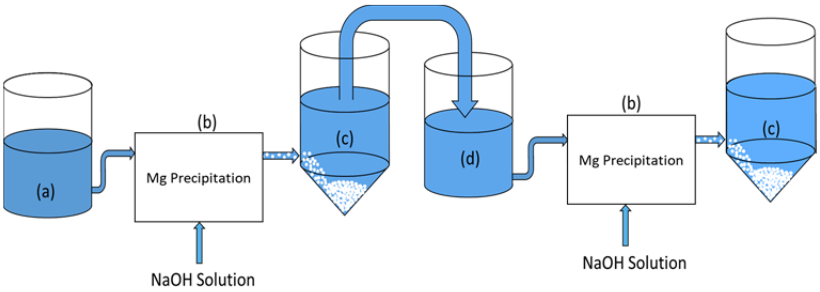

Figure 1. Process scheme of the crystallisation pilot plant. (a) Storage tanks, (b) Precipitation Unit, (c) Settling tank, (d) Intermediate tank.

For tests D, E and F, a pre-treatment was carried out to remove bicarbonate ions from the feed brine. Bicarbonate ions, in fact, can affect the $Mg(OH)_2$ purity as they cause the precipitation of calcium carbonate at pH above 9) (Tai and Chen,1998). The pre-treatment unit is shown in Figure 2.

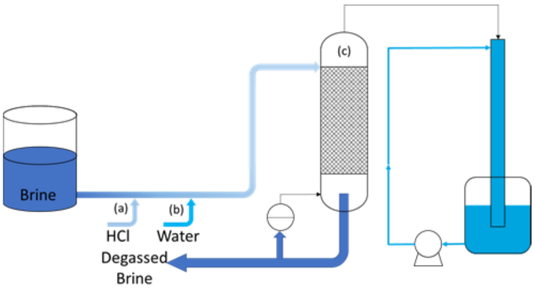

Figure 2, Process scheme of the pre-treatment section.

The pre-treatment step consists of: (a) acidification, where HCl-solution was mixed with the brine until reaching a pH value below 4, to convert bicarbonates into carbon dioxide, (b) water make-up, to restore the water content in the brine compensating the water vapour loss in the stripping column, and (C) stripping unit, where the acidified brine is fed in the top of the packing column, filled with structured packing material (*Flexipac® 700Y, Koch-Glitsch*), and put in contact with the rising stripping vapour. The stripping vapour was produced by in an electrically-driven reboiler at the bottom of the column. More details on the vapour stripping set-up can be found in (Giacalone et al., 2019, Vassallo et al, 2020).

The precipitation test can be divided into three main phases: (i) start-up, in which brine and alkaline solution flow rates are adjusted in order to reach the reaction pH (*i.e.* pH= 10.5 for magnesium precipitation and pH=13 for calcium), (ii), steady-state operation and (iii) cleaning, in which the crystallizer is cleaned using hydrochloric acid solutions and then flushed with tap water. Operating conditions for each precipitation test are reported in Table 2 and Table 3, respectively.

Table 2: Operating conditions for $Mg(OH)_2$ precipitation tests.

Tests	pH		Brine Flowrate [L/min]	NaOH Flowrate [L/min]	Worked Hours [h]
	Without Pre-treatment	With Pre-treatment			
A & D	10.30	10.45	1.71	0.44	2.0
B & E	10.35	10.40	1.46	0.33	2.5
C & F	10.40	10.50	1.00	0.38	3.5

Table 3: Operating conditions for $Ca(OH)_2$ precipitation tests.

Tests	pH Without Pre-treatment	 With Pre-treatment	Brine Flowrate [L/min]	NaOH Flow Rate [L/min]	Worked Hours [h]
A-D	13.0		1.62	0.78	2
B-E	13.0		1.57	0.7	3
C-F	13.0		1.05	0.6	3.5

The pre-treatment test consists of two main steps: (i) start-up, in which the column is filled and heated up to the working temperature, and (ii) steady-state operation. Operative conditions are reported in Table 4.

Table4: Operative condition of the vapour stripping column

Test	HCl Solution Volume [L]	 Concentration [M]	Feed brine Volume [L]	Vapour Stripping column Flowrate [L/min]	 P_{column} [bar]	 $T_{Reboiler}$ [°C]	 Thermal duty [W]
D	1.5	1	200	1.0	0.4	78	1500
E	0.46		200	1.0	0.4	77	1400
G	0.64		200	1.0	0.4	79	1600

During each precipitation test, pH and flow rates were monitored by a pH-meter (KHRONE, mod. PH 8320) and two magnetic flowmeters (KHRONE, mod. OPTIFLUX 4300 C). 1 liter of slurry samples for analytical characterisation were withdrawn during steady-state operation. Samples were filtered and both solids and clarified solution were analysed by means of ion chromatography (IC). The filtered solids were washed with deionized water, dried in an oven at 120°C for 24 hours and then dissolved in acidic deionised water for analyses. Performance parameters for two precipitation steps are defined as:

$$Recovery\ \ (Y)[\%] = \frac{\dot{N}_i^o - \dot{N}_j}{\dot{N}_j^o} \times 100 \tag{1}$$

where $\dot{N}$ is the molar flowrate, the apex ^{o} refers to the inlet stream, subscript $_j$ refers to Mg^{2+} or Ca^{2+}.

$$Purity(\%) = \frac{C_{Mg^{2+}}(\ or\ C_{Ca^{2+}})}{\sum_{i=1}^{N} C_i} \times 100 \tag{2}$$

where $C_{Mg^{2+}}(\,or\ C_{Ca^{2+}})$ is the mass fraction of magnesium (or calcium), while the subscript *i* refers to all cations present in IC analysis of solids.

For the pre-treatment step, the performance parameter adopted was the Removal Efficiency:

$$Removal\ Efficiency(\%) = \frac{N_{HCO_3^-}^o - N_{HCO_3^-}}{N_{HCO_3^-}^o} \times 100 \tag{3}$$

where $N_{HCO_3^-}^o\ and\ N_{HCO_3^-}$ represent the molar concentration of bicarbonate ions in the inlet and outlet brine, respectively.

3. Results and discussion

Solid purity and recovery efficiency for magnesium hydroxide precipitation tests are shown in Figure 2, comparing the selective precipitation performance in the case of untreated and decarbonated feed brine. Magnesium, calcium and bicarbonates concentration in the feed brine are also shown.

As it concerns the solids purity, only Mg and Ca cations were detected in the washed samples. In all tests, the Mg-purity was higher than 90%. Interestingly, a clear influence of bicarbonate ions concentration on purity is shown in Figure 2-A. In fact, the purity increases from test A (91%) to test C (98.7%), with bicarbonates concentration decreasing. The effect of brine decarbonisation pre-treatment is clearly shown in tests D, E and F, which exhibit a $Mg(OH)_2$ purity significantly higher than A, B and C, ranging from 98.3% (Test D) up ~100% (Test F). In particular, the pre-treatment step allowed removing from 55% (Tests F) up to 90% (Test D) of bicarbonate ions, as reported in Figure 2-B.

Also the magnesium recovery efficiency increases in tests D, E and F, thanks to the higher reaction pH.

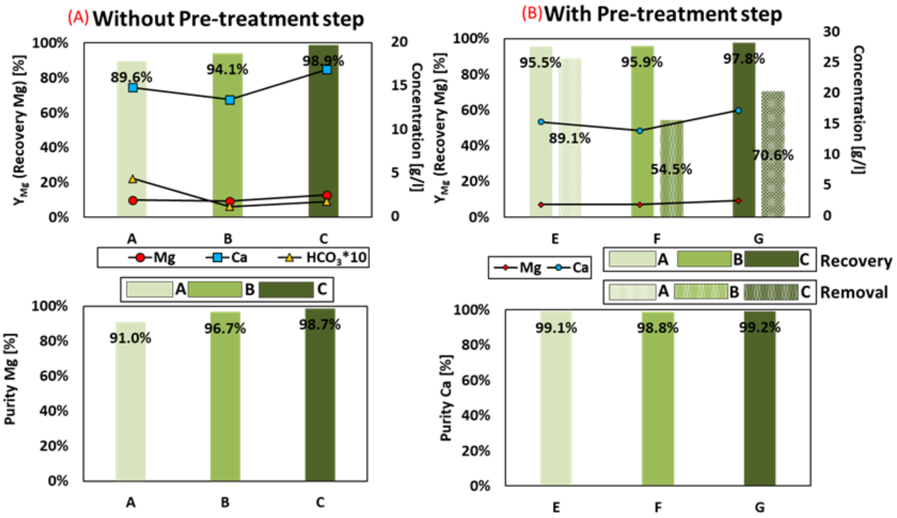

Figure 2: Magnesium recovery and Mg(OH)$_2$ purity for all precipitation tests, accompanied by magnesium, calcium and bicarbonates concentration in the feed brine: ((A) feed brine without pre-treatment and (B) decarbonized feed brine. Bicarbonates removal efficiency is also reported in (B).

The second precipitation step aims at the quantitative removal of magnesium and calcium from the brine. Recovery efficiency (i.e. removal eff.) for calcium and magnesium is shown in figure 3, along with solids purity and magnesium & calcium concentration in the inlet brine. Also, in this case, only Ca and Mg cation were present in the washed solids. The purity in Ca was higher than 98% for all tests, though it was affected by the co-precipitation of magnesium hydroxide, especially for tests with lower magnesium recovery in the first step. Calcium recovery efficiency ranged from 94% up to almost 96%, while magnesium ions were totally removed thanks to the high operating pH.

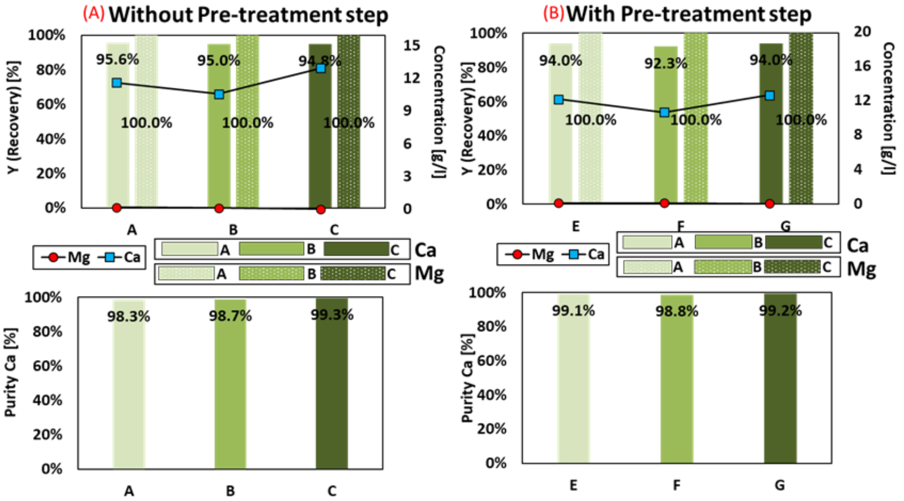

Figure 3: Calcium and magnesium recovery and Ca(OH)$_2$ purity for all precipitation tests, along with magnesium and calcium in the feed brine ((A) feed brine without pre-treatment and (B) decarbonized feed brine. Bicarbonates removal efficiency is also reported in (B).

Conclusions

The recovery of magnesium and calcium precipitated from Ion Exchange resins spent brines was investigated. Magnesium solids, recovered in the form of Mg(OH)2, exhibited a purity between 91% and 98%,with the major contaminant being calcium carbonate. A pre-treatment step consisting in the removal of bicarbonates ions from the feed brine via acidification and vapour stripping was also implemented. Precipitation tests following the pre-treatment step, reached a much enhanced purity in Mg , with values from 98% to 100%. Thus, the de-carbonisation pre-treatment can be proposed as a good strategy to precipitate magnesium hydroxide solids at the highest purity, suitable for very different market applications, such as pharmaceutical, nutraceutical, flame retardant sector. Also the recovered Ca(OH)2 solids, selectively obtained in a second precipitation step, reached a purity above 98% in all tests, with the presence of Mg as Mg(OH)2 as main contaminant. Overall recovery efficiency for Ca was above 92%, while Mg was totally removed in the second precipitation step. Thus, quantitative recovery and removal of bivalent cations is a viable option to regenerate spent brined from IXs softening plants, thus pushing toward process circularity and raw materials recovery from waste streams.

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