Magnesium recovery from exhausted brine

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Introduction

The 20 critical raw materials are crucial to Europe’s economy and essential to maintaining and improving the life.

Reactive crystallization

Magnesium can be recovered from waste brine by means of reactive crystallization. Mg²⁺ reacts with OH⁻ ions forming magnesium hydroxide that is practically insoluble in water.

\[ \text{Mg}^{2+} + 2\text{OH}^{-} = \text{Mg(OH)}_2 \downarrow \]

The source of OH⁻ can be any alkaline solution. The reactants already investigated in our previously studies are: NaOH, Ca(OH)₂, NH₃, Na₂CO₃, NaHCO₃.

Profitability analysis

A new industrial process can be really attractive only when it is economically sustainable. A profitability analysis has been carried out to understand the economic feasibility of the process. The selling price of magnesium hydroxide depends strongly on its purity. Moreover, for a profitability analysis is also important the price of the raw material necessary for crystallization.

European market strengthening

The world production of magnesium (MgO equivalent) is around 12 Mton per year (2012), but only 14% is produced in EU. If the total Mg present in the waste brine of European saltworks would be recovered, the production could grow 5% for the EU area. Moreover, considering the possibility to have an integrated cycle [1] in which the seawater is used to produce potable water by desalination, the desalination brine to produce salt (NaCl) within saltworks and finally the waste brine from saltworks to recover Mg (as magnesium hydroxide), the Euro-Med (i.e. the region around the Mediterranean sea, including Europe North Africa, and Close East) production could become the second in the world. In this way, Europe would become exporter rather than importer of magnesium.

Proof of concept

Tests were carried out to ensure the technological feasibility of the idea with a batch stirred pilot system (fig. 4.a). The goal was to identify the best conditions to obtain magnesium salts with high purity and suitable granularity for rapid separation. The concentration and flow rate of the alkaline solution (NaOH) and the stirring rate of the reaction medium were changed to investigate their effect on the purity and nucleation-growth rates of magnesium hydroxide crystals. Products with purity higher than 99.5% and with good filterability were produced [2]. Following the good results obtained in the preliminary tests, experiments were performed both in a semi-batch and in a continuous 5 liters pilot crystalliser (fig. 4.b-c).

NaOH solutions were adopted as standard alkaline reactant in order to assess the influence of all operating parameters and reactor configuration on the recovery efficiency and purity of the Mg(OH)₂ powder produced [3]. Higher concentrations of alkaline reactant and Mg²⁺ ions allows the formation of larger particles with high Mg purity (99.5±).

An other pilot unit was developed with a plug flow reactor (PFR) configuration, in order to perform further tests of continuous crystallisation (fig. 4.d) towards the process scale-up. Different alkaline solutions (NaOH, Ca(OH)₂, NH₃, Na₂CO₃) were investigated with the PFR pilot unit. Calcium hydroxide has the cheapest price but led to the lowest Mg purity thus not suitable for the purpose.

A latest development focused on the development of a membrane crystallizer reactor using ionic exchange membranes (CrIEM) [5] that can overtake the above problem. In the CrIEM the precipitation reaction occurs avoiding the direct contact between feed brine and alkaline solution, thus allowing in principle the use of any alkaline species, minimising the risk of by-products co-precipitation and enhancing the potential for recovery efficiency. In preliminary tests 99.5% pure Mg(OH)₂ was produced using cheap reactants (e.g. Ca(OH)₂), opening room for the development of a novel and economically profitable process.

Conclusion

Good knowledge has been gained so far and pilot systems have demonstrated the feasibility of Mg recovery from concentrated brines. Exploring scaling-up potentials and facing/solving technological issues for the industrialisation of the process still require joint efforts towards a new leading position of Europe in the Mg world market.

Fig. 1: 20 critical raw materials, EU (2014)

Fig. 2: Prediction of MgO equivalent word production

Fig. 3: Profitability analysis with a magnesium selling price equal to $800/t and the cost of the stoichiometric reactant necessary for the crystallisation.

Fig. 4: Experimental set-up: (a) Batch crystallizer; (b) semi-batch crystallizer; (c) continuous crystallizer; (d) PFR

Fig. 5: Membrane crystallizer reactor (CrIEM)

References