

MAGNESIUM RECOVERY FROM EXHAUSTED BRINE

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1 INTRODUCTION

In the 2014, the European Commission identified 20 critical raw materials, crucial to Europe's economy and essential to maintaining and improving the life.

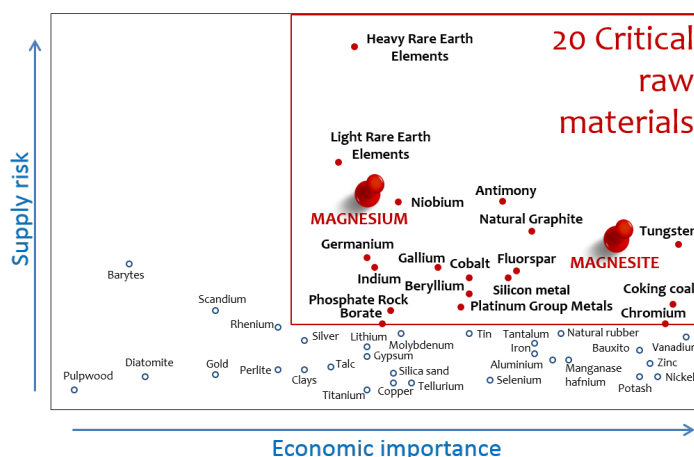


Fig. 1. 20 critical raw materials, EU (2014)

Metallic magnesium and magnesite are among them and, on this basis, the interest of scientific community is growing on the possibility to recover magnesium compounds from waste streams. Magnesium is the third most abundant element in the sea salt, with a concentration between 1 and 1.5 gr/l but it can be up to 30 times larger in waste bittern from saltworks. Reactive crystallization pilot systems have been developed and studied at lab scale to verify the technical and economic feasibility to recovery magnesium from brine.

1.1 European market strengthening

The world production of magnesium (MgO equivalent) is around 12 Mt per year (2012) [1], almost 50% is produced in Russia and China while the European area is around 14%. If the total magnesium presents in the waste bittern of European saltworks was recovered, the EU area production would grow of about 5%. Moreover, this possibility could take advantage from the so-called seawater integrated cycle (ICycle) [2] where the seawater is used to produce potable water by desalination, the desalination brine to produce salt (NaCl) within saltworks (increasing around 30% the production) and finally the waste bittern from saltworks to recover magnesium (in the form of magnesium hydroxide). When the Euro-Med area is considered (i.e. the region around the Mediterranean sea, including Europe, North Africa and Close East), the Magnesium estimated production could become the second in the world (figure 2), thus leading Europe to become exporter rather than importer of magnesium. On this basis, our research group has been focusing on Mg recovery strategies in the last years. The present work reports a brief summary of the corresponding activities and results in this topic.

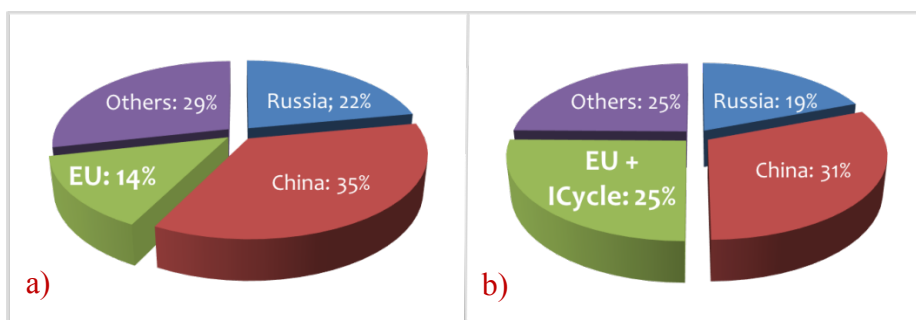
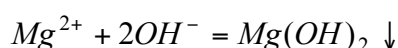


Fig. 2. a) World MgO equivalent production in 2012; b) Theoretical prediction of world MgO equivalent production using the integrated process approach for the EU area.

1.2 Reactive crystallization

Magnesium is present in high concentration in the waste bittern and can be recovered by means of a reactive crystallization. More precisely, Mg^{2+} reacts with OH^- ions forming magnesium hydroxide that has a really low solubility in water:



The source of OH^- ions can be any alkaline solution. The reactants investigated in this studies are: NaOH, $Ca(OH)_2$, NH_3 , Na_2CO_3 .

2 PROFITABILITY ANALYSIS

A profitability analysis was carried out to understand the economic feasibility of the process. The selling price of magnesium hydroxide (strongly dependent on its purity, e.g. 800 \$/t for 98% while 1500 \$/t for 99.5%) and the price of the alkaline reactant necessary for crystallization are crucial input for the engineering economic analysis.

Table 1. Profitability analysis performed by adopting a magnesium selling price equal to 800 \$/t and the average cost of the stoichiometric reactant necessary for the crystallization.

Reactant	NaOH	$Ca(OH)_2$	NH_3	Na_2CO_3
Average price [\$/t]	310	150	650	240
Profitability [\$/t]	375	610	421	364

According to the calculation and the comparison, calcium hydroxide and ammonia are the best reagents to have high profit. However, their use in direct mixing reactors has been found to dramatically affect purity and recovery of the products and NaOH is selected as the best option as it will be shown in the next paragraph.

3 PROOF OF CONCEPT

Tests were carried out to ensure the technological feasibility of the idea with a batch mechanically stirred pilot system (fig 4.a). The goal was to identify the best conditions to obtain magnesium salts with high purity and suitable granulometry for an easy separation. The effect of the alkaline solution (NaOH) concentration and flow rate and the effect of the reactor impeller speed on the purity and nucleation-growth rates of magnesium hydroxide crystals was investigated. Products with purity higher than 99.5% and with good filterability properties were obtained [3]. Following these good preliminary results and considering the discontinuous batch process unsuitable for an industrial continuous production, experiments were performed both in a semi-batch and in a continuous 5 liters pilot crystalliser (fig 4.b-c). In all the tests, 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 [4]. Higher concentrations of alkaline reactant and Mg^{2+} ions allow the formation of larger particles with high Mg purity (99.5 %), thus confirming the results obtained by Almadari et. al. [5].

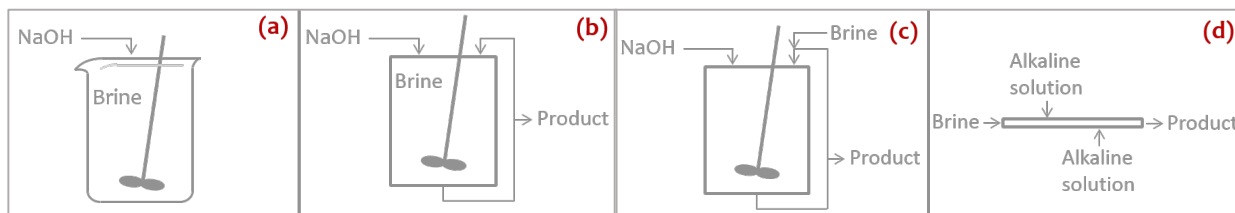


Fig. 3. Experimental set-up: (a) Batch crystallizer; (b) semi-batch crystallizer; (c) continuous crystallizer; (d) PFR

Another 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 ($NaOH$, $Ca(OH)_2$, NH_3 , Na_2CO_3) were investigated with the PFR pilot unit and the *purity* of the powder and the final *conversion* of Mg present in the initial brine into $Mg(OH)_2$ were chosen as performance indicators. The PFR was composed by a main silicon tube 120 cm long, an inlet diameter of 5.3 cm for the brine circulation and other 4 inlets (placed along reactor length) for the alkaline solution. In all the tests, the concentration of OH^- ions was fixed higher than stoichiometric value necessary for the precipitation of magnesium present in the brine. Different alkaline solution concentrations have been used ($NaOH$: 4M; $Ca(OH)_2$: 2M, NH_3 : 4M, Na_2CO_3 : 2M). The results are shown in Fig. 4:

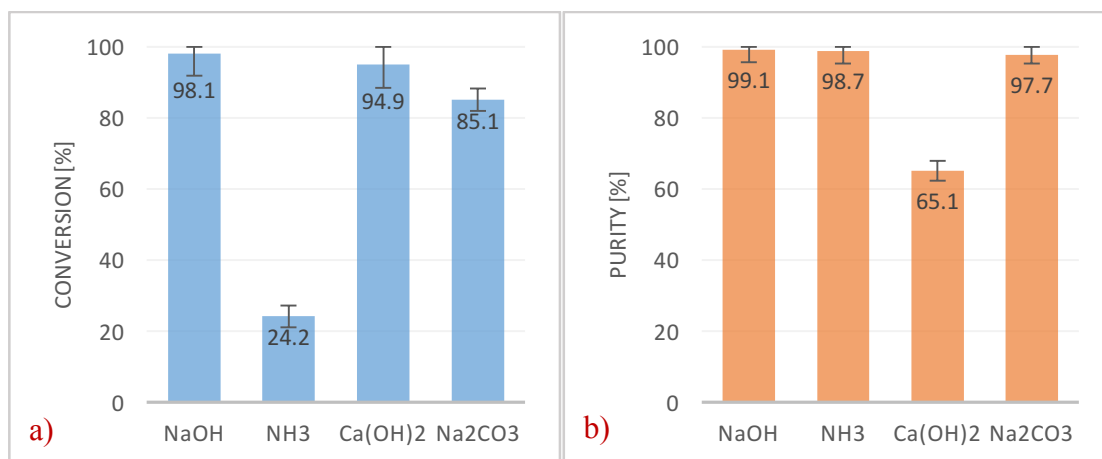


Fig. 4. Performance indicators for different alkaline species. a) Conversion of Mg present in the brine into $Mg(OH)_2$; b) Purity of $Mg(OH)_2$ in terms of Mg concentration.

Sodium hydroxide, ammonia and sodium carbonate have high purity but only calcium hydroxide and sodium hydroxide have a high conversion. With reference to Table 1, although ammonia and calcium hydroxide give the best theoretical profitability, they are not a good option due to the low conversion for ammonia and the low purity for calcium hydroxide. Sodium carbonate has low levels of both profitability and conversion. Only sodium hydroxide appears to be an interesting option due to its high conversion and purity, but it does not lead to the highest profitability margin. In order to tackle this issue, the latest efforts have been devoted to the development of a membrane *Crystallizer Reactor* using *Ionic Exchange Membranes* (CrIEM) [6]. In general, a reactor that uses an ionic exchange membrane can put into *selective* contact the reagents of a reactive crystallization from two different electrolyte solutions, even without direct contact between them.

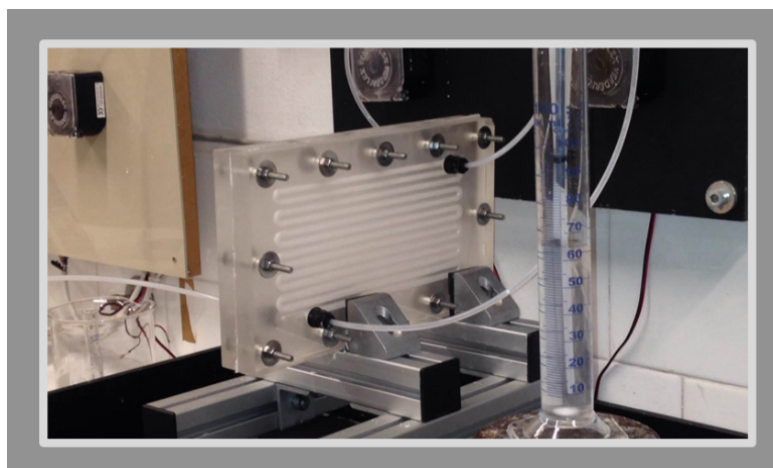


Fig. 5. Membrane crystallizer reactor (CrIEM).

Exploiting the principle described above, in the CrIEM the precipitation reaction between brine and alkaline solution could be done avoiding the direct contact between feeds, 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 $\text{Mg}(\text{OH})_2$ was produced using cheap reactants (e.g. $\text{Ca}(\text{OH})_2$), opening room for the development of a novel and economically profitable process. This new technology has been already patented [6] and it is currently under development to solve possible plugging problems in the channels during the precipitation process. Just as examples, some possible modifications currently under study are reported in the following: cleaning balls for the physical removing of precipitated particles, ultrasound waves to destroy the particles agglomeration or air bubbles to increase the turbulence in the channels.

4 CONCLUSION

The studies carried out and the results collected so far demonstrated the economic and technological feasibility of Mg recovery from concentrated brines via reactive crystallization. High purity Mg can be obtained even by using low-cost reactants. Further development activities along with suitable optimization strategies are currently on going to allow a profitable scale-up of the technology up to industrial level, thus possibly leading Europe to gain a central position in the magnesium global market.

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