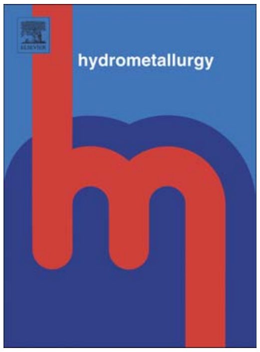


Recovery of magnesium from Uyuni salar brine as hydrated magnesium carbonate

Khuyen Thi Tran, Kyu Sung Han, Su Jin Kim, Myong Jun Kim, Tam Tran

PII: S0304-386X(15)30162-6
DOI: doi: 10.1016/j.hydromet.2015.12.008
Reference: HYDROM 4245

To appear in: *Hydrometallurgy*

Received date: 6 October 2015
Revised date: 11 December 2015
Accepted date: 17 December 2015

Please cite this article as: Tran, Khuyen Thi, Han, Kyu Sung, Kim, Su Jin, Kim, Myong Jun, Tran, Tam, Recovery of magnesium from Uyuni salar brine as hydrated magnesium carbonate, *Hydrometallurgy* (2015), doi: 10.1016/j.hydromet.2015.12.008

RECOVERY OF MAGNESIUM FROM UYUNI SALAR BRINE AS HYDRATED MAGNESIUM CARBONATE

By

Khuyen Thi Tran, Kyu Sung Han, Su Jin Kim, Myong Jun Kim, Tam Tran*

Department of Energy & Resources Engineering, Chonnam National University, Gwangju, South Korea

(*) Corresponding author: tamtran@jnu.ac.kr.

ABSTRACT

Uyuni Salar (Bolivia), the largest resource of lithium (Li) in the world not only contains a high level of Li but also ~1.3% w/w magnesium (Mg) in strong NaCl brines. The recovery of Mg is therefore essential as the resources represent high value of Mg by-products if recovered. High purity hydrated magnesium carbonate (HMC as dypingite or hydromagnesite) could be recovered from the Uyuni salar brines as an easy-saleable product. The precipitation process used for this recovery relies on the selective removal of Ca by adding excess oxalic acid at an oxalate/Ca molar ratio of 6.6:1. The excess oxalate has to be subsequently removed as Mg oxalate by adjusting the pH to pH 4 - 7. HMC products of 97.3 – 99.6% purity could be produced as a result (equivalent to 25.3 - 25.9% Mg in the product compared to a theoretical value of 25.99% Mg for hydromagnesite). Without removing Mg oxalate, products could only reach 23.3-24.3% Mg. The light HMC (hydromagnesite) product could be precipitated at ambient conditions as long as the drying was set at >65 ^{o}C. Precipitation at >55 ^{o}C also yields more crystalline hydromagnesite compared to those obtained at lower temperatures. The light HMC product has a heat adsorbing capacity (endothermic) of 1123-1196 J/g dry product. The product has a sheet-like structure and is easily filtered, compared to magnesium hydroxide.

Keywords: Uyuni salar brine, magnesium, hydrated magnesium carbonate, hydromagnesite, precipitation

1. Introduction

Magnesium (Mg), an alkaline earth metal, is the 8th most abundant element in the Earth's crust. Since its discovery in 1808, Mg has been used in a number of applications such as in the production of magnesium metal used in alloys, aircraft, automobiles, electronics, and in chemical, pharmaceutical and agricultural industries. Due to its highly reactive nature, Mg is rarely found in the pure metallic form in nature. Mg thus is found in natural liquors such as seawater, geothermal water, brines or bitterns and in minerals such as dolomite, magnesite, brucite, carnalite, talc, olivine, etc [Wikipedia-Magnesium, 2014]. A total of 12 billion tonnes of Mg ores (mainly magnesite) is identified in various mineral resources while the Mg in seawater is unlimited [USGS, 2014].

The world production of Mg metal is estimated to have increased from 499,000 tonnes in 2002 to 905,000 tonnes in 2012 [Roskill, 2012]. Industrial Mineral (2015) reported that the global production of magnesia from magnesite is ~8.5 Mtpa (China produces 49% of the total world market, Russia 12% and Australia 3%). Additionally, the global manufacture of synthetic MgO and other Mg chemicals from brines is also estimated to be about 925,000 tpa, mainly from Japan, Brazil, Mexico, Holland, Norway, Russia and USA.

Together with the production of refractory magnesia from minerals, synthetic magnesium products such as Mg chloride, hydroxide, carbonate, etc. can also be produced from brines and bitterns. Located in the highland of Bolivia, Salar de Uyuni contains over 40% of the global lithium and is known to have the richest Li salar brines in the world. Moreover, the Uyuni salar brines also contain a high level of Mg (~13.3 g/L or 1.3 %w/w Mg) compared to other brine sources as shown in Table 1 (Boryta et al., 2011; An et al., 2012; Wikipedia-Sea water, 2015).

The manufacture of Mg products from brines has been in practice on an industrial scale for several decades (Robinson et al., 1943; Panda and Mahapatra, 1983; Dave and Ghost, 2005; CMI Group, 2013; Nakai, 2014) by reacting dolime (CaO.MgO) produced from roasting dolomite or magnesite with the Mg contained in seawater. The resultant Mg hydroxide was then further calcined to produce MgO of 98-99% purity. The use of NaOH has also been extensively applied for the recovery of magnesium from magnesium-rich liquors. Lartey (1997) precipitated magnesium hydroxide from a bittern (4.24% Mg) using NaOH to produce MgO after sintering.

The formation of nano-sized $Mg(OH)_2$ particles of poor cystallinity, which caused difficulty for its recovery when NaOH was used for precipitation, was dealt with in many laboratory studies (Baird et al., 1988; Henrist et al., 2003; Alamdari et al., 2008). Lehmann et al. (2014) proposed a new approach to recover $Mg(OH)_2$ from reverse osmosis brines bearing 2.6 g/L Mg. According to these authors, the process used was based on $Mg(OH)_2$ precipitation on the surface of synthesised magnetite (Fe_3O_4) micro-particles and magnetic separation to recover the product. Thereafter, acid was used to redissolve $Mg(OH)_2$ at pH >4 (to avoid dissolution of magnetite), recovering a high purity (>97% Mg) solution. The recovery of magnesium by adding Na_2HPO_4 at 20 ^oC and controlling pH at pH 8 was conducted to precipitate Mg from seawater (Golubev et al., 1999) or Ca-free seawater (Golubev et al., 2001) as $(Ca,Mg)_4H(PO_4)_3.xH_2O$ or $Mg_3(PO_4)_2.8H_2O$, respectively.

Solvent extraction and ion-exchange were also applied to produce magnesium from brines. Lee and Jackson (1970) patented a process to extract magnesium from a brine containing 1 g/L Mg using alkyl sulphates and sulphonates. After loading, Mg was stripped from the mixture by a water-soluble strippant such as NaCl. Mackay (1977) used 1-dodecylphenyl-3-triflouromethyl-1,3-propanedione to selectively recover Mg from synthetic seawater bearing 1.4 g/L Mg and other elements at pH 6-9. Later, Muraviev et al. (1995) proposed a process to separate calcium and magnesium from artificial and natural seawater, which contained 0.11 g/L Mg and 0.02 g/L Ca, respectively, by carboxylic ion-exchange resins of acrylic and methacrylic types.

For several years, many methods have been studied to synthesise different magnesium carbonate compounds such as nesquehonite ($MgCO_3.3H_2O$), dypingite ($(MgCO_3)_4.Mg(OH)_2.5H_2O$ or $(MgCO_3)_4.Mg(OH)_2.8H_2O$) and hydromagnesite ($(MgCO_3)_4.Mg(OH)_2.4H_2O$). As stated by Canterford and Tsambourakis (1984), dypingite (or heavy hydrated magnesium carbonate, HMC as commonly known commercially) was found in materials yielded during the production of high purity magnesia from crude magnesite by a calcination/CO_2-leaching process. Caceres and Attiogbe (1997) suggested a technique to produce hydromagnesite (or Light HMC) from dolomite which was first roasted in a CO_2 atmosphere at 750 ^oC to obtain semi-calcined dolime ($MgO.CaCO_3$). The semi-calcined dolime was then wet ground at 30-90 ^oC to completely ensure the hydration of MgO. Further re-carbonation of

$Mg(OH)_2$ by reacting with CO_2 under pressure formed an aqueous $Mg(HCO_3)_2$ solution. Hydromagnesite was yielded by heating $Mg(HCO_3)_2$ to 100 ^oC to remove all water and then drying the solid at 120 ^oC. The precipitation of hydromagnesite and dypingite via the formation of magnesium hydroxide slurry and sparging CO_2 gas or reacting with sodium carbonate were also mentioned in several other studies as summarised in Table 2.

In a previous study, Botha & Strydom (2001) showed that different Mg carbonate products were formed depending on (a) precipitation temperature, (b) drying temperature and (c) drying time. Wang et al. (2008) confirmed that the reaction between Mg^{2+} and carbonate will form nesquehonite at a low temperature (30-50 ^oC) whereas hydromagnesite was formed at 60 ^oC. Cheng et al. (2009) produced nesquehonite at 0-40 ^oC, whereas dypingite was formed at 50 ^oC and hydromagnesite at 60-90 ^oC, but no information was given on drying time. The conclusions reached from these studies indicate that (a) at room temperature and low drying temperature and short drying time nesquehonite is preferentially formed, (b) however when the temperature of either precipitation and drying is raised to 65^{o}C or higher dypingite or a transitional species is formed and (c) hydromagnesite is formed at high temperature (65^{o}C or higher) of precipitation and (d) drying at 120 ^oC will produce dypingite (3 h drying time) or hydromagnesite (6-24 h) from nesquehonite.

In our previous studies on the Uyuni salar brines, Mg was first recovered as a low grade Mg hydroxide using lime (An et al., 2012) or high purity Mg oxalate after first selectively removing Ca (Tran et al., 2013) before lithium is recovered. The processes proposed in these studies, although effectively removed Mg, did not produce conventional products ready for sale. They have to be further purified (as in the case of low grade Mg hydroxide) or roasted to produce standard commercial MgO products. The present study therefore aims to recover Mg from the Uyuni salar brine (containing ~13 g/kg Mg) as marketable magnesium carbonate compounds. During the process, Ca was first removed selectively as Ca oxalate by adding oxalic acid, followed by removal of the excess oxalate in the form of Mg oxalate. The Ca and oxalate free brine obtained was subsequently added with sodium carbonate to precipitate Mg as a mixed carbonate product containing nesquehonite and/or dypingite. This precursor was then heat treated at different temperatures to produce hydromagnesite, having superior properties (calorific value, purity and higher MgO content) compared to the original precipitate.

2. Experimental

2.1 Materials and reagents

Approximately 1 m^3 of brine from Salar de Uyuni (Bolivia) was sampled and delivered to South Korea for experiments conducted at Chonnam National University. Chemical analyses using various techniques (ICP-OES and IC) described below determined its composition as shown in Table 3.

Oxalic acid ($H_2C_2O_4.2H_2O$), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) used in this study were of analytical grade and supplied by Duksan Pure Chemicals Co Ltd (Korea).

2.2 Analytical techniques

Several techniques were used for studying the characteristics of various products yielded during the study. X-Ray Diffraction (XRD) using a (Cu-tube 60kv 50 Ma) Phillips instrument was used to determine structures of the crystalline solids. Differential Thermal Analysis and Thermogravimetric Analysis (DTA-TGA) were used to evaluate the decomposition of the products over a temperature range of 25-1000 ^oC using a TG/DTA-200, SEIKO Inc instrument. In addition, a DSC 6000 (Perkin Elmer) apparatus was used to determine the product heat capacity (J/g). Chemical analysis of cations contained in the solutions was carried out by using an Optima 5300 DV (Perkin-Elmer) Inductively Couple Plasma–Optical Emission Spectrometer (ICP-OES). A 790 Personal IC (Metrohm) instrument was employed to determine the concentrations of Cl and SO_4 in the aqueous samples. Meanwhile, the microstructure of the products yielded from precipitation was evaluated by using a Field Emission Scanning Electron Microscope (JOEL JSM-5800 LV).

2.3 Experimental procedures

The process used in this study to recover Mg as Mg carbonate compounds from the Uyuni brine included the following stages:

- Stage 1: Ca removal as Ca oxalate by adding oxalic acid to the brine, reaching pH~1,
- Stage 2: Removal of excess oxalate as Mg oxalate at pH 4-7,
- Stage 3: Precipitation of Mg carbonate at pH 7.6-10.3.

A 2-blade radial impeller was used to agitate the slurries during precipitation tests conducted at room temperature (25 ^{o}C), whereas those conducted at elevated temperatures (55 and 100 ^{o}C) used a heating mantle with a fluctuation of +/-1.5 ^{o}C. The liquors' pH was monitored during the tests.

In stage 1, oxalic acid was added as a precipitant for calcium removal. After such an addition at an oxalic acid/Ca molar ratio of 6.6:1, the pH dropped from pH 6.9 to pH~1 (using simultaneously NaOH at a NaOH/oxalate molar ratio of 1.4:1 to adjust the pH). As oxalic acid has a low solubility in water at ambient conditions, it had to be dissolved in hot water (~60 ^{o}C) before being added into the brine. In stage 2, NaOH was then used to adjust the pH to the desired value (pH 4–7) to precipitate Mg oxalate, which was then filtered from the remaining brine. The last stage involved the addition of 2 M sodium carbonate to the filtrate at carbonate/Mg molar ratios in the range of 0.5-1.9:1. Known quantities of the brine were measured by both volume and weight to ensure the accuracy of the mass balance calculation to derive the Mg recovery (%). Samples were taken at different intervals up to 2 h, filtered and analysed for Mg contents by ICP-OES to ensure the reactions reaching their steady state. During each stage, the slurry obtained after precipitation was filtered using a Buchner flask, funnel and vacuum pump for liquid-solid separation.

All solids yielded were afterward carefully washed by suspending them in distilled water at a solid/distilled water mass ratio of 1:4. Each of the pure samples was then re-filtered prior to be separated into 3 parts and dried at different temperatures of 25, 65 and 100 ^{o}C. The final dried products were then subjected to chemical analysis and characterisation study using XRD, DTA-TGA, DSC and FE-SEM.

3. Results and discussion

3.1 Stabcal modelling to study speciation of Ca-Mg-oxalate and Mg-carbonate systems

As shown in the previous study (Tran et al., 2013), Stabcal software was used to model the speciation of various Ca and Mg species. Developed by Huang (2012), the Stabcal software calculates and plots EH-pH and stability diagrams (Log (concentration) vs pH) for aqueous systems based on the free energy minimisation calculations of all possible reactions involved. This was to determine the optimum pH value and precipitant/Ca or Mg molar ratio for precipitation prior to conducting laboratory experiments. In fact, sequential precipitation of Ca and Mg oxalate could be achieved by adding excess oxalic acid first (at an oxalate/Ca molar ratio of 6.6:1) to reduce the natural pH of the salar brine from pH 6.9 to pH~1 (as shown in Fig. 1a), thus removing only Ca to an equilibrium level of <0.02 g/kg Ca. After filtration, a subsequent adjustment of pH by adding NaOH to pH 4–7 would then precipitate Mg oxalate, to remove the excess oxalate quantity added earlier. After the separation of Ca and Mg oxalate from the remaining brine (by then the original Mg concentration was reduced from 13.3 g/kg Mg to <12 g/kg Mg. Adding sodium carbonate will shift the pH to the range pH 8–10 and precipitate different Mg carbonate species as shown in Fig. 1c.

3.2 Selective recovery of Mg as hydrated magnesium carbonate

Following Stabcal modelling it was possible to then selectively recover Mg from the Uyuni salar brine by sequential precipitation of Ca and Mg as oxalates and carbonates. An addition of oxalic acid at an oxalate/Ca molar ratio of 6.6:1 would selectively precipitate Ca oxalate at pH 0–1. The process used for removing Ca as Ca oxalate has been mentioned in detail in our previous study (Tran et al., 2013). After the excess oxalate was removed as Mg oxalate by adjusting the pH to pH 4–7, an addition of sodium carbonate to the treated brine would recover Mg as high purity Mg carbonate ($MgCO_3.3H_2O$) or Light HMC (hydromagnesite) – $(MgCO_3)_4.Mg(OH)_2.4H_2O$ and Heavy HMC (dypingite, $(MgCO_3)_4.Mg(OH)_2.5H_2O$ or $(MgCO_3)_4.Mg(OH)_2.8H_2O$). Two types of brine were used for the carbonation of Mg as follows:

- High-oxalate brine (obtained after Ca removal only, without further removing Mg oxalate), which was used in a 2-stage process,

- Low-oxalate brine (obtained after Ca removal as Ca oxalate and excess oxalate removal as Mg oxalate), which was used in a 3-stage process.

After the removal of Ca and Mg oxalate, magnesium carbonate (nesquehonite) and HMC of different structures and hydrated water (dypingite and hydromagnesite) could be precipitated from the brines. The composition of the brines at different precipitation stages and their corresponding pH’s (in the range of pH 7.6 – 10.3) are tabulated in Table 4. The precipitation of Mg as magnesium carbonate can be represented by the following reactions:

$$Mg^{2+} + CO_3^{2-} + 3H_2O \rightarrow MgCO_3.3H_2O \qquad \text{(Eq. 1)}$$

In excess CO_3^{2-}:

$$CO_3^{2-} + H_2O \leftrightarrow \underset{\downarrow}{OH^-} + HCO_3^- \qquad \text{(Eq. 2)}$$

$$5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 4H_2O \rightarrow (MgCO_3)_4.Mg(OH)_2.4H_2O \qquad \text{(Eq. 3)}$$

Or

$$5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 5H_2O \rightarrow (MgCO_3)_4.Mg(OH)_2.5H_2O \qquad \text{(Eq. 4)}$$

Or

$$5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 8H_2O \rightarrow (MgCO_3)_4.Mg(OH)_2.8H_2O \qquad \text{(Eq. 5)}$$

As seen above, while a CO_3^{2-} addition can first precipitate nesquehonite ($MgCO_3.3H_2O$) as illustrated by Eq. 1, an excess of CO_3^{2-} added will cause the formations of OH^- and HCO_3^- as demonstrated in Eq. 2 in which the equilibrium is shifted to the right hand side of the equation. The OH^- formed due to an excess of CO_3^{2-} takes part in the precipitation of $Mg(OH)_2$. The formation of HMC is illustrated by Eq. 3 for hydromagnesite – $(MgCO_3)_4.Mg(OH)_2.4H_2O$, Eq. 4 for dypingite – $(MgCO_3)_4.Mg(OH)_2.5H_2O$, or Eq. 5 for dypingite – $(MgCO_3)_4.Mg(OH)_2.8H_2O$, having different hydrated water in the formulae.

Losses of Li and K during the precipitation of the magnesium carbonate compounds were also observed. This was more than likely due to the physical incorporation of Li and K into the precipitate rather than co-precipitation as they could all be removed during subsequent washing. Tables 4 and 5 show the major components of the treated salar brines obtained during the “2-stage process” and “3-stage process”, confirming the effective removal of Ca and/or Mg oxalate and the recovery of Mg carbonate from the original salar brine.

The removal of Ca was completed within 4 h as seen in Fig. 2. Meanwhile, longer time of precipitation up to 8 h at the same oxalate/Ca molar ratio of 6.6:1 also co-precipitated Mg oxalate at pH~1, which is the limit for co-precipitation of Ca and Mg as shown in Fig. 1. This was confirmed by XRD analysis although the co-precipitate’s diffraction pattern is not shown herewith.

During Stage 2 to remove residual oxalate by adjusting the pH to pH 4–7 using NaOH, the precipitation of Mg oxalate took place quickly and was completed within 2 h (Fig. 3). A 99.5%

pure Mg oxalate could be obtained from this stage. It could therefore be used as a precursor for high purity MgO production as dealt with previously by Tran et al. (2013).

After Ca oxalate precipitation by oxalic acid followed by the removal of the remaining oxalate as Mg oxalate, the brine obtained containing 11.8 g/kg Mg was subsequently subjected to Mg carbonate precipitation. The precipitate yielded were afterward dried at 25, 65 and 100 ^{o}C to investigate the effect of drying temperature on the characteristics of the products obtained. Fig. 4 shows an experimentation matrix detailing the precipitation and drying conditions, which yielded either dypingite (containing 5 or 8 hydrated water) or hydromagnesite (containing 4 hydrated water).

3.3 Characterisation of hydrated magnesium carbonate products

3.3.1 X-Ray Diffraction

Fig. 5 shows the XRD patterns of the magnesium carbonate compounds obtained from the low-oxalate brine at a CO_3/Mg molar ratio of 0.9:1 after washing with distilled water, followed by drying at various temperatures. In this case, the precipitation of Mg as carbonate was conducted at ambient temperature while the drying was subsequently carried out at 25, 65, and 100 ^{o}C to investigate the influence of drying temperature on the products' characteristics.

It can be seen that all diffraction peaks of the product obtained after 25 ^{o}C drying (Fig. 5a) were in good agreement with those of dypingite. Meanwhile, the pattern of those obtained from drying at 65 and 100 ^{o}C (Figs. 5b&c, respectively) matched a standard pattern of hydromagnesite. In addition, shapes of their peaks indicate that the magnesium carbonate products were well crystallised.

On the other hand, there is an indication that the products obtained from precipitation using high-oxalate brines, either at 25, 55 or 100 ^{o}C, followed by drying at 100 ^{o}C were identified as hydromagnesite (Figs. 5d,e&f). Therefore, it was found that dypingite was obtained at low precipitation temperature (25 ^{o}C) whereas hydromagnesite was most possibly yielded at higher temperature of precipitation or drying (>65 ^{o}C).

3.3.2 Thermal Gravimetric Analysis (TGA) of Mg carbonate precipitates

The behavior of the precipitates obtained from the low-oxalate brine during thermal decomposition at a heating rate of 10 ^{o}C/min is shown in Fig. 6. The TG curves for the products obtained from precipitation at 25 ^{o}C and drying at different temperatures indicate that their thermal decomposition process can be divided into 3 stages, namely: <140 ^{o}C (1st stage), ~140–320 ^{o}C (2nd stage), and ~320–600 ^{o}C (3rd stage).

Mass losses measured by TGA vary in the range 55.3-58.8% as shown in Table 6, corresponding to the remaining residues containing 41.2% MgO for dypingite and 44.0% or 44.7% MgO for hydromagnesite. The theoretical MgO content after roasting is 41.5% for dypingite and 43.1% for hydromagnesite.

3.3.3 Differential Scanning Calorimetry (DSC) analysis of Mg carbonate precipitates

Together with TGA, thermal properties of the magnesium carbonate products obtained were also characterised by DSC analysis, conducted in a range from ambient temperature to 600 ^{o}C at a heating rate of 10 ^{o}C/min as seen in Fig.7.

As given in Table 7, the endothermic heat adsorbed during decomposition of three magnesium carbonate products yielded at 25, 65, and 100 ^{o}C drying are 1123, 1174, and 1196 J/g, respectively. For the products obtained when Mg oxalate was not removed, a lower heat of adsorption (972-1074 J/g) was measured compared to the higher values above for purer hydromagnesite (Table 8). Compared to the literature, these values represent the highest heat of absorption, compared to reported values in the range of 690 – 860 J/g (Haurie et al., 2006; Bhattacharjya et al., 2011; Ren et al., 2014).

3.3.4 Field Emission – Scanning Electron Microscopy analysis of Mg carbonate precipitates

FE-SEM was used to investigate the surface morphology of the product (hydromagnesite) yielded from ambient temperature precipitation and 100 ^{o}C drying. Its typical SEM images (for 1-100 micron scale) are provided in Fig. 8, showing a sheet-like structure as also found in an earlier study by Bhattacharjya et al. (2011).

3.3.5 Product purity – Chemical analysis

Table 9 shows chemical analysis results for the products obtained from the low-oxalate brine before and after re-slurrying and washing. The re-washing of the precipitate was critical as normal washing by H_2O-spraying of the precipitate on the filter paper did not completely remove the impurities (Li, K and Na). It therefore had to be re-slurried using a solid/water mass ratio of 1:4 to remove them. It can be seen that the Li and K contents could be mostly washed from 0.02% Li and 0.74% K to 0% Li and <0.01% K, respectively whereas the sodium content could be reduced from 1.41% to 0.04%.

In summary, after the removal of Ca and oxalate remained, the products obtained showed that high grades of Mg (~25.9% Mg and 25.3% Mg) could be yielded from precipitation at room temperature and drying at 65 and 100 ^{o}C. These Mg analyses correspond to products of 99.6% and 97.3% purity, respectively, compared to those obtained from the high-oxalate brine which had a lower grade of 23.3–24.3% Mg. A mass balance based on liquor chemical analysis shown in Table 5 shows that the Mg precipitated as Mg oxalate represents 11% of the final product. As the molecular weight of magnesium oxalate (di-hydrate) is 148.35 g/mol much lower than that of hydromagnesite (at 467.64 g/mol) the presence of Mg oxalate would reduce the Mg content of ther final product to 24.4% Mg, which is close to the values analysed (23.3-24.3% Mg) and shown in Table 8. Pure dypingite and hydromagnesite should have 25.02% Mg (~41.5% MgO) and 25.99% Mg (~43.1% MgO), respectively.

The developed process introduced carbonate to the brine if added in excess. As shown in Table 5, when sodium carbonate was added at a carbonate/Mg molar ratio of 0.9:1, 92% of Mg was recovered after Ca is removed, decreasing the brine Mg concentration from 11.8 g/kg original brine to 0.78 g/kg brine, noted that the final volume was increased due to dilution of the added sodium carbonate solution. The residual carbonate in the final brine was calculated as 4.2 g/kg brine by mass balance. Other anions such as chloride and sulphate would be reduced in concentration as the brine is diluted by the addition of sodium carbonate and is expected to remain in the final brine without creating other precipitation products.

4. Conclusion

High purity hydrated magnesium carbonate (HMC as dypingite or hydromagnesite) could be recovered from the Uyuni salar brines which contain ~1.3% Mg. The precipitation process used for this recovery relies on the selective removal of Ca by adding excess oxalic acid at oxalate/Ca molar ratio of 6.6:1. The excess oxalate has to be subsequently removed as Mg oxalate by adjusting the pH to pH 4-7. HMC products of 97.3 – 99.6% purity could be produced as a result (equivalent to 25.3-25.9% Mg in the product compared to theoretical values of 25.99% Mg for hydromagnesite). Without removing Mg oxalate, products could only reach 23.3-24.3% Mg.

The light HMC (hydromagnesite) product could be precipitated at ambient conditions as long as the drying was set at >65 ^oC. Precipitation at 100 ^oC yields hydromagnesite with sharper XRD peaks (indicating more crystalline precipitate) compared to the same products formed at lower temperatures of precipitation. The light HMC product has a heat adsorbing capacity (endothermic) of 1123-1196 J/g dry product. The product has a sheet-like structure and is easily filtered, compared to magnesium hydroxide.

Acknowledgement

We acknowledge the granting of scholarships from the government's "Brain Korea (BK) '21" to conduct this research.

References

Alamdari, A., Rahimpour, M. R., Esfandiari, N., and Nourafkan, E., 2008. Kinetic of magnesium hydroxide precipitation from sea bittern. Chemical Engineering Process 47, 215-221.

An, J. W., Kang, D. J., Tran, T. K., Kim, M. J., Lim, T., and Tran, T., 2012. Recovery of lithium from Uyuni salar brine. Hydrometallurgy 117-118, 64-70.

Baird, T., Braterman, P. S., and Cochrane, H. D., 1988. Magnesium hydroxide precipitation as studied by gel growth methods. Journal of Crysal Growth 91 (4), 610-616.

Beall, G. W., Duraia, E. M., El-Tantawy, F., Al-Hazmi, F., Al-Ghamdi, A. A., 2013. Rapid fabrication of nanostructured magnesium hydroxide and hydromagnesite via microwave-assisted technique. Powder Technology 234, 26-31.

Bhattachrjya, D., Selvamani, T., Mukhopadhyay, I., 2012. Thermal decomposition of hydromagnesite. J. Therm Anal Calorim 107 (2), 439-445.

Boryta, D. A., Kullberg, T. F., and Thurson, A. M., 2011. Production of lithium compounds directly from lithium containing brines. US patent 8,057,764. Nov. 15, 2011.

Botha, A., Strydom, C.A., 2001. Preparation of a magnesium hydroxyl carbonate from magnesium hydroxide. Hydrometallurgy 62, 175-183.

Caceres, P. G., and Attiogbe, E. K., 1997. Thermal decomposition of dolomite and the extraction of its constituents. Minerals Engineering 10 (10), 1165-1176.

Canterford, J. H., Tsambourakis, G., Lambert, B., 1984. Some observations on the properties of dypingite, $Mg_5(CO_3)_4(OH)_2.5H_2O$, and related minerals. Mineralogical magazine 48, 437-442.

Cheng, W., Li, Z., Demopoulos, G.P., 2009. Effect of temperature on the precipitation of magnesium carbonate by reaction of $MgCl_2$ with Na_2CO_3, Product Engineering and Chemical Technology (Chinese Journal of Chemical Engineering) 17(4), 661-666.

CMI Groups. May 2013. Production of high – purity magnesia. Industrial Minerals 49-50.

Dave, R. H., Ghosh, P. K., 2005. Enrichment of bromine in sea-bittern with recovery of other marine chemicals. Indian Acad. Sci. 44 (9), 2903-2907.

Földvári, M. 2011. Handbook of thermogravimetric system of minerals and its use in geological practice. Vol. 213, p. 118.

Golubev, S. V., Pokrovsky, O. S., and Savenko, V. S., 1999. Unseeded precipitation of calcium and magnesium phosphates from modified seawater solution. Journal of Crystal Growth 205, 354-360.

Golubev, S. V., Pokrovsky, O. S., and Savenko, V. S., 2001. Homogeneous precipitation of magnesium phosphates from seawater solutions. Journal of Crystal Growth 223, 550-556.

Haurie, L., Fernández, A. I., Velasco, J. I., Chimenos, J. M., Cuesta, J. M. L., and Espiell, F., 2006. Synthetic hydromagnesite as flame retardant. Evaluation of the flame behavior in a polyethylene matrix. Polymer Degradation and Stability 91, 989-994.

Henrist, C., Mathieu, J. P., Vogels, C., Rulmont, A., and Cloots, R., 2003. Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. Journal of Crystal Growth 249 (1-2), 321-330.

Huang, H. H., 2012. STABCAL software. Montana Tech of the University of Montana, USA.

Industrial Minerals – Magnesia. http://www.indmin.com/Magnesia.html. Accessed on 24 February 2015.

Janet, C. M., Viswanathan, B., Viswanath, R. P., Varadarajan, T. K., 2007. Characterization and photoluminescence properties of MgO microtubes synthesized from hydromagnesite flowers. J. Phys. Chem. C 111, 10267-10272.

Lartey, R. B., 1997. Recovery of useful chemicals from local salt bitterns. Journal of Applied Science and Technology 2 (1-2), 77-84.

Lee, J. M., Jackson, I., 1970. Extraction of magnesium values from brines. US Paten 3,488, 703 (6 January 1970).

Lehmann, O., Nir, O., Kuflik, M., and Lahav, O., 2014. Recovery of high purity magnesium solution from RO brines by adsorption of $Mg(OH)_2(s)$ on Fe_3O_4 micro-particles and magnetic solid separation. Chemical Engineering Journal 235, 37-45.

Li, Q., Ding, Y., Yu, G., Li, C., Li, F., Qian, Y., 2003. Fabrication of light-emitting porous hydromagnesite with rosette-like architecture. Solid State Communication 125, 117-120.

Mackay, K. D., 1977. Process for the recovery of magnesium. US Patent 4,051.223 (27 September 1977).

Muraviev, D., Noguerol, J., and Valiente, M., 1995. Separation and concentration of calcium and magnesium from sea water by carboxylic resins with temperature-induced selectivity. Reactive & Functional Polymers 28, 111-126.

Nakai – Magnesium carbonate. 2014. http://www.naikai.co.jp/leaflet-tanmag-en.pdf. Accessed on 27 February 2015.

Panda, J. D., Mahapatra, S. K., 1983. Process for the production of magnesium oxide from brine or bittern. US Patent 4,370,422 (25 January 1983).

Raade, G., 1970. Dypingite, a new hydrous basic carbonate of magnesium, from Norway. The American Mineralogist 55, 1457-1465.

Rajesh, U. C., Manohar, S., Rawat, D. S., 2013. Hydromagnesite as an efficient recyclable heterogeneous solid base catalyst for the synthesis of flavanones, flavonols and 1,4-dihydropyridines in water. Adv. Synth. Catal. 355, 3170-3178.

Ren, H., Chen, Z., Wu, Y., Yang, M., Chen, J., Hu, H., Liu, J., 2014. Thermal characterization and kinetic analysis of nesquehonite, hydromagnesite, and brucite, using TG-DTG and DSC techniques. J Therm Anal Calorim 115, 1949-1960.

Robinson, H. A., Friedrich, R. E., Spencer, R. S., 1943. Magnesium hydroxide from seawater. US Patent 2,405,055 (30 June 1943).

Roskill Information Services Ltd. Magnesium metal: Global industry markets and outlook 2012.

Tran, T. K., Luong, T. V., An, J. W., Kang, D. J., Kim, M. J., and Tran, T., 2013. Recovery of magnesium from Uyuni salar brine as high purity. Hydrometallurgy 138, 93-99.

Unleur C., and Al-Tabbaaa, A., 2014. Characterization of light and heavy hydrated magnesium carbonate using thermal analysis. J Therm Anal Calorim 115, 595-607.

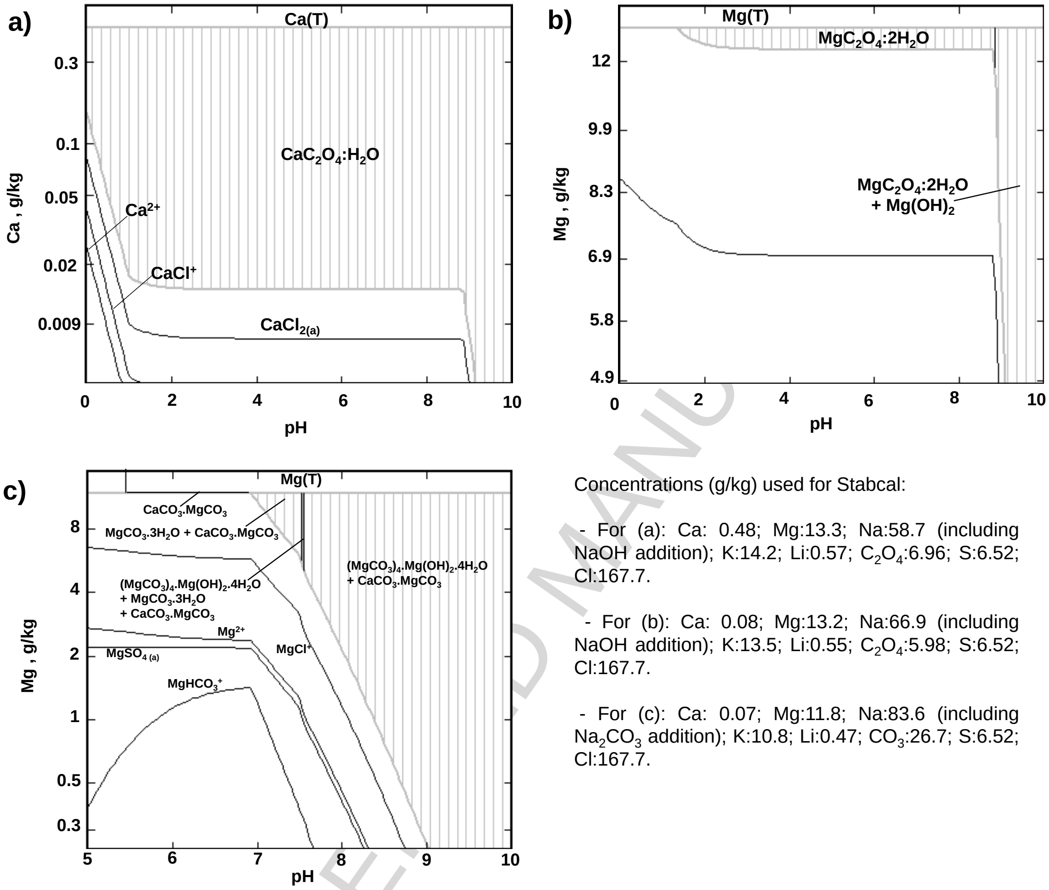
USGS – Magnesium compounds. Mineral Commodity Summaries, February 2014.

Wikipedia – Magnesium. http://en.wikipedia.org/wiki/Magnesium. Accessed on 26 December 2014.

Wikipedia – Seawater. http://en.wikipedia.org/wiki/Seawater. Accessed on 5 February 2015.

Wang, Y., Li, Z., Demopoulos, G.P., 2008. Controlled precipitation of nesquehonite ($MgCO_3.3H_2O$) by the reaction of $MgCl_2$ with $(NH_4)_2CO_3$, Journal of Crystal Growth 310, 1220-1227.

List of Figures



Concentrations (g/kg) used for Stabcal:

- For (a): Ca: 0.48; Mg:13.3; Na:58.7 (including NaOH addition); K:14.2; Li:0.57; C_2O_4:6.96; S:6.52; Cl:167.7.

- For (b): Ca: 0.08; Mg:13.2; Na:66.9 (including NaOH addition); K:13.5; Li:0.55; C_2O_4:5.98; S:6.52; Cl:167.7.

- For (c): Ca: 0.07; Mg:11.8; Na:83.6 (including Na_2CO_3 addition); K:10.8; Li:0.47; CO_3:26.7; S:6.52; Cl:167.7.

Fig. 1. Stabcal simulation at 25^{o}C for precipitation during: (a) Stage 1 – Removal of Ca (oxalate/Ca molar ratio of 6.6:1) showing the Ca concentration profile vs pH, (b) Stage 2 – Removal of residual oxalate as Mg oxalate and (c) Stage 3 – Subsequent recovery of Mg as different Mg carbonate species (CO_3/Mg molar ratio of 0.9:1).

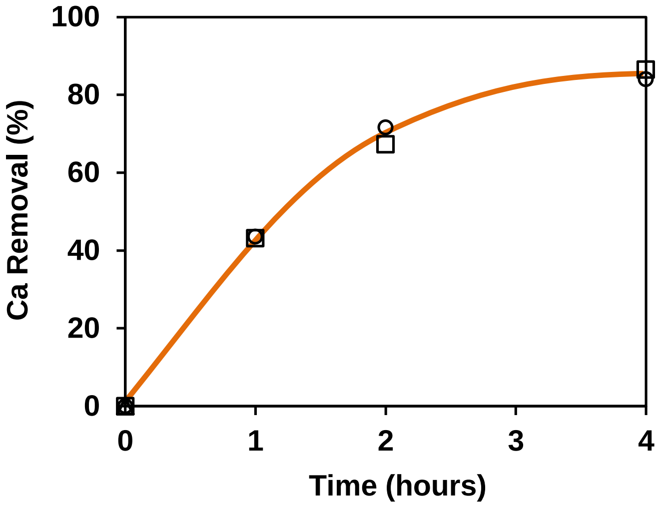


Fig. 2. Removal of Ca from the brine at ambient temperature (25 ^{o}C) using an oxalate/Ca molar ratio of 6.6:1 (conditions shown in Table 4)

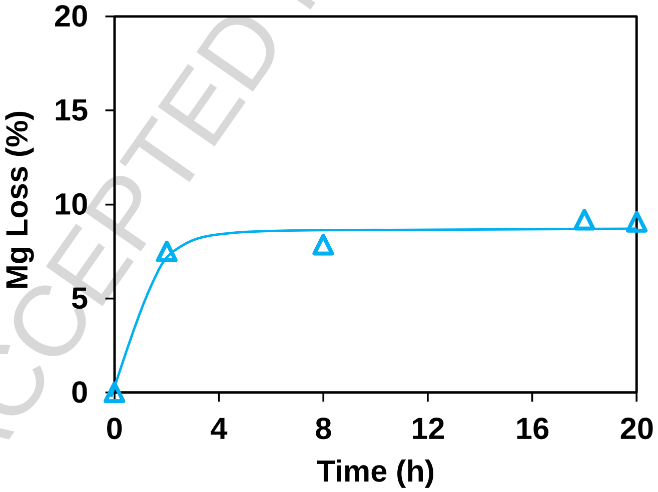


Fig. 3. Mg loss during removal of the remaining oxalate from the brine at ambient temperature (25 ^{o}C) precipitation by adjusting pH to pH 7.1 (conditions shown in Table 5).

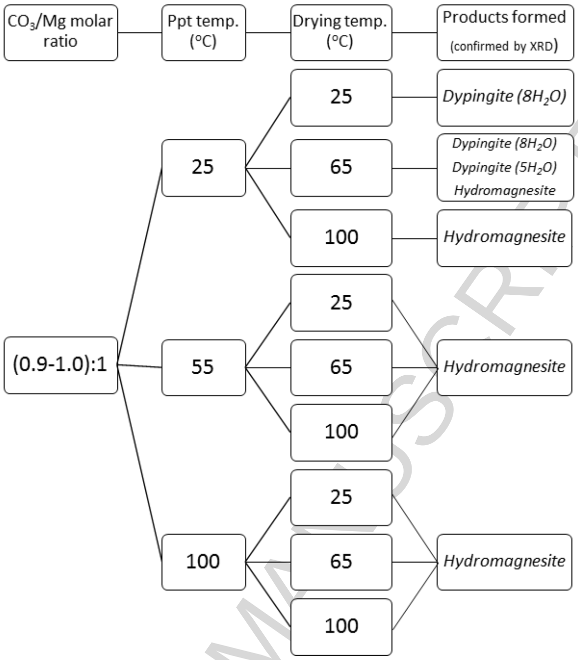


Fig. 4: Experimentation matrix detailing the precipitation and drying conditions and types of product (dypingite or hydromagnesite) formed.

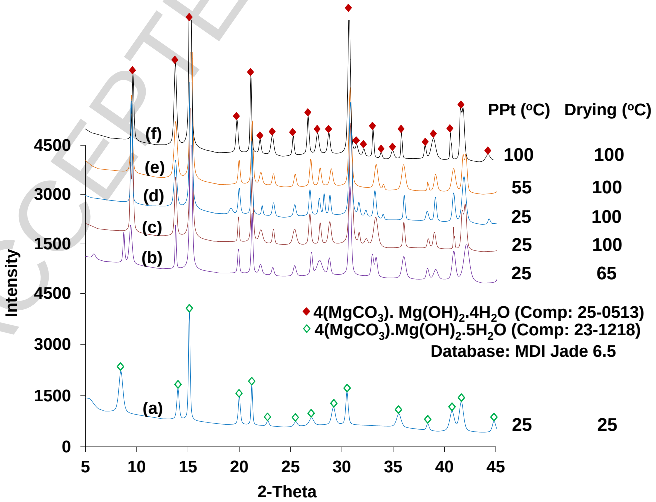


Fig. 5: XRD patterns of Mg carbonate products obtained from (a-c): tests using the low-oxalate brine at room temperature precipitation (25 °C) and different drying temperatures (25, 65, and 100 °C), and (d-f): tests using the high–oxalate brine after drying at 100 °C, independently of precipitation temperature, showing sharper peaks.

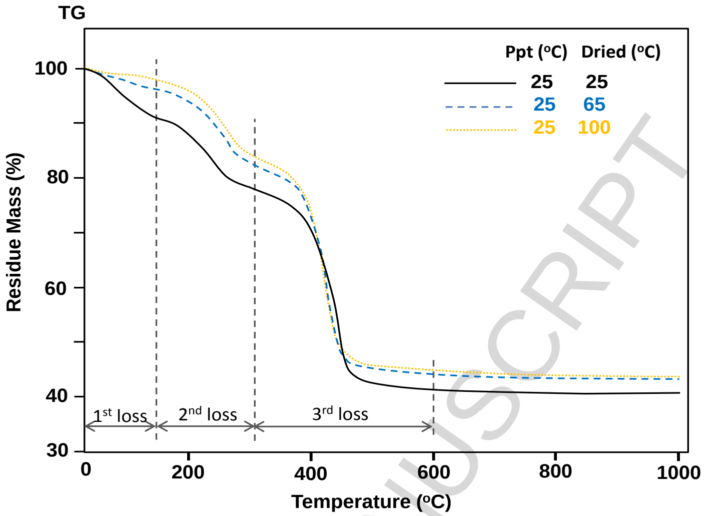


Fig. 6. TGA profiles (at a heating rate of 10°C/min) of Mg carbonate products (after washing) obtained from the low-oxalate brine at ambient precipitation and different drying temperatures using CO_3/Mg molar ratio of 0.9:1.

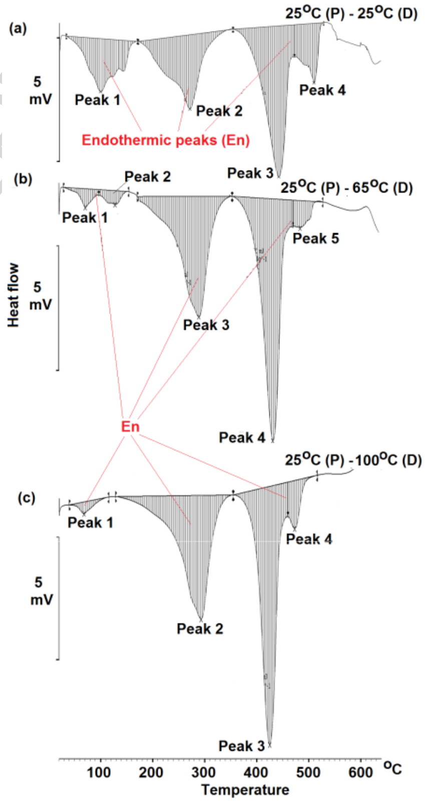


Fig. 7. DSC profiles of the Mg carbonate products obtained from the low-oxalate brine at ambient precipitation (P) and different drying (D) temperatures using CO_3/Mg molar ratio of 0.9:1.

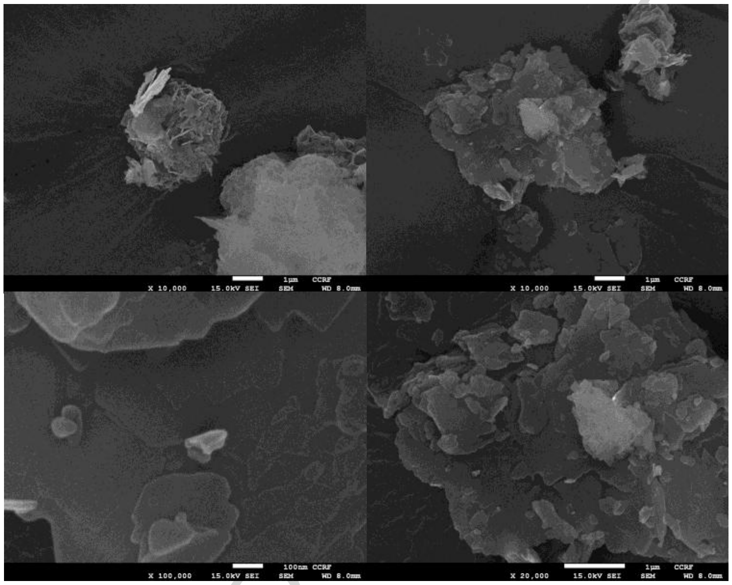


Fig. 8. FE-SEM profiles of hydromagnesite obtained from the low-oxalate brine at ambient precipitation temperature and 100^{o}C drying.

List of Tables

Table 1: Compositions of seawater and various commercial brines around the world (Sources: Boryta et al., 2011; An et al., 2012; Wikipedia, 2015).

Source	Composition (wt. %)						
	Na	K	Li	Mg	Ca	Cl	SO_4
Seawater	1.08	0.04		0.13	0.04	1.94	
Clayton Valley, USA	5.00-7.00	1.30-2.40	0.01-0.04	0.07-0.57	2.26-3.9	14.20-20.90	42-50
Salar de Atacama, Chile	9.1	2.36	0.157	0.965	0.045	18.95	1.59
Salar de Uyuni, Bolivia	5.31	1.42	0.057	1.30	0.048	16.77	1.87
Great Salt Lake, USA	3.70 – 8.70	0.26 – 0.72	0.0018	0.50 – 0.97	0.026 – 0.036	7.00 – 5.60	0.94-2.00
Dead Sea, Israel	3.01	0.56	0.0012	3.09	1.29	16.1	0.061
Salton Sea, USA	5.00 – 7.00	1.30 – 2.40	0.01 – 0.04	0.07 – 0.57	2.26 – 3.9	14.20 – 20.9	42 – 50
Bonneville, USA	8.3	0.5	0.0057	0.40	0.0057	14	
Taijinaier, China	5.63	0.44	0.031	2.02	0.02	13.42	3.41

Tables 2a: Experimental profiles and results of several studies on Hydromagnesite (Light HMC) – $(MgCO_3)_4.Mg(OH)_2.4H_2O$

Reagents	pH	Precipitation temp. (^{o}C)	Drying temp. (^{o}C)	Morphological feature	Temp. range or Peak (^{o}C)	Product predicted after heating	Mass loss (%)		Residue (%)	Source
							Loss	Total		
$MgCl_2$/Mg acetate + Urea-$(Co(NH_2)_2$	10	220	unstated	rosette	150-350	$(MgCO_3)_4.Mg(OH)_2$	15.8	57.0	43.0	Beall et al., 2013
					350-600	MgO	41.2			
$MgSO_4$ + Urea	unstated	100	60	rosette	53-368	$(MgCO_3)_4.Mg(OH)_2$	14.9	55.7	44.3	Li et al., 2003
					368-527	$(MgCO_3)_4.MgO$	15.1			
					527-700	MgO	25.7			
$MgCl_2$ (solution) + ethylene glycol	unstated	110	80	flower-like thin-sheet	100-280	$(MgCO_3)_4.MgO$	17.8	55.7	44.3	Rajesh et al., 2013
					280-480	MgO	37.9			
$Mg(NO_3)_2.6H_2O$ (solution) + Na_2CO_3	unstated	unstated	60	flower	~200	$(MgCO_3)_4.Mg(OH)_2$	~2	~60.0	~40.0	Janet et al., 2007
					~300	$(MgCO_3)_4.MgO$	~16.5			
					350-400	MgO	~41.5			
Acros Organics' commercial product (40-45% MgO)				unstated	266	$(MgCO_3)_4.MgO$	10.1	47.7	52.3	Unluer & Al-Tabbaa, 2014
					458	(MgO	37.6			
Fisher Chemicals' commercial product				unstated	267	$(MgCO_3)_4.MgO$	10.8	47.4	52.6	

					460	MgO	36.6			
Riedel-de Haen’s commercial product				unstated	260	$(MgCO_3)_4$.MgO	11.4	48.6	51.4	
					454	MgO	37.2			
Acros Organics’ commercial product				unstated	266	$(MgCO_3)_4$.MgO	13.3	49.8	50.2	
					469	MgO	36.5			
Commercial product				unstated	227	$(MgCO_3)_4$.MgO	17.9	56.2	43.8	Bhattacharjya et al., 2011
					417.8	MgO	38.3			
$MgCl_2$ (solution) + ethylene glycol	unstated	110±10	unstated	sheet	240	$(MgCO_3)_4$.MgO	13.9	57.9	42.1	
					434.8	MgO	44.0			
$MgCl_2$ (solution) + Na_2CO_3 (in H_2O_2 aqueous medium)	unstated	unstated	unstated	nest	239	$(MgCO_3)_4$.MgO	13.2	56.0	44.0	
					423	MgO	42.8			
$MgCl_2$ (solution) + Na_2CO_3	unstated	90	unstated	unstated	34-301	$(MgCO_3)_4$.MgO	19.3	56.7	43.3	Ren et al., 2014
					301-600	MgO	37.4			

Tables 2b: Experimental profiles and results of several studies on Dypingite – $(MgCO_3)_4.Mg(OH)_2.5H_2O$.

Reagents	pH	Precipitation temp. (°C)	Drying temp. (°C)	Morpho-logical feature	Temp. range or Peak (°C)	Product predicted after heating	Mass loss (%)		Residue (%)	Source
							Loss	Total		
By calcination/CO_2 leaching process with magnesite	unstated	unstated	unstated	unstated	<200	$(MgCO_3)_4.MgO$	18.8	52.9	47.1	Canterford & Tsambourakis, 1984
					>200	MgO	34.1			
Sigma-Aldrich's commercial product				unstated	285	$(MgCO_3)_4.MgO$	16.1	53.0	47.0	Unluer & Al-Tabbaa, 2014
					441;518	MgO	36.9			
Sigma-Aldrich's commercial product				unstated	259	$(MgCO_3)_4.MgO$	9.6	50.9	49.1	
					413;475; 525	MgO	41.3			
Fisher Chemicals' commercial product				unstated	275	$(MgCO_3)_4.MgO$	12.9	51.7	48.3	
					437;517	MgO	38.8			
Mineral in Hungary				unstated	<300	$(MgCO_3)_4.MgO$	21.9	57.6	42.4	Földvári M., 2011
					>300	MgO	35.7			
Mineral in Norway				unstated	<125	unstated	3.5	55.7	44.3	Raade M., 1970
					>125	unstated	52.2			

Table 3: Major chemical composition of the Uyuni salar brine used in this study.

Composition	Ca	Mg	Na	K	Li	Cl	SO_4
g/kg brine	0.48	13.3	53.1	14.2	0.57	167.7	18.7

Table 4: Major components (in g/kg) of various brines obtained after Ca removal and Mg recovery at different molar ratios of (0.5 – 1.9):1 in the “2-stage process”.

Type of brine	Molar ratio (oxalate/Ca or carbonate/Mg)	pH	Components (g/kg)			
			Ca	Mg	K	Li
Original brine		6.9	0.48	13.3	14.2	0.57
After Ca oxalate removal	6.6:1	1	0.08	13.2	13.5	0.55
After Mg carbonate recovery	0.5:1	7.6	0.07	4.98	10.75	0.47
	1.0:1	9.0	0.05	0.57	8.89	0.40
	1.5:1	9.7	0.04	0.36	7.08	0.36
	1.9:1	10.3	0.03	0.39	6.91	0.32

Table 5: Major components (in g/kg) of various brines obtained during the “3–stage process” (Ca+Mg oxalate removal and Mg recovery). Precipitation at 25 ^{o}C, carbonate/Mg molar ratio of 0.9:1.

Type of brine	pH	Components (g/kg)			
		Ca	Mg	K	Li
Original brine	6.9	0.48	13.3	14.2	0.57
After Ca oxalate removal	1.0	0.08	13.2	13.5	0.55
After Mg oxalate removal	7.1	0.07	11.8	10.8	0.47
After Mg carbonate recovery	8.7	0.05	0.78	8.9	0.40

Table 6: Summary of TGA results (at a heating rate of 10^{o}C/min) for the magnesium carbonate products obtained from the low-oxalate brine.

Precipitation temp. (^{o}C)	Drying temp. (^{o}C)	Products formed (confirmed by XRD)	Temp. range (^{o}C)	Mass loss (%)	Total loss (%)	Residue (%)
25	25	$(MgCO_3)_4.Mg(OH)_2.5H_2O$ (Dypingite)	<140	8.8	58.8	41.2
			140 – 320	13.4		
			320 – 600	36.6		
	65	$(MgCO_3)_4.Mg(OH)_2.4H_2O$ (Hydromagnesite)	<140	3.6	56.0	44.0
			140 – 320	15.5		
			320 – 600	36.9		
	100	$(MgCO_3)_4.Mg(OH)_2.4H_2O$ (Hydromagnesite)	<140	1.2	55.3	44.7
			140 – 320	16.3		
			320 – 600	37.8		

Table 7: Summary of DSC results for the Mg carbonate products obtained from the low-oxalate brine at ambient precipitation (P) and different drying temperatures (D). (Peak N^{o} – refers to Fig. 7).

P/D (^{o}C)	Product	DSC analysis	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	**Net Total**
25/25	$(MgCO_3)_4.Mg(OH)_2.5H_2O$ (Dypingite)	Temp (^{o}C)	99.7	271.5	443.5	511.5		
		J/g	**-216**	**-319**	**-459**	**-129**		**-1123**
25/65	$(MgCO_3)_4.Mg(OH)_2.4H_2O$ (Hydromagnesite)	Temp (^{o}C)	71.3	128.5	290.5	433.7	486	
		J/g	**-32**	**-30**	**-475**	**-582**	**-55**	**-1174**
25/100		Temp (^{o}C)	68.3	293.0	425.0	473.2		
		J/g	**-21**	**-527**	**-577**	**-71**		**-1196**

Table 8: Summary of DSC results for the Mg carbonate products obtained from both high and low-oxalate brines at ambient precipitation (P) and different drying temperatures (D), DY: Dypingite, HM: hydromagnesite.

Type of brine	Product (confirmed by XRD)			Hydromagnesite products obtained		
	25^{o}C drying	65^{o}C drying	100^{o}C drying	Heat adsorbed/ DSC, J/g	Purity, wt.% Mg (MgO)	Morphology
High oxalate	DY ($8H_2O$)	Mixture of HM and DY (5 and $8H_2O$)	HM	972-1074	23.3-24.3 (38.6-40.3)	sheet
Low oxalate	DY($5H_2O$)	HM	HM	1174-1196	25.3-25.9 (41.9-	sheet

					42.9)	

Table 9: Chemical analysis of major components (wt.%) of the Mg carbonate products obtained from the low-oxalate brine at CO_3:Mg molar ratio of 0.9:1 after re-slurrying and washing.

CO_3:Mg molar ratio of 0.9:1			Components (wt.%)					
P/D (^oC)	Product (Confirmed by XRD)	Type of product	Mg	Ca	Na	K	Li	MgO
25/25	$(MgCO_3)_4.Mg(OH)_2.5H_2O$ (Dypingite)	On Filter	20.4	0.06	1.40	0.73	0.02	
		Re-slurried	24.4	0.05	0.04	0.01	0.00	40.51
25/65	$(MgCO_3)_4.Mg(OH)_2.4H_2O$ (Hydromagensite)	On Filter	21.7	0.06	1.41	0.74	0.02	
		Re-slurried	25.9	0.04	0.21	0.05	0.01	42.91
25/100		On Filter	22.4	0.07	0.78	0.59	0.02	
		Re-slurried	25.3	0.05	0.49	0.11	0.02	41.91

HIGHLIGHTS

- Magnesium is recovered from Uyuni salar brine as hydrated magnesium carbonate
- Products have 97.3-99.6% purity (25.3-25.9% contained Mg)
- Novel step is the removal of Ca from the brine first as Ca oxalate
- Products have heat absorbing capacity of 1123-1196 J/g, higher than most reported values