



Recovery of magnesium from Uyuni salar brine as high purity magnesium oxalate



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ARTICLE INFO

Article history:

Received 1 February 2013
Received in revised form 3 May 2013
Accepted 28 May 2013
Available online 27 June 2013

Keywords:

Uyuni salar brine
Oxalic acid
Selective recovery of magnesium
Magnesium oxalate
Calcium oxalate

ABSTRACT

Containing 10.2 Mt Li, Salar de Uyuni is known to be the richest resource of Li in the world. A high Mg/Li mass ratio of 21.2:1 of the Uyuni salar brine used in this study is a significant factor hindering the effective lithium recovery. Stabal modelling was first conducted to study the conditions and chemical speciation of various species involved in the selective precipitation of Mg and Ca oxalate. Along with the addition of oxalic acid, the effect of pH was then studied in order to determine optimal conditions to selectively remove Ca and achieve high Mg yield subsequently. At an Oxalate/Ca molar ratio of 6.82:1 and pH <1, ~80% of Ca could be removed from brine without co-precipitation of Mg oxalate. A NaOH/Mg/Oxalate molar ratios of 1.95:1:1 to 3.21:1:1.62 in the range of pH 3–5.5 was used for the Mg precipitation. A recovery of >95% Mg was obtained (precipitate containing mostly Mg oxalate) together with the K and Li losses of up to 35% from the original brine. Washing would remove Li, K contaminants and the co-precipitated sodium sulphate and oxalate. Their absence from the final precipitate was confirmed by XRD analysis. The high purity (99.5% grade) Mg precipitate obtained could be used as a precursor for MgO production.

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1. Introduction

Magnesium and its compounds have been used in many applications such as insulation, agriculture, construction, in chemical and other industries (USGS, 2012). High purity MgO is specifically used in food and pharmaceutical production while Mg(OH)₂ is a major component in the manufacture of fire retarding reagents (Hull et al., 2011). According to the International Magnesium Association, the production of magnesium around the world surpasses 429,000 tonnes/year and steadily increases annually due to the demand of magnesium alloys in the automobile industry (Intlmag, 2012). Magnesium is found in minerals such as magnesite, dolomite, brucite, serpentinite, etc. and is mostly recovered from seawater, brines and bitters. Seawater contains about 1.3 g/L Mg while the resource of magnesium-bearing brines and bitters around the world is estimated to be in the billions of tonnes (USGS, 2012). High contents of magnesium have been found in salar brines located in South America (An et al., 2012) and other salt lakes around the world (Table 1). The high Mg content in Uyuni brine implies it is of high value which should be recovered as a co-product with Li.

Calcined, dead-burned and fused magnesia are produced from magnesite whereas chemical grade Mg(OH)₂ used as fire retarding additives, pharmaceuticals and food additives has been mostly produced from brines and bitters. Lalancette (1978) extracted Mg from magnesium-bearing silicate. During processing, the ores were first digested with

sulphur dioxide at <50 °C and pH 1–2, then purified by precipitation to remove most metallic impurities. Mg was recovered as Mg(OH)₂ at pH 9.5–10.5. Elsner and Roth (1998) extracted magnesium from a magnesite ore by leaching with HNO₃ or HCl. This was followed by purification at pH 5–6 using NH₄OH (or MgO) and H₂O₂ (or Cl₂) and then precipitation to produce Mg(OH)₂. The slurry obtained was thereafter heated at 150–185 °C, to yield high purity Mg(OH)₂. zdemir et al. (2009) produced MgCl₂·6H₂O (91% purity) from magnesite tailings (39.03% MgO) by leaching with HCl at first and then crystallization by evaporation of the leach liquor at 40 °C.

Yildirim and Akarsu (2010) leached a dolomite ore containing 20.6% MgO. After removing Ca as calcium carbonate, the purified magnesium chloride solution was then treated via pyrohydrolysis to yield HCl gas and MgCl₂·6H₂O, which was thereafter decomposed to MgO and HCl. The final MgO product had a purity of 98.86% and HCl gas was then recycled. Recently, Nduagu et al. (2012) treated a serpentinite ore containing 21.8% Mg to produce high purity Mg(OH)₂. Mixtures of the ore with ammonium sulphate at a mass ratio of 0.5–0.7 were first roasted at 400–550 °C. Calcines were then slurried into water to obtain a magnesium sulphate solution. After purification, Mg(OH)₂ was recovered at pH 10–11. During the process, NH₃ gas obtained from roasting is recycled to subsequent precipitation stages. Pyrometallurgy was also used to recover Mg from a hot slag (1300 °C) containing 16–20% MgO (Bodenstein and Farrell, 1985) or a magnesium alloy waste (Faure, 1995).

Robinson et al. (1943) patented a simple scheme for recovering magnesium from sea water as Mg(OH)₂ using lime at pH 10.5 and 25 °C. A patented process for producing MgO from brines and bitters

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Table 1
Composition (wt.%) of different brines (Dave and Ghosh, 2005, 2012).

| Salar brine | Element | | | | | | | | |
|---------------------------|---------|------|-------|------|------|------|-------|-----------------|-------------|
| | Mg | Ca | Li | Na | K | B | Cl | SO ₄ | Mg/Li ratio |
| Uyuni (Bolivia) | 0.65 | 0.05 | 0.035 | 8.75 | 0.72 | 0.02 | 15.69 | 0.85 | 18.6 |
| Atacama (Chile) | 0.96 | 0.03 | 0.150 | 7.60 | 1.85 | 0.06 | 16.04 | 1.65 | 6.40 |
| Hombre Muerto (Argentina) | 0.085 | 0.05 | 0.062 | 9.79 | 0.62 | 0.04 | 15.80 | 0.853 | 1.37 |
| Cauchari (Argentina) | 0.131 | 0.03 | 0.052 | 9.55 | 0.47 | 0.08 | 14.86 | 1.62 | 2.52 |
| Rincon (Argentina) | 0.303 | 0.06 | 0.033 | 9.46 | 0.66 | 0.04 | 16.06 | 1.02 | 9.29 |
| Maricunga (Chile) | 0.69 | 1.31 | 0.104 | 7.14 | 0.75 | 0.05 | 16.06 | 0.06 | 6.63 |
| Silver Peak (USA) | 0.03 | 0.02 | 0.023 | 6.20 | 0.53 | 0.01 | 10.06 | 0.71 | 1.43 |

was developed by Panda and Mahapatra (1983) using calcined magnesite, dolomite, calcite or limestone to precipitate Mg(OH)₂ yielding 98% pure MgO after drying and calcination. In another study, Martinac et al. (1996) used dolime to precipitate Mg from seawater containing 2.42 g/L MgO to produce 98–99% pure Mg(OH)₂. The Mg(OH)₂ yielded was heated at 105 °C before being sintered at 950 °C to obtain MgO. Dave and Ghosh (2005) used hydrated lime to precipitate Mg(OH)₂ from a bittern containing 5.25% w/v Mg at pH 7.0–7.5 as the by-product during bromine processing. In cases where sulphate is present in the liquors, gypsum (CaSO₄·2H₂O) is normally formed as a co-precipitate with Mg(OH)₂ during lime addition (An et al., 2012; Karidakis et al., 2005). This co-precipitation would cause serious contamination of the final MgO product.

Phosphate has also been used to precipitate Mg from synthetic solutions (Cao et al., 2007; Golubev et al., 1999, 2001). Earlier in 1999, Golubev and co-authors reported that an amorphous precipitate phase of Ca–Mg phosphates ((Ca,Mg)₄H(PO₄)₃·xH₂O) was detected when Na₂HPO₄ was added into artificial seawater containing 0–2.48 g/L Mg and 0.4 g/L Ca. In wastewater treatment processes, phosphate was commonly used to remove magnesium as struvite (MgNH₄PO₄·6H₂O) (Lee et al., 2003; Stratful et al., 2001).

NaOH has been widely used to precipitate Mg(OH)₂ from Mg-containing liquors. Lartey (1997) precipitated magnesium hydroxide from a bittern (4.24% Mg) using NaOH to produce MgO after calcination. The formation of nano-sized particles and poor crystallinity of Mg(OH)₂ when NaOH was used for precipitation caused difficulties during filtration (Baird et al., 1988; Henrist et al., 2003). To solve this problem, Alamdari et al. (2008) added Mg(OH)₂ seeds (5–40 μm) during Mg precipitation from a bittern containing 30 g/L Mg to produce a product having particle sizes of 5–60 μm after 1 h crystallization.

In many studies, magnesium could be recovered from mother liquors as magnesium chloride salts. Aubry and Bichara (1979) used 1,4-dioxane to precipitate magnesium as MgCl₂·6H₂O·(C₂H₄)₂ from a brine containing 250–340 g/L MgCl₂. After filtration, the salt was heated at 125 °C to liberate dioxane gas, which was recycled. Hamzaoui et al. (2003) investigated a route to collect Mg from a synthetic brine containing 120 g/L Mg and 0.24 g/L Li using ammonium oxalate to form magnesium oxalate. It was indicated that up to 70% of Li was co-precipitated if Oxalate/Mg molar ratios of ≥0.57 were used. In a recent study, An et al. (2012) developed a two-stage scheme for recovering Li from Uyuni salar brine (Bolivia) containing 16–17 g/L Mg and 0.3–3 g/L Ca. In the first stage, lime or recycled dolime (CaO·MgO) was used to remove Mg and the resultant precipitate is a mixture of Mg(OH)₂ and CaSO₄·2H₂O. Ca and the residual Mg were then removed from the brine using Na₂C₂O₄.

Solvent extraction and ion-exchange were also applied to recover Mg from mother liquors and brines. Lee and Jackson (1970) patented a process to extract Mg from a brine containing 1 g/L Mg using alkyl sulphates and sulphonates. After extraction, Mg was stripped from the mixture by a water-soluble salt such as NaCl. Later, Mackay (1977) used 1-dodecylphenyl-3-trifluoromethyl-1,3-propanedione to selectively recover Mg from synthetic seawater containing 1.4 g/L Mg, 0.37 g/L Ca and other elements (pH 6–9). Muraviev et al. (1996) suggested a new method using carboxylic resins of acrylic and methacrylic

types to uptake Mg from an artificial seawater containing 0.11 g/L Mg and 0.02 g/L Ca. Telzhensky et al. (2011) used nanofiltration membranes DS-5 DL to accumulate Mg from seawater (1.43 g/L Mg) with a recovery of 64% and a new solution containing 3.5 g/L Mg was produced.

As shown in Table 1 and An et al.'s study (2012), the Mg/Li mass ratio in salar de Uyuni brine is 18–20:1 compared to ~6.4:1 and ~1.4:1 in salar de Atacama and salar de Hombre Muerto brines respectively. In our previous study (An et al., 2012) a process was proposed to remove Mg from the Uyuni salar brine by precipitation using lime. Such a step produces a mixture of Mg(OH)₂ and gypsum which requires further processing to recover Mg values. The high level of Ca in the brine would contaminate the Mg products if not removed first. This study therefore aims to recover Ca and Mg separately using oxalate and to produce Mg oxalate as a precursor for high purity MgO production.

2. Experimental

2.1. Materials

Salar de Uyuni brine (200 L) from Bolivia was used as the raw material for this study. Its composition was determined by ICP-MS (for cations) and IC (for anions) as shown in Table 2. Compared to other brines quoted in Table 1, the raw material used in this study has a Mg/Li mass ratio of 21.2:1 much higher than those from other locations.

2.2. Equipment and chemicals

The composition of the original brine before treatment and its components after calcium and magnesium precipitation were analysed by ICP-MS (Agilent A5500) and IC (Metrohm 883 Basic IC Plus). The mineralogy of products obtained from precipitation was determined by X-ray diffraction (XRD) analysis (Cu-tube60kv 50 Ma, Phillips) whereas their constituents were also specified by X-ray Fluorescence (XRF) using an instrument from Rigaku (ZSX Primus II). In addition, Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) using Seiko TG/DTA 200 were used to investigate weight changes and thermal transformations of materials as a function of temperature, respectively. Hot plates were used for all experiments and all chemicals used were of analytical grade. Precipitants used in the study include oxalic acid (analytical grade) and sodium hydroxide (used for pH adjustment).

Table 2
Major components (g/kg) of the original brine and after the removal of Ca (stage 1) at Oxalate:Ca molar ratio of 6.82:1 and Mg (stage 2) at Oxalate:Mg molar ratio of 1.62:1 (Mg/Li mass ratio of the original brine is 21.2:1).

| Components | Ca | Mg | Na | K | Li | Cl | SO ₄ |
|---------------------------|-------|------|------|------|------|-------|-----------------|
| Stage 1 Original brine | 0.476 | 14.2 | 81.4 | 17.4 | 0.67 | 150 | 11 |
| After Ca removal at pH 1 | 0.118 | 14.4 | 82.6 | 17.4 | 0.67 | 147.9 | 8.3 |
| Stage 2 Before Mg removal | 0.025 | 14.6 | 86.3 | 16.3 | 0.67 | 160.1 | 20.6 |
| After Mg removal at pH 4 | 0.003 | 0.83 | 67.6 | 10.6 | 0.41 | 121.0 | 13.0 |

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