

Magnesium Recovery from Desalination Brine

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Abstract

Recovering magnesium hydroxide $Mg(OH)_2$ from the discharged brine from desalination plants has the potential to generate economic, social and environmental benefits. While the concept has not been practised in the industry, it is expected that it can be achieved by adaptation of a conventional method of precipitating $Mg(OH)_2$ from seawater through the addition of lime. This project involves a series of experiments to investigate the feasibility of producing commercial grade $Mg(OH)_2$ from desalination brine utilising this process. The key parameters of interest include the settling rates, the yield of products, and $Mg(OH)_2$ purity. These parameters are being assessed under varying experiment conditions, such as increasing the lime dosage, screening of lime slurry and the use of flocculants. Initial results showed that a major problem with the process is a low product purity, generally below 80% $Mg(OH)_2$. In a recent experiment, however, where the slaked lime slurry was screened, a considerable increase in the product purity has been achieved. Further research is to be undertaken to assess the effectiveness of screening lime slurry and other experimental conditions. These results will provide valuable information as to the product quality and the performance of this process for Water Corporation.

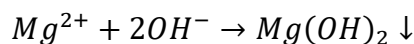
1. Introduction

With a declining rainfall and a rising population, Western Australia has become increasingly reliant on desalination for its potable water supply. The desalination process extracts fresh water from seawater and produces concentrated seawater, also known as brine, as a waste stream. The two desalination plants in Western Australia have a combined capacity of 150 billion litres of fresh water per year (Water Corporation, 2017), accompanied by a massive amount of waste brine discharged back into the ocean. This waste stream, however, contains magnesium ion (Mg^{2+}) up to 2.51 kg/m^3 , which could be converted into valuable products such as magnesium hydroxide ($Mg(OH)_2$). $Mg(OH)_2$ has a versatile range of applications within environmental protection, fire retardant, and pharmaceutical fields. (QYR Chemical & Material Research Center, 2017). Recovering magnesium hydroxide from brine has the potential to generate additional economic, social, and environmental benefits. For these reasons, this concept has recently attracted interest from Water Corporation.

1.1 Magnesium Hydroxide Production from Seawater

Seawater precipitation is one of the conventional methods of producing $Mg(OH)_2$ currently used in industry (QYR Chemical & Material Research Center, 2017). This method uses

‘naturally occurring’ seawater as a raw material, with the addition of an alkaline reagent, to precipitate magnesium hydroxide particles. The alkaline reagents commonly used are caustic soda (NaOH), quicklime (CaO), or ammonia (NH₃) (QYR Chemical & Material Research Center, 2017). The main reaction that occurs in this process is:



The solid products that subsequently form can be separated from the liquids by a series of settling thickeners, washing tanks, and finally by filtration. Depending on its intended application, the filter cake can then either be processed into a slurry form of approximately 60 wt% solid, or into its powder form through a drying operation. Commercial grade Mg(OH)₂ generally have a purity of between 95% to 100% (QYR Chemical & Material Research Center, 2017).

Because of the relative maturity of this technology, it is expected that the same process will be implemented to produce Mg(OH)₂ from brine. Furthermore, low-cost sources of quicklime are readily available to Water Corporation through local WA suppliers. Therefore, this study will only investigate the case where such quicklime is used as the alkaline reagent.

1.2 Desalination Brine Characterisation and Implications

Desalination brine is comprised of the same major constituents as the seawater, but at concentrations approximately twice as high. Table 1 shows the comparative compositions of the brine and seawater. Because brine is significantly richer in Mg²⁺ than seawater, an inherent advantage of this process will be the decreased equipment volume requirements.

Component	Concentration in brine, g/L	Concentration in seawater ^a , g/L
Na ⁺	18.6 ^b	10.5
Mg ²⁺	2.54 ^c	1.29
Ca ²⁺	0.857 ^c	0.410
SO ₄ ²⁻	5.70 ^c	2.72
HCO ₃ ⁻	0.273 ^b	0.150
Cl ⁻	34.0 ^b	18.7

a. Sampled in the seawater intake of the Perth Seawater Desalination Plant.

b. Source of data: preliminary experiments by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ChemCentre WA, 2018).

c. Source of data: hand calculations based on the designed recovery ratio of the desalination plant.

Source of the rest of the data: Water Corporation existing test results (SGS Ltd., 2017)

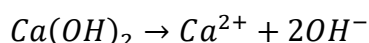
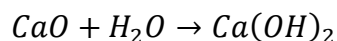
Table 1 Concentrations of major ions relevant to this study in desalination brine, and in seawater.

As a result of these higher concentrations, a problem associated with the use of brine in place of seawater is the increased tendency to form solid impurities. Impurities that might precipitate with the addition of lime include gypsum (CaSO₄·2H₂O) and calcium carbonate (CaCO₃). To eliminate CaCO₃ impurity, the brine is normally pretreated by acidification to *pH* = 4 and purged of CO₂ (Shand, 2006). An analysis of the brine system with a thermodynamic modelling package JESS V8.7 indicated that the starting brine solution is already supersaturated with CaSO₄ (Rowland, 2018), and that this is most likely to precipitate out along with Mg(OH)₂ based on solution equilibria.

1.3 Quicklime Characterisation and Slaking Process

The study used quicklime supplied by Cockburn Cement, commercially known as Quicklime Munster. The main constituent of Quicklime Munster is calcium oxide (CaO), at ~83 wt%. Other notable constituents of the quicklime include silicon oxide (SiO₂), aluminum oxide (Al₂O₃), iron oxide (Fe₂O₃), magnesium oxide (MgO), and sulfur trioxide (SO₃).

As a pretreatment step, quicklime is generally slaked with water to produce a slurry of hydrated lime, where the main constituent is Ca(OH)₂. Slaking is vital as water serves as a medium for easy transportation and release of the hydroxide ions (Oates, 2008). The reactions that occur are:



The effectiveness of the slaked lime may be indicated by the particle size distribution of the Ca(OH)₂ particles. A previous study found that the utilisation efficiency of quicklime, defined as the mass portion of quicklime that participates in the reaction, correlates most strongly with the particle size of the quicklime after slaking (Ineich et al., 2017). It is thus, highly desirable to produce a lime slurry with finer particles, which is associated with higher reactivity.

Among all of the factors that might affect the particle size of slaked lime, temperature during slaking is reported to be the most critical (Hassibi, 1999). While higher temperatures are desirable to produce finer particles, the temperature should not reach the limit where local hot-spots can form causing detrimental effects on slaking (Oates, 2008). Furthermore, the particle size of the lime slurry can be reduced by 'sieving' (size reduction) of either the hydrated lime slurry or the dry quicklime.

1.4 Present State of the Art

There is currently no commercial application of producing Mg(OH)₂ from desalination brine cited in the literature. In the case of using lime or Ca(OH)₂ as the precipitating agent, the few studies found mentioned the main risks of gypsum impurity and poor filterability (Barba et al., 1980, Cipollina et al., 2014). Barba (Barba *et al.*, 1980) recommended an alternative process which essentially produces MgCO₃ solid and further converts it into the desired product. However, within our client's context, it is desirable to utilise an existing mature technology. Hence, this study will investigate the feasibility of recovering commercial grade Mg(OH)₂ from desalination brine using industrial quicklime, with no significant changes to the traditional seawater precipitation process.

2. Methodology

This study is being executed through a series of experiments which aim to replicate the industrial process of Mg(OH)₂ production. A general experimental procedure is illustrated in Figure 1. Brine has been sampled directly from the Perth Seawater Desalination Plant in March 2018, and a sample of Quicklime Munster was supplied by Cockburn Cement. The lime slaking procedure was developed with reference to the Australian Standard AS4489.3.1. This procedure essentially involves mixing quicklime with water at a ratio of 1:4 in an Erlenmeyer flask, and allowing the reaction to occur under agitation at 400 rpm until the reaction is completed.

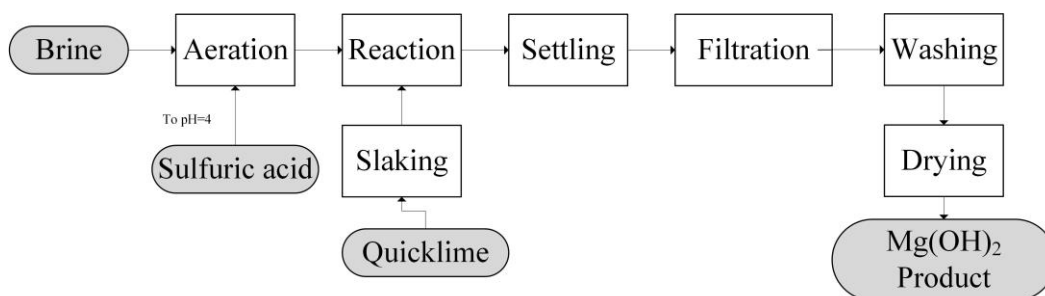


Figure 1 Schematic illustration of a typical experiment procedure.

After adding the hydrated lime slurry to the pretreated brine, the reactions occurred under agitation. When the reaction was complete, the solid was allowed to settle to the bottom, and the settling rate was measured. A small portion of the mixture was also sampled for particle size distribution analysis with a Malvern Mastersizer 2000.

The final product was then further separated from the liquid by filtration, washing to remove soluble salts, and oven drying. To measure the purity of the resulting products, two methods were employed:

1. A small portion of the solid product with a known mass was digested by hydrochloric acid (HCl). The Mg^{2+} concentration of the digested solution was determined by a benchtop spectrometer Hanna HI83300. This value was used to back-calculate the $Mg(OH)_2$ mass fraction in the solid. To verify the validity of this result, the Mg^{2+} concentration in the liquid filtrate was also determined with the same spectrometer, enabling a mass balance to be performed.
2. The bulk solid product composition was also analysed with acid digestion of the solid, followed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

2.1 Experimental Framework

The following framework outlines two sets of experiments discussed in this paper, built on the above procedure.

2.1.1 Effects of Lime Slurry Dosage

Studies have reported that the dosage ratio of the alkaline agent has considerable effects on the composition of the solid products as well as sedimentation rates (Petric and Petric, 1980) (Robinson et al., 1946). Hence, this set of experiments aims to investigate the quality of the product when lime slurry dosage varies from 60% to 120% stoichiometrically equivalent to Mg^{2+} in brine.

2.1.2 Effects of Slaking Condition

Slaking conditions are critical to the reactivity of slaked lime, which affects the utilisation efficiency of quicklime and the $Mg(OH)_2$ product quality. Slaking conditions to be varied in this set of experiments include lime to water ratio, screening of slaked lime by sieves, slaking water temperature, and the possibility of using the original brine as the slaking water.

Other experiments that have or will be undertaken will investigate the effects of addition of seed material, and the effects of flocculant usage.

3. Preliminary Results and Discussions

In a set of experiments to study the effect of the $\text{Mg}(\text{OH})_2$ purity of the precipitate, the results indicated that the purities of $\text{Mg}(\text{OH})_2$ were significantly generally low, as shown in Table 2. Based on the results, a lower dosage of lime slurry appeared to associate with a higher product purity, consistent with the trend reported in another study (Petric and Petric, 1980). Moreover, gypsum contents tend to increase at higher lime slurry dosages, likely due to the increased supersaturation of Ca^{2+} ions. The CaCO_3 contents, however, were significantly higher than expected. In theory, dissolved carbonates were removed under acidification pretreatment of brine, and CaCO_3 precipitation will be minimal. In a further experiment using NaOH instead of lime as the precipitating agent, CaCO_3 content remains ~10%, which eliminated the hypothesis that the CO_3^{2-} was introduced by the lime. It is suspected that the causes of the high CaCO_3 contents are 1) ineffective removal of CO_2 in the acidification pretreatment step; 2) atmospheric CO_2 absorption during the reaction.

Lime slurry dosage, molar equivalence to Mg^{2+} available in the initial brine solution	60%	80%	100%	120%
Purity, mass fraction of $\text{Mg}(\text{OH})_2$	66.3%	65.4%	61.7%	62.3%
CaCO_3 , mass fraction	20.3%	12.9%	13.7%	15.3%
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, mass fraction	7.30%	8.78%	11.3%	12.6%

Table 2 Purity of $\text{Mg}(\text{OH})_2$ at varying lime slurry dosages by ICP-OES.

In another set of experiments, significantly improved product purities were achieved by wet screening of the lime slurry. As shown in Table 3, the resulting $\text{Mg}(\text{OH})_2$ has a purity reaching 91%, when the lime slurry is screened by a 100 μm sieve with before the addition to brine. These results implied that a significant contribution to the impurities in products originates from coarser particles in the lime slurry. Furthermore, high purity $\text{Mg}(\text{OH})_2$ may be recovered from brine through the use of wet-screened lime slurry.

	No Screening	Underflow of a 250 μm sieve	Underflow of a 100 μm sieve
Purity, mass fraction of $\text{Mg}(\text{OH})_2$	68%	79%	91%

Table 3 Purity of $\text{Mg}(\text{OH})_2$ when the lime slurry is directly dosed, wet screened through a 250 μm sieve and a 100 μm sieve respectively.

4. Conclusions and Future Work

Much of the early work has been dedicated to developing an experimental methodology with good reproducibility and consistent mass balance calculations. A functioning experimental procedure with decent reproducibility has been developed, which enables $\text{Mg}(\text{OH})_2$ product quality to be measured under varying experimental conditions. Following this framework, the major shortcoming of the proposed process of recovering $\text{Mg}(\text{OH})_2$ was a low purity obtained. However, it has been shown that wet-screening of lime slurry significantly improves the product purity.

Along with wet screening, it is believed a higher water temperature during lime slaking can further improve the purity of the product, which will be the next phase of the study. It is noted that the $\text{Mg}(\text{OH})_2$ purity measured by the spectrometer has limited value. As a result, it is crucial to analyse the elemental composition of these solid products with ICP-OES, which enables the

impurity contents to be identified. The experimental work will follow the framework outlined above, to investigate the performance of the process with varying lime preparation conditions and the addition of flocculants. In the long term, it will be worthwhile for further study, investigating alternative processes to recover magnesium. For example, it has been argued that recovering magnesium in the form of $MgCO_3$ is more advantageous than the current process (Barba *et al.*, 1980).

5. Acknowledgements

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