Investigation of mechanical properties and associated microstructure of reactive magnesia cement synthesized from reject brine

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**INVESTIGATION OF MECHANICAL PROPERTIES AND
ASSOCIATED MICROSTRUCTURE OF REACTIVE MAGNESIA
CEMENT SYNTHESIZED FROM REJECT BRINE**

Supervisor:

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Submitted by

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2017/18

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A Final Year Project presented to the Nanyang Technological University
in partial fulfilment of the requirements for the
Degree of Master of Engineering

2017/18

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Abstract

This study investigates production scaling up of MgO cement synthesized from reject brine and evaluates the mechanical properties and microstructures of the resulting MgO cement. Hydration process and carbonation degree of the resulting MgO mortar were investigated and compared with commercial MgO cement. Compressive strength, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), particle size analysis, acid reactivity, and thermogravimetric and differential thermal analysis (TG/DTA) were engaged for sample characterization. Results showed that MgO cement synthesized from reject brine possesses higher mechanical strength of 32.5 MPa at the age of 28 days as compared to the commercial MgO cement (20.1 MPa). This is mainly attributed to the high reactivity of the synthesized MgO cement as revealed by the microstructure study.

Keywords : Rejected brine; reactive MgO cement; compressive strength; initial strength; microstructure

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Acronyms

RMC	Reactive Magnesia Cement;
HMCs	Hydrated Magnesium Carbonates
PC	Portland Cement
SSA	Specific Surface Area
EDS	Energy-Dispersive X-ray Spectroscopy
BET	Brunauer–Emmett–Teller
FESEM/SEM	Scanning Electron Microscope
PDA	Particle Size Analyzer
XRD	X-Ray Diffraction
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
RH	Relative Humidity
TG/DTA	Thermogravimetric and differential thermal analysis

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Chapter 1

Introduction

1.1. Background

With increased awareness of the effects of climate change, reducing carbon footprint is a well understood priority of corporations, in general. Especially in the construction industry, this initiative has been on-going for decades[1]. One such development is the consideration of environmentally friendly Magnesium Oxide (MgO) cement to replace conventional Portland cement (PC) which has a much higher carbon footprint [2]. Hence, by adopting MgO cement with lower carbon footprint, the civil engineering industry will take definite steps towards a more sustainable future.

It has been reported [17][35]that MgO cement is often produced by adding NH_4OH or NaOH to the reject brine, and then lime (CaO) [28] or dolomite lime ($\text{CaO}\cdot\text{MgO}$) are used as a base during the synthesis of brucite from the solution. These steps can be followed by calcinating Mg^{2+} containing precipitates, such as magnesium hydroxide and magnesium oxalate. Numerous studies have been carried out to characterize MgO obtained from different sources [28], [34]-[36]. The outcomes of these studies have identified the main factors that influence the properties of MgO producing by dry-route (i.e. decomposition of magnesite), such as the temperatures and the duration time of calcination. Accordingly, increased calcination temperatures and/or prolonged durations lead to the agglomeration of MgO particles due to sintering, which decreases the porosity and reactivity of MgO[34]. However, using MgO cement synthesised from reject brine haven't been report yet.

1.2. Objectives and Scope

The most important goal for this study is using MgO cement (synthesized from rejected brine) to design a Brine-made MgO cement (RMC)-based concrete. Previous studies generate $\text{Mg}(\text{OH})_2$ through a 1L beaker[17][35], which can only produce 2g sample per time. In order to generate enough quantity of MgO, this study increased the scale of the reaction tank from previous 1L to 20L, which could produce 40g sample per time.

Furthermore, the mechanical properties of the resulting synthesized MgO cement from reject brine has not been evaluated, thus, by comparing the carbonation and hydration process difference between Brine-made MgO cement based concrete and commercial RMC-based concrete produced in UK. Compressive strength, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), particle size analysis, acid reactivity, and thermogravimetric and differential thermal analysis (TG/DTA) were engaged for sample characterization. The results will be used to observe the mechanical and microstructural changes undergone by the HMCs and thereby link it to a proper characterization of the cement.

1.3 Organization of Report

Chapter 1 introduces the project, its objectives and the outline of the dissertation. Followed by summarizing the previous researches, with emphasis on some methods used to synthesize MgO from rejected brine and the behavior of MgO cement. This section also briefly discusses the advantages of MgO over conventional PC. Chapter 3 illustrates the experimental procedures. Chapter 4 analyses the results. Chapter 5 serves as the conclusion and offers some feasible ways to further works.

Chapter 2

Literature Review

2.1 Introduction

This chapter will discuss the applications of magnesium oxide (MgO) used in various areas. It will also briefly discuss the previous work done in this field with respect to MgO cement. Furthermore, this section will review different ways that recover brucite ($\text{Mg}(\text{OH})_2$) from seawater/brine.

2.2 Previous study on recovery reactive MgO from reject brine

2.2.1 Desalination plants and reject brine from Singapore

Desalination provides an alternative means to meet the residential and industrial water demands in water-stressed countries like Singapore [2]. Currently, the two desalination plants in Singapore provide 100 million gallons ($448,500 \text{ m}^3$) of drinking water daily, which can meet 25% of Singapore's current water demand. With three additional desalination plants being built, the five desalination plants are designed to provide a total of 190 million gallons ($852,150 \text{ m}^3$) of water per day by 2020 [6]. On a global level, the desalination plants can generate more than 87 million m^3 of waste water per day (18,426 desalination plants) [6]. Production of desalinated water generates an almost equal amount of reject brine [7], a high salt concentration waste by-product produced at the end of the desalination process [8]. Reject brine is often discharged directly back into sea, which threatens the marine life and ecosystem by altering the local flora and fauna due to its high salinity [8]. Therefore, the disposal and management of reject brine remains a major challenge as well as an environmental threat [8][10], which can pave the way for its use in the recovery of valuable metals

and useful solids instead of direct discharge [11].

The desalination process involves the addition of a variety of chemicals to enable the precipitation of the colloidal particles before running through the filtration process. Therefore, the resulting reject brine contains a very high concentration of dissolved salts and suspended constituents, creating variations in its composition in comparison to seawater, natural brine or synthetic solutions. While previous studies [11]- [14] have reported the synthesis of MgO or its derivatives from sea, natural brine or synthetic solutions. The proposed method involves the addition of NaOH, which serves as a pH adjuster and controls the pH of the solution. Unlike Ca-bearing bases, which often lead to the precipitation of a Ca-based compound (e.g. CaCO_3) along with Mg phases, the use of NaOH can increase the purity of Mg-based precipitates [15].

2.2.2 Background of synthetic MgO

From the refractory industry to agriculture, chemical and environmental applications, magnesium oxide (MgO) were widely used[21]. Another increasingly popular use of reactive MgO was reported in the construction industry as an expansive additive [23] and as a novel binder in the development of concrete formulations [21]-[25]. While the majority of MgO produced today is obtained through the processing of naturally occurring minerals such as magnesite (MgCO_3) [21], around the world about 14% of MgO was synthesized by calcinating $\text{Mg}(\text{OH})_2$, which came from seawater or brine sources containing high concentration of Mg^{2+} . The synthetic MgO obtained from seawater/brine demonstrates a higher purity and reactivity compared with MgO produced through the calcination of magnesite [28]. MgO that possesses higher purity and specific surface area (SSA) is widely used in high-end pharmaceutical and semiconductor applications as an additive or a catalyst [20].

2.2.3 Several methods that recover brucite from seawater or brine

Strong bases were always used in recovering brucite from seawater or brine, which can precipitate Mg^{2+} from the solution. During this process, it is essential to reach an appropriate pH level in order to form the precipitates. Previous studies [17] have shown that the ideal pH for the formation of carbonates is above 9, which favors the transformation of carbon dioxide and bicarbonates to CO_3^{2-} . The pH level of gelatinous $\text{Mg}(\text{OH})_2$ could be even higher due to the requirement of surplus hydroxide. These trends were also confirmed by [11], who demonstrated the occurrence of the precipitation process at a pH of 8.5, whereas higher pH values led to increased brucite formation.

Lime (CaO) [28] or dolomite lime ($\text{CaO} \cdot \text{MgO}$) are used as a base during the synthesis of brucite from the solution. By using dolomite lime, can reduce the amount of seawater/brine needed for the production of the same amount of MgO obtained via the use of CaO because dolomite lime itself contains MgO . However, the uses of these Ca-bearing bases often lead to the precipitation of Ca-based compounds (e.g. CaCO_3) and thus reduce the purity and content of Mg-based precipitates. Furthermore, the Ca-bearing bases can react with sulphate (SO_4^{2-}) present in the solution to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which may necessitate the pre-treatment of the solution through the addition of CaCl_2 to remove sulphate in seawater/brine.

Apart from Ca-based bases, several studies have suggested the use of other alkali sources to precipitate Mg^{2+} from seawater/brine [11]. NaCO_3 and NaOH were also reported to recover Calcium and Magnesium from mining wastewater and brine from seawater desalination plants. NaCO_3 can recover more than 94–96% of Ca when the pH above 10 and NaOH can recover more than 97–99% of Mg when pH higher than 11 [33]. Another proposed additive was sodium hydroxide (NaOH) along with oxalic acid, which produce magnesium oxalate (MgC_2O_4) from brine. Previous studies [32] demonstrated the selectively precipitation of Calcium and Magnesium oxalate at

different pH values. Ca-oxalate was precipitated first and removed when oxalate/Ca equals to 6.82, while pH less than 1. This was followed by the precipitation of Mg^{2+} from the brine residue at a Sodium hydroxide/Oxalate/Mg ratio of 3.21:1.00:1.60 at a pH range of 3–5.5, leading to a high yield of pure magnesium oxalate.

These steps can be followed by calcinating Mg^{2+} containing precipitates, such as magnesium hydroxide and magnesium oxalate. Numerous studies have been carried out to characterize MgO obtained from different sources [28], [34]–[36]. The outcomes of these studies have identified the main factors that influence the properties of MgO producing by dry-route (i.e. decomposition of magnesite), such as the temperatures and the duration time of calcination. Accordingly, increased calcination temperatures and/or prolonged durations lead to the agglomeration of MgO particles due to sintering, which decreases the porosity and reactivity of MgO[34].

2.3 Previous study on MgO cement

2.3.1 The relationships between traditional cement and greenhouse effect

The civil engineering industry is a major player in this on-going environmental crisis that about 5% of global CO_2 emissions come from cement production [1]. Portland cement (PC) is the primary ingredient in concrete, which in turn forms the structures of buildings. As CO_2 is a well-known greenhouse gas, the civil engineering industry's contribution to its accumulation in the atmosphere and consequently its effect on the planet's elevated temperatures is undeniable. Hence, the importance of finding effective ways to sequester CO_2 is a well-understood priority of the industry.

Since cement is a major contributor of greenhouse gas emissions, mixing cement with some materials which have a carbon footprints and consuming lower energy are developed. One excellent example would be MgO cement which offers safe and permanent storage of CO_2 [25] and is hence a more sustainable solution compared to

conventional PC.

2.3.2 Different sources of MgO

Generally, there are two ways produce MgO, dry route and wet route. Both two methods produce MgO by calcination, the sources ranging from MgCO_3 , magnesium-rich brine/seawater to MgSiO_3 [21]. In first method, depending on different temperature could be categorized into three groups - light, hard dead burned, temperature ranging from 700°C to 2000°C [36][38]. When the calcination temperature decreased, the specific surface area and reactivity would increase, but high calcination temperature would lead to a high thermal shock resistance[39][40].

2.3.3 The methodology of using MgO as a concrete binder

In MgO based concrete, the carbonation degree of the binder determines the strength directly. While adding MgO into water with some heat, it will transfer into brucite, then, brucite contact with water and CO_2 will generate HMCs, for example hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). Those HMCs above contribute a lot to strength gain. Whole procedures are list below.

Some researches revealed the morphology of HMCs played an important role in strength [41]. HMCs have a lot of morphology, such as needle-like fibrous and rose-like, those structures affect or lock each other and then lead to high strength, in some case the transfer from brucite would increase the volume and stiffness, lower the

porosity. Concrete will have a good performance, because of these characters.

Previous studies already give an elaborate analysis about the microstructural change and strength change during carbonation[25]. Generally, the amount of HMCs added in concrete with aggregates ranging from 4 wt% to 20 wt%. This kind of concrete was mainly used as construction materials, such as blocks. Because of potential to capture carbon dioxide and carbonate, which make it easy to operate[38].

2.3.4 Key factors that influence the carbonation and hydration of RMC

Previous studies[36] revealed that the carbonation and hydration process of RMC were mainly affected by three factors: (1) reactivity of magnesium oxide;(2) water cement ratio and cement aggregate;(3) different conditions of curing, such as relative humidity, the concentration of carbon dioxide and temperature.

2.4 Conclusion

Previous study presented a comprehensive investigation on synthesizing brucite and producing of reactive MgO from reject brine [17][35]. Those studies also proved it is possible to recover reactive magnesia from rejected brine from desalination process. The initial set of experiments successfully demonstrated NaOH could be used as a strong base to recover brucite at an $\text{OH}^-/\text{Mg}^{2+}$ ratio of 2, it has been proved 2 is an optimum ratio which can recover good quality brucite[17][35]. While a certain minimum temperature was required for the complete decomposition of $\text{Mg}(\text{OH})_2$ into MgO, if rising the calcination temperature and prolong the holding time would lower the reactivity of MgO. In order to obtain MgO with high reactivity, calcination temperature should be controlled at 500°C and duration time at 2h is optimum[17][35]. These studies demonstrated that reject brine can be considered as a feasible and economic waste for the sustainable recovery of MgO with a high reactivity, which can be used in various applications within the food, cosmetics, pharmaceutical and

construction industries [18]-[21].

Previous studies about reactive magnesium were mainly focus on carbonation and hydration during curing procedure [36], aims to increasing the ability to sequester carbon dioxide and strength. It also focusses on the microstructure of this kind of concrete, which gives a lot of background about how to reach to an optimize condition to improve the performance of the product.

In conclusion, researches above present a possibility that studying on synthesizing MgO cement from rejected brine and use it to design a brine-made MgO based concrete, which was never investigated before.

Chapter 3

Production Scale-up of MgO Cement Synthesized from Reject Brine

3.1. Introduction

It has been reported [17][35] that MgO cement is often produced by adding NH_4OH or NaOH to the reject brine, and then lime (CaO) [28] or dolomite lime ($\text{CaO}\cdot\text{MgO}$) are used as a base during the synthesis of brucite from the solution. These steps can be followed by calcinating Mg^{2+} containing precipitates, such as magnesium hydroxide and magnesium oxalate. Numerous studies have been carried out to characterize MgO obtained from different sources [28], [34]-[36]. The outcomes of these studies have identified the main factors that influence the properties of MgO producing by dry-route (i.e. decomposition of magnesite), such as the temperatures and the duration time of calcination. Accordingly, increased calcination temperatures and/or prolonged durations lead to the agglomeration of MgO particles due to sintering, which decreases the porosity and reactivity of MgO[34].

3.2. Materials

The rejected brines used in this experiment were taken from a seawater desalination plant called Tuaspring located in western Singapore, which adopts a reverse osmosis (RO) membrane system to purify saline water and produce drinkable water for human use. These membranes reject more than 99.5% of the dissolved salts and suspended materials in the feedwater, resulting in a highly concentrated reject waste stream which contains suspended constituents and a 2 to 7-fold increased concentration of dissolved salts [2]. Before analysis, suspended particles were removed by an injector filter (45 μm). Measured the pH by a pH meter, the result is around 8. Using ICP-OES to analyze

its chemical composition, results shown in Table 1 below. The concentration of Mg^{2+} reaches to 1603 ppm, other impurities such as Na^+ , K^+ and Ca^{2+} were also identified in the reject brine. Sodium hydroxide (NaOH, reagent grade, pellets) produced by VWR Pte Ltd., as an alkaline base during current study.

Table 1 Ions composition of the rejected brine by ICP-OES

Element	Na	Mg	Ca	K	Si	B	Sr	Li	P and Al
Concentration (ppm)	16580	1603	484	998	0.15	4.31	19.6	0.92	< 0.2

Fig. 1 ICP-OES (PerkinElmer Optima 8000) in Environmental Lab 1

3.3. Synthesis of MgO cement from reject brine

3.3.1. Small scale production

NaOH/Mg²⁺ molar ratio equals to 2. Add NaOH solution to the reaction tank and recording pH of solution. The solution was mixed at constant speed of 300 rpm by a magnetic stirrer at room temperature (25 °C)[17]. A pH/thermometer probe was used to monitor reaction degree. When the pH kept stable, it indicates the reaction finished. Followed by separating the precipitant from liquid via centrifuge. Gathering all the solids from tubes to a beaker, and washed by ultra-pure water three times to remove surface-attached ions. The solid-liquid separate procedure also repeated three times. The washed solids were put into an oven drying at 105 °C for 1 day, in order to remove free water before grinding into powder form. The ground samples were calcined at determined temperatures (500 °C) for 2 hours in an electric furnace to make brucite transfer to MgO[17].

3.3.2. Production scale-up

Previous studies generate Mg(OH)₂ through a 1L beaker[17][35], which can only produce 2g sample per time. In order to generate enough quantity of MgO, this study increased the scale of the reaction tank from previous 1L to 20L, which could produce 40g sample per time.

Fig. 2 1 L beaker and 20 L bucket

The scaling up production following the procedures are listed below:

- (1) NaOH/Mg²⁺ molar ratio keeps the same at 2. Add NaOH solution to the 20L reaction tank and recording pH of solution.
- (2) Because of the large size of the reaction tank, the mix force from the magnetic stirrer became negligible, instead, in this scale-up procedure, the well mixing condition was finished by man power shaking, shaking the bucket once an hour for 5 mins, between the 1-hour time interval, measuring the solution pH until it stable, which indicates the reaction finished.
- (3) After 24 hours separating by gravity, liquid phase and solid phase were separate in upper and bottom, respectively. The liquid phase occupied 4/5 space of the bucket, then collecting the solid phase by pour out liquid phase.
- (4) Followed by separating the precipitant from liquid via centrifuge. Gathering all the solids from tubes to a beaker, and washed by ultra-pure water three times to remove surface-attached ions. The solid-liquid separate procedure also repeated three times by following the procedure listed above, (2) - (3).
- (5) The washed solids were put into an oven drying at 105 °C for 1 day, in order to remove free water before grinding into powder form.
- (6) The grinded samples were calcined at determined temperatures (500 °C) for 2 hours in an electric furnace to make brucite transfer to MgO[17].

3.4. Characterization methods

Several techniques were used to analyze the Brine-made MgO. X-ray powder diffraction (XRD) was completed by a Bruker D8 Advance with a Cu K α basis at the set of 40 kV and 40 mA, emitting radiation at a wavelength of 1.5405 Å, scan at 0.02°/step, and a 2 θ range of 5 to 80°. Utilizing a JSM-7600F thermal field emission scanning electron microscopy (FESEM) to investigate the microstructure of the solids by imaging powder surface. The specific surface area (SSA) of the synthesized

samples were obtained by Particle Size Analyzer (MALVERN). The reactivity of MgO was measured by acid neutralization, during which 0.28 g of the synthesized MgO was added into 50 ml of solution at a certain concentration, 0.07 mol/l citric acid, along with phenolphthalein (i.e. pH indicator). The neutralization time was measured and reported as an indicator of reactivity [21]-[23].

Fig. 3 FESEM/SEM and XRD

3.5. Results and discussion

This section will mainly compare the quality of the MgO between the large scale (20L) production sample and small-scale production sample finished by previous researchers [17].

Mg^{2+} in the solution would react with OH^- to generate precipitant $\text{Mg}(\text{OH})_2$ via adding NaOH in to the rejected brine. Meanwhile, HCO_3^- and CO_3^{2-} will also react with OH^- to generate CaCO_3 , which would decrease the purity of the product. The whole procedures happen in the solution were given by four equations below.

In this study, it takes an optimized reaction condition from previous research [15][35], NaOH/Mg²⁺ molar ratio equals to 2. Add NaOH into reject brine at once and recording the pH of solution was recorded. The solution was mixed at constant speed of 300 rpm by a magnetic stirrer at room temperature (25 °C). The washed solids were putted into an oven (105°C for 1 day) to evaporate free H₂O before grinding into powder form. The ground samples were calcined at determined temperatures (500 °C) and durations (2h) in an electric furnace to produce reactive MgO.

Following the best reaction condition from previous study [15][35] Mg²⁺/Ca²⁺ was (19.6) at a NaOH/Mg²⁺ ratio of 2. In order to generate enough quantity of MgO, this study increased the scale of the reaction tank from previous 1L to 20L, which have introduced earlier.

3.5.1. Differences on the raw materials - reject brine

Reject brine is a main material used in this study, a comparison on element difference in reject brine with previous study [17][35] was shown in Table 2, as can be seen, the content of main element Mg and Ca is almost the same, around 1600-1700 ppm and 470-480 ppm, respectively.

Table 2 Comparison on element difference in reject brine with previous study

Element	Na	Mg	Ca	K	Si	B	Sr	Li	P and Al
Concentration (ppm)	16580	1603	484	998	0.15	4.31	19.6	0.92	< 0.2
Previous study	13580	1718	471.3	845.7	3.7	3.8	14.6	0.3	< 0.2

3.5.2. SSA

Particle size of 3 kinds of MgO cement at 10%, 50% and 90% shows in Table 3. Comparing the particle size equals or above 50%, SG sample reaches to the lowest value at 16.294 μm , UK sample has a highest particle size at 34.223 μm , and brine-made sample's 50% particle size reach to 30.516 μm . Besides, the Particle Size Analyzer also gives a Specific Surface Area g/m^2 of 3 kinds of MgO below in Fig. 4.

Table 3 Particle Size Distribution of Brine-Made RMC, UK RMC and SG RMC

	d (0.1) / μm	d (0.5) / μm	d (0.9) / μm
UK RMC	6.016	34.223	84.898
SG RMC	4.807	16.294	61.096
Brine-Made RMC	4.963	30.516	71.426

Fig. 4 Specific Surface Area (g/m²) of Brine-Made RMC, UK RMC and SG RMC

The SSA of the UK, SG and Brine-made MgO are 0.658 m²/g, 0.913 m²/g, 0.483 m²/g, respectively. When compared to two commercial MgO products (produced in UK and SG) other studies, the SSA value (0.658 m²/g for UK, 0.913 m²/g for SG) obtained under these conditions was higher than the results, besides. These values can be optimized even further with an adjustment of the calcination temperature and duration towards the lower range, while enabling the complete decomposition of Mg(OH)₂.

In previous study, which production in small-scale [17], the highest SSA of 51.4 m²/g was obtained (measured via BET) when the synthesized Mg(OH)₂ was calcined at 500 °C for 2 h.

3.5.3. XRD

Fig. 5 illustrates a comparison between MgO synthesized from rejected brine and two commercial MgO products, which introduced before. The most obvious peaks were located at ~37.0°, 42.9° and 62.3° 2θ, which were well-matched with the reference

indicated in JCPDS card no. 89–7746. These peaks were accompanied with some relatively not obvious peaks were led by CaCO_3 .

Fig. 5 XRD comparison between MgO synthesized from rejected brine and two commercial MgO products (produced in UK and SG).

Main differences showed in CaCO_3 , for MgO from rejected brine is behaves as Calcite-III, and Calcite for Commercial MgO. When making comparison between large-scale and small-scale, the main keeps the same, which was given below in Fig. 6 [17].

Fig. 6 XRD diffractograms of reactive MgO produced via the calcination of $\text{Mg}(\text{OH})_2$ under different temperatures and durations [17].

Fig. 7 shows the scanning position of the image, the elementary composition of the Brine-made MgO was given below in Fig. 8. As can be seen, apart from Mg and O, there were small amount of element, such as Na, S, Cl and Pt, which led to impurity of the sample.

Fig. 7 EDS analyze position of MgO synthesized from rejected brine

Fig. 8 Elementary composition of MgO synthesized from rejected brine (EDX)

3.5.4. FESEM

SEM images of Brine-made MgO under a calcination condition at 500 °C-2 h shows in Fig. 9. The microstructure of MgO was composed of a single particle which was a combination of several grains. A plate-like morphology can indicate the parent material ($\text{Mg}(\text{OH})_2$), observed throughout the microstructure of MgO produced at lower temperatures in previous study [15]. The porous structure was led by the losing of water during the decomposition of brucite. The morphology of the large-scale samples are almost the same with previous study which production in small- scale[17].

Fig. 9 FESEM images of Brine-made MgO under a calcination condition at 500 °C-2 h

3.5.5. Reactivity

The reactivity of MgO reflected in acid neutralization time in Fig. 10 This observation doesn't correspond well with the SSA measurements. In theory, MgO samples with higher SSA resulted in shorter acid neutralization times, which was an indication of their higher reactivities. These results were conformed to those reported in earlier studies[45], where a direct correlation between the SSA and reactivity of MgO was reported.

In previous study, which production in small- scale[17], the highest SSA of 51.4 m²/g was obtained (measured via BET) when the synthesized Mg(OH)₂ was calcined at

500 °C for 2 h. But in this study, SSA was analyzed by Particle Size Analyzer, solution used in this study is water, which would react with MgO slightly in room temperature, it would affect the SSA result.

The reaction time with acid in large-scale was 732 s, which was close to the result small-scale, 664 s [17]. A relative more porous mother precursor would result in a more porous MgO, thus a higher reactivity. These values can be optimized even further with an adjustment of the calcination temperature and duration towards the lower range, while enabling the complete decomposition of $\text{Mg}(\text{OH})_2$.

Fig. 10 The reactivity of Brine-made MgO, SG MgO and UK MgO

3.6. Results and discussion

Reject brine is a main material used in this study, a comparison on element difference in reject brine with previous study [17][35] was shown in Table 2, as can be seen, the

content of main element Mg and Ca is almost the same, around 1600-1700 ppm and 470-480 ppm, respectively.

Besides, the other characteristics of this large-scale MgO keeps almost the same with previous study [17][35], for example, the main peaks of the XRD patterns and the reaction time with citric acid, which have shown above. Overall, all results above can prove MgO cement from brine keeps the same quality with previous study [17][35] when scaling-up from 1L to 20L.

Chapter 4

Mechanical Properties and Microstructure of MgO Mortar

4.1. Introduction

In MgO based concrete, the carbonation degree of the binder determines the strength directly. While adding MgO into water with some heat, it will transfer into brucite, then, brucite contact with water and CO₂ will generate HMCs, for example hydromagnesite (Mg₅(CO₃)₄(OH)₂ • 4H₂O), and nesquehonite (MgCO₃ • 3H₂O) dypingite (Mg₅(CO₃)₄(OH)₂ • 5H₂O). Those HMCs above contribute a lot to strength gain. Whole procedures are list below.

Some researches revealed the morphology of HMCs played an important role in strength [41]. HMCs have a lot of morphology, such as needle-like fibrous and rose-like, those structures affect or lock each other and then lead to high strength, in some case the transfer from brucite would increase the volume and stiffness, lower the porosity. Concrete will have a good performance, because of these characters.

Previous studies already give an elaborate analysis about the microstructural change and strength change during carbonation[25]. Generally, the amount of HMCs added in concrete with aggregates ranging from 4 wt% to 20 wt%. This kind of concrete was mainly used as construction materials, such as blocks. Because of potential to capture

carbon dioxide and carbonate, which make it easy to operate[38].

4.2. Experimental program

4.2.1. Materials, mix design and preparation

In this study, a commercial cement binder was set for comparison, which produced by Richard Baker Harrison Ltd. (UK).

Physical characteristics and composition of control samples used in this study were given by Table 4. Besides, aggregates used in mixing concrete was produced by Buildmate Pte. Ltd. (Singapore) the particle size of this aggregates were ranging from 0.05 mm to 1 mm.

Table 4 Physical characteristics and chemical composition of RMC(UK)

	Chemical composition (%)							Physical properties	
	MgO	SiO ₂	CaO	R ₂ O ₃	K ₂ O	Na ₂ O	LOI	Specific	Specific
								gravity (g/cm ³)	surface area, (m ² /g)
RMC (UK)	>91.5	2.0	1.6	1.0	-	-	4.0	3.0	16.3

When preparing concrete cubes, the ratios between binder and coarse aggregates is 1:1, the w/c ratios of synthesized MgO and RMC(UK) is 0.83 and 0.53 (the ratio between water reducer and water is 1:10), respectively.

The size of the mold is 20×20×20 mm, after mixing all the components, adding water into the powder gradually. While it mixed uniformly, it was taking to a vibration table, and sliced flatly by a trowel. After 24 h, cubes were demolded and placed into a curing chamber (temperature: 28 ± 2 °C, relative humidity: 80 ± 5 %, carbon dioxide concentration: 10%). The curing time set as 3, 7 and 28 days.

4.2.2. Test methods

4.2.2.1. Compressive strength

According to the specification of the document ASTM C109/C109M-13[48]. For the compressive strength of the test samples at 3 days, 7 days and 28 days. All the concrete sample are test by a Hydraulic pressing machine (M6 in PE Lab) at a descending speed of 0.5 mm/min.

Fig. 11 Hydraulic pressing machine M6 in PE Lab

4.2.2.2. TG/DTA, XRD and FESEM/SEM analyzes

Cubes after compressive strength test were collected into a tube full of acetone, which can forbid the hydration procedure. Three days after, samples were dried again by an oven at 105 °C. These sample were collected and grinded (125 μ m) for XRD, TG/DTA and A JSM-7600F thermal field FESEM/SEM analyze. Setting for XRD is the same

as previous MgO analyze, phases were analyzed by MDI Jade and the compositions were calculated by a rietveld refinement software called TOPAS with several designed CIFs for different components[48].

TG/DTA was analyzed by a machine called Perkin Elmer TGA 4000, temperature ranging between 30 - 900 °C (temperature increasing at 10 °C/min) and protected by N₂. Before SEM test, using gold to coating the powdered sample. Then, analyzing elemental composition by EDS.

Fig. 12 TG/DTA (SDT Q 600) in SCBE NTU

Fig. 13 Particle Size Analyzer (MALVERN) in Environmental Lab 1

4.3. Results and discussion

4.3.1. Compressive strength

Fig. 14 Comparison of compressive strength of two samples in the given period

The compressive strength of Brine-made MgO sample and commercial MgO cement (UK) sample cured for 3, 7 and 28 days is given in Fig.14. Compressive strength of Brine-made MgO cement sample and commercial MgO cement (UK) samples reached to 32.5 MPa and 20.1 MPa at the final stage (28 days). The strength gain was led by the formation of hydrate phases (i.e. C-S-H), which were formed during the hydration[49]. And due to the carbonation process, the MgO cement obtained a dense carbonate network microstructure[24].

In theory, decreasing the water cement ratio from 0.83 to 0.53 should contribute to an

increased in strength, but this trend hasn't been observed in strength development in this study, it can be explained by the reactivity difference between two samples, because Brine-made sample has a much more higher reactivity than UK sample.

From the perspective of reactivity of the raw materials (RMC) which has been introduced in Fig. 10, Brine-made RMC has a higher reactivity than UK RMC, this could explain why Brine-made sample has higher potential to hydration and carbonation, this also reflected in the amount of brucite and unreacted MgO in XRD TOPAS analyze result. Thus, in this case, the reactivity of the raw materials (RMC) are more important than initial water content on the final strength.

4.3.2. XRD

Fig. 15 XRD patterns of two samples cured for 7 days

The XRD patterns of two kinds of samples cured for 7 days are shown in Fig.15 Focus on the carbonate phase, when compared with dypingite those peaks represent hydromagnesite (PDF #025-0513) were obviously can be observed (15.3° , 30.8° and 13.7° 2θ), which proved the presence of the carbonate phase. The peaks of dypingite were relatively not obvious is because the high background noise and overlap. The MgO peaks can be observed from both sample, which indicates the inadequate hydration procedure. The massive amount brucite observed in graph reveals the low carbonation rate through curing. Overall, it has the potential to reach a higher strength if the hydration and carbonation procedure go further.

Fig. 16 Composition Analyze of UK and Brine-made samples after 7 days of curing by Rietveld Refinement Method (TOPAS)

Fig. 16 above compares the differences between UK and Brine-made sample by TOPAS. The water content is very important for continuing the hydration process.

MgO transfer into brucite through the hydration process, and brucite reacts with CO₂ to form the carbonate phase. Since the water content of UK samples was lower than that of Brine-made samples, the conversion rate of MgO was not lower (79.46 % residue) due to incomplete hydration process. This also led to its lower hydromagnesite content. In contrast, the Brine-made sample has a higher water content and the higher the MgO conversion rate, more opportunity it can react with CO₂, and therefore more hydromagnesite.

This result could relate to the strength performance, the sample (Brine-made) with higher degree of carbonation and hydration process would have a higher compressive strength in the final stage (32.5 MPa vs 20.1 MPa).

4.3.3. TG/DTA

The TG/DTA results of two samples after 7 days curing shows below in Fig.17 and Fig.18. Using double-Y-axis to illustrates the weight loss relate to temperature rising from 30°C-900°C, accompanied with heat flow changes. From the previous studies[38] [41] [41], the whole decomposition follows 3 stages shows in (a)-(c):

(a) First stage (30°C-310°C): weight decreasing was led by the water loss from (HMCs bonded with H₂O): $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} \rightarrow 4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O}$ [41].

(b) Second stage (320°C-480 °C):mass decrease due to:(1) HMCs dehydroxylation ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \rightarrow 4\text{MgCO}_3 + \text{MgO} + \text{H}_2\text{O}$) (2) Un-carbonated brucite decomposition ($\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$) [41].

(c) Final stage (480°C-900 °C: HMCs Decarbonation ($\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$)[41].

Fig. 17 TGA /DSC graph of Brine-made samples cured for 7 days

Fig. 18 TGA /DSC graph of UK samples cured for 7 days

Comparing the peak around 400 °C, it is obvious that the peak of Brine-made sample is sharper than UK sample according to the heat flow changes (25W/g in Brine-made sample vs 10 W/g in UK sample), which illustrates the that the hydration process of Brine-made sample goes much more further than UK sample, this result is consistent with XRD result introduced earlier, brucite content in Brine-made sample is much more higher than it in UK sample (79.46% vs 30.69). This could explain why Brine-made sample has higher potential to hydration and carbonation, then, lead to a higher compressive strength.

Table 5 shows the total weight loss, weight loss at the Second and Final stages and lists the water/CO₂ content from brucite and HMCs, respectively.

Table 5 Mass loss of UK and Brine-made samples calculated by TGA

Species	Weight loss (wt.%)				
	310-490 °C	500-750 °C	H ₂ O (brucite)	CO ₂ (HMCs)	Total
Brine-made	17.3	1.82	7.74	11.38	27.76
UK	7.3	0.9	3.4	4.8	12.33

In contrast to the three-stage reactions given earlier, there are two ways to lose water, one is brucite, and the other is the dehydroxylation process of HMCs, which can be distinguished from the given reference temperature range. Obviously, the higher the water content of the sample, the higher the total weight loss, but also with the higher brucite content. Contrary to previous XRD results, the results were consistent, as the higher HMCs content of the Brine-made samples resulted in higher losses of CO₂, indicating a higher degree of carbonation in the Brine-made samples. A comparison of the strength results shows that the total weight loss (27.76% vs. 12.33%) is also consistent with the final strength results, thus indicating that the degree of carbonation and the degree of hydration directly determine the final mechanical properties of the

samples.

4.3.4. Microstructure analysis-SEM

Fig. 19 compares the differences in microstructure of the UK sample and Brine-made sample after 7 days of curing. Rosette-like carbonate-hydromagnesite was observed in both samples. This is consistent with the results shown by the XRD. Obviously, the hydromagnesite of the Brine-made sample is denser than the UK Sample, which also explains the high strength of the Brine-made sample. In addition, the elemental composition of these two samples is also listed in Fig. 21 which was compatible with the XRD test results, the C content of the Brine-Made sample was higher than UK sample.

(1)

(2)

(3)

(4)

Fig. 19 Pictures of concrete samples after 7 days curing (1) -(4) Brine-RMC and (5) -(6) UK RMC, pictures (7) and (8) are the interfacial transition zone of UK and Brine-made samples, respectively

Picture (4) in Fig. 19 is Needle-like carbonate nesquehonite, observed in the Brine-made sample, but in the UK sample, it's very hard to find the needle-like images. This result is consistent with XRD analyze result, which gives a very low portion of nesquehonite in both sample (1.10 % in Brine-made sample and 0.26 % in UK sample). In-line with TOPAS analyze result, Brine-made sample shows a higher hydromagnesite and nesquehonite content (6.93 % in total) than UK sample (2.17 % in total), which can explain the higher carbonation degree, then higher compressive strength (32.5MPa vs 20.1MPa). This is because the higher reactivity and initial water

content of Brine-made sample lead to a higher hydration degree in Brine-made sample, which has shown in TGA/DSC and XRD result, and then it can explain Brine-made sample has a higher potential to carbonation.

Previous study about the interfacial transition zone (ITZ) illustrates that cement and aggregates bonded closer will lead to a lower porosity[50]. ITZ of UK and Brine-made samples were shown in (7) and (8) from Fig. 19, it's obviously that Brine-made sample has a tighter connection zone than UK sample, and this and explain the higher compressive strength of Brine-made sample.

Fig. 20 EDX analyze position of concrete samples cured for 7 days (a) Brine-RMC and (b) UK RMC

Fig. 21 Elementary composition of concrete samples cured for 7 days Brine-RMC and UK RMC (EDX)

Taking all factors into consideration, the evolution of the microstructure plays a decisive role in the strength of the concrete. The bonding strength of carbonate plays a crucial role in the formation of the network structure [41]. Brine-made sample has a tighter connection zone than UK sample, as can be seen from the ITZ comparison pictures (7) and (8), The tightly bound HMCs crystals form a strong network structure through interconnections. In addition to this, the reaction of brucite and CO_2 leads to the expansion of the carbonate phase and therefore the porosity and degree of densification are reduced. And from the elementary composition result in Fig. 21 can also reflect the higher carbonation degree in Brine-made sample, which shows a much more higher carbon content (35.59 %) than UK sample (9.11%).

4.4. Results and discussion

In summary, after considering all the influencing factors, Rosette-like carbonate-hydromagnesite and Needle-like carbonate nesquehonite have observed in both samples, relating to the XRD analyzed result which has introduced before, the degree of hydration and carbonation process are more important than initial water content on the final strength. Higher degree of hydration and carbonation process will increase the porosity and affect the final strength of the sample.

Chapter 5

Conclusions

This study focusses on using MgO cement (synthesized from rejected brine) to design a reactive Brine-made MgO cement (RMC)-based concrete. And then, comparing carbonation and hydration process difference between Brine-made MgO cement based concrete and commercial RMC-based concrete produced in UK.

The characteristics of this scale-up production MgO kept almost the same with small-scale production MgO in previous study [17][35], the element content of the brine, the main peaks of the XRD patterns and the reaction time with citric acid, which will show in earlier. Overall, all result above can prove MgO cement from brine keeps the same quality with previous study [17][35] when scaling-up from 1L to 20L.

To summarize all the result in this study, there were several factors affect the hydration and carbonation process (the difference of carbonation and hydration degree have reflected in several measurements analyzes, the peak in TGA, carbonate content in XRD and microstructure in SEM), reactivity of raw materials (RMC), initial water content. In this case, Brine-made RMC has a higher reactivity than UK RMC, this could explain why Brine-made sample has higher potential to hydration and carbonation, this also reflected in the amount of brucite and unreacted MgO in XRD TOPAS analyze result. Thus, the reactivity of the raw materials (RMC) are more important than initial water content on the final strength. This study also shows that this new kind of Brine-made RMC has a certain commercial and research value.

In this study, the most important influence parameter was the degree of hydration and carbonation process, which played a crucial role in the final performance, porosity, and microstructure of the product. These effects are mainly reflected in the decrease of the increase the porosity, the increase in strength, and the degree of sufficient

hydration and carbonization. The change in porosity mainly occurs in the melt-state.

In addition, the morphology of the carbonates in the sample is also an important factor affecting the final mechanical properties. Previous studies have shown that this does not depend on their amount [44]. And previous study on interfacial transition zone (ITZ) illustrates that cement and aggregates bonded closer will lead to a lower porosity[50]. By analyzing the microstructure of the comparison sample, it's obviously that Brine-made sample has a tighter connection zone than UK sample, and this and explain the higher compressive strength of Brine-made sample. it can be found that the degree of carbonation and the degree of compactness of the microstructure also determine the strength and mechanical properties of the sample. In this regard, more detailed experimental design and control variables can be further optimized for experimental exploration.

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