PREPARATION OF HIGH PURITY MAGNESIUM OXIDE FROM SEA BITTERN RESIDUAL FROM NaCl PRODUCTION IN Al-BASRAH SALTERN, SOUTH IRAQ

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ABSTRACT

In this study, light and dead-burned magnesia (MgO) were prepared from the sea-bittern residual from the production of NaCl; extracted from sea water (Arabian Gulf) in Al-Basrah saltern in the south of Iraq. Dead burned magnesia of pure and dense form assaying 96.8% MgO, with a bulk density of 3.7 gm/cm^3 was prepared at optimum conditions, including pre-treatment of the sea bittern of 26 Baume with calcium chloride at a ratio of 1.05:1.00 ($CaCl_2:MgSO_4$) to remove calcium sulfate, addition of precipitant (dolime) at a molar ratio of 1:1 ($CaO.MgO:MgCl_2$), and precipitation temperature of about 70 °C for 60 minutes. The precipitated $Mg(OH)_2$ was subjected to calcination at 1000 °C for 60 minutes, whereby a milky soft powder of light-burned (active) magnesia was produced. Dead-burned (inactive) magnesia was then obtained by burning the light-burned magnesia at 1650 °C for 60 minutes. This study provides further benefit, of producing a high purity calcium sulfate ($\geq$ 98%) as a byproduct of the MgO production.

تحضير أوكسيد المغنيسيوم عالي النقاوة من المحلول المر المتخلف عن إنتاج الملح في مملحة البصرة، جنوب العراق

علاء محمد خليل مصطفى و وليد رشيد عبد الله

المستخلص

تم في هذا البحث دراسة إنتاج مادة المغنيسيا الخفيفة ومطلقة الحرق، باستغلال المحلول المر المتخلف عن عملية إنتاج ملح الطعام المستخرج من مياه البحر (الخليج العربي) في مملحة البصرة، جنوب العراق، حيث أمكن تحضير مادة أوكسيد المغنيسيوم مطلقة الحرق وعالية النقاوة (96.8% MgO) وبكثافة كتلية 3.7 غم/سم^3، بعد تثبيت الظروف المثلى لعملية التحضير والتي تضمنت: معاملة أولية للمحلول المر (كثافة 26 بوميه) بمادة كلوريد الكالسيوم وبنسبة 1.05:1.00 ($CaCl_2:MgSO_4$) للتخلص من كبريتات الكالسيوم ولتهيئة المحلول المر للمرحلة التالية. تضمنت المرحلة الثانية إضافة المادة المرسبة (الدولايم) الى المحلول المر وبنسبة مولية 1:1 ($CaO.MgO:MgCl_2$) لترسيب هايدروكسيد المغنيسيوم، وتم التفاعل بدرجة حرارة 70 درجة مئوية لمدة ساعة كاملة. تم حرق هايدروكسيد المغنيسيوم الناتج من عملية الترسيب بدرجة حرارة 1000 درجة مئوية لمدة ساعة للحصول على مادة أوكسيد المغنيسيوم واطئ الحرق (النشط أو الفعال) وبإخضاع الأخيرة للحرق بدرجة حرارة 1650 درجة مئوية، تم الحصول على مادة المغنيسيا عالية الحرق (غير الفعالة). كما يوفر البحث إمكانية إنتاج كبريتات الكالسيوم النقية ($\geq$ 98%) كمنتج عرضي لإنتاج أوكسيد المغنيسيوم.

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INTRODUCTION

Iraq is one of the prosperous countries in the field of industrial ores and minerals. In spite of this fact, there is a lack in some important ore minerals for certain industries. One of these ores is Magnesite ($MgCO_3$), which is considered the primary source for magnesia (MgO) production.

Magnesia (MgO) is one of the several materials that are vital for refractories industry; it is classified under the so called "basic refractories" that are stable to alkaline slugs, dust and fumes at elevated temperatures. These refractories are of considerable importance for furnaces lining, where the environment is alkaline (Bathia, 2011). These characteristics; together with its ubiquitousness, and moderate coast, makes magnesium oxide the right choice for heat intensive metallurgical processes, such as the production of metals, cements, and glasses (Landy, 2004).

Magnesium oxide, however, can be synthesized from some natural sources. The first source is magnesite. Other sources come from sea water, inland brines, salt lakes, which contain soluble magnesium chloride ($MgCl_2$).

Production of synthetic magnesium oxide from sea-bitterns has been practiced worldwide for decades, with some plants operating continuously since 1930. The largest sea water magnesia production plants are found in Japan, Great Britain, United States, and Ireland (Landy, 2004).

Bittern is the dense residual liquor with specific gravity ≥ 1.28 obtained after precipitation and harvesting of NaCl salt from the sea water. The sea water bittern usually contain some sodium chloride, magnesium sulfate, potassium chloride and magnesium chloride, with small amounts of bromine, boron as well as some other trace metals that are occasionally present (Aral *et al*., 2004).

The objective of this study is the production of pure magnesium oxide compatible to the Iraqi Standards for refractory magnesia brick no. 1977 of the year 1995 (Table 1) by utilizing the residual bittern resulted from the production of NaCl from seawater in Al-Basrah Saltern.

Table 1: Characteristics of magnesia brick (Iraqi Standard no.1977, 1995)

Grade \ Characteristic	Grade 1 (Burned)			Grade 2 (Unburned)		
	Class-1	**Class-2**	**Class-3**	**Class-1**	**Class-2**	**Class-3**
MgO Wt.% (Min.)	85	92	95	85	89	93
Apparent porosity % (Max.)	26	23	20	–	–	–
Bulk specific gravity (Min.)	2.70	2.75	2.80	2.75	2.80	2.80
Compressive strength (MPa) (Min.)	29.4	34.3	39.2	39.4	39.4	39.4
Resistance to heat under load (°C) (Min.)	1450	1550	1550	1350	1400	1450

▪ **Previous Works**

Many researchers have investigated the recovery of magnesium oxide from sea-bittern through the precipitation of magnesium hydroxide. Hereinafter, are some assorted studies.

− Panda *et al*. (1983) used calcined dolomite with a molar ratio of $MgO + CaO:MgCl_2$ in the range of 0.66:1 to 0.05:1 or using calcined limestone ratio of $CaO:MgCl_2$ in the range of 0.66:1 to 0.1:1. These ratios used to produce solid mass of $Mg(OH)_2$ at a temperature below 90 °C, which is then dried at a temperature up to 200 °C. Finally, the product was burned

in two steps. **1)** Calcination at 1200 °C, and **2)** Briquetted with binder and fired at a temperature above 1400 °C.

− Balarew *et al*. (2000) have proposed a treatment scheme to recover the salt that remains in the bittern from the sea salt plan "Tchernomorski Solnitzi", in Burges, Bulgaria. Magnesium ions were precipitated in two steps: **1)** Addition of 90% stoichiometric amount of $Ca(OH)_2$ to precipitate a mixture of magnesium hydroxide and sodium chloride, and **2)** further addition of 10% excess of $Ca(OH)_2$ to remove the remainder of the magnesium. The product was calcined at 920 °C to obtain magnesium oxide.

− Gosh *et al*. (2007) applied one-step process for manufacturing of magnesium hydroxide. They added NH_4OH to a bittern containing $MgCl_2$ with mole ratios $MgCl_2:NH_3$ of 1:1.3 – 2.0, the reactions were performed at (45 – 90) °C for (5 – 30) minutes.

− Ghosh *et al*. (2010) invented a process for the preparation of MgO of high purity (> 99%) from salt bittern via intermediate formation of $Mg(OH)_2$; obtained from the reaction of $MgCl_2$ and lime. Although indirectly, i.e., $MgCl_2$ is first reacted with NH_4OH solution and the slurry was then filtered. However, the inventors did not give detailed description to the preparation of MgO.

MATERIALS AND METHODS
▪ Materials
The materials used in this study were:
── **Dolime:** Dolomite $[CaMg(CO_3)_2]$ was provided by the State Company of Mining Industries and Aquatic Insulation. This was calcined at 1000 °C to obtain what is so called dolime (calcined dolomite, CaO.MgO). The chemical composition of the raw and calcined dolomite is shown in Table (2), as where the XRD patterns are shown in Figs. (1 and 2), respectively.

Table 2: Chemical composition of the used raw and calcined dolomite (Dolime)

Composition (%)	I.R.	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I
Dolomite	3.97	0.30	0.21	29.46	20.05	0.57	0.07	45.33
Dolime	4.00	0.62	0.94	51.03	37.45	0.58	0.06	3.72

── **Limestone:** limestone $(CaCO_3)$ was brought from Wadi Ghadaf region, in the Iraqi Western Desert. This was calcined at 1000 °C to produce lime (CaO). The chemical analysis of limestone and lime are given in Table (3), while Figs. (3 and 4) show the XRD patterned of these materials.

── **Sea Bittern:** Sea water was brought from the Arabian Gulf and it was solary evaporated at the Research and Development Section, Central Laboratories in GEOSURV, to obtain bittern solution having density of about 1.22 gm/cm^3 (26 Baume). Its chemical composition is shown in Table (4).

── **Calcium Chloride Hydrate:** The used $CaCl_2.2H_2O$ is of a laboratory grade (72% $CaCl_2$), BDH, England.
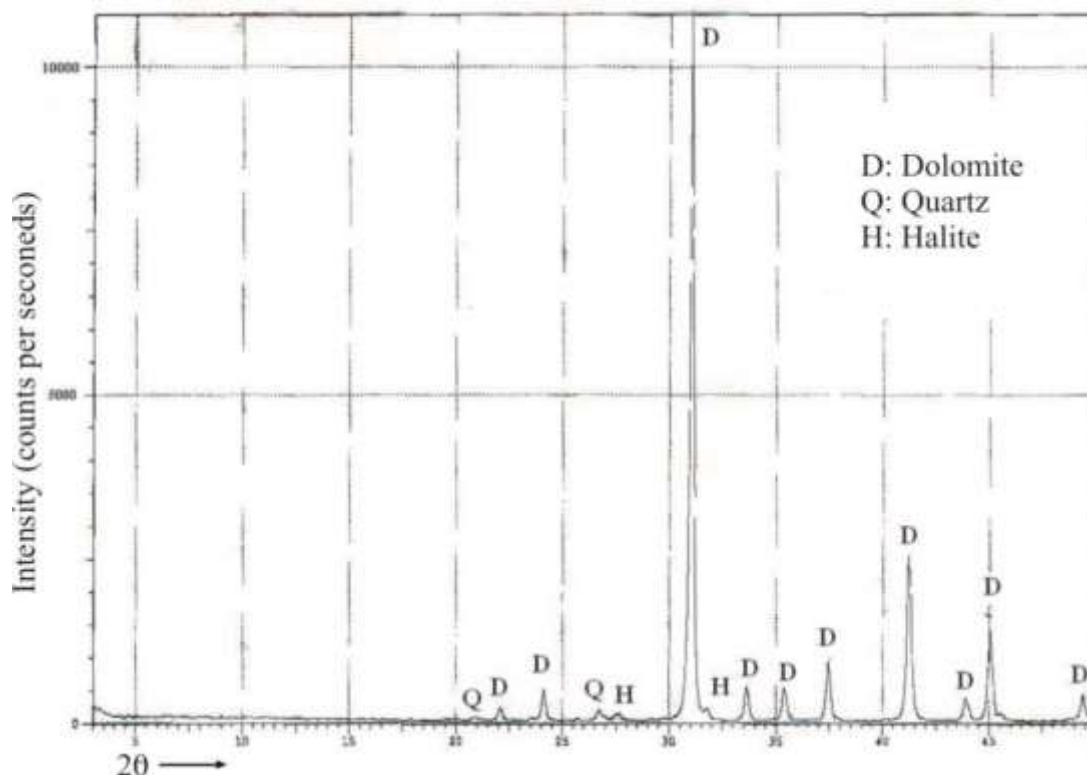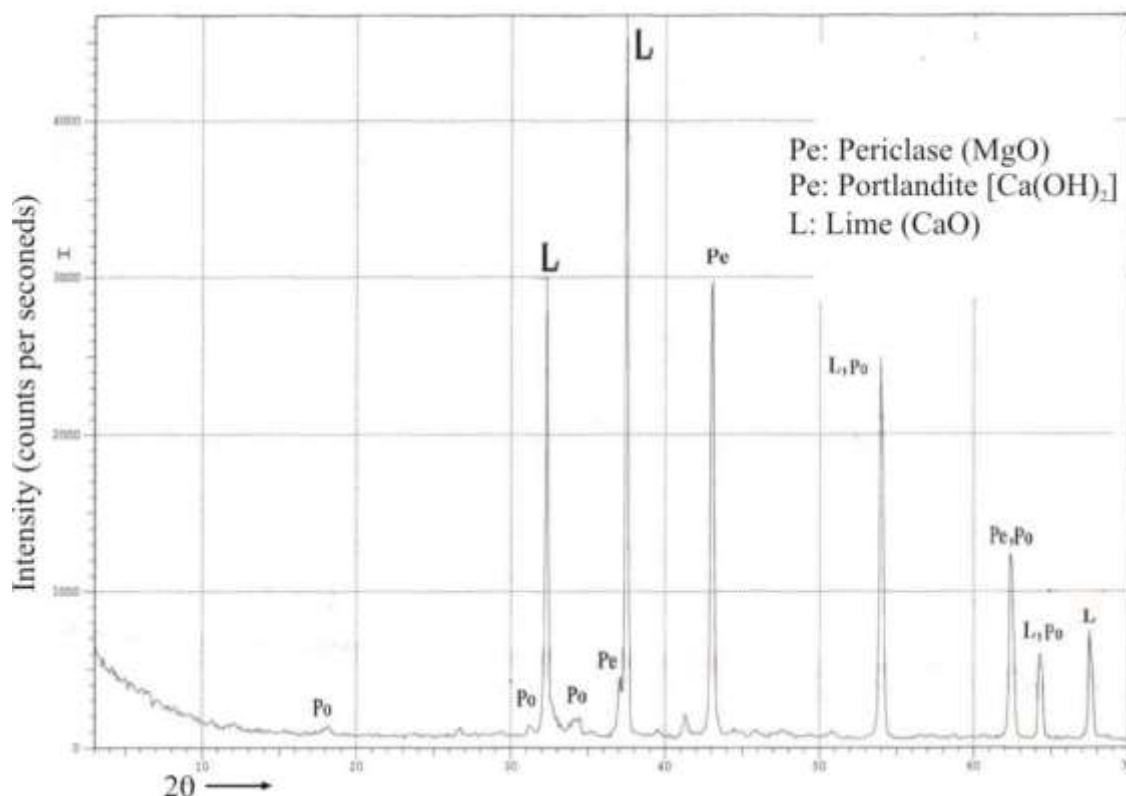
Fig.1: XRD Pattern of raw dolomite

Fig.2: XRD pattern of calcined dolomite (Dolime)

Table 3: Chemical composition of the used raw and calcined limestone

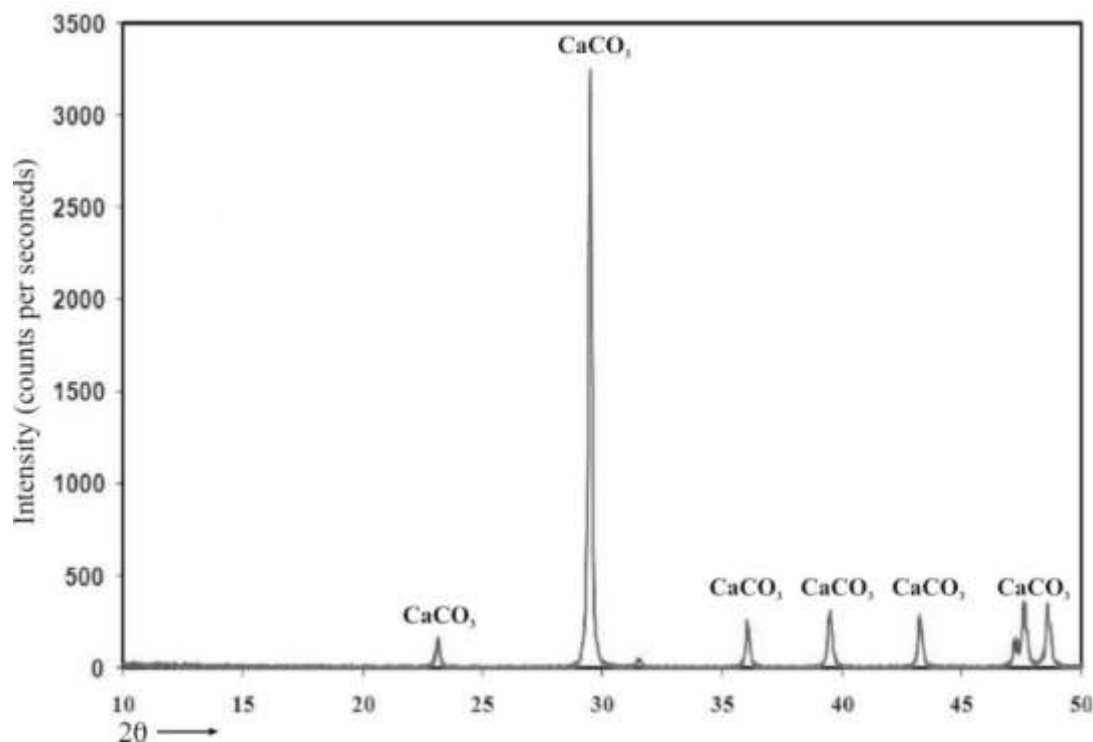| Composition (%)	CaO	MgO	Fe₂O₃	Al₂O₃	SO₃	L.O.I
Limestone (CaCO₃)	54.78	0.15	0.089	0.13	0.07	43.12
Lime (CaO)	88.07	10.81	0.060	0.13	0.08	10.18

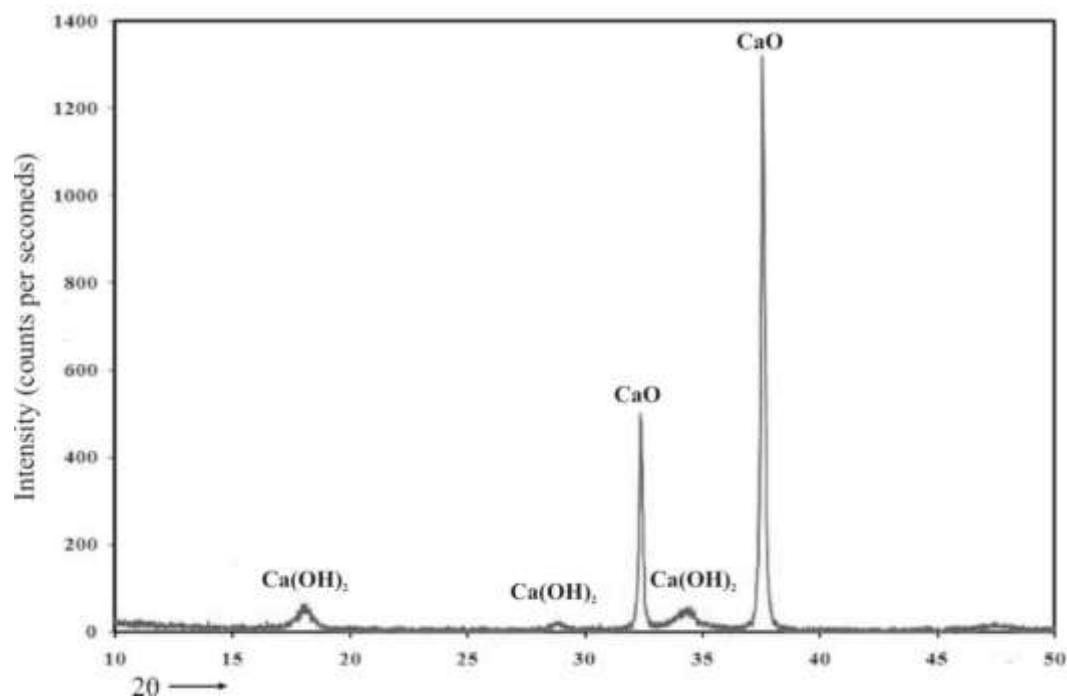

Fig.3: XRD pattern of the raw limestone

Fig.4: XRD pattern of the calcined limestone (Lime)

Table 4: Chemical composition of the used sea water and sea bittern

Composition (g/l)	Na	K	Ca	Mg	SO_4	CO_3	Cl
Sea water (4.9 Baume)	1.719	0.0511	0.028	0.090	0.368	0.012	2.276
Sea bittern (26 Baume)	101.67	4.2468	0.600	15.68	21.57	0.580	191

▪ **Methods**
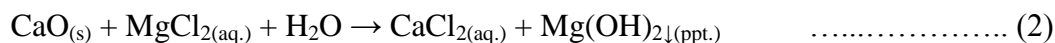The preparation of light-burned magnesia (MgO) was carried out through three stages:
─ **Preparation of Lime, Dolime and Sea Bittern:** This stage includes the preparation of the lime from limestone, dolime from dolomite, and bittern from the sea water. The limestone and dolomite were crushed to – 10 cm partical size, and then calcined in a muffle furnace at 1000 ^{o}C for 1 hour. Sea bittern with a density of about 26 Baume (1.22 gm/cm^3) was prepared by solar evaporation of the sea water of (4.9 Baume).

─ **Precipitation of Magnesium Hydroxide:** This was carried out through two steps: The first step includes the removal of calcium sulfate present in the sea bittern and the conversion of magnesium sulfate into magnesium chloride by the addition of calcium chloride, as it is seen in the reaction equation (1). The $CaCl_2$ was added in a different molar ratio ($CaCl_2$:$MgSO_4$), as from 1:1 to 1:1.1. The precipitated sulfate ($CaSO_4$) was filtered off and the de-sulfated bittern was used for the next step.

$$MgSO_{4(aq.)} + CaCl_{2(aq.)} \rightarrow MgCl_{2(aq.)} + CaSO_{4 \downarrow(ppt.)} \qquad .... (1)$$
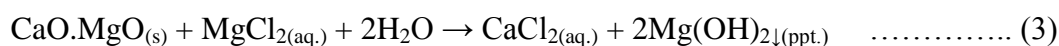
The second step, lime or dolime was added in different ratios to the total magnesium chloride (the original and that generated from conversion of magnesium sulfate) present in the bittern. The reaction of lime or dolime with $MgCl_2$ produces insoluble magnesium hydroxide and soluble calcium chloride, as it can be seen in the chemical equations shown in (2) and (3).

The precipitated magnesium hydroxide $Mg(OH)_2$ was filtered, washed and dried at 100 ^{o}C, and the filterate solution was disposed:

$$CaO_{(s)} + MgCl_{2(aq.)} + H_2O \rightarrow CaCl_{2(aq.)} + Mg(OH)_{2\downarrow(ppt.)} \qquad ….............. (2)$$

or

$$CaO.MgO_{(s)} + MgCl_{2(aq.)} + 2H_2O \rightarrow CaCl_{2(aq.)} + 2Mg(OH)_{2\downarrow(ppt.)} \qquad ….......... (3)$$

However, quick lime as well as hydrated lime can be used as presipitants for $Mg(OH)_2$. Hydrated lime was added to the bittern containing $MgCl_2$ at a molar ratio of 0.1:1, 0.5:1 and 1:1 (CaO:$MgCl_2$), and the reaction was carried out at room temperature for 1/2 and then for 1 hour. Dolime was also added in different ratios (0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1 and 1:1), and the temperature of the reaction was varied from room temperature to 70 °C. The reaction time was also changed from 30 to 60 minutes.

─ **Preparation of Magnesia (MgO):** This was carried out by the calcination of $Mg(OH)_2$ at 1000 °C for 1 hour. The product obtained is a magnesium oxide powder, which is so called "reactive magnesia" or "light-burned MgO". Further burning at 1650 °C produced a dead-burned magnesia.

RESULTS AND DISCUWSSION
▪ **Preparation of Lime, Dolime and Bittern**

The purity of the limestone and dolomite is crucial to the purity of the end product of MgO. The major impurities present in these materials are: SiO_2, Fe_2O_3 and Al_2O_3; some of these impurities are difficult to be removed and, therefore, high-purity source of limestone or dolomite is essential for preparing high-purity products (Shand, 2006). Fortunately, most of Iraqi dolomite and limestone deposits are of high quality; as it can be seen from the chemical analysis (Tables 1 and 2).

Lime was prepared from Wadi Ghadaf limestone by calcination at 1000 °C. The optimum conditions of calcination were based on a previous work (Muslim and Mustafa, 2011), calcination was done at 1000 °C for one hour socking time. The purity of the product was of about 98% CaO.

Dolime was obtained from the calcination of dolomite. Five experiments were conducted for the optimization of calcination process. This was done via measuring the loss in weight upon heating for one hour at various temperatures (750, 800, 900, 1000 and 125 °C), and the results (Table 5) were used as function of calcination efficiency.

Table 5: Loss in weight as a function of calcinations efficiency

Calcination Temperature (°C)	750	800	900	1000	1250
Loss in weight (%)	8.65	20.27	41.87	46.60	46.70

The data (Table 5) shows that the loss in weight significantly increases as the temperature rises from 750 °C to 1000 °C. Rising the temperature above this level had resulted in a minor increase in the weight loss. However, the theoritical calculated loss in weight of dolomite is around 46.75%; based on the chemical analysis of the raw dolomite, thus, the loss in weight at 1000 °C represents about 99.70% of the theoritical loss. Therefore, a temperature of 1000 °C was considered as an optimum temperature for dolime preparation. Higher temperatures may produce a slow hydrated dolime, while calcination at lower temperatures produced light precipitated dolime that is hard to settle during hydration (Shand, 2006).

Sea bittern of 1.22 gm/cm^3 density; about 26 Baume, was prepared by solar evaporation of sea water having 4.9 Baume. The precipitated NaCl salt was separated and the solution left was used to ensure that it is equal or is about 26 Baume. This was done for memicing the production of raw NaCl salt at Al-Basrah Saltern, the sea bittern is drain out for disposal when it reaches 26 Baume.

▪ **Precipitation of Magnesium Hydroxide Mg(OH)₂**

Magnesium hydroxide [$Mg(OH)_2$] is produced worldwide by the treatment of sea water with milk of lime, or calcined dolomite (Shand, 2006, and Gilbert and Gilpin, 1951). In This study, lime (CaO), milk of lime $Ca(OH)_2$ or dolime (CaO.MgO) were used as precipitants for the Mg^{+2}, which is present as chloride and sulfate species in the sea bittern. The sea bittern was pre-treated with calcium chloride to eliminate calcium sulfate, and then it was treated with the aforementioned precipitants to obtain $Mg(OH)_2$.

▪ **Effect of Precipitant Type**

Three types of precipitants were used for the precipitation of $Mg(OH)_2$; lime (CaO), milk of lime $Ca(OH)_2$ and dolime (CaO.MgO), these were added to the pre-treated bittern to

remove $CaSO_4$ and to convert all Mg^{2+} species into $MgCl_2$ form. The precipitation experiments were carried out at room temperature for one hour with a molar ratio of addition 0.5: 1 (precipitant: $MgCl_2$).

The $Mg(OH)_2$ obtained from using different precipitants, was chemically analysed for MgO, CaO and L.O.I. The results are shown in Table (6) and the $Mg(OH)_2$ purity is presented in Fig. (5).

It is obvious from the presented results in Table (6) and Fig. (5) that the purity of the produced $Mg(OH)_2$ was highly enhanced with the addition of dolime and there is no significant difference between the addition of lime and milk of lime. The highest purity, however, was obtained when dolime was used. Moreover, the use of dolime holds some advantages over lime and milk of lime, as it increases the quantity of $Mg(OH)_2$.

Table 6: Effect of precipitating type on the quality of $Mg(OH)_2$ obtained

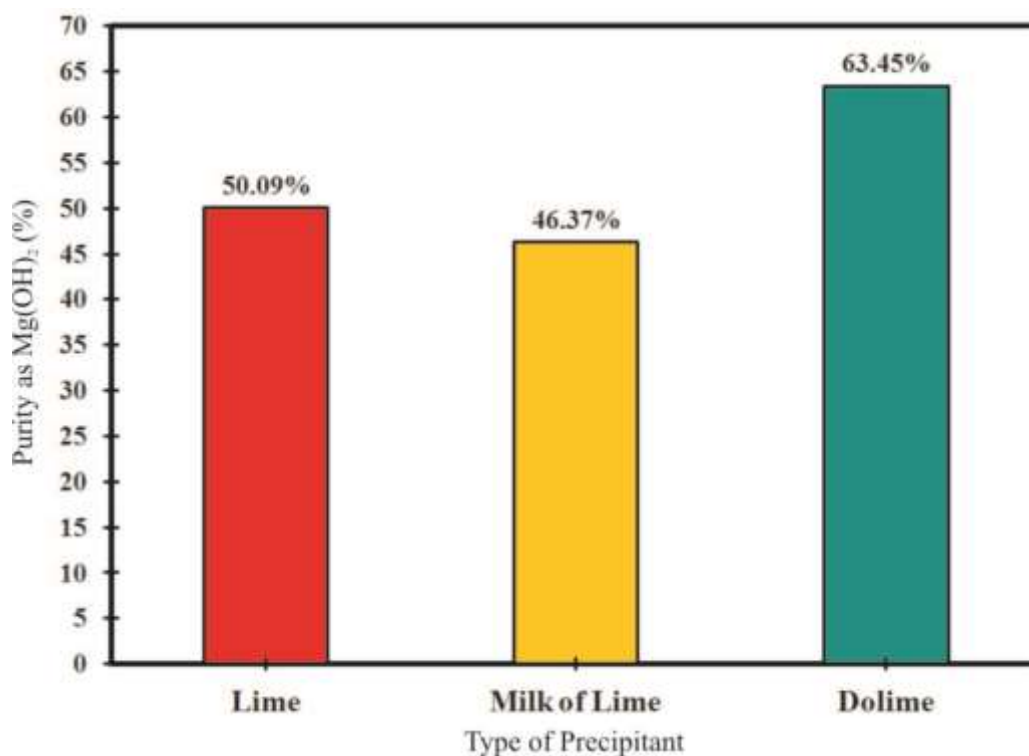| Type of Precipitant	Precipitation Conditions	MgO (%)	CaO (%)	L.O.I (%)
Lime (CaO)	- Room temp. - (1:1) $CaCl_2$:$MgSO_4$ molar ratio - 1 Hour reaction time	34.63	32.12	32.40
Milk of lime [$Ca(OH)_2$]	- Room temp. - (1:1) $CaCl_2$:$MgSO_4$ molar ratio - 1 Hour reaction time	32.06	24.08	36.16
Dolime (CaO.MgO)	- Room temp. - (1:1) $CaCl_2$:$MgSO_4$ molar ratio - 1 Hour reaction time	43.86	23.23	30.45

Fig.5: $Mg(OH)_2$ purity (%) expressed as a function of precipitant type

- **Effect of Mg^{2+} Containing Solution**

The average concentration range for Mg^{2+} ions in sea water is of about 0.9 gm/l (Schwochau, 1984), compared with that of sea bittern (15.689 gm/l). However,a precipitation of $Mg(OH)_2$ from sea water was conducted and the product was analyzed for MgO content and was compared with that of bittern at the same conditions. Table (7) and Fig. (6) show the comparison of MgO content; obtained from sea water and the bittern; as well as the purity expressed as $Mg(OH)_2$, respectively.

Table 7: The effect of Mg^{2+} containing solution

Solution Type	Pretreatment	Precipitation Temperature (^{o}C)	Precipitation Time (Min.)	Dolime:$MgSO_4$ (Molar ratio)	MgO (%)
Sea water	$CaCl_2$ (1:1)	Room temp., 25	60	1:1	36.70
Sea bittern	$CaCl_2$ (1:1)	Room temp., 25	60	1:1	43.86

Note: The World average (Mg) concentration is of about 1.29 g/l (Schwochau, 1984)
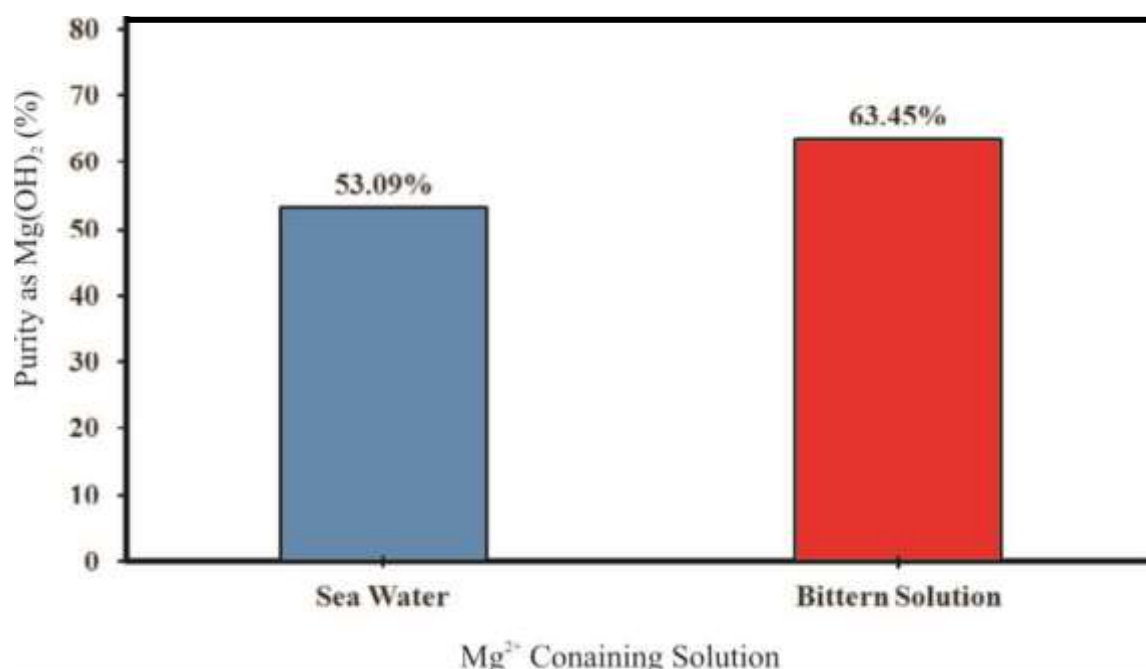

Fig.6: Purity expressed as $Mg(OH)_2$% as a function of Mg^{2+} containing solution

The results of Table (7) and Fig. (6) show that, $Mg(OH)_2$ of better purity can be obtain from sea bittern as compaired with that of the sea water. This can be attributed to the precipitation of some dissolved NaCl, $CaCO_3$ and $CaSO_4$ during the evaporation, and thus, decreasing the possibility of co-precipitation with $Mg(OH)_2$.

On the other hand, and from the technical and economical points of veiw, bittern solution is more conveneint for handling, due to needed small volume to produce an acceptable quantity of $Mg(OH)_2$. For example, each liter of the sea bittern can produce as much as 68 gm of $Mg(OH)_2$, while only 3.7 gm of $Mg(OH)_2$ can be obtaind from one litter of the sea water.

▪ **Effect of Precipitation Time**

To optimize the precipitation time, two precipitation experiments were conducted for (30 and 120) minutes (under the same conditions). Figure (7), represents the results of precipitation time as a function of purity to $Mg(OH)_2$ %.
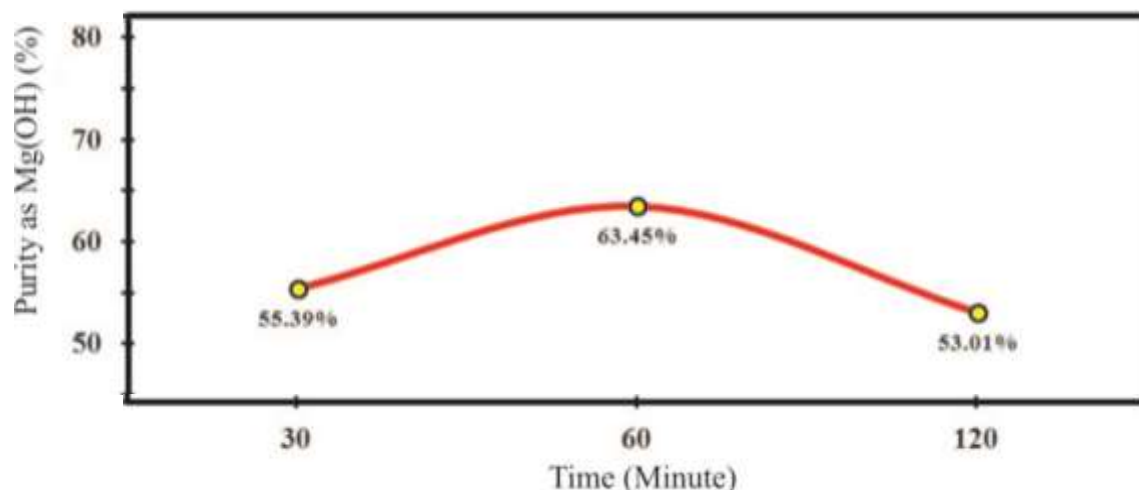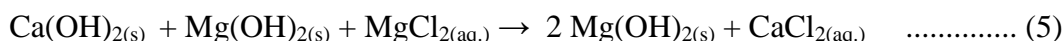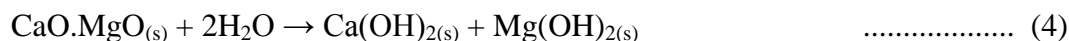

Fig.7: The effect of the precipitation time on the purity of the products

From viewing Fig. (7), it is clear that the purity of $Mg(OH)_2$ is affected by the precipitation time. The results pointed out that a period of 60 minutes is the best precipitation time. The lower purity of $Mg(OH)_2$ obtained at (30 and 120) minutes compared with that of 60 minutes can be attributed to the short time of hydration, resulted in much of the dolime (CaO.MgO); not yet hydrated as in the case of 30 minuts. As the time of precipitation was increased to 120 minutes, chances for more calcium sulfate co-precipitate had occurred.

▪ **Effect of Precipitation Temperature**

It has been stated that increasing the temperature promotes the hydration of dolime components, which in turn will enhance the exchange reaction, and hence increases the precipitation of $Mg(OH)_2$ (Hoda *et al*., 2011). To compare the heat effect on the precipitation of $Mg(OH)_2$ with that conducted at room temperature, further experiment was conducted at 70 ^{o}C, with the same conditions: 0.5:1 molar ratio of dolime to $MgCl_2$ in the sea bittern, 60 min precipitation time, and pre-treatment with $CaCl_2$ in molar ratio: $CaCl_2$:$MgSO_4$ (1:1).

From the results shown in Table (8) and Fig. (8), it can be stated that the temperature of precipitation highly influences the purity of the product, which coincides with the afore described points of view. This can be explained by the following equations:

$$CaO.MgO_{(s)} + 2H_2O \rightarrow Ca(OH)_{2(s)} + Mg(OH)_{2(s)} \qquad \text{...................} \quad (4)$$

$$Ca(OH)_{2(s)} + Mg(OH)_{2(s)} + MgCl_{2(aq.)} \rightarrow 2\,Mg(OH)_{2(s)} + CaCl_{2(aq.)} \quad \text{..............} \quad (5)$$

The equations (4) and (5) can be expressed in one equation (6):

$$CaO.MgO_{(s)} + MgCl_{2(aq.)} + 2H_2O \rightarrow 2Mg(OH)_{2(s)} + CaCl_{2(aq.)} \qquad \text{...................} \quad (6)$$
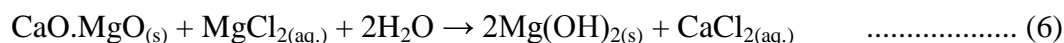
Table 8: The effect of the precipitation's temperature

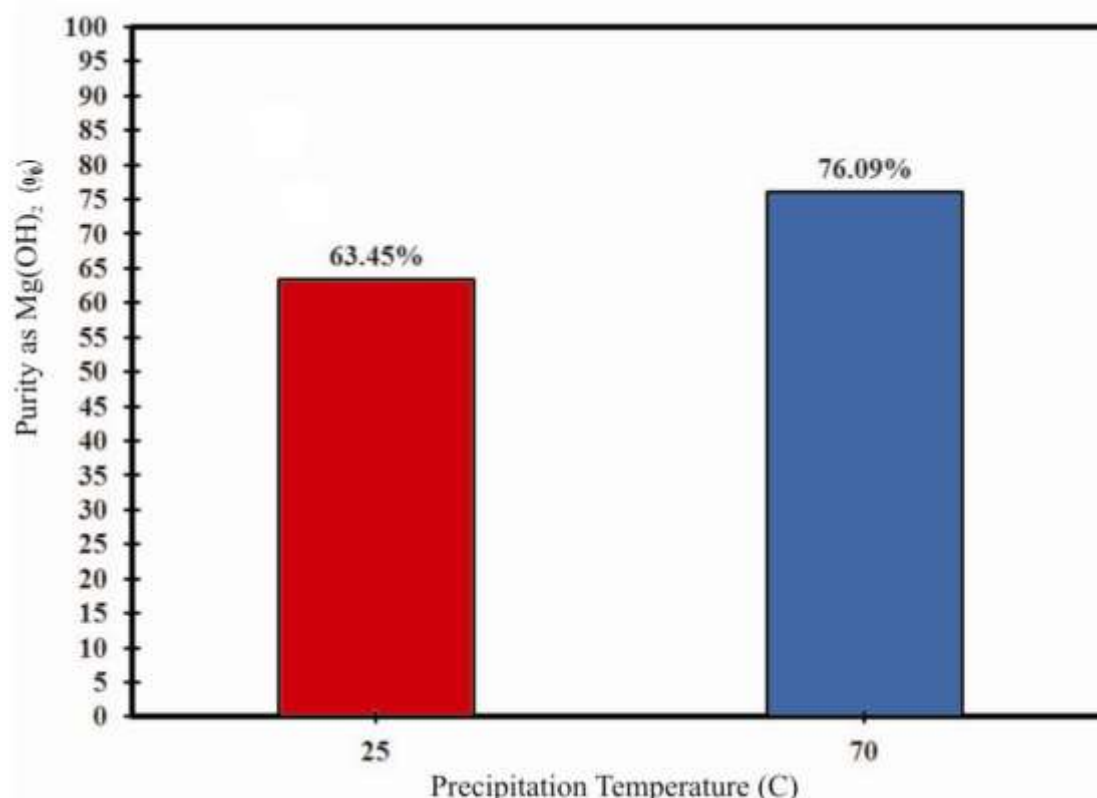| Precipitation Temperature (^{o}C)	MgO (%)	CaO (%)	L.O.I (%)
25 (Room temperature)	43.86	23.23	30.45
70 (Heating)	52.60	4.76	38.15

Fig.8: The effect of the precipitation temperature on the purity of the products

If the reaction in equation No. (4) is not completed, then it means some of the dolime was not yet hydrated, and thus, chances of undesirable substances still remain; such as CaO and MgO may had occurred. These substances are insoluble and tend to co-precipitate with $Mg(OH)_2$, as impurities that are almost unremovable from the final product.

▪ **Effect of Precipitant Molar Ratio (Dolime:MgCl₂)**
The precipitant molar ratio is supposed to be an important factor for the purity of the final product. Accordingly, several experiments were conducted using various molar ratios (0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1 and 1:1) for dolime:$MgCl_2$ at 70 °C and a reaction time of 60 min; after the pre-treatment with $CaCl_2$ (1:1). The products of these experiments were calcined at 1000 °C to produce reactive MgO. The results are given in Table (9) and presented in Fig. (9).

Table 9: The effect of the precipitant ratio on the final product contents

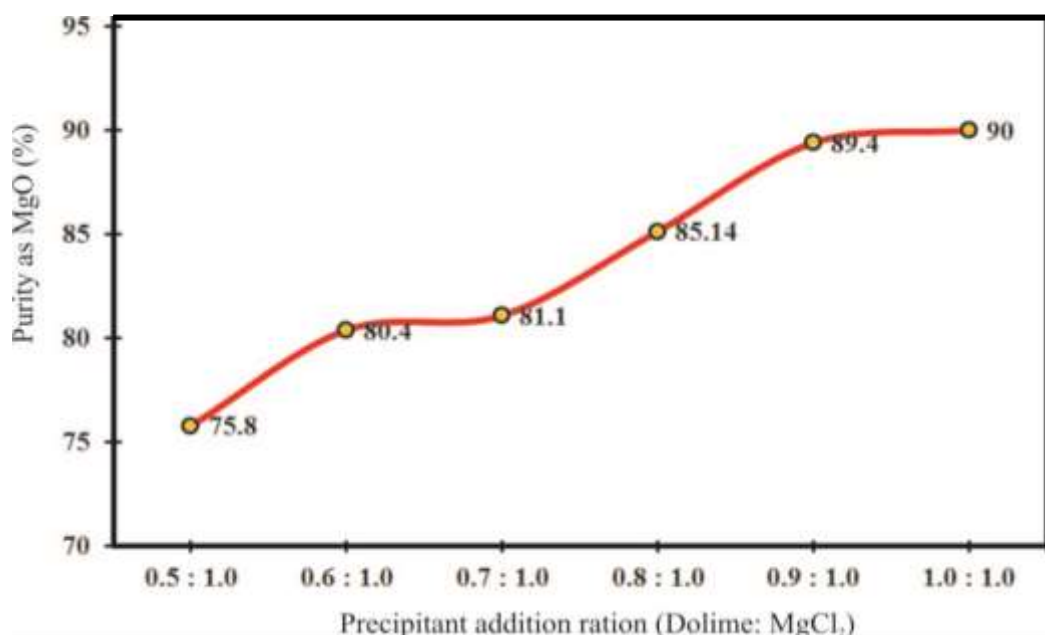| Precipitation Molar Ratio as Dolime:MgCl₂	Purity as MgO (%)	CaO (%)	SO₃ (%)	L.O.I (%)
0.5:1.0	75.80	5.88	5.35	8.12
0.6:1.0	80.40	6.44	4.98	4.81
0.7:1.0	81.10	6.02	5.18	5.53
0.8:1.0	85.14	6.44	4.70	2.23
0.9:1.0	89.40	5.60	0.28	1.87
1.0:1.0	90.00	5.04	0.21	0.23

Fig.9: The effect of the precipitant molar ratio on the purity of the final product of MgO

The results shown in Table (9) and Fig. (9) indicate that the MgO purity is directly proportional with the increase in dolime:$MgCl_2$ molar ratio, and this coincides with all previous works, like Panda (1983) and Balarew *et al*. (2000), which confirm the necessity of controlling the precipitation reaction to avoid the removal of all Mg^{2+} from the sea water, brine or bittern. Uncontrolled precipitation may lead to the possibility of co-precipitation of calcium sulfate, which reaches a critical point of solubility when about 75% of the Mg^{2+} was precipitated. Fortunately, supersaturated solutions of calcium sulfate are quite stable and precipitation dose not normally cause a problem for contaminating the precipitated $Mg(OH)_2$, hence extraction of magnesium from these solutions can be safely carried out up to 95% purity (Shand, 2006).

▪ **Effect of Molar Ratio ($CaCl_2$:$MgSO_4$) Pre-treatment**
To precipitate $Mg(OH)_2$ from the sea bittern containing $MgCl_2$ and $MgSO_4$, the later should be totally converted to $MgCl_2$; therefore, the bittern must be pre-treated with $CaCl_2$. Any addition of $CaCl_2$ less than that required will left some of $MgSO_4$ soluble in the bittern. At the moment of dolime addition, the remaining $MgSO_4$ can be immediately converted to $CaSO_4$, which in turn had co-precipitated as an impurity to the $Mg(OH)_2$. Therefore, the optimization of $CaCl_2$:$MgSO_4$ molar ratio during pre-treatment stage has vital importance to the purity of the final product. This ratio however, is very critical for controlling the solubility and precipitation of Ca^{2+} and Mg^{2+} species.

Three ratios 1:1, 1.05:1 and 1.1:1 of $CaCl_2$:$MgSO_4$ were selected, the results are shown in Table (10) and Fig. (10).

Table 10: The effect of $CaCl_2$:$MgSO_4$ ratio pre-treatment on the MgO purity

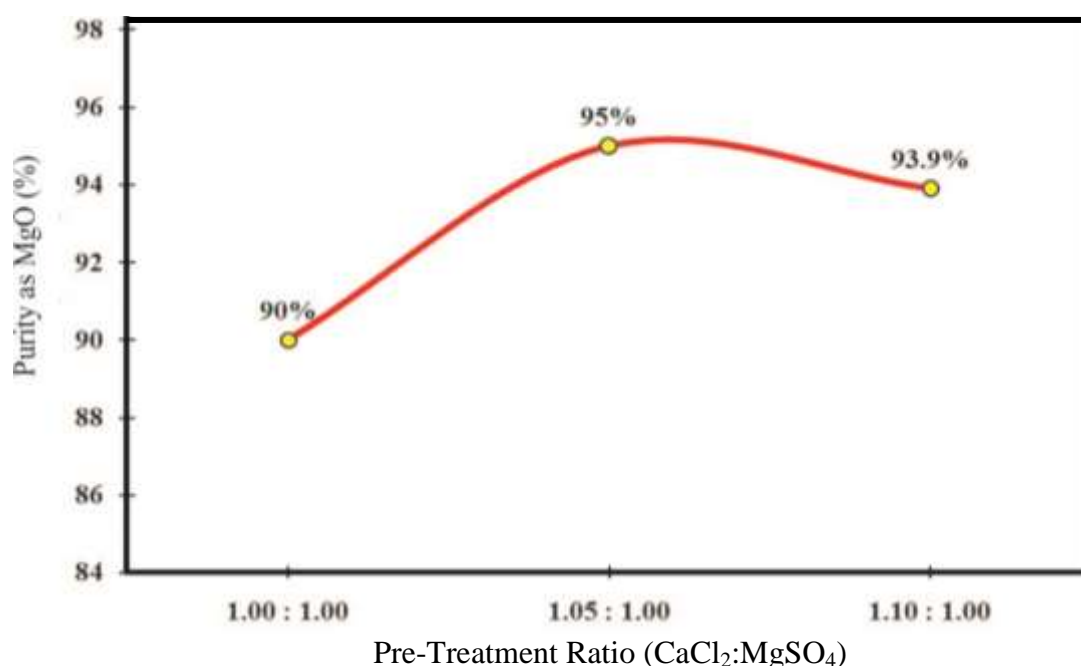| Pre-Treatment Ratio	Precipitation Temp. (°C)	Precipitation Time (Min.)	Precipitation Ratio	Purity as MgO (%)	CaO (%)	SO$_3$ (%)	L.O.I (%)
1.00:1.00	70	60	1:1	90.00	5.04	0.21	0.23
1.05:1.00	70	60	1:1	95.00	2.52	0.32	–
1.10:1.00	70	60	1:1	93.90	3.60	0.25	0.34

Fig.10: Effect of pre-treatment ratio on the purity of the product (MgO)

According to the results shown in Table (10) and presented in Fig. (10), it could be noticed that when the molar ratio increases from 1:1 to 1.05:1, the purity markedly increases, and it decreases again when the molar ratio rises from 1.05:1 to 1.1:1. This may pointed out to the best ratio that controls the contaminants co-precipitation. This supports our conclusions about the role of the addition ratio of $CaCl_2$ as a pre-treatment. This ratio is a controlling factor affecting the purity of the products and this ratio is very critical due to the very complicated composition of the sea bittern. However, the addition of dolime to the sea bittern will cause more complications, as it is shown in Table (10). XRD patterns of the products are shown in Figs. (11, 12 and 13).
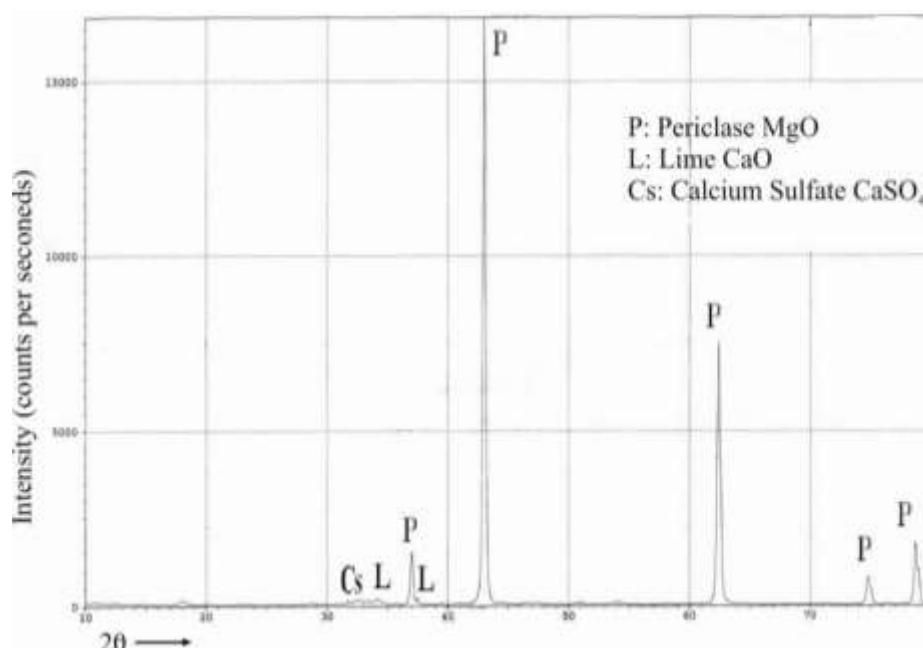

Fig.11: XRD pattern of MgO prepared using 1:1 pre-treatment ratio
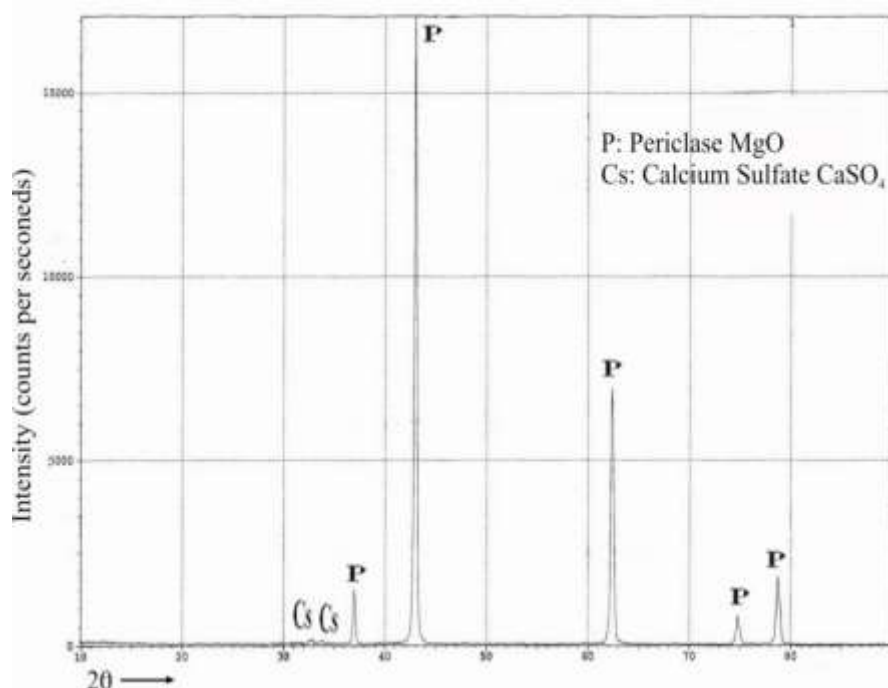
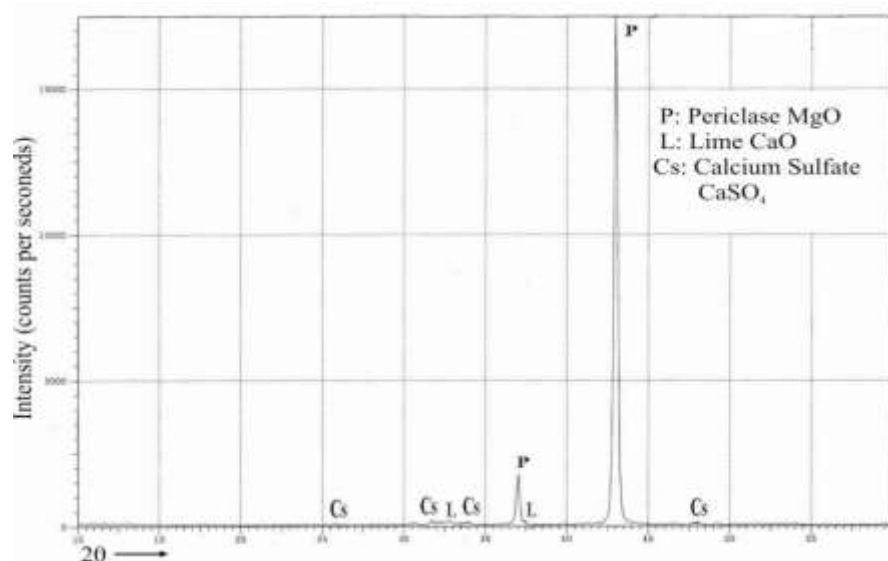Fig.12: XRD pattern of MgO prepared using 1.05:1.00 pre-treated ratio

Fig.13: XRD pattern of MgO prepared using 1.1:1.0 pre-treatment ratio

▪ **Production of Magnesia MgO**
─ **Production of Light Magnesia:** Light magnesia (reactive) was prepared by calcination of the precipitated magnesium hydroxide (prepared at the optimum conditions) at 1000 °C for 60 min. The XRD pattern of the product is shown in Fig. (14). It can be noticed that the pattern of Fig. (14) is quite similar to that in Fig. (12), and the product is pure with a little amount of contaminant represented as calcium sulfate.
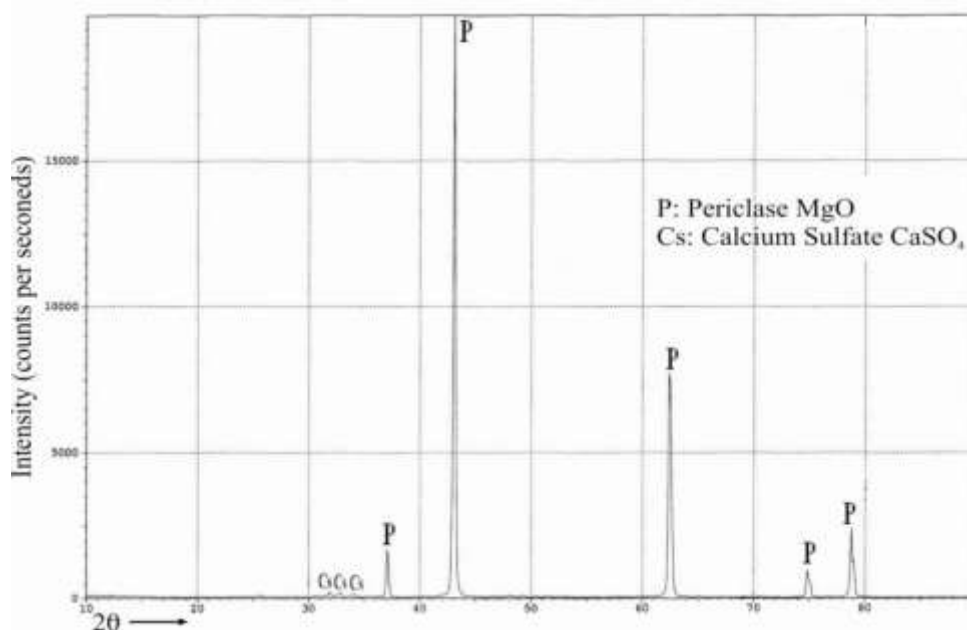
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Fig.14: XRD pattern of light-burned (1000 °C) magnesia

─ **Production of Dead-Burned Magnesia:** To obtain dead-burned magnesia, the powder of the reactive magnesia was briquette and then fired at a temperature of about 1650 °C. The dead-burned magnesia produced was dark green in color. This product was ground to less than 75μ and mineralogically analyzed. The result (XRD pattern) is shown in Fig. (15), this pattern shows absence of calcium sulfate peaks. This can be attributed to the decomposition of $CaSO_4$ starting at 1250 °C and converting to CaO. Furthermore, at 1380 °C melting of eutectic mixture of calcium oxide and non-decomposed calcium sulfate had occurred.
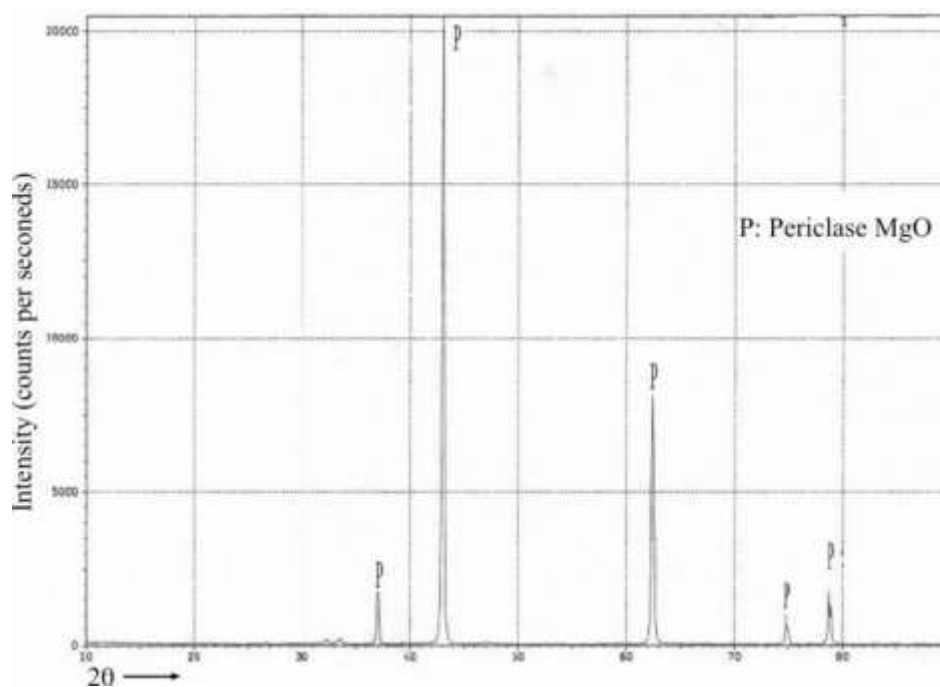

Fig.15: XRD pattern of dead-burned (1650 °C) Magnesia

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Table 11: Chemical composition of MgO produced under the optimum conditions

Optimum Conditions	MgO (%)	CaO (%)	SO₃ (%)	L.O.I (%)	Bulk Density (gm/cm³)
– Pre-treatment with CaCl₂ (1.05:1.00) – Precipitation temperature (70 °C) – Precipitation time (60 min) – Sea bittern (1.22 gm/cm³) – Precipitant ratio (1:1)	96.8	1.96	0.58	0.37	3.79*

* Burning at 1650 °C for 1 hour

As it can be seen from the data presented in Table (11), the dead-burned MgO produced fulfills the Iraqi Standard of Refractory Magnesia Brick (Iraqi Standard No. 1977, 1995).

▪ **Production of CaSO₄ as a Byproduct**

The production of MgO from the sea bittern and calcined dolomite brings other benefit; such as the production of valuable calcium sulfate, which can be produced in various phases like gypsum ($CaSO_4.2H_2O$), bassanite ($CaSO_4.1/2H_2O$) or anhydrite ($CaSO_4$); according to the drying temperature. $CaSO_4$ is precipitated once calcium chloride is added to the sea-bittern and a product of high purity ($\geq$ 98%) was obtained. Table (12), shows the chemical composition of the byproduct calcium sulfate and Fig. (16) shows its XRD pattern.

Table 12: Chemical composition of calcium sulfate, as byproduct of MgO production

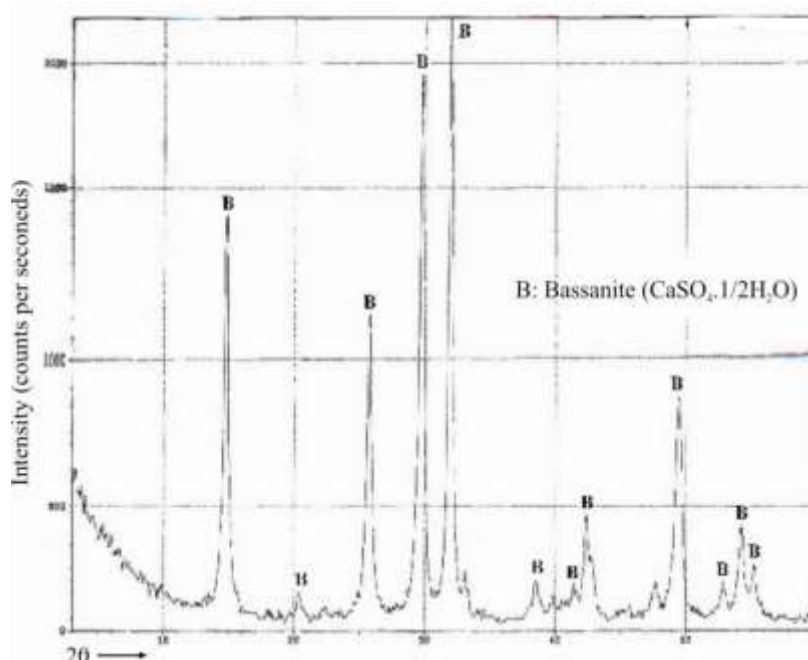| Chemical Composition (%)	CaO	MgO	SO₃	Na₂O	L.O.I
Calcium sulfate (byproduct)	39.66	0.14	54.08	0.52	5.65

Fig.16: XRD pattern of the calcium sulfate byproduct

Figure (16) shows that the calcium sulfate phase is Bassanite ($CaSO_4.1/2H_2O$), and this is confirmed by the chemical composition shown in Table (12). Bassanite phase was produced due to the drying procedure at 100 °C, however, gypsum phase can be obtained by applying another procedure of drying at 40 °C.

Figure (17) shows overall process flow diagram. Shadowed blocks represent the major steps of the process; others refer to the raw, intermediate and final product materials.
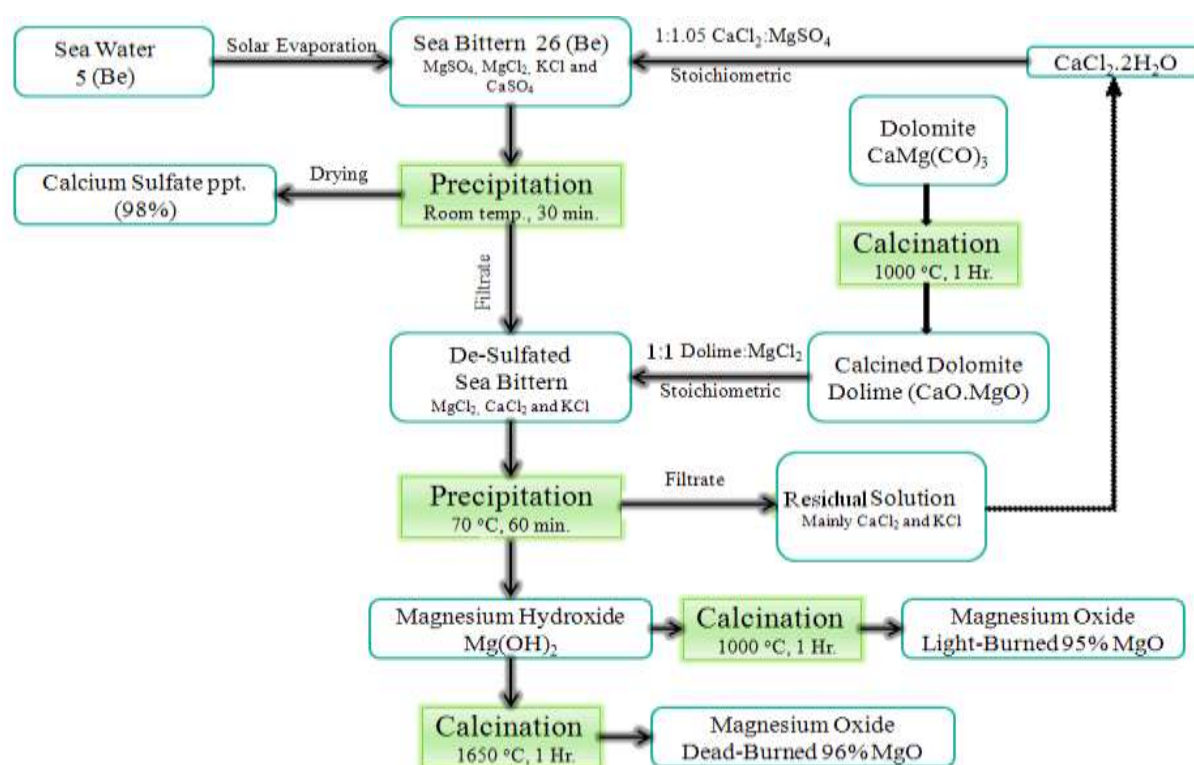

Fig.17: Flow diagram of Magnesia production from the sea bittern and dolomite

CONCLUSIONS AND RECOMMENDATIONS

According to the experimental work, the following points can be concluded and recommended:

- High purity and dense magnesia of > 96% MgO with bulk density of 3.7 gm/cm^3, compatible to the requirements of magnesia refractory brick can be produced under the following optimum conditions:
  - Pre-treatment of the sea bittern with molar ratio 1.05:1.00 of $CaCl_2$:$MgSO_4$.
  - Precipitation of $Mg(OH)_2$ using calcined dolomite (dolime) as a precipitant in a stoichiometric molar ratio (1:1) of $CaO.MgO$:$MgCl_2$. The precipitation reaction should be conducted at 70 °C, and for 60 min.
  - The precipitated $Mg(OH)_2$ should be burnt at (1000 and 1650) °C to obtain light-burned magnesia and dead-burned magnesia, respectively for 60 min.
- A valuable byproduct of the $Mg(OH)_2$ precipitation can be obtained as a high purity (≥ 98%) of Calcium Sulfate.

From the executed study, the following can be recommended:
- It is advisable to carry out a bench-scale study to assure the results of this work.

- It is recommend to use the dolomite of Khadary deposit, located about 40 Km southwest of Samawa city; as it is the nearest deposit to Al-Basrah saltern, to minimize the coast of transportation.
- Planning for establishment a unit of magnesia production from the sea bittern in or near Al-Basrah saltern.

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