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LABORATORY STUDY OF MgO PREPARATION FROM IRAQI DOLOMITE BY LEACH-PRECIPITATION – PYROHYDROLYSIS PROCESS

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ABSTRACT

In this study, a three-process approach was applied for the extraction of Magnesia (MgO) from Iraqi dolomite. The first process comprises leaching of (– 2 mm) raw dolomite in 25% solid by 22% HCl aqueous solution for 10 minutes at room temperature, extracts 99.68% of MgO in the dolomite ore. The second process, which is a separation process, includes two-steps (hydration and carbonation) for the separation of calcium as Precipitated Calcium Carbonate (PCC, 1st stage) of 90.1% purity and a magnesium recovery of 92.8% as dissolved $MgCl_2$. Hydration was carried out by adding 55% by weight ratio of calcined dolomite (dolime)/ leached dolomite at 70 °C for 60 minute; this was followed by carbonation of the slurry formed by CO_2 gas at a pressure of 2 bars for 100 minutes at room temperature. The $MgCl_2$ solution produced was subjected for evaporation to remove the dissolved Calcium Bicarbonate by precipitation as (PCC, 2nd stage) with a purity of 97%. The purified brine was further evaporated till dry salt of $MgCl_2.6H_2O$ (Bischofite) was obtained, and then subjected for pyrohydrolysis, which was the third process, at 650 °C for 60 minutes. 22% HCl was regenerated with a product of 95.48% MgO purity after washing with water and drying.

دراسة مختبرية لتحضير أوكسيد المغنيسيوم من الدولومايت العراقي بطريقة الإذابة – الترسيب – التحلل الحراري

علاء محمد خليل مصطفى، داليا خالد حميد و تانيا فاروجان خاجيك

المستخلص

تم في هذه الدراسة استخلاص المغنيسيا (MgO) من الدولومايت العراقي باعتماد طريقة مكونة من ثلاثة عمليات منفصلة ومتتالية. تضمنت العملية الأولى معاملة خام الدولومايت ذي الحجم الحبيبي (mm 2 –) مع حامض الهيدروكلوريك بتركيز 22% ونسبة صلب 25% لمدة 10 دقائق بدرجة حرارة الغرفة لاستخلاص مايقدر بـ 99.68% من MgO الموجود في خام الدولومايت. في حين شملت العملية الثانية مرحلتين [معاملة الدولومايت المكلسن (الدولايم) مع محلول الاستخلاص ومرحلة الكربنة] لفصل الكالسيوم بشكل كاربونات الكالسيوم المترسبة (PCC، المرحله الاولى) وبنقاوة 90.1% مع استرجاع 92.8% من المغنيسيوم في المحلول بشكل $MgCl_2$ الذائب. حيث أضيفت نسبة 55% وزنا من الدولايم الى الدولومايت المعامل بالحامض بدرجة حرارة 70 °C لمدة 60 دقيقة، اتبعت بحقن غاز CO_2 في اللباب المتكون تحت ضغط 2 بار لمدة 100 دقيقة وبدرجة حرارة الغرفة. تم تبخير محلول $MgCl_2$ الناتج للتخلص من بيكربونات الكالسيوم الذائبة وتحويلها الى راسب كربونات الكالسيوم المترسبة (PCC، المرحلة الثانية) وبنقاوة 97%. وقد تم تبخير المحلول الملحي المنقى لحين ظهور راسب $MgCl_2.6H_2O$ الذي بدوره خضع لعملية التحلل المائي الحراري وهي العملية الثالثة والاخيرة بدرجة حرارة 650 °C لمدة 60 دقيقة. حيث أمكن استرجاع حامض HCl بتركيز 22% مع الحصول على راسب أوكسيد المغنيسيوم الناتج من التحلل الحراري بعد الغسل والتخفيف وبنقاوة 95.4%.

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INTRODUCTION

Iraq has many important industrial ores, but there is a lack in certain important minerals such as, magnesite ($MgCO_3$), which is the primary source of magnesium oxide production (Mustafa and Abdullah, 2013). Magnesium oxide is one of several materials that are vital for refractories industry. It is the basic refractory that withstands alkaline slugs, dust and fumes at elevated temperatures.

Magnesium oxide is usually produced by calcination of the mineral magnesite ($MgCO_3$) or from magnesium hydroxide [$Mg(OH)_2$] obtained from sea water or brine. It is also produced by thermal hydrolysis (pyrohydrolysis) of hydrated magnesium chloride ($MgCl_2$), magnesium sulfate ($MgSO_4$), magnesium sulfide (MgS), and basic carbonates (Ding *et al.*, 2001 and Duhaime *et al.*, 2002). Dolomite is an example of these carbonates, which is a sedimentary carbonate rock, consisting mainly of carbonate of calcium and magnesium [$CaMg\ (CO_3)_2$]. Dolomite occurs either as coarse granular mass or fine-grained compact mass. The crystal structure of dolomite is hexagonal-rhombohedral, and it is naturally white, but may be found as creamy gray, pink, green, and black, or other colors depending on the associated impurities (Brady *et al.*, 1997; British Geological Survey, 2006).

The considerable importance of these refractory materials comes from its uses in furnace linings wherever the environment is alkaline. These characteristics together with its moderate coast, makes magnesium oxide the first choice for heat intensive metallurgical processes, such as the production of metals, cements, and glass (Bhatia, 2011 and Landy, 2004).

Hammodi (1981a and b), prepared MgO of 95.62% and 98.2% purity from dolomite deposit of Al-Khadari (Muthana Governorate) and Rutba city (Al-Anbar Governorate) respectively. His method comprises the following major steps; selective calcination at temperatures between 800 – 850 °C with six periods of time in the range of 10 – 60 minutes. Then he subjected the semi-calcined dolomite for crushing to pass through 2.4 mm. The (– 2.4) mm semi-calcined dolomite was then wetted and ground ball milling to a fineness of (– 90) µm. The ground slurry was heated to 90 – 95 °C, diluted and treated with CO_2 gas under 4 – 5 bar pressure for 30 minutes. The magnesium carbonate produced was then calcined at 1200 °C to produce MgO. The major drawback of this procedure is the low recovery of MgO (60 – 70) %. In addition, the magnesium- bearing carbonate ores contain varying amounts of silica, iron oxide, alumina and calcium silicates, carbonates and oxides, and these may represent impurity in the final product that can not be separated by physical methods. The present work was mainly inspired by the successful experiments carried out by Yildirim and Akarsu (2010) to produce MgO from dolomite by leach-precipitation-pyrohydrolysis process. Optimization of the process in the present work, however, considered the mineralogical and chemical characteristics of the Iraqi dolomite is used as a raw material. Al-Bassam *et al.*, and Barbooti *et al.* (2002), prepared Mg-compounds from Iraqi dolomite deposits. They prepare multi-phase $MgSO_4.nH_2O$ and $Mg(OH)_2$ in pharmaceutical specifications using Al-Khadary dolostone and H_2SO_4.

MATERIALS AND METHODS

▪ Materials

Materials used in this work are described below:

– **Dolomite [$Ca\ Mg\ (CO_3)_2$]:** A dolomite sample of 50 Kg was brought from Al-Khadari deposit; it lies in Al-Muthana Governorate, 41 Km southwest of the city of Samawa near the paved road of Samawa – Salman. These are large deposits having high purity (19% MgO Min.). Average thickness of the dolomite layers is 11.5 m, which lies barren (without overburden), or covered by friable soil with an average thickness of 1.37 m. These deposits belong to the Dammam Formation from the Middle – Eocene age. Reserves put forward for exploitation are 188 million tons (category C2) (Al-Koomy, 1982). The chemical and mineralogical analysis of this dolomite and dolime samples are shown in Table (1) and XRD pattern in Figures (1 and 2).

– **Dolime (CaO.MgO):** This was obtained by calcining the dolomite at 1000 °C for 60 minutes. Figure (2) shows its XRD pattern and Table (1) shows its chemical analysis.

– **HCl:** A commercial grade of concentrated HCl (32%) was obtained from Al-Forate State Company/ Ministry of Industry and Minerals.

– **Carbon Dioxide Gas:** A technical grade CO_2 gas, of no less than 90% purity was obtained from Baghdad Company for Gaseous Drinks Production/ Ministry of Industry and Minerals.

Table 1: dolomite and dolime chemical compositions

Component (%)	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	1.50	0.62	0.94	51.03	37.54	0.19	0.06	3.72

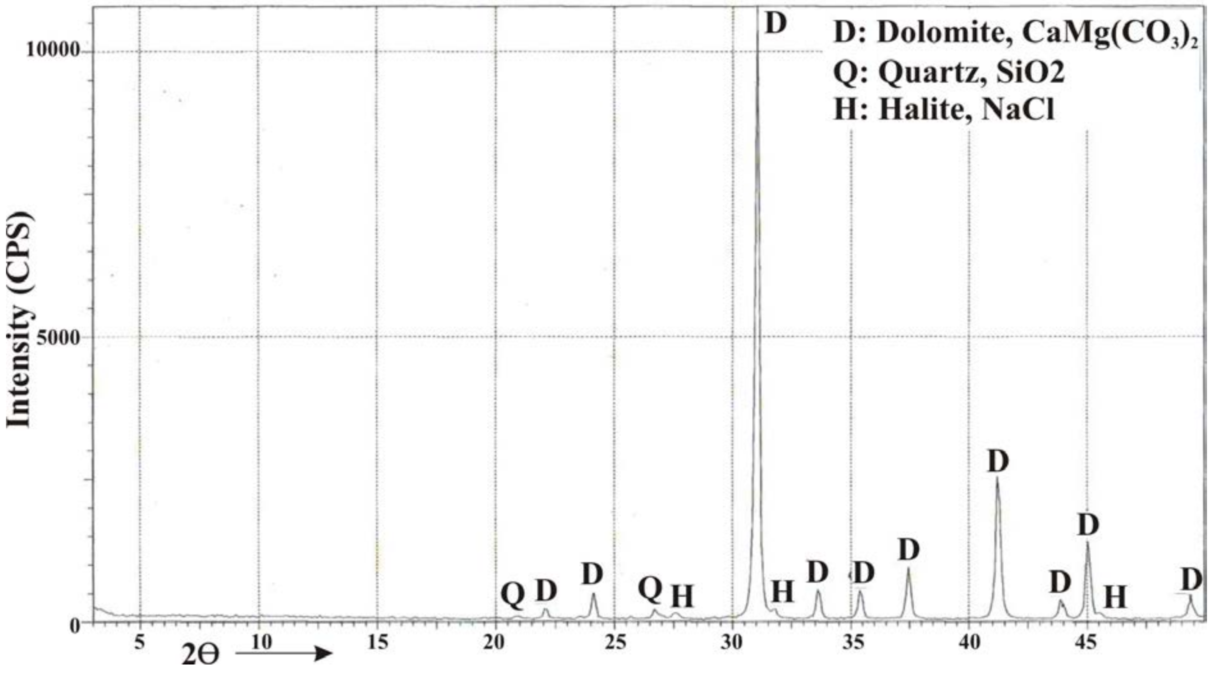

Fig.1: Dolomite XRD pattern

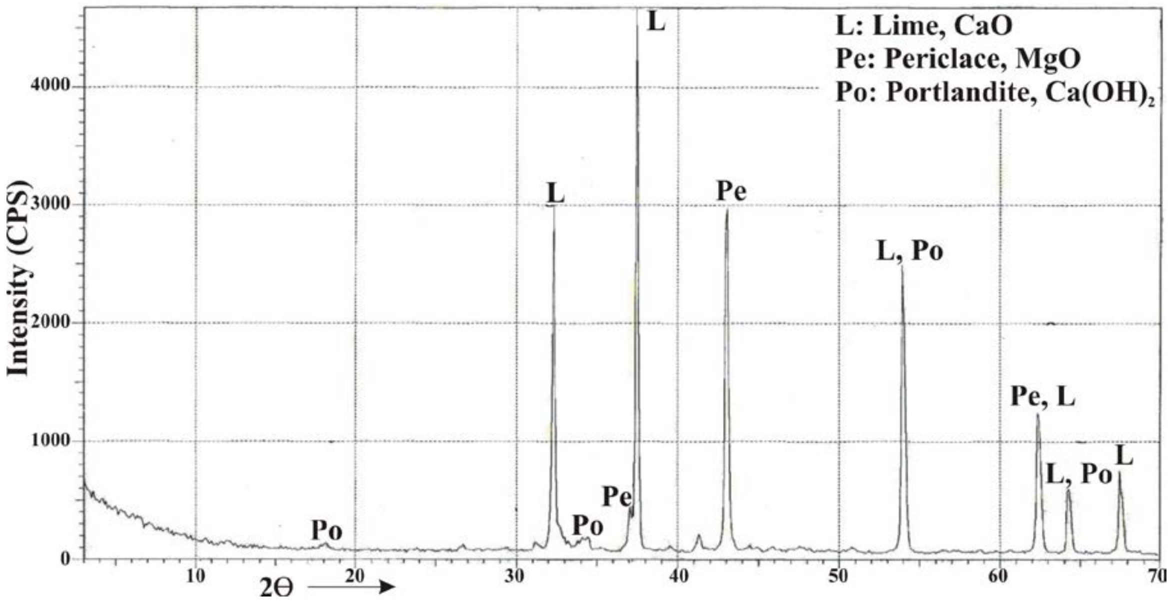

Fig.2: Dolime XRD pattern

▪ **Methods**

– **Sample preparation:** A dolomite sample of 50 Kg was subjected for quartering and dividing to obtain representative samples after crushing and sizing into (– 4 cm) size fractions. These fractions were further ground to pass (– 1 and – 2) mm sieve opening, for leaching experiments. Some samples were calcined at 1000 °C for 60 minutes, and ground to pass 75 µm, to be prepared for separation experiments. The extraction of MgO from the dolomite was carried out over three separated processes:

– **Process Steps:**

- **Leaching (dissolution):** Leaching or dissolution process was conducted using two dolomite particle size (– 1 and – 2) mm samples with various concentrations of HCl (20, 22 and 24) %, at different solid percentages (20, 25 and 30) %, and under two different temperatures (25 and 50) °C for several periods of time (5, 10, 20 and 40) minutes. HCl concentration in the acidic solution was determined by titration with 4N NaOH.

- **Separation:** This process can be subdivided into two steps:

  Hydration: In this step, calcined dolomite (dolime) is added to solution resulted from the leaching (dissolution) of dolomite, containing $CaCl_2$ and $MgCl_2$; Variable (Wt./Wt.) ratios of (dolime/ dolomite) to the leached solution were added (47.5, 50, 52.5, 55, 57.5 and 60) at two different temperatures (25 and 70) °C for 60 minutes. Two volumes of (1000 and 2000) mL/l from the hydration solution, were made.

  Carbonation: In this stage, CO_2 gas was injected into the slurries resulted from the hydration stage. Carbonation induced the separation of calcium ions as a Precipitated Calcium Carbonate (PCC) and mostly $MgCl_2$ remained in the solution after filtration.

Two slurry volumes of (1000 and 2000) mL were made, and the slurry introduced into a reactor under different pressures of (0.5, 1 and 2) bars for two periods of time (60 and 100 minutes). Special apparatus was used to conduct the carbonation stage under pressure, as shown in Figure (3).

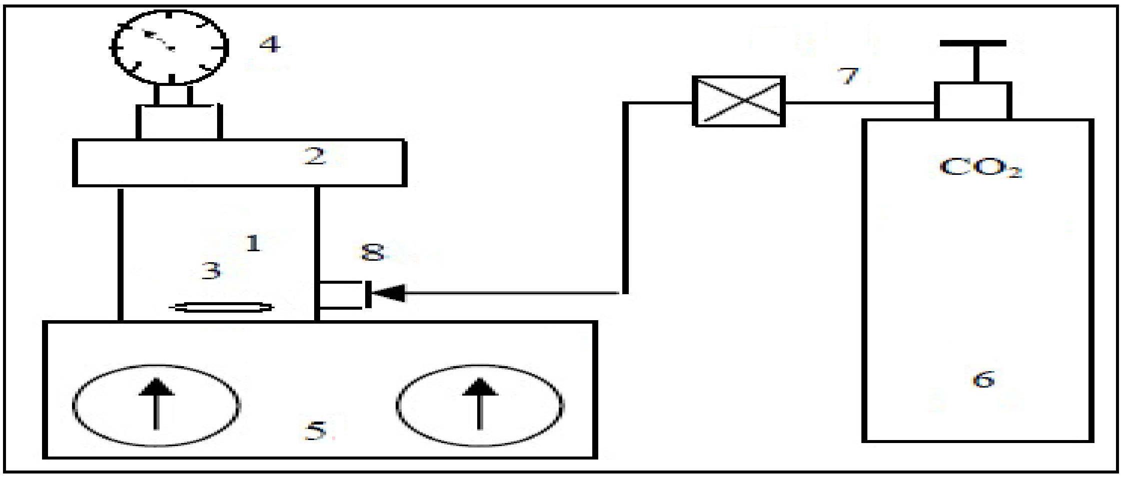

Fig.3: Schematic diagram of the carbonation apparatus: **1)** Stainless steel pressure vessel, **2)** Lid, **3)** Magnetic follower, **4)** Reactor pressure gauge, **5)** Magnetic stirrer, **6)** CO_2 gas cylinder, **7)** CO_2 gas pressure valve, **8)** CO_2 gas inlet controller

– **Pyrohydrolysis:** After the major portion of calcium ions was separated as PCC by filtration, the solution remains were pregnant with magnesium ions as $MgCl_2$. This solution of ($MgCl_2$) was evaporated till it reache a certain volume or till salt crystals appeared (saturation point). Pyrohydrolysis experiments were conducted using $MgCl_2$ as soluble, wet, and dry salt. The latter represent magnesium chloride hexahydrate salt (bischofite) $MgCl_2.6H_2O$. The process was done at different temperatures of (500, 550, 600 and 650) °C for two different periods of time (60 and 120) minutes. Special equipment was used to perform the process of pyrohydrolysis, as shown in Figure (4).

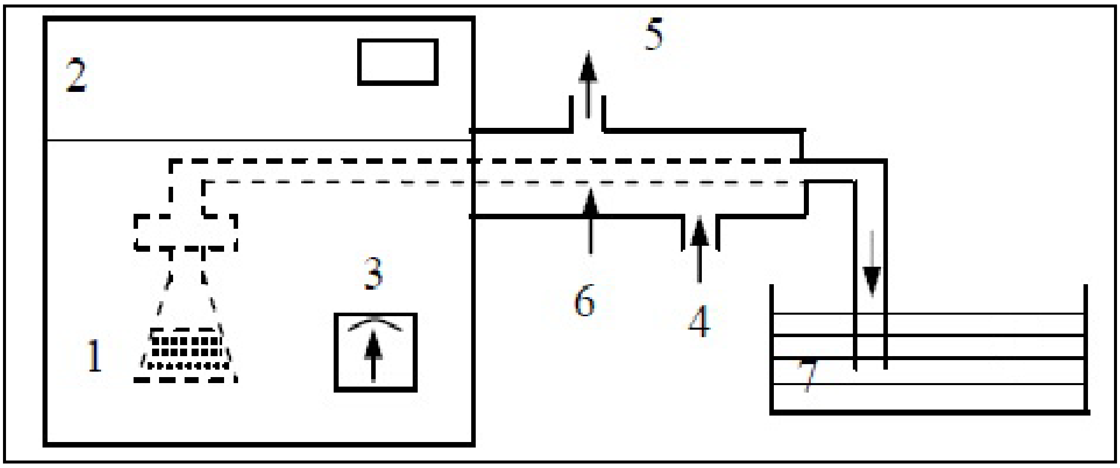

Fig.4: Simplified diagram of the pyrohydrolysis equipment: **1)** Conical flask containing the purified $MgCl_2$ solution, **2)** Heating furnace, **3)** Control unit of the furnace (0 – 1000 °C), **4)** Cool watering in, **5)** Warm water out, **6)** Flue HCl gas and water vapor carrying pipe, **7)** HCl absorber

RESULTS AND DISCUSSION

Obtaining magnesia from Iraqi dolomite was done through three series processes; leaching with HCl, separation of calcium and magnesium ions from each other and finally pyrohydrolysis of magnesium chloride. Each one of these processes, has its own parameters, and thus, optimization of each process conditions was made separately.

▪ Leaching (Dissolution) of Dolomite

Although dolomite reacts rapidly with hydrochloric acid, the reaction can actually be written in two steps (Chou *et al*. 1989), as in equations (1 and 2) below:

$$CaMg(CO_3)_{2(s)} + 2H^+ \rightarrow Ca^{2+} + MgCO_{3(s)} + H_2O + CO_{2(g)}\uparrow \quad \ldots\ldots (1)$$

$$MgCO_{3(s)} + 2H^+ \rightarrow Mg^{2+} + H_2O + CO_{2(g)}\uparrow \quad \ldots\ldots (2)$$

Chou *et al*. (1989) indicated the first step to be very rapid, and the rate of the reaction was controlled by the rate of the second step. Several studies utilize mathematical modeling methods for the optimization of dolomite leaching in HCl solutions. A recent example of these methods used is Taguchi method to determine the optimum conditions for leaching of dolomite ore in hydrochloric acid solutions. The experimental parameters were dolomite particle size, leaching temperature, solid-to-liquid ratio, and acid initial concentration, leaching time and stirring speed. The following optimum leaching parameter levels were found: temperature 50 °C, solid-to-liquid ratio 2%, acid concentration 20 g/mL (2 mol/L) stirring speed 450 min^{-1}, and leaching time 5 min. Under the optimum process conditions, the dolomite ore leaching efficiency was about 83% (Abali *et al*., 2011). Yildirim and Akarsu (2009) also studied the effect of leaching time on the dissolution of dolomite, and they proposed that the recovery of the dolomite dissolution increased with time and reached 92.43% within 5 min., then 98.20% at the end of the total period of 30 min.

The main aim of this study is the optimization of the parameters that affect dolomite leaching in hydrochloric acid solutions. To achieve this aim, a series of experiments were conducted using different dolomite particle size, HCl concentration, leaching time and leaching temperature.

▪ Effect of Dolomite Particle Size

Yilidrim and Akarsu (2010) used Turkish dolomite with a particle size of – 1.7 mm. However, they did not explain their choice, and they obtained an interesting recovery of Ca and Mg in dissolution process with HCl. In the present experiments with Iraqi dolomite particle size of – 2 mm and -1mm were used and evaluated their effect on the leaching process at different dolomite solid% in the HCl solution. The results of these experiments are shown in Figure (5). This set of experiments was carried out at room temperature (25 °C) and for 20 minutes at stirring speed of 500 rpm using 20% HCl. The results displayed in Figure (5), show some proximity, but it can be stated that (– 2 mm) particle size of dolomite is much favored, to avoid further grinding.

▪ Effect of HCl Concentrations

Although, the efficiency of leaching process in HCl was evaluated through a mono-vital factor, which is the extracted MgO%, it is not the only factor that must be taken into consideration. It is a fact that when HCl concentration is reduced, the leaching process of dolomite becomes more economic, e.g., 1 litter of 30% HCl may produce 2 liters of 15% HCl when diluted. Therefore, three HCl concentrations (20, 22 and 24) % were tested for establishing the leaching efficiency of MgO%. The experiments were carried out at room temperature (25 °C) for 20 minutes with a stirring speed of 500 rpm. The results are shown in Figure (6).

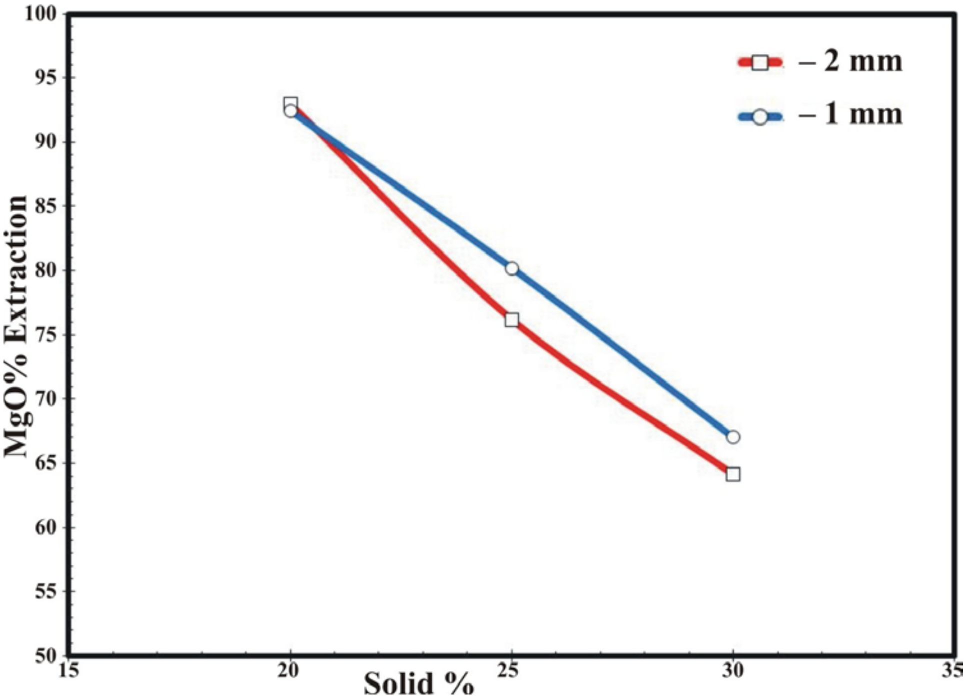

Fig.5: Effect of dolomite particle size at different solid percentage

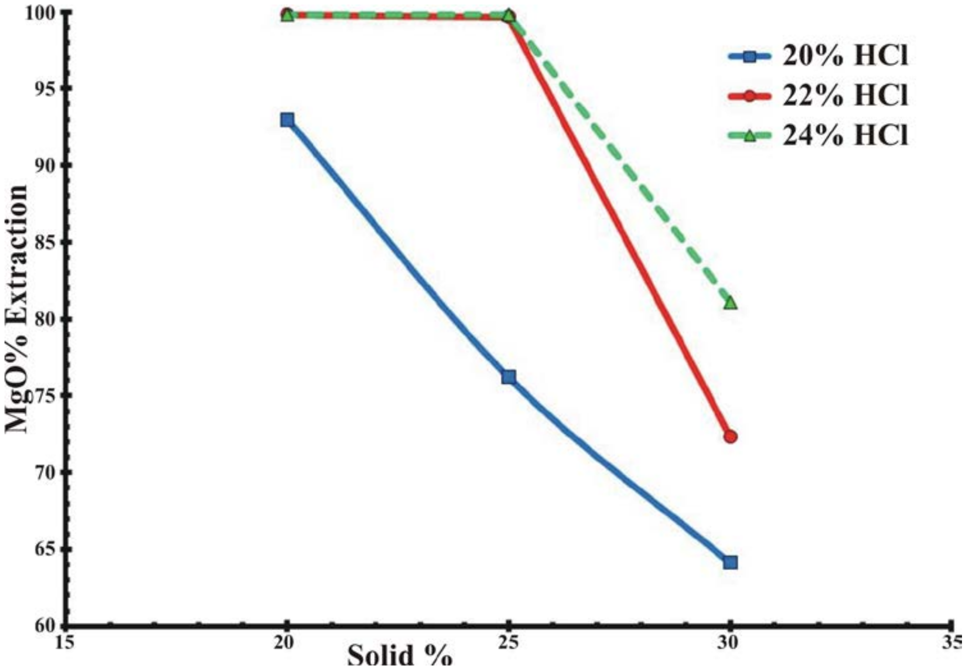

Fig.6: Effect of HCl concentration on the MgO% extraction

As it is clearly shown in Figure (6), the leaching process of MgO was not efficient in accordance with 30% solid for all HCl concentrations. Also it seems that 20% HCl is unsuitable for leaching MgO from dolomite, even at lower solid (20%). However, leaching becomes more efficient when 22 and 24% HCl concentrations are used, particularly at 25 and 20 solid%. Since comparable results are achieved at these percentages of solid and HCl concentrations, partial, logical as well as economical factors outweigh 22% of HCl for leaching of 25% of solid (dolomite).

▪ Effect of Leaching Time

Akarsu and Yilidrim (2008) claimed that, as the time increased, the rate of the dissolution decreased. The dolomite sample to be dissolved was in particular form in the acid solution and reactions (1) and (2) between the solid sample and the liquid solution started as the sample became in contact with the solution. Then, the dissolved product ions were transported from the solid surface to the liquid face due to the local hydrodynamic conditions, created by the gas (CO_2) evolution. This means that the surface area of the dolomite decreased as time proceeded due to the reduction of particles size and the disappearance of the finest particles. This is consistent with Yilidrim and Akarsu (2010) study.

To optimize the leaching (dissolution) process, the role of leaching time, was also studied. Four leaching experiments were carried out at constant conditions including; room temperature (25 °C), 22% HCl, and 25% of solid and with stirring speed of 500 rpm for different periods of time (5, 10, 20 and 40) minutes. The results are shown in Figure (7).

Results, illustrated in Figure (7), point out similar conclusion to the aforementioned previous work. In fact, the only difference found is at the leaching time of 10 minutes. It seems to be more advanced than expected by previous works with an extraction of about 99.68% of MgO presence in the dolomite sample.

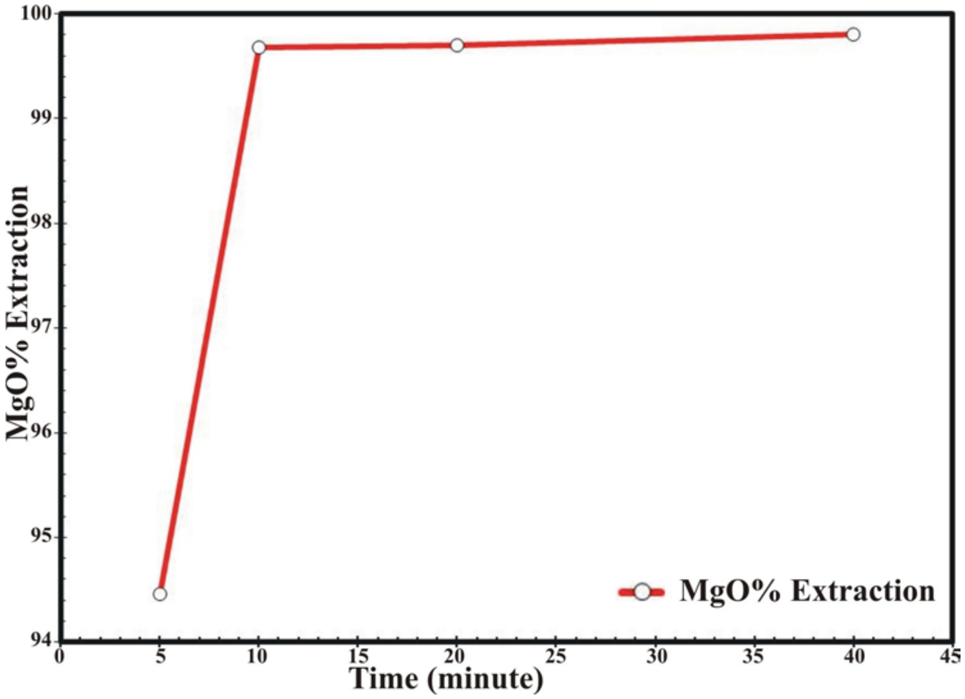

Fig.7: Effect of time on MgO% extraction

▪ Effect of Leaching Temperature

Lund *et al*. (1977) carried out a work on leaching of dolomite in hydrochloric acid. They reported that at 25 °C the dissolution process is surface reaction rate limited. As the temperature is increased up to 100 °C, the dissolution process approaches diffusion limitation even at relatively high stirring speeds (500 rpm). The rate of reaction was found to be proportional to a temperature dependent fractional power on the hydrochloric acid concentration.

To identify the best temperature at which optimum MgO extraction occurred, five experiments were done over different leaching temperatures (10, 25, 40, 50 and 60) °C, and the results of these experiments are shown in Figure (8).

Results of Figure (8) obviously show a significant increase in MgO extraction from 79.29 to 99.68% as leaching temperature increases from 10 to 25 °C, respectively. While increasing temperature from 25 to 40, 50 and 60 °C, brings slight increases in MgO extraction up to 99.8%.

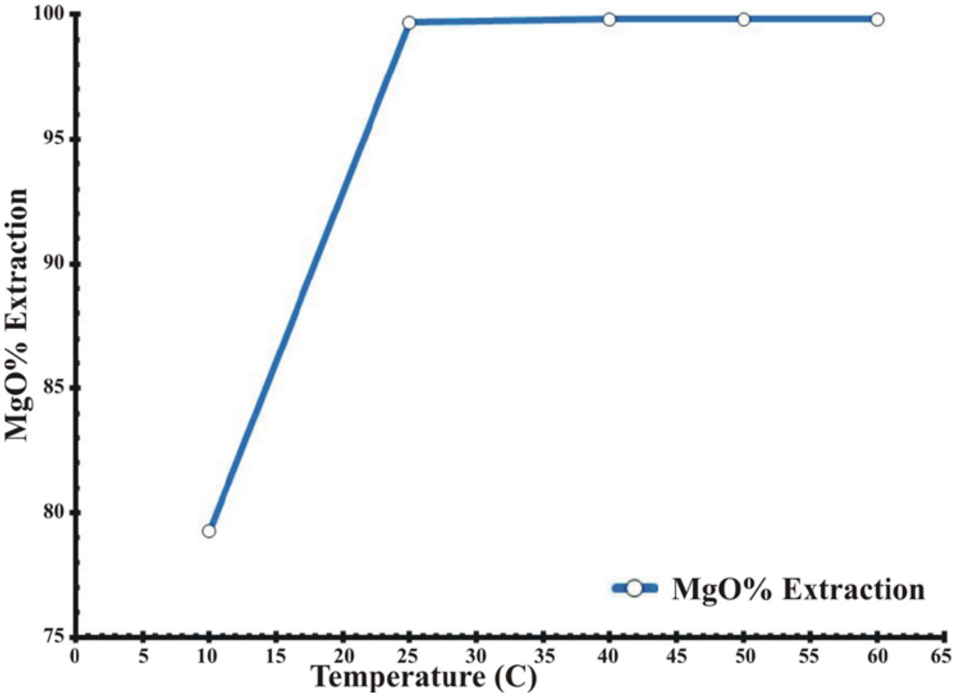

Fig.8: Effect of leaching temperature on MgO% extraction

- **Separation of Ca^{2+} and Mg^{2+}**

The second aim of this study is the optimization of $CaCl_2$ and $MgCl_2$ separation in the leach solution (leachant) produced from the previous stage. Separation of these two cations, (Ca^{2+} and Mg^{2+}) is very hard due to their similar chemical and physical properties. At this stage, separation can be made through two processes:

– **First Process** (Hydration)**:** When calcined dolomite (dolime) added to the leachant, first it will be hydrated by water. Later the hydrated dolime reacts with the leachant component and all Mg^{2+} convert to $Mg(OH)_2$ while the dominant form of Ca^{2+} ions in the solution is $CaCl_2$, as it is shown in reaction (3):

$$Ca(OH)_{2(s)} + Mg(OH)_{2(s)} + CaCl_{2(aq.)} + MgCl_{2(aq.)} \longrightarrow 2Mg(OH)_{2(s)} + 2CaCl_{2(aq.)} \quad \ldots\ldots\ldots (3)$$

– **Second Process** (Carbonation)**:** Dissolved calcium ions in the leach solution were removed by carbonation with CO_2 gas as solid $CaCO_3$ particles. Calcium carbonate precipitation is a process of considerable industrial importance, as it is used in the production of PCC. It was performed according to the following reaction:

$$CaCl_{2(aq.)} + H_2O + CO_{2(g)} \longrightarrow CaCO_{3(s)}\downarrow + 2HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The pertinent ionic reactions which occur are represented by the following steps:

$CO_{2(g)} \longrightarrow CO_{2(aq.)}$ ………………………………………………………(5)

$H_2O + CO_{2(aq.)} \longrightarrow H_2CO_3 \longrightarrow HCO_3^- + H^+$ …………………………………………(6)

$HCO_3^- + Ca^{2+} \longrightarrow CaCO_{3(s)}\downarrow + H^+$ ……………………………………………(7)

Reaction (5) is fast, but not instantaneous, and then may proceed both at the interface and in the bulk. H_2O readily reacts with CO_2 and HCO_3^- is formed in the solution (Eq.6). Chemical equilibrium favors the presence of CO_3^{2-} at pH 11, both CO_3^{2-} and HCO_3^- are formed at pH 8 – 11, while at pH lower than 8 only dissolved CO_2 is present. Calcium Carbonate ($CaCO_3$) forms at pH 7.51 reaction (7), while reaction (9) occurs only at pH above 10.45 (Akarsu, 2004).

$HCO_3^- \longrightarrow CO_3^{2-} + H^+$ ………………………………………………………(8)

$Mg^{2+} + CO_3^{2-} \longrightarrow MgCO_{3(s)}$ …………………………………………………(9)

Actually, $MgCO_3$ precipitation takes place at the beginning, and short after $CaCO_3$ start to precipitate, assisted by the increase in pressure. It means that precipitation of Ca^{2+} ions as $CaCO_3$ increased with time. However, Mg^{2+} ions associated with $CaCO_3$ precipitated first, then slowly detached from the surface of the $CaCO_3$ particles into the solution. pH of the effluent decreased as the precipitation proceeded. The total reaction under pressure can be expressed as:

$Mg(OH)_{2(s)} + CaCl_{2(aq.)} + CO_{2(g)} \longrightarrow CaCO_{3(s)}\downarrow + MgCl_{2(aq.)} + H_2O$ ………………. (10)

- **Effect of Hydration Temperature**

At a ratio of 60 wt% of dolime/ leached dolomite, two experiments were done at (25 and 70) °C to evaluate the role of hydration temperature on the separation of calcium as PCC. These two experiments were carried out under 0.5 bar of CO_2 pressure for 100 minutes. Results are illustrated in Figure (9).

As it clearly appeares in Figure (9), CaO in precipitate and MgO in solution are highly enhanced by the increasing of hydration temperature from 25 to 70 °C. This agrees with a previous work which stated that increasing the temperature promotes the hydration of dolime components which is in turn enhances the exchange reaction no. (3) (Mustafa and Abdullah, 2013). This will pave the ground for the next exchange reaction no. (10).

- **Effect of Carbonation Pressure**

Surveying literatures, it can be noticed that pressure of carbonation was not of interest. Yilidrim and Akarsu (2010), performed their work using $Mg(OH)_2$ as precipitating agent to the leach solution of dolomite with HCl, and they carried out all their carbonation experiments under constant pressure of about (2) bars.

An old United States patent described a work carried out by Pike *et al.* (1944). They stated the possibility of $MgCl_2$ production from $CaCl_2$ and calcined dolomite. They achieved carbonation at about 0.34 bars.

In this study, the effect of carbonation pressure is investigated through applying (0.5, 1 and 2) bar of CO_2 pressure. Results are shown in Figure (10).

The results of Figure (10) show, MgO in solution and CaO in precipitate are increasing with the increase in CO_2 pressure up to 2 bars. Accordingly, all the next experiments were conducted at 2 bars of CO_2.

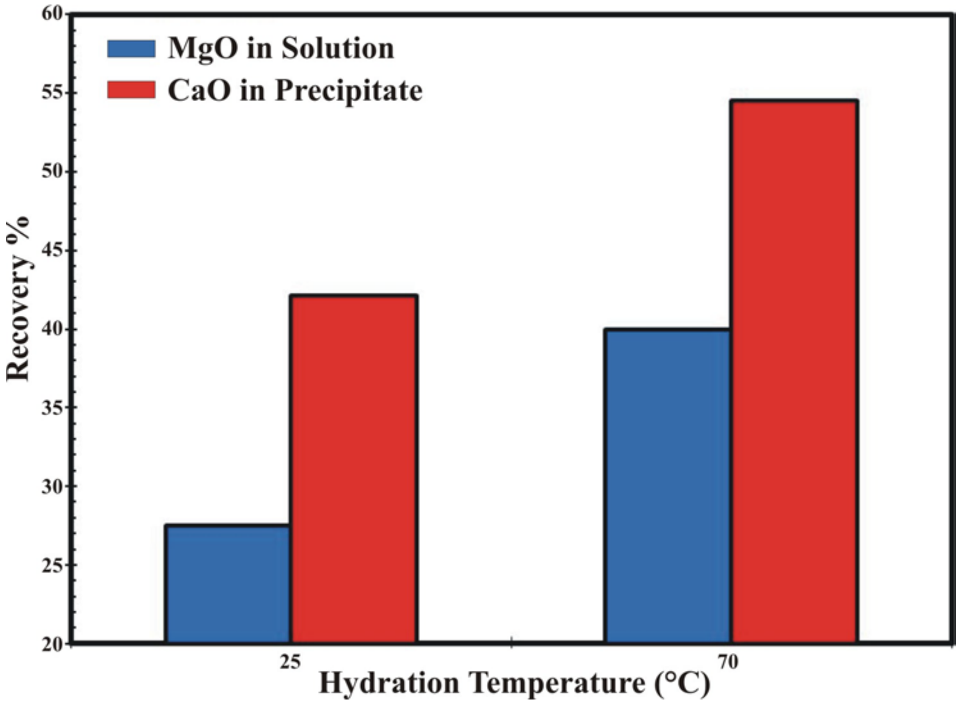

Fig.9: Effect of hydration temperature on the recovery of MgO and CaO

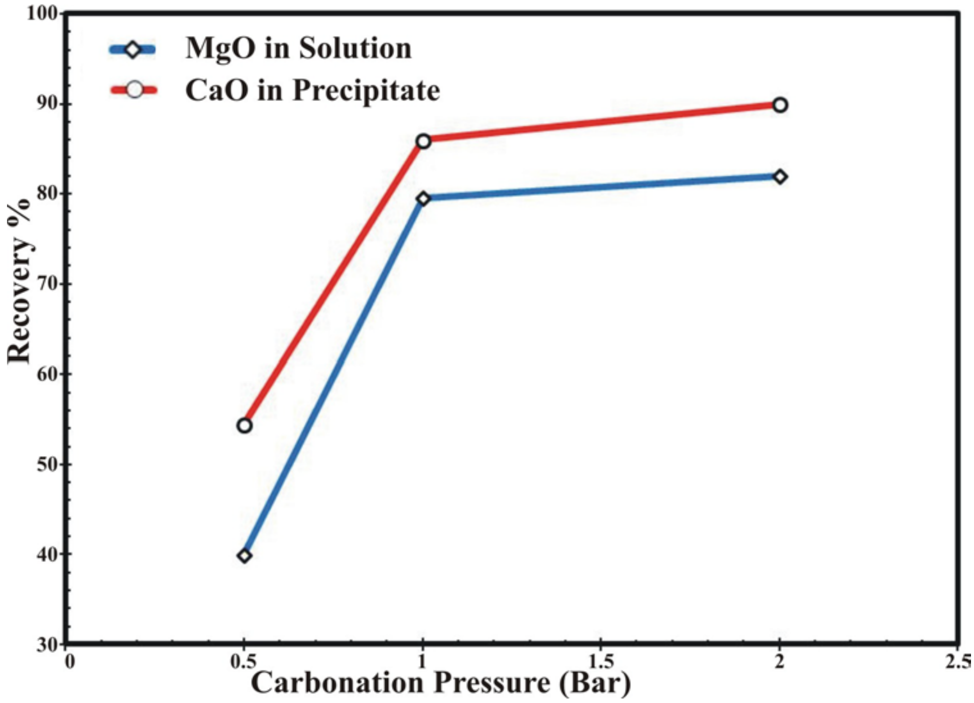

Fig.10: Effect of carbonation pressure on the recovery of MgO and CaO

Effect of Dolime/ Dolomite (wt.%) Ratio

Dolime was used in this work as precipitant for $MgCl_2$ present in leaching solution, allowing all Ca^{2+} ions to be in solution as $CaCl_2$. This will occur in the first stage (hydration) of the separation process. Almost all previous works used pH as an indication for hydration reaction completion, (reaction no. 3). All suggested basic condition with pH of more than 9.1 and 10 (Pike, *et al*., 1944) and (Yilidrim and Akarsu, 2010) respectively. In this work, dolime is added to the leaching solution (1000 ml) at 70 °C for 50 minutes until final pH reach 9.35. The slurry was carbonated at 2 bars of CO_2 for 100 minutes with a slurry volume of (2000 ml). The results of separation process at this condition, show very good recovery of MgO in solution of about 96.9%. The results, unfortunately, refer to a very bad recovery of CaO in precipitate with only 20%. This means that 80% of calcium remains as $CaCl_2$, which will represent an impurity for the final product (MgO). Therefore, other approaches have to be used to indicate completion of hydration reaction.

Stoichiometry of reaction was taken into consideration in an alternative approach. Again, results of an experiment at the same above conditions, but stoichiometric dolime addition to the $CaCl_2$ and $MgCl_2$ in leaching solution, prove weakness of such approach, when only 2.7% of MgO went into solution and 19% of CaO down to the precipitate. This meant that only a very low reaction has occurred.

Another strategy for identification of completion hydration reaction was investigated. In this approach, amounts of dolime were added to the leaching solution in respect to ratio of (dolime/ dolomite). Ratios of (47.5, 50, 52.5, 55, 57.5 and 60) wt.% of dolime/ dolomite, were used. The results are shown in Figure (11).

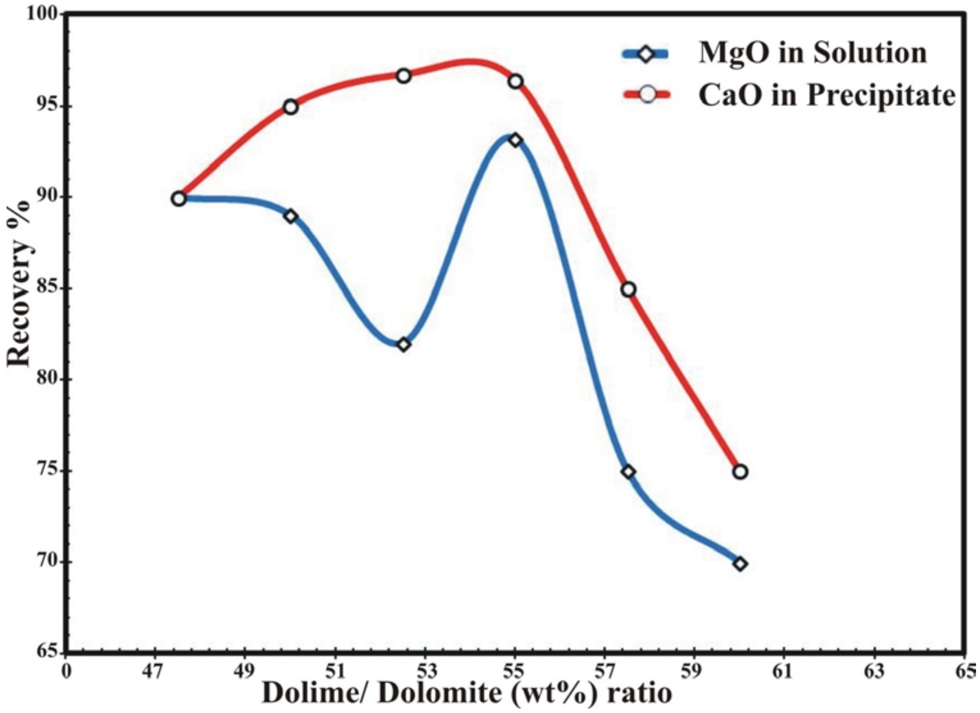

Fig.11: Effect of dolime/ dolomite ratios on the recovery of MgO and CaO

Results illustrated in Figure (11), show the non-doubtful effect of dolime/ dolomite ratio on the recovery of both CaO and MgO. However, optimum ratio is the one when both recoveries are convergent and at top of their record. Based on the aforementioned, 55% of dolime/ dolomite ratio should be considered as the optimum, since MgO in solution and CaO in precipitate are both above 90%.

- **Effect of Leaching Solution Volume**

To evaluate leachant volume on the hydration reaction, and consequently on carbonation reaction that can be expressed as recoveries of MgO and CaO, leachant volumes were made to 1000 and 2000 ml. The results are shown in Figure (12).

Results of Figure (12), show a significant effect of leachant volume on the recovery of MgO in solution and CaO in precipitate. However, results indicate that best recoveries for both MgO and CaO were achieved at low (dilution) volume and vice versa.

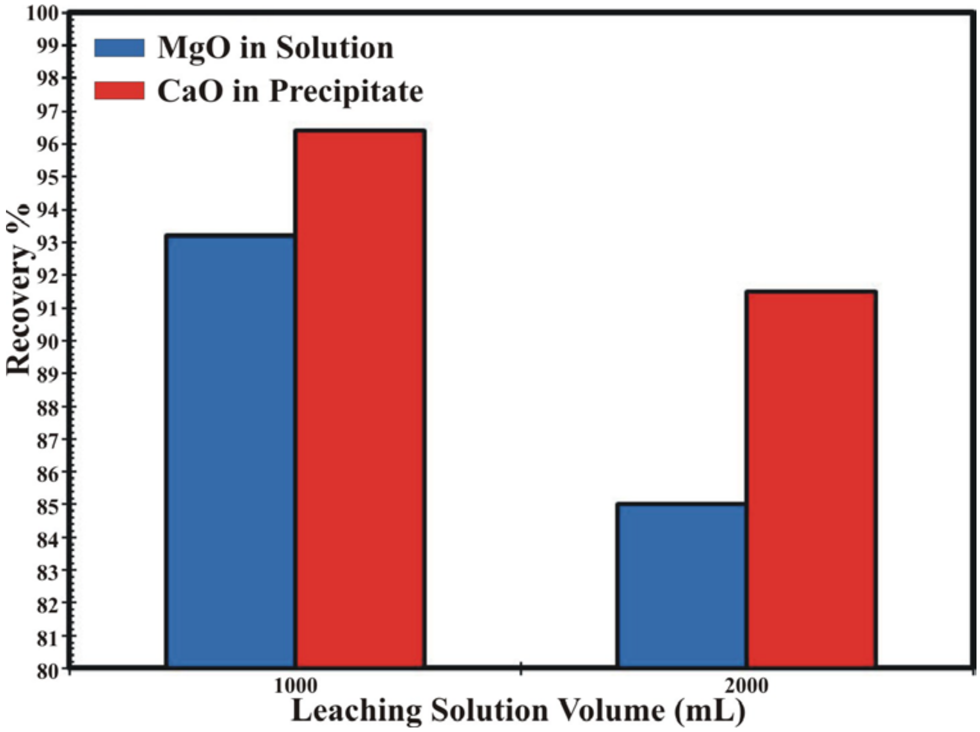

Fig.12: Effect of leaching solution volume on the recovery of MgO and CaO

- **Effect of Slurry Volume**

Slurry is the product of hydration reaction no. (3). Therefore, volume of this slurry may affect the carbonation reaction no. (10) only. To determine this effect, slurry volumes were made to 1000 and 2000 ml. The results are shown in Figure (13).

Results shown in Figure (13), display a clear view of the effect of slurry volume (dilution). This effect is conflicting, as slightly higher recovery of CaO in precipitate was achieved at the lower volume (1000 ml), but with very low recovery of MgO in solution. Meanwhile, much more MgO in solution recovery was obtained at the higher volume (2000 ml), with a considerable recovery of CaO in precipitate.

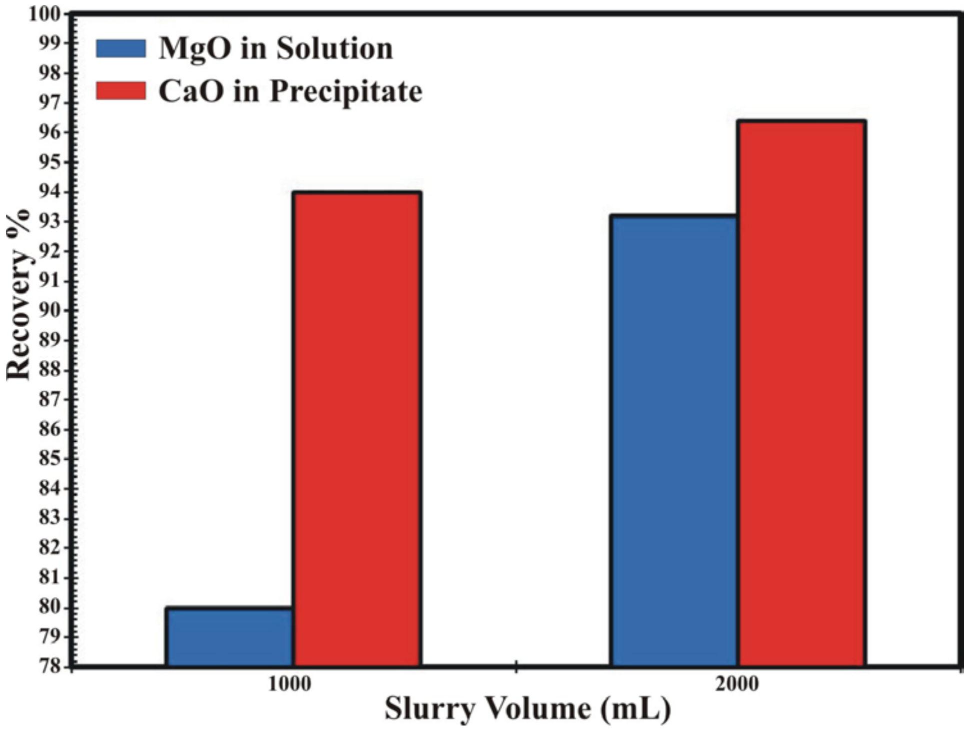

Fig.13: Effect of slurry volume on the recovery of MgO and CaO

- **Effect of Carbonation Time**

Carbonation reaction was applied to precipitate and remove the Ca^{2+} ions in solution as PCC by using CO_2 gas at certain pressure. Like any other reaction, carbonation needs time to reach completion. As aforesaid, precipitation of Ca^{2+} ions as $CaCO_3$ increased with time, and detaching of Mg^{2+} from the surface of $CaCO_3$ particles into solution is a slow reaction. Yilidrim and Akarsu (2010) claim carbonation completion in 7 minutes. Their claim was based on $[Ca^{2+}]$ and $[Mg^{2+}]$ concentrations (mole/l) and pH of the effluent, regardless of the recovery of both ions. They also were using $Mg(OH)_2$ as a precipitant for calcium ions at 50 °C. In this work, recovery of calcium and magnesium were taken into consideration, as well as calcined dolomite was the precipitant and the carbonation experiments were done at room temperature. Therefore, two experiments were conducted for 60 and 100 minutes of carbonation at optimum conditions extracted from the previous experiments. The results are shown in Figure (14).

As it can be seen, the results illustrated in Figure (14) point out that 100 minutes is a better time for carbonation than 60 minutes, particularly in relation to the MgO recovery in solution.

Table (2) shows that the optimum recovery of MgO in solution and CaO in precipitate were obtained by adding 55% weight ratio of dolime/ dolomite to 1000 ml of leaching solution at 70 °C for 60 minutes. Adjusting the slurry formed volume to 2000 ml, and batch reacted at a pressure of 2 bars for 100 minutes at room temperature. Table (3) and Figure (15) show the chemical analysis and XRD pattern of precipitated calcium carbonate (PCC) produced from the separation (hydration and carbonation) process respectively, at the optimum conditions.

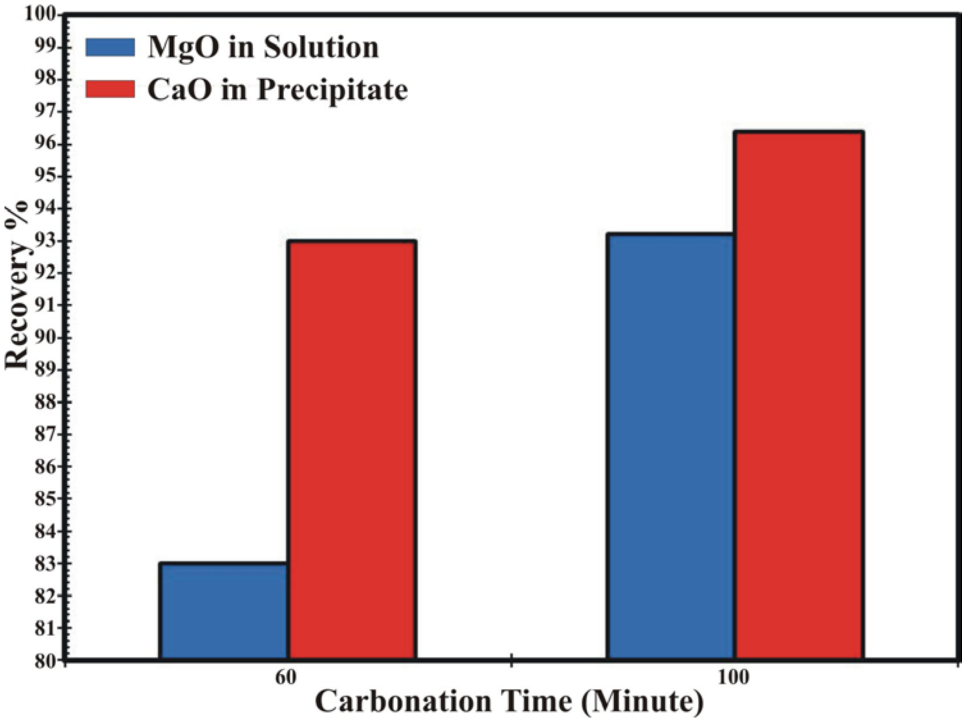

Fig.14: Effect of carbonation time on the recovery of MgO and CaO

Table 2: Recovery of MgO and CaO at the optimum conditions

Description	**MgO in Solution**	**MgO in Precipitate**	**CaO in Solution**	**CaO in Precipitate**
Recovery %	93.2	6.7	3.6	96.4

Table 3: Chemical composition of the 1st stage Precipitated Calcium Carbonate

Chemical Composition	**CaO**	**MgO**	**Cl**	**$CaCO_3$**
%	50.5	2.59	0.204	90.1

To prepare the solution resulted from carbonation (1st stage precipitation) for the next process (pyrohydrolysis), it must be evaporated to a certain volume. Meanwhile, this solution still contains a little amount of calcium ions as bicarbonate. As a result to the evaporation, $Ca(HCO_3)_2$ begins to decompose to $CaCO_3$ and H_2O as soon as temperature reach 70 °C (2nd stage precipitation). This may represent a great opportunity to decrease impurities represented by CaO in the final product (MgO). This can obviously be shown in Table (4), were the chemical analysis of the solution before (1st stage solution) and after (2nd stage solution) evaporation.

Surprisingly, PCC produced from the 2nd stage is quite different from the previous one. It has unique properties; a brightness of 98%, a mono mineral composition of aragonite prismatic shape particles. Table (5) and Figure (16) show, the chemical analysis and mineralogy of this precipitate, namely as second stage PCC respectively.

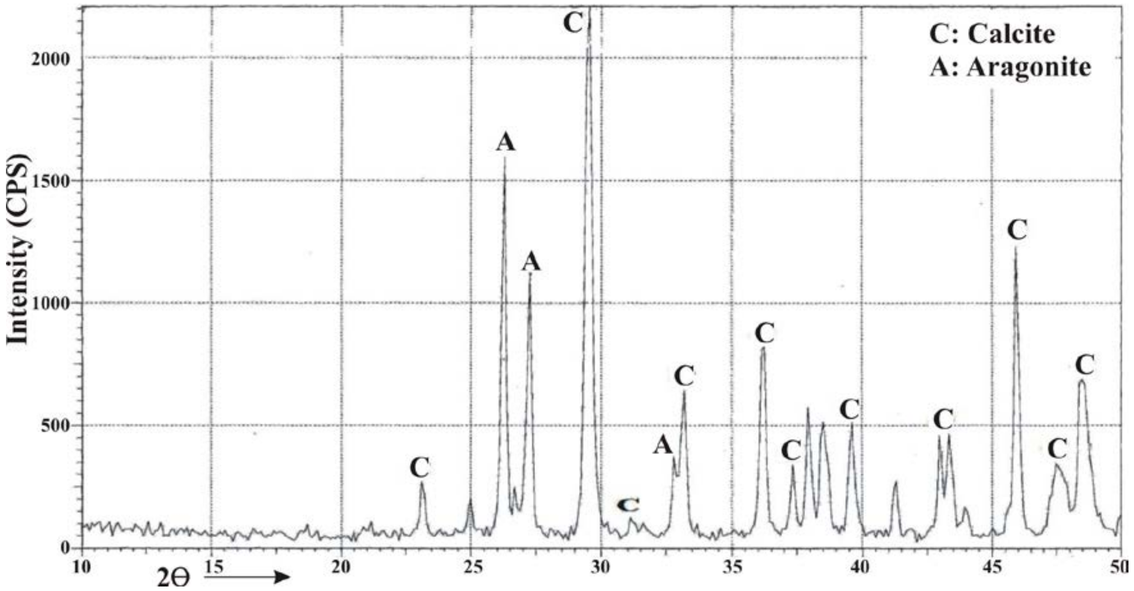

Fig.15: XRD pattern of 1st stage precipitated calcium carbonate

Table 4: Calcium and magnesium ions concentration in the solutions produced from 1st and 2nd stage precipitation and separation recoveries in (gm) and (%)

Described	Mg^{2+}	MgO	$MgCl_2$	Ca^{2+}	CaO	$CaCl_2$
Over all concentration (g/l)	54.46	90.33	215.85	0.72	1.00	2.00
Overall separation recovery (gm)	31	51.41	122.85	0.40	0.56	1.11
Overall separation recovery (%)	92.8			0.75		

Table 5: Chemical composition of 2nd stage precipitated calcium carbonate PCC

Chemical Composition	CaO	MgO	Cl	$CaCO_3$
%	54.32	0.63	0.15	97

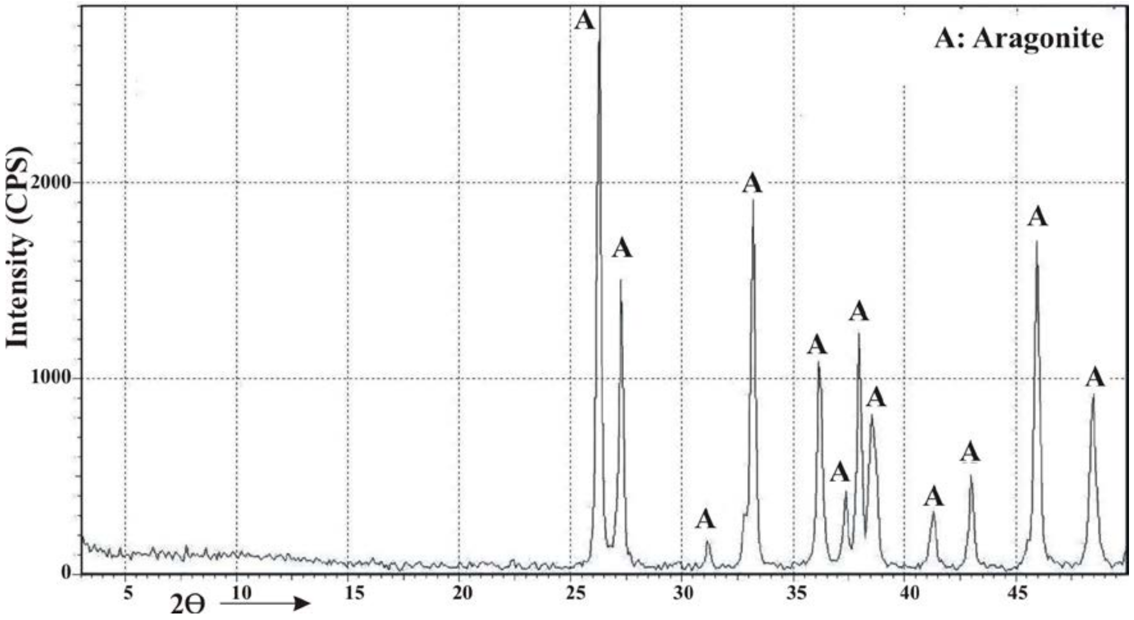

Fig.16: XRD pattern of the 2nd stage precipitated calcium carbonate (PCC)

- **Pyrohydrolysis**

Thermal hydrolysis of hydrated magnesium chloride is a well established technology and has been commercially used for over 30 years. Pyrohydrolysis is the commercial technology of choice when it comes to HCl regeneration (Demopoulos *et al*., 2008). It is thus a proven technology even though it involves a high temperature roast with the evolution of gaseous HCl and the attendant of corrosion problems. In pyrohydrolysis process, the purified magnesium chloride solution is heated and hydrogen chloride gas is evolved in pyrohydrolysing equipment shown in Figure (4). Under these conditions, thermal decomposition produced HCl gas stream absorbed in water to reform HCl which can be recycled to the leach circuit (Kashani-Nejad *et al*., 2005).

$$MgCl_2.6H_2O \xrightarrow{\triangle} MgO_{(s)} + 2HCl_{(g)} + 5H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(11)}$$

Reaction (11) is not a direct reaction; in fact the thermal decomposition of $MgCl_2$ solution is a very complicated process. The first hydrated compound of magnesium chloride produced from evaporation of $MgCl_2$ solution, is $MgCl_2.12H_2O$. This compound is not stable and it tends for further dehydration to become $MgCl_2.6H_2O$, which is the most fully hydrated form of magnesium chloride at room temperature, and its dehydration proceed as appeared in Figure (17) (Kipouros and Sadoway, 2001).

However, the dehydration of hydrated magnesium chloride does not follow this path all the way. Beside temperature, vapor pressure is another factor controlling the dehydration pathways. According to both factors, the dehydration is schematically shown in Figure (18) (Kipouros and Sadoway, 2001).

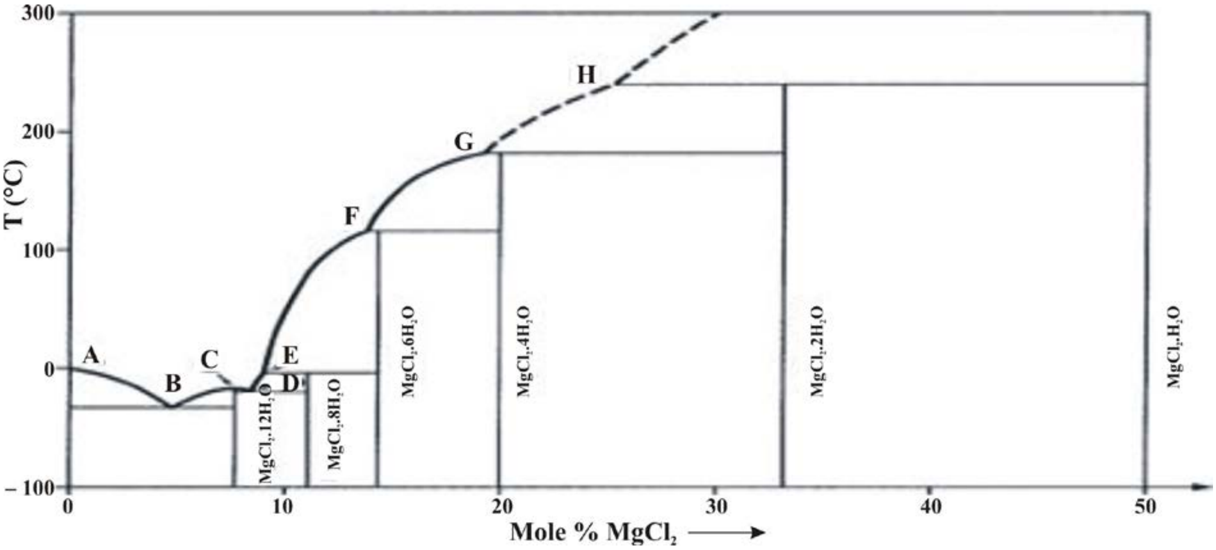

Fig.17: Schematic phase diagram of magnesium chloride – water system

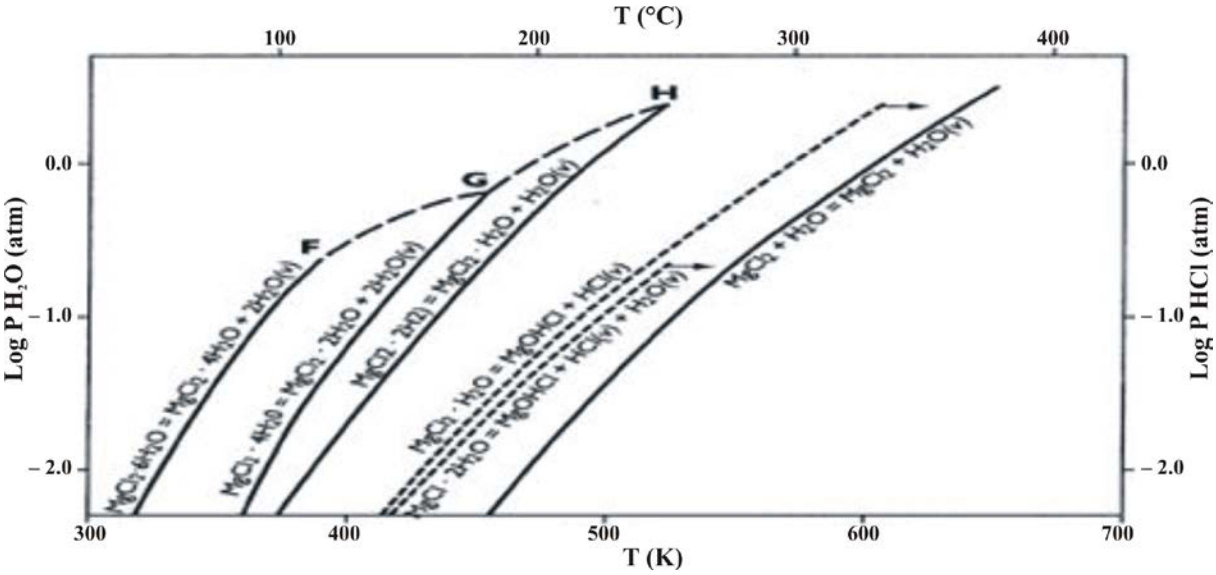

Fig.18: Vapor pressure of H_2O and HCl over the hydrates of magnesium chloride

According to Figure (18) and when magnesium chloride reaches the monohydrate form, the final step before decomposition. Dehydration may produce several possible reactions (12, 13 or 14).

$MgCl_2.H_2O_{(s)} \rightleftarrows MgCl_{2(s)} + H_2O_{(v)}$ …………………………………….………..... (12)

$MgCl_2.H_2O_{(s)} \rightleftarrows MgOHCl_{(s)} + HCl_{(g)}$ ………………………...….…………….. (13)

Figure (18), shows variation in the partial pressure of HCl gas with temperature for reaction (13). Reaction (12 and 13) can be combined to express the hydrolysis of $MgCl_2$ as:

$MgCl_{2(s)} + H_2O_{(v)} \rightleftarrows MgOHCl_{(s)} + HCl_{(g)}$ …………………….….………….. (14)

With respect to the aforesaid, two scenarios can be predicted: the first consisting the production of the magnesium oxychloride (MgOHCl), which decomposes at temperatures above 555 °C as stated by some authors (Kipourose and Sadoway, 2001; Yilidrim and Akarsu, 2010) or at 376 °C as stated by (Kashani-Nejad and Harris, 2005) and its converted entirely to MgO and HCl as shown in reaction (15).

$MgOHCl_{(s)} \rightleftarrows MgO_{(s)} + HCl$ ……………………………….....………………. (15)

The second possible scenario is the least likely, and it is related to reaction (12), where $MgCl_2$ is the final product of the dehydration. Anhydrous $MgCl_2$ is a very hygroscopic compound, and it decompose only at slow heating starting from 300 °C and melt on rapid heating at 714 °C. In fact, a mixture of both of the previous scenarios may occur.

Two objectives can be achieved by this process, the production of valuable MgO and HCl regeneration. In this work, several factors affecting pyrohydrolysis were studied.

- **Effect of Pyrohydrolysis Temperature**

To evaluate the role of pyrohydrolysis temperature on the thermal decomposition of magnesium chloride solution, four temperatures were used for the pyrohydrolysis (500, 550, 600 and 650) °C. The results are illustrated in figure (3 – 15). This figure is drawn according to the MgO and Cl percentages found in the chemical analysis of pyrohydrolysis products produced at these temperatures. MgO component may represent magnesia, magnesium hydroxide or magnesium chloride or one of its hydrates. This can be observed from the mineral composition of each product. This experiment was done using solution of $MgCl_2$ for a period of 60 minutes.

The results shown in Figure (19) indicate an increase in MgO% accompanied with decrease in Cl% as temperatures of pyrohydrolysis rises. As it can be seen, at 500 °C almost no MgO content is found in the product, only a mixture of magnesium chloride hydrates and magnesium oxychloride can be detected. The first presence of the magnesia is observed at 550 °C but in very limited amounts. The magnesia proceeds growing in quantity as pyrohydrolysis temperature rising up to 650 °C, when only anhydrous $MgCl_2$ present as an impurity. The presence of anhydrous $MgCl_2$ may be attributed to the nature of temperature increase in the furnace, since increasing rate dose not offer a rapid heating to avoid the formation of anhydrous $MgCl_2$, at the same time, it is not that slow rate that is capable of decomposing this impurity.

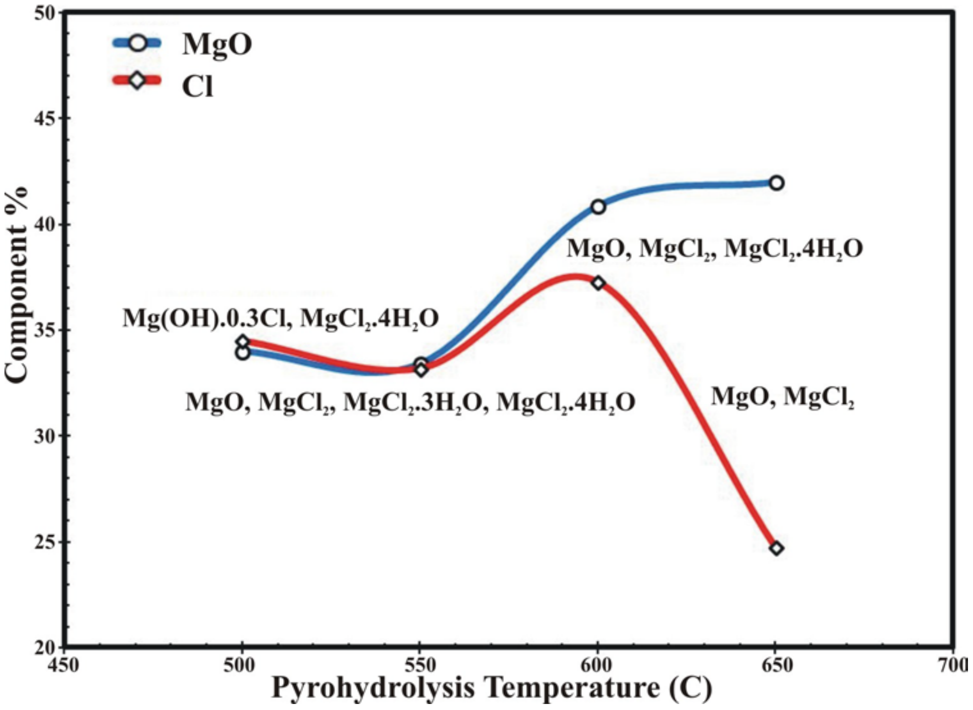

Fig.19: Effect of pyrohydrolysis temperature on the MgO purity

- **Effect of Pyrohydrolysis Time**

Yilidrim and Akarsu (2010) suggest 20 minutes for pyrohydrolysis as a satisfactory period for the production of 98.1% MgO from the Bischofite ($MgCl_2.6H_2O$) reference sample. They built their suggestion on their study to the HCl regenerated from pyrohydrolysis, as it almost reach a constant concentration at a temperature 600 °C. To investigate this suggestion, three experiments were conducted at different periods of time (30, 60 and 120) minutes. The results are shown in Figure (20).

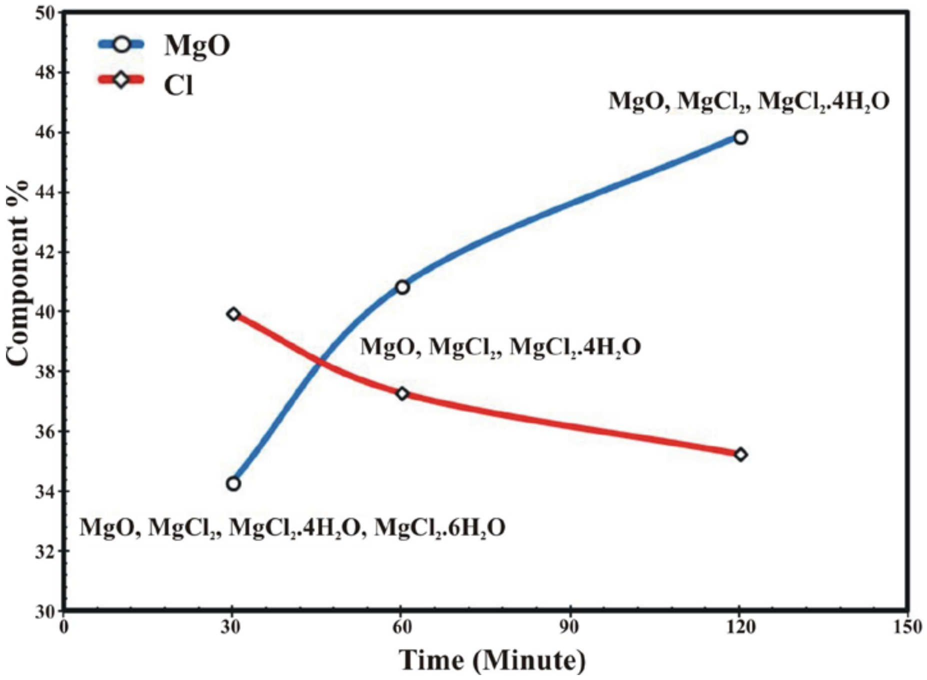

Fig.20: Effect of pyrohydrolysis time on the MgO purity

Results of Figure (20), disagree with the study of (Yilidrim and Akarsu, 2010) because it shows a direct proportional effect of time on both MgO purity and HCl concentration. During the first 30 minutes, a huge vapor evolved contain much more water than HCl gas, and this is reflected on the composition of the product, that contains a lot of Cl percentage. This agrees with the low concentration of 9% HCl collected at the final 30 minutes. On contrast, HCl gas evolved in greater amount than water from pyrohydrolysis conducted for 60 minutes with an HCl concentration of about 18% and with a low Cl percentage in the product. Although, very little amount of HCl was collected after 60 minutes of pyrohydrolysis; the Cl percentage proceeded its decrease in the product and the concentration of HCl collected has risen up to 20%.

Table 6: Increasing MgO purity by washing with water at different temperatures

Pyrohydrolysis Temperature °C	Before Washing		Mineralogy	After Washing		Mineralogy
	MgO%	Cl%		MgO%	Cl%	
600	45.88	35.24	$MgO, MgCl_2$, $MgCl_2.4H_2O$	87.80	3.24	$MgO, Mg(OH)_2$
650	48.03	39.7	$MgO, MgCl_2$	92.02	3.10	$MgO, Mg(OH)_2$

Table (6); show the possibility of increasing the purity of MgO by dissolving almost all the Chloride impurities presented as magnesium chloride and its hydrates. The magnesium chloride dissolved can be recycling to the circuit of pyrohydrolysis.

- **Effect of Magnesium Chloride Feeding Form**

Different forms of feeding samples can be introduced to the pyrohydrolysis process. In this study, feeding samples were a solution, a wet salt of $MgCl_2.12H_2O$ or a dry salt of (Bischofite) $MgCl_2.6H_2O$. All these forms were pyrohydrolysed at 650 °C for 60 minutes. Products resulted from different forms of feeding samples were washed and filtered. Upon chemical analysis it was found that these products have different MgO purity and Chloride impurities as it shown in Figure (21).

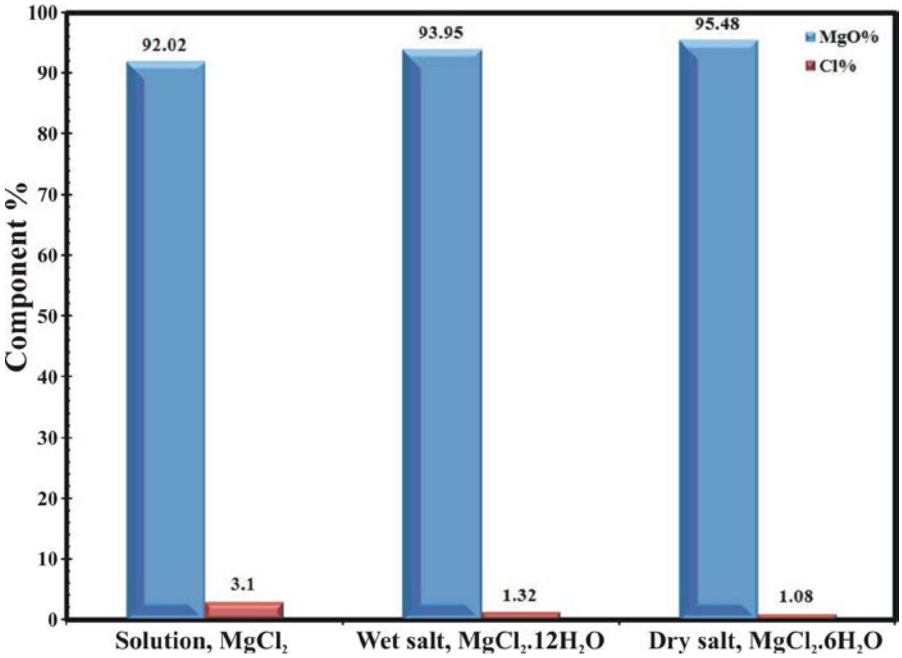

Fig.21: Effect of magnesium chloride feeding form on MgO purity

According to the results illustrated in Figure (21), it is obvious that further evaporation of $MgCl_2$ solution to wet salt of $MgCl_2.12H_2O$ gave enhancement to the products purity in respect to MgO% and chloride impurities remained. It is also obvious, that proceeding evaporation towards a dry salt feeding sample brings more enhancement considering chloride impurities and MgO% of the product. In addition, dry salt feed was easy in handling and in controlling its particle size. Table (7) and Figures (22, 23 and 24) show the chemical analysis and XRD patterns of the three products respectively.

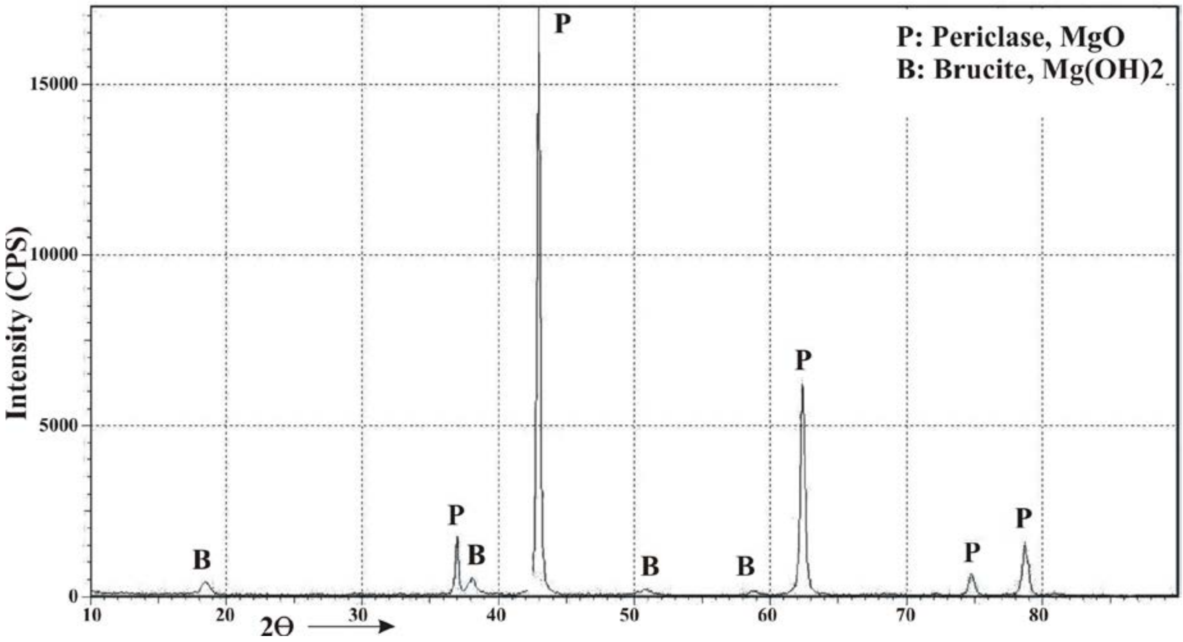

Fig.22: XRD pattern of MgO produced from $MgCl_2$ solution feed

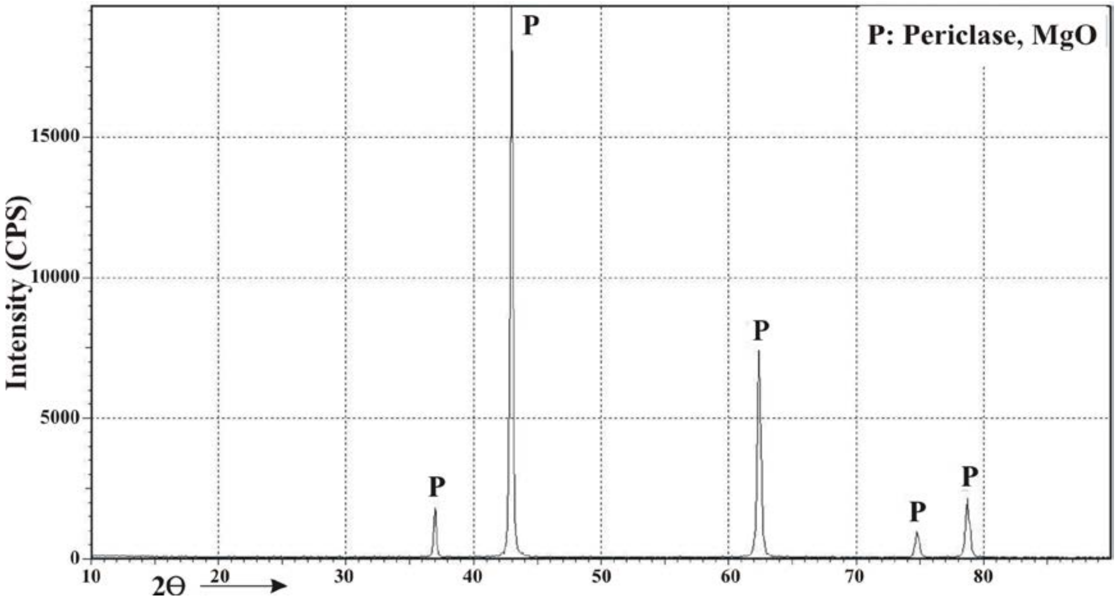

Fig.23: XRD pattern of MgO produced from $MgCl_2$ dry salt feed ($MgCl_2.6H_2O$)

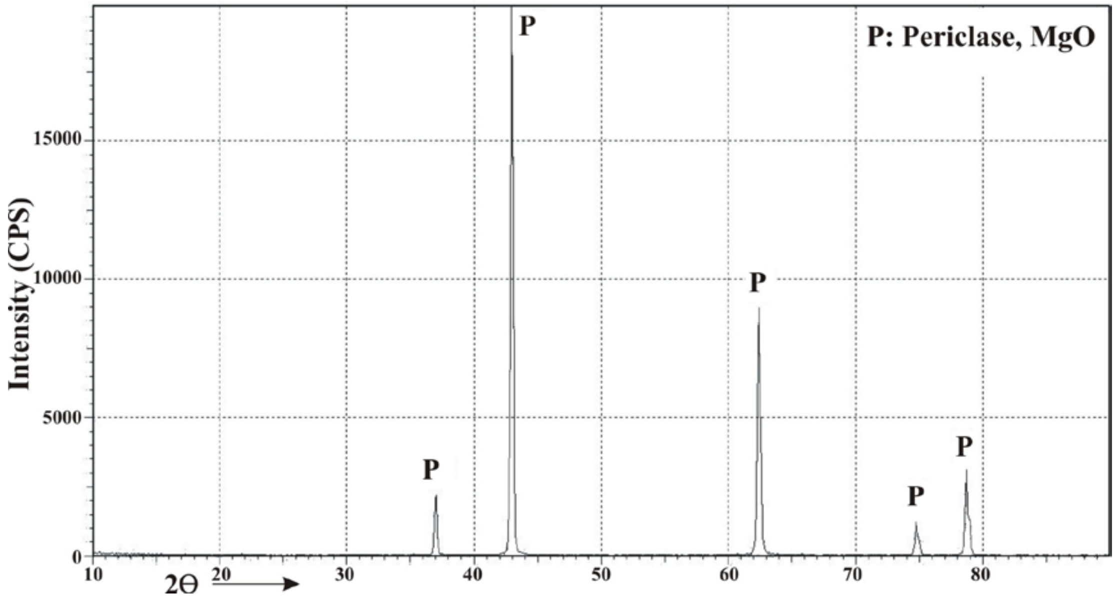

Fig.24: XRD pattern of MgO produced from $MgCl_2$ wet salt feed ($MgCl_2.12H_2O$)

Table 7: Chemical and mineralogical characteristics of the MgO produced

Sample feed	MgO%	CaO%	Cl%	Description	Color
$MgCl_2$ solution	92.02	2.5	3.1	$MgO,Mg(OH)_2$	Slightly Yellowish
$MgCl_2.12H_2O$ wet salt	93.59	1.08	1.32	MgO	Light-Gray
$MgCl_2.6H_2O$ dry salt	95.48	1.07	1.00	MgO	Gray

It is worth to mention that when a dry salt sample used in a fine manner, the MgO produced was in a gray color, inactive, and does not dissolve in any mineral acids even in aqua regia. These properties are similar to those of dead-burned magnesia.

A detail discretion of the method applied for the extraction of MgO from dolomite at the optimum conditions are shown in Figure (25).

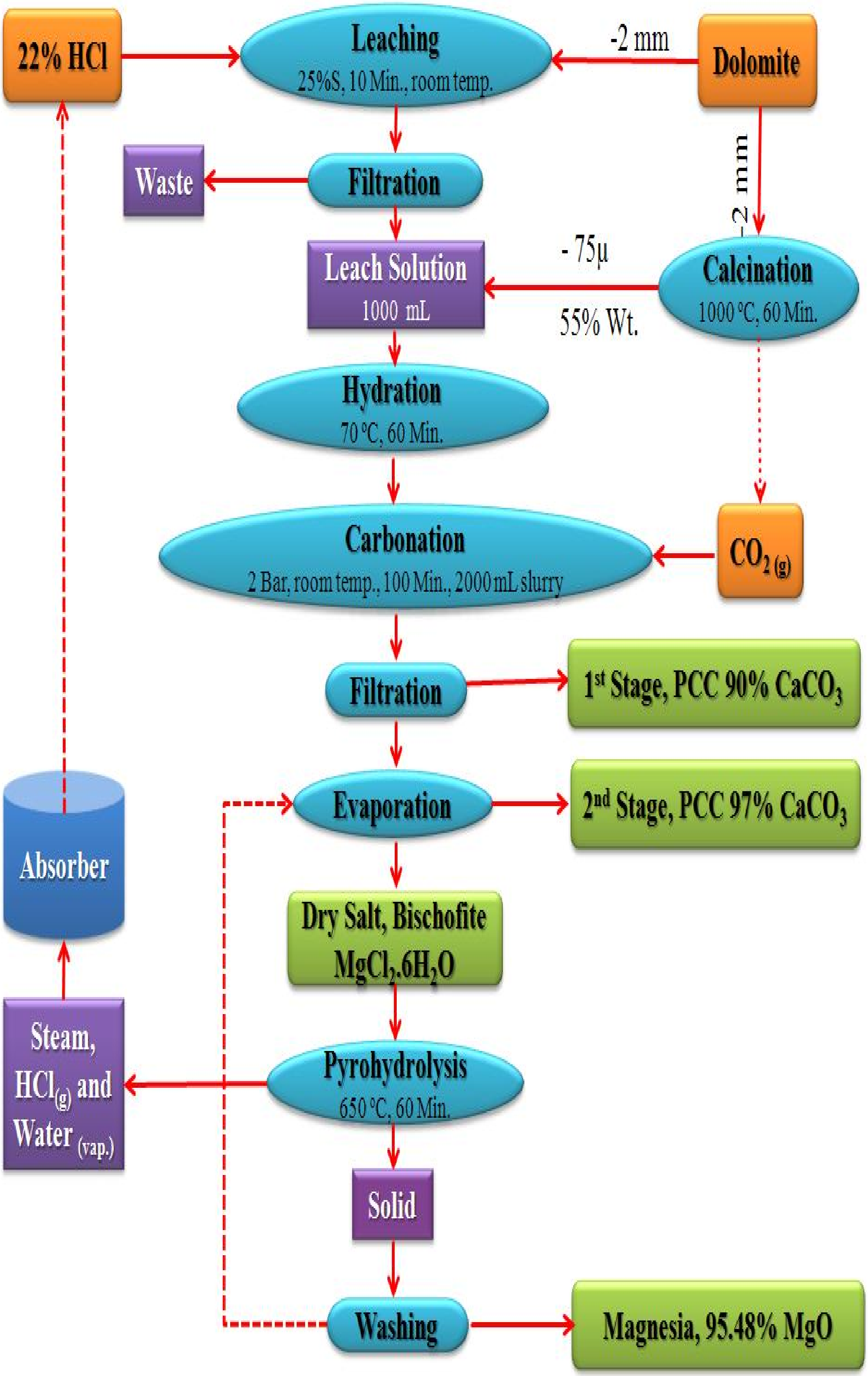

Fig.25: Summary of the process at optimum conditions

CONCLUSIONS AND RECOMMENDATIONS

- According to the present experimental work, the following conclusions can be stated:
  - Leaching of Iraqi dolomite can be done with an extraction of 99.5% MgO in (– 2 mm) dolomite ore using 22% HCl, at 25% solid for 10 minutes at room temperature.
  - The separation of 99.2% CaO as PCC from MgO with a recovery 92.8% in the solution can be carried out in two stages; a. Hydration: using calcined dolomite (dolime) as a precipitant added in a 55% ratio of dolime to a volume of 1000 ml leached dolomite at 70 °C for 60 minutes. b. Carbonation: using 2 bars of CO_2 pressure for a slurry volume of 2000 ml at room temperature for 100 minutes.
  - Pyrohydrolysis can be conducted at the optimum conditions; using 40 gm of $MgCl_2.6H_2O$ (bischofite) feed sample, at a temperature of 650 °C over a period of 60 minutes. Washing of the product to obtain 95.4% MgO, and recycling the filterate to the pyrohydrolysis circuit.
  - A complete pyrohydrolysis of magnesium chloride in any form (solution, wet or dry precipitate) cannot be done using batch furnaces with gradual heat elevation.
- To develop the laboratory experiments of this work, we suggest the following:
  - Ungrounded calcined dolomite should be hydrated with water first and pass over sieve opening 45µ to eliminates SiO_2, then poured to the leach solution at 70 °C for 60 minutes.
  - Build a new apparatus of carbonation provided with an efficient and controllable system of CO_2 gas injection provided with high speed mixer to enhance the separation process.
  - Design a new pyrohydrolysis equipment consisting of either continuous fluidized bed calciner or spray calciner supplied with anti-acid absorber for HCl regeneration and collected tank for MgO.
  - Following this, a bench-scale study should be possible.

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