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PREPARATION OF MAGNESIUM OXIDE (MgO) FROM DOLOMITE BY LEACH-PRECIPITATION-PYROHYDROLYSIS PROCESS

Magnesium oxide suitable for the use in basic refractories was prepared from dolomite $(CaMg(CO_3)_2)$ by hydrochloric acid leaching, precipitation with CO_2 and thermal hydrolysis. Leaching of the dolomite ore in aqueous hydrochloric acid solution was investigated with respect to the effects of time on dissolution of the dolomite sample. The dependence of the observed dissolution rate on pH was established. In the carbonation experiments changes in pH, Ca^{2+} and Mg^{2+} concentrations versus time in the effluent solution were determined. Effects of the temperature on the precipitation rate of Ca^{2+} ions as solid $CaCO_3$ were studied. Experiments were conducted to determine the kinetics of thermal decomposition of $MgCl_2.6H_2O$ during pyrohydrolysis process. From high purity magnesium chloride brine magnesium oxide containing 98.86 % MgO was obtained with the thermal decomposition recovery of 98.10 %.

key words: oxides; dolomite leaching; calcium carbonate precipitation; pyrohydrolysis; fluorescence x-ray analysis

INTRODUCTION

Magnesium oxide is usually produced by calcination of the mineral magnesite $(MgCO_3)$ or magnesium hydroxide $(Mg(OH)_2)$ obtained from seawater or brine by

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liming. It is also produced by thermal hydrolysis of hydrated magnesium chloride ($MgCl_2$), magnesium sulfate ($MgSO_4$), magnesium sulfide (MgS), and basic carbonate (Ding et al., 2001, Duhaime et al., 2002).

One of the operations which have been widely used in the recovery of magnesium oxide from dolomite is the calcination route. Calcite and magnesite decompose at different temperatures, a stepwise decomposition permits the selective calcination in which magnesite is completely decomposed without decomposing calcite. Magnesium oxide is then separated physically from the calcined dolomite by sieving or air separation.

Magnesium bearing carbonate ores contain varying amounts of silica, iron oxide, alumina and calcium silicates, carbonates and oxides. In chemical beneficiation methods, magnesium is dissolved as salt, the insoluble impurities are removed by solid/liquid separation methods, and purified magnesia is recovered by thermal decomposition of the salt solution, which is free from the insoluble residue and the calcium component. The lime-to-silica ratio in magnesia has a major influence on its properties (Kramer, 1992).

U.S. Patent (4370422) proposes a process which comprises: a. adding calcined dolomite to a brine or bittern as a source of MgO and CaO in such amount that the molar ratio of (MgO+CaO):$MgCl_2$ is in the range of 0.66:1 to 0.05:1; b. keeping the mixture at a temperature below 90 ^{o}C until a solid mass is formed; c. drying the solid mass at temperature up to 200 ^{o}C, and d. calcining the solid mass at maximum temperature of 1200 ^{o}C. By this route a product of MgO was obtained and was analyzed to have purity minimum 98 % MgO, but it was an energy intensive process (Panda, Mahapatra, 1983). U.S. Patent (4720375) proposes the use of ammonium chloride to convert the calcined magnesite into $MgCl_2$. The product $MgCl_2$ solution containing also $CaCl_2$ is treated with CO_2 gas to form $CaCO_3$ that can be filtered out of the solution. The resulting $MgCl_2$ solution is then reacted with ammonium carbonate to produce $MgCO_3$ trihydrate crystals. Finally, the $MgCO_3$ is decomposed into CO_2 and MgO. The operation should be carried out in the presence of large amount of the ammonium compounds, the recovery of ammonia is costly (Ainscow, Gadgil, 1988).

In fact, all chemical processing routes based on magnesium bearing minerals rely on leaching process as the first step to selectively dissolve magnesium from the gangue minerals. This is normally followed by precipitation of magnesium from the clarified liquor. The present study pertains to a process for recovering magnesium oxide for refractory applications, and more particularly to a process for recovering precipitated calcium carbonate PCC co-product suitable for the use as a filler in paper and plastics industry.

EXPERIMENTAL

Dolomite ore from Yavca area in Icel province of Turkey was used. After grinding and sizing, its elemental analysis was performed using RIX 3000 Rigaku X-ray spectrometer and SRS 3000 Siemens X-ray fluorescence spectrometer. Mineralogical composition was determined by an electron microscope. Trace elements in the sample were determined by Perkin Elmer 2380 atomic absorption spectrometer (AAS). Analysis of thin sections indicated that dolomite was the major mineral phase whereas limonite, quartz and clay type minerals were minor mineral components of the sample. The chemical analysis results are shown in Table 1.

Table 1. Chemical analysis of the dolomite sample

Component	CaO	MgO	Al_2O_3	Na_2O	K_2O	SiO_2	Fe_2O_3
(%)	31.70	20.60	0.06	<0.002	<0.002	0.30	0.04
Component	CO_2	SO_4	Sr	Li	B	Ti	
(%)	47.30	0.13	0.06	<0.002	0.006	<0.002	

The ore sample was dissolved in hydrochloric acid solution in a 250 cm^3 Pyrex beaker. A predetermined amount of the ore at the required size (-1.7 mm) was added into HCl solution which had a starting concentration of 22 % wt. The initial solid/liquid ratio (21.70 %) was the same in all experiments, and the leaching process was conducted at room temperature (25 ^{o}C). After predetermined time 2 ml sample of the leach solution was withdrawn from the beaker to determine the Ca^{2+} and Mg^{2+} concentrations. pH of the leach solution was measured in each run. The necessary mixing was provided by gas evolving from the dolomite particles reacting with the acid. Filtration was made after each dissolution experiment to remove the undissolved residue and calculate the weight loss. Iron, aluminum and other ionic species were in trace amounts.

Carbonation reaction was applied to precipitate and remove the Ca^{2+} ions in the solution as PCC by using CO_2 gas at certain pressure. Magnesium hydroxide was added to adjust the pH to about 10. A batch reactor with a volume of 370 ml was used, which was equipped with magnetically driven impeller allowing the application of high stirring speed (1000 rpm) in the slurry. Injection pressure of the CO_2 gas was controlled and the temperature of the precipitation in the reactor was regulated by an automatically controlled heater underneath the stainless-steel vessel containing the solution. In each experiment Ca^{2+} concentration in the input and effluent solutions was determined by sampling from these solutions for certain precipitation period. The precipitated product PCC was filtered, dried and sampled for analysis. The experimental set up is shown in Fig. 1.
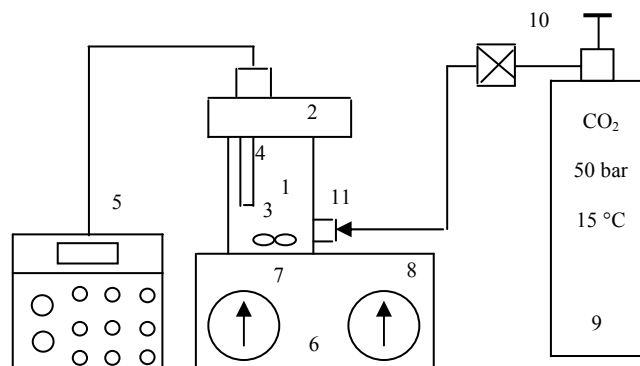
Fig. 1. Schematic diagram of the $CaCO_3$ precipitation apparatus
1. Stainless still vessel containing the leach solution, 2. Lid, 3. Magnetically driven stirrer 4. pH electrode, 5. pH meter, 6. Automatically controlled heater, 7. Stirring rate controller, 8. Temperature measuring unit, 9. CO_2 tank, 10. Gas pressure valve, 11. CO_2 inlet controller

Reference sample of $MgCl_2 \cdot 6H_2O$ (bischofite) was prepared by controlled evaporation of the purified $MgCl_2$ solution at 110 ^{o}C (Kashani-Nejad et al., 2005). The free water of the brine was removed from the sample at 110 ^{o}C. During the evaporation, pH of the solution absorbing the gaseous HCl was continuously controlled. Then 20.3 g of this sample was placed in a 500 mL heat resistant conical flask and heated at 440, 520, 560 and 600 ^{o}C for various periods. Gaseous HCl was absorbed in a 250 mL beaker containing 95 mL of distilled water (Fig.2). HCl concentration of this acidic solution was determined by titration with NaOH solution at the end of each experiment for the different operating temperature. Particle size analysis of the product (MgO) was determined by using the laboratory equipment Mastersizer of the Malvern Instruments Company, SEM micrographs of the sample were also obtained.
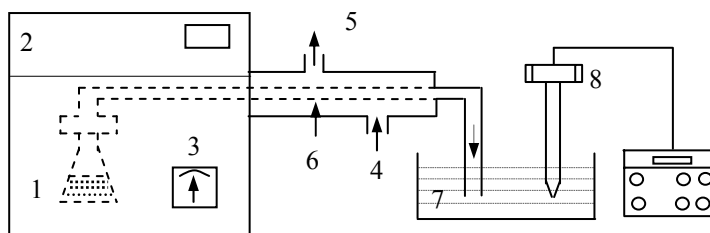

Fig. 2. Simplified view of the pyrodrolysing experiment
1. Conical flask containing $MgCl_2$ solution, 2. Heating furnace. 3. Heat control unit of the furnace (0 – 900 °C), 4. Cool water in, 5. Warm water out, 6. Flue gas ($HCl_{(g)}$) and water vapor carrying pipe, 7. Hydrochloric acid absorber, 8. pH electrode.

RESULTS AND DISCUSSION

LEACHING

The effect of leaching time on the dissolution of dolomite was studied. The results are shown in Fig. 3. Clearly, the dissolution recovery increased with time, the initial dissolution rate of Ca^{2+} and Mg^{2+} being very rapid. The recovery reached 92.43 % in the first 5 min and then, as expected, it continued to increase in the following period of time. After 30 minutes concentration of Ca^{2+} and Mg^{2+} in the leach solution increased with time and attained 1.70 mol cm^{-3} and 1.53 mol , respectively.
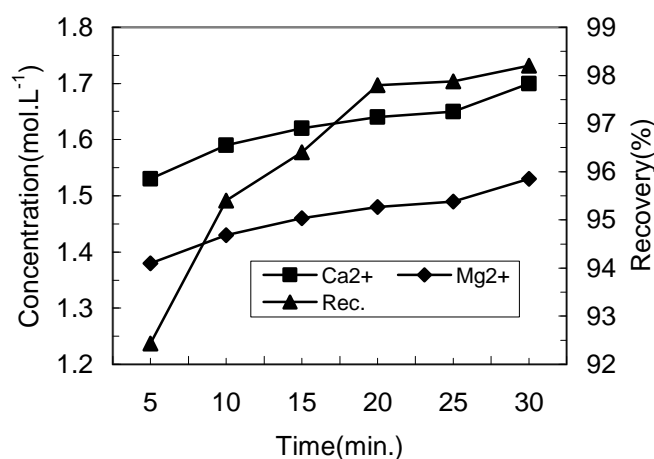

Fig. 3. Changes in the dissolution recovery, Ca^{2+} and Mg^{2+} concentrations as a function of time (HCl concentration: 22 %; solid / liquid ratio: 21.70 %; temperature: 25 °C)
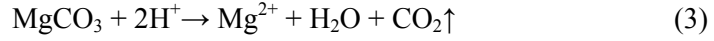
The dissolution rate was calculated using Eq. (1):

$$r=(dw/dt)x(1/sm) \quad (mol\ m^{-2}s^{-1}) \tag{1}$$

Where, dw and dt signify the weight loss of the solid sample and the time elapsed during the dissolution, respectively, s designates the unit specific surface area of the sample not dissolved at the end of the each leaching time, m represents the molecular weight of dolomite (184.41 g mol^{-1}) (Gautelier et al., 1999).

Effect of pH on the rate of dissolution of different carbonates (calcite, magnesite and dolomite) has been studied at 25 °C. At acidic conditions (pH<5), the reaction stoichiometry of dolomite dissolving in hydrochloric acid is (Chou et al., 1989, Lund et al., 1973):

$$CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + MgCO_3 + H_2O + CO_2\uparrow \tag{2}$$

$$MgCO_3 + 2H^+ \rightarrow Mg^{2+} + H_2O + CO_2\uparrow \qquad (3)$$

The rate dependence of the dissolution of dolomite on pH obeys fractional order at low pH values which confirms previously published observations. The dissolution rate (r) observed can be described by the empirical relationship:

$$r = k.a^n_{H^+,b} \qquad (0<n<1) \qquad (4)$$

Where, k is chemical reaction rate constant, n is the reaction rate order, and $a_{H^+,b}$ is the activity of hydrogen ion in the bulk of the solution. It follows from Eq. (4) that the plot of $\log(r)$ against $\log a_{H^+,b}$ for the experiments performed at constant temperature, should yield a straight line with a slope equal to n and intercept equal to $\log ka_{H^+,b}$ as can be determined from Eq. 1. (Lund et al., 1973, Busenberg and Plummer, 1982; Herman and White, 1985: Alkattan et al., 1998). According to Eq. 4. $\log(r)$ is a linear function of $\log a_{H^+,b}$ and the curve drawn through these data, is consistent with this linear relationship, which was used to determine the reaction order n (Gautelier et al., 1999).
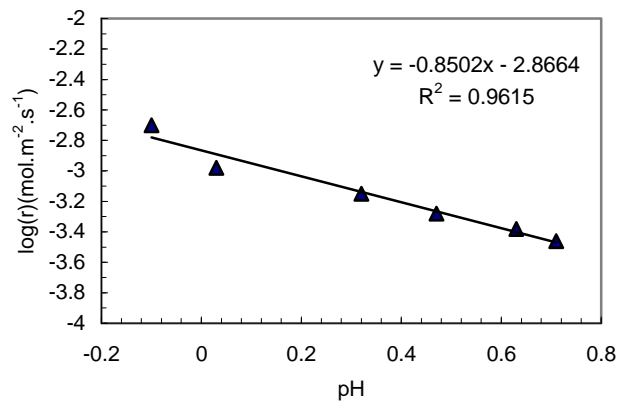

Fig. 4. Logarithm of measured dolomite dissolution rate as a function of pH

The curve illustrated in Fig. 4 was obtained from a fit of a second order functional equation to the experimental results of the dissolution. The value of the functional number n at any pH can be obtained from derivation of this functional expression with respect to the bulk pH. This calculation resulted in n value about 0.85 when pH = -0.1 at 25 °C. One of the researchers found n=0.75 for pH>2.5 at 25 °C, which is somewhat lower than found in this study (Gautelier et al., 1999). Other researchers obtained logarithm of the rate constant: $\log k$ = -2.88 and -2.59 respectively (Chou et al., 1989, Lund et al., 1973). For two component carbonates such as dolomite, the reaction order in respect to pH was determined to be 1 or 2 (Chou et al., 1989). The $\log k$ value was obtained as -2.87 in this study. It is shown in Fig.4 that at very acidic conditions, dissolution rate was dependent on pH and decreased with the increase in pH value.
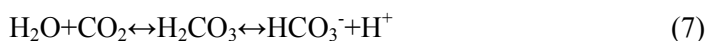
Hence, better dissolution conditions were achieved at high acidity. Figure 5 indicates that the rate decreased as the time increased, but the decrease was significant only up to 10 minutes, and so high recoveries (over 90 %) were achieved within 5 minutes (Fig. 3.) (Akarsu and Yildirim, 2008).

PRECIPITATION

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:

$$CaCl_2 + H_2O + CO_2 \rightarrow CaCO_3 \downarrow + 2HCl \tag{5}$$
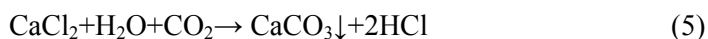
The pertinent ionic reactions which occur are represented by the following steps:

$$CO_{2\,(g)} \rightarrow CO_{2\,(aq)} \tag{6}$$

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{7}$$

$$HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + H^+ \tag{8}$$

Reaction (6) 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. 7.). 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 ($CaCO_3$) (reaction 8) forms at pH 7.51, while reaction (9) occurs only at pH above 10.45 (Akarsu, 2004).

$$Mg^{2+} + CO_3 \rightarrow MgCO_3 \tag{9}$$

As shown in Fig. 5, the concentration of Mg^{2+} in the effluent decreased to 1.03 mol L^{-1} during one minute, then increased again. This indicates that highest amount of Mg^{2+} ion incorporation took place during this period. On the other hand the Ca^{2+} concentration observed in the effluent was 1.6 mol L^{-1}, and then consistently decreased to 0.05 mol L^{-1}. 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 (Fig. 5). Precipitation of calcium carbonate depends on the bicarbonate dissociation in the solution. As the sample is heated up to 70 °C the equilibrium between bicarbonate and carbonate (Eq. 10) is shifted towards carbonate and hence calcium carbonate begins to form and pH tends to decrease.
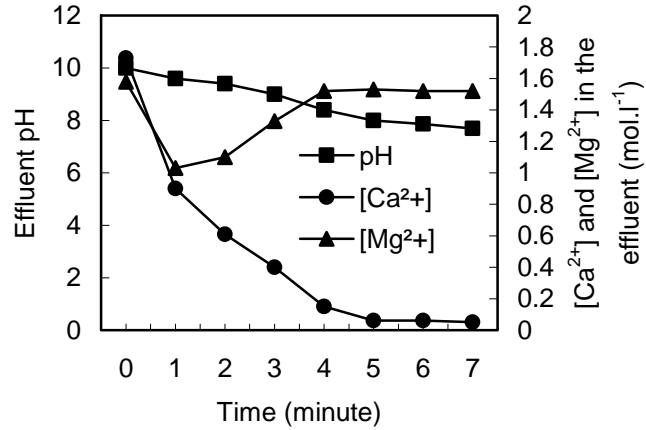
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{10}$$

Fig. 5. Changes in pH, $[Ca^{2+}]$ and $[Mg^{2+}]$ in the effluent solution as a function of time (Temperature: 70 °C; gas (CO_2) pressure: 200 kPa)

The $CaCO_3$ precipitation rate may be given by the following equation:

$$r_p = (1/S)(N/t) \qquad (\text{mol m}^{-2}\text{s}^{-1}) \tag{11}$$

where S represents the final surface area based on the total weight of the solid $CaCO_3$ particles precipitated for the precipitation period of t, N means the number of moles of $CaCO_3$ formed at these period (Levenspiel, 1972).

The curve in Fig. 6 was obtained from a fit of a polynomial to the experimental results. It can be seen in this figure that the precipitation rates of $CaCO_3$ were low up to 50 °C. However the calculated rates tended to increase rapidly with increase in temperature.
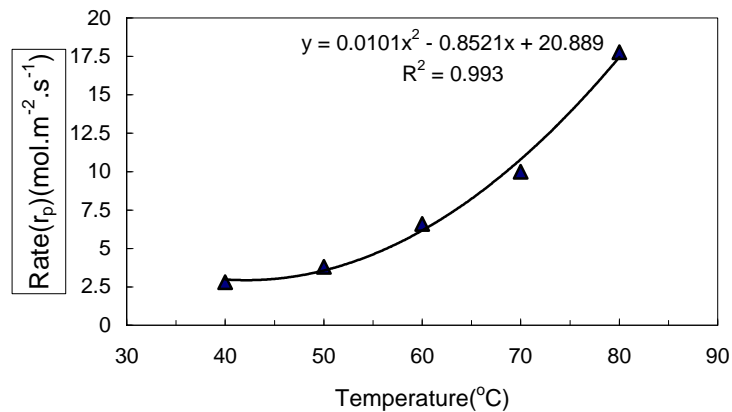

Fig. 6. Precipitation rate vs. bulk temperature (CO_2 pressure: 200 kPa; time: 5 minutes)

There was significant effect of temperature on the rate above 50 °C. It reached to 17.78·10⁻³ mol m⁻²s⁻¹ at 80 °C, while leaving the $MgCl_2$ solution purified from the Ca^{2+} ions. The concentration calculated was about 3.45 mol dm³⁻¹, which is about 20 times higher than that of the seawater. The precipitation rates were obtained for the temperatures using Eq. 11 and variation of $CaCO_3$ precipitation rates with temperature was determined in terms of the Arrhenius equation:

$$r_p = A e^{-Ea/RT} \qquad (12)$$

Where, Ea is the activation energy, the term A is known as the pre-exponential factor, R designates the gas constant (8.314 J.K⁻¹ mol⁻¹) and T signifies the temperature (K). The values of the log rate computed were plotted as a function of the reciprocal temperature in Fig. 7. It follows from Eq. (12) that the slope of the straight line in Fig. 7 is equal to $-Ea/2.303R$. It can be seen from this figure that the apparent activation energy for the precipitation of $CaCO_3$ is 42.5 kJ mol⁻¹. These experiments do confirm strong temperature dependence for the precipitation reaction. In a research work it was found to be 55 kJ mol⁻¹ and the Ea value is usually between 39 and 155 kJ mol⁻¹ (Brecevic, Kralj, 2007) . A PCC product containing 96.70 % $CaCO_3$ was obtained with the precipitation recovery of 94.20 % at the optimum conditions. Its specific surface area was 0.1578 m² g⁻¹. The sizes d_{90} and d_{10} were 7.17 and 1.11 microns, wherein, d_{90} and d_{10} represent the particle sizes account for 90 % and 10 % by number of the total particles respectively. Chemically, it is suitable for making paint, plastic and paper due to its low SiO_2 and Fe_2O_3 contents (Table 2).
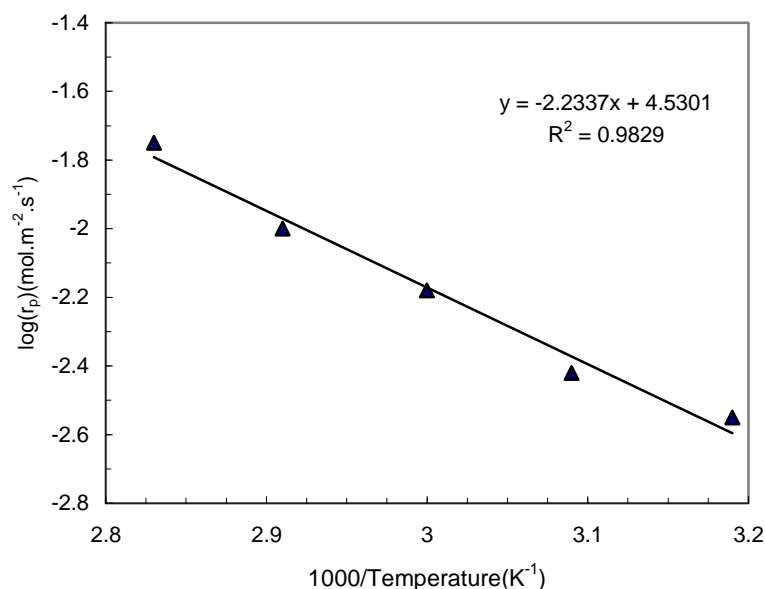

Fig. 7. Arrhenius plot for the precipitation of calcium carbonate particles

Table 2. Chemical analysis of the obtained PCC

Component	CaO	MgO	Al_2O_3	Na_2O	K_2O	SiO_2	Fe_2O_3
(%)	54.70	0.77	0.02	<0.002	<0.002	0.04	0.03
Component	CO_2	SO_4	Sr	Li	B	Ti	
(%)	44.37	0.13	0.01	<0.002	<0.002	<0.002	

PYROHYDROLYSIS

The thermal hydrolysis of hydrated magnesium chloride is a well established technology and has been commercially used for over 25 years. It is thus a proven technology even though it involves a high-temperature roast with the evolution of gaseous HCl and the attendant corrosion problems. In the pyrohydrolysis process, the purified magnesium chloride solution is heated in the pyrohydrolysing equipment shown in Fig. 2 and the hydrogen chloride gas is evolved. Under these conditions, the brine is converted to bischofite ($MgCl_2 \cdot 6H_2O$) while the gas stream is absorbed in water to reform a hydrochloric acid solution which is recycled to the leach circuit. Bischofite is decomposed into MgO and hydrogen chloride gas as shown in Eq. 13. (Kashani-Nejad et al., 2005).

$$MgCl_2 \cdot 6H2O \rightarrow MgO_{(S)} + 2HCl_{(g)} + 5H_2O \qquad (13)$$
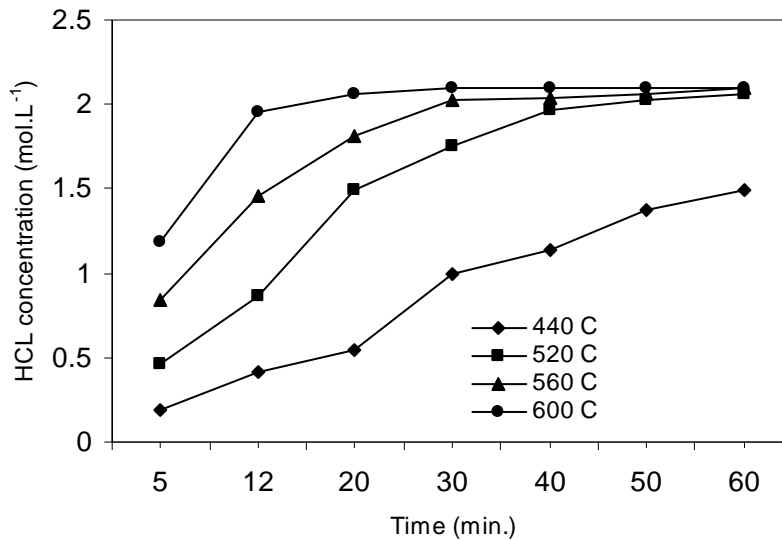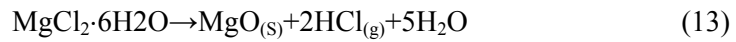

Fig. 8. HCl concentration as a function of time

It is indicated in Fig. 8 that as the time and temperature increased, HCl concentrations in the HCl absorbing solution increased. It reached 0.42 mol dm^{-3} at 440 ^{o}C after 12

minutes. For the same period of time at 600 $^{\circ}$C the concentration attained 1.89 mol dm^{-3}. However it reached the value of 2.06 mol dm^{-3} at 600 $^{\circ}$C for the 20 min. period. That corresponds to 98.10 % decomposition recovery of the HCl associated with the reference sample (MgCl$_2$.6H$_2$O) during this heating period. It means that one of the products of the thermal decomposition of the reference sample was HCl gas. It was consequence of the reaction shown in Eq. 13.
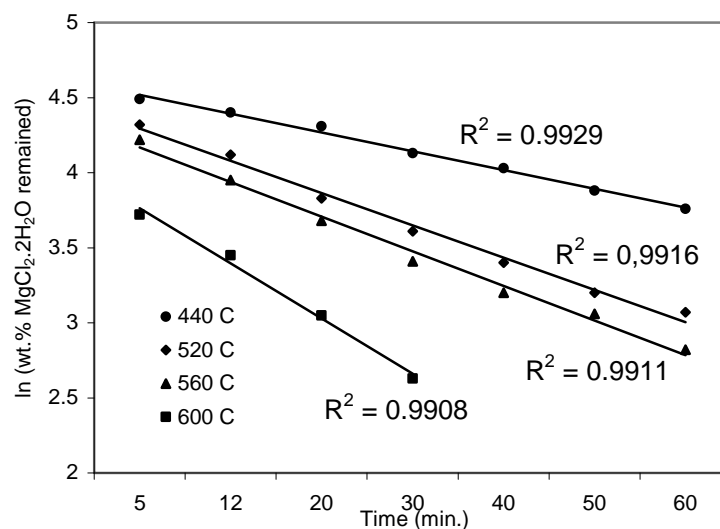

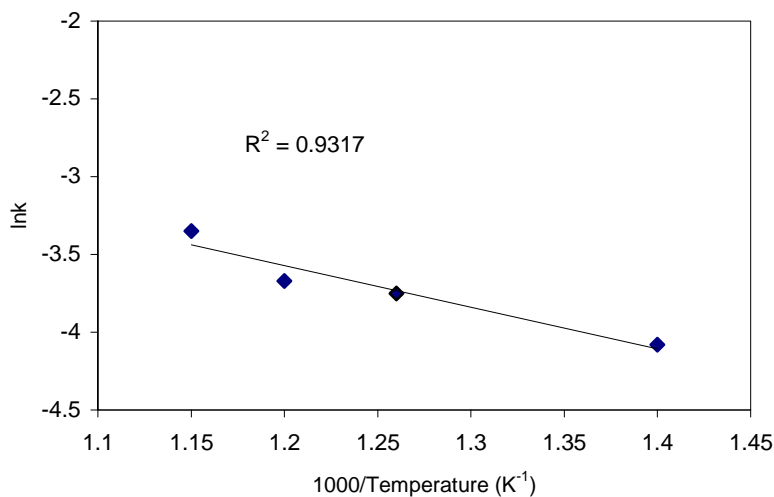Fig. 9. Kinetics of thermal decomposition of the reference sample

Fig. 10. Arrhenius plot of thermal decomposition of the reference sample

The weight loss of the sample determined during the decomposition process was due to the release of HCl gas and H_2O vapor. Therefore, percent of $MgCl_2.6H_2O$ remaining in the sample was found from the weight loss data. A first order kinetic plot of the results obtained in the dehydration process is shown in Fig. 9. This result is in agreement with the result obtained by the earlier researchers (Ainscow and Gadgil, 1988). Reaction rate constant (k) was obtained from the slopes of the curves in Fig. 9., and Arrhenius plot was drawn using the lnk values versus the reciprocal temperatures as shown in Fig. 10. In this figure, function of the curve was determined in terms of lnk and temperature as shown in Eq. 14. Activation energy of the thermal decomposition was obtained to be 19.95 kJ mol^{-1} by calculating the slope of the curve, which is equal to $-Ea/(1000R)$ (Fig. 10). The rate constant, k, was found to have the following dependence on temperature:

$$\ln k = -2400(1/T) + 3.27 \tag{14}$$

Table 3. Chemical composition of the purified brine

Component	Mg^{+2}	Ca^{+2}	SiO_2	Al_2O_3	Fe_2O_3	Na_2O
(g. dm^{-3})	84.32	0.78	0.03	0.02	0.02	0.001
Component	K_2O	SO_4	Sr	Li	B_2O_3	`Ti
(g dm^{-3})	0.004	0.9	0.42	0.006	0.03	0.006

SEI   15.0kV   X300
10μm WD 15.0mm

SEI   15.0kV   X1000
10μm WD 15.2mm

SEI   20.0kV   X30000
100nm WD 15.9mm

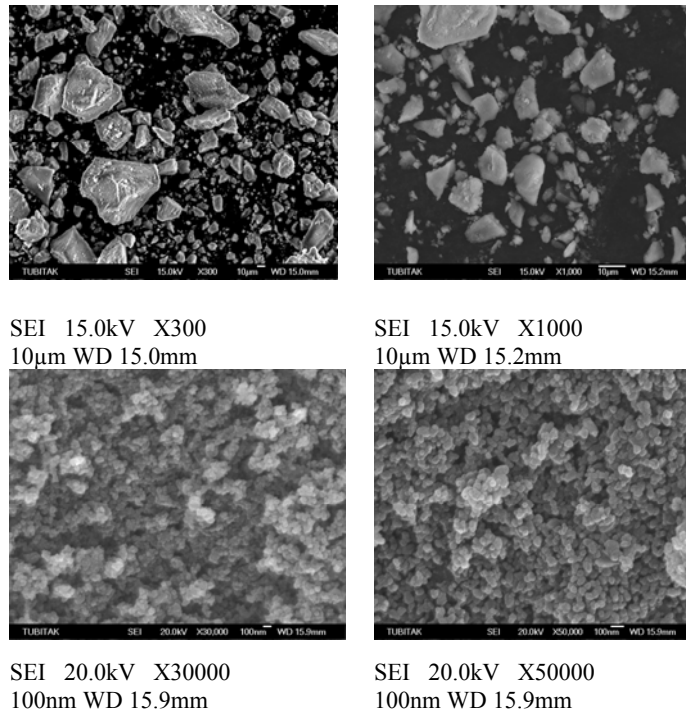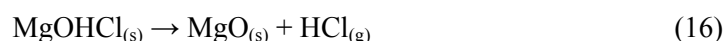SEI   20.0kV   X50000
100nm WD 15.9mm

Fig. 11. SEM micrographs of the submicron MgO particles

It is shown in Table 3 that basic impurity in the purified brine is calcium. It could be reduced by the improvement in the precipitation process. The carbonation is a well known process and it has been used in production of PCC in industry. This may possibly be achieved by changing the hydrodynamic conditions during the precipitation and providing better CO_2/liquid interaction. The SEM images and the particle size analysis of the particulate product MgO samples are shown in Fig. 11 and Table 4, respectively. It is evident that the shape of the particles underwent change and the sample consisted of finely divided particles displaying cubic habit. Shape of the MgO nanoparticles is important in the surface engineering.

In thermal decomposition of the sample $MgCl_2 \cdot nH_2O$; n = 1, 2, 4, 6, water can chemically bind to form a series of hydroxide compounds, and the overall reaction is:

$$MgCl_2 \cdot nH_2O \rightarrow MgOHCl \rightarrow MgO + HCl + H_2O \qquad (15)$$

$$MgOHCl_{(s)} \rightarrow MgO_{(s)} + HCl_{(g)} \qquad (16)$$

On the other hand, it has been known that decomposition of MgOHCl begins at 828 K, and it directly converts into MgO and HCl without undergoing any previous steps. Removal of HCl gas from the MgOHCl particle surface is a significant factor determining the rate of decomposition, and also depends on the amount of MgOHCl in the sample treated (Kashani-Nejad et al., 2005; Kipouros and Sadowayd, 2001). In this work, decomposition was 98.10% at 600 ^{o}C in 20 minutes. The most critical and the final reaction to form MgO is the decomposition of (MgOHCl) (Eq.16). The enthalpy of the decomposition reaction at 600 ^{o}C is ΔH = - 816.1 kJ mol^{-1} which means that the process is highly exothermic. The evaporation of the water is energy consuming, therefore, amount of the net energy to be supplied for formation of the MgO from the brine depends on the $MgCl_2$ concentration of the leach solution. Although the pyrohydrolysis is a highly energy intensive operation, it effectively proceeds in a single step. In the alternative process in which Mg^{2+} ions from seawater is precipitated as $Mg(OH)_2$ several unit operations are required, namely the precipitation and flocculation of $Mg(OH)_2$, dewatering, drying and calcination. The process proposed in this study does not require a pre-calcined CaO that is used to precipitate Mg^{2+} ions from seawater and other Mg^{2+} bearing solutions, which usually may increase the impurity contents of the product MgO.

When the product MgO is used in refractory and ceramic industry, the most important impurities are CaO, Al_2O_3, Fe_2O_3,, SiO_2 and B_2O_3. Generally, dolomites tend to have very low B_2O_3 contents that embrittles the magnesia refractory and ceramics during heat treatment operations. So, dolomite may be used as a raw material in manufacturing refractories and ceramic compounds. It is suitable for chemical reactions where high reactivity and rapid conversion to magnesium hydroxide are required because of its very high surface area. Its fine particle size and high purity make it an excellent magnesium source for the manufacturing of many magnesium compounds. The possible flowsheet proposed to prepare the MgO product is shown in
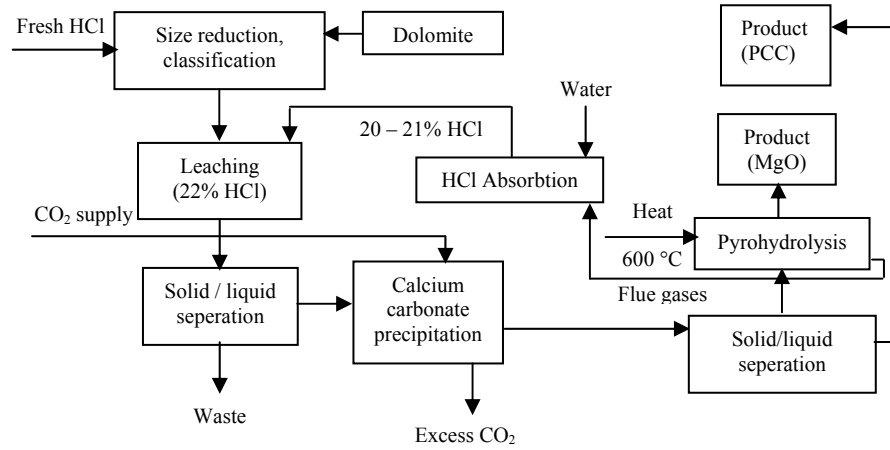
Fig. 12. Simplified flowsheet of the hydrochloric acid leach–precipitation–pyrohydrolysis process

Table 4. Physical properties of the final product MgO

Avarage particle size (microns)	36.96
Top cut	331.77
d_{90}	75.76
d_{50}	28.08
d_{10}	4.32
Surface area ($m^2 g^{-1}$)	0.5231
Whiteness (pure MgO : 100 %)	99.50

Table 5. Chemical composition of the final product MgO

Component	MgO	CaO	SiO_2	Al_2O_3	Na_2O	K_2O
(%)	98.86	0.78	0.02	0.01	0.02	<0.002
Component	SO_4	Sr	Li	B_2O_3	Ti	
(%)	0.003	<0.002	0.005	0.02	<0.004	

CONCLUSIONS

I. 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 (30 min).

II. The dolomite leach solution was cleaned from the Ca^{2+} ions present at 70 °C and 200 kPa CO_2 pressure in 5 min. with the recovery of 94.80 %..

III. Total decomposition of the purified magnesium chloride solution sample was achieved at 300-600 °C within 1 hour. Hydrogen chloride gas evolved was absorbed in water with the recovery of 98 % at 600 °C in 20 min.

IV. In the pyrohydrolysis process, kinetic data showed that removal of the product HCl gas was found to be an important factor controlling the rate of the decomposition. Kinetic data indicated that the thermal decomposition was a first order kinetic process.

V. The hydrochloric acid leach-precipitation-dehydration process offers a method of co-synthesizing high-grade MgO and PCC from a dolomite sample.

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Z dolomitu otrzymano tlenek magnezu przydatny do produkcji zasadowych materiałów ognioodpornych. Otrzymano go za pomocą ługowania kwasem solnym i wytrącania z użyciem CO_2 oraz stosując termiczną hydrolizę. Badano ługowanie dolomitu w roztworze kwasu solnego w odniesieniu do czasu rozpuszczania. Ustalono zależności szybkości rozpuszczania od pH. Określono zmiany pH oraz stężeń Ca^{2+} i Mg^{2+} od czasu w roztworze podczas karbonatyzacji. Badano wpływ temperatury na szybkość precypitacji jonów Ca^{2+} w postaci stałego $CaCO_3$. Przeprowadzono eksperymenty dla określenia kinetyki termicznego rozkładu $MgCl_2 \cdot 6H_2O$ podczas pirolizy. Otrzymano wysokiej czystości tlenek magnezu o zawartości 98.86% MgO z solanki zawierającej chlorek magnezu, przy sprawności termicznej dekompozycji wynoszącej 98.10%.

słowa kluczowe: tlenki, dolomity, precypitacja, piroliza, fluorescencja, analiza rtg