

## **OBTAINING MGO FROM DOLOMITE LOCAL RAW MATERIAL**

## **Kerim Ryzayev**

Supervisor: Dean of Oguz han Engineering and Technology University of Turkmenistan Ashgabat, Turkmenistan

## Almazova Ogulkeyik

Supervisor: Instructor of Oguz han Engineering and Technology University of Turkmenistan Ashgabat, Turkmenistan

## Saparmammedova Aylar

Student of Oguz han Engineering and Technology University of Turkmenistan Ashgabat, Turkmenistan

# **INTRODUCTION**

Magnesium oxide is usually produced by calcination of the mineral magnesite (MgCO<sub>3</sub>) or magnesium hydroxide (Mg(OH)<sub>2</sub>) obtained from seawater or brine by liming. It is also produced by thermal hydrolysis of hydrated magnesium chloride (MgCl<sub>2</sub>), magnesium sulfate (MgSO<sub>4</sub>), magnesium sulfide (MgS), and basic carbonate.

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. 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 is used. 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.

Component	CaO	MgO	$Al_2O_3$	Na <sub>2</sub> O	K <sub>2</sub> O	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
(%)	31.70	20.60	0.06	< 0.002	< 0.002	0.30	0.04
Component	CO <sub>2</sub>	$SO_4$	Sr	Li	В	Ti	
(%)	47.30	0.13	0.06	< 0.002	0.006	< 0.002	

Table 1. Chemical analysis of the dolomite sample

The ore sample is dissolved in hydrochloric acid solution in a 250 cm<sup>3</sup> Pyrex beaker. A predetermined amount of the ore at the required size is added into HCl solution which had a starting concentration of 22 % wt. The initial solid/liquid ratio is the same in all experiments, and the leaching process is conducted at room temperature (25 °C). After predetermined time 2 ml sample of the leach solution was withdrawn from the beaker to determine the Ca<sup>2+</sup> and Mg<sup>2+</sup> 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<sup>2+</sup> 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<sub>3</sub> 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<sub>2</sub> tank,
- 10. Gas pressure valve,
- 11. CO<sub>2</sub> inlet controller

Reference sample of  $MgCl_2 \cdot 6H_2O$  (bischofite) was prepared by controlled evaporation of the purified  $MgCl_2$  solution at 110°C. The free water of the brine was removed from the sample at 110°C. During the evaporation, pH of the solution absorbing the gaseous HCl was continuously controlled.

Then this sample was placed in a heat resistant conical flask and heated. 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.



Fig. 2. Simplified view of the pyrodrolysing experiment

- 1. Conical flask containing MgCl<sub>2</sub> 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<sub>(g)</sub>) and water vapor carrying pipe,
- 7. Hydrochloric acid absorber,
- 8. pH electrode.

#### **RESULTS AND DISCUSSION**

The effect of leaching time on the dissolution of dolomite was studied. 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<sup>-3</sup> and 1.53 mol, respectively.

$$CaMg(CO_{3})_{2} + 2H^{+} \rightarrow Ca^{2+} + MgCO_{3} + H_{2}O + CO_{2}\uparrow$$
$$MgCO_{3} + 2H^{+} \rightarrow Mg^{2+} + H_{2}O + CO_{2}\uparrow$$

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:

## PRECIPITATION

Dissolved calcium ions in the leach solution were removed by carbonation with  $CO_2$  gas as solid CaCO<sub>3</sub> 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:

$$CaCl_2+H_2O+CO_2 \rightarrow CaCO_3\downarrow+2HCl$$

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

$$CO_{2 (g)} \rightarrow CO_{2 (aq)}$$

$$H_{2}O+CO_{2} \leftrightarrow H_{2}CO_{3} \leftrightarrow HCO_{3} + H^{4}$$

$$HCO_{3} + Ca_{2} \leftrightarrow CaCO_{3} + H^{4}$$

## CONCLUSIONS

Recovery of the dolomite dissolution increased with time and reached 92.43 % within 5 min., at the end of the total period. 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. 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 at 600°C in 20 min. In the pyro hydrolysis process, kinetic data showed that removal of the product HCl gas was found to be an important factor controlling the rate of the decomposition.

# REFERENCES

AINSCOW W.S., GADGIL B.B., 1988, Process for producing magnesium oxide, U.S. Patent No. 4720375, January.

AKARSU H., YILDIRIM M., 2008. Leaching rates of Icel-Yavca dolomite in hydrochloric acid solution, Mineral Proc. Extractive Metallurgy Rev., 29, 42-56.

AKARSU A, 2004, The Research of Obtaining High Purity MgO from Icel-Yavca Dolomite, Cukurova University, Ph. D. Thesis, Adana, Turkey.

ALKATTAN M., OELKERS E.H., DANDURAND J.L., SCHOTT J., 1998, An experimental study of calcite and limestone dissolution rates as a function of pH from - 1 to 3 and temperature from 25 to 80 oC, Chemical Geology, 151, 199-214. BRECEVIC L., KRALJ D., 2007, On calcium carbonates: From fundamental research application, Croatica Chemica Acta, 80, 467-484.

BUSENBERG E., PLUMMER L.N., 1982, The kinetics of dissolution of dolomite in CO2-H2O systems at 1.5 to 65 oC and 0 to 1 atm PCO2,, American J. Sci., 282, 45-78. CHOU L., GARRELS M.R., WOLLAST R., 1989, Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals, Chemical Geology, 78, 269-282. DING Y., ZHANG G., WU H., HAI B., LIANGBIN W., QUIAN Y., 2001, Nanoscale magnesium hydroxide and magnesium oxide powders : Control over size, shape, and structure via hydrothermal synthesis, Chemistry of Materials, 13, 435-440.

DUHAIME P., MERCILL P., PINEAU M, 2002, Electrolytic process technologies for the production of primary magnesium, Transactions IMM Sect. C, 111, 53-55. GAUTELIER M., OELKERS E.H., SCHOTT J., 1999, An experimental study of dolomite dissolution rates as a function of pH from -0.5 to 5 and temperature from 25 to 80 oC, Chemical Geology, 157, 13-26.

HERMAN J.S., WHITE W.B., 1985, Dissolution kinetics of dolomite: Effects of lithology and fluid flow velocit, Geochimica et Cosmochimica Acta, 49, 2017-2026. KASHANI-NEJAD S., NG, K.-W., HARRIS R, 2005, MgOHCl thermal

decomposition kinetics, Metallurgical and Materials Trans. B, 36B, 153-157.

KIPOUROS J.G., SADOWAYD.R., 2001, A thermochemical analysis or the production of anhydrous MgCl2,, Journal of Light Metals, 1, 111-117.

KRAMER A.D., 1992, Magnesite and Magnesia, Minerals Yearbook, Metals and Minerals, U.S. Bureau of Mines, Vol. 1, 163-173.

LEVENSPIEL O., 1972, Chemical Reaction Engineering, John Wiley & Sons, Inc., New York.