

# Chemical beneficiation of magnesite

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## INTRODUCTION :

Magnesite is an important refractory mineral used in the manufacture of basic refractories. The total demand<sup>(1)</sup> for various kinds of basic refractories for 1984-85 has been estimated to be 4,68,000 tonnes per annum which is estimated to increase to 5,09,000 tonnes per annum by 1989-90. India has known reserves of 13.6 million tonnes of magnesite. Magnesite occurs mainly in Tamil Nadu, Uttar Pradesh, Karnataka and Rajasthan. The all-India production of magnesite in 1981 was 4,63,000 tonnes. Tamil Nadu produces nearly 76% of the all-India production followed by Uttar Pradesh with 21 %. The remaining 3% of the production comes from Karnataka and Rajasthan.

Natural magnesite is frequently too impure to be used as such in the manufacture of refractories. With the increasing demand for high grade refractories with change over to use of L. D. in the steel industry, the demand for purer grade of magnesite is growing up.

Mechanical/physical beneficiation methods for upgrading the natural magnesite to refractory grade magnesite often neither yield a product of adequate purity nor are economically attractive. When sufficiently pure magnesite is obtained by physical beneficiation methods, the yield is very poor. Chemical methods for purifying the magnesite for various commercial grades have been tried abroad successfully. There are three such methods which require particular mention here. Almost all the chemical beneficiation methods consist in solubilising the magnesium content of the magnesite, filtering off the gangue material, purifying the process liquor and finally precipitating magnesium as magnesium carbonate. The chemically beneficiated magnesite is very pure

and high grade and can be further processed to obtain high quality dead burnt magnesia suitable for use in the production of high grade basic refractories.

## VARIOUS PROCESSES FOR CHEMICAL BENEFICIATION OF MAGNESITE :

### 1st Process : Carbon dioxide atmospheric leaching process<sup>(2)</sup> :

The Carbon dioxide atmospheric leaching process flow sheet is presented in Fig. 1.

The magnesite is crushed and ground to proper mesh size and calcined under controlled conditions to selectively decompose magnesium carbonate as far as possible and leave the calcium carbonate as such. Optimum conditions for selective calcination have to be determined for each magnesite sample. Generally, a maximum temperature of 800°C is adequate for decomposition of nearly all of the magnesium carbonate and leaving most of calcium carbonate undecomposed. Pure magnesium carbonate begins to decompose at 350 °C while pure calcium carbonate begins decomposition at 825°C. The calcined magnesite is then slaked to hydrolyse the magnesium oxide to magnesium hydroxide. The magnesium hydroxide slurry thus obtained is treated with carbon dioxide gas at atmospheric pressure to convert the magnesium hydroxide to soluble magnesium bicarbonate. The slurry is filtered to obtain magnesium bicarbonate solution and the residue containing silica, calcium carbonate, etc. as insolubles is discarded. The magnesium bicarbonate solution is subjected to heating/aeration when magnesium bicarbonate decomposes to basic magnesium carbonate with the evolution of carbon dioxide gas which can be recycled to the carbonating step. The basic

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magnesium carbonate slurry is filtered. The cake containing basic magnesium carbonate is dried, while the filtrate containing residual magnesium bicarbonate may be used again for the next leaching of magnesium hydroxide. The dried/calcined magnesium carbonate is briquetted under pressure and sintered to obtain the refractory grade magnesite product.

### **2nd process : Carbon dioxide pressure leaching process :**

This process is just similar to the first process except that the leaching of the magnesium hydroxide slurry by carbon dioxide is carried out under pressure to obtain the magnesium bicarbonate liquor of higher concentration. In actual experimentation, however, it was observed that the concentration of magnesium carbonate achieved by leaching calcined magnesite with carbon dioxide at ten atmospheres pressure in aqueous medium at 30°C was 2.3 times the magnesium carbonate concentration achieved at one atmosphere pressure at 30°C. The product obtained from the pressure leaching process has the same composition as the product obtained from atmospheric leaching process. This process can be worked within the solubility limits as given in Table-1.

It is evident that the concentration of magnesium bicarbonate in the digest liquor from the pressure leaching process is higher than the concentrations obtained at atmospheric pressure, thereby resulting in the handling of lesser volume of digest liquor per unit of magnesium carbonate produced. However, sophisticated equipment cost such as of autoclaves and pressure control instruments, etc. may outbalance the advantage as compared to the atmospheric leaching process.

### **3rd process : Calcium chloride leaching process :**

Fig. 2 presents the calcium chloride leaching process flow-sheet.

In this process, the steps upto the preparation of magnesium hydroxide slurry starting

from magnesite are the same as in the first process. The magnesium hydroxide slurry is then treated with calcium chloride solution and carbon dioxide gas to obtain magnesium chloride and calcium carbonate. The carbonation of the magnesium hydroxide slurry and calcium chloride results in the formation of magnesium chloride and calcium carbonate. The slurry containing magnesium chloride in solution and calcium carbonate and other gangue materials as insolubles is filtered. The filter cake is calcined and the quick lime goes to the ammonia recovery plant. The filtrate containing magnesium chloride is subjected to purification for removal of residual unreacted calcium chloride. The purified magnesium chloride solution is treated with ammonia and carbon dioxide to form magnesium carbonate and ammonium chloride. Magnesium carbonate is filtered and obtained as filter cake. The filtrate containing ammonium chloride goes to the ammonia recovery plant. The wet magnesium carbonate after drying/calcination goes for briquetting and sintering to obtain refractory grade magnesite product.

## **EXPERIMENTAL :**

### **Preparation of magnesium carbonate from magnesite by carbon dioxide leaching process at atmospheric pressure.**

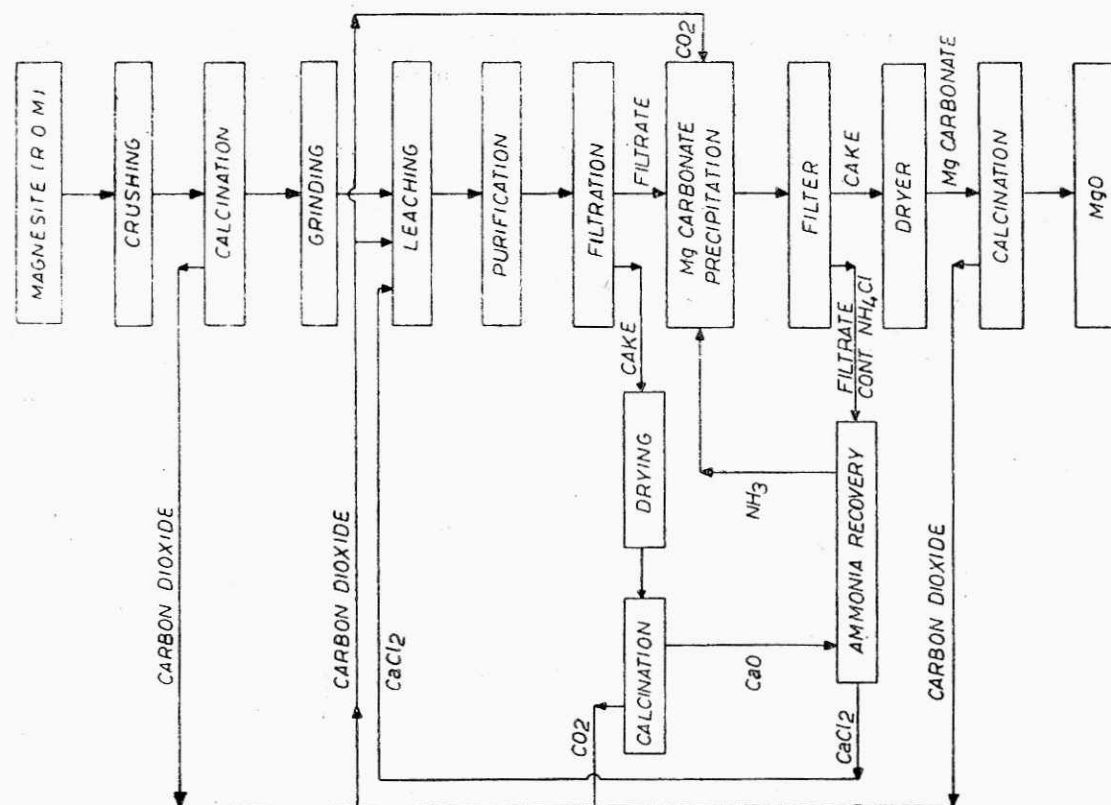
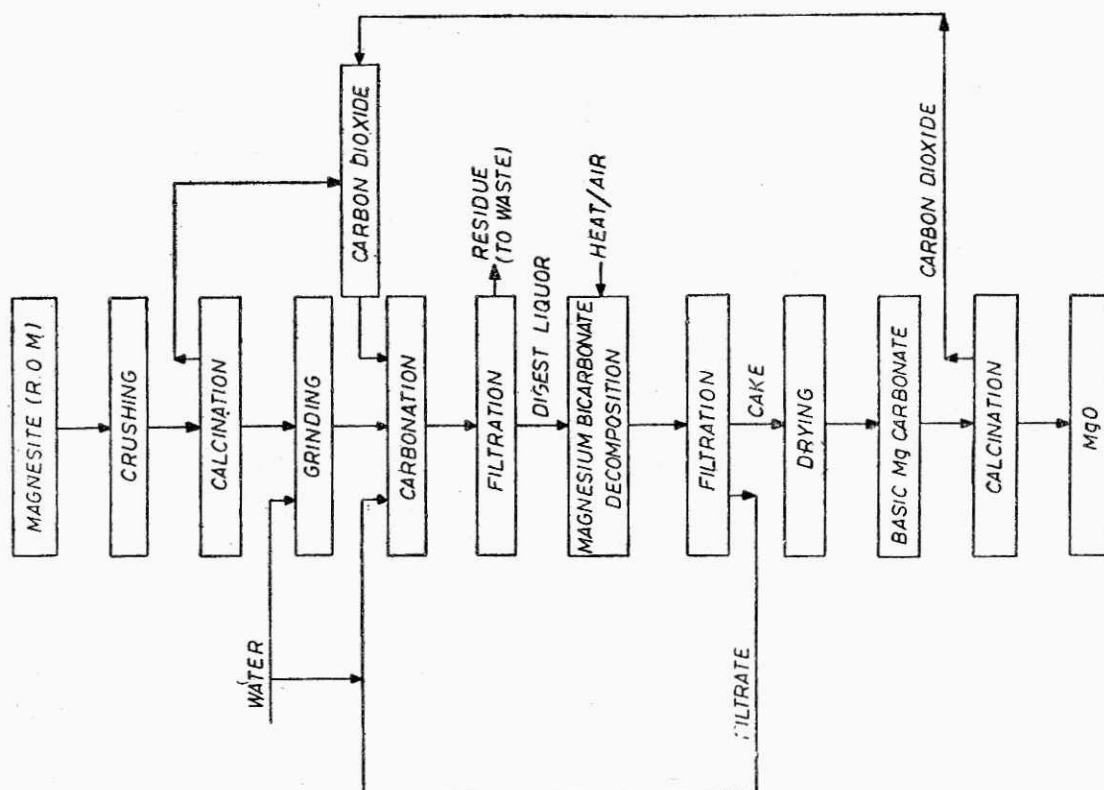
The magnesite sample taken for the studies was from Tamil Nadu. The R. O. M. sample was lumpy and had the size of four to nine inches.

The sample was crushed to -10 mesh and further ground to the finer mesh in the ball mill.

The chemical analysis and mesh size of the sample are given in Table-2.

### **Calcination of magnesite :**

Studies for calcination of magnesite were carried out in an electrically heated muffle furnace at various temperatures and time intervals to ascertain the calcination parameters. The results are given in Table-3 and Table-4.



It may be noted that the magnesite decomposition is almost complete when the sample is calcined at 750°C for one hour.

Although the calcination parameters were studied with the magnesite powder as reported in Table-3 and Table-4, the calcination was also studied with coarser sample and it was found that the mesh size between  $-\frac{3}{4}$ " and  $+\frac{1}{2}$ " was equally amenable to calcination at 750°C for one hour. The magnesite becomes friable after calcination. It is, therefore, suggested that the finer grinding may be carried out after calcination.

#### **Leaching of calcined magnesite :**

Leaching experiments were carried out in a three litre glass beaker fitted with an electrically driven glass stirrer. A glass tube was fitted into the beaker for passing carbon dioxide from a gas cylinder.

The ground calcined magnesite is to be slaked with water for converting magnesium oxide to magnesium hydroxide before leaching. Studies for ascertaining slaking parameters indicated that the conversion of magnesium oxide to magnesium hydroxide was complete when the slurry was agitated in water for one hour. Leaching studies were then carried out by passing carbon dioxide through the magnesium hydroxide slurry with simultaneous agitation. Leaching parameters viz. the amount of calcined magnesite per litre, the time of leaching and the rate of carbon dioxide passed were studied, keeping the temperature of leaching constant i.e. at 30°C  $\pm$  2°C for ascertaining optimum leaching conditions. The results of these experiments are given in Table-5, 6 and 7.

From the results obtained, it may be concluded that with the concentration of ten grams calcined magnesite per litre and passing one litre carbon dioxide per minute for an hour, the leaching was 88% with respect to magnesium oxide.

#### **Precipitation of magnesium carbonate**

The slurry after leaching was filtered and the residue was discarded. The filtrate con-

taining magnesium bicarbonate may be subjected to decomposition by two methods i.e. either by heating or by aeration. Both the methods were studied. When the digest liquor was subjected to boiling for an hour at 95 °C  $\pm$  3°C the decomposition of magnesium bicarbonate was of the order of 98%. While when air was passed through the digest liquor containing magnesium bicarbonate at the rate of 2 litres per minute per litre of digest liquor, 86% magnesium carbonate was precipitated in four hours. The rest 14% remains as a constant component of the process liquor. It may be mentioned that at 30 °C the saturated process liquor contains 7.2 gms MgO per litre. By aeration, 6.2 gms MgO is precipitated out as basic magnesium carbonate and 1 gm MgO remains in process liquor as constant component. The volume of process liquor to be handled for production of a tonne of MgO comes to be 1,61,000 litres.

For comparison sake, it may be mentioned that if heat energy is used for decomposition of magnesium bicarbonate, 7 gm MgO per litre can be obtained as basic magnesium carbonate and volume to be handled in this case comes to 1,43,000 litres/tonne of MgO produced. The energy required for heating 1,43,000 litres of process liquor to 95 °C for one hour is more than the energy required for handling an additional 18,000 litres volume of process liquor. Hence, the decomposition of magnesium bicarbonate by aeration seems to be more economical.

The physical nature and purity of the product obtained by both the decomposition methods i.e. by heating or aeration are same. The basic magnesium carbonate was dried at 120°C and further calcined at 900°C to obtain the magnesia product. The composition of the product obtained is given in Table-8.

The magnesium oxide product obtained by this process is very high grade and is within the desired specifications for its suitability for use in the manufacture of high grade basic refractories.

**Table — 1 : Solubility <sup>(3)</sup> of magnesium carbonate in Water-MgO-CO<sub>2</sub> system at one atmospheric pressure.**

Temp°C	3.5	12	18	22	25	30	40	50
Solubility gm MgO <sub>3</sub> per 100 gm soln.	3.56	2.65	2.21	2.00	1.87	1.58	1.18	0.95

**Solubility <sup>(4)</sup> of magnesium carbonate at 18°C for various partial pressures of CO<sub>2</sub>**

Pressure Atmos.	gms MgCO <sub>3</sub> / 100 gms Saturated solution
2	3.5
4	4.28
10	5.90
18	7.49
56	7.49

**Table—3. Calcination of magnesite at various temperatures.**

Quantity of the sample taken = 25 gms  
Bed thickness = 1.3—1.5 cm  
Time of Calcination = 60 min

S. No.	Temperature °C	Loss in Weight %
1	600	45.00
2	650	45.94
3	700	45.98
4	750	47.07
5	800	47.10
6	850	48.16

**Table—2. Chemical analysis of magnesite**

Constituents	%
Moisture	0.30
L. O. I.	47.97
SiO <sub>2</sub>	5.95
Al <sub>2</sub> O <sub>3</sub>	0.15
Fe <sub>2</sub> O <sub>3</sub>	0.80
CaO	2.18
MgO	42.58

Mesh size	%
+ 200 B. S. S.	2.0
— 200 + 250 B. S. S.	2.0
— 250 + 300 B. S. S.	9.0
— 300 B. S. S.	87.0

**Table—4. Calcination of magnesite for various periods.**

Quantity of the sample taken = 25 gms  
Bed thickness = 1.3—1.5 cm  
Temperature = 750°C

S. No.	Time in min.	Loss in Weight %
1	15	31.96
2	30	44.45
3	45	46.41
4	60	47.07
5	75	47.20

**Table — 5 : Leaching studies on percentage recovery with varying amount of calcined magnesite in the leach liquor**

Volume of the leach liquor = One litre  
 Slaking time given = One hour  
 Rate of carbon dioxide passed = One litre / minute  
 Temperature of the leach liquor = 30°C  
 Time of leaching = Two hours

S. No.	Calcined magnesite taken (gm)	MgO content of calcined magnesite (gm)	Amount of basic Mg carbonate obtained (gm)	MgO content of the product (gm)	Recovery % MgO
1	5.0	4.12	8.57	3.64	88.3
2	7.5	6.17	13.00	5.44	88.2
3	10.0	8.23	17.00	7.25	88.1
4	20.0	16.46	17.25	7.33	44.5

**Table — 6 : Effect of time on percentage recovery in the leaching of calcined magnesite with carbon dioxide at atmospheric pressure**

Calcined magnesite taken = 10 gm  
 MgO content of magnesite = 8.23 gm  
 Volume of the leach liquor = One litre  
 Rate of carbon dioxide passed = One litre/min.  
 Temperature of the leach liquor = 30°C

S. No.	Time of leaching (min)	Weight of Basic Mg. Carbonate obtained (gm)	MgO content of the Basic Mg. Carbonate (gm)	MgO Recovery (%)
1	10	5.62	2.36	28.7
2	20	11.26	4.74	57.6
3	30	13.27	5.58	67.8
4	40	15.90	6.69	81.2
5	45	16.70	6.89	83.7
6	50	16.96	7.14	86.8
7	60	17.00	7.25	88.1
8	70	17.50	7.35	89.3



**Table — 7 : Effect of rate of carbon dioxide passed on percentage recovery in the leaching of calcined magnesite**

Calcined magnesite taken = 10 gm  
MgO content of calcined magnesite = 8.23 gm  
Volume of solution = One litre  
Temperature = 30°C

Expt. No.	Leaching time (min)	CO <sub>2</sub> rate	Wt. of dry (120°C) product (gm)	MgO content of the product	Recovery of MgO (%)
1	60	$\frac{1}{2}$ l/min	10.88	4.58	55.7
2	60	1 l/min	17.00	7.25	88.1
3	60	2 l/min	17.22	7.28	88.4

**Table — 8 : Analysis of MgO obtained by various processes and specification**

Constituents	ISI (Ref. 6) Specifications of magnesite for refractories (%)	MgO (Ref. 5) from CaCl <sub>2</sub> process (%)	U.S. Producers MgO analysis (Ref. 3) (%)	MgO made by NML atmospheric leaching bicarbonate process (%)
MgO	85.0 Min	99.5	98.0	98.3
CaO	2.5 Max	0.2	1.0	0.9
SiO <sub>2</sub>	5.5 Max	0.10	0.4	0.4
Fe <sub>2</sub> O <sub>3</sub>	—	0.10	0.25	0.1
Al <sub>2</sub> O <sub>3</sub>	—	0.10	0.15	0.1

### Conclusion :

It is observed that the chemically beneficiated magnesium carbonate by chloride process is found to be purer than the products obtained by the bicarbonate process, both atmospheric and pressure leaching routes. However, Indian magnesites are amenable for chemical beneficiation to produce high quality magnesia by the above processes.

### Acknowledgements :

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