



ORIGINAL RESEARCH PAPER

Chemistry

PREPARATION OF HIGH PURITY MAGNESIA IN LARGE SCALE EXPERIMENTS FROM SEAWATER AND SINTERING STUDIES

KEY WORDS: bittern, magnesium carbonate, magnesia, desulphation, double salt, sintering

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ABSTRACT

Newer techniques have been developed to prepare high purity magnesia from sea bittern by double salt and desulphation method. The processes are optimized by subjecting one-liter bittern of different density for the preparation of magnesia. Different analytical and physical methods like elemental analysis, X-ray powder diffraction and microscopic study were carried out to characterize various products of the processes. Commercially available Fluka magnesium carbonate and its calcined product have also been simultaneously characterised for comparison. The high temperature strength measurements made solely in order to estimate the performance of refractories. Their sinterability was studied at 1700°C and 1800°C by preparing cylindrical pellets from MgO powders. The boron free magnesia shows high purity of 99 %.

INTRODUCTION

India has no magnesite deposits of acceptable purity and therefore there has been a total dependence on imported sources. India is importing high purity sinters of MgO for production of refractories used by units of both primary and secondary steel sectors. Current import of high sintered magnesia may be around 1,00,000 MT which is expected to increase gradually. This has not only caused an out-flow of valuable foreign exchange but has also throttled the operations of steel industry in sensitive areas such as production of speciality steels.

The sintering studies of magnesium oxide obtained from seawater were studied by Petric, *et al.* in 1994¹. MgO obtained from sea water by precipitation with 80% and 120% of the stoichiometric quantity of precipitating agent and the reagent grade MgO was added with 0.5% TiO₂ at a temperature of 1600 °C, for different duration of isothermal sintering and for different pressures applied in the forming of compacts. The product density, shrinkage, porosity, effect of TiO₂ in MgO on the content of B₂O₃ were examined and analysed. The Uniaxial compacting behaviour of MgO powders calcined at 900 – 1200 °C in air was investigated and the break point in the pressure density curve was found to be effective in elucidating the agglomeration state of the powder. The packing density of MgO powder as a function of calcination temperature was measured before and after milling operations. The plot of relative density vs. logarithmic pressure also exhibits a break point, which indicates the pressure at which the contact points in porous agglomerates began to be destroyed. The agglomerate strength of MgO powders calcined at low and high temperatures (900 –1200 °C) was measured and the micro structural differences between agglomerates in MgO powder and the surface of a compressed powder were examined by SEM². The characteristics of formation of Mg(OH)₂ in a continuous reactor in magnesium chloride-calcium hydroxide water system was studied by Poilov, *et al.* in 1993³. During the formation of Mg(OH)₂ particle size distribution, sp. surface area and particle size were found to vary continuously. The Mg(OH)₂ formation is significantly affected by the agglomeration mechanism of particle growth and nature of excess ions and the effect is analysed of interaction of the CO₂ from air with Ca(OH)₂ on the particle size distribution in Mg(OH)₂^{4,6}.

EXPERIMENTAL

Bittern of 29° Be ' and 30° Be ' were collected from the Huma solar salt plant, Ganjam district of Odisha and Dalmia Salt Works, Gujrat respectively for performing the experiments. The preparation of magnesia in two different process i.e. double salt and desulphation were optimized by carrying out experiments using 1000ml bittern of 29 °Be' and 30 °Be'. Commercial grade reagents like calcium chloride,

ammonium sulphate, ammonium carbonate, ammonium hydroxide and sorbitol were used for the precipitation reaction. Physicochemical methods were employed to characterize the products obtained during the processes.

Preparation of Magnesia through Double salt route

One liter 29° Be' bittern containing 49.607g of magnesium (Table 1.) was subjected to double salt precipitation. 538g of ammonium sulphate was added to it and kept on hot water bath till the temperature reaches ~60 °C. It was kept for another 2 h on the water bath and then cooled to room temperature. The double salt obtained is 937g (wet), which on drying weighs 662.08g. 460.8g of ammonium carbonate dissolved in 500ml water was then added gradually to the double salt solution with constant stirring. It was then kept on hot water bath till the temperature 70 °C and then kept for further two hours. Filtered while hot and then washed several times with one-liter hot water to remove the dissolved impurities. In the last step of washing 2-3 drops of sorbitol was added to the distilled water to make it free from any adsorbed Boron. The magnesium carbonate obtained was dried at 110 °C and further calcined at 1100 °C in a muffle furnace to yield MgO. These samples were then characterized physico-chemically.

Preparation of Magnesia through Desulphation route

One liter 30° Be' bittern containing 80.71g of magnesium and 44.64g sulphate (Table 2) was subjected to desulphation by adding 46.44g of fused calcium chloride. It was then kept on hot water bath till the temperature reaches ~65 °C. The mixture was stirred properly and white precipitate of gypsum was formed immediately. It was kept for another 3h and then the system was removed from the hot water bath and filtered while hot using G2 Buchner funnel. The gypsum separated was washed with a little amount (50-100ml) of water and dried at 110 °C and weighed to be 55.54g. To the mother liquor 1020ml of ammonia (NH₄OH 25%) and 389.46g of ammonium carbonate [(NH₄)₂CO₃] were added and stirred well. The reaction temperature was 33 °C after addition of ammonia and became 39 °C after addition of ammonium carbonate. It was kept on hot water bath till the temperature reaches 65 °C and then continued for another 3h for the complete precipitation of MgCO₃. The precipitated solid was separated by filtration and washed with one liter hot distilled water several times to make it free from other dissolved impurities. The magnesium carbonate formed was dried at 110 °C and calcined at 1100 °C and the resulting products are physico-chemically characterized.

Sintering Study

Sintering study of magnesium oxide was carried out at Tata Refractories Ltd., Belpahar, Orissa using a minimum of one kg prepared sample. Since one litre bittern generates about 60–70g of magnesia several experiments were conducted to

produce one kg of magnesia sample separately in both Double Salt and Desulphation process. Samples were taken to Tata Refractories Ltd. for sintering and allied studies. Cylindrical pellets (40.5 dia x 35.2 h mm) were made with a specific pressure of 154 kg/cm² and with a green B.D of 1.14 (gm/cc). The samples were fired in high temperature tunnel kiln at a temperature of 1700 °C and 1800 °C for 3 h.

RESULTS AND DISCUSSION

Magnesium carbonate was prepared through double salt route following the procedure already outlined. The analysis results of bittern, double salt, magnesium carbonate and mother liquors are presented in Table. 1.

**TABLE- 1
CHEMICAL COMPOSITION OF BITTERN, DOUBLE SALT, MgCO₃ AND MOTHER LIQUOR**

Element	Bittern gms/lit	Double salt (gms)	Mother Liquor (gms)	MgCO ₃ (gms)	Mother Liquor (gms)
Mg	49.607	47.60	0.960	36.394	2.618
SO ₄ ²⁻	64.70	375.6	80.616	nil	325.36
Cl	191.979	50.479	140.66	0.062	39.423
Na	53.75	13.546	40.013	0.008	10.029
K	10.875	5.926	4.553	0.0009	5.104

Similarly, magnesium carbonate has been prepared through desulphation route by processing one liter bittern of 30° Be'. Chemical composition of bittern, desulphated bittern, mother liquor is presented in Table 2.

**TABLE- 2
CHEMICAL COMPOSITION OF DESULPHATED BITTERN, MgCO₃ AND MOTHER LIQUOR**

Element	Bittern gms/lit	Gypsum (63.5384 gms)	Desulphated Bittern (gms)	MgCO ₃ (284gms)	Liquor (gms)
Mg	80.712	0.301	80.43	73.012	1.034
So ₄ ²⁻	44.64	38.68	5.802	Nil	4.011
Cl	229.593	-	263.036	Nil	214.58
Na	17	0.68	16.23	0.46	13.64
K	8.187	0.461	7.603	0.034	5.457
Ca	0.077	14.16	0.592	0.431	0.111

An important finding is that the magnesium loss is less in processing 30° Be' bittern which have more magnesium concentration initially, whereas magnesium loss is more in 29° Be' bittern. Of course, the mother liquor and washings of MgCO₃ in case of double salt route are not rejected but are concentrated and used in the recycle experiments. Magnesium carbonate prepared in both the routes are calcined separately at 1100 °C yielding magnesia. The chemical composition of prepared MgO along with Fluka MgO are presented in Table 3.

**TABLE- 3
CHEMICAL COMPOSITION OF MgO**

Composition (Oxide)	MgO from Desulphation	MgO from Double salt	Fluka MgO
MgO	99.03	99.12	99.265
CaO	0.629	0.027	nd
MnO ₂	0.002	0.002	nd
Fe ₂ O ₃	0.005	0.006	<0.169
Al ₂ O ₃	0.061	0.081	nd
SiO ₂	0.008	0.008	nd
Na ₂ O	0.193	0.008	nd
K ₂ O	0.031	0.002	nd
Cl	nd	0.0896	<0.024
SO ₄ ²⁻	nd	nd	<0.709
B ₂ O ₃	nd	nd	nd

*nd-not detected

The data shows that the purity of MgO in double salt route is

99.12% and the recovery of MgO is 73.82% with respect to magnesium concentration present in bittern. Similarly, the purity of MgO in desulphation route is 99.03% and the recovery is 90.45%. This remarkable recovery in case of desulphation process may be attributed to the presence of high concentration of magnesium in bittern. Hence, it is clearly seen that highly concentrated bittern incurs more recovery and less percentage of magnesium loss in the process. But the calcium contamination is more compared to double salt route due to the addition of CaCl₂ to bittern during desulphation. Hence, the purity is also lowered.

Sintering Studies of MgO

The high temperature strength measurements may be made solely in order to estimate the performance of refractories. The cylindrical pellets prepared from MgO powders are fired at 1700 °C and 1800 °C to study their sinterability. The magnesia powders are calcined again at 1200 °C and their chemical compositions are determined as presented in Table 4. The physical properties of the sintered magnesia are also presented in Table 5.

**TABLE- 4
CHEMICAL ANALYSIS ON LOSS FREE BASIS**

Oxide (%)	MgO (Desulphation)	MgO (Double salt)
MgO	99.13	99.567
SiO ₂	0.10	0.028
CaO	0.57	0.260
Al ₂ O ₃	0.10	0.056
Fe ₂ O ₃	0.05	0.016

**TABLE- 5
PHYSICAL PROPERTIES OF SINTERED MAGNESIA**

Physical properties	MgO of desulphated route		MgO of double salt route	
	Sample fired at 1700°C	Sample fired at 1800°C	Sample fired at 1700°C	Sample fired at 1800°C
% Apparent porosity	7.317	6.1	1.84	0.97
Bulk density in gm/cc	3.145	3.183	3.2323	3.3548
Apparent skeletal density	3.393	3.455	3.2933	3.3872
Mineralogy (Major)	Periclase	Periclase	Periclase	Periclase
Crystal size (Average)	21m	21m	27-28m	27-28m
Range	4-35m	4-35m	8-35m	8-35m

The samples were examined under reflected light and the microscopic study shows that the samples found to contain very fine euhedral direct bonded periclase crystal. The periclase crystal size range and average are given in Table 5. The presence of periclase crystals are further supported by X-ray diffraction study. From the data it is observed that with the increase in sintering temperature the percentage of apparent porosity decreases with the simultaneous increase in bulk density (BD). On comparison, between two samples of magnesia of different preparation methods it is observed that magnesia of double salt route attains the desired BD (3.35gm/cc) at 1800 °C. Whereas magnesia of desulphation route has marginal BD growth when the sintered temperature rises from 1700 °C to 1800 °C. Similarly, there is no appreciable change in apparent porosity also in desulphated magnesia. The effect of density on the high temperature properties of magnesia grain has been an important study for the evaluating the strength of magnesite bricks. As expected the strength increases with decreasing porosity. The reason for not attaining the desired physical parameters in desulphated magnesia even having high purity (>99%) is due to the effect of SiO₂, CaO and other R₂O₃. The desulphated magnesia is having more percentage of SiO₂, CaO and other R₂O₃.

In magnesite bricks (other than those which are deliberately spinel bonded) the essential refractory components are magnesia combined with a refractory silicate which can usefully be either magnesium orthosilicate (forsterite) or calcium silicates. Calcium silicates, especially dicalcium silicate and tricalcium silicate are now the more commonly used secondary components because the principal use of premium grade magnesite bricks is in the basic steelmaking where they are subject to attack by slags of high lime content which rapidly flux forsterite. Di and tricalcium silicates are, however, severely fluxed by all "R₂O₃" group oxides in the order B₂O₃ > Al₂O₃ > Fe₂O₃ > Cr₂O₃ so that these substances are deleterious impurities. The particularly strong fluxing action of boron oxide can be inferred from the work of Flint and Wells⁶ on the system CaO-B₂O₃-SiO₂ taken with the work of Kuzel⁷ on the system MgO-B₂O₃-SiO₂, and more precisely from recent work of White and coworkers^{8,9} on the quaternary system CaO-MgO-B₂O₃-SiO₂. Thus there are good reasons for high purity and for having the lowest practicable contents of at least some of the substances lime, silica, iron oxide, aluminium oxide and boron oxide in premium grade dead-burnt magnesite.

The chemical resistance and stability of magnesia depends on the purity level of MgO. The chemistry and impurity is of great concern, since impurities can affect the magnesite grain. Proper selection of the C:S ratio is important for refractoriness. Boron reduces refractoriness and hot strength; therefore, low boron levels are required. The silica affects the surface of the MgO grains by forming a thin layer of forsterite (2MgO·SiO₂). A high bulk specific gravity is also required. For a high purity magnesite, this is an indication of lower porosity with an inherent lower surface area, which improves the chemical stability of the grain. Periclase bonding is desirable. If this type of bonding is not found, it is only because of some small amounts of high melting impurities present which concentrate at the grain boundaries. Nevertheless, there is a high degree of MgO/MgO bonding found in high purity magnesite grains. Large MgO crystals are preferred. The specific surface of MgO is decreased and its chemical stability is significantly increased by increasing the crystal size.

CONCLUSIONS

Magnesia of two different preparations are studied for their sinterability. It is observed that the large-scale preparation improves the recovery and quality of magnesia 10,11. Simultaneously the loss of magnesium in different stages of process is also minimized. The investigation on the effect of chemical composition on the strength of magnesia grain was undertaken to isolate improved chemical compositions for evaluation of the potential for brick firing, the aim is to develop bond between the magnesia grain particles. It should be noted, however, that for the very high purity magnesia (desulphated magnesia) it has not been possible to achieve quality magnesia grain due to the contamination of impurities. Generally, as soon as the impurity phase in magnesia begins to soften with high temperature sintering the strength of the material markedly decreases and the greater the degree of wetting by the impurity phase on the magnesia crystals, the lower the dihedral angle, the greater the strength decrease. Hence, the effect of the impurities (CaO, SiO₂, Al₂O₃, B₂O₃, Cr₂O₃, Fe₂O₃, Mn₂O₃ and TiO₂) present in refractory grade magnesia is an important factor. With the above observations it may be concluded that the MgO powder prepared in double salt route is more suitable for refractory brick making than desulphated MgO powder. However, the uses of high pure magnesia is manifold and finds use in a range of market. Hence, this investigation will certainly reduce the import load and country's dependency.

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