Preparation of high pure refractory grade magnesium oxide from east coast sea water

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Preparation of good quality magnesium oxide from seawater is the most challenging job because the vast majority of undesired impurities come from seawater during the precipitation stage. Hence, the double salt route has been developed as a very unique technique to prepare refractory grade magnesium oxide from seawater. Controlled addition of carrier reagent at the precipitating stage precipitates magnesium as double salt. The double salt is transformed to magnesium carbonate ($MgCO_3$), which after calcination forms magnesium oxide (MgO). The product quality has been established by elemental analysis, PXRD, FTIR, TG/DTG, and FESEM. Commercially available $MgCO_3$ and MgO of HiMedia have also been characterized simultaneously for comparison. The prepared magnesium oxide shows very high purity of 99.75%, which is shown from EDS measurement and PXRD and can be suitable as basic refractory material for industrial purposes.

Keywords: Sea water, Sea bittern, Double salt route, Double salt, Magnesium carbonate, Magnesium oxide

Salt is the most common mineral on the planet and seawater constitutes a rich source of various commercially important chemical elements. Sea water is the prime source of salts of different alkali & alkaline earth metals[1-2]. Sea water can be the prime source of magnesium, potassium, and sodium salts[3-4]. Magnesium has so many applications in industry and medicinal chemistry[5-7] and hence, much of the world's magnesium is recovered from seawater. Here the main focus is to prepare highly pure magnesium oxide from seawater as the demand for high purity magnesium oxide increases for the use as basic refractory in the lining of furnaces. In the last few decades, there were many research groups did efforts to synthesize high pure magnesium oxide from natural magnesite[8-12], sea water[13-19], and magnesium oxide-rich brine[20-22]. As magnesium ores have limited physical and chemical beneficiation, it is difficult to extract magnesium oxide from the ores. The hydrochloric acid leach route allows direct leaching of magnesium bearing ores to magnesium chloride leach liquor. The use of strong acids causes significant corrosion problems in the leaching plant. As magnesium oxide preparation from seawater is less expensive so it can be used as a good alternative path to the preparation of magnesium oxide from seawater. After continuous evaporation seawater is converted to

bittern which is enriched with magnesium salts so bittern can be used for the production of magnesium oxide. Besides this, the bittern rejected from solar plants could also be considered as the raw material for the preparation of magnesium oxide. $MgCO_3$ or $Mg(OH)_2$ are precipitated from sea bittern using many precipitating agents like Na_2CO_3, NaOH, $Ca(OH)_2$, dolomite, etc. All chemical processes used for magnesium oxide preparation, are nearly same but for refractory purposes, magnesium oxide should be very pure, i.e. >99%. Commercially, magnesium hydroxide will be the intermediate for all chemical processes used for magnesium oxide preparation, and handling this intermediate for the next step of the chemical process is highly complicated as magnesium hydroxide is a very good sorbent. Magnesium hydroxide has a large specific surface area with uncovered OH^- rich faces. Therefore, the use of magnesium hydroxide as an intermediate for the preparation of magnesium oxide shows specific impurities like silicon, aluminium, iron, boron, and calcium, and these impurities reduce the hot strength of magnesium oxide refractory[19,23,24].

In this study, a new process[25] (Double Salt Route) has been evolved to get very pure magnesium oxide from seawater. After continuous evaporation of seawater, bittern is formed. From this bittern, the

basic magnesium carbonate has been prepared, which do not adsorb the impurities in the same extent as does the magnesium hydroxide. Seawater is not a dilute but a multiphase system consisting of a moderately concentrated solution of high ionic strength. The cations generally tend to associate with anions as ion pairs rather than inner sphere complex. Hence, purification of seawater or bittern is a challenging task and therefore, selective precipitation methods are employed to separate the desired chemicals from sea bittern.

Experimental Section

The required raw material, 29 ^{0}Bé sea bittern was made by evaporation of seawater collected from Paradip, Bay of Bengal. Sea water available at the coast is about 3.5 ^{0}Bé density. By evaporating the seawater up to 29 ^{0}Bé, most of the calcium and sodium salts contained in the sea brine are thrown out and at 29 ^{0}Bé where a very high percentage of salts present in the bittern with 25 to 30% sodium chloride (Table 1) and this density (29 ^{0}Bé) is optimum for separation of magnesium oxide from sea bittern[25]. Reagent-grade ammonium sulfate, ammonium carbonate from Merck Chemical, and sorbitol from HiMedia are used in the preparation of magnesium oxide. Magnesium carbonate and magnesium oxide from HiMedia are used as a reference for comparative study in the result discussion part. A set of experiments have been done to get the optimum condition for the precipitation of double salt from sea bittern. 100 mL sea bittern was treated with ammonium sulfate at varied ratios of Mg: $(NH_4)_2SO_4$, i.e. 1:1, 1:1.25, 1:1.5, 1:1.75, and 1:2 at normal temperature. Due to the exothermic reaction

condition, reaction temperature increased to ~45°C. After that, the reaction mixture was kept in a hot water bath at 65°C with continuous stirring for 2 h. Then on cooling double salt precipitated out from the reaction mixture and the precipitate is filtered and dried at 110°C.

Similarly, a set of experiments has been done to get the optimized condition for the precipitation of magnesium carbonate. 100 g double salt $(MgSO_4(NH_4)_2SO_4.6H_2O)$ dissolved in 500 mL deionized water and reacted with the precipitating agent, ammonium carbonate at varied ratios of Mg: $(NH_4)_2CO_3$, i.e. 1:1, 1:1.25, 1:1.5, 1:1.75 and 1:2 at normal temperature. Ammonium carbonate is added to the reaction mixture with continuous stirring. Then the reaction mixture is kept in a hot water bath at 40°C for 1 h to start the precipitation process and then the temperature is increased to 70°C for 2 h to complete the precipitation process of magnesium carbonate[26]. After cooling, the precipitate is filtered and washed several times with deionized water to make it impurities free and a few drops of sorbitol were mixed with deionized water and washed the precipitate to get boron free product. Then the product is dried at 100°C and calcined at 1100°C to get high pure magnesium oxide. The flow chart for the synthesis process is shown in Scheme 1.

Sea bittern and seawater were analyzed by AAS (SHIMADZU AA- 7000), ICP OES (iCAP7000), and Flame Photometer (SYSTRONICS Flame Photometer 128) for the major and trace elements, and pH & EC were determined by WTW Kit (Model Multi 340i). Synthesized and commercially available magnesium carbonate and magnesia were characterized by XRD (RIGAKU ULTIMA IV), FTIR (BRUKER ALPHA II), TG-DSC (NETZSCH-STA449F3), and FE SEM (ZEISS SUPRA 55) techinques.
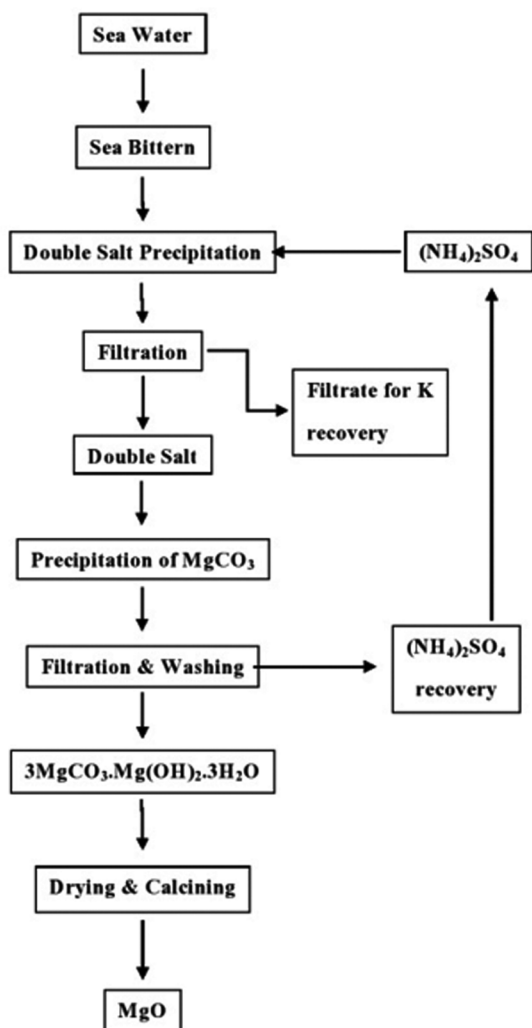
Results & Discussion

Analysis of sea bittern

The analyzed sea water and bittern of 29 ^{0}Bé show the concentration of major elements and the trace elements are given in Table 1. Sodium chloride, magnesium chloride, magnesium sulfate, and potassium chloride are the major components present in the sea bittern with minor quantities of sodium sulfate, bromides, and other components[27-29]. Normally, the pH of seawater is in the range of 7.8 to 8.4 i.e., alkaline in nature for the presence of carbonates, $H_2BO_3^-$ and bicarbonates[30]. During the thermal evaporation of seawater, the pH of sea bittern

Table 1 — List of major and the trace elements present in sea water and sea bittern

| Constituent elements	Elements	3.5° Be' Sea Water	29° Be' Sea Bittern
Major elements (g/L)	Mg	1.254	51.336
	Ca	0.289	0.112
	Na	5.12	57.45
	K	0.11	11.256
	SO_4^{2-}	1.996	65.64
	Cl^-	18.893	195.92
Trace elements (mg/L)	Co	0.129	2.59
	Fe	0.210	7.1
	Mn	0.240	0.69
	Ni	0.18	0.115
	Cr	0.22	1.77
	B	4.5	47.42
	Sb	0.0005	6.05
	Al	0.01	ND
	Si	3	ND

Scheme 1 — Flow diagram of pure MgO through double salt route

is not alkaline because carbonates and bicarbonates are removed as $CaCO_3$. Thus, the pH of the 29 ^{0}Bé shows 6.74 and the electrical conductivity shows 506000 μS/cm due to the ionic strength and ionic mobility of the ions in the sea bittern.

Preparation of double salt

The double salt is prepared from the sea bittern by the addition of a stoichiometric amount of ammonium sulfate to the bittern. Due to the exothermic reaction condition, the solubility of ammonium sulfate in the bittern solution increases with increasing the temperature and by further heating, sulfate ions spread homogenously throughout the solution which is rich in magnesium. On cooling the reaction mixture, the precipitation of double salt is started and separated from the solution at room temperature.

The precipitation process is generally a heterogeneous precipitation method by which the solid alkali sulfate is separated from the solution. In this study, the different ratios of magnesium and ammonium sulfate have been used to get the optimum reaction condition for the preparation of double salt i.e. $MgSO_4$. $(NH_4)_2SO_4.6H_2O$[31]. It is observed that in the second experiment (1:1.25 ratio), the recovery of Mg in the double salt is more (98.74%). With increasing the addition of more amount of ammonium sulfate in the ratio of 1:1.5, 1:1.75, and 1:1.2, more amount of double salt obtained as unreacted ammonium sulfate has also been co-precipitated along with double salt. So, to reduce the impurity of the carrier reagent in the double salt, the addition of ammonium sulfate in the ratio of 1:1.25 is taken as an optimized condition for the double salt precipitation. Theoretically, for 100% recovery of Mg, the amount of double salt formation from the sea bittern should be 76.037g. For the double salt formation, the possible reaction equation is

$$MgCl_2(in\ bittern) + 2(NH_4)_2\ SO_4 \rightarrow$$
$$MgSO_4(NH_4)_2\ SO_4.6H_2O + 2NH_4Cl$$
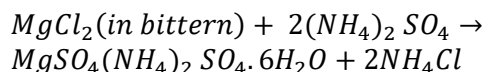
In seawater, Mg is present as magnesium sulphate in appreciable amounts along with magnesium chloride. Sodium Chloride and magnesium Chloride are the predominant salt components of sea water. When ammonium sulphate is added to the bittern, the magnesium chloride present is converted to magnesium sulphate. Simultaneously, potassium sulphate, sodium sulphate and calcium sulphate are formed and their solubility increased by the formation of more and more ion pairs between Mg^{2+} and SO_4^{2-}. The extent of association of Mg^{2+} and SO_4^{2-} increases with decrease in temperature, thereby, forming double salt. Sulphate compounds of other cations remain in solution. The solubility of other components increases by the formation of ion pairs between Mg^{2+} and SO_4^{2-} in the solution as Mg^{2+} is very effective in terms of effectiveness in complexing[32,33].
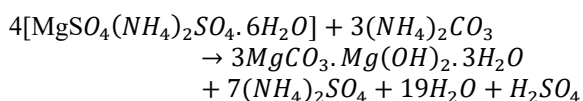
Preparation of magnesium carbonate

The preparation of magnesium carbonate from bittern has been done by using many precipitating agents, like sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and ammonium carbonate[34]. The use of sodium or potassium carbonate shows the presence of a trace number of cations (Na^+ or K^+) in the MgO that affects the base strength of magnesium oxide and reduces the strength of magnesium oxide bricks. So, to obtain the

Table 2 — Extraction percentage of double salt and hydromagnesite at varied ratios

Varied Ratio	Double salt			Hydromagnesite		
	Wt. of dry double salt Expt. (Theo) in g	Mg in double salt in g	Recovery of Mg in double salt (%)	Wt. dry hydromagnesite Expt. (Theo) in g	Mg in hydro-magnesite in g	Recovery of Mg as hydromagnesite (%)
1:1	59.2(76.04)	5.004	97.48	19(26.16)	5.011	71.68
1:1.25	72.5(76.04)	5.068	98.74	21(26.16)	5.538	79.11
1:1.5	83.5(76.04)	5.012	97.64	21.5(26.16)	5.671	80.11
1:1.75	95.6(76.04)	5.021	97.81	21.9(26.16)	5.772	81.54
1:1.2	102.4(76.04)	5.028	97.95	22.2(26.16)	5.855	83.69

precipitate of magnesium carbonate from the double salt solution [MgSO$_4$(NH$_4$)$_2$SO$_4$.6H$_2$O], ammonium carbonate has been tried as a precipitating agent to get high pure magnesium oxide. Here the purpose of mild heating (70°C) is to convert any occluded magnesium sulphate or insoluble double salts of ammonium magnesium sulphate for homogenization, which leads to the complete precipitation of magnesium carbonate and soluble ammonium sulphate. A varied amount of ammonium carbonate was added to the double salt solution for Mg present in the double salt to precipitate magnesium carbonate. The reaction has been done by the slow addition of ammonium carbonate to the double salt solution. Magnesium recovery as magnesium carbonate and experimental conditions are given in Table 2 and the possible reaction equation for the formation of basic magnesium carbonate is as follows.

$$4[MgSO_4(NH_4)_2SO_4.6H_2O] + 3(NH_4)_2CO_3$$
$$\rightarrow 3MgCO_3.Mg(OH)_2.3H_2O$$
$$+ 7(NH_4)_2SO_4 + 19H_2O + H_2SO_4$$

It is observed that the addition of excess (NH$_4$)$_2$CO$_3$ increases the extent of Mg recovery in magnesium carbonate from a 1:1 to 1:2 ratio. The percentage of Mg in hydrated magnesium carbonate varies from 71.68% to 83.69%. Here, the 1:1.5 ratio has been chosen for Mg recovery as magnesium carbonate due to less consumption of reagent materials, and also the impurities, particularly boron present in the basic magnesium carbonate will be less.

Boron is found in sea water in the form of non-dissociated orthoborate acid (H$_3$BO$_3$) and partly in the form of borate ion (H$_2$BO$_3^-$). The concentration of higher oxidation level ions (HBO$_3^{2-}$, BO$_3^{3-}$) is very low. It is well known that at low or neutral pH boron compounds do not dissociate into ions. As pH increases boron assumes the form of borate ion. In case of magnesium hydroxide precipitation from sea water by the addition of hydroxyl ions borate ion adsorbed on to the surface of Mg(OH)$_2$. This is because hydroxyl ion has high surface area with abundance of exposed OH$^-$ rich faces. In a highly alkaline medium (pH=12.5) boron desorbed thereby preventing further contamination. Hence, the boron content is reduced by rinsing the precipitate by (1) alkalised distilled water or slaked lime, (2) complexing agents as polyhydric alcohol, (3) Ion exchange resins or (4) adding caustic soda to volatilise boron. Moreover, EDS analysis of magnesium carbonate shows the absence of boron peak confirming that boron has been removed from the final product. Many research groups have reported the preparation of magnesium carbonate using various precipitating conditions and reagents[35-40]. In the previously reported methods, the cost of chemical processes is high due to the consumption of reagents for the precipitation of magnesium hydroxide. Whereas in the double salt route, ammonium sulfate was regenerated during the conversion of basic magnesium carbonate from the double salt, which could be reused for double salt precipitation, and also in basic magnesium carbonate, the presence of impurities is lower than in magnesium hydroxide. So, magnesium oxide prepared from basic magnesium carbonate is pure with good chemical activity.

Physico-chemical characterization

The prepared and HiMedia magnesium carbonates (Fig. 1) were subjected to XRD analysis for ascertaining the mineral phases. The X-ray diffractogram for prepared magnesium carbonate shows four major peaks with d spacing values 5.809, 2.902, 2.15, 2.5Å, and their corresponding 2θ are (15.52º, 30.8º, 41.92º, 36º) in good agreement with hydromagnesite (3MgCO$_3$.Mg(OH)$_2$.3H$_2$O) as described in the JCPDS file (JCPDS Card 25-513)[41]. Both the reference (HiMedia) and prepared magnesium carbonates reveal almost a similar pattern and confirm the structure of hydromagnesite as the monoclinic. This ensures that the hydrated magnesium carbonate is successfully prepared from

the double salt. Besides, the XRD of prepared and reference (HiMedia) magnesium oxides (Fig. 2) shows the same pattern and has five peaks with d spacing (2.412, 2.085, 1.512, 1.2541, 1.224 Å) and 2θ (37.22º, 43.18º, 62.56º, 74.9º, 78.84º) which are well accordance with the JCPDS (JCPDS Card-78-0430)[42] of magnesium oxide. Therefore, it can be confirmed that magnesium oxide is formed which is further supported by TG-DTG and FTIR analyses.

The FTIR study for the reference (HiMedia) magnesium carbonate and the synthesized magnesium carbonate are almost similar. From the FT IR spectra, the $\nu(OH)$ mode appears as a broad band in the region 3200-3600 cm^{-1} in both the samples for the water molecules and hydroxo groups. From FTIR spectra, ν_1 mode appears single sharp band at 1102 cm^{-1}, and ν_2 mode is also a single sharp band at 846 cm^{-1}.
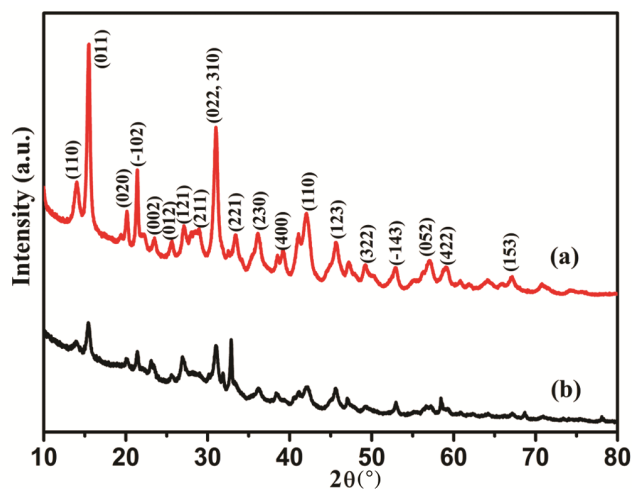
Fig. 1 — Comparative XRD patterns of (a) reference (HiMedia) MgCO$_3$ and (b) prepared MgCO$_3$

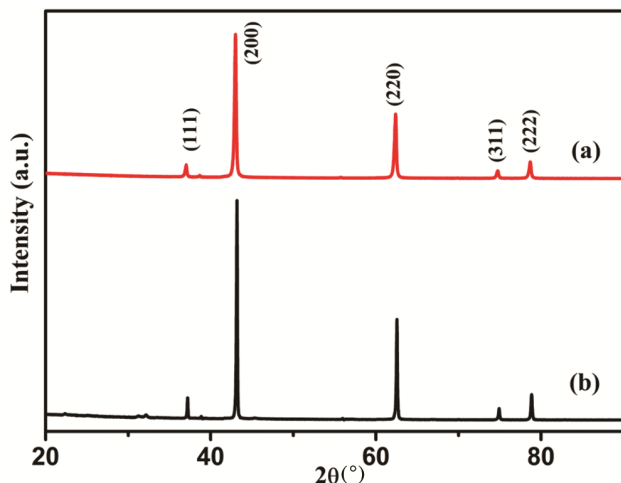Fig. 2 — Comparative XRD patterns of (a) reference (Himedia) MgO and (b) prepared MgO

The distinct doubling of ν_3 modes appear at 1509 & 1408 cm^{-1} for CO$_3^{2-}$ absorption bands[43,44]. The reference sample also shows a similar type of absorption band as shown in Fig. 3. So, from FTIR analysis, it is confirmed that the synthesized sample is hydromagnesite (3MgCO$_3$.Mg(OH)$_2$.3H$_2$O).

The TG-DTG curves of reference (HiMedia) and synthesized hydromagnesite (3MgCO$_3$.Mg(OH)$_2$.3H$_2$O) studied between 27 to 1000°C are shown in Figs 4a and b. It is found that the decomposition begins very early at 37°C and ends at ~500°C for both the samples demonstrating similar decomposition behaviour. The percentage of weight loss from the TG curve is observed to be 55.4% for reference MgCO$_3$ whereas that of synthesized 3MgCO$_3$.Mg(OH)$_2$.3H$_2$O is 86.4%. This indicates the presence of more intermediate inorganic molecules (H$_2$O, OH, and CO$_3$) and the compound seems to be non-stoichiometric. As the general formula of hydromagnesite is xMgCO$_3$. yMg(OH)$_2$. zH$_2$O[(Ref.45)], the possible intermediate species are H$_2$O (water of crystallisation), Mg bound OH, and CO$_3^{2-}$ molecules which are already confirmed from FTIR. Therefore, the DTG profile exhibits a minor endothermic decomposition between 37-127°C and two strong peaks between 157-317 and 332-527°C. The lower endothermic peaks are seen for synthesized MgCO$_3$ at 212.5 and 397.5°C as compared to HiMedia MgCO$_3$ at 262.5 and 442.5°C. The minor decomposition is due to the removal of H$_2$O (water of crystallisation) molecules while at ~200°C ± is assigned to loss of Mg bound OH species. Finally, a strong peak at ~400°C ± is owing to the decomposition of Mg bound CO$_3^{2-}$. Although synthesized 3MgCO$_3$.Mg
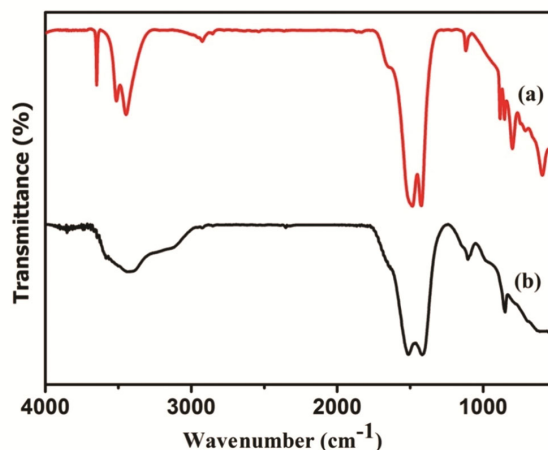

Fig. 3 — Comparative FTIR study of (a) reference (HiMedia) MgCO$_3$ & (b) synthesized MgCO$_3$

$(OH)_2.3H_2O$ resembles the reference $MgCO_3$, the decomposition appeared at a lower temperature and the formation of MgO occurred at 467°C for synthesized compared to the reference (507°C). After 500°C, both the samples display a stable behaviour because of the formation of MgO.

The FESEM micrographs of as-prepared $3MgCO_3.Mg(OH)_2.3H_2O$, calcined at 700°C, 900°C,

and 1100°C are illustrated in Fig 5a-d. It can be seen that there is a remarkable morphology evolution from the microwires to microparticles upon the calcination temperatures. A closer view of each sample can be observed through the higher magnification images which are presented as insets. The as-prepared $3MgCO_3.Mg(OH)_2.3H_2O$ reveals a distinct and smooth morphology of microwires (Fig. 5a) with a
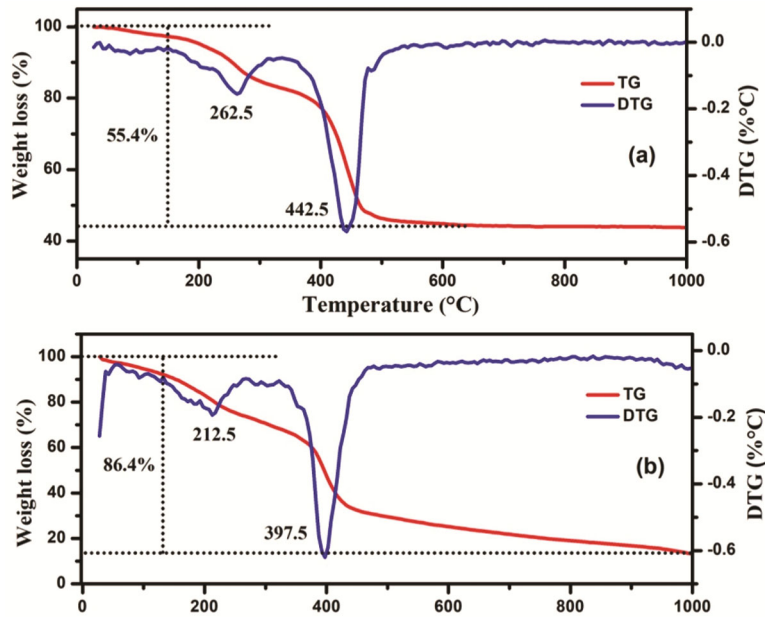

Fig. 4 — TG curves of (a) reference (HiMedia) $MgCO_3$ and (b)synthesized $MgCO_3$
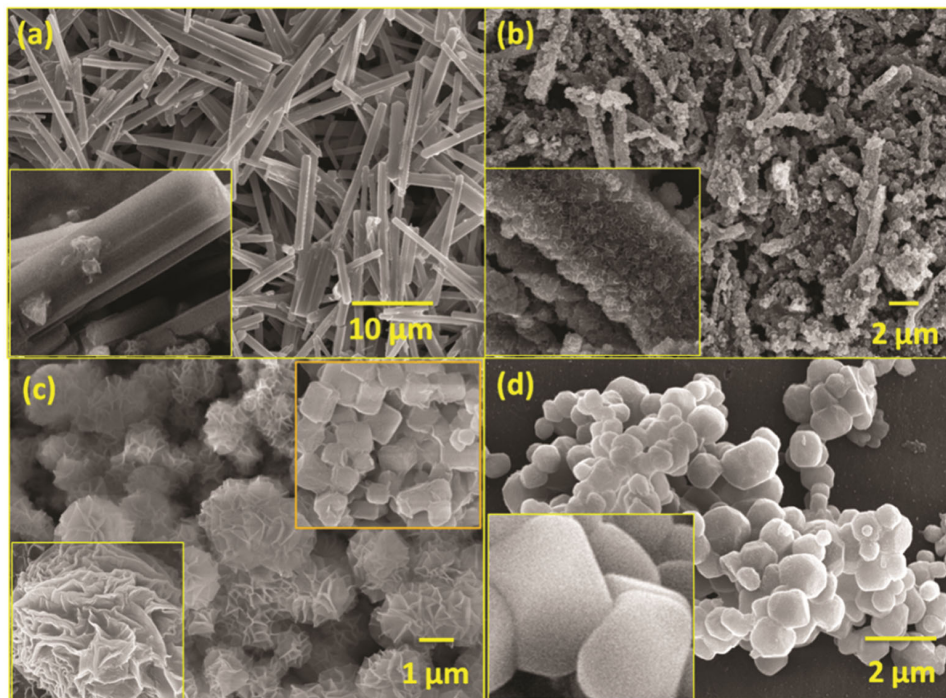

Fig. 5 — FESEM micrographs of (a) as-synthesized $MgCO_3$, calcined at (b) 700°C, (c) 900°C and (d) 1100°C

length and a width of 14.3 and 1.1 µm, respectively. However, this morphology becomes highly destroyed when the sample was subjected to calcination. At 700°C, the microwires are changed into several polycrystalline grains (Fig. 5b) on the wires having 6.6 µm lengths and 0.8 µm widths. On increasing the temperature to 900°C, a complete morphology change is observed from microwires to hierarchical spherical structures along with micro cubes structure with an average diameter of 2.3 µm. Thus, the hierarchical structures have been made up of several nanosheets as displayed in Fig. 5c., the hierarchical structures have further transformed into a typical spherical particle (0.74 µm) when the temperature is maintained at 1100°C (Fig. 5d). From the above observations, one can confirm that the calcination temperature is entirely modified the morphology of the as-prepared $3MgCO_3.Mg(OH)_2.3H_2O$ (microwires) into pure MgO (microparticles).

The morphology evolution of $3MgCO_3.Mg(OH)_2.3H_2O$ microwires into MgO micro particles due to calcination temperature could be governed by the re-crystallization process followed by 'neck growth' (Fig. 6). It is found that clear microwires have been viewed for the as-prepared $3MgCO_3.Mg(OH)_2.3H_2O$ phase. Upon heating the sample, CO_3^{2-} species start to evaporate as evidenced from TG-DTG and therefore the recrystallization process tends to collapse the microwires to form a new entity for the 700°C calcined sample. During this scenario, several polycrystalline structures are started to grow on the body of the wires. Interestingly, beautiful hierarchical spherical structures along with microcubes have been grown on further increasing the temperature at 900°C, as a result of grain boundary formation owing to the increase in the surface energy[46]. At a very high temperature of 1100°C, the entire structures transformed into densified microparticles via the continuous 'neck growth' and a strong agglomeration of the hierarchical structures and nanocubes. Consequently, a single envelope of MgO microparticles has been grown resulting from the recrystallization cum neck growth mechanism which is already explored in the literature[47].

The EDS spectra (Fig.7) of prepared magnesium carbonate contains the elemental atomic percentage such as Mg (16.26%), C (15.18%) and O (68.56%) indicating the formation of $3MgCO_3.Mg(OH)_2.2H_2O$. Also from EDS spectrum, weight% values of Mg (23.61%), C (10.89%) and O (65.50%) nearly matched with prepared $3MgCO_3.Mg(OH)_2.3H_2O$. However, the excess of oxygen, that reflects in the EDS spectrum in both the cases is ascribed to the interference of atmospheric O_2 during the synthesis and drying process. Upon calcining the samples, CO_3^{2-} species evaporated and only Mg and O elements are observed with a total at.% of 100, 99.13, and 99.75 for 700, 900, and 1100°C, respectively. This concludes that the prepared samples at the various calcination

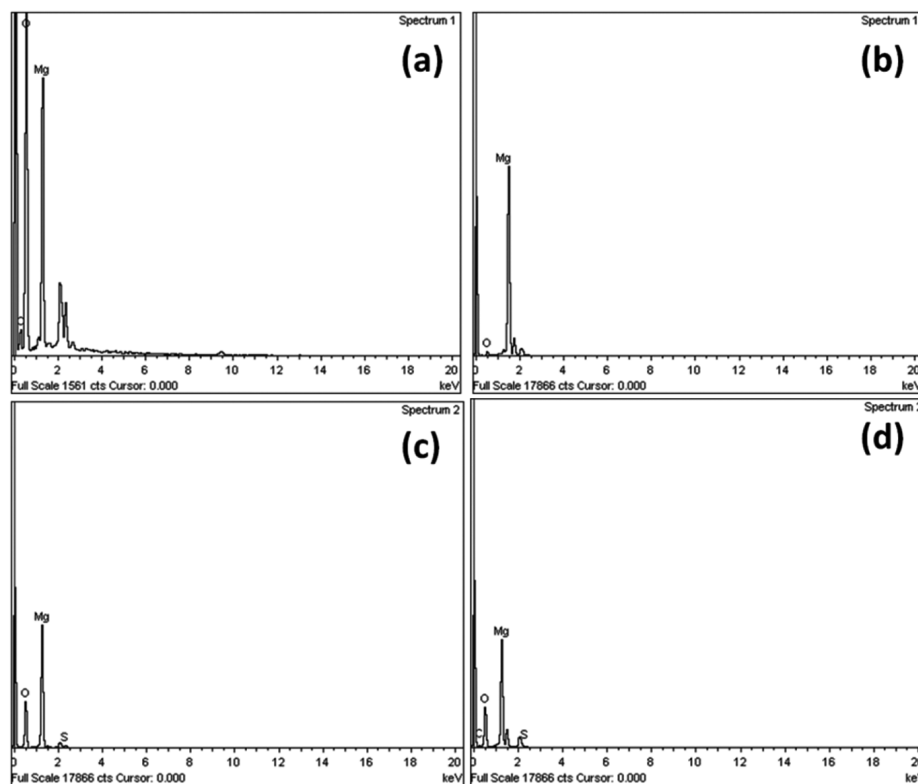Fig. 6 — Morphology variations as a function of the calcination temperatures

Fig. 7 — EDS spectra of (a) as-synthesized $MgCO_3$, calcined at (b) 700°C, (c) 900°C and (d) 1100°C

temperatures display the almost successful formation of pure MgO.

Conclusion

Earlier there were many known procedures for the preparation of magnesia but the preparation of magnesium oxide from seawater by double salt route is a new chemical process that has been developed to control the working difficulties already present in the magnesium hydroxide process. In this process, no need for a separate boron removal step as only a few washings of sorbitol and distilled water are required. The recovered magnesium oxide (MgO) is in a very pure state nearly free from boron and other elemental impurities. Ammonium sulphate is recycled in this procedure to achieve a more economically feasible path to recover magnesium oxide from seawater. From this process, the Mg recovery is 80.11% on a 100 mL scale and 80.54% on a 1000 mL scale. More than 99% pure magnesium oxide is prepared in this process.

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