



**ORIGINAL RESEARCH PAPER**

**Chemistry**

**RECOVERY OF MAGNESIA FROM SEAWATER-A REVIEW**

**KEY WORDS:** Precipitation, Magnesium, Magnesia, Seawater

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**ABSTRACT**

Seawater magnesia has, with great success replaced the refractories, used in the Iron & Steel Industries. Magnesia recovered from natural resources like magnesite ore by physical means such as magnetic separation, heavy media separation or floatation have certain limitations regarding the purity of the product. So continuous efforts has been made by the scientist to establish a novel route for the preparation of high purity magnesium oxide from seawater bittern. This review describes various processes, characteristics of the precipitation agents and the impurity introduced by the seawater and the means by which they can be reduced.

**INTRODUCTION**

Seawater is a multi-component system that contains various metals, non-metals, organic salts and other dissolved solids. It contains an average of 3.5% of various elements in solution and hence each cubic mile of seawater holds 166 million tons of solids. Of the 60 elements reported from seawater nine most abundant elements constitute over 99% of the total dissolved solids out of which sodium and chlorine constitute 85.2% of dissolved solids in seawater [1]. The elements which are in constant proportion to one another are chloride 54.8% of total salt, sodium ion 30.44%, sulfate ion 7.5%, magnesium ion 3.7%, calcium ion 1.2%, potassium ion 1.1%, carbonate ion 0.3%, bromide ion 0.2% and the borate ion 0.07% [2].

The resource potential of seawater is immense and yet to be fully realised. The chemical industry has started exploiting it for the chemical raw materials present in the beaches, floors of bays and estuaries, continental shelf region and the ocean basin. It is possible to recover sodium chloride, sodium carbonate, bromine, magnesium, magnesium salts and potassium salts. Besides, marine algae also serve as a major industrial source for iodine, bromine, and potash. Considerable attempts have been made to extract minerals from seawater by the technologists and technologies are evolving rapidly in these directions in the form of research papers and Patents. Economic feasibility has been a major factor in the adoption of any extraction technique. A survey of brine processing technology made by Christensen *et al.* [3] showed that a relatively small number of basic methods being used for the separation of products from seawater. These include evaporation, precipitation, electrolysis, adsorption, distillation, solvent extraction, ion exchange, floatation and oxidation. However, evaporation, precipitation, electrolysis and floatation methods are mostly adopted.

**HISTORY**

The history of extraction processes goes back to the Chinese who started extraction of common salt prior to 2200 BC, after which seawater became the principal source of salt production [4]. With the development of technology more and more methods evolved and many chemical compounds like sodium chloride, magnesium and its compounds and bromine are being extracted with the production of calcium and potassium compounds are produced as the by-product. Recovery of KCl from the Dead Sea in Israel and Jordan [5], potassium sulfate from the Great Salt Lake in Utah USA [6] and lithium, boron, soda, potassium from the Searles lake in USA [7] are best examples of extraction of useful chemical compounds from seawater and estuaries. Magnesium was first obtained from sea water in England [5] and the first large scale plant for the extraction of magnesium from sea water was Free port, Texas, that was put into operation in early 1941 by Dow chemical company. However, the complex utilization of the whole spectrum of valuables like KCl, NaCl, Br, MgO, MgCl and hydrochloric acid from the Dead Sea water [8] still remains as a milestone.

**REFRACTORY MAGNESIA**

Earlier magnesite (MgCO<sub>3</sub>) was only raw material for the

production of magnesium oxide. In India the natural magnesite deposits are of poor quality (80-85% MgO) and their chemical composition has shown a wide variance. As such the purity and mineralogy of Indian magnesite are unable to meet the stringent specification of High quality Sintered Magnesia (HOSM). But the chemical process for preparing magnesium oxide from seawater has provided another alternative source of magnesium. A process for obtaining synthetic MgO from sea water in significant amounts was first produced by the California Chemical Company in 1931[9] and now the major producers of seawater magnesia are North American Magnesia producer viz. Harbison-Walden Refractories Cvo, Marine Magnesium Co., Premier Periclase Ltd. of Irish Republic, Billiton Refractories BV of Netherlands, Dead sea Periclase of Israel, Ube Chemical Industries Co. Ltd. of Japan and Steetley Magnesia Products Ltd. of U.K. However, good improved refractory magnesia should be high pure i.e., 99.88% and contains negligible amount of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Magnesium recovered as magnesium oxide from brine or bittern can solve the increasing demand of high purity magnesia as refractory.

**PRECIPITATION OF MANESIA FROM SEAWATER**

**Precipitation of Mg(OH)<sub>2</sub> using Ca(OH)<sub>2</sub>**

A new method of preparation of high purity brine magnesia comprising concentrated CaCl<sub>2</sub> medium and lime slurry precipitation was invented by Zhai and Miao [10] in 1993 and the main difficulty and breakthrough points in the production technology was also studied. The resulted dead burnt magnesia has MgO 98.97%, c/s ratio of 3.62, B<sub>2</sub>O<sub>3</sub> 0.017%, bulk density of 3.48g / cm<sup>3</sup>. Yumanuradav *et al.* [11] prepared magnesium oxide concentrate containing 6.5% B<sub>2</sub>O<sub>3</sub> from chloride containing natural brine by treating milk of lime at 95°C, maintaining CaO :MgO ratio 1.0-1.5, for 2 h.

Tanaka Kinji [12] described a process in which sea water was mixed with Ca(OH)<sub>2</sub> powder to adjust the pH at 11.0, diluted with water, mixed with 7% HCl to adjust the pH to 8.0, pressurized to 3.0 kg/cm<sup>2</sup> by blowing air into the solution, mixed with 1.0 ppm anionic polymer coagulant and treated in a press floatation tank. The resulting floated scum containing Mg(OH)<sub>2</sub> was separated. Dorr Co manufactured Mg(OH)<sub>2</sub> of desired physical characteristics obtained from MgCl<sub>2</sub> brines by treating Ca(OH)<sub>2</sub> to control the pH (9.6-11.5 for sea water, 9.5-12.5 for brine of low Na content), maintaining the Mg ion concentration (0.01-0.8 g/l), and the contact time (20-90 min, depending on agitation, particle size of lime bearing solids, and degree of extraction of Mg ions from the brine) [13].

Preparation of Mg(OH)<sub>2</sub> containing minimum amount of B & Ca from sea water by adding Mg(OH)<sub>2</sub> seed crystals and excess alkali was studied by Brown *et al.* [14]. The slurry of Mg(OH)<sub>2</sub> formed is treated with sea water and to react with remaining alkali. Addition of Zn(OH)<sub>2</sub> prior to the addition of Ca(OH)<sub>2</sub> to sea water also show good result giving rise to Mg(OH)<sub>2</sub> containing 21.62-65.45 ppm of Boron [15].

In the production of  $Mg(OH)_2$  from sea water by precipitation with milk of lime, filtration and rinsing are difficult. When the NaCl lime suspension increases the filtration rate increases. The favourable condition for filtration is NaCl lime suspension containing 11-14% salts (2.5%  $CaCl_2$  and 9% NaCl) and the  $Mg(OH)_2$  precipitated together with  $CaCO_3$  serve as raw material for production of Mg salt [16]. The properties of  $Mg(OH)_2$  precipitate are studied to facilitate the separation of these precipitate industrially by Terada M. [17].

According to Asahi Chemical Industry Co. Ltd.,  $CaC_2$  waste also serves as precipitating agent for the preparation of high purity  $Mg(OH)_2$ . The  $CaC_2$  waste is separated mechanically into coarse and fine slurry and then added to seawater in 2 steps. The resultant precipitate passed through a cyclone separator producing a light, high purity  $Mg(OH)_2$  (94.87% MgO) and a heavy crude  $Mg(OH)_2$  (80.84% MgO) [18]. During the reaction of  $CaC_2$  with bittern the effect of temperature crystal growth are also studied [19].

A method for obtaining  $Mg(OH)_2$  from sea water with higher precipitation rate using  $Ca(OH)_2$  is described by Keisuke *et al.* [20]. Lime stone is mixed with either 5%  $MgCl_2 \cdot 6H_2O$  or 10% raw bittern, sintered for 4 h at  $1000^\circ C$  to produce CaO and then slaked to  $Ca(OH)_2$ . A flow sheet for the preparation of  $Mg(OH)_2$  showing the requirements like 2.2 tons of lime stone, 0.45 tons of fuel, 12 cu.m of fresh water, and 120 kw. H of power per ton of magnesia was demonstrated by Goldberg [21]. A mathematical statistics was also used to study the two stage removal of  $Mg^{2+}$  from Sivash brine in the manufacture of  $Na_2CO_3$  by Itskov *et al.* [22]. The loss of milk of lime for precipitation of  $Mg(OH)_2$  was found to be diminished by recycling the sludge from the 1<sup>st</sup> stage into the 2<sup>nd</sup> stage.

Shoikhet *et al.* [23] established the possibility of producing  $Mg(OH)_2$  from Sivash brine which is suitable for use in refractories. MgO is obtained by treating brine with milk of lime under conditions of complete calcination of limestone; otherwise the brine MgO contains > 2-3% CaO. The rate of formation of  $Mg(OH)_2$  is limited by diffusion through the surface films which causes slow reaction and gradual growth of  $Mg(OH)_2$  particles and yield of  $Mg(OH)_2$  increases with increase in temperature. In another process described by B.A. Shoikhet [24] brine is treated with  $Ca(OH)_2$ , followed by settling, decantation, treatment with  $CO_2$  to precipitate  $MgCO_3$  which on ignition yields MgO.

A review of 101 references describe the salt deposits for the production of MgO with all technical and economical aspects and of their qualifications for the manufacture of refractory materials [25]. The flow sheet for manufacture of high purity MgO and a B concentration from Sivash brine was demonstrated with 16 references [26]. Lopez Gomez [27] discusses the process for the recovery of MgO from seawater and desalinated brine. The Chesny method of MgO removal by precipitation with lime following removal of bicarbonates and sulfates are also presented. Sea water brine reacted with  $Ca(OH)_2$  in a  $Ca(OH)_2 / Mg^{2+}$  in an equivalent ratio of 1.05 - 1.20 and pH 10.6. The resulting crude  $Mg(OH)_2$  is refined by calcination, hydration, further calcined, molded and sintered to obtain high-density, high purity MgO.

#### Precipitation of $Mg(OH)_2$ using $Ca(OH)_2$ & Alcohol

According to Postoronko *et al.* [28] use of an organic additive to sea water during the precipitation of  $Mg(OH)_2$  using milk of lime decreases the chloride content of the product. Thus  $Mg(OH)_2$  is obtained by using 0.001-0.1 wt% of Polyvinyl alcohol. The same is also tried using a polyhydric alcohol namely sorbitol by Suzukawa *et al.* [29] in 1973. For accelerating the precipitation of  $Mg(OH)_2$  addition of a mist of polyethylene glycol esters of higher aliphatic alcohol  $RO(CH_2CH_2O)_nH$  (R= alkyl alc. radical, n= 20) to sea water is also suggested]. The process is carried out by addition of  $10^{-4} - 10^{-2}$  wt% mist. of polyethylene glycol ester of higher aliphatic alcohol to sea water followed by addition of milk of lime [30].

#### Precipitation of $Mg(OH)_2$ using Ammonia

Zhai *et al.* [31] described a brine-ammonia process for continuous precipitation of  $Mg(OH)_2$  which is ready to filter and was proposed based in the analysis of the kinetics of crystal growth of  $Mg(OH)_2$ . In another process saline mine water containing  $MgCl_2$ , 20-250, NaCl 70-270, KCl 4-5 g/L,  $I^-$  0.5 and  $Br^-$  1g/L was concentrated at  $90^\circ C$  to remove NaCl and KCl followed by precipitation of  $Mg(OH)_2$  with gaseous  $NH_3$ . The contamination of NaCl and KCl in the precipitate decreases with increase in Mg content in initial brine whereas the contamination by  $NH_4Cl$  increases. Thus potable carbonate free water was used for washing and the calcinations product is found to contain 75-92% MgO [32].

A process for production of  $Mg(OH)_2$  using aqueous Ammonia and its recycling was patented by Romania, Ministry of Chemical industry in 1957. A sea water containing 12.50 NaCl, 1.95  $MgCl_2$ , 1.65  $MgSO_4$ , 0.68  $CaSO_4$  g/l, total salts including 1.26g/l MgO as Mg salt is preliminary treated with equivalent quantity of dolomite milk or heating 30 min. at  $90^\circ C$  for eliminating  $CO_2$  and bicarbonates. The resulted seawater is mixed with 25%  $NH_4OH$  maintaining the pH 10-11. The  $Mg(OH)_2$  formed is filtered and calcined at  $1600^\circ C$  to give MgO containing 2.1% CaO. The output of Mg extraction was 91.8%. The filtrate after  $Mg(OH)_2$  separation is treated with a stoichiometric quantity of caustic dolomite milk for the decomposition of  $NH_4$  salt [33].

#### Precipitation of $Mg(OH)_2$ using NaOH & $Na_2CO_3$

Preparation of MgO from sea water lake brines and well brines by neutralization with  $Ca(OH)_2$  and NaOH were reviewed with 16 references by Ohta, Chisato [34]. Separation of Mg & B from seawater using an alkaline substance and bubbling  $SO_2$  was described by Tanigachi, Yoshio [35]. The concentrated sea water was treated with 20% NaOH at pH 10 to precipitate  $Mg(OH)_2$ , which was filtered off and then suspended as a 11.7% solution.  $SO_2$  was bubbled till the pH reached 8.5 resulting co precipitation of B (90%) and liberation by  $SO_2$  was 75%.

Mario Gianattasio (1958) mixed seawater with stichiometric amount of  $Na_2CO_3$  to precipitate Mg as  $MgCO_3$ . The  $MgCO_3$  filtered and converted to MgO by heating at  $650^\circ C$  [36]. The conditions for precipitation of  $Mg(OH)_2$  using  $Na_2CO_3$  from a solution containing 127g mg/l was described by Bruno Riva [37]. Seawater is diluted with 5 volume of soft water to prevent the precipitation of NaCl and then treated with a filtered solution of calcined  $Na_2CO_3$  in 5 volume of  $H_2O$ . The  $MgCO_3 \cdot 3H_2O$  formed is dried at  $110^\circ C$  forms a basic salt and at  $900-950^\circ C$  forms 98.6% MgO. A rational method of MgO production from brines of Malinove lake by utilization of mother liquor from  $Na_2CO_3$  production was described by V.G. Ediger [38]. The intermediate product magnesia Alba ( $3MgCO_3 \cdot Mg(OH)_2 \cdot H_2O$ ), produced is calcined to prepare MgO.

#### Preparation of MgO using Dolomite

In most of the processes dolomite is used as the precipitating agent for the preparation of  $Mg(OH)_2$  and MgO. A review with 35 references on the manufacture of MgO from dolomite, seawater, waste Mg salt, lean magnesites and serpentinite is described [39]. A study on recovery of magnesia using Egyptian bittern 27<sup>Be</sup> and dolomite gives better result as MgO concentration increases from 1.5g/l at 4<sup>Be</sup> to 65g/l at 31<sup>Be</sup>. Dolomite calcined at  $1150-1200^\circ C$  reacted fastest, where as dolomite calcined at  $1500-1550^\circ C$  resulted in the fastest settling rate of  $Mg(OH)_2$ . However a compromise temperature of  $1300-1350^\circ C$  results a reasonable reaction time, with good settling rate, filterability and wash ability [40]. Similarly MgO slurry is produced by hydrate process from Black sea water and calcined dolomite, which on dehydration yields MgO suitable for preparation of brick [41].

Bittern of various concentrations on treatment with calcined dolomite results  $Mg(OH)_2$  contaminated with less amount i.e: 2-3%  $Ca(OH)_2$  [42]. Magnesia of 94-95% purity containing 3-5% CaO and 1-2%  $SO_3$  was obtained using suspension (1-8%)

of dolomite burnt at 700-1000°C. Whereas Slaked lime needs freshly prepared milk of lime to decrease the CaO content [43]. Examination was also made for the qualities of Mg(OH)<sub>2</sub> prepared by treating bittern with quick lime or light burnt dolomite. It is concluded that MgO low in CaO can be obtained by treating freshly prepared dilute milk of lime at low temperature in the absence of CO<sub>2</sub> [44].

A process for production of high density MgO was described by Fred A. De Maestri [45]. Treatment of sea water with dolomite of 48-100 mesh size, followed by washing, filtration gives rise to Mg(OH)<sub>2</sub> which on calcination yields MgO. A magnesium product containing MgO-92.4, SiO<sub>2</sub>-2.1, Al<sub>2</sub>O<sub>3</sub>-1.4, Fe<sub>2</sub>O<sub>3</sub>-1.4 and CaO-2.7% known as Britmarg was prepared by W.C. Gilpin [46]. Sea water, previously treated with lime to precipitate carbonates and sulfate, is then treated with dolomite hydrated lime in proper amount to precipitate Mg(OH)<sub>2</sub> and to keep Ca salts in solution. Thickening, filtering and calcining of the precipitate yields the product. In some cases the particle of dolomite are large enough thus the unreacted materials settles at the bottom giving rise to a floc of Mg(OH)<sub>2</sub> in a reactor [47].

Addition of Dolomite mixed with 3-5% limonite, calcined at 900°C to diluted bittern of 32° Be' yields Mg(OH)<sub>2</sub> containing 4-5% lime [48]. A.D. Pelish [49] developed a commercial method of extraction of natural magnesium oxide of low calcium oxide content using brines of Perekop lake using calcined calcareous dolomite or tech. CaO of 0.5mm. Slaking of CaO takes place and Mg(OH)<sub>2</sub> formed at temperature 80°C.

Arther W. Vettel reported a process for making Mg(OH)<sub>2</sub> by mixing a concentrated aqueous solution of MgCl<sub>2</sub> with seed crystals of Mg(OH)<sub>2</sub> and agitating with 100 mesh, dry, calcined dolomite (58% CaO and 41% MgO) at 1250°C. The underflow is removed as an impurity and the overflow is removed as a slurry containing Mg(OH)<sub>2</sub>. In this process a very pure Mg(OH)<sub>2</sub> containing < 1% CaO is obtained [50].

Rastrelli, Joel E. [51] worked with the recovery of synthetic magnesia with low B value. Sea water passed over lime, dolime to precipitate the Mg values along with the least part of the B values to give a thickened precipitation of Mg(OH)<sub>2</sub>. As boron reduces the strength of the brick two classes of magnesia of different B content are produced to solve the purpose.

MgO clinker containing ~ 90% MgO can also be prepared from seawater using dolomite or limestone. Heating the sample at 1500°C to vapourize SO<sub>3</sub> purifies it to > 98% MgO. Use of limestone shortened the processing time and increases the purity of MgO [52].

Panda *et al.* [53] studied the suitable ratio of precipitation agent and solution containing MgCl<sub>2</sub> to get pure magnesia. The precipitating agents used are MgO, Mg(OH)<sub>2</sub>, calcined magnesite, calcined dolomite, calcined calcite / lime stone. In case of MgO, Mg(OH)<sub>2</sub> or calcined magnesite, the molar ratio of MgO : MgCl<sub>2</sub> is 1:1.5-1:15, in case of calcined dolomite the molar ratio of (MgO + CaO) : MgCl<sub>2</sub> is 0.66:1 - 0.05:1 or in calcined calcite/lime stone the molar ratio of CaO : MgCl<sub>2</sub> is 0.66:1 - 0.1:1 at < 90°. Addition of calcined MgO to MgCl<sub>2</sub>. 6H<sub>2</sub>O at 27° Be' in a ratio MgO : MgCl<sub>2</sub> 1:4, followed by drying at 110°C and heating at 800°C, yields a fine powdered MgO of 99% purity [54].

#### Preparation of MgO using Boron-ion-exchange resin

An economical process for manufacturing MgO from brines or bittern is described by Panda [55]. B<sub>2</sub>O<sub>3</sub> is removed from brine by passing the brine through an ion exchange resin. The resulting brine is mixed with crushed and calcined magnesite, dolomite or calcite. The mass obtained on further calcination, washing, briquetting and sintering yields 98% MgO. In another process H<sub>3</sub>BO<sub>3</sub> removing resin containing NMeC<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> groups (N-methyl glucamine derivative) was used. The brine on treatment with CaO or dolomite yields

high purity Mg(OH)<sub>2</sub>. The calcination product yields MgO of 99.54, CaO 0.25, SiO<sub>2</sub> 0.11% and B<sub>2</sub>O<sub>3</sub> 0.03% [56].

#### Recovery of MgO through Desulphation process

Magnesium oxide can be recovered from seawater brine by primary desulphation followed by precipitation using various precipitating agent. A two step process for preparation of Mg(OH)<sub>2</sub> was reported by Rabadzhieva *et al.* [57]. In the first step brine is desulphated using CaCl<sub>2</sub> crystal or its solution and in the 2<sup>nd</sup> step Mg(OH)<sub>2</sub> is precipitated using milk of lime and dolomite milk. Similarly Nabi *et al.* [58] prepared Mg(OH)<sub>2</sub> of 99% purity from waste bittern by treating commercial CaCl<sub>2</sub> followed by treatment with lime water.

Seawater on treatment with CaCl<sub>2</sub> gives an easily filtered - Gypsum and the filtrate on evaporation crystallize out NaCl. The liquor obtained after NaCl precipitation, treated with Ca(OH)<sub>2</sub> to separate Mg(OH)<sub>2</sub>. The residual CaCl<sub>2</sub> rich solution is used for the first stage. Thus a continuous crystallization process is found to be possible with a 27° Baume feed [59]. As in some cases Mg(OH)<sub>2</sub> contain CaSO<sub>4</sub> impurities, a carbocation-decarbocation process is suggested by Barba *et al.* [60] to remove the impurities.

While studying the recovery of Magnesia from bittern Bakr and El-Abd [61] used CaCl<sub>2</sub> for desulphation and dolomite for the precipitation of Mg(OH)<sub>2</sub>. Dolomite was calcined for 2 h at 1300-1350°C. The recovery of Mg is 96% containing 2.6% CaO. Similarly, another process of manufacturing MgCl<sub>2</sub> from sea brine after desulphation was suggested by Wang and Li [62]. The process comprises heating brine to 35-125°C and adding 5-30% NaOH for neutralization (pH 6-7.5). Then gypsum is removed by the addition of 10-40% CaCl<sub>2</sub> followed by settling at 40-100°C in settling tank for 1.5 hour. The supernatant after SO<sub>4</sub><sup>2-</sup> removal is recycled to the settling tank by addition of a bleaching agent NaCl, which on evaporation to 165-170° under atmospheric pressure yields MgCl<sub>2</sub>.

Desulphation of brine of Sivash using Cl-Ca lye, before and after the beginning of settling of NaCl in the production of MgO was also studied by Shoikhet and Sologubenko [63]. In case of weak and strong brines, the continuous desulphation process can be carried out cyclically with the production of MgO. The possibility of producing Mg(OH)<sub>2</sub> from brine of Perekop lake and desulphated brine of Sivash was reported by Shoikhet and Sologubenko. Brine is treated with milk of lime under condition of complete calcination of lime stone for precipitation of Mg(OH)<sub>2</sub> containing < 2-3% CaO. The rate of formation of Mg(OH)<sub>2</sub> is limited by the diffusion through the surface films that causes slow reaction and gradual growth of Mg(OH)<sub>2</sub> particles [64].

Oscar and Waters [65] described a process for recovery of pure gypsum and Magnesium hydroxide after distillation of seawater, which had been acidified with H<sub>2</sub>SO<sub>4</sub> to prevent scale. Addition of lime to the liquor to pH 7.0-9.5 followed by CaCl<sub>2</sub> to balance total Ca with SO<sub>4</sub><sup>2-</sup> ion precipitates pure gypsum. The liquor limed further to pH 10.4 precipitates Mg(OH)<sub>2</sub>.

Shoichiro *et al.* [66] reviewed various methods of obtaining MgO from magnesite, brucite or sea water and the method of manufacturing MgO from sea water, brine or bittern by treating calcined dolomite or lime was found to be best. Dilute solution (15-20 Be') of bittern or brine was mixed with a slaked solution of calcined dolomite in 2 steps: First small amounts of calcined dolomite equivalent to SO<sub>4</sub><sup>2-</sup> are added to precipitate CaSO<sub>4</sub>. 2H<sub>2</sub>O and then a calculated amount of dolomite equivalent to Mg<sup>2+</sup> are added to precipitate Mg(OH)<sub>2</sub>.

#### Precipitation Kinetics

As precipitation of Mg(OH)<sub>2</sub> is the first step of production of Mg compound from seawater [67]. Carson *et al.* studied the kinetics of precipitation and the effect of temperature & particle size on it. The precipitation kinetics of CaCO<sub>3</sub> and

Mg(OH)<sub>2</sub> from natural NaCl brine was also studied by Khazin *et al.* [68]. It is found that temperature has a negligible effect on the initial precipitation rate, which was attributed to the simultaneous formation, growth and decomposition of metastable modifications. The equilibrium concentration of impurities in the solution during final precipitation was attributed to the solubility of sub micro particles. The compactness of the precipitate of CaCO<sub>3</sub> and Mg(OH)<sub>2</sub> was favoured by solid-phase aging and the aggregation of submicro particles. The nucleation and growth rate of CaCO<sub>3</sub> and Mg(OH)<sub>2</sub> particles during their removal were measured for the electrolytic recovery of NaOH and Cl<sub>2</sub>. Recirculation of the pulp was recommended to increase the particle size by extending the residence time of the solid phase in a flow-through apparatus [69]. Kinetics of precipitation of Mg(OH)<sub>2</sub> from sea water was investigated by monitoring the total Ca and Mg composition of species < 2 m. The effect of temperature and dolomite particle size on the kinetics of Mg(OH)<sub>2</sub> precipitation were also studied by Carson *et al.* [70]

#### Preparation of Mg(OH)<sub>2</sub> by Sedimentation

One of the difficulties in the production of magnesia from sea water is the slow settling rate of Mg(OH)<sub>2</sub>. Thus the addition of sedimenting agents such as carboxy methyl cellulose, separation, starch in small amounts increase the settling of Mg(OH)<sub>2</sub> [71]. Similarly the effect of flocculants like polyamide, separan NP 10 etc. on the sedimentation behavior of Mg(OH)<sub>2</sub> suspensions have been studied [72,73].

#### Preparation of MgCO<sub>3</sub>

Sea bittern can serve as a basic raw material for the production of lightweight magnesium carbonate. Experiments have been carried out to optimize various parameters, which affect the bulk density of product. The main controlling factors are found to be rate of agitation and concentration of reactants. The suitable combination for preparation of lightweight MgCO<sub>3</sub> is rate of agitation (280/560 rpm) and concentration of reactants (Mg<sup>2+</sup> 20-25g ml<sup>-1</sup>; Na<sub>2</sub>CO<sub>3</sub> 250-265g ml<sup>-1</sup>) [74]. Kappanna *et al.* [75] suggest a method for preparation of light basic MgCO<sub>3</sub> using a calculated amount of soda ash solution to bittern with agitation and bubbling air under pressure. After precipitation, it was washed for removal of SO<sub>4</sub><sup>2-</sup> & Cl<sup>-</sup> and the moist cake was dried at 120°C to get fine light basic MgCO<sub>3</sub>. Belyaev *et al.* [76] studied the precipitation of MgCO<sub>3</sub> by NaHCO<sub>3</sub> using artificial brines, similar in composition to the water of lake Sivash, which is free of Ca<sup>2+</sup>.

Preparation of MgCO<sub>3</sub> by treating MgCl<sub>2</sub> solution with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> or distillation gas cooler condensate from Solvey process was studied by Maurer, Bruno. The NH<sub>4</sub>Mg carbonate formed is washed with neutralize condensate and treated at high temp with Cl free water to make the Cl content < 0.01 wt%. The basic MgCO<sub>3</sub> formed is calcined to give pure MgO and the NH<sub>3</sub> & CO<sub>2</sub> are recycled [77].

Seshadri *et al.* [78] reported a useful method for preparation of basic MgCO<sub>3</sub> from bittern using NH<sub>3</sub> and CO<sub>2</sub> at 50°C. The removal of Mg was 90.5% when molar ratio of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> to Mg was 2:1 and calcination of the MgCO<sub>3</sub> at 600-700°C gave light weight MgO of bulk-density of 180g/l. Similarly the Mg containing solution obtained from acid extraction of magnesite or bittern reacts with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> producing light wt MgCO<sub>3</sub> which can be fired to get light weight MgO [79].

Andrianov *et al.* [80] studied the preparation condition for pure magnesia product. The main impurities, which affect the quality of MgO, are Ca, Fe, Mn and Si. In order to remove these impurities from Mg(OH)<sub>2</sub> prepared from sea water, it is completely dissolved in NH<sub>4</sub>Cl at 25°C. Ca is also removed by carbonation giving rise to high quality MgO. In order to decrease the Ca content 80.5% stoichiometric amount of soda can be added during the washing [81]. Purification of the starting reagents like MgCl<sub>2</sub> and NaOH is also found to be responsible for the production of high purity MgO [82].

#### Recovery of MgO through Double salt process

Magnesium forms a number of double salts like K<sub>2</sub>SO<sub>4</sub>.MgSO<sub>4</sub>.6H<sub>2</sub>O (Schoenite), KCl. MgCl<sub>2</sub>. 6H<sub>2</sub>O (Carnallite) and NH<sub>4</sub>Cl. MgCl<sub>2</sub>. 6H<sub>2</sub>O (ammonium carnallite). It is recovered as double salt from sea water brine, by natural evaporation till the inception of the precipitation of epsomite followed by addition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The Mg.NH<sub>4</sub> double salt MgSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O (Tuffon's salt) further reacts with milk of lime to form Mg(OH)<sub>2</sub> [83].

#### CONCLUSIONS

During the last few decades, there have been major changes in the refractory practices of Iron and Steel industries. Fire clay which was the first refractory material to be used in furnaces [84] got rejected due to its variable composition and properties and materials such as alumina, silica and magnesia began to be used. A good refractory material should be infusible at higher temperature, chemically inert, resistant to abrasion and have the ability to expand and contract uniformly without cracking and has in size when heated and cooled. Magnesia (MgO) is found to comply with all the requirements and hence is a very good refractory material. Two processes have been developed for recovering high pure manesia from sea water bittern. Seawater bittern 30° Be' subjected to 90% desulphation using CaCl<sub>2</sub>. The desulphated bittern is then treated with stoichiometric amount of ammonia and ammonium carbonate to form magnesium carbonate which on calcinations yields 99.3% pure magnesia [85]. A process of recovery of 99.5% pure magnesia is obtained from bittern 29° Be' by precipitation of double salt using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> followed by MgCO<sub>3</sub> precipitation using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> followed by calcination of magnesium carbonate [86].

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