

## Production of Magnesia from Sea Water and Dolomite

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OF THE normal domestic consumption of magnesium compounds more than half is used for the manufacture of refractories, about one quarter for insulating materials and the remainder for textiles and paper, magnesium metal, oxychloride cements, adsorptive powders, catalysts and catalyst carriers, rubber products and various magnesium chemicals. In wartime further very large quantities are required to make additional magnesium metal for incendiary bombs and the light magnesium-aluminium and magnesium-beryllium alloys.

For refractories, magnesium oxide is calcined at a temperature of 1,600 to 1,700°C until it is chemically inert and for thermal and sound insulation basic magnesium carbonates are required. The lightly calcined oxide, the sulphate and the chloride largely satisfy the remaining demand.

The approximate present consumption figures, computed as magnesium oxide in tons *per annum*, are:

refractory oxide	40,000
basic carbonate for insulation	25,000
magnesium sulphate	5,000
magnesium metal	5,000
miscellaneous	5,000

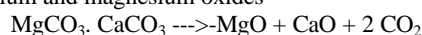
Until comparatively recent times the commercial magnesium compounds were mostly derived from magnesite, the naturally occurring magnesium carbonate, large deposits of which occur in Austria and Greece. Manufacture from seawater was commenced in this country in 1937 to ensure an adequate supply of home produced magnesia for the steel and magnesium industries.

Seawater, although it contains only about 0.5 per cent of soluble magnesium compounds, was the obvious alternative source to meet the requirements of the expanding magnesium metal industry and also to maintain production of the refractories required by the steel industry. The basic idea was not a new one; in fact a small plant was operated for a few months in 1885 on the south coast of France, and prior to this had been mooted for several decades especially in Germany. Lack of suitable equipment, and the difficulty of handling the precipitates obtained appear to have prevented much progress and it was not until about 1930 that production approached the large scale. Since then a number of works have been built and operated notably in England and the

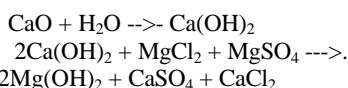
United States and a great deal of research has been carried out. The production of magnesium from sea water has also begun in Norway. The present article describes the process used at Hartlepool in the Ministry of Supply works operated by the British Periclase Co. Ltd; this development dates from 1937, when a pilot plant was erected, to the present time when the works are scheduled to produce in excess of 50,000 tons of magnesia a year.

### CHEMISTRY OF THE PROCESS

The extraction of magnesia from seawater depends on the reaction of soluble magnesium salts with a base to form insoluble magnesium hydroxide. The base commonly used on account of its cheapness and availability is calcium hydroxide and this may conveniently be provided by dolomite, which contains approximately equimolecular amounts of magnesium carbonate and calcium carbonate. It is first calcined to give a mixture of calcium and magnesium oxides



and these are then slaked and added to sea water when the lime is converted to the relatively soluble hydroxide which subsequently precipitates magnesium hydroxide and passes into solution as a mixture of soluble calcium salts.



The precipitate is recovered by filtration and is composed of magnesium hydroxide precipitated from the seawater and unchanged magnesia from the calcined dolomite. As, when using dolomite only half of the magnesia is derived from magnesium salts present in the seawater, for the same production the size of the precipitation and settling section of the plant is much smaller than when using limestone.

In practice the process is not as simple as has been described since dolomite always contains impurities which may be increased on calcination by contamination with fuel ash, and sea water is not just a pure solution of magnesium chloride and sulphate but also contains a variety of other salts. Insoluble impurities are recovered with the precipitate so that the preparation of the purest dolime is of primary importance. Similarly the seawater

must also be subjected to a preliminary treatment to ensure that the precipitation of insoluble calcium salts does not occur during the main reaction process. This is because the addition of dolime to seawater to precipitate the magnesium increases the alkalinity from pH 8.1 to 11.0 and the calcium ion content from 10.23 mg to 65.3 mg per litre and at equilibrium over 99 per cent of the bicarbonate and 20 per cent of the sulphate are precipitated as calcium carbonate and sulphate.

It is also very important that the magnesium hydroxide be precipitated in a form, which will settle rapidly and yield a sludge that can be readily dewatered. If this cannot be achieved production per unit of capital invested will be small and cost per ton high. The magnitude of this problem is indicated by the fact that each ton of magnesia produced must be separated from some 300 tons of water. Much ingenuity is therefore required to obtain a good separation and a high quality product.

### RAW MATERIALS

*Dolomite*- Dolomite of a suitable quality cannot be found near Hartlepool, where the underlying rocks are largely obscured by thick glacial deposits, and must be brought from quarries at Coxhoe about seventeen miles to the west. The deposits here form part of the Lower Magnesian Limestone division of the Permian system and give rise to a bold escarpment very suitable for quarrying. The rock, probably deposited in an ancient dead sea, is brown-grey and evenly bedded with very few fossils. It has percentage composition: silica (SiO<sub>2</sub>) 0.6, alumina (Al<sub>2</sub>O<sub>3</sub>) 0.5, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) 0.4, calcium carbonate (CaCO<sub>3</sub>) 57.10, magnesium carbonate (MgCO<sub>3</sub>) 41.40.

Sea water-Since strong tides run parallel to the coast no trouble due to dilution of the sea water with river water or 'spent' sea water from which magnesium has been removed is experienced at Hartlepool. Pipelines run 900 feet into the sea, but tides do not permit pumping for more than seven hours consecutively. Pumping capacity must, therefore, be such that seawater can be stored during this period for use during the remaining five hours. The seawater has the following composition (in gm/l):

chlorine	(Cl)	19.50
sulphate	(SO <sub>4</sub> )	2.72
bromine	(Br)	0.06
bicarbonate and carbonate	(HCO <sub>3</sub> + CO <sub>3</sub> )	0.13
borate	(H <sub>3</sub> BO <sub>3</sub> )	0.02
sodium	(Na)	10.75
magnesium	(Mg)	1.31
calcium	(Ca)	0.42
potassium	(K)	0.39
strontium	(Sr)	0.14

The content of bromine is noteworthy because, notwithstanding the minute amount, its recovery from seawater is a commercial proposition. Trials have been made in Norway to extract potassium salts economically from seawater. The problem here is to find a reagent, which precipitates potassium but leaves sodium in solution. Dipicrylamine satisfies the condition but is relatively costly.

### PROCESSING

*Dolime burning*- At Coxhoe the stone is quarried and crushed and then calcined with coke as fuel in mixed feed' lime kilns. The mixture of calcium and magnesium oxides obtained should contain the minimum of insoluble calcium compounds and the maximum of reactive calcium oxide. Calcium carbonate results from incomplete decomposition, calcium sulphate is derived from the sulphur of the fuel, and calcium silicates, ferrites, and aluminates from the reaction between calcium oxide and the impurities in the stone and fuel ash. All these compounds are insoluble in seawater and contribute to the calcium content of the precipitate, but calcium carbonate is the most serious contaminant. Since the refractories industry demands a low-lime magnesia, with less than 3 per cent of calcium oxide, calcination is controlled so as to obtain maximum decomposition without 'overburning' and thereby seriously reducing the reactivity of the calcium oxide.

At Hartlepool the shaft kiln product contains about 1 per cent of carbon dioxide, which is equivalent to some 1.7 per cent of calcium oxide in the final calcined magnesia. The calcium silicates, ferrites and aluminates are, after calcium carbonate, the most important source of calcium oxide in the magnesia. Their contribution, amounting to about 0.8, per cent, depends mostly on the inherent impurities of the dolomite rock.

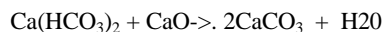
*Dolime hydration and purification* ---The calcined dolomite reaches Hartlepool by rail in sheeted wagons where it is crushed to about ½ in (1.27 cm) size and hydrated or slaked by what is known as the 'dry' process. The amount of water added is such that the small excess, which does not enter into chemical combination, is evaporated by the heat of hydration. The resulting hydrate is a very fine free-flowing powder which is air classified to remove the coarser and heavier impurities introduced from the fuel during calcination. The impurities inherent in the Coxhoe dolomite are more finely and uniformly disseminated and so do not tend to segregate on this treatment.

The resulting hydrated dolime has the following percentage composition

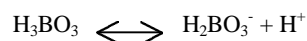
silica	(SiO <sub>2</sub> )	1.2
alumina	(Al <sub>2</sub> O <sub>3</sub> )	0.9

iron oxide	(Fe <sub>2</sub> O <sub>3</sub> )	0.8
lime	(CaO)	49.7
magnesia	(MgO)	30.3
carbonate	(CO <sub>2</sub> )	0.6
sulphate	(SO <sub>3</sub> )	0.4
water	(H <sub>2</sub> O)	16.1

*Seawater pretreatment-* Prior to the removal of magnesium hydroxide the seawater is treated with a small amount of lime to precipitate bicarbonate as calcium carbonate. If this is not done calcium carbonate will subsequently precipitate with and contaminate the magnesium hydroxide.



Seawater contains basic radicles in excess of the equivalent of strong acid radicles, this excess being balanced by borate, bicarbonate, and carbonate ions. Borate ions arise from the ionization of the small but approximately constant content of boric acid.



Bicarbonate and carbonate ions result from the equilibrium established between themselves, hydrogen ions, undissociated carbonic acid and dissolved carbon dioxide.



These are the only weak acids present in sufficient amounts to affect the equilibria. If the total alkalinity and pH of the seawater have been measured, the carbonate alkalinity may be calculated and hence the relative amounts of carbonate and bicarbonate. On the addition of lime the equilibrium is displaced and the carbonate ion concentration increased, until the limit is reached beyond which precipitation of calcium carbonate should occur. At some further point, as more lime is added, magnesium hydroxide will commence to precipitate but theoretically it should be possible to precipitate 98 per cent bicarbonate as calcium carbonate without removing magnesia. In practice difficulties arise as at normal temperatures no precipitate is produced for several hours owing to the tendency of calcium carbonate to form supersaturated solutions. If calcium carbonate seed is added in the form of previously precipitated sludge it tends to destroy the supersaturation and under the proper conditions (requiring, however, special equipment) a rapidly settling precipitate can be obtained.

At Hartlepool desupersaturation and the formation of a precipitate of the required properties are accomplished in Dorr hydrotreaters. These machines are cylindrical tanks each with three separate and distinct zones. In the lower part of the tank is the flocculation zone where seawater and dolomitic lime are mixed with previously formed

sludge returned by gravity from the clarification zone above. In the clarification zone a flocculate of calcium carbonate separates from the water which discharges over a weir into a peripheral launder. Beneath the flocculation zone at the tank centre is a thickening zone where excess sludge is continuously concentrated before discharge. The overflow water passes along open troughs to rapid gravity sand filters, which further reduce the small amount of suspended solids present. The treated and clarified water contains only about 0.005 gm of suspended solids and 0.06 gm. of dissolved calcium carbonate per litre.

*Precipitation of magnesium hydroxide-* The reaction between calcined dolomite and treated sea water must be carried out so as to ensure not only complete reaction of calcium oxide, but also to prevent precipitation of substances other than magnesium hydroxide and to yield a precipitate which settles rapidly and can be easily dewatered. This is the most critical part of the whole process since its success depends on the qualities of the magnesium hydroxide obtained. The problem of obtaining the precipitate in an easily separable form has been the subject of a voluminous patent literature, but very little fundamental information seems to be available. In theory it should be possible to obtain a product that settles rapidly by controlling precipitation so as not to exceed rate of crystallization from solution on to existing nuclei, possibly magnesium hydroxide from the calcined dolomite. In practice it is very difficult to prepare a coarse crystalline material in this manner since the very low solubility of magnesium hydroxide makes it almost impossible to balance rate of solution of base against rate of precipitation of product. An adequate rate of crystallization must be ensured to allow precipitation to take place at an economic rate and good results can be achieved by adding ' seeding ' nuclei such as previously formed precipitate. Here the only difficulty is the amount of seed, which may reasonably be kept in suspension.

It has already been stated that if all the magnesium present is precipitated the solubility of calcium sulphate in the spent seawater is exceeded and precipitation of this salt should occur. From this source alone 7.7 per cent of calcium oxide could become associated with the final product. The limiting concentration of calcium ion is attained when 72.5 per cent of the total magnesium has been removed. In practice precipitation does not take place immediately and the supersaturated solutions of calcium sulphate produced are sufficiently stable to allow complete precipitation of magnesium hydroxide. Calcium sulphate does, however, deposit on long standing. Full reaction of calcium oxide is ensured by subsequently washing the magnesium hydroxide with fresh pretreated seawater and this also removes any precipitated calcium sulphate.

The means for the proper proportioning of dolime and seawater depend on the method of working, but generally the flow of seawater is manually set to a definite rate to correspond with the appropriate amount of dolime. Seawater is measured by a weir, orifice or venturi and calcined dolomite by means of a continuous weight feeder. Any adjustments are made according to chemical tests.

*Treatment of the precipitate---* The precipitate passes as a dilute slurry from the reaction tanks to the settling tanks which vary in size up to 240 ft in diameter with conical floors falling to a maximum depth of 23 ft at the centre. These are equipped with Dorr thickener mechanisms, which consist principally of specially designed mechanically rotated raker arms, fitted with inclined rakes. These work the magnesium hydroxide to the centre of each tank from where it is withdrawn and pumped to the wash tanks. Spent seawater overflows into a launder and is discharged.

A concentrated slurry is produced with a magnesium hydroxide content of about 300 gm/l. The importance of a rapidly settling precipitate is now evident since the greater the settling rate of the precipitate the greater is the production that can be obtained from equipment of a specified size. This slurry is pumped to the filter house. In some plants the slurry must be heated to render it rapidly filterable and the expenditure of fuel to produce the necessary steam may be considerable. The qualities of the precipitate now produced at Hartlepool, however, render this operation unnecessary.

Rotary disk filters, arranged in batteries and partly immersed in slurry, are used for filtration. They have proved very satisfactory over a number of years. Each filter, which is divided into compartments, consists of a disk covered with stout cotton twill and mounted with a number of others on a hollow shaft from which filtrate can be withdrawn. The compartments are separately connected to the hollow shaft and arranged so that on immersion suction is applied and magnesium hydroxide deposited. When the compartment emerges from the slurry, during rotation, compressed air is blown through in the opposite direction and the paste coating removed from the surface of the cloth by contact with a fixed scraper wire. The paste, which contains about 33 per cent of magnesia, drops on to a moving belt and is conveyed to the rotary kiln plant for calcination. Continuous vacuum filters cannot satisfactorily dewater unflocculated colloidal solids since they tend to choke the filter cloth. No difficulty is experienced, however, if the precipitate consists of crystalline or well flocculated material. The behaviour of the precipitate at this as at the settling stage can determine the degree of success of the whole plant.

*Calcination of precipitate----* The subsequent use of the calcined magnesia determines the method of calcination employed. If it is to be employed for refractories it is burned at the highest possible temperature in rotary kilns similar to, but generally shorter than, cement kilns. A typical rotary kiln is a gently inclined revolving steel cylinder approximately 150 ft long by 9 ft in diameter and lined with refractory brick. The front of the kiln is closed by a hood, which carries the burner, a simple tube open at one end, through which a mixture of powdered coal and

air is blown. Ignition of this mixture produces an intensely hot highly luminous flame. The magnesia paste is fed into the upper end of the kiln and as the furnace rotates gradually works its way down towards the burning zone and the discharge port. During its passage water and alkali salts are volatilized and the residue partially fuses or sinters to form the brownish granules known to the refractories industry of this country as *Britmag*. The maximum temperature attained is probably in the region of 1,650°C.

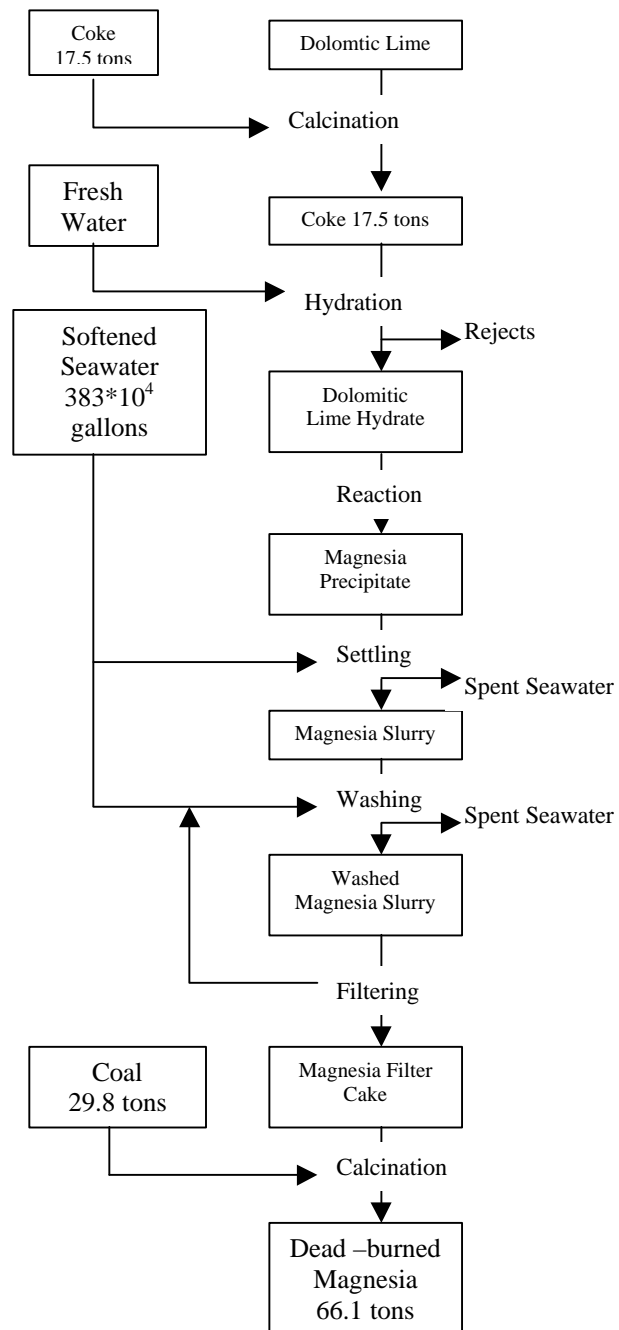


Figure 1. Hartlepool process: flow diagram

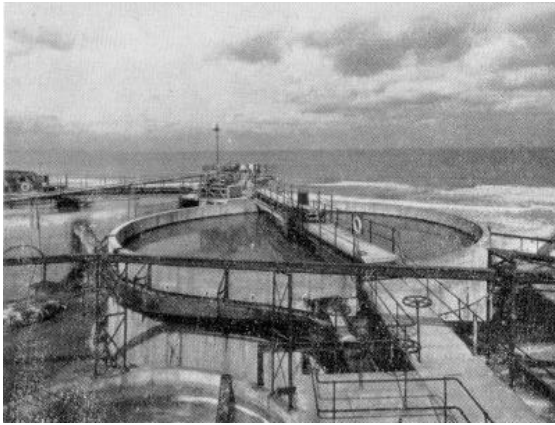


Figure 2. Seawater pretreatment: Dorr hydrotreator

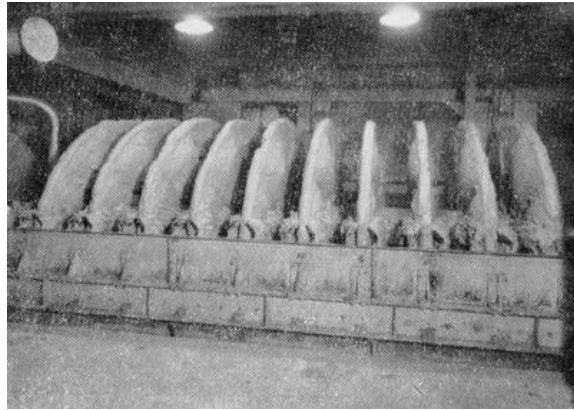
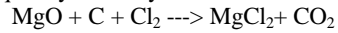


Figure 4. Magnesia slurry filtration: ten disk rotary vacuum filter

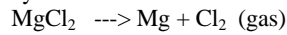
The *Britmag* clinker is virtually inert to the action of atmospheric moisture and is said to be 'dead burned'. It forms the chief product of the Hartlepool works for the manufacture of magnesia bricks elsewhere. An average percentage composition is as follows: silica (SiO<sub>2</sub>) 2.1, alumina (Al<sub>2</sub>O<sub>3</sub>) 1.4, iron oxide Fe<sub>2</sub>O<sub>3</sub> 1.4, lime (CaO) 2.7, magnesia (MgO) 92.4.

If the product is to be used for the manufacture of magnesium metal it must be calcined, again in rotary kilns, at the much lower temperatures of 800<sup>o</sup> to 1000<sup>o</sup>C to form the chemically active variety known as 'caustic magnesia'. During the 1939-45 war precipitation from sea water and calcination to the caustic grade was principally carried out at the Harrington works, near Workington, in Cumberland. After transport to the magnesium metal works the reactive magnesia is treated with coal and chlorine

at about 850<sup>o</sup>C to form molten magnesium chloride which is subsequently electrolysed :



On electrolysis:



The electrolysis cells are operated at about 700<sup>o</sup>C and the liberated magnesium floats as liquid on the surface of the cell contents. A flow sheet of the process worked at Hartlepool is shown in *Figure 1* *Figures 2-5* illustrate the various aspects of the plant operation described in the preceding pages.

It is doubtful if the position of the Hartlepool plant could be improved upon, since nowhere else in Britain are large deposits of dolomite found so near the coast and yet within such easy reach of the chief steel producing centres.

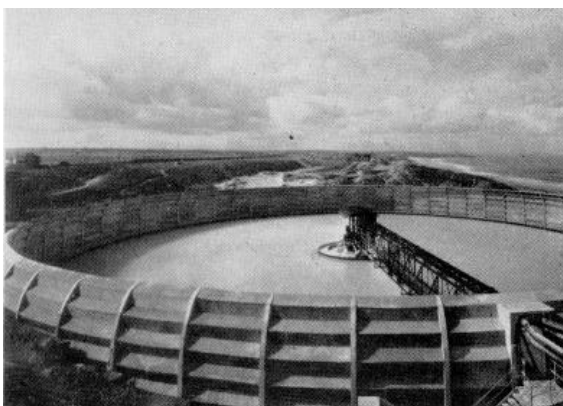


Figure 3. Magnesia settling: 240ft Dorr thickener with windshield

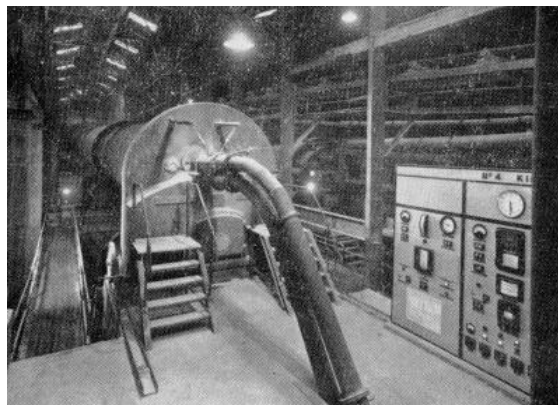


Figure 5. Magnesia calcination: 185ft rotary kiln (P.F. firing)

In the United States some sea water plants have made themselves independent of limestone and dolomite by the use of oyster shells, large deposits of which occur at various points near the coastline in shallow water. They are recovered by dredging and when calcined give a very pure calcium oxide which has been proved eminently suitable as a precipitant.

The seawater process, both in this country and the United States, would probably not have attained its present development without the wartime stimulus caused by the lack of natural imported Austrian magnesite. This was partly due to long established commercial relations with the Austrian producers, and partly because the refractory brick plants had organized their processes and products completely to the use of the Austrian material.

Seawater magnesia now has, however, the advantage over natural magnesite that, within limits, its composition can be adjusted at will. This makes it possible to produce material of the quality found by research to give the most satisfactory service in the steel furnace.

#### BIBLIOGRAPHY

For the general reader the best volume on the production of magnesium and other substances, including bromine, and potassium salts, from the sea is probably *Raw Materials from the Sea* by E. F. ARMSTRONG and L. M. MIALL, Leicester. This volume is useful also in that it details numerous references to journals and periodicals, which will be of interest to technical readers. Some of the more important of these are :

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