

DEPARTMENT OF ENERGY, MINES AND RESOURCES MINES BRANCH OTTAWA

REFRACTORY-GRADE MAGNESIA IN CANADA

M. PALFREYMAN

MINERAL PROCESSING DIVISION

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by

M. Palfreyman*

ABSTRACT

The increasing demand for magnesia refractories is a direct result of the increasing use of the basic oxygen furnace in the steel industry. This trend may be expected to continue, at least until the open-hearth furnace has been phased out. At the same time, the specifications for refractory-grade magnesia are becoming more rigid, particularly with respect to iron oxide and to boron, which is present in seawater magnesia. As a result, more interest is being shown in the beneficiation of natural magnesitic ores to produce high-purity magnesia free from boron and very low in iron oxide.

This bulletin discusses the properties of refractorygrade magnesia, reviews the magnesia industry in Canada both past and present, and lists known Canadian sources of magnesitic rock.

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RÉFRACTAIRE DE QUALITÉ DE MAGNÉSIE AU CANADA

par

M. Palfreyman*

RÉSUMÉ

A cause de l'utilisation croissante du four basique à oxygène dans l'industrie d'acier, il y a une demande progressive pour des réfractaires de magnésie. On peut s'attendre à ce que cette tendance continue au moins jusqu'à ce que le four à sole disparaîtra. En même temps, les spécifications des réfractaires de qualité de magnésie deviennent de plus en plus rigides particulièrement en ce qui concerne l'oxyde de fer et aussi le bore qui est présent dans la magnésie d'eau de mer. Par conséquent, il y a plus d'intérêt dans l'enrichissement des minerais magnétiques naturels pour produire de la magnésie d'une pureté élevée, libre du bore et d'une teneur très basse en oxyde de fer.

L'auteur discute dans ce bulletin des propriétés des réfractaires de qualité de magnésie et il présente une revue du passé et du présent de l'industrie de magnésie au Canada. De plus il donne une liste des sources canadiennes connues de roches magnétiques.

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INTRODUCTION

In 1950, the quantity of refractory-grade magnesia sold or used by United States producers amounted to 335,000 short tons(1), including both calcined and dead-burned varieties. By 1965 this figure had increased to 897,000 short tons and the projected figure for 1975 is 1,367,000 tons. Canadian production of dead-burned magnesite in 1970 was 60,000 tons. The greater part of this material has been and will continue to be consumed by the iron and steel industry, where the largest single factor contributing to the increasing use of magnesia is the basic oxygen furnace (BOF). The production of steel by the BOF process has shown a dramatic increase since 1955, and it is certain that it will replace the open-hearth process by 1980(2). The refractories requirements of the BOF are very different from those of the open-hearth. Very little fire clay and much more magnesite and dolomite is required. Rapid changes have taken place in the types of refractories used in basic oxygen steel making since 1955. At that time, basic magnesite, chromite, and dolomite brick were used. The use of chromite has since decreased to almost zero and dolomite or magnesite or combinations of the two are now universally used in the process. Tar is the common bonding agent.

In non-ferrous smelting and refining, the variety of metals, furnaces, and fuels demands a wide variety of

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refractories. However, except in electric furnaces, the refractories used are usually basic, made of magnesite, dolomite, or chromite, either in blends or alone.

It should be noted that whereas the names magnesite, magnesite-chrome, and chrome-magnesite are in universal use in the refractories industry, they are mineralogically misleading. The material in the refractories is actually magnesia, which is produced by calcining the mineral magnesite.

In Canada, numerous occurrences of magnesite have been reported, several of which may be classed as deposits with commercial potential. At least one of these deposits is being worked commercially as a source of refractory-grade magnesia.

Magnesia may also be obtained by the precipitation of magnesium salts from seawater. For refractory use, both mineral and seawater magnesias should be dead-burned (i.e. calcined to 1700°C(3092°F) or higher) to give a suitable product. The mineral and seawater dead-burned products differ to some extent, both chemically and physically, but technological developments have enabled the manufacturers of both types to produce very high-quality materials.

MAGNESITE AS A SOURCE OF REFRACTORY-GRADE MAGNESIA

Magnesite is essentially magnesium carbonate $(MgCO_3)$, which may occur in the pure form or in association with other minerals, notably dolomite. From the refractory point of view, other important impurities are iron as pyrite, hematite,

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magnetite, or siderite, and silicon as quartz. Magnesite suitable for the production of refractory-grade magnesia commonly occurs as breunnerite, compact magnesite, and as brucite.

Coarsely crystalline magnesite is mined at Veitsch, in Austria. The Austrian product is often referred to as breunnerite because the dead-burned product may show from 4 to 8 per cent of Fe_2O_3 . Most breunnerites as mined contain large quantities of dolomitic impurity which must be removed prior to deadburning.

Crypto-crystalline or "compact" magnesite is usually white in colour and very hard. This material occurs in Greece, Yugoslavia, India, Australia, South Africa, and in California in the United States. It is normally low in iron and, if fired to a sufficiently high temperature, provides a very good magnesia for refractory production.

Brucite, which is essentially hydrated magnesium oxide $(Mg(OH)_2)$, and often occurs in association with limestone. Such material is normally referred to as brucitic limestone, which is found in considerable quantities in Ontario and Quebec. It is usually found with substantial amounts of other minerals and must be concentrated prior to dead-burning.

As mentioned above, the undesirable impurities in magnesite destined for use in refractories are lime, in the form of calcite or dolomite, iron compounds, and silica. The CaO-MgO system(3) does not show the formation of any liquid phases below 2370°C(4298°F) so that fluxing by lime would not occur under normal steelmaking conditions. However, free lime would render

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the final product prone to hydration by atmospheric moisture thereby restricting the storage life.

Magnesia forms a continuous series of solid solutions with ferrous oxide (wustite)(4), such that considerable substitution of the refractory oxide by the flux may occur before a composition is reached which melts at the operating temperature of the steelmaking furnace.

The most important impurity is probably silica which is not only detrimental in itself but combines with other impurities to form compounds which are very detrimental. The system Mg0.SiO₂ shows a eutectic at 35 per cent by weight MgO that melts at $1543 \circ C(2810 \circ F)(5)(6)$. It also shows two compounds; clinoenstatite (Mg0.SiO₂), which is 40 per cent by weight MgO and melts incongruently at $1557 \circ C(2835 \circ F)$, and forsterite $(2Mg0.SiO_2)$, which is 57.14 per cent by weight MgO and melts congruently at about $1900 \circ C(3452 \circ F)$. Magnesia and forsterite form a eutectic system with a melting point of $1850 \circ C(3362 \circ F)$. Both natural and synthetic forsterite refractories are employed in steel plants and are characterized by their stability of strength and volume at high temperatures.

The combination of silica and lime is extremely important in magnesia refractories in that the lime: silica ratio determines the nature of the compounds formed in the bond between the magnesia grains. Relatively refractory minerals such as dicalcium silicate (2CaO.SiO₃) are tolerable but less refractory minerals such as wallastonite (CaO.SiO₂), merwinite (3CaO.MgO. $2SiO_2$), or monticellite (CaO.MgO.SiO₂) are undesirable. If the

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lime content of the magnesite is high, considerable quantities of dicalcium silicate may be formed during dead-burning and this can lead to "dusting" of the refractories in service when they are cooled to below 675°C(1247°F). The "dusting" results from the $\beta - \delta$ transformation in the dicalcium silicate which is accompanied by a 10 per cent volume change. In general a lime: silica ratio of about 2:1 is desirable. With a higher ratio, the possibility exists of forming low-melting dicalcium ferrite (2CaO.Fe₂O₃) and tricalcium silicate (3CaO.SiO₂), which are unstable in the temperature range to which magnesia refractories are normally subjected. The formation of such a liquid phase between the magnesia grains reduces the resistance to deformation or rupture of the hot refractory. Recent work(7) has shown that the hot strength of magnesia grain is increased by increasing the lime:silica ratio beyond 2:1 for silica contents up to 0.85 The lower the silica content the higher the lime:silica per cent. mole ratio required to obtain maximum strength. The explanation for this phenomena is that at high temperatures the lime distributes itself between the magnesia and silicate phases. Several workers have found lime existing in solid solution in magnesia crystals in materials of similar chemical purity to those used in the production of refractories(8)(9)(10)(11). When part of the lime enters into solid solution with the magnesia, the lime:silica ratio of the silicate phase is lowered favouring the formation of merwinite (3Ca0.Mg0.2Si0₂) and monticellite (Ca0.Mg0.Si0₂), which liquify at lower temperatures than dicalcium silicate (2CaO.SiO₂). Therefore, excess lime is required above the 2:1

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ratio in order to maintain the dicalcium silicate in the bond phase. The solution of lime in the magnesia becomes more critical at lower silica contents; therefore a greater overall lime: silica ratio is necessary to maintain the dicalcium silicate phase.

The occurrence of alumina (Al_2O_3) as an impurity in magnesite is normally very small and in magnesia refractories the alumina and silica together would be less than 2 per cent. The system MgO-Al_2O_3-SiO_2 shows a eutectic which melts at 1355°C (2471°F), but this would not be expected to be present in any great quantity in a magnesia refractory which has been fired to a high temperature. The eutectic can be formed by reaction between magnesia and fireclay refractories indicating the desirability of separating these refractories either by a neutral course or by ensuring that they are not used in contact at temperatures above about 1300°C(2372°F).

For refractory uses, the magnesia content of a deadburned product should be not less than about 90 per cent. The lime content should be as low as possible.

PROCESSING OF MAGNESITE

In order to produce a refractory-grade magnesia from any natural magnesite the latter must be processed in two stages. The first stage is to reduce the quantity of undesirable impurities to an acceptable level, and the second stage is to calcine the material to a very high temperature so as to render the

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final product resistant to attack by atmospheric moisture and to volume changes in any subsequent heating process.

The impurities may be reduced or removed by various processes such as heavy-media or magnetic separation. Chemical analyses of some samples of dead-burned magnesite from various locations, as quoted by Chesters(12), are given in Table 1. In some cases the analyses are for beneficiated materials including magnetic separation of the fired products. The Canadian material was produced by dead-burning a magnesitic-dolomite rock found at Kilmar, Quebec(13); no attempt was made to beneficiate the raw material.

The process of calcining magnesitic rock to produce a refractory-grade magnesia is referred to as "dead-burning" because after calcination it is unreactive or "dead" in that it may be used in brick-making or monolithic forms without such ensuing difficulties as hydration and shrinkage. Dead-burning is usually performed in either rotary or shaft kilns at about 1700°C(3092°F) or higher. The main advantage of the rotary kiln is that the product receives a more uniform treatment. Material which is calcined at lower temperatures, in the range 900° to 1100°C(1652° to 2012°F), is usually referred to as caustic calcined magnesia or simply, calcined magnesia. This product is unsuitable for the production of refractories but finds many other uses as described below. Although the chemical reactions are different, the same basic principles apply whether the material is produced from the carbonate (magnesite) or the hydroxide (brucite). The dissociation temperature of the

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TABLE 1

Chemical Analyses of Dead-Burned Magnesite From Various Locations

Source	Austria		Greece	Russia	Manchuria	India	Canada	U.S.A.	
	Veitsch	Radenthein	Euboea	nussia	Manchuria	тиата	vanaua	Washington	
	%	%	%	%	%	%	%	%	
Si0 ₂	1.7	2.1	2.6	4.7	2.8	5•4	7.9	3.2	
Al ₂ 03	0.9	2.4	0.4	1.1	2.3	0.4	0.2)	3.2	
Fe203	8.2	3.9	0.5	2.7	1.9	0.7	7.8)	<i></i>	
CaO	2.5	2.3	2.0	5.7	1.8	2.6	19.5	2.0	
MgO	86.9	89.0	95.3	85.2	90.8	90.8	64.5	91.6	

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carbonate is much higher than that of the hydroxide and basic carbonates dissociate over a long intermediate temperature range(12).

From the steelmaking standpoint the important feature is the effect of the calcination temperature and the fluxes present upon the rate of crystal growth and the stability of the final product. The specific gravity of the latter should be as close to 3.56 g/cm³ as possible. However, if the final product contains considerable quantities of iron oxide this value may be exceeded. As a rough approximation the specific gravity may increase by 0.01 g/cm³ for each 1.0 per cent of iron oxide, although this fails to take into account the effect of other impurities. In general it may be stated that as the specific gravity increases the crystal size also increases whilst the hydration tendency decreases. If the hydration tendency exceeds the safe value, or if reactive material is present, difficulties may be encountered in storage or in actual brick-making. The safe value is really a comparative value as storage conditions may vary from place to place. For example, a figure which is acceptable in a locality where the relative humidity is normally low may not be acceptable where it is normally high. Similarly, the safe value may vary according to the drying procedure adapted in the brick-making process.

Equally important to the hydration tendency is the firing shrinkage or "after contraction" of the dead-burned material. When the firing shrinkage is excessive, brick produced from such a material may crack during firing or be under

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size. Furthermore, brick or a monolithic furnace lining made from this material may shrink and crack in subsequent service causing a shutdown of the furnace.

THE MAGNESIA INDUSTRY IN CANADA - A REVIEW

Prior to World War I, Austria was the dominant producer of magnesitic rock, clinker, and brick. The production of certain basic refractories from magnesitic rock began in Canada in 1918 and by 1936 an apparent 85 per cent of the domestic requirement for magnesite brick was being satisfied(13). The true value was in fact much lower than this due to the export of large quantities of raw material to the United States and Great Britain. In 1938, Quebec ranked amongst the world's leading producers of magnesitic rock and clinker. The raw material was mined at Kilmar, Argenteuil County, Quebec, and consisted essentially of crystalline magnesium carbonate intimately mixed with dolomite, which occurs with magnesium silicate rocks in the Precambrian The deposit was exploited by open pits until 1927, but terrain. by 1938 this practice had been replaced by stope mining. The chemical analysis of the crude rock was as follows: 2.0 to 3.5 per cent SiO_2 , 0.2 to 0.3 per cent Al_2O_3 , 0.2 to 0.4 per cent Fe_20_3 , 9.0 to 12.0 per cent CaO, and 32.0 to 38.0 per cent MgO; the loss on ignition was 46.0 to 48.0 per cent. This material was processed at the Canadian Refractories Limited plant at Kilmar, Quebec. After reduction to 100 mesh, the rock was deadburned in a rotary kiln fired with Bunker "C" fuel oil in the

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temperature range 1482° to 1788°C(2700° to 3250°F). The chemical analysis of the dead-burned clinker was as shown in Table 1 with minor variations. The large content of iron oxide in the clinker is due to the fact that extra iron oxide was added in the rotary kiln to promote sintering of the magnesia and to stabilize the lime. The final product contained considerable dicalcium silicate. In terms of the steelmaking practices of that time the clinker was acceptable in many applications. However, in view of the large flux content it would not qualify as magnesia by present day standards.

In 1937, brucite was discovered by Goudge(14) in the Precambrian limestone of the Rutherglen district of Ontario. The occurrence of limestone in that area had been known for many years and references had been made to it since 1845. It was apparently used by the early settlers of the district for making Brucite was found in the Bryson area of Quebec in 1938 lime. and in 1939, a very large deposit was discovered at Farm Point, Quebec, which is about 18 miles north of Ottawa and 3 miles south of Wakefield. The brucite occurs as granules disseminated through white Precambrian limestone of the Grenville series. This rock may be referred to as predazzite or pencatite. However, the term brucitic limestone is generally used to designate limestone in which brucite is developed. The magnesia content of the rock does not approach that of magnesite in any of the deposits, so it was necessary to develope a means of concentrating the brucite. A process of beneficiation was developed by Goudge and Phillips (15), which involved calcining the rock,

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adding sufficient water to convert the lime to a dry hydrate leaving the calcined brucite in granular form, and finally separating the brucite from the lime and serpentine. The separation was effected by air flotation, washing, and screening. The final product contained about 92 per cent magnesia and 3 per cent lime.

In 1942 the Aluminium Company of Canada Limited started to produce magnesia by this process. Most of the initial magnesia production was consumed in the manufacture of basic refractories and in the paper industry.

In 1945, Canadian Refractories Limited was taken over by the Harbison-Walker Refractories Company, Pittsburgh, Pa., and modernization of the plant at Kilmar, Quebec, was started in 1946. This was completed in 1948 and included a 245 foot tunnel kiln and a sink-float plant which enabled lower grade ores to be beneficiated by heavy-media separation. The construction of a second plant for production of basic refractories was started in 1951 at Marelan, Quebec, 10 miles south of Kilmar. This plant opened in 1953.

In 1959, the General Refractories Company Limited installed facilities at Smithville, Ontario, for the production of basic refractories from imported dead-burned magnesia. In the same year, the Aluminium Company of Canada Limited closed the magnesium metal plant at Arvida, Quebec, which had used magnesia from the plant at Wakefield, Quebec, as raw material. In the following year, Refractories Engineering and Supplies Limited installed a plant at Bronte, Ontario, to produce ramming mixes from imported dead-burned magnesia. At Chippawa, Ontario, the

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Norton Company began producing fused magnesia from imported raw materials.

The first recorded shipments of brucitic limestone from the deposits in the Rutherglen district of Ontario were made in 1961. However, the material was not destined for refractory usage.

The following year, the A.P. Green Firebrick Company drilled and sampled an occurrence of magnesite at Briscoe in southeastern British Columbia, and Canadian Magnesite Mines Limited began exploration of an occurrence in Deloro and Adams Townships in Ontario(11). In 1963, the latter company announced its intention to construct a pilot plant at Beaucage, Ontario as a further step in the evaluation of the magnesite deposits in Deloro and Adams Townships. The plant opened in 1964 to process only a few hundred tons of magnesite as will be discussed below in greater detail. Also in 1963, Canadian Refractories Limited installed new equipment at Kilmar, Quebec, to process magnesite concentrates.

In February 1968 the Aluminium Company of Canada ceased operations at Wakefield. At present the only operations producing magnesia for basic refractories are the Canadian Refractories Limited plants at Kilmar and Marelan in Quebec. On September 1, 1971, Canadian Refractories Limited became a wholly owned subsidiary of Dresser Industries Canada Limited.

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KNOWN OCCURRENCES OF MAGNESITIC ROCK IN CANADA

British Columbia

Magnesite occurs at Marysville between Kimberley and Cranbrook where it forms part of the Cranbrook Formation(17); at the northwest end of Liza Lake in the Bridge River map areas of the Killooet district(18); and at numerous other points as noted by McCammon(19) who has published extensive details of occurrences of brucite and hydromagnesite $(3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O)$ in British Columbia. A deposit of magnesite on Mount Brussilof, which lies between the Kootenay and Banff National Parks, has been examined for purity and suitability as a refractory raw material(20)(21)(22).

Ontario

Almost pure magnesite occurs in veins in a serpentinecarbonate rock in the southern point of Deloro Township(23).

Brucite occurs in the Rutherglen district(14) in Olrig and Calvin Townships(24)(25), and in Hinchenbrook Township(26).

Breunnerite occurs in Rothburn Township on the east shore of Wanapitei Lake, in Scadding Township(27) and has been reported in the southern part of Deloro Township(23).

Quebec

Magnesian limestone occurs at Kilmar, in Harrington Township about 10 miles north of Grenville(28); in Bolton and Sutton Townships(29); and in Montauban Township(30).

Brucite occurs at the Martin-Bennet chrome pit in

Ireland Township, Megantic County(31), and near Asbestos(32). Extensive deposits of brucitic limestone are found in Bryson and on Calumet Island(14)(33), and in Wakefield, Masham, and Hull Townships(14(34).

Atlantic Provinces

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Magnesite has been reported in Nova Scotia at Malagash in Cumberland County(35), and on the Point Road near Orangedale in Inverness County(36).

Brucite occurs in the Meat Cove zinc deposit on the headwaters of French Creek, two miles south of Meat Cove on the northern tip of Cape Breton Island(37).

Breunnerite occurs in the ultrabasic rock which extends northward from half a mile north of the Trans-Canada Highway in the Terra Nova and Bonavista map-areas in Newfoundland(38).

Northwest Territories

Hydromagnesite has been reported along the south shore of Deare Bay, Great Bear Lake(39).

CURRENT COMMERCIAL EXPLOITATION OF MAGNESITIC ROCK IN CANADA

Apart from the deposits of magnesian limestone at Kilmar, Quebec, and the brucitic limestones of Wakefield, Quebec, and Rutherglen, Ontario, no other Canadian source of magnesitic rock has been exploited successfully for the recovery of magnesia. There is no doubt that many factors such as the size of deposit, problems in beneficiation, and location have contributed to this situation.

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The deposits of magnesite at Marysville, between Kimberley and Cranbrook in British Columbia(17), were acquired by the Consolidated Mining and Smelting Company in 1935(40). They contain considerable alumina and silica, and over about ten years, attempts were made at beneficiation, but the operations never amounted to production.

The deposits that have been examined most recently with a view to the commercial production of magnesia are those in the southern part of Deloro Township in Ontario(23) and on Mount Brussilof in British Columbia(20)(21)(22).

Preliminary tests on the material from Deloro Township were made by Lakefield Research of Canada Limited, Lakefield, Ontario(41). Their results, based on calculations from chemical analyses, indicated that the principal constituents were magnesite (55.5 per cent), talc (28.6 per cent), quartz (10.3 per cent), and hematite (5.5 per cent). Subsequent tests by the Mines Branch, Department of Mines and Technical Surveys, Ottawa, showed that the principal constituent was magnesite of practically stoichiometric composition(42).

Initial work on the physical beneficiation of the raw material(43)(44)(45) showed that a product high in magnesia and low in lime and silica, with a moderate iron content could be prepared by flotation followed by magnetic separation. It was first necessary to remove the talc by flotation followed by either floating and cleaning of the magnesite, or alternatively to remove the quartz, hematite and silicates by flotation. The second alternative was deemed to be preferable. It was found

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necessary to grind the raw material to liberate the silicates. Part of the iron remained with the magnesite and could not be separated.

At about the same time a process for the chemical beneficiation of the raw material was being investigated by Battelle Memorial Institute, Columbus, Ohio, with a view to producing a high-quality magnesia(46)(47).

As a result of these investigations, a pilot plant was built at Beaucage, Ontario in 1964, in which 500 tons of magnesite concentrate were produced from about 2000 tons of ore. Some of the concentrate was dead-burned. Brick made from this material showed encouraging refractory properties. A typical chemical analysis of the dead-burned product showed 92.5 per cent MgO, 6.0 to 6.5 per cent Fe_2O_3 , 1.0 per cent SiO_2 , and less than 0.2 per cent CaO. Further work carried out at the Mines Branch in Ottawa showed that by careful control of grinding techniques and calcination temperatures it was possible to obtain magnesia grain with densities between 3.45 and 3.47 g/cm³ with a deadburning temperature of $1650 \circ C(3002 \circ F)(48)$.

In order to compete with seawater magnesia, it became evident that the iron content of the Canadian Magnesite Mines Limited product must be reduced. A chemical process to reduce the iron and other impurities was devised by Opatowski(49), and in 1969, a pilot plant designed to use this process was put into operation. The plant was capable of producing several pounds per hour of high-purity magnesia (99.7 per cent MgO, 0.01 per cent SiO_2 , 0.20 per cent CaO, and 100 ppm Fe₂O₃). Canadian Magnesite Mines Limited considers that the economics of the Opatowski process are such that it may be possible to produce a high-purity magnesia which can subsequently be doped with controlled amounts of lime, silica, and iron oxide, to impart ideal properties for producing refractories. In 1971, the company planned a one-tpd pilot plant to produce the high-purity product. This plant would also provide the data necessary to design a commercial plant. The company is also interested in installing flotation facilities to work in conjunction with the commercial plant. The flotation plant would provide tailings containing about 50 per cent magnesite, which would serve as feed for the chemical plant and, by suitable blending prior to dead-burning, it should be possible to produce a wide selection of refractory magnesias.

The Deloro deposits have a particular advantage in that they are near the main Canadian steelmaking centres. The magnesite deposits on Mount Brussilof in British Columbia are more remote. Mount Brussilof lies in a 15-mile wide corridor between the Banff and Kootenay National Parks on the Alberta-British Columbia border. Samples of rock taken from the western face of the mountain showed that the magnesite content was either zero or between 40 and 99 per cent(20). The principal impurity was dolomite.

Chemical analyses of samples of magnesite are taken from Mount Brussilof in 1970 showed approximately 95.9 per cent MgO, 1.40 to 3.12 per cent CaO, 0.26 to 0.35 per cent SiO_2 , 0.76 to 0.99 per cent Fe_2O_3 , and 0.21 to 0.25 per cent $Al_2O_3(50)$.

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These samples were subsequently evaluated as a refractory raw material by the Mines Branch in Ottawa(21)(22).

The evaluation showed that magnesia grain, with densities between 3.39 and 3.49 g/cm^3 , could be produced by a twostage process, in which the raw material was calcined at $1100 \circ C(2012 \circ F)$, comminuted, pressed into pellets and dead-burned at $1650 \circ C(3002 \circ F)$. The variation in bulk density was attributed to the differing lime contents. Because the lime: silica ratio is much greater than 2:1 it is considered preferable to remove some of the lime rather than add silica because the latter process would reduce the refractoriness.

The deposits have now been taken over by a major mining company(51), for further exploration and sampling.

A chemical process for the extraction of magnesia from magnesian limestone has been developed by Spring Chemicals Limited, Toronto, Ontario. The company is interested in producing a dead-burned magnesia for refractory and ceramic uses, and a sample of its product from a pilot plant situated at Masson, Quebec, was evaluated as such by the Mines Branch in Ottawa(52). The material is very pure (99.4 per cent MgO), the principal impurity being iron oxide. Magnesia grain with a density of 3.27 g/cm^3 was obtained after calcining the raw material at $1150 \circ C(2102 \circ F)$ followed by pelletization and dead-burning at $1650 \circ C(3002 \circ F)$. Higher bulk densities can be achieved by doping the magnesia with controlled amounts of lime, iron oxide, and silica.

The pilot plant at Masson is temporarily shut down

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as the company has been obliged to attend to other commitments.

SEAWATER MAGNESIA IN CANADA

In 1968, the Sea Mining Corporation, a joint venture of the Continental Ore Corporation (New York) and Frederick J. Gormley Limited, began development of a process for extracting magnesium hydroxides from seawater at Aguathuna, near Stephenville, Newfoundland. The plant is the first of its kind in Canada. The raw materials involved are seawater, sulphuric acid, and local limestone. The extraction of magnesia from seawater is made economic by virtue of the low solubility of magnesium hydroxide which can be precipitated from solutions of magnesium salts by bases that provide only a moderate concentration of hydroxyl iron.

In order to work the seawater magnesia process, either limestone or dolomite is calcined in vertical or rotary kilns to give an oxide mixture,

 $CaCO_3 \cdot MgCO_3 \longrightarrow CaO + MgO + 2CO_2$

the lime in which, when added to seawater, hydrates and reacts with the magnesium salts, to precipitate magnesium hydroxide. The calcium ions pass into solution, i.e.,

 $\begin{array}{ccc} \text{CaO} + \text{H}_{2}\text{O} & & & \text{Ca(OH)}_{2} \\ \text{Ca(OH)}_{2} + \text{Mg}^{2+} & & \text{Mg(OH)}_{2} + \text{Ca}^{2+} \end{array}$

The magnesium hydroxide is subsequently settled, thickened, filtered, pelletized, and dead-burned in a rotary kiln. In actual practice, the process is more complex than indicated above. Up to 1970, the plant at Aguathuna had produced only magnesium hydroxide slurry. In that year, the project was taken over by Lundrigans Limited (53), a Newfoundland constructionoriented company, which planned to install the new equipment necessary to fulfil a 5 year contract for \$10 million worth of magnesia to Corhart Refractories Division, Corning Glass Works Inc., Corning, N. Y.

The main disadvantage of seawater magnesia is that it contains boron which lowers the hot strength of magnesia refractories.

SUMMARY

At present, the only Canadian producer of dead-burned magnesia for refractories is the Canadian Refractories Division of Dresser Industries Canada Limited.

Due to the small size of the Canadian steel industry, a magnesia producer must be prepared to export most of his product. The nearest market is the United States which consumes vast quantities of magnesia. However, the magnesia industry in the United States is large and well established so that the market could be expected to be very competitive. Nevertheless, as the specifications for refractory-grade magnesia become more rigid, the quantity of readily available acceptable material will no doubt decrease. Under these circumstances, a highpurity Canadian product could be more competitive.

Whilst this bulletin is principally concerned with

the production of dead-burned magnesia for refractory or ceramic use, it is pointed out that calcined magnesia is used in the production of flooring cements, rayon, insulation, specialty fertilizers, rubber, pulp and paper and a variety of chemicals including magnesium metal. Therefore, a magnesia producer need not design solely for, nor depend on, the refractories industry as a market.

REFERENCES

- 1. W.S. Miska, "Refractory Use Patterns in the Iron and Steel Industry of the United States", U. S. Dept. of the Interior, Bureau of Mines Information Circular No. 3282 (1968).
- 2. D.J. Kusler and R.G. Clarke, "Impact of Changing Technology on Refractories Consumption", U. S. Dept. of the Interior, Bureau of Mines Information Circular No. 8494 (1970).
- R.C. Domon, J.B. Barr, R.N. McNally, and A.M. Alper, "Phase Equilibria in the System CaO-MgO", J. Amer. Ceram. Soc. <u>46</u>, (7), 314, (1963).
- 4. N.L. Bowen and J.F. Schairer, Am. J. Sci., 5th Ser. 29, 153, (1935).
- 5. N.L. Bowen and O.Andersen, Am. J. Sci. (4), 37, 488, (1914).
- 6. J.W. Grieg, Am. J. Sci., (5), <u>13</u>, 15, 133-154, (1927).
- 7. D.R.F. Spencer, "Basic Refractory Raw Materials", Trans. Brit. Ceram. Soc., <u>71</u> (5), pp. 123-134, (1972).
- 8. D.G. Jones and D.A. Melford, "Comparison of the High-Temperature Constitution of Seawater Magnesites with that of Natural Greek Material", Trans. Brit. Ceram. Soc.,<u>68</u> (5), pp. 241-47, (1969).
- 9. J.W. Henney and J.W.S. Jones, "The Solid Solubility of CaO and SiO₂ in MgO and its Effect on the MgO-CaO-SiO₂ System at 1750°C", Trans. Brit. Ceram. Soc.,68 (4), pp. 201-203, (1969).

10. T. Hatfield, C.Richmond, W.F. Ford, and J. White, "Compatibility Relationships between the Periclase and Silicate Phases in Magnesite Refractories at High Temperatures", Trans. Brit. Ceram. Soc., <u>69</u> (2), pp. 53-8, (1970).

- 11. D.R.F. Spencer, T.W. Beamond, and D.S. Coleman, "The Solubility of CaO in MgO and its Effect on the CaO-MgO-SiO2 System at 1800°C", Trans. Brit. Ceram. Soc., <u>70</u> (1), pp. 31-3, (1971).
- 12. J.M. Chesters, "Steelplant Refractories ", The United Steel Companies Limited, Sheffield, England, (1963).
- 13. J.W. Craig, "Manufacturing Magnesite Brick in Canada", J. Can. Ceram. Soc., 7, 25, (1938).
- 14. M.F. Goudge, "A Preliminary Report on Brucite Deposits in Ontario and Quebec and their Commercial Possibilities", Bureau of Mines, Mines and Geology Branch, Dept. of Mines and Resources, Ottawa, Mem. Ser. No. 75, December, (1939).
- 15. M.F. Goudge and J. G. Phillips, "Canadian Brucite as a Material for the Production of Basic Refractories", Am. Ceram. Soc. Bull., <u>25</u> (3), 87, (1946).
- 16. J.S. Ross, "Magnesite and Brucite", Canadian Minerals Yearbook, Minerals Report 9, (1962).
- 17. H.M.A. Rice, Geol. Surv. Can., Paper 37-27, p. 17, (1937).
- 18. C.W. Drysdale, Geol. Surv. Can., Sum. Report, pp. 75-85, (1915).
- 19. J.W. McCammon, "Magnesite, Hydromagnesite and Brucite Occurrences in British Columbia", B.C. Dept. Mines and Pet. Res., January, (1968).
- 20. G.B. Leech, Geol. Surv. Can., Paper 66-1, p. 65, (1966).
- 21. M. Palfreyman, "Evaluation of a Sample of a British Columbia Magnesite as a Refractory Raw Material", Dept. of Energy, Mines and Resources, Ottawa, Canada, Mines Branch, Investigation Report IR 71-27, February, (1971).
- 22. M. Palfreyman, "Further Evaluation of a British Columbia Magnesite as a Refractory Raw Material", Dept. of Energy, Mines and Resources, Ottawa, Canada, Mines Branch, Investigation Report IR 71-31, April, (1971).

23.	A.G. Burrows, Ont. Dept. Mines, Ann. Report Vol. 33, Part II, p. 39, (1924).
24.	W.D. Harding, Ont. Dept. Mines, Ann. Report Vol. 53, Part VI, p. 43, (1944).
25.	M.C. Cooke, Geol. Surv., Can., unpublished file 21-C- 10, p. 1, (1938).
26.	W.D. Harding, Ont. Dept. Mines, Ann. Report Vol. 56, Part VI, pp. 44-5, (1947).
27.	L.F. Kindle, Ont. Dept. Mines, Ann. Report Vol. 41, Part IV, p. 4, (1932).
28.	M.E. Wilson, Can. Mining J., 55, pp. 239-241, (1934).
29.	N.E. Logan, Geol. Surv. Can., Geology of Canada, p. 457, (1863).
30.	J.R. Smith, Que. Dept. Mines, Geol. Report 65, p. 30, (1956).
31.	H. Merman and C.D. West, Amer. Mineral., 17, p. 313, (1932).
32.	J.D.G. Dounay, Univ. Toronto Stud., Geol. Ser., 49, R5, (1945).
33.	F.F. Osborne, Que. Dept. Mines, Prelim. Report 139, pp. 13-14, (1939).
34.	Ibid, pp. 7-11.
35.	H.C. Rickaby, Univ. Toronto Stud., Geol. Ser. 16, p. 50, (1923).
36.	L.M. Dobbel, Amer. Mineral., 8, p. 223, (1923).
37.	W.M. Tupper, Can. Mineral., 7, p. 796, (1963).
38.	S.E. Jenness, Geol. Surv. Can., Mem. 327, p. 89, (1965).
39.	G.C. Hoffman, Geol. Surv. Can., Ann. Report XII, p. 22R, (1899).
40 <u>.</u>	M.F. Goudge, "Magnesite in 1935", The Canadian Mineral Industries, Mines Branch, Dept. of Mines, Ottawa, February, (1936).

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- 41. R.J.C. Tait et al, "An Investigation of the Recovery of Magnesia from Ore Submitted by McIntyre Porcupine Mines Limited", Project Report No. 1, Project No. L. R. 866, Lakefield Research of Canada Limited, Lakefield, Ontario, September 15, (1961).
- 42. R.M. Buchanan, "Mineralogical and Petrographic Examination of Magnesite-Talc Rock from Deloro Township, Ontario", Mines Branch Test Report MPT 63-21, May, (1963), Dept. of Mines and Technical Surveys, Ottawa, Canada.
- 43. F.H. Hartman, "Concentration of Magnesite from Deloro Township; Progress Report No. 1", Mines Branch Internal Report MPI 63-61, October, (1963), Dept. of Mines and Technical Surveys, Ottawa, Canada.
- 44. F.H. Hartman and R.A. Wyman, "Concentration of Magnesite from Deloro Township, Ontario, Progress Report No. 2: Pilot Plant Operations", Mines Branch Investigation Report IR 64-90, (1964), Dept. of Mines and Technical Surveys, Ottawa, Canada.
- 45. F.H. Hartman, "Concentration of Magnesite from Deloro Township, Ontario, Progress Report No. 3", Mines Branch Investigation Report IR 64-104, (1964), Dept. of Mines and Technical Surveys, Ottawa, Canada.
- 46. J.W. Cookston et al, "The Recovery of High-Purity Magnesia from Magnesite", Research Report, July, (1963), Batelle Memorial Institute, 505 King Avenue, Columbus, Ohio, U.S.A.
- 47. G.R. Smithson Jr. et al, "The Recovery of High-Purity Magnesia from Magnesite", Research Report, January, (1964), Batelle Memorial Institute, 505 King Avenue, Columbus 1, Ohio, U.S.A.
- 48. V.D. Svikis, "Dead-Burned Magnesia from an Ontario Magnesite Concentrate", Amer. Ceram. Soc. Bull., <u>48</u> (7), 724-28, (1969).
- 49. "The Potential of Canadian Magnesite Mines Limited", Industrial Minerals, No. 43, pp. 40-43, April, (1971).
- 50. K.M. Pople, Acres Western Limited, Vancouver, B.C., Letter to I.F. Wright, Mines Branch, Dept. of Energy, Mines and Resources, Ottawa, December 8, (1970).
- 51. J. Robertson, Acres Western Limited, Vancouver, B. C., Private Communication, October 26, (1972).

- 52. M. Palfreyman, "Evaluation of a Chemically Prepared Magnesia as a Refractory Raw Material", Dept. of Energy, Mines and Resources, Ottawa, Canada, Mines Branch, Investigation Report IR 71-66, September, (1971).
- 53. Dept. of Energy, Mines and Resources, Ottawa, Canada, Mineral Resources Branch, Internal Report MRI 458/70, p. 8, (1970).

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