Mines Branch Information Circular IC 280

CANADIAN MINERALS FOR REFRACTORIES

by

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ABSTRACT

Most of the minerals employed in Canadian refractory production are imported, in fact most of the refractories consumed in Canada are imported. Whereas this situation is partly due to a definite shortage of suitable raw materials, e.g., fireclays, it is possible that the potential of certain mineral deposits which could be usefully exploited has not been recognized. There are exceptions, notably magnesite and dolomite, from which refractories are produced in Canada.

In many cases, known mineral deposits are located in either inaccessible areas or in areas where transportation would be a major economic factor. This paper lists some minerals and their respective known deposits which could be employed in the production of refractories irrespective of economics.

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Direction des mines
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Les Minéraux canadiens pour la production de réfractaires

par

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Résumé

La plupart des minéraux utilisés dans la production canadienne de réfractaires est importée, en fait la plupart des réfractaires consommés est importée. Tandis que cette situation est causée en part par une pénurie de matières premières convenables, par exemple les argiles réfractaires, il est possible que le potentiel de certains gisements minéraux qui pourraient être exploités, n'a pas été reconnu. Il y a des exceptions, notamment le magnésite et la dolomite dont les réfractaires sont produits au Canada.

Dans plusieurs cas, ces gisements minéraux sont situés soit dans des régions inaccessibles soit dans des régions où le transport deviendrait un problème économique. On trouve dans ce circulaire une liste de quelques minéraux et leurs gisements qui pourront être utilisés dans la production de réfractaires sans tenir compte de leur rentabilité.

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INTRODUCTION

The refractories industry in Canada is smaller than in either the United States or the United Kingdom. This is largely due to the facts that the major refractory consuming industries in Canada are small, and furthermore, most of the refractories consumed are imported. In the United States, 61 per cent of the total refractory production is consumed by the iron and steel industry(1). On the same basis, the total Canadian refractory consumption would be expected to be small, because the Canadian steel output is smaller.

Although there are advantages to be gained by processing Canadian raw materials in Canada, namely expansion of Canadian industry and production of finished goods that may replace imports or may themselves be exportable, minerals of the required quality (from quarries or mines in Canada) may be exported for processing by foreign refractory producers.

The purpose of this paper is to specify the minerals known to occur in Canada that could be used in the production of refractory products. The latter term includes fireclay*, basic, high-alumina, and insulating refractories in the form of brick, shapes, rammables, mouldables, and castables. Constituents of refractory cements and mortars have also been considered.

No attempt has been made to provide values either for the available tonnage of any particular mineral or for the tonnage which could be consumed annually in any given operation.

In certain cases, brief details of refractory production techniques are given.

*Note: The terminology used in this paper is in accordance with ASTM Standards, Part 13, April, 1972

Refractory Clays

A refractory clay is basically kaolinite, ($Al_2O_3 . 2SiO_2 . 2H_2O$) which, in the purest form, melts at above Cone 35 (1785°C, 3245°F). However, almost all refractory clays contain other materials such as alkalis, iron oxide, titania, lime, magnesia, etc. which lower the refractoriness.

The most useful materials in this field are fire clays and kaolin. Fire clays*are employed principally in the production of fireclay brick and shapes but also find uses in the manufacture of monolithic refractories i.e. castables, rammables, mouldables, gunning materials, and refractory cements and mortars.

In monolithic refractories the fire clay may be in either the raw or calcined state.

The field of fireclay refractories covers all types from low through super duty firebrick* in the form of brick and shapes and includes specialties such as pouring-pit refractories. The term firebrick refers only to products made from fire clay and does not include other types of refractory brick.

In the American classification (ASTM C27-70) five types of fireclay brick are recognized, namely: super-duty fireclay brick having a P.C.E. not lower than Cone 33 (1743°C, 3169°F) on the fired product, less than 1 per cent shrinkage in the reheat test (1599°C, 2910°F) and less than 8 per cent loss in the panel spalling test; high-duty fireclay brick which should have a P.C.E. not lower than Cone 31½ (1699°C, 3090°F); medium duty fireclay brick which should have a P.C.E. not lower than Cone 29 (1659°C, 3018°F); low-duty fireclay brick which should have a P.C.E. not lower than Cone 15 (1430°C, 2606°F); and semi-silica brick having not less than 72 per cent SiO_2 and 1.5 per cent subsidence at 1349°C (2460°F).

Kaolin may be employed in the production of the above mentioned refractories but finds more extensive use in the production of high-temperature (hot-face) insulating brick and shapes.

Known Sources of Fire Clay and Kaolin

Fire Clay

Canada unfortunately does not have deposits of highest-quality fire clays. Canadian fire clays are used largely in the production of medium-and high-duty firebrick. Known Canadian fire clays are not sufficiently refractory for the production of super-duty fireclay brick without the addition of extra alumina.

A variety of good quality fire clays occurs in the Whitemud formation in Saskatchewan(2), on Sumas Mountain in British Columbia(3), and some low-quality fire clays occur in Manitoba (4). Some of the fire clay from the Sumas Mountain deposit is exported to the United States and a little is used at plants in Vancouver.

Fire clay and kaolin occur in the James Bay watershed in northern Ontario along the Missinaibi, Abitibi, Moose, and Mattagami rivers(5)(6)(6a). Terrain and climate have made exploration difficult in this region in the past but considerable exploration has been carried out in recent years.

In Quebec, kaolinitic fire clays occur at Schefferville, Chateau Richer, St. Remi d'Amherst, Brébeuf, Labelle, and Point Comfort(6)(7). The Schefferville fire clay is suitable for the

* See note on p. 1.

manufacture of medium-duty refractories if mixed with a clay of higher refractoriness. The materials from St. Remi and Brébeuf are suitable for the manufacture of low-duty refractories if mixed with clays of higher refractoriness. The material from Point Comfort is possibly suitable for refractory manufacture. Excess quartz in some of this material may make the manufacture of good-quality products difficult.

Fire clay deposits occur at Shubenacadie and Musquodoboit in Nova Scotia(8)(9). Some of these materials are suitable for the manufacture of medium-duty fireclay brick and preliminary work has been performed on their potential use as ladle brick. Fire clay from Musquodoboit has been employed by foundries in the Atlantic provinces.

Kaolin

Most of the known kaolin deposits in Canada are small, and, owing to problems in beneficiation, none has been developed. Deposits of sandy kaolin occur near Wood Mountain, Fir Mountain, Knollys, Flintoft and elsewhere in southern Saskatchewan(2).

A deposit of clay similar to a secondary china clay occurs on the Fraser River near Prince George in British Columbia (3). This clay varies from plastic to sandy and the upper layers are iron-stained.

Kaolinitic rock deposits have been investigated in Manitoba at Cross Lake and Pine River in the northwest, on Deer Island and Black Island in Lake Winnipeg, and at Arborg(4). Some kaolinitic clays occur near Kergwenan, although they are more like fire clays or stoneware clays.

In Quebec, kaolin-bearing rock occurs at St. Remi d'Amherst in Papineau County, at Brébeuf in Terrebonne County, at Point Comfort on Thirty-One Mile Lake in Gatineau County, and at Chateau Richer in Montmorency County(7).

In general, the Quebec deposits contain excessive quartz and iron minerals, the kaolinite content being variable but usually less then 50 per cent.

In Ontario, extensive kaolin-sand deposits occur along the Missinaibi and Mattagami rivers(6). Some good-quality clays and glass sands, as judged by laboratory test work, have been obtained from this region. Algocen Mines Limited, Sault Ste. Marie, has investigated the deposits along the Missinaibi river north of Hearst(6a) and Indusmin Limited, Toronto, has shown interest in the clays along the Mattagami river.

High-Alumina Materials

Naturally occurring high-alumina materials are normally alumino-silicates containing from 60 to 90 per cent Al_2O_3. Included in this range are mullite ($3Al_2O_3.2SiO_2$), bauxite, which is largely gibbsite ($Al_2O_3.3H_2O$), kyanite, sillimanite, and andalusite all of which can be represented by the empirical formula, $Al_2O_3.SiO_2$.

These materials are employed in all types of high-alumina refractories, i.e., brick and shapes, monolithic refractories, and refractory cements and mortars. They may also be employed in the production of synthetic refractory materials such as calcined alumina and mullite.

The field of high-alumina refractories extends through alumino-silicates containing from about 50 to 100 per cent Al_2O_3. Alumino-silicates containing from 40 to 50 per cent Al_2O_3 are normally referred to as aluminous fire clays.

High-alumina refractories are divided into seven different classes according to ASTM C27-70, viz.,

50 per cent alumina
60 " " "
70 " " "
80 " " "
85 " " "
90 " " "
99 " " "

The existence of these classes stems mainly from the use of different materials for the major constituents of the refractory.

Refractories in the range 50 to 70 per cent Al_2O_3 can be composed of combinations of mullite, kyanite, andalusite, sillimanite, and clay, the latter acting as a bond and plasticizer. Other bonding agents such as phosphoric acid may be used in preference to clay. Calcined bauxite or tabular alumina (sintered calcined alumina) may also be employed as components in this type of refractory.

In the range 70 to 90 per cent Al_2O_3, the main component would probably be calcined bauxite in combination with kyanite, andalusite, or sillimanite and bonding agents. Tabular alumina may also be used.

The range 90 to 100 per cent Al_2O_3 is based on tabular alumina which normally is diluted with silica. To boost the alumina content of calcined bauxite containing 85 to 87 per cent Al_2O_3 is not a practical proposition.

The calcined bauxite described above refers to South American material. The beneficiation of lower grade bauxites from the southern United States to produce 70 per cent Al_2O_3 refractories(10) is a process which will probably undergo considerable expansion in the future.

A somewhat more specialized branch of high-alumina refractories is the production of synthetic mullite. Kyanite is used extensively in this field(11). The expansion of raw kyanite on calcination is made use of in certain types of monolithic refractories to counteract firing shrinkage.

Known Sources of High-Alumina Materials

Because bauxite is not found in Canada and tabular alumina is imported from the United States, the Canadian interest in high-alumina refractories depends upon the minerals kyanite, andalusite, and sillimanite.

Kyanite

Kyanite is a common mineral in aluminous rocks which have been subjected to regional metamorphism(12). It occurs as disseminated crystals in schists, quartzites and gneisses. Coarsely crystalline kyanite occurs in pegmatites, quartz veins and quartzose masses (13).

Deposits of kyanite-bearing rock have been reported in British Columbia in the Big Bend area of the Columbia River(14)(15), south of Summit creek(14)(16), between the Salmo and Kootenay rivers in the Nelson mining division(14), in the Albreda district near mile 2487 west of Jasper(17), in the North Thompson river region(14)(18), 7 miles south of Tete Jaune Cache in the Cariboo mining district(19) and at several other points accurately noted by McCammon(14); in Ontario at the Golden Fleece Mine in Kaladar Township(20), in Clarendon Township 50 miles northeast of Kingston(15), in Carlow Township(22), in gneissic outcrops,12 miles east of Sudbury(15), 20 miles north of Mattawa(15) and in Dryden Township(22); in Quebec at Témiskaming(15) and at the Normetal property in Abitibi County(23).

The most important deposits so far discovered in Canada occur at Wanapitei, about 12 miles east of Sudbury, Ontario(15); 20 miles north of Mattawa, Ontario(15); near Témiskaming in Quebec(15); and in the Big Bend area of the Columbia river, British Columbia(14)(15).

The kyanite of the Wanapitei district is a coarse-grained mineral making up 15 to 30 per cent of the kyanite-garnet-biotite-quartz-feldspar gneiss in which it occurs. The bands of gneiss are from a few feet to 400 feet wide and,in some cases,are 2500 feet long.

In the Mattawa deposit, the kyanite gneisses are interbonded with hornblende and biotite gneisses. The beds strike northeast and dip 30° to 45° northwest. The southeast ridge of kyanite gneiss is about 1200 feet wide and the northwest ridge about 300 feet. The composition of the kyanite gneiss varies but generally shows from 10 to 15 per cent kyanite.

The Témiskaming deposit, which is under investigation by Narco Mines Limited, a subsidiary of North American Refractories, typically contains about 8 per cent kyanite. This may be too low to be of economic value.

The deposits in the Big Bend area of the Columbia river consist mainly of coarsely crystalline kyanite aggregates associated with pegmatitic material. The kyanite gneiss is very similar to the material found in Ontario and contains about 10 per cent kyanite.

The kyanite has to be separated from the other minerals present such as mica, garnet, etc., and considerable work in this field has been carried out by Wyman et al (24)(25)(26).

The fact that Canadian kyanite concentrates can be used successfully in high-alumina refractories has been demonstrated by Svikis et al (27)(28)(29).

Sillimanite

Sillimanite has the same empirical formula as kyanite and occurs in alumino-silicate rocks in the form of long needles or slender crystals hence the old synonym of fibrolite.

Deposits of sillimanite have been reported in British Columbia at several locations, all of which have been accurately noted by McCammon(14); in Manitoba, in the nickel ore of the Thompson-Moak Lake belt(30); in the Northwest Territories in the Chidliok Fiord area on Baffin Island(31); in Nova Scotia on the seashore at Eastern Head, Liverpool Bay, Queens County(32); in Ontario, in Dungannon Township, Hastings County(33), in Carlow Township, Hastings County(34), in Lyndoch Township(35), on the northern portion of Beaverstone Bay near Collins inlet on Georgian Bay(36), and in Dryden Township east of Wanapitei(37).

In Quebec, sillimanite has been reported on an island (not named) opposite Romaine near the confluence of the Romaine and St. Lawrence rivers(38), in the paragneiss of the upper Romaine river area in Saguenay County between the Petite Romaine and Touladis rivers(39), 7 miles south of Irene Lake in the Nipissis river area, Saguenay County(40), at the south end of Papineau Lake in the Swan Lake area(41), and in the ore zone at Montauban-les-Mines and Tetrault Mines, Portneuf County(42).

No Canadian sillimanite deposit has been developed as a continuous enterprise.

Andalusite

Andalusite is a mineral similar in composition to kyanite and silliminate and takes its name from the province of Andalusia in Spain where extensive deposits occur.

Occurrences of andalusite have been recorded in British Columbia northeast of Deer Park(43) and at other points that have been accurately noted by McCammon(14); in New Brunswick at St. Stephen and Moores Mills in Charlotte County(44); in Newfoundland along the highway a mile to the north of the bridge at the east end of Gander Lake(45); in the Northwest Territories at Outpost Island in the east corner of Great Slave Lake(46), in the Yellowknife Group, Basler Lakes(47), and at a point about 55 miles northeast of Yellowknife Bay(46); in Nova Scotia at Geizer's Hill west of Halifax, Halifax County(48), inland from Yarmouth and Pubico, Yarmouth County(49), at Red Head and Goose Neck Point near Point Latour in Shelburne County(50), and at Shelburne Harbour(48) along the Broad River about 1½ miles from its mouth(51), and along the Gaspereau River(52); in Ontario at the Cochenour-Willans Mine(53); in Quebec in Bornston, Hatley, and Stanstead Townships, Stanstead County(54), in Compton, Eaton, and Hampden Townships, Compton County(54), in Marston Township, Frontenac County(54), in St. Samuel de Gayhurst, Frontenac County(48), and Lake St. Francis, Frontenac County(20); in the Yukon Territory at White Channel on the east side of Clear Creek, opposite Gauvin's Cabin, Barlow(55).

Some work has been performed by Wyman(56) on the concentration of andalusite, but, at the present time none of the known Canadian deposits is being exploited commercially. The known deposits in Nova Scotia have not proven to be of economic importance.

Silica

Silica has the chemical formula SiO_2 and occurs in nature in various forms, most commonly as quartz or as cryptocrystalline varieties such as chalcedony. Free silica also occurs commonly as quartz sands, sandstones, and quartzites in which the grains may be bonded with precipitated silica or as the result of metamorphism.

For refractory uses, the preferred materials are quartzite and ganister, which is a hard, dense, comparitively uniform sandstone consisting essentially of fine-grained quartz. The selection of quartzite or ganister for refractories is often made according to the clay content of the rock because small amounts of clay lower the refractoriness of the finished product. The quartzite or ganister are normally used directly for brick production without any chemical or special processing. They may be employed in the ground form in ramming mixes or for fettling purposes.

Silica sand is used extensively in foundries for moulding purposes.

For use in refractories, i.e., specifically silica brick, any quartz or silica sand should be at least 98 per cent silica, less than 1.0 per cent alumina and less than 1.5 per cent combined alumina and ferric oxide. Lime and magnesia should be as low as possible.

Known Sources of Refractory-Grade Silica

Silica occurs abundantly in Canada. Most of the production is low-grade lump silica and low-grade silica sand for use as metallurgical flux. Some high-grade silica sand for use in glass and foundry moulding is produced in Canada from quartzite and sandstone although a substantial quantity is still imported.

The Dominion Steel and Coal Corporation Ltd., Sydney, Nova Scotia, formerly obtained high-grade quartzite from a deposit at Chegoggin Point near Yarmouth(57). This was shipped by rail to Sydney for the production of silica brick. The plant is no longer in operation. Much of the Lorraine quartzite of the Sault Ste. Marie-Sudbury area is suitable for the manufacture of silica brick(58). Such material was quarried for this purpose by the Algoma Steel Corporation from a deposit at Bellevue, 20 miles north of Sault Ste. Marie(57). Indusmin Limited has a silica processing plant at Midland, Ontario. Raw material for this plant is obtained from a deposit of Lorraine quartzite on Badgeley Island, situated near Killarney, which is 120 miles north of Midland on Georgian Bay(59). The deposit consists of pure Precambrian Lorraine quartzite and has a good economic life. Production of silica for glass and ferrosilicon started in 1971 and the material may be useful for refractories as well as for ceramics.

For use in high-alumina refractories (above 90 per cent Al_2O_3), any silica must be in a finely ground form and, therefore, high-purity silica sand could be used as an alternative raw material to silica rock. The type of sand used in the manufacture of glass would be suitable, i.e., low in Fe_2O_3 and TiO_2. Alumina is obviously not a detrimental impurity in a siliceous material which is to be employed in the production of high-alumina refractories. As in the case of material used in the production of silica brick, lime and magnesia should be low.

Silica sands are presently being produced in Canada in commercial quantities from deposits of sandstone and/or quartzite in Quebec, at St. Canut and St. Donat northwest of Montreal(57) and in Manitoba, on Black Island in Lake Winnipeg(57).

Many other deposits of silica sand occur throughout Canada, and have been tabulated by Traill(60). However, other than those mentioned here, none is being exploited commercially.

Basic Raw Materials

For refractory purposes, minerals are generally referred to as either acidic or basic. Silica and alumino-silicates are acidic, whereas materials such as chrome, dolomite and magnesia are basic. Alumina is generally regarded as neutral. The commonly used basic materials are chrome, magnesite, and dolomite, although brucite, hydromagnesite, and breunnerite are employed to a lesser extent. Forsterite is a mineral which is finding increasing use in the refractory field. These materials all require some form of processing to make them suitable for refractory production. In the processing of dolomite, the silica content is often controlled by the addition of serpentine. Basic materials may be employed in all types of refractories, though their use has been limited in the field of insulating refractories.

Chrome ore consists essentially of a mixed spinel phase together with impurities which may constitute up to 40 per cent of the orebody. These impurities may be largely serpentine. A vast amount of work has been carried out in this field and is amply reported in the literature. In short, it may be stated that for a chrome ore to be suitable for refractory manufacture the Cr:Fe ratio should be approximately 4:1.

Magnesite is essentially magnesium carbonate, $MgCO_3$, which may occur in the pure form or in association with other minerals, notably dolomite.

Dolomite is a mineral having the empirical formula $CaMg(CO_3)_2$. It may occur as dolomitic limestone which is a mixture of calcite and dolomite. Not all dolomitic limestone is suitable for the production of refractories; for this purpose, the material should contain between 40 and 46 per cent $MgCO_3$.

Forsterite is a mineral with the empirical formula $2MgO.SiO_2$ which corresponds to 57.3 per cent MgO and 42.7 per cent SiO_2. Its melting point is 1900°C (3452°F), which makes it a useful refractory material for many high-temperature operations.

The mineral olivine is usually a solid solution of forsterite and the corresponding iron mineral, fayalite, $2FeO.SiO_2$. It is present in high-silica magnesite brick and forms the normal bond in chrome-magnesite refractories.

Brucite is essentially hydrated magnesium oxide, $Mg(OH)_2$, and often occurs in association with limestone. Such material is normally referred to as brucitic limestone. Hydromagnesite may be regarded as a mixture of magnesite and magnesium hydroxide and has the empirical formula $3MgCO_3.Mg(OH).3H_2O$. Breunnerite is a ferrous-magnesite complex.

A special source of magnesia is sea-water. The extraction is made economic by virtue of the very low solubility of magnesium hydroxide so that it can be precipitated from solutions of magnesium salts by bases that provide only a moderate concentration of hydroxyl ion.

In order to carry out the sea-water magnesia process, a source of dolomite or lime is required. The dolomite is first calcined in vertical or rotary kilns to give an oxide mixture.

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

When the calcined product is added to sea-water the calcium oxide hydrates and reacts with the magnesium salts, precipitating magnesium hydroxide. The calcium ions pass into solution, i.e.,

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + Mg^{2+} \longrightarrow Mg(OH)_2 + Ca^{2+}$$

The magnesium hydroxide is subsequently settled, thickened, filtered, pelletized, and dead-burned in rotary kilns. (In actual practice, the process is much more complicated than indicated above).

Processing of Raw Materials for Basic Refractories

Chrome brick were originally made by simply grinding chrome ore with water and possibly some bonding material followed by pressing, drying, and firing. They were used initially in applications where it was desired to separate basic materials from acidic materials. Very few chrome brick as such are made today, it being normal practice to add at least 10 per cent magnesia to increase the refractoriness of the mineral impurities(61).

The term magnesite is a misnomer when applied to refractories, because any natural magnesite (or brucite) must first be calcined to produce magnesia, MgO, which is subsequently formed into refractory products.

Calcination of magnesite to produce refractory magnesia is normally referred to as "dead-burning" and the product is known as dead-burned magnesia. The objectives of dead-burning are twofold, firstly to render the material inactive to atmospheric moisture, i.e., to prevent hydration and, secondly, to render the material volume-stable, i.e., to eliminate after-contraction in the magnesia clinker or grog. Calcination may be carried out in rotary or shaft kilns between 1650°and 1750°C (3000°and 3182°F). The advantage of the rotary kiln is uniformity of the firing treatment.

The principal impurities in magnesia produced either from natural magnesite or from sea-water are lime, silica, iron oxide, and alumina. When present as single impurities these compounds may not have too serious an effect on the refractory properties of the magnesia. However, in combination, the effects can be very detrimental(61). It is generally accepted that lime should be less than 2.5 per cent and that silica and alumina should be less than 2.0 per cent. With certain natural magnesite ores the iron oxide (Fe_2O_3) may run as high as 8.0 per cent.

Dolomite is the most readily available basic material of high melting point. Before being used as a refractory material, the raw dolomite must first be calcined to produce doloma. Doloma consists of the oxides produced from dolomite in the same way that magnesia consists of the oxides produced from magnesite. The basic reaction is the removal of carbon dioxide i.e.

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

If this reaction is stopped immediately after the CO_2 has been removed, the product is too reactive and porous for use as a refractory material. Calcination is usually carried out at a temperature of about 1700°C (3092°F), which reduces the porosity to an acceptable level of about 15 per cent. This allows the material to be stored for several weeks without serious deterioration.

Unstabilized dolomite refractories suffer from two weaknesses, both of which can be connected with the silica content. The first,known as "perishing", results from the hydration of uncombined lime by atmospheric moisture. The second, known as "dusting", occurs in service owing to the $\beta \rightarrow \gamma$ change in dicalcium silicate, $2CaO.SiO_2$. Thus, if the silica content is too low, the doloma is prone to hydration in storage and, if too high, dusting may occur in service.

A method of controlling the silica content is to calcine the dolomite with a second material such as serpentine so as to combine the lime in the form of tricalcium silicate which does not undergo any detrimental phase transformations. For example, the calcination may follow the reaction:

$$6(CaCO_3.MgCO_3)+3MgO.2SiO_2.2H_2O \rightarrow 2(3CaO.SiO_2) + 9MgO + 2H_2O + 12CO_2$$

It is safer to work on the silica-rich side and any dicalcium silicate formed can be stabilized by small additions of boric acid or calcium phosphate(61).

Both alumina and ferric oxide lead to fluxing action in dolomite refractories and should therefore be as low as possible, preferably less than 1.0 per cent total.

The calcination may be carried out in either rotary or vertical shaft kilns. After calcination, the doloma clinker is crushed and screened to give a material which may be formed into refractory brick or shapes in a variety of ways. For example, tar may be used as the bonding agent.

Chrome-magnesite and magnesite-chrome refractories are made from mixtures of chrome ore and dead-burned magnesia. The chrome-magnesite type normally contains a ratio of 60:40 or 70:30, chrome:magnesia, whereas the magnesite-chrome type contains less than 50 per cent chrome.

The production techniques for both types of refractory are similar. In the case of brick, firing may be carried out in the range 1400° to 1700°C (2552° to 3092°F). The present tendency is to fire at the high-temperature end of the range.

Forsterite refractories are normally made either from natural olivines or mixtures of serpentine and magnesia. The refractoriness of the commercial products is less than that of pure forsterite but they are still very refractory and, in addition, show high refractoriness under load. Forsterite refractories exhibit very desirable stability of strength and volume at high temperature.

Known Sources of Basic Raw Materials

Chromite

No chromite is produced in Canada at the present time because the known occurrences are generally low-grade. Chromite occurs in British Columbia at Highland Valley in the Ashcroft area(62); at Chrome Creek at a point about one third of a mile above its entrance into Scottie Creek, which is about twenty miles north of Ashcroft(63), in the Bridge River Mining Camp(64); and in the Bridge River area on the northwest corner of Taylor Basin(65). There are occurrences in Manitoba in the Bird River Sill, a folded peridotite-gabbro intrusion in the Lac du Bonnet district(66)(67)(68)(69); in New Brunswick at the Atlantic Nickel Mine on Rogers Farm in Charlotte County(70). Chromite occurs in the region of the Bay of Islands igneous complex in western Newfoundland at (a) the Blow-Me-Down Mountain pluton on the Fox Island river, (b) the Lewis Hills pluton on the Fox Island river, (c) the Chrome Point deposits on a small hill southeast of the Fox Island river and south of Springers Hill, (d) Mine Cove in the Lewis Brook area, and (e) as lenses in the upper part of the ultrabasic zone in the Bay of Islands(71). Chromite also occurs in Ontario in Steele Township(72), in Dundonald Township(73), and in Réaume Township(74). It occurs in Quebec in South Main and Garthby Townships, Wolfe County, in Coleraine Township, Megantic County, in Awantgish Township, Matapedia County, in Mount Albert, Gaspé County, in Bolton Township, Brome County, and in Brampton, Cleveland, and Melbourne Townships, Richmond County(48).

Magnesite, Brucite, and Sea-Water Magnesia

Magnesite occurs in British Columbia at Marysville in the Nelson area where it forms part of the Cranbrook Formation(75), at the northwest end of Liza Lake in the Bridge River map-areas of the Lillooet district(76), and at numerous other points, all of which have been noted in detail by McCammon(77) who has also produced extensive details of occurrences of brucite and hydromagnesite in British Columbia. Deposits of magnesite on Mount Brussilof and Mount Eon between the Kootenay Provincial Park and the Banff National Park have been examined for purity and suitability for a refractory raw material(77a)(77b)(77c).

Breunnerite occurs in the ultrabasic rock which extends north from one-half mile north of the Trans-Canada Highway in the Terra Nova and Bonavista map areas in Newfoundland(78).

Magnesite has been reported in Nova Scotia at Malagash in Cumberland County(79), and on the Point Road near Orangedale, in Inverness County(80). In Ontario, breunnerite occurs in Rothburn Township on the east shore of Wanapitei Lake in Scadding Township(81) and has been reported in the southern part of Deloro Township(82) (see below). In Quebec, magnesite occurs at Kilmar(83), in Harrington Township about 10 miles north of Grenville(84), in Bolton and Sutton Townships(85), and in Montauban Township(86).

Brucite occurs at various points in British Columbia which have been recorded by McCammon(77); in Nova Scotia, at the Meat Cove zinc deposit located on the headwaters of French Creek, two miles south of Meat Cove on the northern tip of Cape Breton Island(87); in Ontario in Olrig(88), Calvin(89) and Hinchenbrook Townships(90); in Quebec, at the Martin-Bennett chrome pit in Ireland Township, Megantic County(91), in the Asbestos district of Quebec(92), in the Calumet Island area(93), and in Wakefield, Masham, and Hull Townships(94).

Hydromagnesite, which is nominally $3MgCO_3.Mg(OH)_2.3H_2O$, occurs extensively in British Columbia at various points which have been tabulated by McCammon(77), and in the Northwest Territories along the south shore of Deare Bay, Great Bear Lake(95).

As late as 1969, the only Canadian producer of magnesite on a commercial scale was Canadian Refractories Limited. The material is obtained from a magnesite-dolomite rock located at Kilmar, Quebec. The raw material is mined underground, crushed, and beneficiated by heavy-media separation(83). The beneficiated ore is calcined in an oil-fired rotary kiln to produce a dead-burned magnesia clinker. The latter is manufactured into refractories (magnesite and chrome-magnesite) by Canadian Refractories Limited at their Marelan plant in Quebec.

Attempts to develop magnesite deposits located at Deloro and in Adams Township near Timmins, Ontario have been made by Canadian Magnesite Mines Limited. A considerable amount of work has been carried out on these materials from the refractory, beneficiation and mineralogical points of view(96)(97)(98)(99). Difficulty has been experienced in developing a process for a marketable dead-burned magnesia.

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 sea-water at Aguathuna, near Stephenville, Newfoundland. This plant is the first of its kind in Canada. The raw materials involved are sea-water, sulphuric acid, and local limestone. It was planned to produce a dead-burned magnesia as the final product, though at the present time only magnesium hydroxide slurry has been produced. In 1970 the project was taken over by Lundrigans Limited(100), a Newfoundland construction-oriented 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.

Dolomite

Dolomite is a common rock constituent throughout Canada. It occurs in the Northwest Territories at White Eagle Silver Mine on the north bank of the Camsell river about nine miles east of its mouth in Conjuror Bay(101); in Ontario in Herschel(102)(103) and Bagot Township(104); and at Haley Station, Ross Rownship, in the Renfrew area(105). Chemical analysis of the material from Haley Station showed it to be of good quality(106)(107) and it is mined by Chromasco for production of magnesium and calcium metals.

Steetley Industries Limited, Hamilton, Ontario is the only company listed(108) as supplying dolomite for fluxing and fettling purposes. The material is obtained from a quarry at Dundas.

Scotia Limestone Limited, Sydney, Nova Scotia, quarries dolomite in the Frenchvale and Upper Leitches Creek areas in Cape Breton(109)(110). The material is used at the steel plant in Sydney. Dolomite also occurs in Nova Scotia at Ingonish in Victoria County(110).

Serpentine

The serpentine which may be employed as an addition in the calcining of dolomite should be ground massive serpentine rather than fibrous asbestos (chrysotile). Massive serpentine and asbestos always occur together, though the ratio of one to the other may vary widely. Numerous deposits of serpentine occur in Canada, the most productive being in the Thetford mines area of Quebec. All the known occurrences have been listed by Traill(60).

Forsterite

The only known deposit of forsterite of any potential commercial value occurs on the Gaspe Peninsula in Quebec, about

10 miles south of the village of Ste. Anne-des-Montes(111). The deposit has been explored by the Conwest Exploration Company Limited, Toronto, though no development has been carried out to date. The occurrence is massive and the material would require crushing prior to shipment. At the present time, the only projected use is as a steel-foundry moulding sand.

Insulating Materials

The minerals which are employed in the production of insulating materials can be divided into groups, i.e., minerals which are naturally low in density or are such that the density can be reduced by simple processing, and denser minerals which are used to form insulating bodies by more complex processing.

The first group includes minerals such as diatomite, fibrous asbestos, vermiculite, and perlite, all of which are employed in the production of low-temperature insulating materials. The second group includes fireclay, kaolin, silica, high-alumina minerals, basic minerals and pyrophyllite. These minerals may be used in the production of all types of insulating materials from low to high temperature, the insulating properties being more a function of the processing involved than of the nature of the mineral.

Insulating refractories may take the form of brick, shapes or castables. Insulating brick have been classified by the A.S.T.M.(C155-68) into the following groups:

Group Identification	Reheat Change not More than 2% at:	Bulk Density not Greater than:
16	1550°F (845°C)	34 lb/ft^3
20	1950°F (1065°C)	40 "
23	2250°C (1230°C)	48 "
26	2550°F (1400°C)	54 "
28	2750°F (1510°C)	60 "
30	2950°F (1620°C)	68 "
32	3150°F (1730°C)	95 "
33	3250°F (1790°C)	95 "

The Group Identification number when multiplied by 100 gives the maximum temperature, in degrees F, to which the hot face of the brick may be exposed.

The methods of manufacturing insulating brick and shapes may vary according to requirements. For example in the case of diatomite, blocks may be sawn directly from the face of the deposit to give a natural grade. These blocks may be used as such or they may be heated to make them suitable for use up to a higher temperature. Alternatively, brick or shapes may be pressed from powdered diatomaceous earth with or without clay binder and heated to a suitable temperature. The porosity of the product may be increased by additions of combustibles such as sawdust, powdered coal, coke, or paper pulp. Large or complex shapes are produced almost entirely by sawing massive natural or heat-treated blocks.

The production of brick or shapes from asbestos and vermiculite is limited. Light pressures are employed with small amounts of bonding agent, probably of the clay type, and the final shape is obtained by machining or sawing small units from large blocks.

With materials such as fireclay, kaolin, silica etc. the porosity may be introduced either by adding combustibles as described above, which are removed during the firing process, or by adding foaming agents to the mix. Some materials such as perlite or vermiculite can be expanded into a porous aggregate by the application of heat alone.

Basic materials such as magnesite or chrome-magnesite have been produced in insulating form. Insulating brick have also been manufactured from raw dolomite-silica mixtures and from serpentine-magnesite mixtures by use of foaming agents or the addition of combustibles(61).

Known Sources of Insulating Materials

Diatomite

Diatomite or diatomaceous earth is a fine-grained chalk-like material formed from the silica skeletons of diatoms, which are minute organisms that live in water. It occurs in beds of widely varying thickness.

Diatomite occurs at numerous points in British Columbia (112)(113) and Nova Scotia(113) and some deposits have been reported in the Muskoka district of Ontario(113). A few small deposits occur in Quebec(113).

More than 100 occurrences have been noted in the Maritime Provinces, the majority of which are in northwestern Nova Scotia(113)(114)(115)(116)(117). The largest sources in Nova Scotia occur on Digby Neck and Long Island in Digby County. The beds of diatomaceous earth are up to 24 feet thick. The material, taken from 4 to 8 feet, calcines to buff or cream whereas that taken from a depth of 12 feet or more tends to be brownish. The quality is reported to be from good to very good(118).

At least 20 deposits of diatomite are known in British

Columbia, the most important of which is at Quesnel. Crownite Industrial Minerals Limited are producing powdered diatomite from the Quesnel deposits, some of which is being used in refractory production by Canadian Refractories Division, Dresser Industries Canada Limited, at Abbotsford, B. C.(119). Fairey and Company Limited, Vancouver, is also using Quesnel diatomite in refractory production.

Vermiculite

Vermiculite belongs to a group of micaceous minerals which are all hydrated silicates closely related to the chlorites but of widely varying composition. They are alteration products chiefly of the micas biotite and phlogopite and retain more or less perfectly the micaceous cleavage. The vermiculites useful for insulating purposes are characterized by their ability to exfoliate on heating thereby greatly increasing their volume and allowing air to become entrapped in the cleavage planes.

Vermiculite mixed with biotite occurs in crystalline limestone near the Blue River in the Kamloops area of British Columbia(120).

In Ontario, deposits have been reported at Loughborough Township, Frontenac County(121), in the Stanleyville area at North Burgess Township, Lanark County(122), and near Mississauga Lake in Cavendish Township, Peterborough County(123). The Stanleyville deposits, which consist of vermiculite mixed with phlogopite, have been exploited commercially but at the present time are not being worked.

Asbestos

Asbestos is a name applied to a group of naturally fibrous minerals. The principal commercial variety is chrysotile, a hydrous magnesium silicate having the theoretical formula $3MgO.2SiO_2.2H_2O$.

Canada produces about 35 per cent of the world's asbestos production. The vast majority of Canadian material is mined from the layer of ultrabasic rock that stretches through the Eastern Townships of Quebec. Asbestos is also mined at Cassiar in British Columbia(124). It was formerly mined in Northern Ontario(125) but the operation has now been closed down. Asbestos is being mined in Newfoundland at Baie Verte and in the Yukon at Clinton Creek. Prospects in Quebec at Asbestos Hill in the Ungava region, at Abitibi, and at Chibougamau promise to be fruitful.

Perlite

Perlite is a volcanic glass, granules of which, on heating, expand to cellular particles suitable for low-temperature insulation. The only known occurrences of perlite in Canada are found in the Prince George region of British Columbia at Francois Lake, at Doyeezcha Mountain which is some 25 miles south of Burns Lake(126)(127)(128), and at Big Bar Creek, northwest of Clinton in the Yukon Territory. None of these occurrences is being exploited commercially.

Fire Clay

This material was discussed above in the section pertaining to refractory clays. However, whereas good quality fire clays are essential for the production of high- and super-duty firebrick, this may not necessarily be true for insulating refractories in the low-temperature category.

Low-temperature insulating aggregate is now being produced by the process of "expansion". In this process, ground clay is mixed with a combustible material such as pulverized coal, pelletized, and passed rapidly through rotary kilns or sintered on travelling grates operating at about 1300°C (2372°F). The release of volatiles from the combustible renders the clay mass porous thereby decreasing the density and thermal conductivity. The process would obviously be aided by using a clay having a high flux content. Therefore, low-quality fire clays (with respect to firebrick production) could be employed in the production of low-temperature insulating aggregate.

Miscellaneous Refractory Minerals

Included in this section are the minerals spinel (magnesium aluminate), zircon (zirconium silicate), and pyrophyllite which are employed in the production of refractory specialties.

The term spinel covers a large group of oxides having the empirical formula $R^{I}O.R^{II}{}_2O_3$, where R^{I} is one or more of the divalent metals Mg, Fe, Mn, Zn, Ni, and R^{II} is one or more of the trivalent metals Al, Fe, Cr, Mn or tetravalent Ti. Natural spinels fall into three groups viz., spinel, magnetite, and chromite. In the spinel group, the dominant R^{II} metal ion is Al^{3+} and, within the group are end members such as spinel ($MgO.Al_2O_3$), hercynite ($FeO.Al_2O_3$), galaxite ($MnO.Al_2O_3$), and gahnite ($ZnO.Al_2O_3$). For refractories, only spinel ($MgO.Al_2O_3$) and chromite are of interest.

Zircon or zirconium silicate is a common constituent of igneous rocks, especially those of the more acidic feldspathic groups of the kind derived from magmas containing much soda, such as granite, syenite, or diorite. It is generally present as minute crystals, but some pegmatites contain large, well-formed individual zircons.

Spinel ($MgO.Al_2O_3$) and zircon are employed in the production of certain types of castable refractories for small special applications though they are also produced in the form of brick and shapes. Spinel brick are extremely resistant to molten aluminum but their high cost precludes them from everyday use. Zircon is used extensively in the production of tundish nozzles for the continuous casting of steel.

Known Sources of Spinel ($MgO.Al_2O_3$), Zircon, and Pyrophyllite

Spinel

Occurrences of spinel have been reported in Newfoundland at Ackley Batholith, north of Pine Hill(129); in the Northwest Territories at the north end of Brown Inlet, Baffin Island (130); in Ontario in South Burgess Township, Leeds County(131), and also in Ross Township, Renfrew County(20); in Quebec in Portland Township, Papineau County(132), in the Seigniory of Daillebout, Joliette County(20), in Bigelow Township, Labelle County(133), in Bouchette Township, Gatineau County(133), in Aylwin Township, Gatineau County(134), and in the dalmationite at Amulet Mine near Noranda, in which it is abundant(135).

At the present time none of these deposits is being developed commercially.

Synthetic spinel has been produced experimentally by the Aluminum Company of Canada in Arvida(136) from Canadian magnesite and calcined alumina, but the process was discontinued in 1966 on economic grounds.

Zircon

Numerous occurrences of zircon are known in Manitoba, Ontario, Quebec, and Nova Scotia and have been noted by Traill(60). The majority of the reported occurrences are in Ontario. All the occurrences are of mineralogical interest only, none having been developed commercially.

Pyrophyllite

Pyrophyllite is a hydrated alumino-silicate of the general formula $Al_2O_3.4SiO_2.H_2O$. In nature, it may occur in foliated form, radiated, lamellar, fibrous, or compact massive. The latter form may be white, greyish, or greenish and resembles compact steatite.

Three occurrences of pyrophyllite have been reported in British Columbia at Kyuquot Sound on the west side of Kashute

Inlet(137)(138), at Riverside just south of the C.P.R. tracks at Semlin Siding(138), and in the Pyro Group at the 3,500 foot elevation, one-half mile east of the Coalmont-Princeton road, 3 miles east of Coalmont(138).

Pyrophyllite occurs in large replacement lenses in schists south of Long Pond near Manuels in Newfoundland(139)(140)(141). These deposits lie in a narrow belt extending about 6 miles south from Manuels. The belt contains large areas of quartz-pyrophyllite schists, a number of which show a high percentage of pyrophyllite in addition to scattered lenses of almost pure pyrophyllite. The depth of the deposits varies up to about 35 feet. They are being exploited commercially(142), and ceramic tests on the material show it to be comparable to North Carolina pyrophyllite(143).

A pyrophyllite deposit to the north of Senneterre, in Quebec, has been investigated for refractory purposes by Domtar (144). Some refractory brick were produced from this material but the operation has since been discontinued.

CONCLUSIONS

Many minerals exist in Canada which could be usefully employed in the production of refractories.

Recognizing the facts that transportation may be a major economic factor in exploiting certain mineral deposits and that domestic consumption of finished refractories is relatively small, it is not difficult to see why the Canadian refractories industry has not expanded. A further factor to be considered is the close proximity of the United States, and its vast refractories industry which renders importation of finished refractories easier and, perhaps, more economical than making them in Canada.

However, there is no reason why the Canadian industry should not look beyond the domestic requirements for finished refractories and the simple exportation of refractory raw materials and why it should not endeavour to produce finished refractories from Canadian resources for export to foreign consumers.

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