CHAPTER 14. WOLLASTONITE

The mineral wollastonite is a natural calcium silicate ($CaSiO_3$) usually occurring in cleavable or fibrous masses and sometimes granular and compact. It is usually white, sometimes greyish or brownish, has a hardness of 5 on Mohs scale and a density of 2.9. Wollastonite can be distinguished from other white fibrous silicates, such as sillimanite and tremolite, by its solubility in HCl with the separation of silica. Wollastonite is formed by the metamorphism of siliceous limestones at temperatures around 450°C and higher, and therefore occurs in high grade regionally metamorphosed rocks and near igneous contact zones (Berry and Mason, 1959). Synthetic wollastonite can be manufactured by high temperature sintering of quartz flour and finely ground limestone.

Synthetic wollastonite is crystallized from a homogeneous mixture of raw materials in a 1:1 molecular ratio when heated in a rotary kiln to a temperature below the melting point of wollastonite. A melting phase occurs through reaction with the raw materials aided by the addition of fluxing agents. The crystallization process is carefully regulated using special mineralizing compounds and precise temperature control in the firing zone where the temperature of formation of synthetic wollastonite is around 1450°C.

PRODUCTION AND USES

In 1983 the total world production was estimated at 125 743 t, but this figure does not include production figures from the U.S.S.R., China and smaller operations in Namibia, New Zealand and Japan. A dramatic increase in production over the past 10 years has been encouraged by market demand for various wollastonite products. The wollastonite market is split into two sectors which are differentiated by the degree of acicularity of the material. Low aspect ratio (the ratio between the length of the crystal and its width) wollastonite, commonly in the range of 1:3-1:5, has little potential for reinforcing applications so markets are primarily confined to the ceramics, metallurgical fluxes, and simple filler and coating applications (Power, 1986). High aspect ratio wollastonite that generally ranges from 1:15 to 1:20 is greatly prized as a semifibrous replacement for asbestos and finds high potential growth as a performance filler in the various plastic and resin systems becoming increasingly more common today. Apart from the high aspect ratio, whiteness of the mineral and loss on ignition (LOI) values are very important if the product is going to satisfy criteria required by the various uses. Most wollastonites have good brightness values owing to minimal contamination from iron oxides; these factors are very important in most filler, coating and ceramics applications. LOI values must be $<1\%$ in most ceramic and metallurgical applications. Carbon dioxide derived from calcite is emitted during firing of the wollastonite so the more calcite removed during beneficiation techniques, the better the wollastonite in terms of LOI characteristics.

Wollastonite is a comparative newcomer to the mineral filler market and therefore has to show either a competitive price with other alternative materials or prove its worth in terms of performance. In ceramic applications, the largest volume of wollastonite is consumed in wall tile bodies and coating glaze formulations. Fast-firing processes have revolutionized the ceramic body firing times, but the increased speed of production has also brought with it associated physical and chemical problems. Thermal shock, increased mechanical handling and reduced evacuation of the gas phase evolved during firing have all added to the new demands which are being placed on ceramic raw materials employed in this process. In wall tile and glaze applications wollastonite has made considerable inroads into the market as a reinforcing, dimensionally stable, low gas producing additive that has found various degrees of replacement for the more traditional ceramic materials such as limestone, dolomite, talc and feldspar.

CERAMIC APPLICATIONS

The following list of physical and chemical properties of wollastonite illustrates its benefits in ceramic body and glaze formation (Power, 1986):

Acicular Crystal Shape

1. Contributes mechanical reinforcement to the strength of the body and improves pressing quality and green strength to allow new mechanical handling techniques.

2. Imparts high impact strength and dimensional stability to the fired product.

3. Acicular particles also promote good acoustical properties to tile surface.

4. Drying rates are improved in tile and plastic brick bodies owing to the elongated nature of the crystal which acts as a channel for the rapid passage of moisture and thereby reduces moisture expansion.

Thermal Expansion Characteristics

Wollastonite has a low, straight line, thermal expansion coefficient which reduces shrinkage and other dimensional instabilities such as cracking, dunting, grazing and glaze defects.

Loss on Ignition

1. Wollastonite generally shows a <1% LOI value which gives minimal gas evolution during firing, especially when compared to that volume of gas generated by the more traditional carbonates and hydrated minerals used in ceramics.

2. As the mineral melts with the minimal of bubbling, this leads to a smooth surface with diminished pin-holing.

Chemical Purity

1. Since iron, titanium and manganese impurities are minimal the mineral retains its high whiteness value on firing.

2. The absence of alkalies also contributes to excellent electrical insulation properties.

3. The mineral has a low sintering temperature around 991-1196°C, similar to that of most natural frits, and fuses readily with alumina and silica, therefore the mineral is most suitable for fast firing techniques.

4. Contributes CaO to alkaline glaze formulations to improve glaze strength, improve surface finish and, in the right quantity, produce matt finish in low-fired glazes.

PAINT APPLICATIONS

Wollastonite as a simple paint system filler has to compete with a variety of cheaper materials and, unless supplies are cheap and readily available, it has limited use. However, in speciality paints such as industrial anticorrosive coatings and textural paint, powder and acicular materials play an important part. The following list outlines the properties effective when wollastonite is used in paint systems (Power, 1986).

Acicular Crystal Shape

1. Needle-like particles act as a good flattening agent and allow paint to settle out after application to produce a dry filler of uniform thickness.

2. Interlocking particles improve toughness and durability of coat with excellent tint retention, scrub and weather resistance.

Colour and Oil Absorption

1. High brightness and whiteness reduces pigment load.

2. Very low oil absorption reduces volume of binder required and contributes to reduced pigment costs.

Chemical Characteristics

In a 10% slurry wollastonite has a pH of 9.9. Although this renders the material unsuitable for some paint systems, it is particularly advantageous in polyvinyl acetate paints (PVA) where it helps to neutralize acidity shift. PVA can decompose into vinyl alcohol and acetic acid, but the presence of wollastonite maintains the alkaline nature of the paint combating corrosion (Power, 1986).

METALLURGICAL APPLICATIONS

Since wollastonite is a natural low temperature fluxing material, significant high volume markets have been developing in steel casting and welding formulations. In recent years, with the establishment of a continuous casting process in the European steel industry, a growing market has developed for wollastonite in fluxing formulations employed in the continuous casting route for steel. When molten steel is poured from the bottom of the refining ladle into the refractory tundish, a flux composite powder is applied to the continuous stream of molten metal. This practice maintains the surface of the flow in a molten state and minimizes surface defects such as scratching that could arise during the pour. Flux formulations containing wollastonite are reported to give better surface finishes to the steel than can be achieved by silica and lime composites. Welding powder formulations also use large tonnages of wollastonite as a flux and slag-forming additive. Wollastonite is favoured because of the improved burn characteristics of the mineral and the inhibition of sparking during the weld owing to its inherent fluxing characteristics (Power, 1986).

ASBESTOS REPLACEMENT

With increasing health legislation over the use of asbestos in various reinforcement applications there exists a growing large volume market for the use of wollastonite as an asbestos substitute. This market, however, is open only to the high aspect ratio materials and then wollastonite is not a perfect substitute because the crystal cannot match the length and flexibility of asbestos fibres. Nevertheless, wollastonite crystals are acicular enough to use as semifibrous reinforcement fillers for boards and panels used in various heat containment applications. Wollastonite is also enjoying increasing use in the replacement of asbestos in certain cement formulations, in ceiling and floor tiling, and in friction applications such as brake linings (Power, 1986).

PERFORMANCE FILLERS IN PLASTICS

There is great potential for the use of the more acicular wollastonite material as a performance filler in the resins and plastics industry. Wollastonite not only reduces the volume of expensive media consumed, but also contributes to physical, chemical and electrical properties of the finished product. In most cases wollastonite offers improved tensile and flexural strength over most other mineral fillers with particularly good moisture repellent properties (Power, 1986).

The following mineralogical properties illustrate the beneficial effects of wollastonite used in thermoplastic (PVC, nylon, polypropylene) and thermosetting resin systems (epoxy, phenolic, polyester).

Acicular Shape of Crystals

1. The crystal structure reinforces the media increasing impact, tensile and flexural strengths.

2. The high hardness of the mineral adds to wear resistance although this may cause abrasion problems in the extrusion casting.

3. High dimensional tolerance reduces shrinkage.

Moisture Pickup and Absorption Properties

1. Very low water absorption in comparison with other mineral fillers.

2. High loadings possibly due to low plasticizer absorption.

3. Also demonstrates low viscosity at high loadings.

4. Compatibility with organic plastic system enhanced by chemical surface coating of grains.

Colour Characteristics

1. High brightness and whiteness together with opaque properties saves pigmentation costs.

2. Smooth surface finish to shapes with high degree of stain resistance due to low water absorption.

Electrical Properties

1. Very good electrical insulation due to low levels of impurities. In polypropylene at 40% loading dielectric constant of 2.74 (Power, 1986).

MARKETS

The two major markets for wollastonite are: (1) as a ground 'powder' material used in ceramics and coating/filler applications, and (2) high aspect ratio material used in asbestos replacement and performance filler applications.

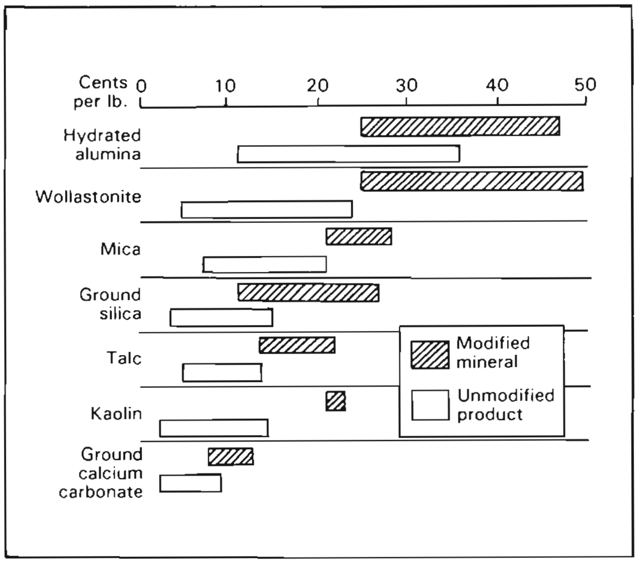
The 'powder' market is not likely to grow due to the plentiful supplies of cheaper and more traditional raw materials for the ceramics industry.

However, the metallurgical markets show considerable potential for growth along with some filler and extender applications where high aspect ratio wollastonite is used in fibreboards and panels as a replacement for asbestos. The lucrative plastics and fillers market where reinforcing characteristics are required has excellent growth prospects for the future where the current United States market of around 8000-10 000 tpa is expected to grow 10-12% per annum. Since many of the applications in thermosetting and thermoplastic media require some degree of chemical surface treatment, this provides considerable added income to the mineral producer. Figure 44 shows the added value effect in cost per pound that is generated by the chemical surface processing of various mineral fillers in the United States.

The trend now for the existing powder wollastonite producers is to invest in sophisticated milling equipment and chemical coating facilities to increase the acicular nature of their products in order to make them more attractive to the plastics and resins market.

FUTURE MARKETS

Future prospects for the wollastonite market appear to be very good with a great deal of healthy investment being concentrated on the long-fibre market. Supplies of ground powder material are totally adequate for future growth and the only area of concern is whether or not producers can satisfy demands for the more acicular material.



Source: C. H. Kline & Co. Chemically Modified minerals – United States 1985
Industrial Minerals, 1986

Figure 44. The added value effect in cost per pound that is generated by the chemical surface processing of the various mineral fillers in the United States.

NOVA SCOTIA POTENTIAL

The only known locations within Nova Scotia where siliceous limestones have been subjected to temperatures in the 450°C and higher range occur near areas of regional metamorphism in the George River Group of Cape Breton Island. The only known occurrence of wollastonite to date is located at Lime Hill, Inverness County (Figs. 45 and 46). George River Group carbonates have been metamorphosed by Hadrynian intrusive rocks as well as Devonian granites. The range of metamorphic temperatures, based on the silicate assemblages, is from 250-600°C (Hattie, 1975), well within the range for wollastonite formation.

The fine- to medium-grained, clear to grey calcite marble of the George River Group is interlaced with white to buff, nematoblastic subhedral, acicular aggregates of banded wollastonite up to 1.5 cm in thickness. Wollastonite also occurs in blebs up to 3.0 cm in size. Numerous inclusions of fine, pale green grains of pyroxene (possibly diopside) up to 1 mm in size are disseminated in both the wollastonite and carbonate. Minor quartz is found as interstitial grains in the marble. Very fine grains of pyrite are visible with some of the wollastonite.

Trenching conducted by Bluestack Resources Ltd. in 1986 delineated three wollastonite zones, referred to as the Eastern, Central and Western Zones (Pegg, 1987) (Fig. 45).

The Eastern Zone strikes approximately north-south and extends for over 180 m. The wollastonite varies between 2 and 3 m wide and contains between 25 and 50% wollastonite. The dip appears to be 70°W.

The Central Zone is defined as a multiple zone where several bands of wollastonite are exposed in trenches and intersected by drillholes. The bands dip about 60°W and contain 25-30% wollastonite on average. The bands range from stringers to thicknesses in excess of 2.5 m. The wollastonite content seems to increase to the south. A few deeper drillholes (+150 m) should be drilled on this Central Zone to determine if the wollastonite increases with depth.

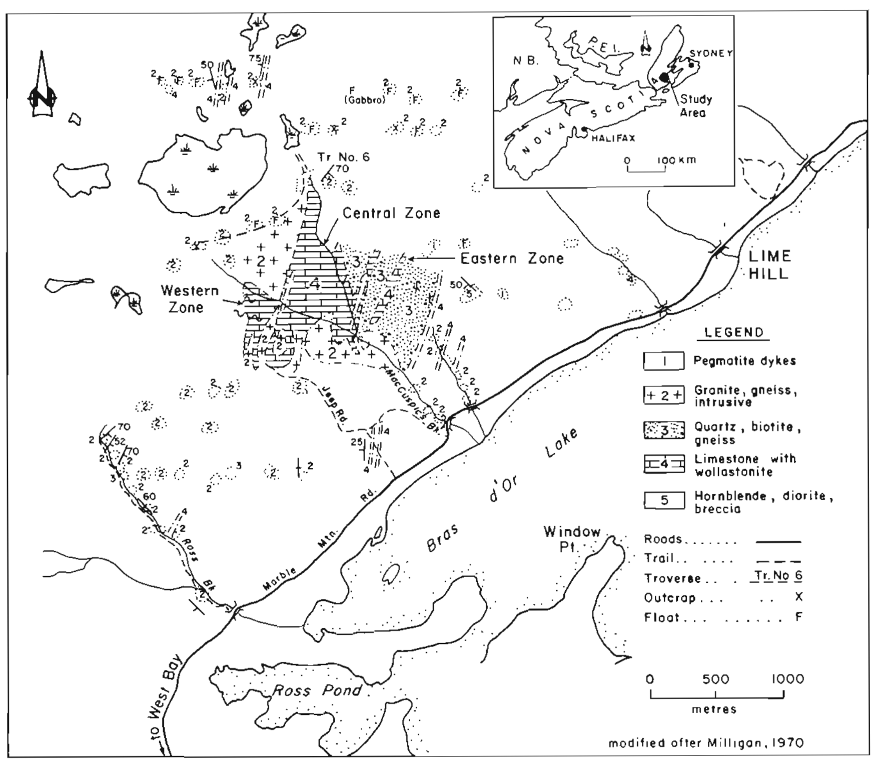


Figure 45. Location and geology map of wollastonite deposit at Lime Hill, Inverness County.

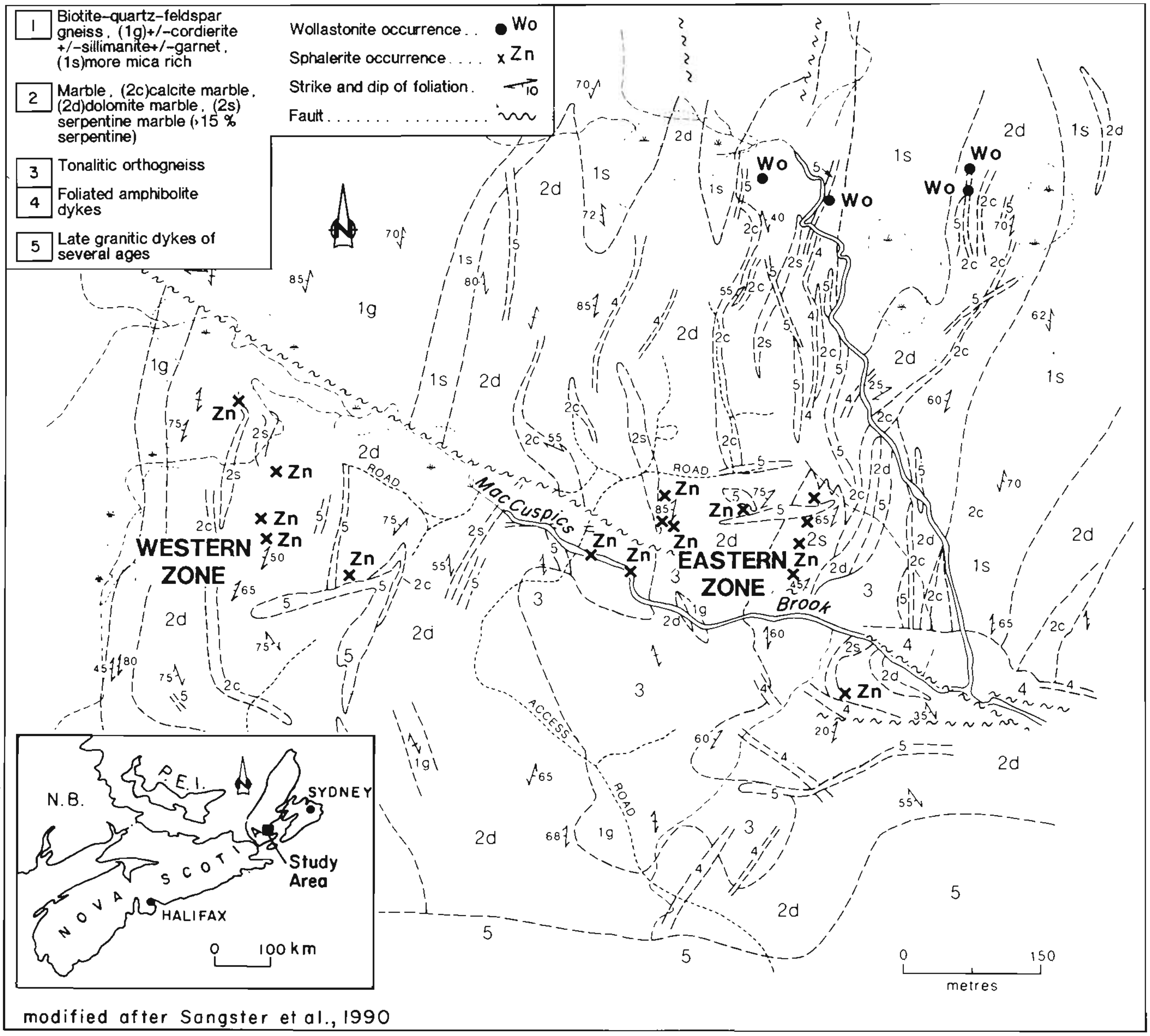


Figure 46. Geology and location of the zinc and wollastonite occurrence, Lime Hill, Inverness County.

The Western Zone appears to be a single horizon reaching a maximum thickness of 2.1 m, although one previous drillhole intersected three bands of wollastonite 1 m, 0.6 m and 0.3 m wide over 12 m. The Western Zone contains an average 25-30% wollastonite. More drilling at depth is necessary on this zone.

During the term of the Various Commodities Project in September 1986, a 4 kg sample of wollastonite ore was collected from the Lime Hill deposit and forwarded to the Mineral Processing Laboratory of the Canada Centre for Mineral and Energy Technology in Ottawa for preliminary assessment testing. This work indicated that the wollastonite could be concentrated by a combination of magnetic separation and flotation. Magnetic separation reduces iron oxide levels to 0.22% Fe_2O_3 in the -600 +300 μm fraction and to 0.28% Fe_2O_3 in the -300 +150 μm fraction. Subsequent reverse flotation of calcite on material ground to -300 μm removed approximately 85% of the calcite, resulting in a concentrated wollastonite product. Aspect ratios of this concentrated product were estimated at between 10:1 and 12:1. Brightness values of this same product are between 68 and 71%.

The results of this preliminary test work indicate that the wollastonite from the Lime Hill deposit can be successfully beneficiated to meet the requirements for use as a filler or extender material in paints and plastics. Further work on a larger representative sample is recommended (Andrews and Kelly, 1987).

Other wollastonite deposits may be possible in other sections of the George River Group carbonates that have been subjected to the same degree of metamorphic temperatures evident at Lime Hill. Temperature is the controlling factor and to date the Lime Hill location is the only known occurrence where the degree of metamorphism was high enough to produce wollastonite.