Additional Reading: Chemical Properties

About This Document

NYCO has the benefit of many years of experience in the production, handling and marketing of wollastonite products. The purpose of this document is to share some of this accumulated knowledge and experience with NYCO's customers, associates, agents and distributors with a view towards the successful usage and application of NYCO's wollastonite products.

The document provides a basis for understanding and for obtaining more definitive information or advice. This guide in no way represents a definitive reference for wollastonite. In consideration of the peculiarities of wollastonite, NYCO strongly recommends that the appropriate professionals carry out any design of products, processes, installations or modifications. NYCO also recommends that any test work deemed necessary by those involved in these endeavors be carried out on the appropriate NYCO products. NYCO can provide contacts that have had past experience working with wollastonite.

Where specific information is given, this is based on NYCO's experience and as such is offered as an example only. Situations and conditions in other's facilities will be different enough to warrant that a qualified professional makes specific recommendations. NYCO can provide assistance in contacting individuals with past experience.

Feel free to contact NYCO for additional information.

Chemical Properties

Wollastonite is a mineral comprised chemically of calcium, silicon and oxygen. Its molecular formula can be expressed as $CaSiO_3$ or as $CaO \cdot SiO_2$. It is commonly referred to as calcium metasilicate according to the now obsolete classification of silicates as oxyacids of silicon, a salt of hypothetical metasilic acid: H_2SiO_3. It has a theoretical composition of 48.28% CaO and 51.72% SiO_2. Natural wollastonite however, may contain trace or minor amounts of various metal ions such as aluminum, iron, magnesium, manganese, potassium and sodium. Any of these ions may partially substitute for calcium if they are present.

Wollastonite is rarely found by itself, and ore zones in the major deposits contain 20-98% wollastonite. Associated minerals are most often calcite, garnet, and diopside.

Synonyms and Trade Names

CAS Registry No.: 13983-17-0

Chem. Abstr. Name: Wollastonite

Synonyms: tabular spar, table spar, okenite, vilnite, rivaite, schalstein, gillebachite, aedelforsite

NYCO Trade Names include: NYAD, NYGLOS, NYCOR, WOLLASTOCOAT, ULTRAFIBE, NYCEM, HARRP

Chemical Reactivity

Wollastonite being relatively inert, has a low solubility in water although it does result in a basic pH (9-10 typically) upon contact with water. It is hydrolyzed according to the reaction:

$$CaO \cdot SiO_2 + nH_2O >> Ca(OH)_2 + SiO_2 \cdot (n-1)H_2O$$

The increased pH results from the presence of $Ca(OH)_2$ in solution in the water. The resulting pH with freshly ground wollastonite is typically close to 10. Aged samples however, typically result in lower pH. It is thought that this is due to the gradual liberation of calcium ions over time as surface moisture accumulates from the ambient atmosphere. The pH effect lessens as the calcium depleted surface layer increases in thickness and the transport of calcium ions becomes more difficult. In acidic solutions however, wollastonite has a buffering action due to readily available calcium ions. Maintaining the low pH of a wollastonite slurry demands the constant addition of acid. Without it the pH will rapidly return to 8 or more. Maintaining the pH of a wollastonite slurry much below 4 is difficult (if not impossible).

Wollastonite reacts readily with acids, especially hydrochloric acid. In fact, samples of pure wollastonite can be completely dissolved with concentrated hydrochloric acid under the right conditions. Incomplete dissolution results in a silica gel. Dissolution by hydrochloric acid is useful as a measure of certain insoluble impurities (such as quartz, sphene, etc.). Other acids, which are known to dissociate wollastonite, include sulphuric, phosphoric, acetic, citric, lactic, and formic acids.

Reaction of wollastonite with phosphoric acid can result in special cements with good cast-ability and which can be subsequently fired to produce a white body of high strength, which can easily be machined. The optimum amount of phosphoric acid for binding purposes is indicated by the following equation:

$$3\ CaO \cdot SiO_2 + 2H_3PO_4 >> Ca_3(PO_4)_2 + 3H_2SiO_3$$

Since this reaction proceeds quickly, boric acid or borax is generally added as a retardant. Wollastonite with a coarser particle size also acts as a retardant however it may not react completely if this is a requirement. By varying the proportions in the mixture, good casting compositions can be obtained with setting times in excess of two hours. Fired shapes can be sawed, drilled, nailed, and cut without tearing or splitting. This is sometimes referred to as an "inorganic polymer" and has been the subject of recent patents.

Reactivity with bases or dissociated salts appears to be limited at ambient temperatures. At elevated temperatures however, ion exchanges (Na and K) can be effected.

Being calcium silicate, wollastonite is readily compatible with portland cements in concrete mixes. Wollastonite readily bonds with portland cements which are themselves composed mainly of tricalcium silicate and dicalcium silicate ($(CaO)_3SiO_2$ and $(CaO)_2SiO_2$ respectively). Wollastonite tends to improve many of the properties of concrete including tensile strength, chemical resistance, density and fracture resistance. Chemical modifiers may be required to achieve optimum properties.

Surface Enhanced Chemistry

Surface chemistry is important in applications where wollastonite is added as a reinforcement in other materials. Coupling agents or surface-modifiers enhance the performance of wollastonite in the matrix. Generally surface treatment of wollastonite is to enhance its role as a functional filler in plastics however, it can also be important in other materials systems.

The properties of filled plastics can be significantly improved by surface treatment of the filler minerals. Surface treatment of wollastonite with coupling agents enables a superior bond with the resin. Stronger bonding with the matrix enhances mechanical properties, reduces shrinkage, increases weather resistance, and lessens or eliminates surface or internal defects. In addition, surface treated wollastonite permits higher filler loadings; improves dispersion; and improves powder flow characteristics, as well as flow during mixing and molding in compounding systems.

The three main groups of chemical agents used for treating plastic fillers are acids, organosilanes and organometallics. Both silanes and titanates are used to treat wollastonite. The use of stearic acid and acid esters is largely for calcium carbonates. Of the two, the organotitanates have relatively small and specialized markets. The surface treatment method actually used plays a major part in the success of a treated wollastonite product. After treatment, handling wollastonite is a concern as broken particles expose untreated mineral surface, which are potential weak points. NYCO has many years of experience in consistently providing customers with high quality surface treated wollastonite products.

High Temperature Chemistry

Wollastonite has a basic chemistry that is desirable in many applications requiring the melting of refractory type materials. Wollastonite forms low-melting point eutectics with more refractory phases such as Al_2O_3 and MgO. Wollastonite ($CaO.SiO_2$) itself, has a lower melting point (1540^{O}C for pure wollastonite) than either CaO at 2570^{O}C or SiO_2 at 1723^{O}C. Moreover it is a previously combined source of both CaO and SiO_2. As a source of CaO, wollastonite is less refractory than either calcite (effectively CaO which has a melting point of 2570^{O}C) or dolomite (effectively (Ca,Mg)O which has a melting point of about 2500^{O}C). Wollastonite also contains little or no chemically bound CO_2 or H_2O. The addition of wollastonite to feldspar raw materials can lower their effective melting point by as much as 100^{O}C.

Loss-On-Ignition (LOI)

Loss-on-ignition (LOI) is the amount of volatile matter driven off when the mineral is heated to 1000^{O}C. Commercial wollastonite products have an ignition loss ranging from 0.5% to 2.0%. The LOI for NYCO's wollastonite products are typically less than 0.7%.

Loss-on-ignition can be attributed primarily to the decomposition of carbonates (mainly calcite) however, such things as water of hydration, organic materials (roots, wood, plants, etc.) and sulphur-containing minerals may also contribute in part for some wollastonite.

LOI is important in ceramics as gas evolution affects the quality of glazes (pinholes) and leads to shrinkage and warping during the firing of ceramic bodies. Gas evolution is also undesirable in metallurgical applications as it can affect surface finish, release of hydrogen can lead to embitterment and micro-cracking, and lead to poor end-use characteristics (sparking, spitting, etc.).

Ceramics

Wollastonite is considered the preferred raw material source for calcium oxide in glazes or in glaze frits. Wollastonite is a water insoluble calcium base in glazes and compared to calcium carbonate plus flint, dissolves much more readily, permitting the glaze to smooth out more rapidly and completely. In such applications it is important that the wollastonite contains as little coloring oxides as possible and has low loss-on-ignition. This allows the production of high quality glazes with no pinholes and no opacity from unmelted silica. Certain calcium-based pigments, particularly the chrome tin pink pigment used widely, will be brighter in a glaze containing wollastonite. The wollastonite saturates the glaze in calcium, protecting the pigment from dissolution by the glaze itself. This reduces pigment requirements. As a quality requirement, any dark colored particles (black specks) that remain after firing will exclude some wollastonite from being used in glazes.

The usage of wollastonite in ceramic bodies can amount to as much as 40% or more. Wollastonite serves as a reliable sintering aid to vitrified bodies. The addition of wollastonite results in many positive effects such as less fired shrinkage, low water absorption, lower fast firing temperature, higher green strength, less cracking and shorter firing times.

Wollastonite can also replace limestone and silica sand in a glass batch where it reduces the melting temperature and inhibits scum and seed formation. This is can be important in the production of specialty glasses and fiberglass.

Metallurgical Fluxes

In metallurgy, wollastonite finds application where there is a need for water insoluble, low loss-on-ignition, low melting calcium bases. Wollastonite is commonly added to formulated powders for steel casting and welding. A CaO/SiO_2 ratio of 1 readily absorbs Al_2O_3 that is detrimental to finished steels. The addition of wollastonite to metallurgical fluxes provides ready fusibility, good insulating qualities and low viscosity slags. Additionally wollastonite is generally low in phosphorous and sulphur that are detrimental. Some metallurgical fluxes can have 60% or more wollastonite content.

Because wollastonite is a natural, low temperature flux, it has found acceptance in fluxing formulations used in the continuous casting of steel. When molten steel is poured continuously from a ladle or tundish, a casting powder is applied to maintain and protect the surface of the molten metal. An effective casting powder minimizes surface defects, prevents oxidation of the steel, lubricates the mold wall and absorbs harmful inclusions. Because of it's very low loss-on-ignition, wollastonite reduces the chances of embrittlement and micro cracking. In the finished steel, wollastonite modifies non-deformable Si-Mn deoxidation inclusions ($MnO \cdot Al_2O_3 \cdot SiO_2$) to form anorthite ($CaO \cdot Al_2O_3 \cdot SiO_2$) inclusions. Anorthite inclusions are desirable because they are deformable during hot rolling or fine wire drawing. Anorthite inclusions have a similar degree of deformation as steel. Anorthite inclusions are amorphous and do not crystallize during cooling. Wollastonite used in weld powder formulations improves burn characteristics and minimizes splatter during welding, as well as acting to maintain the arc.

Paints and Coatings

The alkaline nature of wollastonite is advantageous in paints and coatings where it acts as an anti-corrosive agent. This property is important for architectural and industrial applications including primers, textured paint; putty, caulks, and sealants; roof coatings; stucco and block fillers.

Wollastonite with its high pH, for example is advantageous in polyvinyl acetate (PVA) paints where it helps to neutralize acidity shift. PVA can decompose into vinyl alcohol and acetic acid, but wollastonite maintains the alkaline nature of the paint and so can combat corrosion.

Other Chemical Uses for Wollastonite

Wollastonite has been found useful as a soil conditioner and an additive to plant fertilizer for it’s reactivity in acid conditions. As opposed to lime or calcite, it offers long-term protection against the acidification of soils. In some countries, wollastonite has also found use as an inert carrier for pesticides and insecticides.

Suggested References

Deer, Howie, and Zussman, Rock Forming Minerals, v. 2A, p. 547-563, New York, Longman-Wiley, 1978.

Bolger, R., "Wollastonite, Quality Remains the Key Aspect," Industrial Minerals, Nov ’98, p. 41-51.

Fattah, H., "Wollastonite, New Aspects Promise Growth," Industrial Minerals, Nov ’94, p. 21.

The Economics of Wollastonite, Sixth Edition 1996, London, Roskill Information Services, 1996.

Harben, Peter W., The Industrial Minerals Handybook, 2nd Edition, p. 197-199, London, Industrial Minerals Information, 1995.

Bauer, Copeland, and Santini, "Wollastonite" in Industrial Minerals and Rocks, 6th Edition, p. 1119-1128, Society for Mining Metallurgy, and Exploration, 1994.

Robbins, M., Fluorescence, Gems and Minerals Under Ultraviolet Light, p. 266-267, Phoenix, Geoscience Press, 1994.

"Wollastonite" in IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Silica and Some Silicates, Volume 42, 1986, 15 pp.

Andrews, R.W., Wollastonite, Monograph, Institute of Geological Sciences, Her Majesty’s Stationary Office, London, 1970, 114 pp.

Amberg and McMahon, Wollastonite, An Industrial Mineral, Bulletin No.4,New York State College of Ceramics,1949,60 pp.

Touloukian, T.S., Judd, W.R., Roy, R.F., Physical Properties of Rocks and Minerals, McGraw