Manufacture of Synthetic Wollastonite

[1]F. M. Z, KAIFI*, [1]M. AURANGZEB, [1]B. AHMED AND [2]M. KHAN
[1]*PCSIR Laboratories Complex, Jamrud Road, Peshawar, Pakistan*
[2]*Chemistry Department, University of Peshawar, Pakistan*

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Summary: Synthetic wollastonite a calcium silicate has received much attention over the last decade. It is largely chemically inert and biologically safe. Due to its immense properties, the production capacity has increased substantially in recent years. Synthesis of wollastonite was investigated with regard to optimum parameters at laboratory scale; such as mesh size of raw material, (calcium carbonate, silica) time duration, sintering temperature, stoicheiometric ratio and characterization of product. It was found that wollastonite may be synthesized at maximum degree with varying sets of parameters. The maximum yield of the product with ratio 26:15 for one hour was suitable to produce commercially acceptable product which is economically feasible.

Introduction

Wollastonite is the mineral form of calcium metasilicate. It occurs in nature having acicular shape. It has the chemical formula $CaSiO_3$. [1,2]. It was first mined in California in 1935 to supply material for a white mineral wool. It was also used experimentally during the second world war, but it was not until late 1949 that construction was started on an industrial plant in New York state to manufacture Wollastonite products [3].

Wollastonite has a theoretical composition of CaO (48.3%) and SiO_2 (51.7%) when pure, [4] but in nature the calcium component is often substituted by iron, magnesium or manganese and commonly associated minerals include; diopside ($CaMgSiO_6$), tremolite [Ca_2 $(MgFe)_5$ Si_8 O_{22} $(OH)_2$] idocrase [$Ca_{10}AI_4$ $(MgFe)_2$ $(Si_2O_7)_2$] $(SiO_4)_5$ $(OH)_4$], grossular garnet [Ca_3 AI_2 $(SiO_4)_3$)] and andradite garnet [Ca_3 Fe $(SiO_4)_3$] [5]. Deposits of sufficient size and purity to be economically exploitable are rare.

Although the mineral is white when pure it is often coloured grey or brown due to impurities, and it is the nature of these impurities which obviously determine whether the mineral is economically exploitable or not. For example, if the mineral impurity is iron contained in associated minerals this can be removed fairly easily using magnetic separation. Calcite is however less easily removed.

Quartz is the most abundant silica mineral and its α ↔ β inversion has been studied extensively. The temperature of this inversion reaction is almost constant at 573°C and it is in fact sometimes used as fixed point for the calibration of the temperature scale of DTA apparatus.

However, already Fenner [6] found some variation of this temperature between quartz samples from various geological sources. Keith and Tuttle [7] demonstrated this by DTA techniques that α ↔ β inversion of quartz are variable. The energy change in the reaction is only about 1.4 cal g-1 [8].

White and Grimshaw [9] found that quartz determination by DTA based on the reaction at high temperature on cooling after standard test. Calcium silicate may be synthesized by treating limestone or dolomite are quartz sand under different conditions. Dempster and Ritchie [10] have demonstrated that finely ground quartz gives erroneous results, unless that distorted layer on the surface caused by grinding is removed by hydrofluoric acid, or NaoII.

The simplest silicates contain the SiO_4^{-1} ion and are represented by Mg_2SiO_4 (Olivine) and the synthetic β- Ca_2 SiO_4, an important constituent of cement, which sets to a hard mass when finely ground and mixed with water; one of the products of this reaction has the composition Ca_2 $(SiO_3$ (OH) (OH). Boyer [11] Grimshaw [12] and Roberts [13] have shown that the DTA estimation of quartz give lower results for silica content than x-ray or chemical methods.

Dawson and Willburn [14] list a complex set of peaks at 100-130. 130-140, 150-170, 200-250 and 300-350°C. The temperature variation is assumed to

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*To whom all correspondence should be addressed.

be caused by chemical impurities (solid solution) within the structure and possibly by formation of glass around the impurity. Plumat [15] had also suggested of tridymite crystals at low temperature inversion and at higher temperature (163°C) inversion was also observed [16,17,18].

Theoretical composition of pure wollastonite is CaO (48.3%) and SiO_2 (51.7%), but in nature the calcium component is often substituted by iron, magnesium or manganese, and commonly associated minerals include, diopside (CaMg SiO_6), tremolite Ca_2 $(MgFe)_5$ Si_8 O_{22} $(OH)_2$ [19.20].

When two SiO_4 units share an oxygen, the resulting $Si_2O_7^{-6}$. The cyclic anions $Si_3O_9^{-6}$ and $Si_6O_{18}^{-12}$ in which each SiO_4 unit shares two corners, occurs in $Ca_3(Si_3O_9)$ (α - wollastonite). While in β-wollastonite the SiO_4 units share two corners from an infinite chain i.e. Si:O is again 1:3. Though it occurs in short chain polysilicate anions but are uncommon [21,22], these occur in a few rare minerals. If the SiO_4 units sharing two corners form an infinite chain, the Si:O is again 1:3, this is found in $CaSiO_3$ (β-wollastonite and CaMg $(SiO_3)_2$ diopside, a member of a pyroxene ground of minerals [17,23].

The main use of wollastonite in industrial applications has widened as the importance of its properties (some of which are unique) have become better understood. Traditionally wollastonite is recognized as a filler in a number of products such as ceramics, paints, plastics, adhesives, resins, wallboards, floor tiles and insulating materials. In the majority of ceramic formulations wollastonite can prevent cracking, dunting, crazing breakage and glaze defects.

Wollastonite can also be used as a non-moisture absorbent fillers in thermosetting, thermoplastic moulding compounds and casting resins, as extender in vinyl plastiols and linoleum. Wollastonite is a dry clean filler which is compatible and easy to disperse.

Color, particle shape and oil absorption all make wollastonite particularly useful in paints. In white and clear color paints, the brilliant white color of wollastonite is exceptionally useful. It also helps good tint retention.

In ceramic artware wollastonite reduces, drying and firing shrinkage, improves quality and appearance of finished products, increases dry, bisque, and ghost transverse strengths, reduces moisture expansion, and increases impact strength.

A greater fluxing rate and high thermal shock resistance had been achieved when wollastonite was used in the production of ceramic-bonded abrasives, and abrasive wheels. Some wollastonite was used as a filler in grinding wheel bonding formulations. When wollastonite emulsion paints were applied to the surface of ceiling tiles the whiteness and acicular particle shape of the wollastonite enhanced burnish resistance, colour, and acoustical properties to the surface of these tiles. In the production of porcelain enamels wollastonite acted as a natural frit, and the use of calcium metasilicate in the form of wollastonite had proven more economical than pre-fritting with limestone and silica.

As an extender, wollastonite was used as a replacement for non-fibrous materials, and regular asbestos. It improved physical, electrical, and chemical properties in moulded brake linings, polyethylene (low-density), polyesters, epoxies, vinyls, caulking compounds, adhesives, cements, and automotive under-coating. Wollastonite had been used as a metallurgical flux, and had in addition been used as a coating on welding rods to ease flux applications. Wollastonite was used (in place of limestone) in the manufacture of glass as it did not only act as a source of lime but added silica to the melt as well.

Wollastonite was also recommended for specialized ultra-high frequency electronic equipment such as high temperature porcelains, high tension circuit breakers, phenolic-bonded electrical resistors, and as inorganic insulation for applications involving temperatures up to 500°C. This was due to the ultra-low loss.

Pakistan possesses large resources of goods quality minerals and rocks. Despite this fact Pakistan mineral industry remains backward due to low technical and financial inputs, poor infrastructure, general lack of technological expertise and absence of developed domestic consumer market. Large deposits of minerals occur, which have a potential for providing strength to mineral industries are baryte ($BaSO_4$) bauxite clay, china clay, dolomite, fullers earth, gypsum ($CaSO_4$) limestone, magnesite ($MgCO_3$) marble, nephline syenite, phosphate, rock-salt, silica sand, feldspar, antimony miscellaneous.

Results and Discussion

The results of synthetic wollastonite are summarized in table 1-8.

It may be observed from the Table 1-7 that synthetic wollastonite at 650°C in the time limit of one hour with the ratio (2:1) i.e. (silica 26gm:calcite 15gm) can be achieved 98.72%.

Repetition of this experiment with same ratio did not indicate any change in the percentage yield. Such a high recovery was not obtained by changing the parameters as shown in the Table (9,1-5). In these experiments the ratio of the raw material (calcite) and temperature are varied. With the change of duration of time and temperature a decrease in yield was observed. It indicated that by fixing the temperature, time and ratio of raw material (silica) higher yield was obtained. With the variation of temperature, ratio and fixing time, a decrease in the yield up to 49.63% was obtained. It is indicated that at 650°C with 2:1 ratio of silica and calcite exhibited maximum yield 98.72% of synthetic wollastonite.

The purity of the synthetic wollastonite was checked through analytical method, which confirmed CaO 47.9% and SiO_2 50.86%. These results are closest to chemical formula of naturally occurring wollastonite.

Results of chemically prepared calcium silicate (calcium chloride and sodium silicate) are summarized in Table (7). It was observed that with the variation of ratio in sodium silicate, and keeping calcium chloride ratio constant, the percentage of reagent was 82.6%. This shows that beyond 1:1.5 ratio the yield of calcium silicate gets decreased. It was derived from these studies that naturally occurring calcite and silica are the cheap materials that can easily be obtained from mine owners or open market being economical.

While chemically prepared calcium silicate is not economically feasible as both the reactants are expensive. The product (synthetic wollastonite) as well as commercial calcium silicate analytical grade are being imported. This data has been acquired from "Trade Statistics of Pakistan", April-June 1998.

Synthetic calcium silicate (wollastonite) manufactured through naturally occurring raw materials is cheaper and it costs about Rs. 40-60/Kg, while the chemically prepared $CaSiO_3$ costs up to Rs. 60-80/kg. Synthetic wollastonite cost has been worked on laboratory scale preparation. The laboratory preparation parameters could be optimized to pilot plan production. At pilot plant about 200 Kg wollastonite synthesized at commercial level which cost about Rs.30-35/kg. Overall wollastonite has unique properties that increases its demand. The home demand could easily he met from execution of pilot plant production.

Experimental

The raw materials used for synthetic wollastonite are calcite ($CaCO_3$) and silica (SiO_2), which occur in abundance in N.W.F.P. They were analysed first then set optimum parameters and combined in stoicheiometric ratio, sintered to obtain product. The chemical analysis of raw materials is given in Table-9.

Several experiments were conducted, out of which 24 experiments result are mentioned. Ratio of the silica kept constant and the amount of calcite varied from 30 gms to 15 gms at variable temperature ranging from 1000°C to 650°C as given in the Table 1-7.

Similarly, for comparative study, calcium silicate was also prepared by reacting calcium

Table-1:

S. No.	Experimental Ratio			
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
1.	26:30	1000	1	50.63
2.	26:25	1000	1	62.91
3.	26:20	1000	1	70.80
4.	26:15	1000	1	73.50

Table-2

S. No.	Experimental Ratio			
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
5.	26:30	950	1	50.87
6.	26:25	950	1	55.92
7.	26:20	950	1	65.24
8.	26:15	950	1	74.43

Table-3

S. No.	Experimental Ratio			
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
9.	26:30	900	1	49.63
10.	26:25	900	1	55.24
11.	26:20	900	1	60.80
12.	26:15	900	1	75.45

Table-4

S. No.		Experimental Ratio		
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
13.	26:30	850	1	54.32
14.	26:25	850	1	65.72
15.	26:20	850	1	72.06
16.	26:15	850	1	80.48

Table-5

S. No.		Experimental Ratio		
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
17.	26:30	750	1	59.32
18.	26:25	750	1	70.39
19.	26:20	750	1	78.66
20.	26:15	750	1	84.92

Table-6

S. No.		Experimental Ratio		
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
21.	26:30	650	1	86.82
22.	26:25	650	1	90.58
23.	26:20	650	1	93.60
24.	26:15	650	1	98.72

Table-7

S. No.		Experimental Ratio		
Sample	(SiO_2: $CaCO_3$)	Temp. °C	Time hr	Yield%
1.	26:15	1000	1	73.50
2.	26:15	950	1	74.37
3.	26:15	900	1	75.69
4.	26:15	850	1	80.35
5.	26:15	750	1	84.92
6.	26:15	650	1	98.72

Table-8

S. No.		Experimental Ratio		
Sample	$CaCl_2$	:	Na_2SiO_3	Yield%
1.	100	:	25	45.72
2.	100	:	50	51.82
3.	100	:	75	57.00
4.	100	:	100	63.24
5.	100	:	125	75.43
6.	100	:	150	82.61

Table-9:Chemical analysis of Raw Materials (Calcite and Silica)

Element	Calcite % ($CaCO_3$)	Silica % (SiO_2)
Loss on ignition (L.O.I)	44-47	0.41-0.57
Iron oxide (Fe_2O_3)	0.2-0.56	0.53-0.83
Aluminium oxide (Al_2O_3)	0.6-2.30	2.62-3.07
Calcium oxide (CaO)	27-28	<0.35
Silicon dioxide (SiO_2)	0.16-2	95.00-96.22

chloride (Anal-R grade) with sodium silicate (commercial) in a hot solution of calcium chloride dehydrate sodium silicate added, a precipitate obtained was filtered through sintered glass crucible. The precipitate was dried at 110°C for two hours.

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