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Beneficiation of A Wollastonite From Sirohi, Rajasthan

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Abstract

Low grade Wollastonite samples from Sirohi, Rajasthan were received with the aim of evolving a beneficiation process to produce ceramic grade wollastonite concentrate containing wollastonite>97% and trace amounts of calcite, iron oxides and clay [<1% each]. The as received sample whitish coloured lumps [50mm size] with considerable of fines. The sample analysed 43.43% CaO, 2.70% Fe_2O_3, 2.21% Al_2O_3, 46.69% SiO_2 and 4.10% LOI. It contained mainly wollostonite with subordinate amounts of calcite with minor amounts of garnet, hornblende, iron oxides, quartz and clay. The diagnostic amenability test at -65mesh indicated that ceramic grade wollastonite concentrates may be obtained by removal of carbonates and ferruginous impurities. The process comprises of soap flotation followed by WHIMS of non float at mesh of grind of -150#. The above flotation –WHIMS process yielded a ceramic grade concentrate assaying 97%CaO.SiO_2, 0.49 % Fe_2O_3, 1.01% Al_2O_3 and 0.45% LOI at weight % yield of 75.0. The cleaner calcite float assaying 45.6% CaO, 7.20% Fe_2O_3, 4.21% Al_2O_3, 5.89% SiO_2 and 36.22% LOI may be used as by-product as it meets cement grade

Keywords: *Wollastonite, flotation, Cemamic grade, cement grade lime stone.*

1 Introduction

Wollastonite, a met silicate of calcium (CaSiO3), contains theoretically 48.3% CaO and51.7% SiO_2 with hardness of 4.5 on Moh's scale. It occurs as aggregates of bladed or needle-like crystals.The resources of wollastonite, as per UNFC system are placed at 16.57 million tons. Out of total resources, about 88% (14.58 million tons) including 2.49 million tons reserves are located in Rajasthan and the remaining about 12% resources (1.99 million tons) in Gujarat. Meager resources are located in Tamil Nadu (3,533 tons). India is the 2nd largest producer of wollastonite.

The use of wollastonite depends on the accicularity or the aspect ratio; i.e., ratio between length and width of a crystal. Wollastonite having aspect ratio in the range from 3:1 to 5:1 has little potential for reinforcing applications and hence, market is primarily confined to ceramic, metallurgical fluxes and simple filler and coating applications. Wollastonites acicular nature allows it to compete with other acicular materials, such as ceramic fibre, glass fibre, steel fibre, and several organic fibres, such as acramid and polyethylene etc. It reduces the volume of the expensive plastic or resin medium and contributes to physical and chemical properties of the finished products. It improves tear strength, dielectric properties and retains mechanical properties at elevated temperatures. Wollastonite is used primarily in automobile brakes, ceramics, metallurgical processing, paper paint, plastic, cosmetics, adhesives and as a replacement of asbestos in asbestos, cement boards and sheets. Some of the properties that make it useful are high brightness and whiteness, low moisture and oil absorption, low volatile content, and the acicular nature of some wollastonite. A better compatibility between the polymer and the filler is achieved by chemical surface treatment of the mineral filler. Wollastonite, when treated in such a manner, results in improved flexural modules in polypropylene and improved reinforcement in nylon. Bulk demand for wollastonite in the country is in the ceramic industry for the manufacture of floor and wall tiles. In ceramics, wollastonite decreases shrinkage, low and gas evolution during firing. Small quantities are used in asbestos-cement products as a partial replacement for short fibre asbestos, paint, insecticide, marine wallboard, and welding rod industries. In metallurgical applications, wollastonite serves as a flux for welding, a source for calcium oxide, as slag conditioners and to protect the source of molten metal during the continuous casting of steel.

Wollastonite is mined by open cast mining method along the strike of wollastonite mineralized zone of skarns. The ROM is crushed ~50mm size and is hand sorted to remove associated gangue minerals like calcite, diaspore, garnet, quartz and iron oxides. The hand sorted concentrate is milled and labeled based on brightness. The sub grade rejects are stacked separately. 50 kgs of mine hand sorted reject wollastonite sample from Sirohi, Rajasthan was collected with a view to study the amenability of sample beneficiation techniques like flotation, magnetic separation. The aim of the investigation was to produce a wollastonite concentrate containing a minimum 97% wollastonite, 0.5% maximum LOI, 1% [max] Iron oxides, 1% [max] Al_2O_3 and 1% [max] carbonates, besides a possibility of generation of calcite based co products. The review of processing of wollastanite centers on hand sorting and flotation as enumerated by IBM.

2 Material and Methods

Low grade Wollastonite samples from Sirohi, Rajasthan were received with the aim of evolving a beneficiation process to produce ceramic grade wollastonite concentrate containing wollastonite>97% and trace amounts of calcite, iron oxides and clay [<1% each]. The as received sample was stage crushed to -10 mesh using primary lab jaw crusher[150 x225mm – 25 mm set], lab roll crusher [200mm x 150mm] 300 mmx600mm 10 mesh screen. The crushed sample was subjected to standard feed preparation by adopting sampling procedures. The sample was ground in 175mm x 350 mm rod mill 7 kg rod charge -10 Nos of 40mm, 25mm and 20mm dia varying grinding time. The ground pulp was subjected to froth flotation using D12 Denver type lab sub aeration flotation machine. The non float was subjected to Wet High Intensity magnetic separation [Eriez-Carpco] to remove magnetic impurities. The feed and products after dewatering followed by drying were weighed, sampled and subjected to characterization studies. 10% Sulphuric acid was used to adjust pH to 7.5. Oleic acid [BDH] was saponified with NaOH [BDH] stoichimetrically to get sodium oleate soap to be used as collector.

3 Results and discussion

3.1 Characterization studies**;** The as received sample consisted of whitish gray coloured hard and compact lumps of50mm max size with considerable fines with bulk density of 1.7t/m^3 and 53^o angle of repose. The Bond's ball mill work index was found to be 10Kwh/short ton. The sample contained mainly fine grained acicular wollastonite intimately associated with subordinate to minor amounts of fine grained aggregates of calcite quartz. Iron oxides, clay and feldspar occur in minor to trace amounts and occur as fillers between calcite – wollastonite interstitial space. The mean aspect ratio of wollastonite was 3. The sample analyzed 43.43% CaO, 2.70% Fe_2O_3, 2.21% Al_2O_3, 46.69% SiO_2 and 4.10% LOI. Fair degree of liberation is noticed at ~65 mesh size. The diagnostic amenability test on -65 mesh sample involving leaching with acetic acid followed by Frantz iso dynamic magnetic separation of leach residue yielded a non magnetic leach residue containing about 97% wollastonite.

The representative. -10 mesh samples were stage wet ground in rod mill to -65 /-150/-270 mesh size and samples were subjected to size analysis. The data is given in Table 1. The grindability data indicated that the sample was medium soft in nature

Table 1 Size analysis of rod mill grindability

Conditions; 500 gms of – 10 mesh sample stage wet ground in 175mm x 350mm rod mill with 7 kg rod charge at for 3' time to -65/-150/-200 mesh

Stage	Cell gms	rpm	Reagent	Dosage kg/t	CT min	FT min
RF	250	1200	Sod Oleate	0.8/1.0 /1.2/1.4	3 each	4 each

Mesh	Aperture microns	Cum Wt% Passing		
-72+100	212	100.0	100.0	100.0
-100+150	150	85.2	100.0	100.0
-150+200	106	64.8	88.1	100.0
-200+325	75	35.2	65.2	100.0
-325+400	45	28.0	55.2	78.7
-400	37	20.2	40.0	55.5
D_{80} microns		140	80	45

3.2 Effect of mesh of grind; Flotation tests were conducted varying MOG -65/-150/-200 # respectively at pH of 7, with 2kg/t sulphuric acid and1.2 Kg/t sodium oleate. The results are given in Table 2. The results indicated that the LOI content reduced to a minimum at mesh of grind of -150 mesh and hence was chosen. The fall in grade in coarse grind of -65 mesh was due to lack of liberation of calcite values while the fall in grade in very fine grind of -200 mesh was attributed to interference of slimes

3.3 Effect of collector dosage; Flotation tests were conducted varying collector sodium oleate from 0.8/1.0/1.2/1.4kg/t at MOG of -150mesh, pH of 7 with 2kg/t H_2SO_4. The results are given in Table 3 which indicated that the LOI content reduced with sodium oleate dosage. 1.2kg/t oleate was chosen. The fall in grade in lower collector dosages was due to lack of collector to float calcite while the fall in yield was due to collection of wollastonite at collector exceeding 1.2kg/t.

Table 2; Effect of MOG on flotation

Conditions; Mesh of grind -65/-150/-200 mesh Flotation pH 7, % S 20, 2 kg/t Sulphuric acid

Stage	Cell gms	rpm	Reagent	Dosage kg/t	CT min	FT min
RF	250	1200	Sod Oleate	0.5+0.3+ 0.2+0.2	3 each	4 each

Results

Mesh of grind	Product	Wt%	% LOI	
			Assay	Distn
-65 mesh D_{80} 140 microns	Float reject	15.5	22.36	84.6
	Concentrate	84.5	0.75	15.4
	Head Cal	100.0	4.11	100.0
-150 mesh D_{80} 80 microns	Float reject	21.0	17.77	90.1
	Concentrate	79.0	0.50	9.9
	Head Cal	100.0	4.00	100.0
-200 mesh D_{80} 45microns	Float reject	40.0	9.25	89.8
	Concentrate	60.0	0.70	10.2
	Head Cal	100.0	4.12	100.0

Table 3; Effect of collector dosage on flotation

Conditions; Mesh of grind -150mesh, Flotation pH 7, % S20, Sulphuric acid 2kg/t

Results

Sod. Oleate kg/t	Product	Wt%	% LOI	
			Assay	Distn
[0.2+0.2+ 0.2+0.2] 0.8	Float reject	15.0	22.33	79.8
	Non float	85.0	1.00	20.2
	Head Cal	100.0	4.20	100.0
[0.4+0.2+ 0.2+0.2] 1.0	Float reject	20.0	18.00	90.0
	Non float	80.0	0.50	10.0
	Head Cal	100.0	4.00	100.0
[0.5+0.3+ 0.2+0.2] 1.2	Float reject	21.0	17.77	90.1
	Non float	79.0	0.50	9.9
	Head Cal	100.0	4.00	100.0
[0.6+0.4+ 0.2+0.2] 1.4	Float reject	28.0	13.85	92.3
	Non float	72.0	0.45	7.7
	Head Cal	100.0	4.19	100.0

3.3 Effect of pH: Flotation tests were conducted varying pH from 7/8/9 using H_2SO_4&Na_2CO_3. The test results are shown Table 4. The results indicate that pH 7 yielded low LOI concentrate

Table 4 Effect of pH

Conditions; Mesh of grind -150mesh, Flotation, % S 20 , 1.2 kg/t sodium oleate

Stage	Cell gms	rpm	pH	Reagent	Dosage kg/t	CT min	FT min
RF	250	1200	7/ 8/ 9	Sod Oleate	0.5+0.3 +0.2+ 0.2	3 each	4 each

Results

pH	Product	Wt%	% LOI	
			Assay	Distn
7 With 2kg/t H_2SO_4	Float reject	21.0	17.77	90.1
	Non float	79.0	0.50	9.9
	Head Cal	100.0	4.00	100.0
8 Natural pH	Float reject	21.0	17.61	90.2
	Non float	79.0	0.51	9.8
	Head Cal	100.0	4.10	100.0
9 With 1kg/t Na_2CO_3	Float reject	33.0	10.96	90.0
	Non float	67.0	0.60	10.0
	Head Cal	10.0	4.02	100.0

3.4 Effect of %solids; Flotation tests were conducted varying % solids from 20 to 33from at MOG of -150mesh, pH of 7 with 2kg/t H_2SO_4 and 1kg/t sodium oleate. The results are given in Table 5 which indicated that the LOI content reduced with % Solids. Flotation at33%S yielded 0.4% LOI concentrates but the Fe% content was 2.64, indicating it's unsuitability to ceramic grade.

Table 5; Effect of %S on flotation

Conditions; Mesh of grind -150mesh, Flotation pH 7, Sulphuric acid 2kg/t

Stage	Cell gms	rpm	% S	Reagent	Dosage kg/t	CT min	FT min
RF	250	1200	20 /33	Sod Oleate	0.4+0.2 +0.2+ 0.2	3 each	4 each

Results

% Solids	Product	Wt%	% LOI	
			Assay	Distn
20	Float reject	20.0	18.00	90.0
	Non float	80.0	0.50	10.0
	Head Cal	100.0	4.00	100.0
33	Float reject	25.0	15.00	92.6
	Non float	75.0	0.40	7.4
	Head Cal	100.0	4.05	100.0

3.5 Reduction of Fe values in Wollastonite non float concentrate by WHIMS**;** The optimum flotation tests at-150 mesh of grind D_{80} 80microns, 33%S, pH 7 using 2kg/t H_2SO_4 as pH modifier and 1kg/t sodium oleate as collector yielded a wollstonite concentrate assaying ~95% wollastonite,2.64% Fe_2O_3 and 0.40% LOI which failed to meet ceramic grade due to ferruginous impurities. The non float was subjected wet high intensity magnetic separation using Eriez –Carpco 1X4L at 18000 Gauss intensity to remove the ferruginous impurities. The result of final test is given in Table 6. The final test comprising of soap flotation, WHIMS of non float yielded a wollastonite concentrate assaying 97%$CaO.SiO_2$, 0.50% Fe_2O_3, 0.95% Al_2O_3, and 0.41% LOI meeting the ceramic specifications at wt% yield of 70.0.

3.6 Final test: The beneficiation process comprises of [1] Rougher calcite flotation at -150mesh,D_{80}80 microns, 33%S, pH 7 using 2kg/t H_2SO_4 and 1kg/t of sodium oleate [2] two cleanings of rougher calcite float and recirculation of dewatered cleaner tails to rougher feed[3] Wet high intensity magnetic separation of Rougher tails at 19200 gauss. The results are given in Table 7. The above flotation –WHIMS process yielded a ceramic grade concentrate assaying 97%$CaO.SiO_2$, 0.49 % Fe_2O_3, 1.01% Al_2O_3 and 0.45% LOI at weight % yield of 75.0. The cleaner calcite float assaying 45.6%

Table 6; Final test- Flotation any WHIMS of non float

Conditions; Mesh of grind -150mesh, Flotation pH 7, % S 33, Sulphuric acid 2kg/t

Stage	Cell gms	rpm	% S	Reagent	Dosage kg/t	CT min	FT min
RF	250	1200	33	Sod Oleate	0.4+0.2 +0.2+ 0.2	3 each	4 each

WHIMS; 1x4 L Eriez-Carpco WHIMS, Ball matrix 6mm dia, 1 kg ball matrix, Current 4Amps [max], Intensity ~18000 gauss, Feed pulp 20%S at 0.2LPM, Wash water 1LPM, loading and unloading cycle time 2' each

Results;

Product	**Wt%**	**% Assay**		**%Distn**	
		LOI	**Fe_2O_3**	**LOI**	**Fe_2O_3**
Wollastonite Conc.	70.0	0.41	0.50	7.1	11.7
Mag rejects	5.0	0.20	33.00	0.3	55.0
Float rejects	25.0	15.00	3.99	92.6	33.3
Head [Cal]	100.0	4.00	3.00	100.0	100.0
Non Float [Cal]	75.0	0.40	2.67	7.4	66.7

Table 7; Final locked test- Flotation & WHIMS of non float
Conditions; Mesh of grind -150mesh, Flotation pH 7, % S 33, Sulphuric acid 2kg/t

Stage	Cell gms	rpm	% S	Reagent	Dosage kg/t	CT min	FT min
RF	250	1200	33	Sod Oleate	0.4+0.2 +0.2+ 0.2	3 each	4 each
I Cl	250	1200	19	-	-	-	3
II Cl	250	1000	10	-	-	-	3

Results

Product	**Wt %**	**% Assay**		**%Distn**	
		LOI	**Fe_2O_3**	**LOI**	**Fe_2O_3**
Wollastonite Conc.	70.0	0.40	0.49	7.0	13.3
Mag rejects	20.0	0.10	9.51	0.5	72.4
II Cl Float co conc	10.0	36.22	7.20	92.5	14.3
Head [Cal]	100.0	4.00	2.63	100.0	100.0
I&II Cl tails	10.0	3.99	2.50	10.0	9.5
Rougher feed	110.0	4.00	2.61	110.0	109.5
Non Float	90.0	0.33	2.50	7.5	85.7
Rougher float	20.0	20.51	3.12	102.5	23.8

4 Conclusions

Low grade Wollastonite samples from Sirohi, Rajasthan were received with the aim of evolving a beneficiation process to produce ceramic grade wollastonite concentrate containing wollastonite>97% and trace amounts of calcite, iron oxides and clay [<1% each]. The as received analysed 43.43% CaO, 2.70% Fe_2O_3, 2.21% Al_2O_3, 46.69% SiO_2 and 4.10% LOI. It contained mainly wollostonite with subordinate amounts of calcite with minor amounts of garnet, hornblende, iron oxides, quartz and clay. The beneficiation process comprises of [1] Rougher calcite flotation at -150mesh,D_{80} 80 microns, 33%S, pH 7 using 2kg/t H_2SO_4 and 1kg/t of sodium oleate [2] two cleanings of rougher calcite float and recirculation of dewatered cleaner tails to rougher feed[3] Wet high intensity magnetic separation of Rougher tails at 19200 gauss. The above flotation –WHIMS process yielded a ceramic grade concentrate assaying 97%CaO.SiO_2, 0.49 % Fe_2O_3, 1.01% Al_2O_3 and 0.45% LOI at weight % yield of 75.0. The cleaner calcite float assaying 45.6% CaO, 7.20% Fe_2O_3, 4.21% Al_2O_3, 5.89% SiO_2 and 36.22% LOI may be used as by-product as it meets cement grade.

Reference

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