Dispersion and Upgradation of Limestone from new Umrangshu, Assam, India

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Abstract

North Cachar district of Assam, India is endowed with a vast deposit of limestone at New Umrangshu (25°31'51" to 25°32'8" N latitude and 92°48'1" to 92°48'7" E longitude). The deposit contains about 116 million tones of limestone extended over an area of 3.5 square km, which is used presently for manufacturing cement. The limestone contains over 91% $CaCO_3$ (~ 51-52% CaO) with ~2.1-2.7% MgO, ~1.5-2.2% SiO_2 and ~0.8-0.9% Al_2O_3 mostly in the form of calcite with small to trace amounts of impurities like kaolinite, pyrite, illite. It was earlier reported that size classification leads only to marginal improvement of the limestone. The coarser fraction contains the maximum amount of CaO and minimum amount of SiO_2, Al_2O_3 and Fe_2O_3, whereas, the fine fraction contains the minimum amount of CaO and maximum amount of SiO_2 and Fe_2O_3. The impurities are evenly distributed in the limestone. The present communication reports the results of further works carried on beneficiation of the limestone. Fine grinding leads to liberation of the clay minerals; the major impurities of the limestone which may be removed by adopting dispersion-cum-settling technique resulting a fraction containing ~97% $CaCO_3$ (~54.3% CaO) with ~0.5% SiO_2 and ~0.6% Al_2O_3.

INTRODUCTION

Limestone is one of the most extensively exploited minerals. It finds use in manufacture of cement, building lime, paper, calcium carbide, bleaching powder, iron and steel, glass, ferro-alloys, fertilizers, rubber, toothpaste etc. The specifications of limestone for different purposes are different.

Almost all the states of NE region of India is endowed with vast deposits of limestone. R.R.L. Jorhat has initiated a program to systematically characterize the prominent limestone deposits of the region to access their utility and possibility of value addition [1,2]. Directorate of Geology and Mining, Govt. of Assam proved a limestone deposit containing about 116 million tones of limestone in a 3.5 square km area in New Umrangshu, North Cachar Hills, Assam (25°31'51" to 25°32'8" N latitude and 92°48'1" to 92°48'7" E longitude).

In an earlier communication [1] we reported the physicochemical characteristics of the limestone and possibility of upgrading the same by dry beneficiation technique. The limestone contains over 51% CaO and mineralogically it is calcite contaminated with small to trace amount of clay minerals, of which kaolinite is the major phase. Size classification reveals that the coarser fraction contains the maximum amount of CaO (51.79%) and minimum amount of SiO_2 (1.53%), and Al_2O_3 (0.79%) whereas, the fine fraction contains the minimum amount of CaO (50.92%) and maximum amount of SiO_2 (2.25%). The present communication reports the results of further works carried on upgrading the limestone by fine grinding followed by separation using dispersion cum settling technique.

MATERIALS AND METHODS

About 10 tones of limestone were procured from New Umrangshu deposit through Assam Mineral Development Corporation, Govt. of Assam, Guwahati. It was then subjected to size reduction in a jaw crusher followed by separation in to three fractions: $-25mm+18.75mm$, $-18.75+12.5mm$ and $-12.5mm$, which are marked as ULA, ULB and ULC respectively. A representative sample ULR, prepared by mixing the different sized fractions in the same proportions as obtained during crushing was further pulverized to $-150\mu m$ size in a planetary ball mill. A suspension (2 liter) of the pulverized representative sample in water 1% (w/v) was subjected to stirring (14 000 rpm) in a Hamilton beach mixture (NL Baroid, USA, Model 936-31S-1) in presence of dispersing agents (~1.0 g of $(NaPO_3)_6$ and ~0.1 g Na_2CO_3). The suspension (pH ~ 8.5) was then transferred to a cylindrical column and allowed to settle the $+70$ μm fraction by maintaining the appropriate sedimentation time worked out as per Stoke's law. The sediment was collected and dried at 100 ± 10 °C. The dispersed phase was further separated into three different size fractions (viz. ~ -70 $\mu m + 20$ μm, ~ -20 $\mu m + 2$ μm and $\sim - 2$ μm) by adopting dispersion cum settling technique and using Stoke's law and the separated fractions were washed and dried at 100 ± 10 °C. The procedure adopted for processing the limestone is schematically shown in Fig. 1.
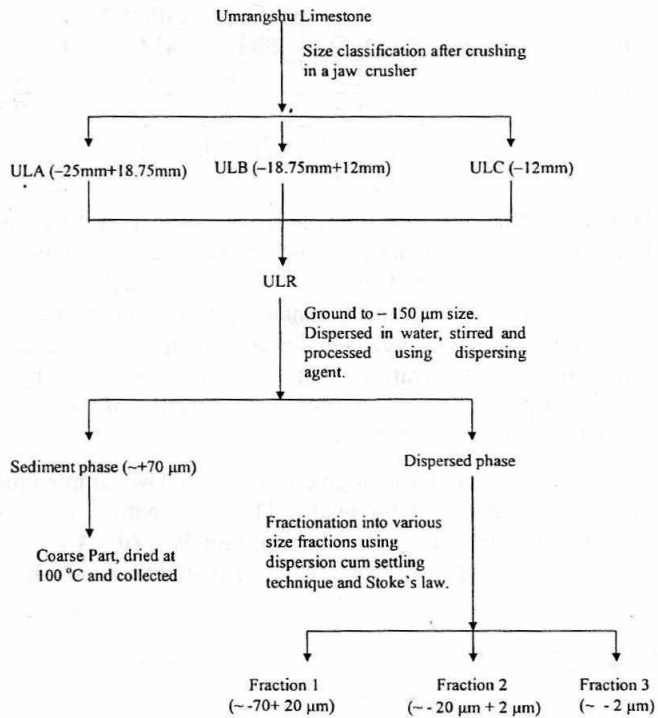

Fig. 1: Scheme for Recovering Various Fractions of Limestone Sample

The chemical analyses of the samples were done by standard methods of analysis [3]. The CaO, MgO and Fe_2O_3 contents were determined volumetrically using EDTA for the former two and potassium dichromate as oxidant for the later. The amount of SiO_2 and Al_2O_3 were estimated gravimetrically. Mineralogical characterization of the limestone sample and it's size fractions were performed using XRD analysis of random powder samples (Philips X-ray Diffractometer, Type PW1710, UK and Brucker D8 advance XPS, Germany) using Cu K_α X-radiation; Thermal analysis (TA instrument, model STD 2960, USA) under air flow rate of 100 ml/min, heating rate of 10 °C/min up to 1000 °C

and using calcined α-Al_2O_3 as the reference material in a platinum crucible; FTIR (Perkin Elmer System 2000 spectrophotometer, USA) using KBr pellet method; SEM (model LEO S430) coupled with EDXA (LINK ISIS, OXFORD INSTRUMENTS, UK) and particle size analysis (Laser Particle Size Analyser, Model CILAS 1180, France).

RESULTS AND DISCUSSIONS

The yield and chemical analyses of different size fractions obtained by processing the limestone sample are shown in Tables 1 and 2 respectively.

Table 1: Percentage Yield of Various Fractions Obtained on Processing of the Limestone

Fractions.	Yield (% w/w)
Coarse Part	57.23
Fraction 1	11.83
Fraction 2	25.02
Fraction 3	5.88

Table 2: Chemical Compositions of Feed Limestone ULR and its Fractions

Size Fractions	Chemical Composition (% w/w)					
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	LOI
ULR	51.75	2.57	1.70	0.83	0.81	41.50
Coarse Part	52.60	1.97	0.51	1.02	0.95	42.03
Fraction 1.	54.28	1.10	0.53	0.62	0.71	42.53
Fraction 2.	53.35	0.96	0.55	0.65	0.78	42.16

It is observed that the Coarse part contains about 57.23% of the limestone and its CaO and Al_2O_3 content is higher and SiO_2 and MgO contents are lower than the parent sample ULR. It's SiO_2 content (0.51%) is comparable to that of Fraction 1 and Fraction 2 and much lower than that in the parent sample (1.70%). Similarly the Fractions 1 and 2 contain higher amount of CaO (54.28-53.35%) and lower amount of Al_2O_3 than the parent sample. The Fe_2O_3 contents of all the fractions are comparable with that of the parent sample. Pulverization of the limestone followed by wet separation using dispersion cum settling technique leads to liberation and separation of the clay minerals present in it leading to a limestone fraction enriched with CaO.

The XRD pattern of the parent sample ULR is given in Fig. 2. The sample contains calcite (d=3.84, 3.02, 2.81, 2.47, 1.91, 1.59, Å) as the major phase. The XRD pattern of the Coarse part (Fig. 3.) indicates presence of Boehmite (d=6.2, 3.17, 2.35 Å), Goethite (d= 4.16, 2.68, 2.44 Å), Siderite (d=2.82, 1.74, 1.73 Å) and Pyrite (d=2.72, 2.42, 1.61 Å) in addition to Calcite (d=3.84, 3.02, 2.84, 2.48 Å).
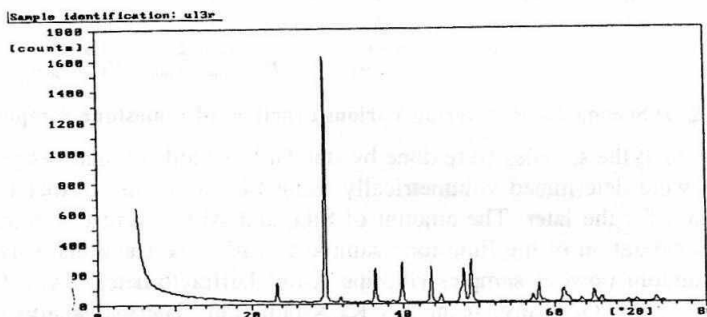

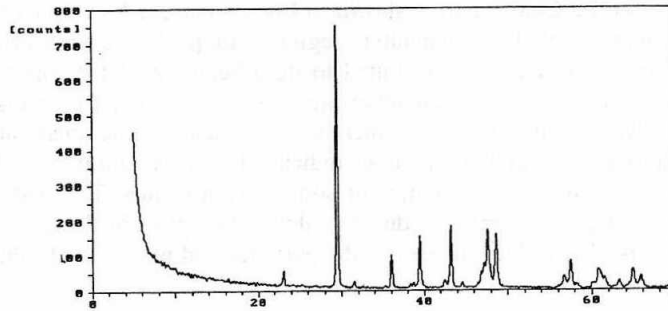**Fig. 2: XRD Pattern of ULR Sample**

Fig. 3: XRD Pattern of Coarse Part

The XRD patterns of Fractions 1 and 2 (Patterns not shown) also show paeks at d =3.84, 3.02, 2.84, 2.48, 1.91, 1.86, 1.59 Å due to calcite with small peaks for pyrite (d= 1.91, 1.62 and 1.44 Å), Kaolinite (d=7.15, 3.58, 1.49 Å) and Illite (d=4.46, 3.34, 2.55 Å).

The XRD pattern of Fraction 3 (Fig. 4.) reveals the presence of Kaolinite (d=7.15, 3.58, 1.49 Å) as the major phase, with small peaks due to Illite, Calcite and Pyrite. Peaks due to Boehmite, Goethite and Siderite are not observed in the patterns of Fractions 1, 2 and 3 [4].
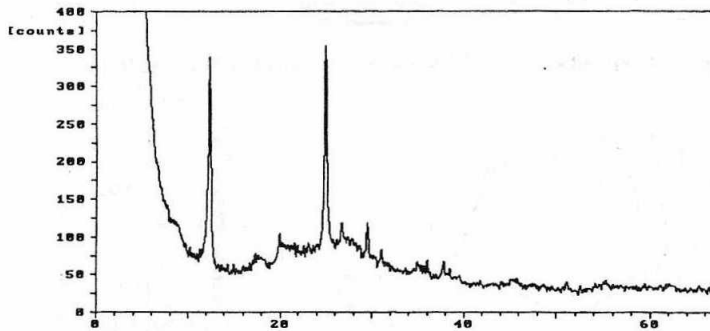
Fig. 4: XRD Pattern of Fraction 3

The particle size of the parent sample ULR ranges from 0.04 to 260 μm with (Table 3) the mean diameter of 57.46 μm. The Coarse part contains particles of even less than +70 μm size (32 % material). It is possible that Pyrite, Goethite, Boehmite etc. heavy minerals (as reveled by XRD) exist in the fraction which might be of finer size. The fraction 1 and Fraction 2 also contain particles finer than the targeted +20 μm and +2 μm size respectively. The latter may be due to clay minerals. On the other hand, Fraction 3 contains 66.43% particles in the size range −70 μm +2 μm. This indicates that many of the fine and medium sized limestone particles get dispersed under the condition and composition employed for dispersion. Optimization of dispersant dosage and composition may lead to selective separation of the particles.

Table 3: Particle Size Distributions in Different Size Fractions

Size Fractions (μm)	Particle size range (μm)	Mean Diameter (μm)	Diameter (μm) at cumulative %				
			90	70	50	30	10
Coarse Part	0.07-260	96.33	162.54	122.2	96.43	66.32	29.70
Fraction 1	0.07-71.00	17.09	32.02	22.10	16.24	10.50	1.42
Fraction 2	0.07-12.00	3.70	7.86	5.10	3.14	1.70	0.38
Fraction 3	0.04-71.00	13.98	36.01	20.10	9.17	1.70	0.66

Thermal analysis pattern of the Coarse part is shown in Fig. 5. The DTA curve of the coarse fraction exhibits sharp endotherm at 600-800 °C temperature regions with peak at around 770 °C, accompanied by weight loss in TG and DTG curve is attributed to decarbonation of the limestone. The thermal curves of Fraction 3 (Fig. 6.) show weak endothermic trend accompanied by weight loss at around 100 °C, attributed to dehydration of clay minerals. The endothermic peak at around 500 °C accompanied by weight loss in TG and DTG curves indicate dehydroxylation of kaolinite. Exothermic trend noted above 850 °C is also characteristics of some clay minerals. The pattern also exhibits a weak endotherm at ~650 °C, which may be due to calcite. The drop in decarbonation temperature from 750 to 650 °C may be due to the fineness of the particles and presence of other materials as the major phase [5,6].
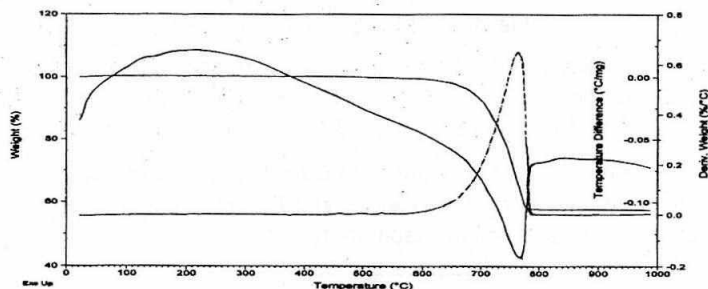

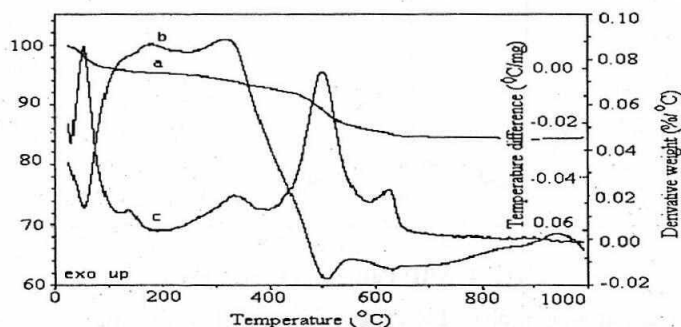**Fig. 5: Thermal Curves of Coarse Part, (A) TG (B) DTA, (C) DTG**

Fig. 6: Thermal Curve of Fraction 3 (A) TG, (B) DTA, (C) DTG
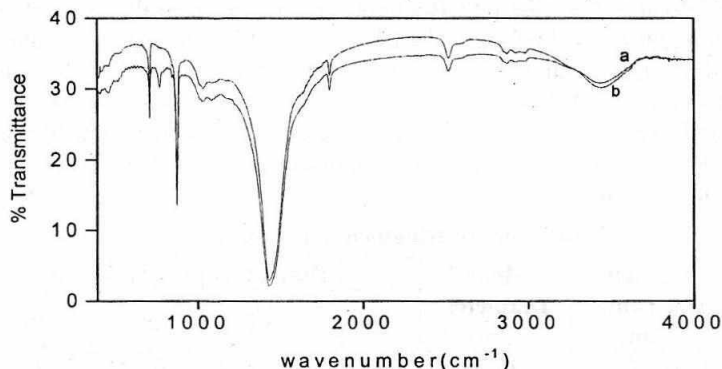

Fig. 7: FTIR Spectra of (A) ULR and (B) Coarse Part

The FTIR spectra of parent sample ULR and Coarse part are shown in Fig. 7. In the spectra, IR bands at ~713, 876, 1427 and 2514 cm^{-1} are diagnostic bands for calcite. The weak peaks at ~470 and 537

cm^{-1} are assigned for $\equiv$Si-O asymmetric bending vibrations of quartz, feldspar and other alumino/aluminiumsilicate group of minerals. Small peak at ~913 cm^{-1} is due to Al...O-H$^-$ vibrations. Bands at 1008 and 1032 cm^{-1} are indicative of ν_{Si-O} vibration. The peaks at ~1084 and 1112 cm^{-1} are due to ν_{as} vibrations of Si-O-Si. Presence of water in the sample is revealed by peaks at ~3447 and 1799 cm^{-1} [7]. The small peaks at the region ~2598 – 2983 cm^{-1} may be for organic matters present in the sample.

The FTIR spectra of Fraction 3 (Fig. 8) exhibits sharp peaks at ~470, 537, 753, 913, 1032, 1108, 3694 and 3620 cm^{-1}, characteristics of the clay mineral kaolinite. Band in the region ~1430 cm^{-1} indicates presence of carbonate bearing minerals [8].
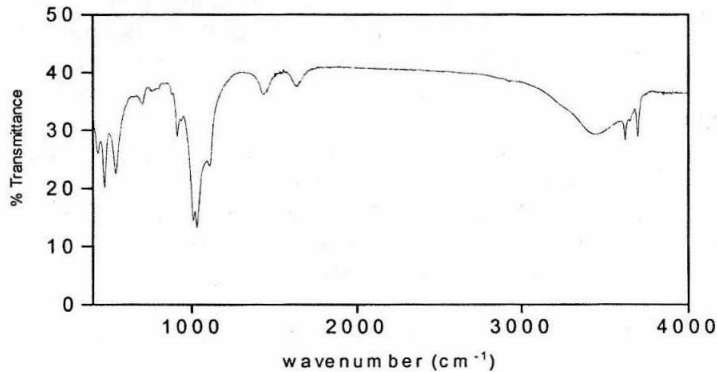

Fig. 8: FTIR Spectra of Fraction 3

The SEM-EDXA pattern of Fraction 3 (Fig. 9) shows combination of plate like, layered and irregular shaped flaked particles characteristics of clay minerals [9]. The EDXA data also suggest presence of clay minerals and aluminosilicate in addition to calcite.
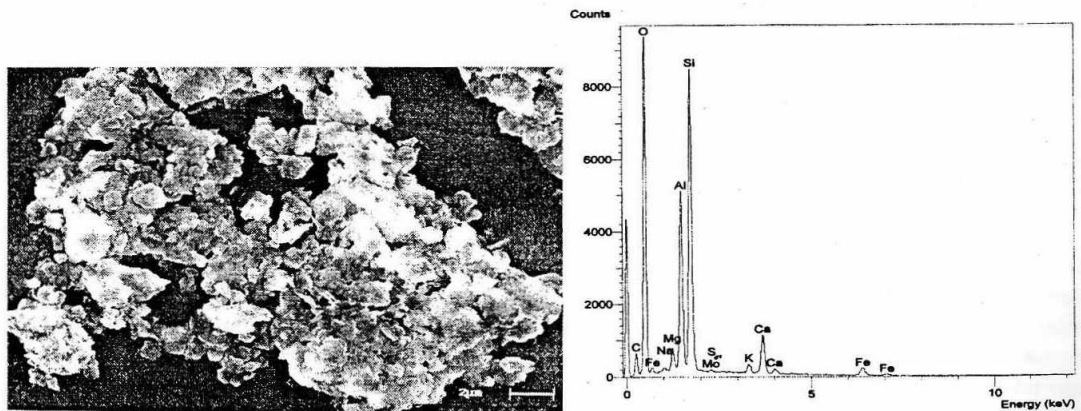

Fig. 9: SEM-EDXA of Fraction 3

CONCLUSIONS

The clay minerals present as the major impurity in Umrangshu limestone are liberated by fine grinding and are separated by adopting dispersion cum settling technique. A limestone fraction (~12%) with ~97% $CaCO_3$ may be obtained from the parent sample containing ~91% $CaCO_3$. It may be possible to improve the yield and quality of the limestone fractions by optimizing the grinding parameters, nature and dose of the dispersing agent etc.

ACKNOWLEDGEMENTS

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