Pakistan J. Sci. Ind. Res., Vol. 18, Nos. 3–4, June–August 1975

EVALUATION OF MUSAKHEL LIMESTONE FOR MAKING COLOURLESS GLASS

AHMAD DIN, MOHAMMAD ASHRAF and M. R. ARIFF

PCSIR Laboratories, Lahore

(Received June 5, 1974; revised January 4, 1975)

Abstract. Six limestone formations of Sakesar, Nammal, Khairabad, Ceratite and Productus beds were studied from Musakhel in detail for their uses in colourless glass manufacture. The Productus limestone samples of Permian system contain the minimum Fe_2O_3 contents. After beneficiation one of the samples of this system in combination with Daud Khel[1] sand was used for making colourless glasses and the results were found very satisfactory.

This work is part of the programme being conducted in these Laboratories on the evluation, beneficiation and utilisation of indigenous glass raw materials. Sand and limestone are the naturally occurring rocks which are incorporated in the glass batches to the extent of 70–74% and 10–13% respectively. Although a good deal of work on the evaluation of glass making sands[1,2] has been undertaken, no comprehensive study has been reported on the evaluation and utilisation of limestone available in the country.

Large deposits of limestone are found in the bare and well exposed mountains of Chidru, Marmandi, Sakesar, Nammal, Daudkhel and other areas of the Salt Range. The outcrops extend for a distance of more than one hundred miles from Katha in the east and beyond Kalabagh in the west. Limestone can be found in many hundred feet thickness from Permian to Eocene systems in and around the Nammal Gorge area which can be approached directly by metalled road from Mianwali.

Glass industrialists using the Musakhel limestone as such complain of the inferior properties of their finished products; most prominent amongst them being the undesirable green colour, caused by the presence of colour impurities present in limestone.

It is of practical interest, therefore, to undertake investigation for the evaluation and utilisation of this limestone for making colourless glass.,

Scope of Investigation

Representative bulk samples of limestone were collected by one of the authors personally. On preliminary studies, it was found to contain impurities in three distinct form : (a) as surface stains; (b) specks of limonite; and (c) as acid insolubles.

In the light of the above facts it was planned to include, in the present study the following operations for the evaluation and utilization of the limestone.

(1) Microscopic study to categorise limestone samples according to their ages and to know which deposit is better as far as its CaO and Fe_2O_3 contents are concerned.

(2) Surface stains removal and subsequent water washing to remove the surface scale containing most of the Fe_2O_3 contents and the limonite fractions present as iron oxide specks.

(3) Chemical analysis to find out the CaO content and impurities present in the limestone and determine the grade to which the various samples belong.

Experimental

Field Study. Six different samples of limestone from L-1 to L-6, from different formations of Musakhel have been studied in the present investigation. The stratigraphic position of different samples is (iii) Sakesar limestone (L–1); (ii) Nammal limestone (L–2) of Eocene system; and (i) Khairabad limestone (L–3).

(C) Upper Jurassic limestone; (B) Ceratite (beds) limestone (L–4) of Triassic system; and (A) Productus limestone (L–5 and L–6) of Permian system.

Chemical Analysis. About 200 g solid samples were thoroughly ground. The sample was spread out in a layer and portions were taken from different parts to yield a sample of approximately 20 g. This sample was further finely ground and dried at 110°C in an oven for chemical analysis. Samples were then analysed chemically, according to British Specifications.[3] The constituent determined were insoluble matter including silica, Fe_2O_3, Al_2O_3, CaO and MgO. The results are given in Table 1.

Petrological Examination. Suitable samples were first studied microscopically for colour, hardness, lustre and structure. The better samples of limestone, i.e. L–1, L–5, L–6 as shown by chemical analysis, were studied under a microscope for identification of undesirable impurities like iron oxide, dolomite and quartz (Table 2).

Beneficiation of the Limestone. After rubbing off the surface scale containing most of Fe_2O_3 the different bulk samples were further washed with water to remove the loosely held impurities such as limonite. The washed samples were dried at 110°C in an oven, finely ground for chemical analysis (Table 3).

Preparation of Colourless Glass. A commercial glass composition[4] used for tableware and beverage industry was selected for the present study. The batch compositions are given in Table 4. The raw materials used were the Musakhel limestone (L–6) and the Daudkhel sand studied previously.[1] The minimum quantity of selenium and cobalt oxide used for were taken from the work of Löffler[5] and the amounts varied to match the domestic raw materials. The batch glass weighing 821 were melted in fire clay crucibles at 1400°C. The maximum temperature was maintained for 3 hr and the temperature was then lowered to 1260°C and maintained for another 2 hr to dissolve the occulded gases. Melts were poured and the glass samples annealed. The glass composition No. 4 was also tried on commercial scale by one of the authors.

Discussion

The results of the chemical analysis of limestone samples are given in Table 1. Sample Nos. L–5, L–6 and L–2 have high calcium oxide and low insoluble matter. The rest of the samples show a low CaO content. According to Pakistan Standards[6] L–5 and L–6 can be categorized as grade 'A' limestone as far as the glass manufacturing side is concerned. The field study[7] of this area (see experimental) reveals that the samples L–5 and L–6, frcm separate and thick beds, belong to the Productus limestone of Permian system. The chemical analysis (Table 1) further shows that the iron content of the Productus limestone samples is very low as compared to the Ceratite limestone, L–4 of Triassic system and Sakesar limestone L–1, Nammal limestone L–2, Khairabad limestone L–3 of Eocene system. From the foregoing facts it is advisable to select from the Musakhel region abundantly available Productus limestone of Permian system because of its high CaO, low acid insolubles and Fe_2O_3 content.

The petrographic analysis (Table 2) conducted on limestone samples reveals that Productus limestone of Permian system L–5 and L–6 are almost white rocks with a few limonite specks in some places. The rest of the samples show regular iron oxide specks and high contents of quartz, dolomite and limonite. The beneficiation of the Musakhel limestone samples reduces the Fe_2O_3 content (Table 3) from 5.9 to 63%. The maximum reduction is in case of L–5 and L–6 samples belonging to the Productus limestone series which shows that the ferruginous matter containing mostly Fe_2O_3 is loosely held and is removed by scratching with iron or brass brushes and subsequent water-washing. The maximum percentage of iron oxide that can be tolerated in a good decolourised glass is 0.06%. The sands of Daudkhel region after water–washing, exhibit Fe_2O_3 content from 0.02 to 0.05%. Therefore, limestone samples L–5 and L–6 are suitable for blending with the above mentioned sands for making colourless glass. These limestone samples adding 8.7% CaO to the total glass composition contribute roughly 0.01% to 0.004% to the total iron content of 0.06%.

In view of the low Fe_2O_3 content only the L–6 limestone was blended with a representative glass sand from Daudkhel region,[1] using a standard glass composition used for glass tableware and beverage bottles. As is evident from Table 4 only the amount of selenium and cobalt oxide is varied. Increasing the cobalt oxide beyond 0.02 g/1000 g of sand yields a glass of undesirable tint (composition No. 3). Keeping cobalt oxide constant at 0.02 g/1000 g sand the amount of selenium is increased (glass composition Nos. 4 and 5) the resulting glass No. 4 containing 0.002 g cobalt oxide and 0.045 g selenium/ 1000 g sand is completely decolourised. Increasing the selenium-content beyond 0.045 the tinge of the decolourised glass aft r annealing turns reddish which may be du to the excessive use of selenium. The best selected composition 4 was tried on a commercial scale and the results are found very satisfactory.

TABLE 1. CHEMICAL ANALYSIS (wt%).

No.	Insoluble matter including silica (%)	CaO (%)	R_2O_3 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	MgO (%)
L-1	0.535	51.48	0.77	0.271	0.499	0.76
L-2	1.290	54.20	10.71	0.399	0.311	Traces
L-3	1.33	51.68	1.22	0.439	0.781	Traces
L-4	3.64	50.80	1.32	0.399	0.921	Traces
L-5	0.46	55.04	0.64	0.159	0.481	0.68
L-6	0.47	55.10	0.325	0.127	0.198	Traces

TABLE 2. PETROGRAPHIC ANALYSIS.

Megascopic examination	Microscopic examination
L-1 *Colour.* Light grey with occasional yellowish and bluish tints. *Hardness.* 3·5 *Lustre.* Vitreous. *Structure.* Crystalline form of grains of calcite which are not perfectly developed, i.e. they are corroded and compact.	*Texture.* Fine, medium and coarse-grained crystals which are cemented together. *Minerals* *Calcite.* Thin section is almost colourless to grey shows cloudiness. Minerals assemblage is fine to coarse-grained and anhedral, but foraminifra are perfectly developed showing each chamber of their growth. Cleavage is poor. *Quartz.* Three scattered medium and subhedral grains are present in the section studied. *Iron Oxide.* Fine-grains and specks of iron oxide are present.
L-2 *Colour.* Grey with some bluish tint. *Hardness.* 3·5 *Lustre.* Vitreous. *Structure.* Crystalline form of grains corroded and compact.	
L-3 *Colour.* Dark grey with some yellowish and brownish tints. *Hardness.* 3·0 *Lustre.* Earthy. *Structure.* Consists of fine-grained crystals of calcite and clay. Small pure and white calcite veins are also present in some of the hand-specimens. The rock is compact.	
L-4 *Colour.* Light yellow and cream-coloured limestone. *Hardness.* <3 (2·5) *Lustre.* Earthy. *Structure.* Micro-fossiliferous clayey limestone, grains are very fine. The sample is not very compact.	
L-5 *Colour.* Almost white with some yellowish specks. *Hardness.* 3·0 *Lustre.* White, vitreous. *Structure.* Consists of medium-grained to coarse-grained crystals which are corroded. Grains are highly tightened together.	*Texture.* Fine, medium and coarse-grained crystals, which are compactly cemented together. *Minerals* *Calcite.* Almost the whole thin section consists of calcite. It shows light grey colour. Grains are fine, medium and coarse. Some shows well developed rhombohedral and parallel cleavages while fine aggregates are without cleavages (98 %). *Dolomite.* Only two grains give properties of dolomite. Dolomite grains show highly well-developed rhombohedral cleavage (1 %). *Quartz.* One medium grain of quartz is present. Which is subhedral in form (0·5 %). *Iron Oxide.* Very fine grains and a few specks of iron oxide are present (1 %).
L-6 *Colour.* Almost white with some yellowish specks. *Hardness.* 3·0 *Lustre.* Vitreous. *Structure.* Consists of mostly coarse-grained crystals, most of the grains are well developed while others are corroded. Some genera of foraminifera are also present. Grains are highly cemented together.	*Texture.* Medium to coarse grains crystals with foraminiferal fossils. *Minerals* *Calcite.* It is predominant, well-developed and is from fine to coarse-grained in size. It is colourless and cloudy thin section. Shows anhedral to subhedral aggregate. cleavages are perfect rhombohedral and parallel. Foraminifera are well developed (99 %). *Iron Oxide.* Very fine-grains and some specks of iron oxide are visible in the thin section (0·8 %).

TABLE 3. COMPARISON OF Fe_2O_3 CONTENTS OF BENEFICIATED AND UNWASHED SAMPLES.

No.	Percentage of Fe_2O_3 in unwashed samples	Percentage of Fe_2O_3 in washed sample	Decrease in Fe_2O_3 content (%)
L-1	0.271	0.255	5.9
L-2	0.399	0.303	24.0
L-3	0.439	0.342	22.0
L-4	0.399	0.375	6.2
L-5	0.159	0.110	30.8
L-6	0.127	0.047	63.0

TABLE 4. COMPOSITION OF VARIOUS BATCH FORMULATIONS EXPRESSED IN PARTS BY WEIGHT (g).

Glass No.	Silica sand	Feldspar	Limestone	Soda ash	Saltpeter	Arsenic	Selenium	Cobalt oxide	Resulting colour
1.	1000	46	224	367	5·1	1·5	0·02	0·001	Yellowish green
2.	1000	46	224	367	5·1	1·5	0·03	0·002	Yellowish green
3.	1000	46	224	367	5·1	1·5	0·04	0·003	Colourless with greenish tinge
4.	1000	46	224	367	5·1	1·5	0·045	0·002	Colourless
5.	1000	46	224	367	5·1	1·5	0·050	0·002	Colourless with slightly reddish tinge

Acknowledgements. The authors wish to thank Mr. Zia Haider for the chemical analysis of the limestone samples and Mr. M.R. Sheikh for his help in the preparation of the manuscript.

References

1. Ahmad Din, Ghulam Rasul and M.A. Rana, Commercially Exploited Glass Sands of West Pakistan, Pakistan J. Sci. Ind. Res., **15,** 1 (1963).
2. F.A. Faruqi, *Glass Sands of Pakistan,* PCSIR Laboraatories, Lahore, 1969 Bull. No. 7.
3. B.S.I. No. 3108 (1959).
4. S. R. Scholes, *Modern Glass Practice* (Industrial Publications, Chicago, 1953).
5. H. Löffler, *Entfarbung von Glas*, Glashutten-Handbuch, (HVG, Frankfurt, 1941) R41–1–R41–5.
6. Pakistan standard for limestone for making colourless glass (private communication, 1973).
7. M. Ashraf, M.R. Shaikh and M.R. Ariff, Pakistan J. Sci. Ind. Res., **10,** 296 (1967).
8. F.V. Tooley, *Handbook of Glass Manufacture* (Ogden, New York, 1961), p. 294.