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COMMERCIALLY EXPLOITED GLASS RAW MATERIALS OF PAKISTAN*

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Representative samples of sand, dolomite, marble/limestone and soda feldspars now being commercially exploited by the glass industry have been evaluated for their chemical and mineral contents and utility. Sands from Mianwali possess a SiO_2 content over 99% and of Fe_2O_3 of less than 0.04% after simple water washing. The Fe_2O_3 content of Thana Bullah Khan samples is in the range of 0.09 – 0.1%. On the basis of the Fe_2O_3, CaO and mineral contents of the marble/limestone, samples from Swawai (Swabi) and Pampokha (Swat) areas are rated as the best calcite limestones. The pampokha limestone has some streaks of dolomite embeded in it. The feldspars from Dadar Sanitorium and Jaba are good soda feldspars, while the feldspar from Dalbori shows some Ca spar contents as is also confirmed by chemical analysis. The dolomite of Gundai Turrako Hills shows iron contents of 0.1 – 0.2%.

INTRODUCTION

The basic raw materials for all types of glasses may be divided into two categories: (i) chemical and (ii) naturally occurring materials. Soda ash, potash, sodium sulphate, borax, boric acid, zinc oxide and many others including minor ingredients belong to the first category. These chemicals are of constant composition and are available from the market. The materials of the second category, i.e. naturally occurring materials are silica sand, marble/ limestone, dolomites feldspar. Huge deposits of these naturally occurring raw materials have been discovered in Pakistan but their compositions vary from one deposit to another.

The suitability of a particular raw material depends upon its purity, availability at a reasonable cost and grain size distribution. Utmost importance is therefore attached to the quality of raw materials to prevent undesirable impurities from entering the finished glass. Iron oxide is probably the most troublesome impurity encountered in glass. Uniformity of grain size allows a uniform melting rate. Coarse grains, which take longer time to melt, may create areas of different viscosity and may even survive the melt to leave small crystalline imperfections in the finished glass. Grains that are too fine will also cause melting difficulties.

Since the inception of the Glass and Ceramics Division of the PCSIR Laboratories, Lahore, special attention has been diverted to the problems having a direct bearing on the industrial needs of the country. Realising the fact that minerals are indispensable to the industrial economy of the country, the research activities of the division has been directed towards assessing the quality and evaluating the minerals [1-4] used in glass industry of Pakistan. Development work was also carried out to make various glass products utilising the available glass raw materials and the results were made known to the industry. The aim of this paper is to evaluate and to compile data of some of the most valuable sources of glass raw materials now being utilised and needed by glass industries of Pakistan. Moreover the present data will be a great help to those engaged in the field of glass and ceramics industries.

SCOPE OF INVESTIGATION

Bulk samples of sand, feldspar, limestone, dolomite and magnesite were collected either from quarries or from the bulk storage of glass industries and represent the actual industrial feed samples. On preliminary studies the limestome, feldspar and dolomite samples were found to contain the impurities in three distinct forms: (i) surface stains, (ii) minor impurities in the main body, and (iii) 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 above minerals.

1. Microscopic and geological study: To categorise the deposits according to their ages and to know the extent of deposits and impurities in the deposits.

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2. Surface Stains: Removal of the surface scale containing most of the Fe_2O_3 content and the limonite fractions present as iron oxide specks.

3. Grading and chemical analysis of the washed beneficiated samples: To determine grade to which the various minerals belong.

Only the water washed and density separated samples of sand (except in the case of Kutki-Chopri) were analysed for their chemical content and grain-size distribution.

EXPERIMENTAL

1. Petrographic Examination. – Five different samples of marbles/limestones, 4 samples of feldspar and dolomite were first studied microscopically for colour, lustre and structure and then for impurities like iron oxide, dolomite and quartz. The results were shown in Table 3, 4 and 5.

2. Chemical Analysis. – After rubbing off the surface scale and following the standard methods of chemical analysis, the limestone/marbles, dolomite and magnesite samples were analysed for CaO, MgO, Fe_2O_3, Al_2O_3 and SiO_2. Results are given in Tables 3 and 4. Using the same techniques the beneficiated sand samples and feldspars were analysed for their chemical content and the results are presented in Table 1 and 5.

RESULTS AND DISCUSSIONS

1. Glass sands. – Silica sands are composed predominantly of quartz grains with minor but variable amounts of silicates, carbonates and iron oxides. Sometimes these grains are loosely cemented and do not need any crushing and subsequent sieving operations. This is usually the case with the Karachi area sands. The deposits of these sands are 44-60 miles away from Karachi on both sides of the National Highway. The silica sandstone from Mianwali area is comprised of cemented but friable sand grains and requires crushing and sieving. At present the main centres of their commercial exploitation are the Khairabad mines, Zahri Banda (Qamar Mashani) and Kutki-Chopri. The deposits are extensive and located about 45 miles from Mianwali city.

Silica sand constitutes about 70% of all the glass raw materials and its quality determines the end products. According to BS 2975, 1958, optical glass requires the purest sand (minimum silica, 99.5%, maximum iron oxide, 0.008%), and at the lower end of the scale is the sand for the general colourless container and flat glassware (minimum silica, 98.5%, maximum iron contents, 0.03%). It should be noted that many flat window glasses are actually green if viewed from an oblique angle but are, for practical purposes, regarded as colourless. An iron content of 0.1% may therefore be quite acceptable in a sand used for such glasses and the minimum silica content, as is practised in the country's sheet glass industry, may also be waived off if the silica is partially replaced by a non harmful or even beneficial impurity such as alumina.

As far as granulometry is concerned, KTG recommends a retention of greater than 85% of the sand on a 100-mesh Taylor Sieving System. These sands conform to this standard (Table 1).

In the light of the BS specifications all the sands studied except those of the Thana Bullah Khan (Table 1), are suitable for making medium quality tablewares and good quality containers and flat glasses. Using the modern techniques of scrubbing and water washing the sands from Qamar Mashani, Kutki-Chopri are being used for the manufacture of good-quality containers and tableware. Results of the simple water washed Thana Bullah Khan sand are given in Table 1. The iron oxide content is slightly higher than desired for colourless containers. The Thana Bullah Khan sand is being exploited for colourless containers by the Baluchistan glass industry after scrubbing and water washing. The sheet glass industry of Pakistan may use the unwashed sands provided the iron oxide content does not exceed 0.1%. If these industries desire to manufacture good quality sheet glass, they must include the techniques of scrubbing and density separation in their units. The coarser fraction in density separation carries most of ferrugenous fraction (see Table 2) and makes the above 500 micron sand unfit for colourless glass manufacture. The coarser fraction of the density separator carrying most of the iron oxide may be used for amber and green glass production.

2. Limestone Marble and Dolomite. – Limestone and dolomite from Swawai, Gundai Terrako and Pampokha which are now being used in the glass industry have been studied. In addition to this, limestone from the Jamshoro area has also been investigated. The results are given in Table 3. The limestones of Gundai Terako-Swawai-Pampokha area were formed as a result of metamorphism and belong to the Cambrian age. The deposits are of two types: compact white and friable (loosely cemented grains). The second type of limestones are finding use in the glass industry because of their low Fe_2O_3 and high CaO contents. They are also easy to crush. Their occurrence is widespread and the rock is generally granoblastic. The extent of the deposits is still to be reinvestigated. The minor impurities are surface scaling and quartz. The CaO content is 55-56% and approaches the average chemical formula $CaCO_3$.

Table 1. Chemical composition and physical characteristics of commercially exploited glass sands of Pakistan

Locality / Chemical Constituents	Thana Bullah Khan Karachi	*Khairabad Mines/Daudkhel	Kutki Chopri/ **Mianwali	Zohri Banda (Qamer Moshani)
	100-500 microns (%)	100-500 microns (%)	100-500 microns (%)	(%)
I/L	0.2	0.2	0.18	0.12
SiO_2	99.05	99.56	99.38	99.40
Al_2O_3	0.38	0.24	0.12	0.2
Fe_2O_3	0.096	0.025	0.035	0.03
CaO	0.21	0.05	0.06	0.15
MgO	–	0.02	0.03	0.01
Total	99.906	100.095	99.805	99.91
% Retained on Taylor Mesh No. 100-500 microns.	⩾ 85	⩾ 85	⩾ 85	⩾ 85
Bulk Density lb/ft^3	95	103	103.5	100
Grains	Angular-round	–	Angular-round	Angular-round

* Sand obtained by crushing sand stones.
** Results of a floated scrubber and density separator plant.

Table 2. Beneficiation of the Kutki Chopri sand by scrubbing and density separation-floatex plant.

State of Sand / Chemical contents	Run of *mines %	100-500 micron sand scrubbed and density separated %	Above 500 microns %
I/L	0.38	0.18	0.25
SiO_2	98.16	99.38	97.81
Al_2O_3	1.10	0.12	1.7
Fe_2O_3	0.095	0.035	0.1
CaO	0.26	0.06	0.2
MgO	0.01	0.03	.005
Total	99.995	99.805	100.065

* The above are the average results of various samples.

The average Fe_2O_3 in a furnace-feed descaled limestone is 0.006/.

According to the BSI the Fe_2O_3 in common glass must normally be less than 0.06% and for special optical glass the maximum acceptable upper limit may be 0.01 – 0.02%. The limestone from Swawai-Gundi-Terako-Pampokha area conforms to BS specifications. The black streaks in the Pampokha area limestones are the result of dolomitisation process.

The Jamshoro and other Karachi region limestones are fossiliferous limestone of the Eocene period. The deposits are extensive. These limestones are fine to medium-grained of about 99% purity. Minor impurities are in the form of clay and quartz minerals. The result of chemical contents are shown in Table 3. The average CaO content is 54.40% and Fe_2O_3 0.027% and these are suitable for making the common type of glass.

The delomite of Ghundai Terako [6] is white to light grey and weathers to a brown colour. It is fine to coarse grained as compared to the Hazara dolomite. Dolomite is Ghundai Terako is about 50-65' thick with a dip of about 40-45^o N.E. The dolomite is quite massive and well joined. The contact of different formations is gradational except for limestone which shows sharp contact with the dolomite. The best exposed contacts are seen at Gundai Terako Hill where quartzite gradually changes to siliceous dolomite and finally to dolomite. The dolo-

Table 3. Chemical analysis including physical characteristics of the commercially exploited limestone/calcite

Locality Chemical constituents %	Swawai A	Swawai B	Pampokha	Ghundai Terako Hills	Jamshoro
L/I	43.8	43.6	66	43.6	44
SiO_2	0.14	0.2	0.18	0.3	0.25
Al_2O_3	0.06	0.05	0.04	0.75	0.01
Fe_2O_3	.006	.005	.007	0.015	0.027
CaO	56.0	55.48	55.6	54.80	54.40
MgO	0.04	0.02	0.23	0.2	0.05
K_2O	0.1	0.48	0.08	0.22	0.03
Na_2O	0.04	0.05	Nil	0.03	0.28
Total	100.18	99.86	100.18	99.815	99.317
Colour	White	White	White with patches or grey colour.	Greyish	Almost white
Texture:	Grano-blastic highly-pure.	Grano blastic highly pure.	Medium to fine grained.	Granoblastic micro to criptocrystalline.	Hydrated Limestone fine to medium grained.
Minerals:	Nonen	Nonen	Traces of Apatite and Quartz	Traces of Quartz	99% Calcite, minor clay, one to two grains of quartz.
Age of Formation:	Cambrian age	Cambrian age	Cambrian age	Cambrian age	Eocene age group.

Table 4. Chemical and mineralogical composition of some of the dolomite and magnesite deposits of Pakistan.

Locality: Chemical constituents %	Gundai Terake Hills G1	G2	G3	G4	Aaluli (Tanol) A1	A2	Muslimbagh Magnesite
SiO_2	1.85	1.02	0.6	0.75	0.43	0.28	0.51
Al_2O_3	2.14	1.85	1.00	0.48	1.40	1.02	0.11
Fe_2O_3	0.23	0.2	0.14	0.14	0.2	0.24	0.1
CaO	31.73	30.39	30.26	29.29	31.56	31.45	0.6
MgO	19.01	20.83	21.11	21.86	21.11	21.21	47.72
L.O.I.	45.0	45.7	46.97	47.26	45.26	45.40	51.03
MgO/CaO	0.599	0.635	0.698	0.746	0.669	0.674	79.53
Colour:	Light Grey to White				Light Grey		White
Minerals	Calcite, limonite, magnetite and quartz				Calcite, limonite and traces of quartz.		Traces of quartz and calcite; almost a pure mineral.
Texture:	Mostly fine and medium in size, coarse grains are present in veinlets only.				Fine to very fine. Crystals are mostly subhedeal to anhedral.		Fine to medium grain. Very pure type of magnesite

Table 5. Chemical analysis and physical characteristics of some of the soda feldspar deposits of Pakistan.

Locality: Chemical Analysis (wt %)	Bousa Char	Dadar Sanitorium	Jaba	Dilbori
L.O.I.	0.40	0.3	0.4	0.2
SiO_2	67.80	70.05	66.20	67.50
Al_2O_3	2.0	18.30	23.50	16.80
Fe_2O_3	0.06	0.05	0.04	0.03
Na_2O	11.50	10.75	9.20	12.23
K_2O	0.10	0.08	0.20	0.04
CaO	0.03	0.35	0.25	2.90
MgO	0.3	0.04	0.04	0.13
P_2O_5	Nil	Nil	Nil	Traces
Total	100.19	99.22	100.79	99.83
Colour after firing at 1000°c	White	Buff	White	White
Minerals:	Albite, traces of quartz and dolomite	Free quartz; albite	Traces of mica; main body is albite.	Apatite, major albite, traces of plagioclase, quartz, sphene, muscovite. All in traces except for apatite and sphene.
Texture:	Fine grained.	Fine grained. Well cemented.	Fine grained; most of the material is powdered.	A mixture of compact and powdered material.

mite portion is fine grained coarsening towards the approach of marble. Moreover, gradual change in colour is also observed towards increased whiteness.

The results of the chemical analysis of dolomite are shown in Table 4. The MgO and CaO contents approach the desired limits but the Fe_2O_3 contents are a little higher. Considering the allowable limit of 0.1% Fe_2O_3 in sheet glass the dolomite of Ghundai Terako is quite suitable for sheet glass manufacture. Factories desiring good-quality glass products may incorporate Muslimbagh magnesite along with limestone in their batch formulations.

3. *Feldspars of Pakistan.* – The chemical and mineral contents of the feldspars from Bousa Char, Dadar Sanitorium and Dilbori can be seen from Table 5. The main mineral is albite with traces of quartz and dolomite in the Bousa Char feldspars. Dadar Sanitorium has got free quartz in it while traces of muscovite are found in the Jaba feldspar. The minerals of Dilbori feldspar are apatite, traces of plagioclase, sphene Muscovite and quartz. The Al_2O_3 contents of all these feldspars are 17-23% and the Na_2O content is 9-12%. The Fe_2O_3 content is very low. At present these are good soda feldspars deposits being exploited commercially.

The impurities are not objectionable but thanks to the suppliers, the factory owners are forced to use aluminium hydrate instead of the cheap naturally occurring raw material feldspars. Foreign countries are beneficiating feldspars to upgrade the feldspar. The Fe_2O_3 contents in the upgraded feldspars is 0.05%. Pakistani feldspars mentioned in the paper are good quality feldspars but care must be taken on the part of the suppliers mining the minerals.

4. *Glass Manufacture.* – The glass obtained by using density separated sands of Chopri, Pampokha limestone and feldspars from Dilbori and proper adjustment of minor ingredients was colourless. The glass composition was SiO_2 (73%), CaO (11%), Na_2O (13.8%), and Al_2O_3 (1.2%). The results have been verified on a 40 ton/day furnace.

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