Pakistan J. Sci. Ind. Res., Vol. 31, No. 9, September 1988

STUDIES ON ECONOMIC POTENTIALS OF NEPHELINE SYENITE OF KOGA (SWAT) FOR MAKING COLOURLESS GLASS

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(Received May 22, 1988; revised September 17, 1988)

Six samples of Nepheline syenite collected from Koga area (Swat, NWF) have been investigated to find their suitability for the manufacture of colourless glass. This work involves geology, microscopic study, crushing grinding, grading, chemical analysis, magnet treatment and glass melting. The iron content in the raw samples varied in the range 0.87 to 2.7 % rendering them unsuitable for colourless glass making. After magnetic separation, Fe_2O_3 is reduced (0.06 %) to a level which is acceptable for colourless glass making. Two glass compositions containing Al_2O_3 1.5 % and 4.0 % suitable for container and fiber glass have been melted to produce colourless glass. The results are satisfactory.

Key words: Nepheline, Glass raw material, Nepheline for glass making.

INTRODUCTION

The Glass industry in Pakistan is expanding rapidly, and new factories for the manufacture of more sophisticated products are coming up almost every year. With the expansion of this industry, demand for new glass raw materials is also increasing. Sand, feldspar, soda ash, limestone and dolomite are the main raw materials which are incorporated in almost all types of glass batches. With the exception of soda ash, all are naturally occurring materials. A good deal of work [1-4] has been done on the evaluation and utilization of these materials in the glass industry of Pakistan.

The present study deals with the evaluation and utilization of nepheline syenite from Koga (Swat) in the manufacture of colourless glass. Nepheline syenite is a naturally occurring dark grey crystalline rock composed of predominantly nepheline and alkali feldspar. The rock looks like an ordinary granite but mineralogically it consists mainly of feldspar and nepheline with minor amount of calcite, alkali-amphiboles, biotite and magnetite.

Nepheline syenite is found in many areas of the world [5] but uptil now only Canada, Norwary, USSR and United States have been able to utilize this rock for their glass and ceramics industries.

Nepheline syenite finds its main application in the glass industry especially for container and sheet glass. The main constituents of this rock are SiO_2, Al_2O_3, Na_2O and K_2O. The presence of Al_2O_3 plays vital role in the glass composition as it inhibits devitrifaction, improves strength and durability of the glass. The amount of Al_2O_3 varies from 2.0 to 24 percent in various types of glass compositions [6]. The incorporation of alumina in the glass composition as calcined or hydrated alumina is avoided because of its high cost and the poor fusion characteristics. The choice of a natural mineral as an alumina source depends upon its relative cost and its melting rate. The two most important, natural alumina sources are feldspar and nepheline syenite. Nepheline syenite has advantages over feldspar as it has a higher alkali and alumina content and a lower fusion point.

The second main constituent that is being supplied by the nepheline syenite is its sodium and potassium contents. Sodium oxide being a strong flux, melts the batch easily and rapidly and lowers the viscosity of the glasses. Potassium oxide is similar to soda in its general effects and in addition, its presence in the glass batch improves appearance and brilliancy of the glass. At the same time it has been observed that mixed alkali glasses are invariably more durable.

In soda-lime-silica glasses, the requirement of Na_2O goes upto 20 % [6]. Since the price of soda ash has increased considerably over the past few years, the high cost will influence the ultimate cost of the finished product. Great efforts are being made all over the world to use cheap alkali-rich raw materials. With this point of view, the nepheline syenite rocks are most suitable to provide both Na_2O and K_2O at economical cost.

The present studies were undertaken for the economic utilization of Koga Nepheline syenite of Swat, as raw material for the manufacture of colourless glass.

Geology of Koga nepheline syenite. The Koga nepheline syenite complex occurs in the Buner sub-Division of Swat District, a place about 56 kilometer from Mardan.

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The estimated reserves of this rock reported in 1975 are about five million metric tons. The nepheline syenite rock and the associated carbonatites were first reported by Siddique [7]. However, the first field and petrological account was presented by Siddiqui *et al.* [8]. The nepheline syenite complex is associated with "Ambela granite" and Swat-Chamla metasedimentary group. Siddiqui and Siddiqui *et al.* [8,9] regarded it as a single horse-shoe shaped body. However, detailed geological work carried out by Chaudry *et al.* [10] showed it to be a composite body of oblong oval shape composed of syenite, pulaskite, calcite bearing syenite and nepheline bearing syenite (containing upto 15 %) nepheline, and a number of feldspathoid rich dykes to the NE and E of this intrusion. The dykes are emplaced in an intrusion called the Babaji Syenite. The syenite complex with associated pegmatites and fenites is a result of multiple magmatic intrusions in the country rocks. The location map and out line map of the intrusion are given [11] as Fig. 1.

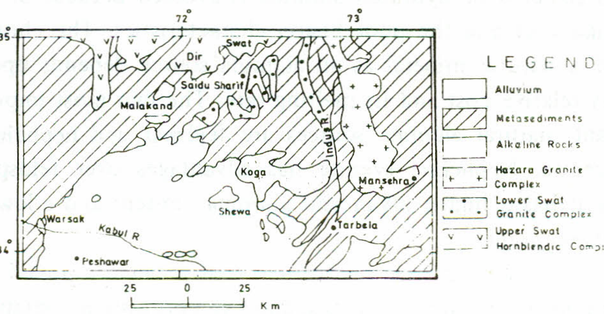

Fig. 1. Geological sketch map showing location of Complex and other alkaline and acidic complexes of NW Himalayas [11].

The Koga nepheline syenite complex occurs as a part of the alkaline province of NW Himalya. It occurs within the Indian Shield just South of the leading edge (South of MMT [7-10,12].

The tectonic setting of the alkaline rocks within the broad tectonic net of NW Himalya has been discussed [12,13]. They showed these rocks to be clearly tension related and discussed origin of this tension.

Rock types. The rock types recognised in this complex are nepheline syenite, sodalite nepheline syenite, litchifieldite, foyaite and pegmatites.

Mineral composition. The bodies (feldspathoids bearing) are composed of variable amount of microcline, albite and nepheline. Biotite, muscovite, sedapyriboles (pyroxene and amphibole), ilminite, melanite, zircon, sphene, sodalite, cancrinite, epidote, pyrite, apatite and haematite may occur as accessories. Zeolites, fluorite and astrophylite may occur rarely. The mineral parameters are given in Table 3.

Texture and structure. These rocks are generally medium to coarse grained and hypidiomorphic and hypidiomorphic porphyritic to sub-porphyritic fine grained facies occur as minor associates. Replacement by sodalite and cancrinite may be seen in some bodies. Aplitic textures are rare. Flow structures may be seen at some places. Foyaites are generally very coarse grained and look like granitoids and at places are pegmatitic.

Intergrowths of felsic constituents with the mafics is common. Inclusions of ferromagnesians and iron and iron-titanium oxides in feldspars and feldspathoids are common in many parts of the nepheline syenite complex, especially where feldspathoids are abundant. This restricts the areas amenable to upgradation. This also necessitates detailed exploration.

EXPERIMENTAL

Preparation of the sample. The lumps of rock samples extracted from the deposit were crushed primarily to pieces between 80 mm and 100 mm diameter. These pieces were further crushed to reduce their size between 50 to 60 mm dia and finally between 7 mm to 8.0 mm. It was then milled carefully to avoid the fines to a grain size of 0.97 mm approximately.

Grading. About 500 gm of raw sample after milling was subjected to sieve analysis using B.S. test sieves Nos. 30, 44,60,100 and 200 mesh. Mechanical shaking machine was employed to facilitate the sieving process. The material retained on each sieve and that passing through 200 mesh was weighed. The results are shown in Table 4.

Purification. Minus 200 mesh fraction being very fine was rejected for any test work. The other fractions i.e. −30+44, −44+60, −60+100 and −100+200 mesh size were subjected to magnetic separation. The magnetic particles i.e. magnetite, biotite amphibole and pyroxenes were separated at various current intensities. The removal of Ferromagnetic mineral was effected at low current intensities i.e. at 0.2 to 0.5 amp. The speed of the rollers of the magnetic separator was adjusted so that the non-magnetics might not be carried away along with the magnetic ones. It was observed that the speed of rollers should be maintained 35 cycles per minute in case of +44, +66 and +100 and 45 cycles per minute in case of −100 and +200 fractions. The magnet current in case of +44, +60 and +100 was varied as 0.2. 1.0, 1.5, 2.0 and 2.5 amps while the variation in case of −100 +200 was 0.5, 1.0, 1.5, 2.0 and 2.5 amps successively. At higher intensity magnetic separation stages, the pramagnetic and traces of ferromagnetic minerals were separated which still remain after the first magnetic separation stage. After passing the samples at

0.2 and 0.5 amp, the middlings were once again recirculated at 1.0 amp. Subsequently only the non-magnetics were re-circulated at higher current intensities to get the end product almost free from ferromagnetic and paramagnetic minerals. The percentages recovery of non-magnetic middlings and magnetics are given in Table 5.

Chemical analysis. Chemical analysis of the raw rock samples and the purified samples was carried out according to B.S.S. 1958 [14] and by Vogel [15]. Iron was determined by spectrophotometer and Na_2O and K_2O were determined by flame photometer. The samples for chemical analysis were taken by the usual coning and quartering method. The results are tabulated in Table 1 and 2.

Batch formulation and glass meltings. Two commercial glass compositions i.e. (wt. %) SiO_2 72.5, Al_2O_3 1.5, Na_2O 15.5, CaO 10.5 and (2) SiO_2 65.0, Al_2O_3 4.0, Na_2O 8.5, Cao 14.0, MgO 3.0, B_2O_3 5.5 suitable for container, sheet and glass fiber insulation[16] were selected for the present study. The batch compositions corresponding to these glasses are given in Table 6. Raw materials used were either of good quality or pure chemicals. The minimum quantity of selenium and cobalt oxide was adjusted to match the indigenous raw materials. The glass batch weighing 1000 gms was melted in an ordinary clay-grog crucible at 1400°.

The maximum temperature was maintained for 3 hours and then the temperature lowered to 1250° and maintained for one hour to dissolve the occluded gases. Melts were then poured on a hot steel plate and the glass samples were annealed. It was observed that all the glass melts obtained from the two compositions were almost colourless and free of bubbles and seeds. The general observation was that the batch free time in this case was less as compared to ordinary glass batch.

Table 1. Chemical analysis of the raw samples of nepheline syenite (wt. %).

Locality with co-ordinates	Agarai 5600-3680	Landi patao 5320-3573	Miane Kandao 5296-3311	Bagoch Sar	Shpala 5073-3493
SiO_2	55.54	58.16	56.74	47.95	54.02
TiO_2	0.60	Traces	0.1	0.00	0.00
Al_2O_3	23.50	22.38	22.16	23.74	23.31
Fe_2O_3	2.06	2.70	2.68	0.87	1.18
MnO	0.00	0.00	0.00	0.00	0.00
MgO	1.00	0.83	0.38	0.72	0.43
CaO	1.85	1.40	1.61	5.75	3.01
Na_2O	10.63	9.98	10.37	8.98	9.45
K_2O	3.96	4.38	4.80	4.94	6.08
P_2O_5	0.00	0.00	0.00	0.00	0.00
Loss on ignition	1.0	0.79	1.03	6.78	2.67

RESULTS AND DISCUSSION

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 raw materials.

The chemical analysis of the raw nepheline syenite is given in Table 1. It can be seen that iron content as Fe_2O_3 exceeds 0.87 % in all the five samples rendering them unsuitable for the manufacture of colourless glass.

Table 2. Chemical analysis of purified samples of nepheline syenite.

Locality with co-ordinates	Agarai 5600-3680	Patao 5320-3573	Miane Kandao 5296-3311	Bagoch Sar	Shpala 5073-3493	Canada
SiO_2	57.20	59.00	58.14	49.47	55.00	60.00
TiO_2	0.41	Traces	0.1	0.00	0.00	–
Al_2O_3	23.57	23.24	23.02	23.02	23.00	23.3
Fe_2O_3	0.07	0.06	0.10	0.08	0.06	0.08
MnO	0.00	0.00	0.00	0.00	0.00	–
MgO	1.02	0.84	0.39	0.72	0.43	0.1
CaO	1.88	1.42	1.65	5.80	2.84	0.4
Na_2O	10.84	10.17	10.68	9.05	9.54	10.0+
K_2O	4.0	4.44	4.94	4.95	6.54	5.0+
P_2O_5	0.00	0.00	0.00	0.00	0.00	–
Loss on ignition	1.0	0.80	1.06	8.80	2.60	0.7

However, samples from Bagoch Sar and Shapala containing Fe_2O_3 0.87 % and 1.18 % respectively may be used for the production of green, amber and heat absorbing glasses. These samples can also be used for the manufacture of fiber glass as colour does not matter in this case. Iron is very valuable when glasses for goggles for protection against intense light and heat are to be made. Ferrous oxide has a powerful absorption for long wave radiations centering around 10,500 A, and sheet glass containing 0.1 % ferrous ion is made to keep out solar radiations from buildings in warm weather.

Table 3. Petrographic composition of nepheline syenite.

Samples mineral	Agarai	Landi-patao	Miane Kandao	Bagoch Sar	Shpala
K-Feldspar	8.00	47.00	50.00	53.00	42.00
Albite	22.00	18.00	12.00	15.00	20.00
Nepheline	38.00	20.00	33.00	15.00	17.00
Cancrinite	0.50	–	2.00	–	
Pyroxene	–	–	–	–	1.50
Sodalite	6.00	6.00	–	–	
Fluorite	–	–	–	–	
Amphiboles	5.00	0.50	–	5.00	2.00
Garnet	–	–	–	–	
Epidote	–	–	0.50	–	1.00
Biotite	4.00	4.00	0.50	1.00	5.00
Muscovite	–	–	–	–	–
Sphene	–	–	–	1.00	–
Calcite	–	0.50	–	10.00	7.00
Clay	–	–	–	–	–
Apatite	0.50	–	–	–	–
Zircon	–	–	–	–	–
Magnetite/ Iliminite	2.0	3.00	2.00	–	2.50
Pyrite	–	0.80	–	–	2.00
Haematite/ Limonite	–	0.20	–	–	–

The colouring effect of iron, which is present as an impurity, gives rise to the problem of decolourizing. It becomes of great importance in the manufacture of crystal glass and tableware which should be colourless as well as transparent. It is possible to overcome this colour effect by the use of chemical decolourizers provided the iron content does not exceed beyond certain limits set out for different glass materials. In nepheline syenite Fe_2O_3 should be less than 0.1 % for colourless glass making [17,18]. The petrographic results (Table 3) revealed the presence of a substantial amounts of magnetite, biotite amphiboles and pyroxene. As these minerals are magnetic in nature and, therefore, their removal by magnetic separation is possible. Other predominant minerals present in these samples are K-feldspar, albite, nepheline, calcite, and sodalite. It can be seen from the chemical analysis of the purified samples (Table 5) that Fe_2O_3 has reduced from 2.06 % to 0.07 %, 2.7 % to 0.06 %, 2.68 % to 0.10 %, 0.87 % to 0.08 % and 1.18 % to 0.06 % after the removal of the magnetic portion.

The total reduction in the iron content is 90 % to 97 % which is appreciable. Percent recovery of the non-magnetics varies from 38 % to 63 % which is comparable with the reported results [17]. The iron oxide content of

Table 4. Sieve analysis.

BSS mesh No.	Opening in mm	Agarai % retained	Landi patao % retained	Maine Kandao % retained	Bagoch Sar % retained	Shpala % retained
+ 30	0.590	0.00	0.00	0.00	0.00	0.00
– 30 + 44	0.350	21.38	25.28	19.05	23.94	22.08
– 44 + 60	0.250	16.13	14.57	16.16	14.91	16.19
– 60 + 120	0.149	22.51	20.52	22.92	21.39	22.04
– 100 + 200	0.074	17.74	16.89	16.82	17.30	16.93
– 200	–	21.23	22.73	25.02	22.45	22.75

Table 5. Magnetic separation.

Locality	% recovery of non-magnetic (−30+200) mesh size	% Fe_2O_3 before magnetic separator	% Fe_2O_3 after the magnetic separator	% Fe_2O_3 reduction
Agarai	48.0	2.06	0.07	96.60
Landipatao	56.0	2.70	0.06	97.78
Miane Kandao	42.0	2.68	0.10	95.52
Bagoch Sar	38.0	0.87	0.08	90.80
Shpala	63.0	1.18	0.06	94.92

Maino Kando is slightly higher than desired for colourless containers. This can be used for the manufacture of good quality sheet glass and fiber glass. Thus simply by dry magnetic separation process, the iron level has reduced to 0.06 % in case of Agarai, Landi Patao and Shapala. It is comparable with the other nepheline syenite of the world being used in the manufacture of glass. For instance, the upgraded nepheline syenite of Canada contains Fe_2O_3 0.08 % [17] (Table 2). The percentage of MgO and CaO is all the samples is higher but not objectionable as these oxides are present in almost all the glass compositions. MgO in small amount is desirable as it controls devitrification in the glass. Total alkalies and alumina contents are comparable with the Canadian nepheline syenite.

The standard glass melts were made using the purified samples. The results are given in Table 6. The melting tendency of the nepheline syenite samples in both the glasses was normal. Both the glasses were easy to melt and refine. Moreover, no unmelted material was observed when seen under a microscope. In case of glass [1] containing Al_2O_3 1.5 %, all the purified samples produced transparent, colourless and seed free melts. The glass melt obtained with the Maine Kando, gave slightly bluish green tinge. This colour can be further decolourised by the proper adjustment of decolourisers selenium and cobalt oxide. The composition [2] containing 4 % Al_2O_3 were also colourless and seed free with the exception of Miane Kando and Bagoch Sar. In the manufacture of fiber glass the choice of composition is governed largely by chemical durability and resistance to weathering rather than by colour. In fiber glass Al_2O_3 can be added upto 24 % depending upon its use [16].

CONCLUSION

These nepheline syenite samples from Koga areas (Swat, NWFP) are basically feldspathic and feldspathoidal (Soda potash feldspars and feldspathoidal) and contain a considerable amount of magnetite, biotite, amphiboles and pyroxene which are magnetic in nature and their removal by magnetic separator is possible. A considerable improvement in iron reduction (92 %) is achieved by magnetic

Table 6. Batches corresponding to glass compositions [1] and [2] raw materials by parts.

Locality		Sand	Nepheline syenite	Soda ash	Lime stone	Dolomite	Borax	Sodium nitrate	Arsenic	Resulting colour
Agarai	1	1000.0	92.35	349.00	268.33	–	–	20.00	2.00	Brilliant, colourless, seed free
	2	1000.0	307.70	100.27	301.00	260.46	272.56	15.00	2.00	Colourless and free of seeds.
Landi-patao	1	1000.0	93.84	350.00	269.75	–	–	20.00	2.00	Transparent colourless
	2	1000.0	94.72	348.00	314.52	266.62	276.35	15.00	2.00	Colourless and seed free.
Miane-Kandao	1	1000.0	94.72	348.00	270.50	–	–	20.00	2.00	Slightly bluish green tinge
	2	1000.0	315.76	94.72	307.24	271.42	273.79	15.00	2.00	Bluish colour but seed free
Bagoch Sar	1	1000.0	93.87	347.86	260.42	–	–	20.00	2.00	Colourless and seed free
	2	1000.0	305.15	101.10	302.67	258.95	266.56	15.00	2.00	Slightly bluish green.
Shpala	1	1000.0	94.54	347.13	264.00	–	–	20.00	2.00	Transparent, colourless and seed free
	2	1000.0	313.54	91.23	305.42	268.28	271.53	15.00	2.00	Colourless

treatment. Fe_2O_3 content in the purified samples has reduced to 0.06 %. Transparent, colourless and seed free glass has been obtained with the purified samples.

Acknowledgement. The authors are thankful to M/s. Younis, Junior Technical Officer and Muhammad Boota, Laboratory Assistant, for their assistance in carrying out the chemical analysis and experimental work.

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