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UTILIZATION OF NEPHELINE SYENITE IN GLASS FOUNDING

Arshad Ali Naqvi*, M. Khalid Farooq, M. Sohail and M. Siddique Choudhry

PCSIR Laboratories, Lahore

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A large deposit of nepheline syenite has been discovered in Koga, Tehsil Bunnair, Swat (Pakistan). It is acidic igneous rock but it does not contain free quartz, being silica deficient as compared with granites and syenites and mineralogically is a mixture of several minerals of which major ones are: albite, microcline and nepheline. In this paper the use of nepheline syenite in glass-founding of four kinds with a skeleton formula of 75 % SiO_2, 15 % NaO and 10 % CaO is discussed at length.

Key words: Nepheline syenite; Glass.

INTRODUCTION

Nepheline syenite is a quartz-free rock consisting essentially of the felsphathoid mineral nepheline possessing the general formula $K_2O.\ 3Na_2O.4Al_2O_3.9SiO_2$ and theoratically containing 7 % K_2O, 15 % Na_2O, 33 % Al_2O_3, and 45 % SiO_2.

It has been also suggested (1) that the natural nepheline may be a molecular combination of $K_2O.\ Al_2O_3.2SiO_2$ and $Na_2O.Al_2O_3.2SiO_2$. In addition to nepheline the nepheline syenite rock also contain other feldspathoid minerals such as sodalite and concrinite and feldspar such as albite and microcline. The accessory minerals like biotite, magnetite ($FeO\ Fe_2O_3$), Zircon ($ZrO_2 .\ SiO_2$), aegirine and Pyroxine may also be present.

Nepheline syenite rock is used [2] in the manufacture of glass where high alumina content is particularly desired for which the usual specifications are: 0.05-0.07 % Fe_2O_3 content, uniform granular product, minus 30 mesh maximum grain size and low in fines. It is also used as a vitrifying agent in white-ware and sanitaryware, as a source of alumina and alkalies in glazes and porcelain enamels, as a ceramic bond: in abrasive grinding wheel, in refractory cement and in some types of heavy clay products. Its many advantages over feldspar include high alumina content, lower fusion temperature and high in alkalies (high soda and low potash). In Russia an economically process for the commercial extraction of alumina from nepheline syenite has been successfully evolved during the second World War. However, the starting point there is more or less pure nepheline obtained as a by product from their apatite Russia is also reported to be using nepheline in making portland cement in addition to its general use in glass and ceramic industries. Although, nepheline syenite possesses piezoelectric properties yet it is not used for this purpose as the crystals are usually small and imperfect.

EXPERIMENTAL

The present studies were undertaken on 13 bulk samples of nepheline syenite received as lumps. Each sample weighed about 60 kg. The colour of all the samples was identical which varied from grey to dark grey and hardness was between 5.5-6.5 on Moh's scale. The quality of the samples could not be simply judged from the colour alone as mineral nepheline was seen to be present in white, greyish, dark green and greenish colours depending upon the quality of the mineral itself and associated coloured minerals such as biotite, aegerine, sodalite etc.

To obtain a representative sample for chemical analysis and glass founding the entire lot of individual nepheline syenite samples were crushed in a jaw crusher. The resultant crushed aggregate was quartered and coned to obtain 2 kg samples which were manually ground in agate mortar to obtain minus 100 mesh material.

The chemical analysis of these ground samples were done in accordance with ASTM method of chemical analysis [3]. The alkalies were determined by flame-photometer. Iron was determined by colorimetric method [4,5]. The analytical results are reported in Table 1. However, before embarking on the chemical analysis of these samples, about 500 g of randomly chosen and finely ground samples Nos. 2,9,10,11 & 12 were tried for iron removal by a high intensity magnetic separation technique. It was observed

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*Present address: Construction & Building Materials Section; Saudi Arabian Standards Organization, P.O. Box No. 3437 Riyadh Kingdom of Saudi Arabia.

that fairly large quantities of iron impurity could be removed in this way (Table 6).

Although it was expected that loss on ignition in these samples will be negligible, yet it was also determined to provide a uniform ground for comparison. After chemical analysis, these samples have been arranged according to the rising loss on ignition. For the purpose of glass batch calculations (Table 2) the average chemical analysis** of the thirteen nepheline syenite samples is also reported in Table 1.

To undertake glass founding a skeleton glass formula containing 75 % SiO_2, 15 % Na_2O and 10 % CaO was considered to be studied. This formula is commonly used in glass container industry. The glass foundings were done utilizing various percentages of nepheline syenite, as per Table 2 to obtain 2 kg of the founded glass.

Other batch materials used for glass founding were also chemically analysed. The chemical analysis of these raw materials is given in Table 3.

The weighed out batch materials were thoroughly mixed so as to achieve homogeneous mixing. The silica sand was water washed and so was limestone. Later limestone was crushed and ground to obtain minus 100 mesh material.

The properly mixed glass batches were transferred to sillimanite crucibles which were fired in a gas fired furnace at 1500 + 5° for 2 hours. The expected iron and alumina content as also the colour of the founded glasses are given in Table 4. For amber colour, 3 % carbon and 1 % sulphur was added to the batch. To act as oxidising/refining agent, 1 % sodium nitrate and 0.3 % arsenic oxide was added to the three batches. All the chemicals were analytical grade.

At the time of glass-foundings only limited facilities were available for the mineralogical studies, and no more than five samples could be studied. Therefore, at random these samples were chosen for the purpose and mineralogical findings thereof are presented in Table 5 for sample Nos. 2,3,4,11 and 13.

The mineral contents were determined by standard point counting techniques, by measuring across several traverses of thin sections of a rock. Table 5 shows that minerals contributing for Na_2O are abundant such as albite, sodalite, nepheline, aegerine and microcline (soda rich variety). The K_2O is contributed by microcline, nepheline and biotite minerals. This is indicated in Table 1 which show Na_2O content ranging from 7.22 to 10.46 and K_2O content from 3.28 to 7.09 percent in these rocks.

RESULTS AND DISCUSSION

By undertaking chemical analysis of the samples it was expected that loss on ignition will be neligible; maximum 0.5 %. But Table 1 shows that it steadily rises from minimum of 0.49 to maximum of 3.62 %. This steady rise of loss of ignition can be attributed to the presence of

Table 1. Chemical analysis of nepheline syenite samples (in %)

Sample	L/I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Total
1.	0.49	61.03	20.07	1.48	2.83	Nil	4.62	9.53	100.05
2.	0.58	62.95	17.59	2.44	0.72	0.48	5.13	10.46	100.35
3.	0.71	59.88	20.59	1.52	4.68	Nil	5.80	7.51	100.69
4.	0.76	59.60	21.59	0.78	3.06	Tr.	6.48	7.37	99.64
5.	0.92	45.62	39.42	0.43	1.58	1.63	4.32	6.85	100.77
6.	1.08	62.15	21.11	2.43	0.96	Nil	5.05	7.49	100.25
7*.	1.23	59.54	22.30	0.33	2.15	Nil	3.28	10.42	99.25
8*.	1.58	55.62	21.66	2.05	3.16	1.69	4.82	9.01	99.59
9*.	1.90	56.54	22.01	2.50	2.72	0.52	3.98	9.87	99.98
10.	1.98	57.42	22.38	1.08	1.09	1.31	5.01	10.21	100.52
11.	1.98	57.42	19.71	3.75	1.83	0.83	6.62	7.22	99.36
12.	2.08	59.55	20.82	1.34	1.90	0.43	6.02	8.21	100.35
13.	3.62	56.13	19.67	0.71	5.21	0.34	7.09	7.87	100.69
**.	–	58.79	22.56	1.62	2.49	0.91	5.33	8.75	100.45

*Contains traces of phosphate (P_2O_5).

**Average chemical analysis of nepheline syenite samples, excluding loss on ignition.

Table 2. Batch weighings of the glass foundings based on varying percentage of nepheline syenite.

Nepheline Syenite		Weights of other batch raw materials				
Added (%)	Weight' (g)	Silica sand (g)	Soda ash (g)	Lime-stone (g)	Total batch weight (g)	Total decrease in Batch weight (%)
–	–	1500	513	357	2370	–
5	100	1441	479	293	2313	2.41
10	200	1382	445	230	2260	4.64
25	500	1205	344	39	2088	11.90
35	700	1087	277	*	2064	12.91

*No limestone was added; instead 41.28 g of B203 was added which is equivalent to 2 % of the total batch weight.

Table 3. Chemical analysis of raw materials used in glass founding.

Constituents	Silica sand	Limestone	Soda ash
L/I	0.62 %	41.76 %	Na_2CO_3 = 82.5 %
SiO_2	98.30 %	3.14 %	NaCl = 16.74 %
Al_2O_3	0.54 %	5.21 %	Loss of volatiles in the range of 110 - 140° = 27.32 %
Fe_2O_3	0.08 %	0.13 %	
CaO	0.36 %	48.78 %	
Others	0.98 %	Tr.	
			Fe_2O_3 = 0.17 %

Table 4. Expected alumina and iron content of the founded glasses.

Sample No.	Nepheline syenite used (%)	Expected alumina (%)	Expected iron (%)	Colour	Remarks
B.	–	1.14	0.11	Green	Neat batch
1.	5	1.87	0.17	Whitish green	Refining/ oxidizing agent used
2.	10	2.42	0.26	Green	Blank
3.	10	2.60	0.23	Bluish green	Blank
4.	10	2.78	0.17	Light yellowish green	Refining/ oxidizing agents used.
5.	35	13.27	0.21	Did not melt	Blank
6.	25	5.45	0.66	Dark green	Blank
7.	10	2.85	0.13	Light green	Blank
8.	5	1.94	0.19	Light bluish green	Blank
9.	10	2.81	0.32	Amber	Clouring agent used.
10.	10	2.83	0.19	Light bluish green	Refining/ oxidizing agent used.
11.	10	2.62	0.43	Amber	Colouring agent used
12.	25	5.38	0.40	Green	Blank
13.	10	2.59	0.16	Light yellow green	Refining/ oxidizing agent used

Table 5. Mineralogical composition of nepheline syenite.

	2	3	4	11	13
Aegerine	9.8	3.9	–	4.1	3.0
Albite	17.0	15.1	6.2	26.8	9.1
Arfvedsonite	–	–	10.0	1.9	4.0
Biotite	1.0	1.7	0.8	2.4	1.1
Calcite	–	–	–	–	4.0
Cancrinite/ sodalite	2.2	2.1	–	–	0.9
Microcline	53.7	33.4	51.1	45.3	36.8
Muscovite	–	0.7	1.0	–	–
Nepheline	13.6	39.9	27.2	15.4	39.7
Accessorise (sphene)	2.6	3.1	3.5	4.1	1.5

accessory minerals in the rock. A close look at Table 5 reveals that sample Nos. 2,3,4,11 and 13 contain several accessory minerals, five of them shall contribute towards the (greater) loss of ignition through their own decompositions.

Table 6. % Iron in samples before and after treatment.

Sr. No	Sample No.	iron present Before treatment %	 % After treatment %	Reduction (% age)
1.	2	2.44	0.88	64
2.	9	2.50	0.98	61
3.	10	1.08	0.45	58
4.	11	3.75	1.20	68
5.	12	1.34	0.54	60

For the purpose of glass founding the total alkalies content is very important. In Table 1 notice that five samples (Nos. 1,2,10,12 and 13) contain upto or more than 15 % total alkalies. In addition to them, seven other sample Nos. 3,4, 6-9 and 11 contain 13 to 14 % of total alkalies and in case of sample No. 5 only, the total alkali content stands at 11 %. This indicates that in respect of total alkali content all those nepheline syenite samples may be classified as fairly good. However, while looking at their iron content it is notice that it varies from a minimum of 0.33 % (sample No. 7) to a maximum of 3.75 % (sample No. 11). This means that by using nepheline syenite in glass batch it is unlikely to obtain a clear, colourless glass. As has been reported earlier [6] , iron removal was effected with high intensity magnetic separation technique so as to enable colourless glass to be manufactured.

From the Table 6, it is observed that a fair amount of iron has been removed from the samples by the treatment. Table shows that the iron removal is minimum e.g., 58 % in case of sample no 10, whereas it is maximum e.g., 68 % in case of sample No. 11.

Table 2 gives the weights of the batch weighings undertaken along with the chemical analysis reported in Table 3 of the raw materials used for glass founding. This was done to indicate the expected iron contamination in the founded glass. Table 4 gives a general picture of the founded glass series with the details of expected alumina and iron content, and colour of the glass.

For glass founding four types of glasses were kept in view: colourless, amber, green and neutral clear. Normally a colourless glass will be obtained if the total iron content of the batch does not exceed 0.1 %. However, the iron content of nepheline samples varies from 0.33 to 3.37 %. Additional iron is also likely to come from batch materials (limestone, soda ash, silica, sand; (Table 3). Therefore, in routine glass foundings using nepheline syenite, would give green to deep green glass. This effect of iron could be minimised either by using refining/oxidising agents [7] or iron removal magnetically. Alternatively, one could either embark on amber glass founding or green glass bottles manufacturing.

For soda-lime-silica neutral clear glass a batch containing upto 7 % Al_2O_3 was needed to be melted. In normal glass melts, alumina content upto a maximum of 2 % is allowed. It is known that alumina apart from causing increase in durability, crushing and tensile strength, resistance to thermal and mechanical shock and imparting brilliance, also increases the viscosity of the melt making refining and homogenizing processes very difficult. Moreover, the usual melting temperature (1450-1550°) of glass is increased with the addition of alumina. However, in special glasses such as fibre glass, sodium resistant glass, glass insulators, the alumina content of upto 14 % tolerable.

All the present glass foundings were done using formula 75 % SiO_2, 15 % Na_2O and 10 % CaO. As pointed out earlier, this formula is chiefly used in containers glass industry. And this was chosen to be studied because containers, in general, are subject to several endurances such as those of filling, rough transportation, resistance to mechanical and thermal shocks, general wear and tear, as compared with other glass products. Moreover, of all the hollow glass ware manufactured world wide about 60 % is produced as container glass. And in relation to the needs of Pakistan, it was considered for manufacturing glass containers for domestic use and for export.

Table 3 outlines the chemical analysis of commercial grade batch raw materials used for the glass founding in this study. As we see, all the batch materials contain iron impurity while limestone also containing 5.12 % alumina. Though iron free sillimanite crucibles have been used for glass founding yet colourless clear glasses could not be founded. This means beneficiation studies are needed for the silica sand and limestone and simple water washing was not sufficient as has been done in these cases. A curious fact, however, is noted in case of commercial grade soda ash which surprisingly contained 16.74 % NaCl as impurity. It is unlikely that common salt impurity is due to manufacturing defect. It may be that ratailer who may have deliberately added common salt as an adultrant to supplement his profiteering. On laboratory scale glass founding, this impurity of common salt did not manifest any harmful effect. However, in tank furnace, it shall sublime at the batch melting end and condense on the cooler parts of the furnace at the working end to drop back into molten glass and cause problems: of cords, or in homogenuity, of stones [8]. Further more, it shall initiate corrosion process at higher temperature on the refractory crown of the furnace thereby reducing its life. It may be pointed out that halogens are known to help refining and if used in excessive quantities, cause opalescence [9].

Table 4 gives the complete history of the founded glasses. As already expected, the neat batch (B) and all the blank founded glasses for sample Nos. 2,3,5,6,7,8 and 12 were not colourless clear but possessed a distinct hue varying in intensity from light bluish green to green with the expected alumina content rising from 1.14 to a maximum of 13.27 %. For studying the comparative degree of refining achieved amongst these founded glasses careful visual examination of the six founded glasses (except sample No. 5 of which the description follows here after) were conducted. There were no unmelted batch particles entrapped in these founded glass specimens. Of these series of seven blank foundings sample No. 5, containing the highest amount of nepheline syenite at 35 % of the glass batch (as also to give an expected alumina content of 13.27 %, also the highest, in the founded glass), did not melt. In this case the sillimenite crucible was cut into two halves by means of a diamond cutter and its contents examined visually; which revealed that vigorous batch-reactions have been initiated since numerous bubbles were trapped in fused and/or partially melted batch. The raising of the founding temperature from 1500° to say 1550° and/or prolonging the founding time beyond two hours could have resulted in a clear, founded glass in this case too. But these possibilities were not explored.

The next in the series of glass foundings were amber coloured glasses which were attempted in cases of sample Nos. 9 and 11. Since these two samples were expected to contain about 3 % iron content, hence 3 % carbon and 1 % sulphur of commercial grade were added to these batches. The amber colour obtained was, to the naked eye, almost equal in intensity. By varying the amount of carbon and sulphur additions deeper or lighter amber coloured glasses could be obtained. The third series were founded using 1 % sodium nitrate and 0.3 % arsenic oxide as an oxidising agent and as a refining agent respectively for sample Nos. 1,4 and 13 only. All the three samples contained about 0.2 % of iron and it was hoped that the additions of oxidising/ refining agents will give light coloured green glasses in comparison to neat and blank founded glasses. And in actual practice, we did obtain lighter glasses, in greenish hue. If beneficiated nepheline syenite samples with low iron contents is used it is likely to produce faintly coloured clear glass. Better grade glass could also be founded (in case of third series) by incorporating complimentary colour producing ions like cobalt, manganese and nickle. However, these possibilities needed to be explored.

In conclusion it may be said that the nepheline syenite rock can be utilized in any type of glass founding as tried above.

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