Research Paper

Assessment of Orangi Sandstone Unit of Nari Formation, Karachi: Industrial Applications with Special Focus on Glass Making

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Abstract: Glass manufacturing is one of the important industrial activities in Karachi but raw material is still being imported from other countries due to unexplored potential of indigenous silica sand deposits. Therefore, this is an attempt to assess the quality of Orangi sandstone of Tertiary age for its industrial applications which is exposed in and around Karachi city. Sandstone samples (n=14) were collected from areas extending between Surjani town to Hub Dam. Textural, mineralogical and chemical analyses were carried out through sieving, XRD and SEM-EDS techniques respectively. Mineral composition of Orangi sandstone varies in the order of quartz > kaolinite > feldspar > calcite > lizardite > ferric oxide > zinnwaldite. Texturally, the grain shape of sandstone is angular to sub-angular and the size is fine sand (0.075mm). The chemical analysis revealed that the major oxides (Si, Al, Fe, Ca, Mg, Na, K) are found to be 83.16%, 4.75%, 1.06%, 0.24%, 0.56%, 0.27% and 0.45% respectively. Mineralogical, Chemical and textural results of analyzed samples suggest that Orangi sandstone can be used as potential raw material for industrial applications where beneficiation may increases its grade up to 95% silica.

Keywords: Orangi sandstone, economic evaluation, industrial application, glass making.

Introduction

Silica sand is one of the most common minerals occurring on the earth's crust (Edem et al., 2014) which occurs in the last stage of rock weathering and an important part of the rock cycle (Shaffer, 2006).The deposits of silica sand are extensive throughout the world, mostly in non-tropical regions of the world which are used for different purposes (Freestone, 2005; Heck et al., 2002). Good quality silica sand reserves are reported in Germany, UK, Belgium, Brazil, France etc (Sundararajan et al., 2009).The demand for glass plants are increasing around the world, especially in the developed countries (Fox, 1994). The uses of silica sand depend on its mineralogy, chemistry and physical properties. It is mainly utilized in making glass and glass fiber, portland cement, silicon carbide, sodium silicate, silicon alloys and metals, filter media in water treatment, sand paper, foundry sand, sand blasting, hydraulic fracturing, paint and a host of other applications (Sundararajan et al., 2009). The quality of the commercial glass produced is highly dependent on mineral raw material used in the process (Hamidullah et al., 1996).

Main deposits of silica sand are fluvial, marine, lacustrine, glacial, residual and windblown/ loess (Hamidullah et al., 1996).Characterization of silica sand for potential of glass making from river and weathering products of sandstone deposits have been reported worldwide (Howari, 2015; Edem et al., 2014). However, very limited work has been carried out in Pakistan (Nizami and Farooqi, 1990) which is geologically inherited by sedimentary rocks where surface rocks (Tertiary age) are dominated by clastic sediments in the southern part of the country. Silica sand can provide job opportunity, if properly assessed and utilized by industries for the development of the country, but unfortunately it has been neglected for so long in the country. In Pakistan, silica sand has been used mainly by glass, ceramics, steel and soap industries (Hamidullah et al., 1996). Good quality silica sand is reported from rock deposits in Munda Kuchha area; district Manshera, Punjab province (Hamidullah, 1996; Alauddin et al., 1992). However, no such work is reported from Sindh province therefore, this study is aimed at assessing the quality of Orangi sandstone for its industrial applications through textural, mineralogical and chemical analyses.

Study area:

The study area is extended from Surjani Town to near Hub Dam site which lies between latitude 25° 04′ 56″ N to 25° 13′ 29″ N and longitude 67° 03′ 23″ E to 67° 07′ 57″ E. It is located in the northwestern part of Karachi with the Hub River on its west, while Kirthar Mountain on the north and Gadap syncline in south east (Fig. 1). Orangi sandstone is widely exposed in the form of ridges in and around Karachi which is easily accessible through road.

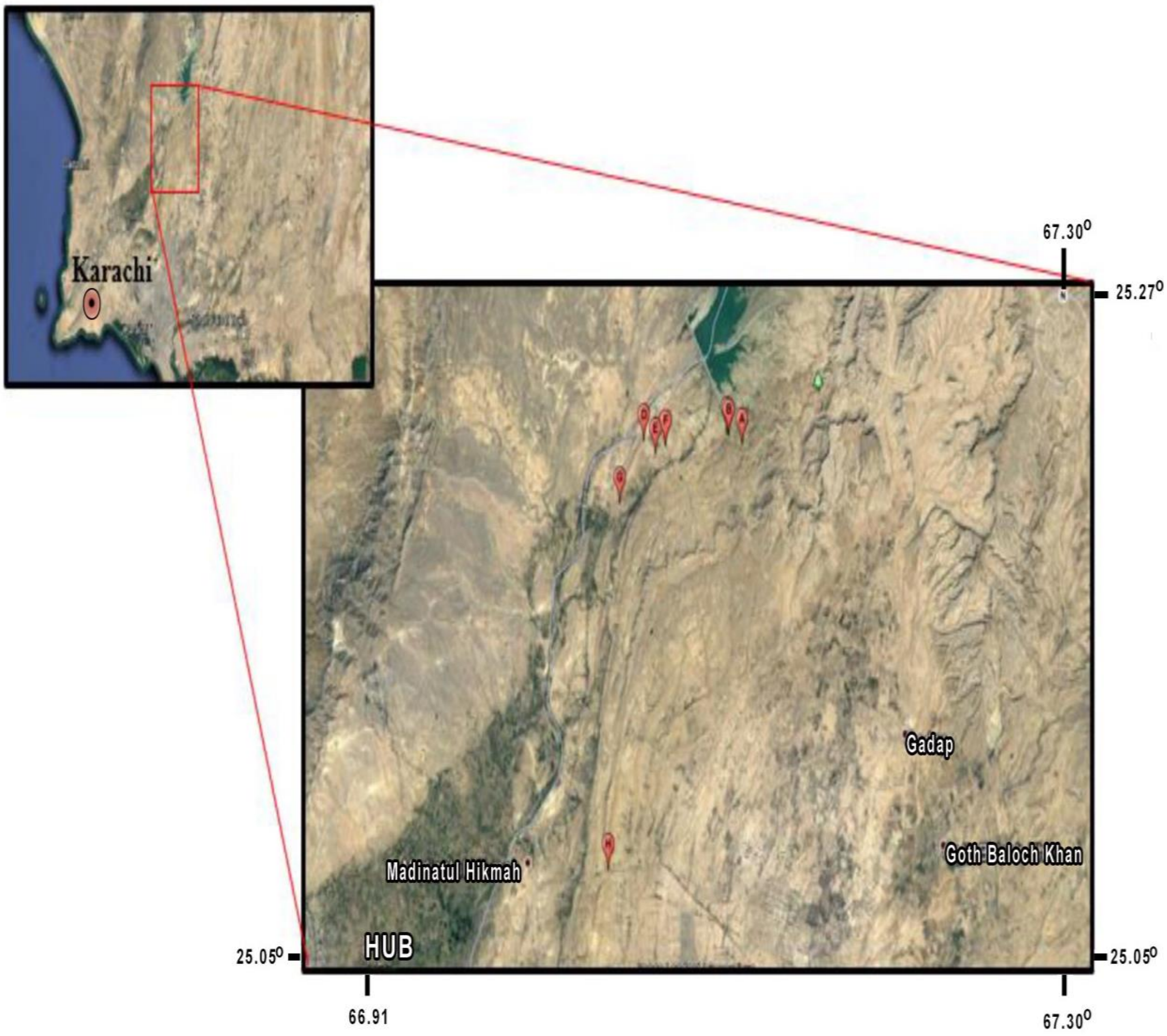


Fig. 1 showing the location of study area through Google Map.

The Nari and Gaj formations of Oligocene and Miocene age are exposed in the study area which is mainly clastic in nature (GSP, 1980). Orangi sandstone (Fig. 2) is the youngest member of Nari Formation which is mainly comprised of sandstone. Basal part of Orangi sandstone is medium bedded and compacted, whereas its middle part is thin to thick bedded limestone. The upper part is multicolored, massive, thick to thin bedded sandstone, medium to coarse grained and friable in nature which at some places is gritty.

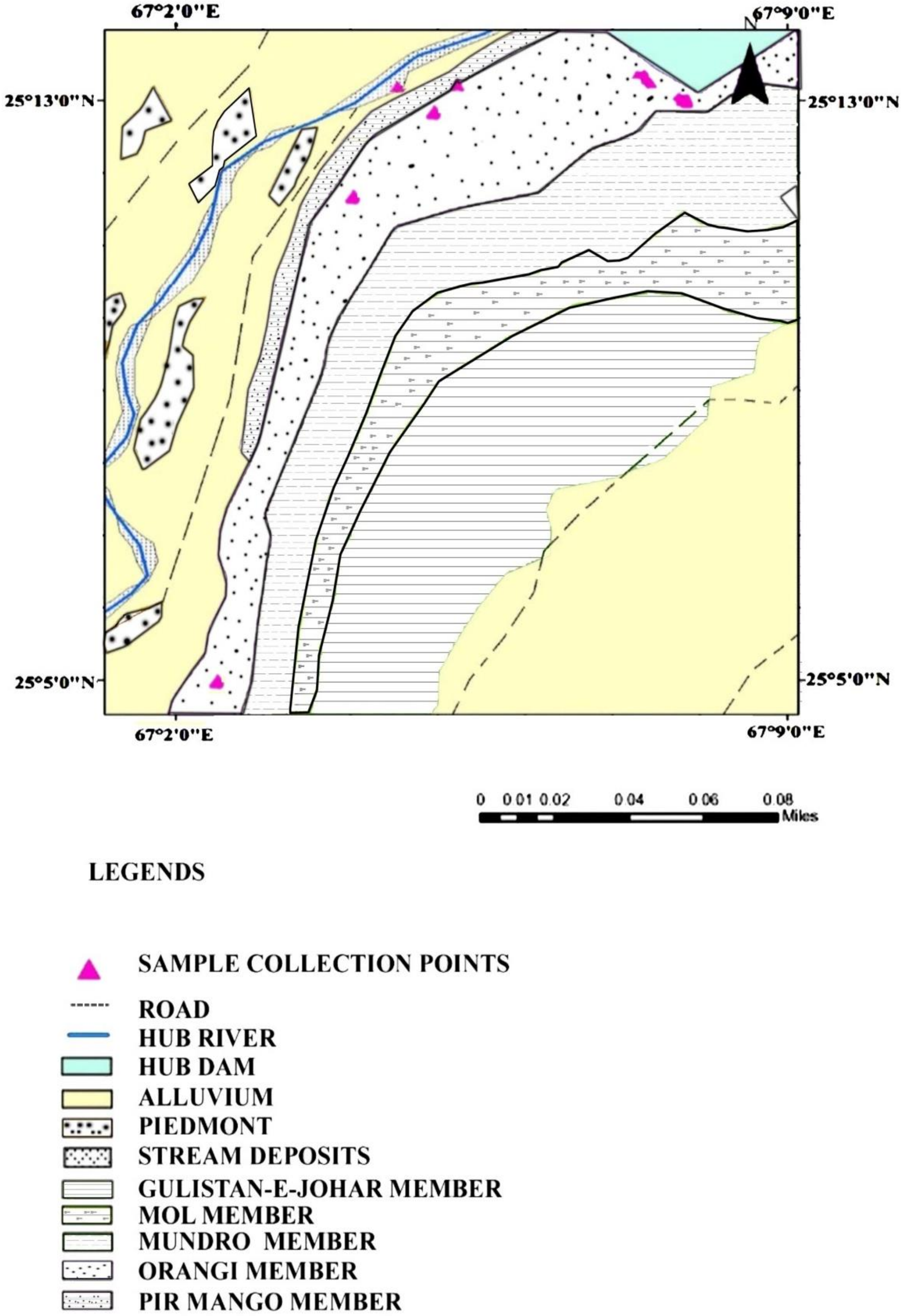


Fig. 2 Geological map of study and adjoining areas.

Materials and Methods

Grain size analysis

Two hundred grams each of the collected samples was oven dried and placed in a set of stacked sieves of various mesh sizes ranged between 4.75mm-0.062mm. The set of sieves was arranged in such an order that the coarsest sieve was at the top followed by finer ones with a pan at the bottom. The sieves were shaken mechanically through sieve shaker (Model: H-4325.5F). After 15 minutes of shaking, the sediments collected on each sieve and pans were weighed on electronic balance (Model: PCB350-3).

SEM-EDS analysis

Scanning Electron Microscope with Energy Dispersive Spectrum analysis was carried out to determine elements (major oxides) of collected sand samples. The analysis was carried out using Scanning Electron Microscope (SEM) fitted with EDS (Model: JEOL-JSM-6380A). The grains were mounted on a SEM brass stub. The mounted grains were coated with gold in a vacuum evaporator while the sample was being slowly rotated. Usually 15-20 grains were studied in detail and typical micrographs were taken by using SEM. The results were expressed as percent of oxides concentration.

X-Ray Diffraction (XRD) Analysis

XRD technique was used to identify the mineral phases present in the sand samples. Sample preparation for XRD was done as per the standard practices. The powder of samples for XRD patterns were obtained on a diffractometer system XPERT-PRO with the help of a Goniometer model PW3050 using Cu K(alpha) radiation operating at 45KV and 40mA on a diffraction range 5-70° (2θ) with a scan rate of 2°/min.

Petrography

All samples were examined under polarizing microscope (model: B-165POL) on ×4 magnification to visually inspect the mineral constituents and grain morphology (size and shape along with iron coating on mineral grains).

Results and Discussions

Grain size distribution:

Particle size is very critical for glass making as large grains do not mix properly with the other grains in the batch while too fine grains create air bubbles in the final product of glass making (Robert, 2002; Corning Glass Works, 1967; Crockford, 1949). Collected samples were analyzed for size distribution by sieving through various size intervals ranged between 4.75mm-0.062mm. The results of screened samples (n=14) have been summarized in Table 1. Data revealed that Orangi sandstone is mainly composed of fine to very fine sand with subordinate silty-clay. Relative abundance of grain size (Fig. 3) retaining on the sieves of various intervals are 0.075mm (51.75%) > 0.15mm (31.61%) > 0.425mm (8%) > less than 0.062mm (7.94%) > 1.18mm (5.66%) > 2.36mm (2.53%) > 2mm (1.52%) > 4.75mm (0.44%) respectively. According to Wentworth (1922) classification of grain size the data of present study lies between very fine (0.0625mm-0.125mm) to fine (0.125mm-0.25mm). Although the Orangi sandstone falls in fine category but these particles are dominated by non-clay fraction and these occur in very low amount which can be eliminated by washing process (Sundararajan et al., 2009).

The occurrence of gravel is reported in five samples out of which only one was gritty (16.3% gravel) and four samples had <10% gravel (Table 1) which could easily be removed by screening process (Edem et al., 2014). Microscopic examination of sediments revealed that mostly the grains were angular to sub-angular (Fig. 4) which was good for melting because roundness of the grain is a negative factor in such way that higher the roundness of the grains lower the melting rate (Hamidullah et al., 1996). It is also observed that the grains were free from iron coating which means that the sand needed no processing to remove grain coated iron.

Chemical analysis

Elemental distribution

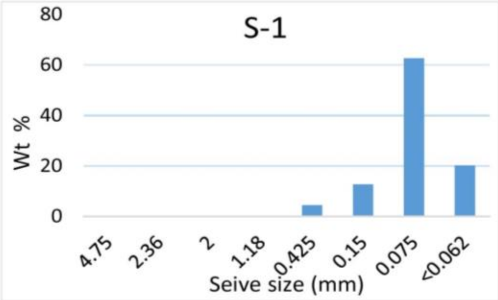
Major element geochemistry of rocks gives clues about weathering conditions and provenance (Ben et al., 2016). Detailed description of results for major oxides (wt%) of the collected samples are listed in Table 3 which reveal that SiO2 dominate over other oxides (Fig. 4). According to Highly et al., (2007) about 70-74% SiO2 is required for soda-lime-silica glass. The mean silica content is found to be 83.16%.Hence the silica content of Orangi sandstone qualifies for making such glass. General specification of chemical composition for glass sand is given in Table 2 which shows that the green glass, amber glass, insulating fibre, clear/float glass manufacturing require 95% SiO2 and the present samples shows that the potential for these manufacturing after the beneficiation process may increase up to 95%.

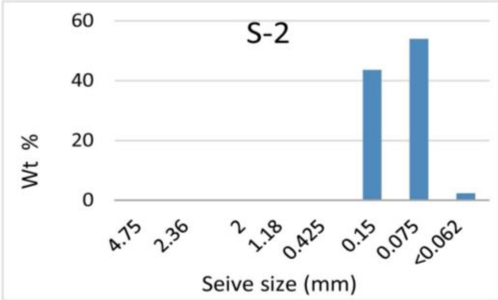
Table 1 Grain size distribution of Orangi sandstone collected between Surjani town and Hub Dam.

SAMPLE NO.		1	2	3	4	5	6	7	8	9	10	11	12	13	14
size mm	mesh ϕ	wt. (gm)													
4.75	-4	0	0	0	0.29	0	0	0	0	0	1.23	0	0	0	0
2.36	-1.25	0	0	0	10.66	0	0	0	0	0	0.45	0	0.23	0.96	0
2	-1	0	0	0.08	7.85	0	0	0	0	0	0.16	0	0.65	0.69	0
1.18	-0.25	0	0	0.09	31.97	0	0	0	0	0	0.45	0	0.89	9.43	1.01
0.425	1.25	8.83	0.09	0.86	39.73	0.52	0.33	0.43	1.3	3.02	3.69	0.17	8.63	102.99	17.12
0.15	2.75	25.1	86.63	136.14	10.67	34.19	70.84	42.52	22.66	34.85	125.91	95.28	53.4	56.35	66.43
0.075	3.75	124.13	107.16	58.84	11.02	150.05	113.46	138.14	151.88	128.18	57.62	81.58	118.45	14.45	81.09
<0.062	4>	39.99	4.7	3.2	3.07	13.48	14.25	17.75	22.36	33.46	9.43	14.6	16.43	5.06	18.67
TOTAL		198.05	198.58	199.21	115.26	198.24	198.88	198.84	198.2	199.51	198.94	191.63	198.68	189.93	184.32

SAMPLE NO.		1	2	3	4	5	6	7	8	9	10	11	12	13	14
size mm	mesh ϕ	Wt (%)													
4.75	-4	0	0	0	0.25	0	0	0	0	0	0.62	0	0	0	0
2.36	-1.25	0	0	0	9.25	0	0	0	0	0	0.23	0	0.12	0.51	0
2	-1	0	0	0.04	6.81	0	0	0	0	0	0.08	0	0.33	0.36	0
1.18	-0.25	0	0	0.05	27.74	0	0	0	0	0	0.23	0	0.45	4.96	0.55
0.425	1.25	4.46	0.05	0.43	34.47	0.26	0.17	0.22	0.66	1.51	1.85	0.09	4.34	54.23	9.29
0.15	2.75	12.67	43.62	68.34	9.26	17.25	35.62	21.38	11.43	17.47	63.29	49.72	26.88	29.67	36.04
0.075	3.75	62.68	53.96	29.54	9.56	75.69	57.45	69.47	76.63	64.25	28.96	42.57	59.62	7.61	43.99
<0.062	4>	20.19	2.37	1.61	2.66	6.8	7.17	8.93	11.18	16.77	4.74	7.62	8.27	2.66	10.13
Wt (%)		100	100	100	100	100	100	100	100	100	100	100	100	100	100

TEXTURE														
Gravel %	0	0	0.04	16.3	0	0	0	0	0	0.93	0	0.45	0.87	0
Sand %	79.8	97.6	98.36	81	93.2	92.8	91.1	88.8	83.2	94.37	92.4	91.25	96.43	89.9
Mud %	20.2	2.4	1.6	2.7	6.8	7.2	8.9	11.2	16.8	4.7	7.6	8.3	2.7	10.1
Texture	sand	sand	sand	sand	sand	sand	sand	sand	sand	sand	sand	sand	sand	sand


S-1
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)


S-2
Wt %
0
20
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60
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2
1.18
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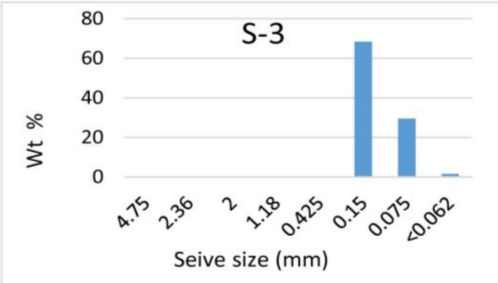
Seive size (mm)


S-3
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
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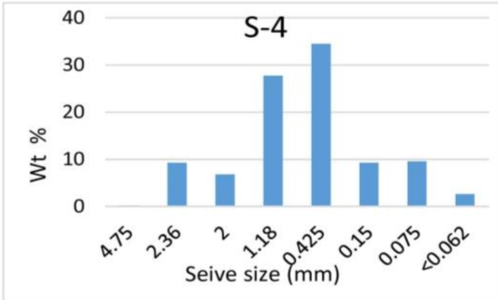
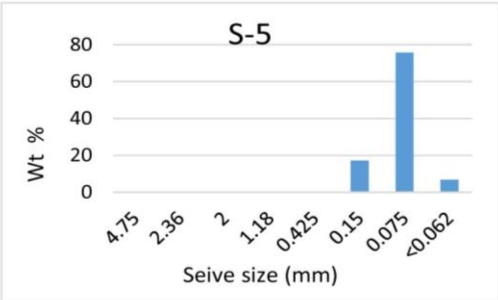
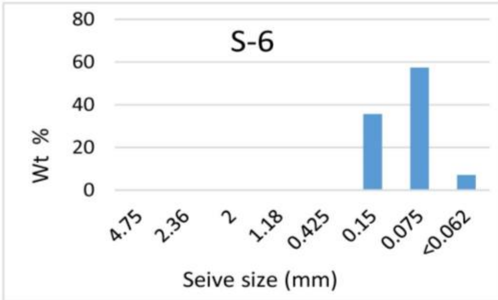
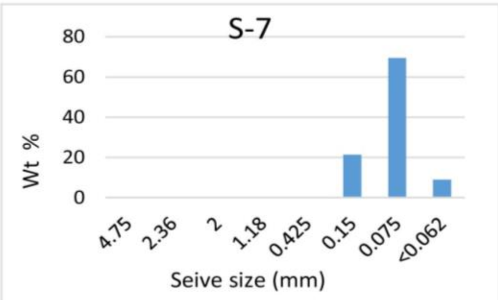
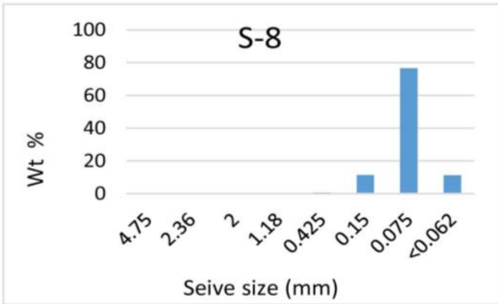
0.075
<0.062
Seive size (mm)

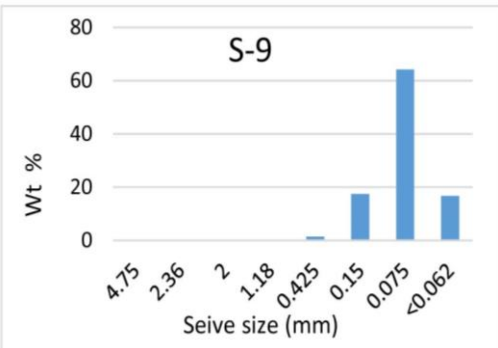

S-4
Wt %
0
10
20
30
40
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)

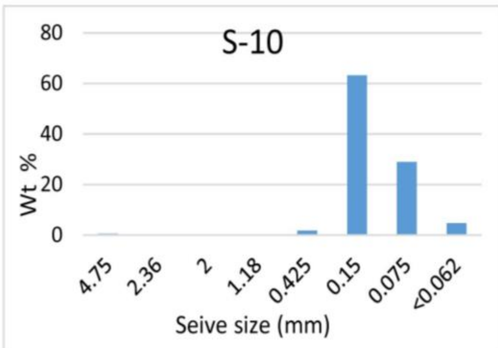

S-5
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)


S-6
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)


S-7
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)


S-8
Wt %
0
20
40
60
80
100
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)


S-9
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)


S-10
Wt %
0
20
40
60
80
4.75
2.36
2
1.18
0.425
0.15
0.075
<0.062
Seive size (mm)

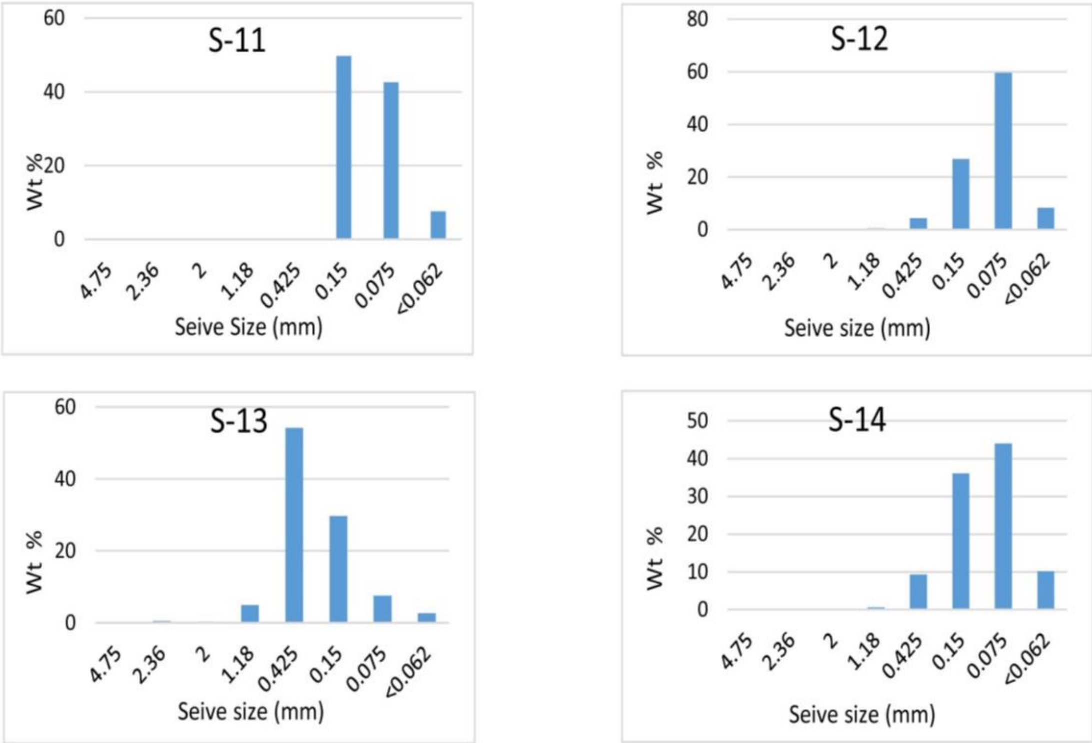


Fig. 3 Graphical representation of grain size distribution.

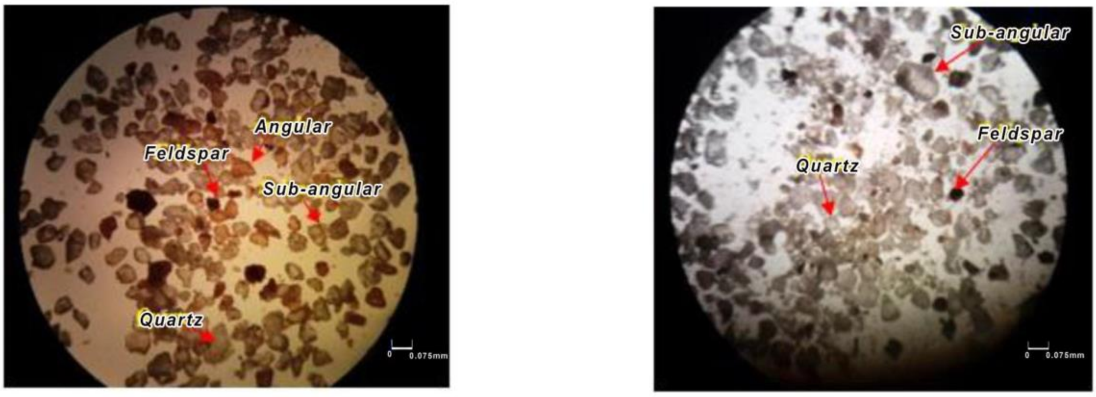


Fig. 4 Microscopic observations of selected samples for mineral composition and degree of angularity.

Table 2 General specification of chemical composition of glass sand.

Glass quality	SiO_2%	Fe_2O_3%	Al_2O_3%	CaO/MgO%	TiO_2%
Optical glass	99.80	0.005	0.100	0.100	-
Borosilicate glass	98.50	0.05	0.50	0.20	0.012
Colorless container glass	98.50	0.150	0.50	0.50	0.100
Clear/Float glass	95.00	0.200	4.00	0.50	0.100
Insulating fibre	95.00	0.300	0.50	0.50	0.100
Amber glass	95.00	1.00	4.00	0.50	0.100
Green glass	95.00	1.00	4.00	0.50	0.100
Grain shape: Angular, round and sub-angular melt easily.					

Table 3 Chemical composition of selected samples determined through SEM-EDS.

OXIDES	S-3	S-6	S-8	S-9	S-10	S-11
SiO_2	92.47	81.26	75.32	81.73	82.74	85.46
Al_2O_3	3.85	5.58	8.64	3.51	2.44	4.52
Fe_3O_4	1.36	1.14	1.74	0.74	0.65	0.73
CaO	0.15	0.57	0.05	0.08	0.55	0.05
MgO	0.21	0.57	1.3	0.67	0.32	0.3
Na_2O	0.2	0.26	0.66	0.14	0.27	0.1
K_2O	0.13	0.3	1.22	0.58	0.23	0.27
Cr_2O_3	0.04	0.01	nd	nd	0.06	nd
CoO	0.05	0.15	nd	nd	nd	0.04
NiO	0.09	0.07	0.13	0.11	0.12	nd
CuO	1.46	1.18	1.45	0.67	1.28	1.25
ZnO	nd	0.43	nd	nd	nd	nd

The other oxides such as CaO, MgO, Na_2O, K_2O, NiO, CuO, Cr_2O_3, CoO and ZnO showed low concentration (less than 1.2%) whereas Fe_3O_4 and Al_2O_3 ranges from 0.65%-8.64%. Calcium oxide (CaO), magnesium oxide (MgO) and alumina (Al_2O_3) are added for glass manufacturing in order to give the glass stability and durability. Hence, natural occurrence of these oxides in Orangi sandstone may increase its value for such glass manufacturing.

Deleterious oxides like Cr_2O_3 and CoO are found as traces in three out of six samples which range between 0.01-0.06 and 0.04-0.15 respectively. ZnO is reported only in one sample which is not significant in quantity (0.43 wt %) and can be neglected during the processing. On the other hand, Fe_3O_4 (magnetite) is found in all six samples but in three samples concentration is low (0.65%-0.74%) and in remaining samples it is relatively high (1.14%-1.74%). Microscopic inspection revealed that Fe_3O_4 (magnetite) occur as residual grains hence it can be eliminated by turboelectric method (Dolley, 2004; Chang, 2002; Goldman, 1994).

Silica richness

Chemical maturity is an index to express the relative abundance of quartz. For this purpose the ratio between SiO_2 and Al_2O_3 is used where high values of ratio means that the sand is rich in quartz. This ratio for Orangi sandstone is found to be 17.5 which according to Potter (1978) indicate moderate chemical maturity. On the other hand, these collected samples have low alumina (4.75 wt%) and CaO (0.24 wt%) contents. According to Tsai (2004), low values of Al_2O_3 and CaO reflect moderately siliceous sand which is consistent with the finding of Potter (1978) as discussed earlier. According to Crook (1974), ratio between K_2O and Na_2O indicates the relative abundance of quartz and feldspar. If $K_2O/Na_2O > 1$ it indicates quartz richness in the sandstone. The ratio between K_2O and Na_2O content is found to be greater than 1% in the analyzed samples (Table 3) which is consistent with the petrographic observations showing high quartz and low feldspar content.

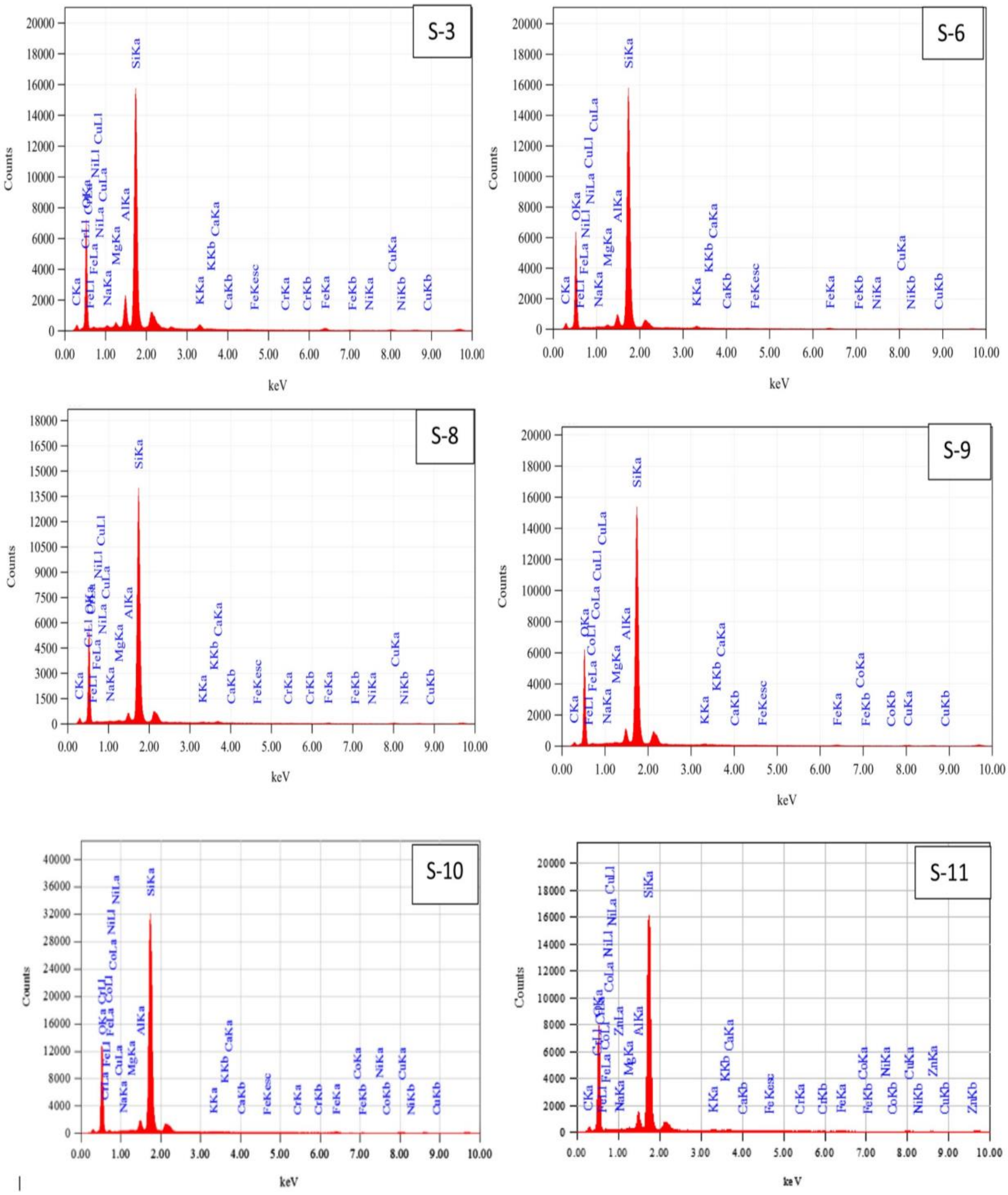


Fig. 5 SEM-EDX micrographs showing SiO_2 as major oxide.

Mineral determination

The minerals identified in the representative samples have been summarized in Table 4. X-ray profiles (Fig. 5) confirmed that quartz is the dominant mineral where relative abundance of other minerals follows the order kaolinite, feldspar, calcite, lizardite, ferric oxide, zinnwaldite.

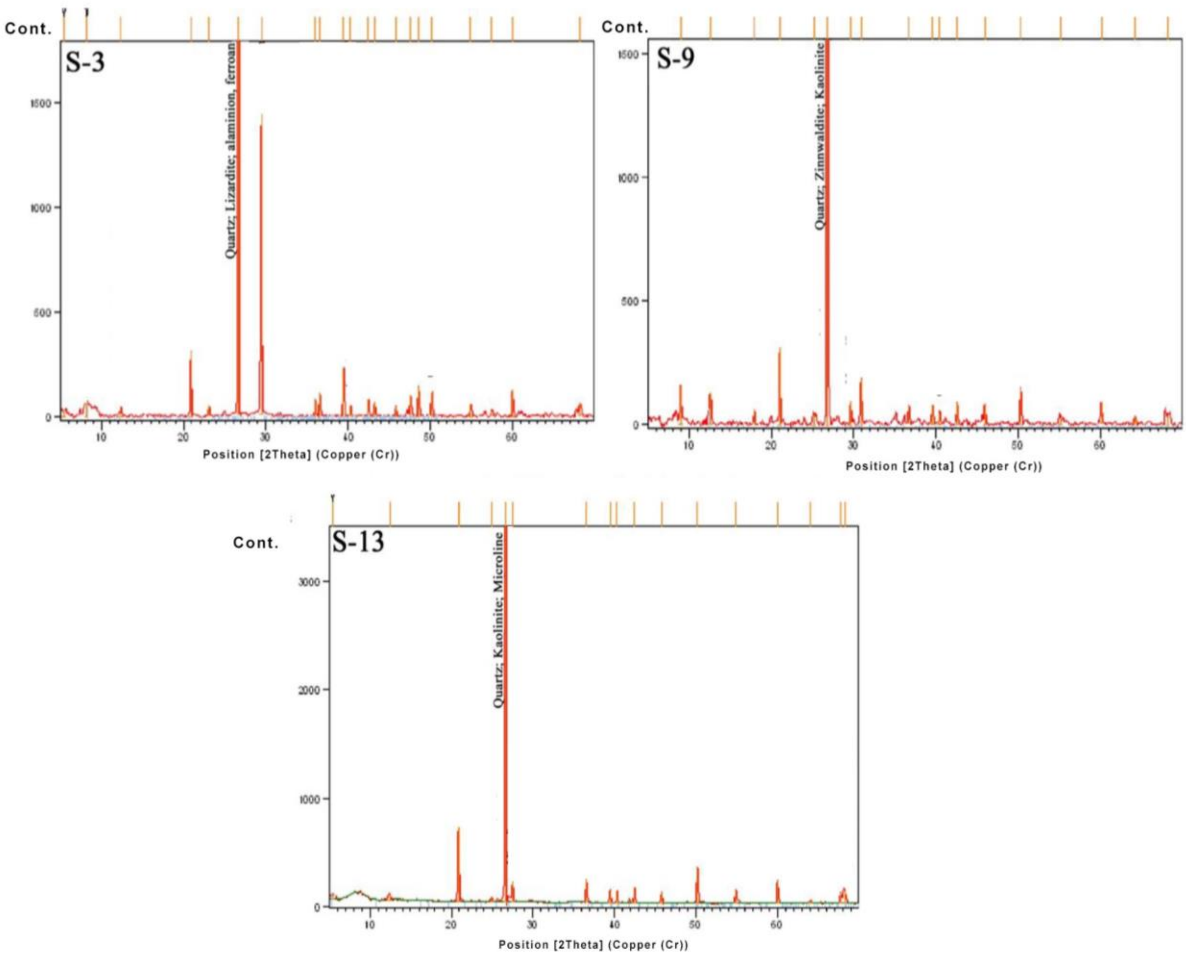


Fig. 6 X-ray profiles of selected samples.

Sample S-13 is gritty in nature which is relatively higher in quartz content as compared to other samples (Fig. 6). Kaolinite is found in two samples (S-13 and S-9) which is formed at the expanse of feldspar alteration which is relatively higher in the sample (S-9). This sample was collected from the basal part of Orangi sandstone in the proximity of Hub Dam. Whereas, feldspar is found only in one sample (S-13) where the kaolinite is in low quantity. Calcite and lizardite are reported only in one sample where both show about 31% and 15% of the total minerals present in S-3. Ferric oxide (magnetite) and zinnwaldite (variety of mica) are reported in S-9 which are in low quantity (11% and 2% respectively). Ferric oxide can be removed by gravity separation using spiral separators in which lighter particles are pushed to the outside of spiral pans (Edem et al., 2014) and zinnwaldite (variety of mica) and other undesirable minerals can be eliminated through Flotation process (Edem et al., 2014).

Table 4 XRD results of selected samples.

SAMPLES	MINERALS	WEIGHT %
S-13	Quartz	73
	Feldspar	20
	Kaolinite	7
S-9	Quartz	63.4
	Kaolinite	23.8
	Ferric oxide	10.9
	Zinnwaldite	2
S-3	Quartz	54
	Calcite	31
	Lizardite	15

Conclusion

Textural, chemical and mineralogical evaluation of Orangi sandstone reveal that grain size of sandstone is generally fine but quartz rich which is confirmed by mineralogical study. Chemically, high silica content (75%-92%) is found which regard Orangi sandstone for using in glass industry especially for soda-lime-silica glass. Clay (zinnwaldite, kaolinite) and heavy minerals (magnetite, chromate) are serving as impurities but in a very subtle quantity and can be eliminated through physical operations such as size separation (screening), gravity (spiral concentration), and magnetic separation. The removal of these unwanted minerals may increase grade of silica up to 95% which can be used for more advance uses including green glass, amber glass, insulating fiber, clear/float glass, colorless glass container and borosilicate glass manufacturing. Since present work is based on limited number of samples which are showing sketchy picture of the Orangi sandstone. Detailed study is required to evaluate potential of Orangi sandstone for its industrial applications.

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