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CHARACTERISTICS OF GLASS MAKING SANDS OF KHISORE - MARWAT RANGES OF D.I. KHAN DIVISION, N.W.F.P., PAKISTAN

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Extensive deposits of silica sand are found in the basal part of Dutta formation (Jurassic) in the Khisore and Marwat ranges, D.I.Khan division, NWFP. The chemical composition, grain size distribution and physical characteristic of eleven samples from these areas were determined. Beneficiation by physical and chemical methods were undertaken to reduce the colour imparting impurities mostly iron. The objectives of the work was to investigate whether the silica sand deposits of Khisore and Marwat ranges were suitable for the rapidly expanding glass industries of Pakistan. The results showed that the silica sand in its original form is not suitable for the production of colourless container glass. However, it is suitable for the production of sheet glass/green glass. After beneficiation, majority of the samples were up graded to meet the specification for the production of colourless container glass.

Key words: Glass sand, Khisore, Marwat ranges, Silica sand, Beneficiation.

Introduction

North-West Frontier Province (NWFP) of Pakistan and Federally Administered Area (FATA) have several silica sand deposits. Prior to this study several areas of this region were explored for quality silica sand to meet the requirement of glass industries of the region, as silica is essentially a major component of glass composition [1]. Among areas previously covered include Mohmand Agency silica sand FATA [2] and Kurd silica sand, Karak District (NWFP) [3].

Silica sand deposits of the area under present investigation i.e. Khisore and Marwat ranges are being used without purification by a number of industries for the production of sheet glass. Glass produced from the above untreated sand exhibit inferior properties due to the presence of colour imparting impurities in the glass sand. The glass and bulb industries of NWFP are getting their supplies of silica sand from Daudkhel in Mianwali district [4]. The transportation cost of silica sand is very high. It was,therefore, decided to undertake the upgrading of Khisore-Marwat ranges silica sand with a view to meet the specification of container glass industries. The deposits of Khisore and Marwat ranges are large. It is situated on Bannu-D.I. Khan road and also lies on a narrow gauge railway line connecting Bannu with Mari Indus [5].

The object of this work was to minimise all the objectionable impurities by means of grading, water washing, magnetic separation and various chemical treatments and thus make the sand sample useful for the production of colourless glass.

Geology of the area. Marwat range trends east-north-east and extends for about 35 miles, with an average width of five miles [5]. Khisore range is almost parallel to Marwat range and its average width is 6 miles. Sheikh Budin, the highest point in the range is 4500 feet above the sea level. General elevation in the Marwat range is between 2000 - 3000 feet, while in Khisore range it is 3500 feet above sea level. The silica sand deposits of Khisore and Marwat range are located near Pezu and Paniala town respectively [6].

The oldest rock unit of Marwat range are of Permain age and the youngest units are of Pliocene age. The thickness of the sedimentary sequence is about 9500 feet. In Khisore range rock units range from Cambrian to Pliocene [5]. Surfacial deposits of recent age overlie the older rocks. Stratigraphic thickness of Cambrian to Jurassic rocks in Khisore range is 4,400 feet.

The Marwat range silica sand comprises irregular zones and patches of milky white, dirty white, yellowish and reddish colour. The outcrop extends for about 5 miles [5]. The silica sand samples of this area contain clay impurities showing high alumina content.

The silica sand bed of Khisore ranges extends to about 4 miles. It is thin bedded. The sand is dirty white to white in colour with yellowish patches at places. In the eastern part of the exposure the colour gets more yellowish and reddish showing increase in the incidence of impurities [5]. The sand is very friable and medium to fine grained. Its grains are sub-angular to rounded. Combined reserves of silica sand deposits of Marwat and Khisore ranges are approximately 31/32 million tonnes [6].

Silica sand sample Nos. (1-6) have been quarried from the location of Paniala channel and sample Nos. (7-11) have been collected from the adjacent location of Pezu area respectively. Samples from the middle areas of Paniala channel (sample Nos. 2,3 and 5) contain iron oxide in lesser quantity (below 0.1%) as compared to samples collected from the beginning and end of the channel which shows greater iron oxide (range

0.14 to 0.25%). On the other hand Pezu silica sand are better as in all the silica sand from the area, iron oxide is generally below 0.1% with the exception of sample No. 10 which has 0.229% Fe_2O_3 (Table 1).

Materials and Methods

Eleven representative samples were received from two different localities namely Pezu and Paniala of Khisore and Marwat range respectively. Research and development work was carried out on these eleven samples.

(i) Chemical analysis. 100 gm of the sand (original and water washed) were ground to a fine powder (-100+120) and analysed using standard method of chemical analysis [7] the constituents determined were SiO_2, Fe_2O_3, Al_2O_3, TiO_2, P_2O_5, CaO, MgO, Na_2O, K_2O and loss on ignition etc. The results of the chemical analysis of original and water washed silica sand samples are given in Table 1. Iron, titanium etc., were determined spectrophotometrically.

(ii) Water washing. The clay fraction was removed by washing the sand with water. For this purpose [3], sand and water was taken in a 3 liter beaker and stirred with a glass rod. The resulting dirty liquid carrying ferrugenous clay particles were decanted after 1.5 min. The process were repeated till the washing were free from any dirty liquid. Effect of water washing in the improvement of Fe_2O_3 was calculated and incorporated in Table 1.

(iii) Grading. 100 gm of each of the original and water washed samples were taken and the sieving was done by means of ASTM standard sieves of 25, 36, 52, 72, 100 and 120 mesh. Each sample was shaken for 5 min in a mechanicals shaking machine and the amount retained on every mesh was weighed [3]. From the percentage retention for glass industries (-25+12 mesh) were found out and given in Table 2. Improvement of iron contents of glass sand after grading and water washing are given in Table 3.

(iv) Magnetic separation. In order to remove the ferromagnetic particles, the washed and raw silica sand were subjected to manual magnetic separation. A strong permanent magnet was passed over a sand bed in a glazed paper. No particles were attracted by the magnet in any one of the eleven silica sand samples. All the samples were free from ferromagnetic particles.

BENEFICIATION BY CHEMICAL TREATMENT

(a) Hydrochloric acid treatment. 100 gm of silica sand was boiled with 200 ml commercial hydrochloric acid. The sand was then boiled with distilled water for 1/2 hr. to wash the chloride completely [8]. It was dried in oven at 105° and Fe_2O_3 was determined spectrophotometrically. The above experiment was repeated with 1:1 HCl and iron was determined and percentage reduction of iron by this process was calcu-

TABLE 1. CHEMICAL ANALYSIS OF KHISORE AND MARWAT RANGES SILICA SAND (RAW AND WATER WASHED).

Sample No.	Raw sand or water washed	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	TiO_2 (%)	MnO (%)	P_2O_5 (%)	CaO (%)	Mgo (%)	Na_2O (%)	K_2O (%)	Loss on ignition (%)	Total (%)
S-1	Raw sand	97.12	0.14	2.03	0.038	Nil	Nil	0.62	Nil	0.035	0.082	0.46	100.525
	Water washed	97.48	0.068	1.25	0.003	Nil	Nil	0.33	Nil	Trace	0.02	0.02	99.25
S-2	Raw sand	97.02	0.074	3.20	0.021	Nil	Nil	0.30	Nil	Trace	0.016	0.32	100.95
	Water wasged	97.10	0.064	2.78	Trace	Nil	Nil	0.18	Nil	Nil	Nil	0.11	100.234
S-3	Raw sand	97.70	0.07	2.01	0.01	Nil	Nil	0.75	Nil	0.02	0.02	0.17	100.75
	Water washed	97.50	0.07	1.36	Trace	Nil	Nil	0.13	Nil	Nil	Nil	0.08	99.14
S-4	Raw sand	96.32	0.25	1.02	0.09	Nil	Nil	0.98	Trace	0.02	0.03	0.35	99.06
	Water washed	97.80	0.15	0.49	0.01	Nil	Nil	0.69	Nil	0.01	0.01	0.10	99.26
S-5	Raw sand	98.80	0.061	1.67	0.01	Nil	Nil	Trace	Trace	0.01	0.02	0.07	100.641
	Water washed	98.38	0.03	1.20	0.008	Nil	Nil	Nil	Nil	0.008	0.007	0.01	99.703
S-6	Raw sand	97.80	0.91	1.31	0.01	Nil	Nil	0.52	Nil	0.135	0.05	0.15	100.165
	Water washed	98.80	0.05	0.78	Nil	Nil	Nil	0.27	Nil	0.01	0.009	0.03	99.949
S-7	Raw sand	96.98	0.07	2.56	0.01	Nil	Nil	0.21	Trace	Nil	Nil	0.26	100.09
	Water washed	97.60	0.048	2.19	0.01	Nil	Nil	0.11	Nil	Nil	Nil	0.12	100.078
S--8	Raw sand	97.15	0.09	2.66	Nil	Nil	Nil	Trace	Nil	Nil	0.015	0.04	99.955
	Water washed	98.24	0.05	1.69	Nil	Nil	Nil	Nil	Nil	Nil	Nil	0.01	99.99
S-9	Raw sand	97.92	0.088	1.71	0.05	Nil	Nil	0.22	Nil	0.08	0.02	0.01	100.098
	Water washed	98.06	0.074	1.01	0.01	Nil	Nil	0.10	Nil	0.03	0.02	Nil	99.304
S-10	Raw sand	92.54	0.229	5.32	0.05	Nil	Nil	0.58	Nil	0.025	0.025	1.22	99.989
	Water washed	96.84	0.11	1.84	0.012	Nil	Nil	0.02	Nil	0.01	0.014	0.30	99.14
S-11	Raw sand	96.82	0.094	2.30	0.045	Nil	Nil	0.52	Nil	0.015	0.10	0.27	100.164
	Water washed	97.76	0.051	1.30	0.01	Nil	Nil	0.23	Nil	0.005	0.018	0.09	99.364

lated and given in Table 4.

(b) Oxalate process (Adam's process). Adam removed the iron coating of sand grain by treating the samples with solution of sodium acid oxalate containing some $FeSO_4$, $7H_2O$. The method [9] has been commercially exploited for a long time in many countries. The reacion was undertaken at 65 ± 5°. The supernatent liquid was decanted off. The sand was further washed with distilled water till the washings gave no indication of iron and the washed sand was dried at 105°. Iron was then determined in usual manner. The results are given in Table 5.

(c) Sulfite process. The sand was mixed thoroughly with 0.4% sodium sulfite and the mixture transferred to 600 ml polythene beaker, to which water containing hydrofluoric acid

TABLE 2. GRAIN SIZE ANALYSIS RESULT OF KHISORE AND MARWAT RANGES SILICA SAND (RAW AND WATER WASHED).

Sample No	Raw sand or water washed	0-25 mesh (%)	-25 mesh (%)	-36 mesh (%)	-52 mesh (%)	-72 mesh (%)	-100 mesh (%)	-120 mesh (%)	Total (%)	Sieve loss (%)	Useful fraction -25 + 120 mesh (%)
S-1	Raw	13.19	1.44	0.37	4.20	2.81	15.53	61.86	99.30	0.70	24.95
	Water washed	0.20	0.02	0.06	3.74	3.59	19.10	73.15	99.69	0.31	26.83
S-2	Raw	4.80	6.58	6.79	37.63	5.72	11.88	26.41	99.73	0.27	68.79
	Water washed	0.12	4.80	6.52	37.20	5.78	16.65	28.48	99.55	0.45	72.40
S-3	Raw	16.18	4.82	2.90	19.98	8.13	14.36	33.41	99.78	0.22	50.41
	Water washed	0.30	3.42	3.45	30.59	7.80	20.23	33.45	99.24	0.76	66.25
S-4	Raw	21.47	3.56	1.10	6.21	4.36	14.70	48.22	99.72	0.28	30.31
	Water washed	2.38	7.32	0.68	10.75	5.55	22.68	56.58	99.94	0.06	41.04
S-5	Raw	12.39	31.90	18.15	24.91	1.43	5.04	5.89	99.71	0.29	81.72
	Water washed	1.96	33.16	22.36	32.83	1.75	4.39	1.13	99.68	0.32	96.81
S-6	Raw	6.68	27.80	15.35	25.83	2.24	7.57	14.63	99.60	0.40	78.69
	Water washed	2.52	32.07	18.93	34.61	3.53	5.89	2.24	99.99	0.01	95.24
S-7	Raw	00.97	8.25	7.49	32.18	3.26	14.64	32.97	99.76	0.24	66.06
	Water washed	00.99	10.80	9.49	39.97	5.48	16.72	15.80	99.25	0.75	83.21
S-8	Raw	0.78	20.86	13.55	28.63	2.62	10.34	22.46	99.34	0.66	76.56
	Water washed	0.22	18.11	13.52	35.33	4.27	14.57	13.10	99.56	0.44	86.68
S-9	Raw	0.50	14.26	18.68	36.38	3.86	10.26	15.66	99.60	0.40	83.84
	Water washed	0.25	13.63	20.69	46.29	4.04	9.88	5.58	99.66	0.34	94.57
S-10	Raw	32.44	4.28	1.93	13.22	3.45	10.72	33.80	99.84	0.16	33.76
	Water washed	11.67	3.42	2.98	30.20	10.83	24.91	15.76	99.27	0.73	82.57
S-11	Raw	0.41	2.47	0.94	15.27	5.03	17.50	57.61	99.23	0.77	58.02
	Water washed	0.19	0.42	0.73	22.68	11.30	33.20	30.90	99.67	0.33	68.91

TABLE 3. IMPROVEMENT OF THE IRON CONTENTS OF GLASS SANDS AFTER GRADING AND WATER WASHING.

Sample No.	% Fe_2O_3 in original sand	%Fe_2O_3 in useful fraction -25+120 mesh	%Fe_2O_3 retained in water washed sand	%Reduction of Fe_2O_3 after garding	%Reduction of Fe_2O_3 after water washing
S-1	0.14	0.073	0.068	47.85	51.42
S-2	0.074	0.069	0.064	06.75	13.51
S-3	0.075	0.074	0.072	01.33	04.01
S-4	0.25	0.187	0.15	25.20	40.00
S-5	0.061	0.052	0.03	14.75	50.81
S-6	0.19	0.134	0.05	29.47	73.68
S-7	0.07	0.061	0.048	12.85	31.42
S-8	0.09	0.059	0.05	34.44	44.44
S-9	0.088	0.069	0.074	21.59	15.90
S-10	0.229	0.15	0.11	34.79	51.96
S-11	0.094	0.085	0.051	09.57	45.74

(pH 2.7) was added [8]. The amount of water being sufficient to cover the mass completely. The slurry was stirred with wooden rod for 5 mins. The resulting turbid liquid was decanted off. The sand was further washed with water and dried as usual and iron oxide was subsequently determined. Comparison of improvement of Fe_2O_3 by Adam's process and sulfite process are given in Table 5.

(d) Sodium hydroxide process. The sand was wetted with 4% sodium hydroxide solution and the wetted mass heated to 160° to convert the iron oxide to sodium ferrite [8]. The above mass was then stirred with sufficient water to hydrolyse the ferrite, allowed to stand for sometime to separate the liberated iron oxide and the supernatent liquid decanted off. The sand was further washed with 2% sulphuric acid to remove traces of free ion oxide still left and then washed with water. Iron was determined by usual method after drying. Results are given in Table 6.

(e) Sodium chloride process. The sand was mixed mechanically with 2.5% of sodium chloride and the mixture heated at 1100° for 1/2 hr [8]. It was then cooled, washed with water to remove surplus sodium chloride and other soluble impurities. After drying as usual, iron was determined in the sample by spectrophotometric method. Results are given in Table 6.

Results and Discussion

Table 1 shows that the iron oxide content in the raw samples of silica sand varies from 0.061 to 0.25%. Water washing reduced the iron content ranging from 4.01% to 73.68%. The more effective water washing in some samples (Table 3) implies that it contains a large part of ferrugenous clay minerals which are removed by water leaving behind a comparatively good quality of silica sand (enhancing the percentage of silica in the sand) (Table 1).

TABLE 4. IMPROVING OF THE IRON CONTENTS AFTER BENEFICIATION WITH COMMERCIAL HYDROCHLORIC ACID (CONC & 1:1).

Sample No.	% Fe_2O_3 in original sand	%Fe_2O_3 after treatment with HCL		%Reduction of Fe_2O_3 after treatment with HCL	
		Conc.HCL	1:1 HCL	Conc. CL	1:1 HCL
S-1	0.14	0.051	0.083	64.28	40.71
S-2	0.074	0.037	0.048	50.00	35.13
S-3	0.075	0.057	0.064	24.00	14.66
S-4	0.25	0.22	0.24	12.00	04.00
S-5	0.061	0.059	0.061	03.27	Nil
S-6	0.19	0.037	0.043	80.52	77.36
S-7	0.07	0.02	0.039	71.42	44.28
S-8	0.09	0.01	0.023	88.88	74.44
S-9	0.088	0.028	0.039	68.18	55.68
S-10	0.229	0.031	0.15	86.46	34.49
S-11	0.094	0.019	0.036	79.28	61.70

TABLE 5. IMPROVING OF THE IRON CONTENT IN SILICA SAND AFTER BENEFICIATION THROUGH OXALATE AND SULFITE PROCESS.

Sample No.	% Fe_2O_3 in original sand	%Fe_2O_3 after oxalate process	%Fe_2O_3 after sulfite process	%Reduction of Fe_2O_3 fter oxalate process	%Reduction of Fe_2SO_3 after sulfite
S-1	0.14	0.04	0.048	71.42	58.57
S-2	0.074	0.05	0.03	32.43	59.45
S-3	0.075	0.07	0.047	Nil	32.85
S-4	0.25	0.14	0.029	44.00	88.49
S-5	0.061	0.038	0.051	37.70	16.39
S-6	0.19	0.093	0.034	51.05	82.10
S-7	0.07	0.006	0.06	91.42	14.28
S-8	0.09	0.009	0.017	90.00	81.11
S-9	0.088	0.032	0.057	65.90	35.22
S-10	0.229	0.056	0.04	75.54	82.53
S-11	0.094	0.034	0.034	63.82	63.82

TABLE 6. IMPROVING OF THE IRON CONTENT IN SILICA SAND AFTER BENEFICIATION WITH SODIUM HYDROXIDE AND SODIUM CHLORIDE PROCESS.

Sample No.	% Fe_2O_3 in original sand	%Fe_2O_3 after sodium hydroxide process	%Fe_2O_3 after sodium chloride process	%Reduction of Fe_2O_3 after sodium hydroxide process	%Reduction of Fe_2O_3 after sodium chloride process
S-1	0.14	0.085	0.067	39.28	52.14
S-2	0.074	0.034	0.04	54.05	45.94
S-3	0.075	0.065	0.064	07.14	08.57
S-4	0.25	0.194	0.25	22.40	Nil
S-5	0.061	0.04	0.038	34.42	37.70
S-6	0.19	0.068	0.10	64.21	47.36
S-7	0.07	0.03	0.03	57.14	57.14
S-8	0.09	0.02	0.028	77.77	68.88
S-9	0.088	0.05	0.088	43.18	Nil
S-10	0.229	0.045	0.068	80.34	70.30
S-11	0.094	0.039	0.01	58.51	89.36

Glass making sands should pass through a 25 mesh sieve and a major part should be retained on 120 mesh sieve. The useful fraction (-25+120 mesh) of the sand samples vary from 24.95 to 83.48%. (Table 2). Samples of silica sand having high useful fraction (around 80%) are commercially viable. The rest of the samples are uneconomical and useless for the glass industry. However, these can be exploited for the manufacture of sodium silicate and amber glass/earthenware industries.

The silica sand samples were free from ferromagnetic particles as was evident during the magnetic treatment. Even after the two operations i.e. grading and water washing, the residual iron contents is too high for the manufacture of colourless glass. With a view achieving further substantial reduction in iron content, leaching with commercial hydrochloric acid was done using varying concentration (i.e. conc. HCl and 1:1 HCl). Notwithstanding the necessity of acid resisting equipment and cost factor involved for setting up a plant, laboratory scale experiment was performed as commercial hydrochloric acid is available at a reasonable price. The range of percentage reduction of iron oxide with conc. and dil. (1:1) HCl are 3.27 to 88.88% for conc. HCl and 0 to 77.36% for dilute (1:1) hydrochloric acid (Table 4). The results of beneficiation by Adam's process are moderately successful (0 to 91.42%) (Table 5). The process is suitable for sand beneficiation because of the easy and economical recovery and re-use of the reagent [3].

Treatment of sand with sulfite process gives a far better reduction in the iron oxide content 14.28 to 88.49% (Table 5). Beneficiation by sodium hydrochloride and sodium chloride process (Table 6), is not generally encouraging and limited in scope for these sand samples. But the methods are selectively suitable for some of the samples. The silica sand of Khisore and Marwat ranges are worth trying for local glass industries as after beneficiation majority of the sand samples meets the specification for colourless container glass industries at a competitive price as a result of saving of transportation cost to the glass industries of NWFP and Northern Punjab.

Conclusion

The glass industry in Pakistan uses 96% indigenous raw materials and low valued minerals, most important of them is silica sand. The silica sand deposits of Khisore-Marwat range have the potentiality to become a valuable source of glass making sand after various treatment suggested in the text. The main objective of this work was to minimise all the objectionable impurities by physical and chemical methods and upgrading the sand to meet the specification of colourless container glass industries. Results of some of the samples are very encouraging. The present study was an humble effort to help glass industries of NWFP finding suitable raw material in the area.

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