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CHARACTERISTICS OF SOME RIVER BED SANDS AND THEIR SUITABILITY FOR MAKING COLOURLESS GLASS

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ABSTRACT

While it is pertinent to note that sharp sand is a representation of a high energy environmental deposit of river and tidal channels activities in the Niger Delta Area, gravimetric methods were used for the characteristics of some river bed sands from various river locations in River Niger, Wilbros dockyard, Port Harcourt, Ughelli River, Ubangwe River, River Ethiope, in Abraka and Sapele, Ikpoba River and the Ogedegbe River all in Nigeria and their suitability for the making of colourless glass were analyzed. Gravimetric methods were used to determine the Loss on Ignition (LoI), Silica (SiO_2) and fusion were examined. The separation method was used in the determination of R_2O_3 and Fe_2O_3 Compounds. Grain size distribution analysis and the beneficiation and up gradation of samples were also examined. The silica sand samples were randomly collected in duplicate from the flowing point of the river and at position of approximately 20cm below the surface water level at an interval of 100meters. The results of the analyses revealed that silicon dioxide (SiO_2) formed the predominant metal oxide in the entire samples. . However further beneficiation of the obtained silica sand samples revealed an increase in SiO_2 with a decrease in iron (Fe_2O_3) content, thus implying that the samples can be used for glass making. Grain size distribution analysis revealed that a high percentage of the samples grains size distribution fraction were within the recommended screen sizes (40-100 mesh). Results obtained indicated that majority of the sands met the specification for Grade C and under British standard for colourless glass and just slightly fell short for the Grades A and B specifications and they also met the specification for the American standard for second and third quality flint glasses. Hence, it is time the federal government, nongovernmental organization, private individual and other stake holders to partners with stake holders in the region to take advantage of the availability of the minerals in the region to establish medium enterprises and firm, which in turn, will not only help engage the youth, nor potentially reduce the tension in the region or to generate revenue for government especially in these period of economic meltdown, but will also help diversify the Nigerian economy and reduce the country dependency on oil.

KEYWORDS: Silica, Quartz, Sand, River Bed, Loss On Ignition, Gravimetric Method, Chemical.

INTRODUCTION

Sand could be described as the product of the chemical and mechanical disintegration of rocks under the influences of weathering and abrasion. When freshly formed, the particles are usually angular and sharply pointed, becoming smaller and more rounded by attrition by the wind or by water [Microsoft Encarta, 2009]. It is a loose, incoherent mass of mineral materials in a finely granular condition, usually consisting of quartz (silica), with a small proportion of mica, feldspar, magnetite, and other resistant minerals. Sand is an important constituent of most soils and is extremely abundant as a surface deposit along the courses of rivers, on the shores of lakes and the sea, and in arid regions. It is generally mixed with cement to make concrete for construction work, mortar, clean up oil leak and as industrial cleaner to strip paint off the building and very importantly, in making glass. Sand is a major constituent of glass constituting from 52 to 65% of the mass of the original mixture, or from 60 to 75% of the finished product after melting has driven off carbon dioxide, sulphur dioxide, and other volatile materials. Thus, glass is made from a combination of network formers, modifiers and stabilisers; silica (SiO_2) is the most common network former in ancient glasses. They are material made by the rapid cooling of molten silica (sand) in such a manner that they do not crystallize but remain in an amorphous state.

Glass could be described as a fused mixture of the silicates of alkalis, alkaline earths, and of more common metals. Usually the alkaline bases are sodium and potassium; the alkaline earth is calcium, and the common metallic element is lead. All of these are used in the form of salts. In melting together the various ingredients employed in the batch or mixture, the silica, under the influence of heat in the presence of a flux, forms silicates with sodium or potassium, and calcium, lead, etc., and the alkaline silicate then dissolves 'the remaining silicates. This solution thus solidifies into glass on cooling. The Contributions to Economic Geology (1905) in their study, examined sand samples in order to ascertain its value for glass-making purposes, stated that inspection with a magnifying glass were the best preliminary test. They note the following observation that sand should be at least, white in color; it should be of medium fineness (passing a 20 to 50 mesh horizontal sieve); also, the grains should be uniform in size, even, and angular, or, less preferably, they may be rounded. Again, they suggested a simple chemical test by heating the sand in a dilute acid. Effervescence indicates the presence of lime; loss of color shows the presence of clay impurities.

They reported that iron in the minutest quantity may be detected by dissolving sand in hydrofluoric acid and adding potassium ferrocyanide, which produces a blue precipitate if iron is present. They thus suggested that the complete quantitative analyses as well as a furnace test should be made as a final determination of the character of prospective glass sand. The sample sites in this study has white quartz sand which is evidently a near-shore deposit, and its purity, freedom from mud and other fine detritus, the uniform size of its particles, and their sub-rounded character indicate long-continued sorting action at this part of the shore. The grains are of medium fineness, practically all passing a 40-mesh sieve and 25 per cent passing a 60-mesh sieve. While it is necessary to note that sharp sand is a representation of a high energy environmental deposit of river and tidal channels activities in the area, the factors on which sand deposit depends for its possible value for glass making are firstly, chemical composition; secondly, the physical character; thirdly, the amount available; again , location with respect to fuel supplies; also, conditions of quarrying or mining; furthermore, the location with respect to transportation routes, and lastly, location with respect to markets. The sample sites used in this study - River Niger in Itobe; Wilbos dockyard, Port Harcourt; the Ughelli River; the Ubangwe River; the River Ethiope, in Abraka and Sapele, Ikpoba river and the ogedegbe river all in Nigeria has large deposit of silica sand along its shore. These deposits do not only cause obstruction to free flow of inland water way transportation of goods and services but also prevent the generation of revenue due to under utilization. Though, silica deposit from these sample sites is dredged and used for construction purpose, there is need to investigate the potentials of this vast silica sand deposit within the State for the establishment of glass and other allied industries. Hence, the aim of this study is to study the characteristics of some river bed sands and their suitability in the making of colourless gasses.

MATERIALS AND METHODS

The Geology of the Niger Delta

Glass sand is associated with the coastal plain of sedimentary areas in the southern part of Nigeria, although deposits also occur in some inland areas. The Niger Delta topography generally is sub – horizontal – undulating. The area is low lying and is drained and criss – crossed by an anastromosing network of river distributaries. Youdeowei and Nwankwoala, (2012) in their study reported that the modern Niger Delta was formed during the third and last depositional cycle of the southern Nigerian basin which started in the paleocene. It was recorded that the region was formed during the tertiary period as a result of the interplay between subsidence and deposition arising from a succession of transgressions and regressions of the area. These phenomena evolved the three main lithostratigraphic units of Akata, Agbada and Benin formation with an overall approximate thickness of over 5000m of sediment body. Table 1 show the geologic unit of the study area.

Table 1: Geologic unit of the Niger Delta

Geologic Unit	Lithology	Age
Alluvium (General)	Gravel, Sand, Clay, Silt	
Fresh Water Backswamp, meander belt	Sand, Clay, Some Silt, Gravel	
Salt water Mangrove Swamp and backswamp	Medium – fine sands, clay and some silt	Quaternary
Active / Abandoned beach ridges	Sand, clay, and some silt	
Sombreiro – Warri deltaic plain	Sand, clay, and some silt	
Benin formation (coastal plain sand	Coastal to medium sand, subordinate silt and clay lenses	Miocene – Recent
Agbada formation	Mixture of sand, clay and silt	Eocene – recent
Akata formation	Clay	Paleocene

Source: Akpokodje (1989)

Sample Collection

The silica sand samples were randomly collected in duplicate from the flowing point of the river and at position of approximately 20cm below the surface water level at an interval of 100meters from each other and from various river locations in River Niger, Wilbos dockyard, Port Harcourt, Ughelli River, Ubangwe River, River Ethiope, in Abraka and Sapele, Ikpoba river and the Ogedegbe river all in Nigeria. Sample collection was done between the month of December and January to reflect the late dry season periods when water tidal influence is at low level. The collected samples were each separately prepared by thoroughly blending the material by “centre displacement method” so as to obtain a homogenous material. 100kg of each sample was heaped, thoroughly mixed and quartered. Quartering was repeated and duplicated samples of homogeneous mixture were obtained. The well labeled samples were then put into sample bags to distinguish them from each other. The labeled silica samples were taken to the laboratory for pretreatment and preparation.

Sample Pretreatment and Preparation

The collected samples were each poured on a 200 mesh screen and placed in a plastic container, scrubbed and de-limed (thoroughly washed with water to remove impurities such as clay and soluble materials) and finally with distilled water (Allen,1974). After washing the samples were air-dried in the open for one week and finally dried in the oven at a temperature of 110^oC for seven hours. After drying, about 100g were taken from each samples, weighed and homogenized into fine grain. The crushed fine grain particles were further sieved using a 100 mm mesh screen to ensure homogeneity of particle size (Plate 2). To avoid contamination of samples, the crusher and mesh were repeatedly washed and rinsed with distilled water each time a new sample was to be crushed and sieved. Each of the pulverized samples was poured in a clean dried universal bottles and sets for chemical analysis while the other remaining parts of the uncrushed samples were preserved for physicochemical analysis.

Sample Analysis

Gravimetric Methods

Loss on Ignition (LoI) Determination

1gm, of the prepared sample was placed in an ignited weighed platinum crucible. It was the heated to a temperature of 1100^oC in a partially open muffle for about one hour. The crucible and its contents were then allowed to cool in desiccators.

$$\%\,loss\ on\ ignition = \frac{wt\ of\ crucible + sample - wt\ of\ crucible\ and\ sample\ after\ ignition}{wt of\ sample}\ x\ 100$$

Determination of Silica (SiO_2)

Few drops of conc. Sulphuric acid and 5ml of hydrogen fluoride was added to the sample and fumigated on a hot plate. Care was taken to avoid loss by spotting. After cooling, the side of the crucible was washed down by distilled water, and a further 3ml of hydrofluoric acid was added and the fumigation repeated to dryness. The residue was ignited first at 800^0C and then at 1100^0C in a muffle furnace.

$$\%\,SiO_2 = \frac{wt\ after\ ignition - wt\ before\ fumigation}{wt of\ sample}\ x\ 100$$

Fusion

After determination of the percentage SiO_2, the contents of the crucible were fused with $NaKCO_3$ and 0.3gm tetraborate at 1100^oC in a muffle furnace. A stock solution was then produced by dissolving the fused contents of the crucible in HCl (1:1) and this was stored in a 250ml volume flask, which was then made to the 250ml mark with distilled water.

Determination of R_2O_3 Compounds

Separation Method

To determine the value for R_2O_3 compounds present, 100ml of the stock solution was pipetted into a beaker and to this solution was added NH_4Cl salt. The R_2O_3 compounds present were then precipitated using NH_4OH on hot plate. The precipitate formed was filtered off using 41 Whatman filter paper. The residue and the filter paper was burnt in a crucible of known weight using a muffle furnace. The crucible and its content was then allowed to cool in a decimator and it was then weighted.

$$\%\,R_2O_3 = \frac{wt\ of\ crucible + burnt\ filter\ paper - wt\ of\ empty\ crucible}{wt of\ sample}\ x\ 100$$

Determination Fe_2O_3

After the determination of the total R_2O_3 value, the crucible content was dissolved using HCl (1:1) in a beaker. $SnCl_2$ was added to this solution so as to reduce the iron thus: Fe^{3+} - Fe^{2+} + e^-. The mixture was then allowed to cool in a cold bath and $HgCl_2$ was then added to react with the excess $SnCl_2$. Also a specific acid mix was added to mask the reactivity of the other elements apart from iron. A few drops of Diphenylamine were then added to act as an indicator. Finally, a titration was carried out on the mixture using $K_2Cr_2O_7$ (0-IN).

$$\%\,Fe_2O_3 = (Titre\ value\ X\ 4)\ X\ F_{factor\,x\,1.429\ constant}$$

Where F_{factor} = Correction factor for the preparation of (0.IN) $K_2Cr_2O_7$. Therefore, percentage Al_2O_3 is thus; % $Al_2O_3 = R_2O_3 - Fe_2O_3$

Grain Size Distribution Analysis

The grain-size analysis was carried out to determine the percentage ideal fraction of the silica sand samples using a standard set of sieves (from 20-140 mesh).100g of each of the dried sample was poured into an Endoctts sieving machine model EFL 2000/1 with standard mesh range of 20-140. The machine was electrically agitated for 30 minutes and the percentage retentions of grain size of each sample on each sieve calculated. (Freestone, 2005; Ushie *et al.*, 2005; Sundararajan *et al.*, 2009). Further, the silica sand samples grains shape distribution patterns were observed using a magnifying machine, Suntex colony counter model 560 (Ushie *et al.*, 2005).

Beneficiation and Up Gradation of Samples

The beneficiation of the silica sand samples was done by taking 20g of the representative samples and were weighed and placed in a 250 mL flask and 100mL of oxalic acid added. The mixture was placed on a heating plate and agitated (870 rpm) at a temperature of 80^0C to 90^0C for 2hours.To ensures uniformity; the agitation was kept constant for all the experiments. A watch glass was fitted to the flask to prevent evaporation during each experiment, the samples were filtered and the residue washed with distilled water and dried in an oven and the percentage concentration of metal oxides in each sample determined using XRF method.

RESULTS AND DISCUSSIONS

The results of analysis for the characteristics of some river bed sands and their suitability in the making of colourless gasses is shown in table 2 to 6 below

Table 2: Percentage Composition of Sands of Various Quality Based on Ignited Samples

Qualities	Si_2O	Al_2O_3	Fe_2O_3
First quality optical glass	99.80	0.100	0.020
Second quality flit glass containers, tableware	98.50	0.500	0.035
Third quality flint glass	95.00	4.000	0.035
Fourth quality sheet glass rolled and polished plate	98.50	0.500	0.060
Fifth quality sheet glass rolled and polished plate	95.00	4.000	0.060
Sixth quality green glass container and window glass	98.00	0.500	0.300
Seventh quality green glass	95.00	4.000	0.300
Eight quality amber glass container	98.00	0.500	1.000
Ninth quality amber glass containers	95.00	4.000	1.000

America Standard for Silica for glass making

Table 3: the British Limits for Chemical Composition of Sand for Making Colourless Glass Based on Materials Dried at 110°C.

Grade of Sand	Minimum Silica (SiO_2) Content (%)	Minimum Total Iron (as Fe_2O_3) Content (%)	Aluminium Oxide (Al_2O_3) Content
A	99.50	0.008	
B	99.50	0.013	
C	98.50	0.030	

Grade A: Fine – grade optical glass ware; **Grade B**: High grade domestic glass ware; **Grade C**: General colourless glass ware including containers.

Table 4: Tabulated Results of LoI Values, SiO_2, Fe_2O_3 and Al_2O_3 that are Present in Samples

Locations (Towns)	Parameters present in samples (%)			
	LoI	SiO_2	Fe_2O_3	Al_2O_3
River Niger	4.56	90.70	3.07	2.68
Ekpoma	0.32	90.70	2.46	1.77
Benin	0.30	91.60	2.92	2.18
Abraka	0.11	97.50	0.62	1.68
Sapele	0.17	96.90	0.52	0.98
Warri	0.18	97.90	0.52	0.98

Table 5: Grain size distribution analysis of silica sand samples from form various location

Mesh no	Sieve size (mm)	River Niger	Wilbros Dockyard	Port Harcourt	Ughelli River	Ubangwe River	River Ethiope (Abraka)	River Ethiope (Sapele)	Ikpoba River	Ogedegbe River
20	0.840	0.32	0.24	0.00	0.00	0.04	0.06	0.05	0.10	0.03
30	0.600	1.37	1.48	1.60	1.28	1.32	1.40	1.48	1.32	1.39
40	0.425	18.90	17.85	18.45	17.70	17.07	17.13	18.18	18.78	17.42
50	0.300	35.89	36.40	37.50	38.90	38.26	38.97	38.84	36.48	38.47
70	0.212	30.40	32.10	31.48	32.23	31.11	33.19	31. 49	31.23	30.70
100	0.150	7.90	8.60	8.27	8.19	7.30	8.36	8.89	7.81	7.70
140	0.100	2.10	1.38	1.93	0.67	0. 03	0.76	1.00	1.63	0.02

Table 6: Beneficiation percentages composition of metal oxides in the silica sand samples from various River

Locations	Parameters Present in Samples (%)		
	SIO_2	Fe_2O_3	Al_2O_3
River Niger	94.70	1.97	0.07
Ekpoma	95.40	1.34	0.08
Benin	96.60	1.52	0.07
Abraka	99.50	0.32	0.05
Sapele	99.40	0.49	0.02
Warri	99.98	0.39	0.00
Ughelli	99.40	0.83	0.00
Port Harcourt	99.99	0.49	0.00

Silica

Data in this study reveals that the high SiO_2 content trend in all the samples shows that all the silica sand generally consist of high SiO_2 content. This is in agreement with the study of Edem *et. al.,* (2014); Shakila *et. al.,* (1999); Sundararatan *et. al.,* (2009); Pisutti *et. al.,*(2008); Babasaheb, (2010). To the glass manufacturer, high silica content is most desirable. A look at the results on Table 4 reveals that the samples collected from the River Niger at Itobe, Ogedegbe River at Ekpoma and the Ikpoma River with percentage silica content of 90.70, 90.40 and 91.60% respectively do not meet both the British and American standards for any grade of glass. However, on considering the sample collected from Abraka with silica content of 97.50 per cent, it does not meet with the British standard but it can be seen to have met with the American specification for third quality flint glass, fifth quality sheet glass rolled and polished plate, seventh quality green glass and ninth quality amber glass. The samples from Sapele, Warri and Ughelli with silica content of 96.40%, 97.90% and 97.80% respectively. This sample meets the American specifications for third quality flint glass; fifth quality sheet lass rolled and polished plate, seventh quality green glass and ninth quality amber glass. But on the other hand they do not meet the British specifications for any grade of glass. From Table 4, it can be seen that only the samples collected form Port-Harcourt with silica content of 98.50 per cent clearly met with the British specification (i.e. for grade C sand) and the American specifications for second quality flint glass containers, third quality flint glass, fourth quality sheet glass rolled and polished plate, fifth quality sheet glass rolled and polished plate, sixth quality green glass, seventh quality green glass, eight quality amber glass and ninth quality amber glass. Data from this study reveals that the sample collected from the River Niger – Itobe has the lowest silica content of 89.70 per cent while those collected from Port-Harcourt has the highest silica of 98.50 per cent. The various concentration of SiO_2 observed though may be attributed to some geological factors such as type of weathering and distance travelled by particle size from source rock of the individual rivers. However further beneficiation of the obtained silica sand samples revealed an increased in SiO_2 with a decrease in iron (Fe_2O_3) content of which means that the samples can be used for glass making (Ushie *et al.,* 2005). The various concentration of SiO_2 observed though may be attributed to some geological factors such as type of weathering and distance travelled by particle size from source rock of the individual rivers.

Iron Oxide

Iron oxide content is perhaps the most critical chemical component for all glass raw materials. Data from this study as shown in table 4 reveals that the samples collected is form river Niger – Itobe, River Ogedekpe Ekpoma, Ikpoba River Benin, River Ethiope Abraka, River Ethiope Sapele, Warri River, Ughelli River and Wilbras dockyard Port-Harcourt with iron content of 3.07, 2.46, 2.92, 0.62, 0.69, 0.52, 1.20 and 0.85% respectively has not met the British specification for any grade of glass. Notwithstanding, it can be seen that samples collected from Abraka, Sapele, Warri and Port-Harcourt met the American specification of iron required for eight quality amber glass and ninth quality amber glass. The concentration of Fe_2O_3 in any silica sand deposit determines the quality of glass to be produced. A slight increased in Fe_2O_3 content gives the glass a green, yellow or red colour as a result should not exceed 0.005 percent. This colouration to a certain extent can be neutralized by the addition of manganese resulting to a faint shade or purple colour (Horst, 1991; Goldman, 1994; Heck, 2002). Hence results from this study reveals that silica samples are not suitable for making colourless glass of flint. However, Edem *et. al.,* (2014) in their study, carried out further benefication on the silica sample and they obtained improved SiO_2 content and thus decrease their iron (Fe_2O_3) content which thus made the silica sample useful for their desire use.

Aluminium Oxide

Aluminium oxide content does not affect the colour of glass to be made. General survey reveals that the limit of aluminium oxide content, if required, is regularly fixed by agreement between the glass manufacturers and sand suppliers. Data from table 4 reveals that the sample collected from Port-Harcourt has aluminium oxide content of 0.45% while the silica sample collected from River Niger at Itobe has alumina content of 2.68%. data further reveals that the silica sample collected from Port Harcourt with Al_2O_3 content of 0.45% met with the American specifications for second quality flint glass, fourth quality sheet glass rolled and polished, sixth quality green glass and eight quality amber glass. Furthermore it can also be deduce from table 3 that the samples collected from Ughelli River, Warri River, Ethiope River Sapele, River Ethiope Abraka, Ikpoba River Benin, Ogedekpe River Ekpoma and River Niger – Itobe with Al_2O_3 content of 0.64, 0.98, 211, 1.68, 2.18, 1.77 and 2.68% respectively met with the American standard specification for Al_2O_3 required for second quality flint glass, third quality flint glass, fourth quality sheet glass rolled and polished plate, sixth quality green glass, seventh quality green glass, eight quality amber glass and ninth quality amber glass.

Grain Size Distribution Analysis

Data from this study revealed that the highest percentage retention fraction of the silica sand sample was between mesh number 40 to 70 (98%), This implies that silica sand samples met the requirement of sieve size retention fraction at different significant percentage levels of between 40 – 100 sieve size. Grain size distribution plays an important part in silica sand requirement. Large grain do not mixed proper with the other grains in the batch while too fine grain create air bubble in the glass final product. (Edem, *et. at.,* 2014). Hence, this study further reveals that the grain size distribution fraction from from the various locations in the Niger Delta Area of Delta State, Nigeria falls within the recommended size range of 40 to 100 screen mesh (Crockford, 1949; Sundeen, 1978; Robert, 2002).

CONCLUSION

The study reveals the large glass sand deposit in the Niger Delta region of Nigeria with great prospect for investors, private partnership, NGOs and most especially, the federal government of Nigeria taking advantage of the huge mineral deposit not just to invest with the aim to generate revenue for the country, or to reduce the rate of youth unemployment in the region, but they should seize the opportunity to diversify the economy and reduce the country dependency on oil

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