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CHEMICAL EVALUATION AND YIELD ESTIMATE OF ALLUVIAL SEDIMENTS OF FIVE MAJOR RIVERS IN SOUTHWESTERN NIGERIA FOR GLASS RAW MATERIALS

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ABSTRACT

Alluvial sands are detrital materials which are transported by a river and deposited, usually temporarily, at points along the flood plain of the river. These sands are majorly consumed in construction industries, especially in developing countries like Nigeria. However, with value addition, it could have a high value-to-mass ratio. The alluvial sands of five major rivers in southwestern Nigeria were investigated. A total of 51 samples were collected along the channels of River Yewa, River Ogun, River Ona, River Osun, and River Shasha during the dry season in 2024. The objectives were to: assess the major chemical composition of alluvial sand vis-à-vis specification requirements for various glass industries; determine the beneficiation requirements where necessary for the silica sand to meet specification; and determine the tonnage of sediments and silica yields per year. The samples were analysed using (XRF) and XRD. The mean percentage of major oxides for the five rivers are SiO_2 75.78%, TiO_2 1.97%, Al_2O_3 8.96%, Fe_2O_3 4.45%, MnO 0.27%, MgO 1.25%, CaO 2.49%, Na_2O 0.08%, P_2O_5 0.52%, Cr_2O_3 0.23%, and LOI 9.79%. Based on the chemical specification, it was found that the sands are not suitable for the production of first-quality glass materials. However, they are suitable for glass wool, optical glass, flat glass, glass ceramic, container glass etc. based on Best Available Techniques BAT, (2013). The Chemical Index of Alteration (CIA) was adopted to estimate the sediment yield of all the rivers. The average sediment yield of all the rivers was estimated at 2772.64t/km^2/yr. Out of which 1981.71t/km^2/yr of silica was generated. It was concluded that such an estimate could boost the GDP of the country if well-harnessed.

Keywords: Silica sand, Weathering, Specification, Beneficiation, CIA

INTRODUCTION

Alluvial sand is a terrigenous sedimentary rock belonging to the arenite family and the subfamily of unconsolidated arenites (Mambou and Mvogo, 2020). It is an accumulation of sediment deposited from running water in a channel or coastal or deltaic plain and comprising gravel, sand, mud, coal and chemical precipitates (Phillip, 2001). Larger particles are granules, pebbles, cobbles, or boulders (>256 mm) and smaller grains are silt (0.0625 mm) or clay (<0.004 mm) (Shaffer, 2006).

The term 'Silica Sand' is used to identify sand that conforms with the specifications of the main composition of about 95% SiO2 with an impurity of less than 5% (Sara *et al.*, 2003). Silica sand forms the major ingredient among natural raw materials needed for glass making (Ramag,2021). It provides the SiO_2 component of glass formulation. These command higher prices than construction sands and serve a wider geographical market, including exports (BGS, 2020), as it has wide industrial uses. For instance, in 2022, Glass fibres were the world's 271st most traded product (out of 1218), (OEC,2022), the top exporters are China ($3.7B), the USA ($1.32B), Germany ($1.06B), Belgium ($696M), and France ($640M).

However, Nigeria has extensive deposits of good quartz silica sands (RMRDC,2010). However, there is a research gap in areas of exploration, exploitation and end uses. Some of these deposits either require more geological investigation or are not being exploited (RMRDC, 2010) except for use in civil engineering construction that harnesses the physical properties; and represent more than 99% of the 50 billion tonnes of sand extracted (FEVE,2020). The chemical industry represents less than 1% of the 50 billion tonnes (FEVE,2020) among this, is the glass industry. FMI, (2023) had estimated that the global silica sand for glass-making market is expected to register a compound annual growth rate (CAGR) of 4.1% between 2023 and 2033. The valuation is projected to cross US$ 8.5 billion by 2033(FMI, 2023). This is due to the surge in the construction sector, rapid urbanisation worldwide, product innovations-introduction of solar power glazing, application of nanotechnology, usage of hybrid guide plates, as well as the new technology of recycling collected glass that has been found to replace the batch virgin ingredients to the tune of 52%(FEVE,2020). It is therefore desirable to investigate the chemical composition of the vast silica sand deposit in Nigeria, as the only reliable way of assessing the proportions of silica, iron and other constituents within the sands (Thompson and Poole, 2016) for glass making. The iron level is the most critical parameter in determining whether particular sand can be used to make clear or coloured glass (David, 2016). Also, many other chemicals can be added to the mixture to create certain properties which make it one of the most versatile engineering materials (RMRDC, 2001). To this end, southwestern Nigeria has been taken as a case study, thereafter, the research could be extended to other regions.

MATERIALS AND METHODS

Location, Climate, and Drainage of the study area

The study area is a part of southwestern Nigeria. It occupies parts of Meko Topographic sheet 59A, Ibadan sheet 59, Ilesha sheet 60 and Akure sheet 61, within longitude 2^{0}45'E and latitude 5^0 00'E and longitude 6^{0}30'N and latitude 8^{0}00'N (Fig. 1). The area falls within the humid tropical climatic zone which has prominent wet and dry seasons. Annual rainfall ranges between 100 mm and 1500 mm, with average wet days of about 100mm. Annual temperature varies between 18^{0}C and 34^{0}C (IIoeje,1980).

Drainage of the area

Streams flowing across the area are widely spaced, deeply incised and consist of south-flowing consequent streams as well as south-east flowing subsequent ones. This drainage direction is controlled by foliation and joints in the Basement Complex.

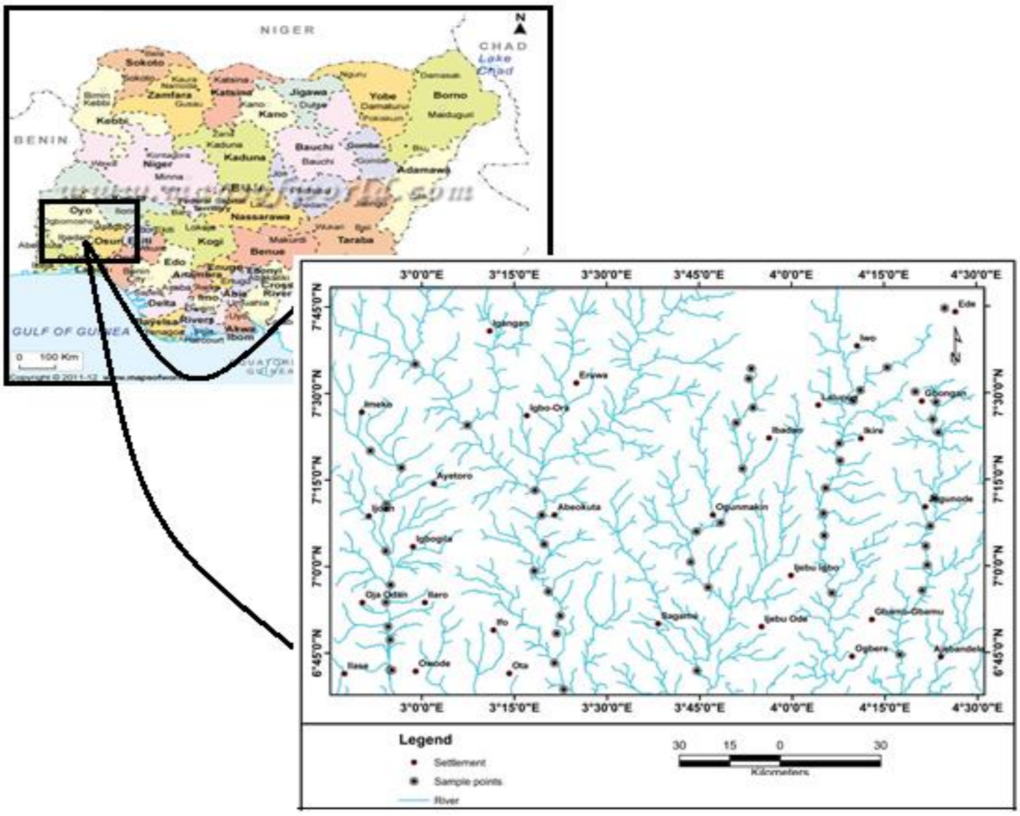

Figure 1: Location map of the study area showing the sample points along the major river channels

The major rivers of the study area are the Shasha, Owena, Ona, Oshun, Ogun and Yewa. The drainage density of the Oshun and Owena basins is lower than that of the Oshun and Yewa basins (Azeez, 1972). Most of the rivers are generally turbid during the wet season owing to high clay content in their upper reaches. In the dry season, flow is considerably reduced and sustained by effluent seepage. The smaller streams become local puddles with small connecting trickles (Azeez, 1972).

Geology of the area

The Basement Complex terrains of South-western Nigeria consist of Precambrian basement rocks, which comprise crystalline igneous and metamorphic rocks mostly granite/porphyritic granite, granite-gneiss, quartz-schist, migmatite as well as Augen-gneiss, Pegmatite intrusions and variably Migmatized Biotite-hornblende Gneiss (Lateef,2012; Aizebeokhai *et al*.,2016; Bayewu, 2017).

The southern part of Ogun State is underlain by Sedimentary rocks which consist of sandstone and shale (mudstone) of Cretaceous to Tertiary age. Abeokuta formation of the Cretaceous age consists of sandstone, which forms an excellent aquifer. Ewekoro/Imo shale and Oshosun Formation are mudstone covering Abeokuta Formation. Overlying the above formations, the Ilaro and Ameki Formations consist of mainly sandstone and form an aquifer. (JICA, 2014). Along the coastal plain in the south of the Ogun-Osun Basin is the Quaternary Formation (JICA, 2014) is an Alluvial Formation distributed on small to large scale (Fig. 2). It consists of unconsolidated and half-consolidated sand and clay with high permeability forming an aquifer.

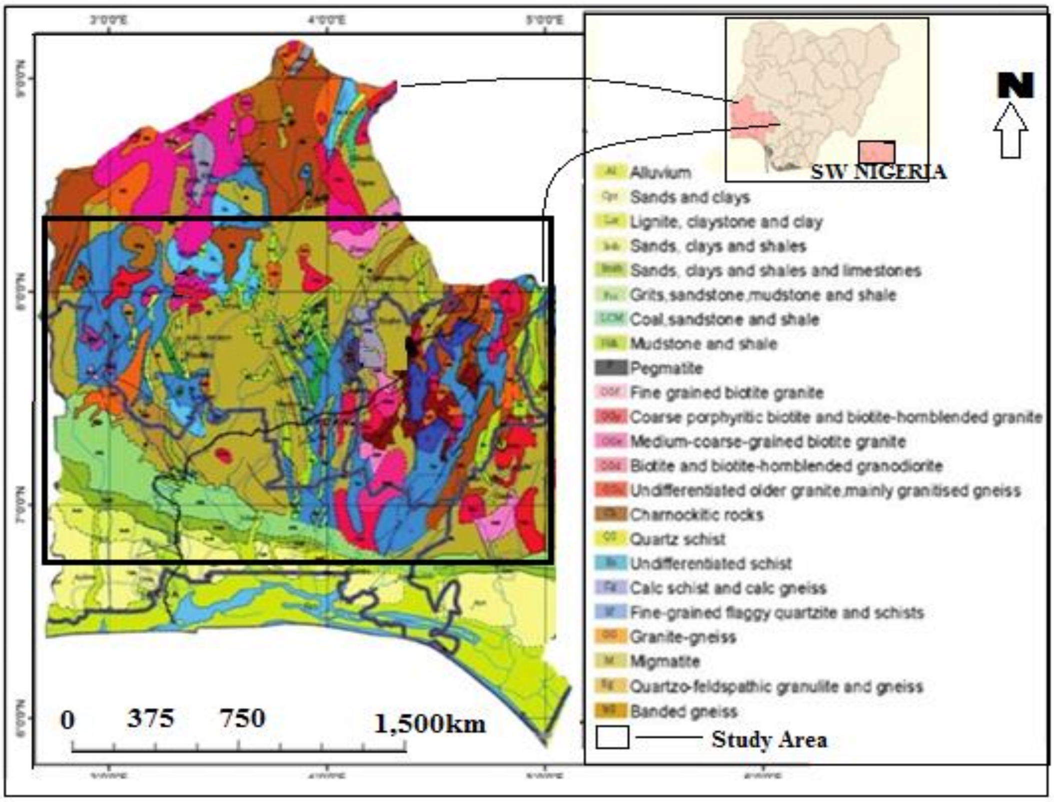

Figure 2: Geology map of the study area (adapted after NGSA, 2008)

The research questions

How do the chemical compositions of each river (sub-basins) differ from each other?

Is there any difference in the quantity of silica sand generated through the Chemical Index of Alteration by each river (sub-basin) despite being from the same Crystalline Basement Rocks?

Sample site selection

The fieldwork was designed to capture the geology and the weathering products within the drainage pattern of the area. The area is basement terrain and drainage patterns are dendritic, it was designed that sampling be carried out at the tributary's junctions, especially at the 2nd and 3rd order of the sub-basin units, to reflect the mineral compositions of inland areas traversed by each stream. The samples were collected from the exposed bars or inside bends of a river meander or behind the boulders and in still water close to the edge or border where water hugs the land.

Sample collection

A 45- 50 kg wet-weight bulk sample was obtained in each location, and a total of 51 samples were collected along the five major rivers in southwestern Nigeria between January and March 2024. The rivers are River Yewa, River Ogun, River Ona, River Osun, and River Shasha. Within the dry channels, a hand trowel covered with polythene was used to scoop sands at the channel centerline and at both sides of the channels to cater for site variability, while a 140mm width by 600mm long polyvinyl chloride (PVC) pipe was inserted into a channel with water, and samples were collected using a plastic cup and polythene to prevent fines from getting lost along the water column. These were then sieved using a 4.75mm mesh (fine gravel) to guaranteed homogeneity. Other precautions and procedures adopted were as given in ASTM D75- a guiding principle in the sampling procedure. ASTM C702 informed and guided the sampling procedure employed in reducing the field sample to obtain the required test portion for each of the tests performed.

Sample Types and Depth

The top layer of the dry sand and still water sand interface (0 -2cm) was first removed to reduce organic contaminants in the samples. Thereafter, samples were taken at 2.0-20cm,20-30cm and 30-40cm within the same hole to cater for sediment heterogeneity. By visual inspection, particles of the sediments more than 2.5mm in diameter were manually removed, and the composition mainly consisted of fine gravels, sands, silts and clays. The average thicknesses of the sediment in all the channels were between 2.0 -40.5cm, as most of the channels are characterized by chaotic arrangement of gravels and boulders.

Sample preparation and treatment

The samples were wrapped into black polythene bags and labelled with their code (e.g. YE 01 representing Yewa River location 1), and coordinates were recorded to avoid mix-ups before transportation to the laboratory. The distances of sampling between one location and the other vary from 100m to 4000m, according to the intervals between the one tributary and the other. The problem encountered was accessibility and insecurity in some of the areas. The samples were sealed in second black polythene bags to prevent sample busting and to reduce moisture losses. The samples were later transferred to the Soil Laboratory of the National Water Resources Institute, Kaduna where they were air dried at room temperature (26^o - 27^oC) for three weeks after some parameters had been measured. This is because air drying helps stabilize the moisture content of the soil, which is crucial for consistent results when analyzing physical and chemical properties.

Processing of the River Sands: Some quantities of sand samples were subjected to some basic sand processing and beneficiation procedures. These include washing, scrubbing and acid leaching. During processing, the sand samples were first washed with water while scrubbing at the same time, then washed with dilute HCl, and then dried before taking for further chemical analysis.

The Acid Solubility Test (AST) is a measure of soluble carbonates or hydrogen carbonates in the sample. The AST was carried out according to the methods of WHO (2004). Four hundred (400) grams of sand sample were taken from the washed stock and recorded (W_1). The weighed sample was then immersed in 40% (by volume) of hydrochloric acid (HCl) + 60% distilled water for 24 hours (1 day) in a plastic bucket, to dissolve any organic matter present in the sample. The sample was then filtered with the aid of filter paper and a funnel to collect the residue (sand sample). The residue collected was properly rinsed with distilled water and then oven-dried for 2 hrs at 105 ℃ and later weighed (W_2) to determine the loss in weight. The percentage Solubility was then calculated as follows:

$$\%Solubility = \frac{W1-W2}{w1} x100 \quad (1)$$

Where: w_1= Initial weight of the sand sample, w_2 = Final weight of the sand sample, w_1- w_2= Loss in weight of the sand sample.

Laboratory Analysis

For the chemical analysis, those samples that were within the same micro catchment were mixed together in equal proportion as composite samples (using coning and quartering method). The percentage concentration of metal oxides in each sample determined using XRF The X-ray fluorescence Spectrometry (XRF) method was used to analyse the major oxides and elemental concentrations (in percent weight), while X-ray diffraction (XRD) method was adopted for heavy minerals at the National Steel Raw Materials Exploration Agency, Kaduna and Nigerian Geological Survey Agency (NGSA) Kaduna respectively. The results of these oxides SiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, CaO, MgO, K_2O, MgO, MnO, Na_2O, TiO_2 and LOI were subjected to T-test at $P \leq 0.05$ to analyze the level of variation in chemical composition at different rivers across the project sites.

RESULTS AND DISCUSSION

Geochemical analysis

The geochemical analyses carried out on the samples using XRF yielded data for the concentration of 10 major elements (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MgO, CaO, Na_2O, K_2O, P_2O_5, and MnO and LOI (Table 1). From Table 1, it is observed that the mean percentage of SiO_2 as a major raw material in all the samples were below 90%; and are not the same. The SiO_2% shows that River Shasha > River Ona> River Osun> River Yewa> River Ogun. Other oxides display an interchanging proportion. All these varying geochemical parameters are a demonstration that the geology of the area is not homogenous. Table 1, shows that there is a significant difference (at $P \leq 0.05$) in the composition of major oxides in all the river channels, even though they traverse the same region with the same Crystalline Basement Rocks of southwestern Nigeria. This can be attributed to alterations in the mineralogy of the preexisting rocks during the tectonic-metamorphic events of the Pan- African orogeny (Dada,2008).

Table 1: Mean variation of Major Oxides (wt%) and weathering indices of sediments of five major Rivers in Southwestern Nigeria

Analytes	River Yewa	River Ogun	River Ona	River Osun	River Shasha	P- value
SiO_2	70.01±0.83	62.83±1.64	76.66± 3.03	70.11 ±0.51	85.49±0.51	
	(69.12 -711)	(60.95- 4.72)	(73.07-9.98	(69.45-70.46)	(84.83-85.85)	4.54 x10^{-6}
TiO_2	0.55 ±0.26	2.17±0.50	0.56±0.05	5.07±1.52	1.52±0.51	
	(0.34-0.90	(1.51-2.52)	(0.14-0.26)	(69.45-70.46)	(0.86-1.87)	1.22 x 10^{-6}
Al_2O_3	9.54 ±0.51	11.1±0.51	8.94±0.51	9.92± 5.3	5.3±0.51	
	(8.88-9.89)	(10.44-11.45)	(8.28-9.29)	(4.41-5.42)	(4.64-5.65)	2.79 x 10^{-6}
Fe_2O_3	2.52 ±0	7.2±0.51	3.56±0.51	6.33±2.64	2.64±0.50	3.03 x 10^{-6}
	(2.51-2.85)	(6.54-7.55)	(2.90-3.91)	(9.29-10.27)	(1.98-2.99)	
MnO	0.2±0.05	0.24 ±0.008	0.19±0.01	0.58 ±0.32	0.13±0.04	0.0427
	(0.13-0.25)	(0.23-0.25)	(0.17-0.20)	(5.67-6.68)	(0.08-0.16)	
MgO	0.001±ND	±ND	6.19±0.51	0.001 ±ND	0.11 ±0.09	1.43 x 10^{-7}
	(---------)	(-----)	(5.53-6.54)	(------)	(0.01-0.23)	
CaO	0.87 ±0.51	6.6±0.51	0.95±0.51	2.74 ±0.51	1.3 ±0.50	1.11 x10^{-6}
	(0.12-1.22)	(5.94-6.95)	(0.29-1.30)	(2.08-3.09)	(0.64-1.65)	
Na_2O	0.02 ±0.51	0.04±0.51	ND ±ND	±0.51	ND ±ND	
	(0.64-0.37)	(0.35-0.65)	(-------)	(0.38-0.63)	(-------)	4.48 x 10^{-4}
K_2O	0.12 ±0.04	5.44 ±0.51	1.38±0.51	2.98 ±0.51	1.44 ±0.50	1.92 x 10^{-6}
	(0.08-0.16)	(4.78-5.79)	(0.72-1.73)	(2.32-3.33)	(0.78-1.79)	
P_2O_3	ND±ND	2.07±0.51	0.16±0.02	0.36 ±0.05	ND ±ND	7.88 x 10^{-6}
	(--------)	(1.41-2.42)	(0.14-0.18)	(0.30-0.43)	(-------)	
Cr_2O_3	0.09±0.008	0.04±0.02	0.07±0.01	0.05 ±0.02	0.88 ±0.07	2.37 x 10^{-10}
	(0.08-0.10	(0.02-0.06)	(0.06-0.08)	(0.04-0.08)	(0.81-0.96)	
LOI	10.1±0.508	9.7±0.51	11±0.51	10.5 ±0.51	8.74 ±0.51	
	(9.44-10.49)	(9.04-10.05)	(10.34-1.35)	(9.84-10.85)	(8.08-9.09)	-----------
Values are mean (%) ± S.D(%), (Minimum – Maximum% values in parenthesis), P≤ 0.05						
CIA (%)	79.74	53.72	77.16	55.26	58.86	
Acid Solubility(%)	1.60	1.75	0.95	1.20	1.04	

From Table 2, over 40% of the correlations vary between the very strong to strong correlation. The very strong positive correlations are MnO versus TiO2, Fe_2O_3 versus K_2O, CaO versus (K_2O and P_2O_5), K_2O versus P_2O_5. While the strong negative correlations are: SiO_2 versus Fe_2O_3 and K_2O, Al_2O_3 versus Cr_2O_3. It is an interplay between the mobile (e.g. SiO_2, CaO, MgO, and Na_2O) and immobile (e.g. Al_2O_3, Fe_2O_3, and TiO_2) elements occasioned by chemical weathering. Those oxides with high positive correlation coefficients probably have similar geochemical characteristics.

Table 2: Pearson's correlation matrix of major oxides in the alluvia sediments of five rivers in southwestern Nigeria

Oxides	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cr_2O_3
SiO_2	1										
TiO_2	-0.5269	1									
Al_2O_3	-0.7702	0.2606	1								
Fe_2O_3	-0.9725	0.6915	0.6931	1							
MnO	-0.4957	0.9241	0.4506	0.6176	1						
MgO	*0.0622*	-0.4289	-0.0218	-0.2383	-0.2526	1					
CaO	-0.8791	0.3670	0.5887	0.8769	0.2067	-0.3631	1				
Na_2O	-0.7839	0.5436	0.8021	0.8277	0.5359	-0.5718	0.8125	1			
K_2O	-0.9201	0.4947	0.5181	0.9299	0.3171	-0.2495	0.9654	0.7271	1		
P_2O_5	-0.8599	0.1972	0.6179	0.8137	*0.0662*	-0.2345	0.9808	0.7532	0.9283	1	
Cr_2O_3	0.6141	-0.1702	-0.9455	-0.5105	-0.4527	-0.2214	-0.3182	-0.5868	-0.2764	-0.3669	1
Status	Very strong correlation ± (0.9- 1.0) = 29%			Strong correlation ± (0.7-0.89) = 17%			Moderate correlation ± (0.4-0.69)= 27%		Weak correlation ±(0.1-.39) = 27%		

The strong negative correlation between Fe_2O_3 and SiO_2 suggests the incorporation of Fe_2O_3 and SiO_2 in different mineral phases (Ndema *et al*., 2020); and that as weathering or leaching advances, the ratio between concentrations of immobile and mobile elements progressively increases (Martins and Adeleye,2023).

The moderate positive correlation groups are: SiO_2 versus Cr_2O_3, TiO_2 versus Fe_2O_3, TiO_2 versus (Na_2O and K_2O, Al_2O_3 versus (Fe_2O_3, MnO_2, CaO, K_2O and P_2O_5), Fe_2O_3 and MnO and Na_2O, while the moderate negative correlation group include SiO_2 versus (TiO_2 and MnO), TiO_2 versus MgO, Fe_2O_3 versus Cr_2O_3, MnO versus Cr_2O_3, as well as Na_2O versus P_2O_5. All these associations probably reflect the heterogeneous nature of the underlying geology of the area, environmental influence and possible occurrence of mineralization.

The heavy minerals present in the samples using the XRD method include silica, orthoclase, albite and muscovite. The presence of muscovite is an indication that the weathering process is still at the incipient stage. The coexistence of muscovite, quartz, and kaolinite suggests a sequence of weathering, where muscovite-bearing rocks underwent initial breakdown, leaving behind muscovite and quartz. Further weathering led to the formation of kaolinite, indicating more advanced stages of alteration (Ekele *et al*., 2024). The result of the mean weight percent concentration of silica using XRF and XRD methods (Table 3), both confirm that the SiO_2 is not of high grade.

Table 3: Comparison between SiO_2 wt. % using XRF and XRD methods

Analytes	River Yewa	River Ogun	River Ona	River Osun	River Shasha
SiO_2 (XRF method)	70.01	62.83	76.66	70.11	85.49
SiO_2 (XRD method)	77.57	65.56	87.14	62.62	80.18

Suitability for glass-making

From the result, (Table 1), it was observed that the alluvial sands of southwestern Nigeria are generally containing less than 90% silica. This implies that they are not suitable for the production of first-quality glass with the batch formulation of SiO_2, 99.8±0.1%; Al2O3, 0.1±0.05%; Fe_2O_3 max%, 0.02±0.005; CaO+ MgO%, 0.1±0.05 (US Bureau of Standard for Glassmaking). However, science and technologies are continuously developing and new or emerging processes are being successfully introduced into the industries, according to Best Available Techniques (BAT) Reference Document for the Manufacture of Glass (2013), several other varieties of glasses of less than 90% silica are now available. These include (a) soda-lime glass (b) Lead crystal and crystal glass, (c) Borosilicate, and (d) special glass, majorly from the recycling of old and broken glasses. From Table 1, it was observed that the mean average Acid Solubility Value are 1.60% for the Yewa River, 1.75% for the Ogun River, 0.95% for Ona River, 1.20% for Osun River and 1.04% for the Shasha River. The samples generally show AST value an indication of low soluble carbonates content present in the silica sand sample from the five Rivers. This low AST may be attributed to the leaching and removal of soluble carbonate minerals during the weathering process. To this end, the major oxides of the samples of alluvial sand from southwestern Nigeria were compared with the Best Available Techniques (BAT) Reference Document for the Manufacture of Glass (2013) specification, the results are shown in Tables 4, 5, and 6.

Suitability of southwestern Nigeria Sediments for various types of glasses based on the specification of the Best Available Techniques (BAT) Reference Document for the Manufacture of Glass (2013)

Soda-lime Flat glass: The river Ogun sediment also required upgrading in SiO_2 content. All the rivers have low percent weight of Na_2O and CaO. While only River Ona has more MgO (6.19%) than required. The Al_2O_3 content, just like the specification for Container glass, needs to be reduced. Soda-lime glasses are used for bottles, jars, flaconnage (perfumery and cosmetics), everyday tableware and window glass. Also, it is used in operations requiring higher thermal expansion and resistance to thermal shock and chemical attack.

Glass fiber products: The SiO_2 and TiO_2 wt. % of all the sediments of the five major rivers meet the specification for the Glass fibre. However, CaO and Al_2O_3 percent weights have to be increased, while K_2O and Na_2O, as well as Fe2O3, have to be reduced. Also, the percentage composition of F^- and B_2O_3 should be 0- 1% and 0- 10% respectively. Continuous filament glass fibre is used (approximately 90 %) in the production of composite materials (glass-reinforced plastic, GRP), by reinforcement of both thermosetting and thermoplastics resins.

Container glass: All the rivers in the areas have the required percent of silica- a major ingredient in Container glass production, except River Ogun (62.83%). This needs to be upgraded. However, more addition of minor ingredients like Na_2O, and CaO are needed for all the sediments of the rivers. River Ona sediments have an excess of MgO (6.19%) (MgO, K_20, and SO_3, are used as fining agents). The Al_2O_3 content of all these rivers cannot be used directly without reduction. While the K_2O content of River Ogun needs to be reduced. The SO_3 content of all the rivers needs to be ascertained too. Container glass is found useful in the manufacture of packaging glass based on soda-lime and modified soda-lime formulations by fully automated processes. Specialized containers for chemicals and pharmaceuticals may be made from borosilicate glasses, which have increased durability and do not release sodium into the contents through a chemical attack on the glass (Shelby, 2005).

Glass wool: All the rivers meet the specifications of SiO_2 and P_2O_5, while TiO_2 and Fe_2O_3 percents have to be increased. Also, the proportions of K_2O, Na_2O, CaO and MgO have to be reduced during beneficiation before the sediments can be used in the manufacturing of Glass wool. Mineral wool has applications as a fireproofing material due to its inherent fire resistance, manufacture of resin-bonded panels, gaskets, brake pads, automotive components, filtration products, and as a substrate in hydroponic agriculture. Mineral wool has applications as a fireproofing material due to its inherent fire resistance, manufacture of resin-bonded panels, gaskets, brake pads, automotive components, filtration products, and as a substrate in hydroponic agriculture.

Glass-ceramics: The sediments met the SiO_2, CaO and MgO percent specifications (except for River Ona which has excess MgO of 6.19 weight %, Al_2O_3 content has to be increased, Fe_2O_3 contents of all the rivers have to be reduced, while K_2O and P2O5 are not required. The Sb_2O_3 (0. 02wt %; and AS_2O_3 (0 -1.5 wt %) have to be tested as additional trace elements.

Table 4: Comparison of alluvial sands from SW. Nigeria with End Use Specifications

End-use	Key Requirements: Best Available Techniques (BAT) Reference Document for the Manufacture of Glass (2013)		Percentage Oxides in alluvial sands of southwestern Nigeria: River Yewa	River Ogun	River Ona	River Osun	River Shasha
Container glass	SiO_2	71—73 (%)	70.11	62.83	76.66	70.12	85.49
	Na_2O	12—14 (%)	0.02	0.04	---	0.03	---
	CaO	9—12 (%)	0.87	6.60	0.95	2.74	1.30
	MgO	0.2—3.5(%)	0.001	0.001	6.19	0.001	0.11
	Al_2O_3	1—3 (%)	9.54	11.10	8.94	9.92	5.30
	K_2O	0.3—1.5 (%)	0.12	5.44	1.38	2.98	1.44
	(SO_3)	0.05-0.3(%)	NT	NT	NT	NT	NT
	Colour modifiers, etc.	Traces	Cu^{2+}, Cr^{3+}, Cr^{6+}, Fe^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+} etc. are present in all the samples				
Soda-lime Flat glass	SiO_2	72.6 (%)	70.11	62.83	76.66	70.12	85.49
	Na_2O	13.6(%)	0.02	0.04	---	0.03	---
	CaO	8.6(%)	0.87	6.60	0.95	2.74	1.30
	MgO	4.1(%)	0.001	0.001	6.19	0.001	0.11
	Al_2O_3	0.7(%)	9.54	11.10	8.94	9.92	5.30
	K_2O	0.3(%)	0.12	5.44	1.38	2.98	1.44
	SO_3	0.17(%)	NT	NT	NT	NT	NT
E-glass composition for glass fibre products used in general applications	B_2O_3	0 -10 (%)	NT	NT	NT	NT	NT
	CaO	16- 25(%)	0.87	6.60	0.95	2.74	1.30
	Al_2O_3	12- 16(%)	9.54	11.10	8.94	9.92	5.30
	SiO_2	52- 56(%)	70.11	62.83	76.66	70.12	85.49
	MgO	0-5 (%)	0.001	0.001	6.19	0.001	0.11
	$CaO+K_2O$	0 -2 (%)	0.99	12.04	2.33	5.72	2.74
	TiO_2	0 -1.5(%)	0.55	2.17	0.56	5.07	1.52
	Fe_2O_3	0.05 -0.8(%)	2.52	7.20	3.56	6.33	2.64
	Fluoride	0 -1.0 (%)	NT	NT	NT	NT	NT
Glass wool	SiO_2	57-70(%)	70.11	62.83	76.66	70.12	85.49
	K_2O+Na_2O	12-18(%)	0.14	5.48	1.38	3.01	1.44
	CaO+ MgO	8-15(%)	0.87	6.60	7.07	2.74	1.41
	B_2O_3	0-12(%)	NT	NT	NT	NT	NT
	Fe_2O_3	<0.5(%)	2.52	7.20	3.56	6.33	2.64

Al_2O_3	0-5(%)	9.54	11.10	8.94	9.92	5.30
TiO_2	Trace (%)	0.55	2.17	0.56	5.07	1.52
P_2O_5	0-1.5(%)	0.001	2.07	0.16	0.36	0.001

Table 5: Comparison of major oxides of alluvial sands of southwestern Nigeria with Batch formulation for glass ceramics and Optical glass

Different End use of glass					**Percentage Oxides in alluvial sands of southwestern Nigeria**				
Oxides*	**Glass ceramic**	**Quartz glass**	**Optical glass**		**River Yewa**	**River Ogun**	**River Ona**	**River Osun**	**River Shasa**
			Boron crown	**Optical flint**					
SiO_2	55-70	99.9	35-70	25-60	70.11	62.83	76.66	70.11	85.49
Al_2O_3	15-25	0.005	0-10	0-15	9.54	11.1	8.94	9.92	5.30
Fe_2O_3	0-0.2	NR	NR	NR	2.52	7.20	3.56	6.33	2.64
CaO	0-4.0	0.001	0-10	NR	0.87	6.60	0.95	2.74	1.3
Sb_2O_3	0 -2	NR	0 -0.3	0- 0.1	NT	NT	NT	NT	NT
As_2O_3	0-1.5	NR	0-0.3	0-0.3	NT	NT	NT	NT	NT
MgO	0 -1.0	0 -3	NR	NR	0.001	0.001	6.19	0.001	0.11
Na_2O	0.5-1.5	0-2	0-10	0.5-10	0.02	0.04	--	0.03	---
K_2O	NR	0-2	0-20	0.5-8	0.12	5.44	1.38	2.98	1.44
P_2O_5	NR	NR	NR	NR	--	2.07	0.16	0.36	---

* Source: Special, Glass compositions, 2008 (in Best Available Techniques (BAT) Reference Document for the Manufacture of Glass (2013)

Table 6: Comparison of major oxides of alluvial sands of southwestern Nigeria with Batch formulation for CRT and Glass tube

Oxides* (wt %)	**CRT glass Panel**	**Glass tube**		**Natural suitability of alluvial sands of southwestern Nigeria**				
		Soda lime silica	**Boro-silicate**	**River Yewa**	**River Ogun**	**River Ona**	**River Osun**	**River Shasha**
SiO_2	60-63	69	67-81	70.11	62.83	76.66	7.12	85.49
Al_2O_3	2 -3.4	2 -4	2.0-7	9.54	11.1	8.94	9.92	5.30
Fe_2O_3	NR	0- 1	0.01 -2	2.52	7.20	3.56	6.33	2.64
CaO	0 -3.2	4-5	0.01- 1.5	0.87	6.60	0.95	2.74	1.30
TiO2	NR	NR	NR	0.09	0.04	0.07	0.05	0.88
MnO_2	NR	NR	0.01-5	0.2	0.24	0.19	0.58	0.13
MgO	0 -1.2	2--3	0.01-0.5	0.001	0.001	6.19	0.001	1.30
Na_2O	6.6 -9.4	9-16	3.5-12	0.02	0.04	--	0.03	---
K_2O	6.6- 8.4	1--11	0.01-2.5	0.12	5.44	1.38	2.98	1.44

* Source: Special, Glass compositions, (2008)

NR means: Not Required oxides, and have to be removed via beneficiation

Borosilicate glasses have applications that include chemical process components, laboratory equipment, pharmaceutical containers, lighting, cookware, and oven doors and hobs. A further application of borosilicate glass is in the production of glass fibre, both continuous filaments and glass wool insulation.

Sediment yield estimate from Chemical Index of Alteration (CIA)

To estimate the quantity of sediment yield in each of the five major rivers in southwestern Nigeria, The Chemical Index of Alteration (CIA) approach was adopted. It is an important indicator to judge the degree of chemical weathering and is widely used in the study of rock weathering. This index takes the assumption that Ca, Na and K decrease as the duration and/or intensity of weathering increases (Duzgorein-Aydin *et al*., 2002). The CIA is represented (Chakrapani, 2005) as:

The molar ratios of $[Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O]*100$ as measured in sediment……. (2)

The results are shown in Table 7. It shows that the weathering intensity varies as follows: 79.74>77.16>58.86>55.26>53.72, with 64.95 as the average CIA for the region associated with secondary minerals. Karina and Pedro (2014) indicated that smectite and illite groups have values ranging from about 70 to 80 and that primary minerals have much lower CIA values: plagioclase and K-feldspars are 50; biotite, 50 to 55. Hence, the CIA value of a bulk sample will vary substantially depending on the proportions of clay minerals and primary minerals in it (Nesbitt and Markovics 1997). River Yewa is underlain mostly by sedimentary rocks, while others are essentially mixtures of the migmatite gneiss and schist in varying degrees of weathering.

Table 8, shows a One-way ANOVA of SiO_2 across the five rivers revealing that there is a significant difference (at $p \leq 0.05$) in the amount of CIA and the Silica yield across all the rivers. This further confirms that the area is heterogeneous in geology, and hence different rates of weathering generate sand.

Table 7: Summary of the estimated sediment and Silica yields by the five major rivers from southwestern Nigeria

Features	River Yewa	River Ogun	River Ona	River Osun	River Shasha	Average or Total
CIA (%)	79.74	53.72	77.16	55.26	58.86	Av.64.95
Sediment Yield (Ton/km^2/yr)	78.61	1055.48	101.69	905.03	631.83	Total=2772.64
Area of the sub-catchment (Km^2)	6000.50 (a)	24096.00 (a)	6775.30 (a)	9741.00 (a)	6623.00 (a)	Total= 53235.80
Silica (SiO_2) %	83.87	62.83	76.66	70.11	85.49	Av=75.79
Length of river (km)	177(b)	480 (c)	55 (d)	267 (e)	55 (c)	
Estimated quantity of Silica yield (Ton/km^{2}yr^{-1})	65.93	663.16	77.96	634.51	540.15	Total= 1981.71

Ref. (a) Eruola, (2017); (b)FAO, (1969); (c)Wikipedia; (d) Ganiyu *et al*., (2021) ;(e) Adebanjo *et al*., (2019).

Table 8: Anova test of variance of SiO_2 within the major river channels SW Nigeria

Source of variation	SS	df	MS	F	P-value	F critical
Between Groups	525.318	4	131.3295	1.187795	0.417603	5.192168
Within Groups	552.829	5	110.5658			
Total	1078.147	9				

Sediment and silica sand yield of the rivers in the area

CIA reflects the integrated weathering history in the drainage basins. This was used to estimate the sediment yield of the five major rivers in the area. According to Li, & Yang, (2010), by assigning CIA values representative of unweathered (50) and extremely weathered (100) sources to extreme denudation values, a relationship could be constructed between weathering and denudation as shown in equation 3:

$$\text{Sediment yield (t/km}^2\text{/yr.)} = (2.25*10^5)\,(10^{-0.04335(CIA)}) \quad ...(3)$$

The sediment yield estimates for each of the rivers are shown in Table 5. It follows the decreasing order as Ogun> Osun> Ona> Shasha> Yewa. This is in direct relationship with the catchment of each river. This indicates that the catchment area of the rivers determines the sediment yield in this study. The total sediment yield for the area is 2772.64 t/km^2/yr. The silica sand generation aligned with the size of the basin, in the order of Ogun> Osun> Shasha> Ona rivers. The total SiO_2 yield within the area annually is estimated at 1981.71 tons/km^2/yr.

CONCLUSION

The alluvial sediments of southwestern Nigeria are not the high-quality silica type (99.98% silica). However, they are still found useful in the manufacture of some glass products having specifications of between 50-80% silica. The end-use glass materials include container glass, flat glass, glass wool and some varieties of optical glasses. The alluvia sand in the area should not therefore be rated as only being suitable for civil construction, they have a relatively high value-to-mass ratio for other products like glass manufacturing industries, which Nigeria has not contributed its quota to the world market. The major rivers (Yewa, Ogun, Ona, Osun, and Shasha) in southwestern Nigeria produce an estimated quantity of 1981.71 ton/km^{2}yr-^{1}, this is quite substantial and can contribute to the GDP in the solid mineral sector, with very minimal beneficiation.

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