

CHEMICAL CHARACTERIZATION OF SILICA SAND DEPOSIT FROM RIVER KATSINA-ALA, NORTH CENTRAL REGION OF NIGERIA.**S.P.Malu¹, .C.A.Edem², and B.I.Ita²**¹ Department of chemical sciences, Federal University Wukari, Taraba State, Nigeria² Departments of Pure and Applied Chemistry, University of Calabar, Calabar, Nigeria.**Correspondence Author:** S .P. Malu, Dept. of Chemical Sciences, Federal University of Wukari, Taraba State Nigeria.

ABSTRACT: Analytical techniques such as X – Ray Fluorescence Spectroscopy (XRF) and Atomic Absorption Spectroscopy (AAS) coupled with statistical package for multivariate analyses were employed to characterize silica sand deposit obtained from River Katsin-Ala in Benue State, North Central Region of Nigeria. The results of analyses reveal that silicon dioxide (SiO₂) forms the predominant metal oxide in the entire samples with a percentage mean concentration of 95.904 ± 0.2539%, followed by (Fe₂O₃; 0.3856 ± 0.0406%), (MnO; 0.1170 ± 0.0085%), (PbO; 0.0714 ± 0.0027%), (TiO₂; 0.0420 ± 0.0019%), (BaO; 0.0344 ± 0.0033%), (P₂O₅; 0.0360 ± 0.0062%) (NiO; 0.0280 ± 0.0178%), (Na₂O; 0.0109 ± 0.0012%), (K₂O; 0.0146 ± 0.0017%), and trace amounts of CaO, MgO, Al₂O₃, ZnO and CuO. Further beneficiation (using acid leaching method) of the silica sand samples reveal an increased silica (SiO₂) content from 95.904 ± 0.2539% to 97.850 ± 0.1052% with a corresponding decrease in Fe₂O₃ content (0.3856 ± 0.0406% to 0.0530 ± 0.0035% across samples. Physico-chemical analysis shows a moderate pH value of 7.03 signifying high basic oxides content in the silica sand samples. Acid Demand Value (ADV) test reveals a moderately low ADV in samples of 15.14, signifying the presence of low soluble carbonates in the silica sand samples. Grain size distribution analysis reveals that a high percentage of the samples grains size distribution fraction are within the recommended screen sizes (40-100 mesh). Heavy liquid separation test reveals a significant trace amount of principal minerals such as ilmenite, magnetite, mica, calcite and kaolinite. A correlation between the mean values of SiO₂ and Fe₂O₃ in all the samples reveals a direct relationship between SiO₂ and Fe₂O₃ which implies that as the values of SiO₂ increases that of Fe₂O₃ also increases and vice versa. Furthermore, comparison of observed mean of SiO₂, Fe₂O₃, CaO, Al₂O₃ and TiO₂ with their observed minimum standard (95.00%; 0.005%; 0.1000% and 0.0120%) shows that the silica sand samples from River Benue can be used as a source of SiO₂ for glass making.

KEYWORDS: Glass sand; Silica sand, Grain size, Metal Oxides, Beneficiation, Acid demand values.

INTRODUCTION

Silica sand is an industrial term used for sand or easily disaggregated sandstone with a very high percentage of quartz (silica) grains. Quartz is the most common silica crystal and the second most common mineral on the earth's surface. It is found in almost every type of rock; igneous,

metamorphic and sedimentary (Ketner, 1973; Bourne, 1994). While quartz deposits are abundant, and quartz is present in some form in nearly all mining operations, high purity and commercially viable deposits occur less frequently. The composition of silica sand is highly variable, depending on the local rock sources and conditions.). Silica exists in nine different crystalline forms or polymorphs but the three main forms being quartz, which is by far the most common, tridymite and cristobalite. It also occurs in a number of cryptocrystalline forms. Fibrous forms have the general name chalcedony and include semi-precious stone versions such as agate, onyx and carnelian. Granular varieties include jasper and flint. There are also anhydrous forms - diatomite and opal (Press, 2001; Tsoar, 2004; Wilkinson, 2005).

The silica in the sand will normally be in the crystalline form of quartz. For industrial use, pure deposits of silica capable of yielding products of at least 95% SiO₂ are required. Often much higher purity values are needed. Silica sand may be produced from sandstones, quartzite and loosely cemented or unconsolidated sand deposits (Press, 2001; Tsoar, 2004; Wilkinson, 2005). High grade silica is normally found in unconsolidated deposits below thin layers of overburden rocks. It is also found as "veins" of quartz within other rocks and these veins can be many meters thick. On occasions, extremely high purity quartz in lump form is required and this is produced from quartzite rock. Silica is usually exploited by quarrying and it is rare for it to be extracted by underground mining (Press, 2001; Wilkinson, 2005). Silica sand deposits are most commonly surface mined in open pit operations or on riverine surface deposit due to erosion but in some cases, dredging and underground mining is also employed. Extracted sand undergoes considerable processing to increase the silica content by reducing impurities. It is then dried and sized to produce the optimum particle size distribution for the intended application (Langer, 2003; Dolley, 2004a). For industrial and manufacturing applications, deposits of silica sand yielding products of at least 95% SiO₂ are preferred. Industrial sand's strength, silicon dioxide contribution and non-reactive properties make it an indispensable ingredient in the production of thousands of everyday products. (Samtur, 1979; Bolen, 1996; Crossley, 2001; Chang, 2002).

In the United States for instance, silica sand production increased from 2.5 to 28.5 metric tons from 1996 to 1997 and out of this about 37% is used for glass making while 23% was used as foundry sand. Other uses were hydraulics fracturing (6%) and abrasive (5%) (Bourne, 1994; Wallace, 1997; Langer, 2003). The US produces 30% of the world total silica sand from more than 150 operations and about three-fourths of production coming from the central US alone in 1992 (Chang, 2002; Dolley, 2004a). In Africa, especially In Nigeria however, the use of silica sand is limited on the domestic scale, as most of the teeming population only utilize it for road and building construction, while the vast spread deposits are left unattended to and this has prevented their exploration (Plate.1) are left underutilized in spite of their valuable economic mineral content (Chang, 1991; Claude, 2002). Available evidence shows that this silica sand contain a high proportion of pure quartz (SiO₂) and can be directly or indirectly used in the manufactured of various industrial products especially glass products (Bajah, 1986; Malu and Bassey, 2003). It is therefore desirable to investigate the potentials of this vast silica sand deposit within the State for its potentials especially for the establishment of Glass and other allied industries.

MATERIALS AND METHODS

The Study area

The study area covers Katsina - Ala River and its environs, it is one of the major tributaries of River Benue in Nigeria, has large deposit of silica sand along its shore, it is located on coordinates 7°8'N, 9°8'E (Fig. 1). This river has its source from the Bamenda highlands in Cameroon. It flows 200 miles (320km) northwest in Cameroon passing through the Eastern Nigerian-Cameroon border into Nigeria. The River is mainly found in Benue State, North Central Region of Nigeria. It empties into the River Benue. Its length and size makes it one of the largest tributaries of River Benue. (Neba, 1999; Chisholm, 2010).

Sample collection

Five silica sand samples were collected along the river bank of River Katsina-Ala, as indicated on the map of the study area (Fig. 1). The samples were collected at different points at an interval of 100 meters apart from each other between the month of September and December to reflect the late dry season periods when water depth is at low level. The samples were each separately prepared by thoroughly blending by using the "centre displacement method" so as to obtain a homogenous material. 100kg of each silica sand sample was heaped at one spot and then the entire material was shoveled and heaped on a second spot (thus displacing the center). This process was repeated for about 10 times (five heap at each spot), to obtain a homogenous mixture. The samples were then put into sample bags. (Calico bags) and labeled A, B, C, D and E to distinguish them from each other. The labeled silica sand 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°C for seven hours. After drying, about 100g were taken from each sample, weighed and homogenized into fine grain using a crusher-Mangan Model BB200. The crushed fine grain particles were further sieved using a 100 mm mesh screen to ensure homogeneity of particle size. 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 digestion

The digestion of the pre-treated samples, for metallic oxides analysis was carried out using 10mL concentrated hydrochloric acid (HCl) and Perchloric acid (HClO₄), to release metal oxides content into solution (Allen, 1974; Rantalla and Lorrington, 1992; Ademoroti, 1996). For each of the representative pretreated samples, 0.2g was carefully weighed and placed in a clean-dried crucible. 5mL mixture of nitric and perchloric acid in the ratio of 3:2 was added followed by 10mL of hydrofluoric acid (HF) and refluxed for one hour (1h). The mixture was then heated to

dryness on a hot plate in a fumed cupboard at a temperature of 90-100⁰C. The mixture was then cooled to room temperature and 5mL concentrated hydrochloric acid (HCl) was added and allowed to settle, and then filtered into a 100 mL plastic flask and made up to mark with de-ionized water and allowed to stay for three days before analysis using atomic absorption spectrophotometer (AAS). All glassware and specimen bottles used were initially washed thoroughly with HNO₃ and rinsed with distilled water (Harries, 1975; Sinex *et al.*, 1980; Asuquo, 1999).

Determination of metal oxides concentration

This was carried out using atomic absorption spectrophotometer (AAS), Shimadzu model AA 6800; x-ray fluorescence spectrophotometer (XRF) Mini Pal Model 4 version PW430 and UV-spectrophotometer model 2400 Hatch. The atomic absorption spectrophotometer was used for each determination of MnO, MgO, PbO and K₂O. Working standard solution for each element was prepared and the standard solutions and aliquots of the diluted clear digest were used for the determination. Standard curve was used to establish the relationship between absorption intensity and concentration of each element (Boyd, 1994; Underwood and Day, 1988; Emufurieta *et al.*, 1992). The detection limit of the AAS was < 0.001mg /L. The X-Ray fluorescence spectrophotometer was used for the determine SiO₂, Fe₂O₃, CaO, Al₂O₃, Na₂O, TiO₂, NiO, ZnO, BaO and CuO. To a specific amount of each of the pulverized samples, a binder (PVC dissolved in toluene) was added carefully, mixed and pressed in a hydraulic chamber to form a pellet. The pellet was then loaded into the sample chamber (Analyzer) of the spectrophotometer and a voltage (30 KV maximum) and a current (1mA maximum) was applied to produce the x-rays. The analyzer was then calibrated using the software attached to it and run for about 30-60 seconds and the result automatically printed out. The process was repeated until all the samples were analyzed.

Determination of phosphorous

About 5g each sample was weighed into a 250mL plastic beaker and 100mL of 0.1M HCl added, corked and shaken for 30 minutes and allowed to settle. The mixture was then filtered using Whatman filter paper No. 42. 10mL of each filtrate was introduced into a curvette cell and another 10mL of distilled water into a separate curvette bottle to produce a blank. 1mL of phosphate reagent was then added to each of the filtrate and the blank. The UV spectrophotometer was then calibrated using the blank to mark zero and the filtrate inserted into the curvette hole and read at a wave length of 690nm. Standard solutions of phosphate reagents were prepared and calibration curve constructed and with the help of the curve the concentration of phosphorous in the samples were determined in mg/L. (Harries, 1975; Christian, 1980).

Beneficiation and up gradation of samples

The beneficiation of the silica sand samples was done according to the method of Veglio *et al.*, 1999 and Tarasova *et al.*, 2001. 20g of the representative samples 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 80⁰C to 90⁰C 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 as in (2.5) above.

Determination of loss on ignition (LOI) and pH

10_g of each sample were taken and carefully poured in a clean crucible and weighed using analytical balance. The weighed samples were then placed in an electric muffle furnace and heated for 1 hour at 950°C to determine the loss on ignition.

The pH of the samples was determined electronically using a pH meter of ± 0.1 percent sensitivity model WTW pH 422. (The instrument was calibrated using a buffer solution) (Harries, 1975; krist and Rump, 1988).

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 (Plate 2). 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).

Determination of acid demand values of samples

Acid Demand Values (ADV), is a measure of soluble carbonates present in a given silica sand sample. It value determines a low or higher concentration of alkali or carbonates reacting materials present in given silica sand sample. Their presence is an indicator of whether given silica sand sample can be used for glass making. It is therefore important that the presence of these reacting materials be measured so that uniformity and formulation control may be achieved. The ADV was therefore carried out according to the methods of Sundeen (1978).

Heavy liquid separation of minerals

Heavy liquid separation of minerals was carried out according to the wok of Muller and Burton, 1965; Robert *et al.*, 2002 and Sundararajan *et al.*, 2009 while the beneficiation and up gradation of samples was done according to the method of Veglio *et al.*, 1999 and Tarasova *et al.*, 2001. 20g of the representative samples 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°C to 90°C 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 as in (2.5) above.

RESULTS AND DISCUSSION

The results concentration of silica sand samples obtained from River Katsina-Ala have been analyzed using some analytical methods. The results are as presented in Table 1.

Metal oxides concentration

The mean percentage metal oxide concentration (SiO_2 , Fe_2O_3 , K_2O , NaO , CaO , Al_2O_3 , MgO , TiO_2 , ZnO , NiO , PbO , BaO , P_2O_5 , MnO , and CuO) in the silica sand samples are presented in Table 1 and depicted in a three dimensional graph of Figures 2. The result revealed that the highest percentage mean concentration of SiO_2 in the silica sand samples was ($95.904 \pm 0.2539\%$), followed by Fe_2O_3 (0.3856 ± 0.0406), MnO (0.1170 ± 0.0085), PbO (0.0714 ± 0.0027), TiO_2 (0.0420 ± 0.0019), P_2O_5 (0.0360 ± 0.0062), BaO (0.0344 ± 0.0033), NiO (0.0280 ± 0.0178), K_2O (0.0146 ± 0.0017), Na_2O (0.0109 ± 0.0012) and significant amounts of, CaO , Al_2O_3 , ZnO , CuO and MgO . This high SiO_2 content trend in all the samples revealed that silica sand generally consist of high SiO_2 content (quartz) (Sosman, 1954; Bajah, 1986, Siever, 1988). The concentration of SiO_2 in silica sand samples in this study to be similar to those obtained by other research studies (Shakila *et al.*, 1999; Sundararatan *et al.*, 2009; Pisutti *et al.*, 2008; Babasaheb, 2010). Comparison of the observed mean values of SiO_2 , Fe_2O_3 , CaO , Al_2O_3 , MgO and TiO_2 (Table 6) in the silica sand samples with their glass making standard using a population t-test revealed the concentration of SiO_2 ($93.946 \pm 0.4775\%$), CaO , Al_2O_3 and MgO was below the minimum standard, while those of Fe_2O_3 and TiO_2 were above the minimum standard which imply that the entire silica sand sample require further beneficiation to reduce the Fe_2O_3 content to a more acceptable standard level as stipulated by the American ceramic society and the National Bureau of standards (Frank, 1972; Enuvie, 2003; James, 2007). 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 (Host, 1991; Goldman, 1994; Heck, 2002).

However further beneficiation of the silica sand samples revealed and increased in SiO_2 from 95.904 ± 0.2539 to 97.850 ± 0.1052 % with a decrease in iron content of 0.0530 ± 0.0035 % from $0.3856 \pm 0.0406\%$ (Table 2) which means that the samples can be used for glass making (Ushie *et al.*, 2005; Marson, 1978). Comparison of the percentage concentration of SiO_2 obtained in this study with those of other authors revealed that although most of SiO_2 concentration were below minimum standard, they however fall within the range after further beneficiation was undertaken, their SiO_2 content was upgraded to the minimum standard. 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 river. Silica sand constitute about 60% of the raw batch composition used by most container and flat glass producers and as a result, the quality of the sand is a primary factor in determining the quality of the finish glass product. Since the present of Fe_2O_3 in silica sand determine its suitability for making glass (Marson, 1978; Patridge, 1994) and as a result a pearson moment correlation was computed to determined (Table 5). The results revealed that the correlation between SiO_2 and Fe_2O_3 is strong but positive ($r=0.741$) which implies that there is a direct relationship between SiO_2 and Fe_2O_3 in the samples that; that is as the value of SiO_2 increases that of Fe_2O_3 also increases and vice versa. Most high-quality glass sand can exceeds 99.5% SiO_2 when processed and would average close to the 99.80% level. However, silica content in the sand is not the problem; rather, it is that fraction which is not silica which include clays and a host of minerals which contribute Iron, Aluminum, Titanium, Calcium, Magnesium and various trace constituents. Any constituent in the silica sand other than silica is therefore considered as a

contaminant, principal of which is iron, aluminum, and titanium. (Charles, 1974; Marson, 1978; Stocchi; 1975)

Grain size distribution analysis

The mean grain size distribution analysis of the silica sand samples is presented in Tables 5. The result shows the mean grain size distribution among the silica sand samples from River Katsina-Ala to be 0.110-37.864. The result revealed that the highest percentage retention fraction of the silica sand sample was between mesh number 40 to 70 (98%), This implies that having met the requirement of sieve size retention fraction at different significant percentage levels of between 40 – 100 sieve sizes, the mean percentage retention fraction among the five samples were significantly not different from each other. 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. (Crockford, 1949; Corning Glass Works, 1967; Robert, 2002), as a result the grain size distribution should falls within the 40-100 screen mesh size. From the analysis so far carried out the grain size distribution fraction from River Katsina-Ala, falls within the recommended size range of 40 to 100 screen mesh (Crockford, 1949; Sundeen, 1978; Robert, 2002).

Mineralogy

The principal minerals present in the silica sand samples is presented in Table 4. The result shows the principal minerals present in silica sand from River Katsina-Ala to be Quartz, mica, Kaolinite, ilminite, magnetite and calcite. The results revealed that quartz in form of silica (SiO_2) form the predominant mineral in all the silica sand samples The grain shape of the silica sand samples observed ranges from angular to sub-angular with an average diameter range of 0.05mm to 0.125mm. However, most of the grain shapes would be classified as sub-angular. (Thomas, 2001; Robert, 2002; Sundararantan *et al.*, 2009).

Acid demand values (ADV)

The mean values of the acid demand values (ADV) of the silica sand samples are presented in Table 3. The result revealed that the highest Acid Demand Value is obtained from samples D (15.32) This result is similar to those obtained by other researchers (Crockford, 1949; Robert *et al.*, 2002; Mclaws, 1971). The acid demand values measures the amount of alkaline materials that should not be present in already processed washed and classified silica sand. Acid Demand Values(ADV) range from 1 to a maximum of 50, a low ADV(near zero) is an indication of either no acid was consumed ,and so virtually no soluble carbonates are present in the sample or low alkaline materials in the samples while a high ADV(values in upper 40's to 50) is an indication of nearly all acid added in the test was consumed or a high soluble carbonate and salts that can be deleterious in the application of the silica sand for glass making (Sundeen, 1978; Hrdina, 1999; Pisutti, 2008).From Table3,it was observe that the Acid Demand Values of the silica sand samples falls within the moderately acceptable range of 15.14 which is an indication of low soluble carbonates content present in the silica sand sample from the five Rivers. This low ADV may be attributed to the leaching and removal of soluble carbonate minerals (primarily calcite) by downward percolating oxidizing surface waters (Sundeen, 1978; Hrdina, 1999; Pisutti, 2008).

Loss on ignition and pH

Table 1 also shows the results of the mean percentage weight loss on ignition (LOI) of the silica sand samples which is 2.11%. Loss on ignition (LOI) is the combined loss of volatile matter such as combined structural water (H_2O^+) and carbon dioxide from carbonates. It is used as a quality test, commonly carried out for solid mineral deposits to ascertain the level of loss of volatile matter when a sample is subjected to a temperature of 950°C or 1000°C (Dean, 1974; Bengtsson, 1986; Velda, 1992; Ademoroti, 1996; Oliver, 2001). The pH of the silica sand samples is presented in Table 3. The results revealed the pH value to be 7.03. The pH of a given sample gives the water soluble level of alkalinity or acidity of the silica sand (Doremus, 1973; Sell, 1981). A higher or lower pH values signify the present of acidic or basic oxide in given silica sand sample. Sand with a pH close to neutral (7.00) is therefore the best for glass making (Doremus, 1973; Sell, 1981; Paul, 1982).

CONCLUSION

Five silica sand samples obtained from River Katsina-Ala have been analyzed using some analytical and statistical techniques. From the results obtained, the following conclusions can be drawn:

- (i) The silica sand samples generally contain a high percentage concentration of silicon dioxide (SiO_2) content with significant amount of Al_2O_3 , K_2O , MgO , Fe_2O_3 and trace amount of CaO , TiO_2 , NiO , ZnO , PbO , Na_2O , BaO , P_2O_5 , MnO and CuO .
- (ii) The silica sand samples contain a moderate to low concentration of iron oxide (Fe_2O_3).
- (iii) The grain size distribution of most of the silica sand samples falls within the recommended screen size (40-100 mesh), for glass making
- (v) The silica sand deposit from River Katsina-Ala are suitable for glass making due to their high SiO_2 content and low Fe_2O_3 , Acid demand values (ADV) coupled with suitable grain size distribution fraction and angular to sub-angular shape.
- (vi) The silica sand from River Katsina-Ala fall within the recommended sixth quality (Grade iii glass) for the manufacture of commercial coloured container and window glasses.
- (x) Water for the beneficiation of the silica sand can be available from these Rivers the year all round.
- (xi) Whereas this silica sand deposit can be used for glass making, there are other uses which might expand the market, these are: The manufacture of silica brick to line furnaces; making of asbestos pavement; used as engine sand to give traction to locomotive, filter sand remove foreign matter from water reservoirs etc.

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ACKNOWLEDGEMENTS

We acknowledged the assistance of National Research Institute for Chemical Technology Zaria, Center for Energy Research and Development Zaria, Benue Cement Company Gboko and Urban and Regional planning Center for the use of their laboratory facilities for this study.