THE STUDIES OF CHEMICAL ANALYSIS OF RAW MATERIALS FOR GLASS INDUSTRY IN THE ARID ZONE OF NIGERIA

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ABSTRACT
Results of chemical analysis of some sands in the arid zone of North Eastern Nigeria have shown that the sands are suitable raw materials for the glass industry. The major glass forming oxide which is silica, has been determined to be high, ranging from 74 to 94%. In particular, samples three (Dapchi) and five (Ngala) are suitable for all glass making. The extent of substitution of ammonia group, (R_2O_3) for the metal oxides was determined in percentages for all the samples. It was found to be a function of the percentage composition of silica. The deleterious heavy metals were not detected, a fact which also makes the sample suitable for glass making. The percentage of oxide of iron (Fe_2O_3) is relatively high in these samples ranging between1.20% and 1.59% thus making them viable for colour and amber glasses.

INTRODUCTION

The Glass industry is very important in any country which is aspiring to be technologically advanced. Glass is useful in the building sector, research laboratories, house holds, manufacturing industries and many other sectors.

In Nigeria the government has been spending substantial amounts of hard-earned foreign currencies to import glasses into the country. This is because there are very few glass industries in the country, which cannot cope with the demand for glasses. The raw materials to be used in producing glasses can be found in many parts of the country, however much has not be done to source for these materials.

For most commercial glass families silica sand, is the main material, but to obtain melting economy and flexibility of properties, additions of other substances are made, particularly of oxides [1]. Most commercial sand for glass making are obtained from river beds in which organic materials and other impurities have been separated. Desert sand can also be used for glass making but it has to be washed before melting in the furnace. This is to separate the pure silica sand from organic materials and other impurities [2].

However, glass is essentially an amorphous solid made by fusing silica (silica dioxide) with basic oxides which have been cooled to a hard condition without crystallization [3]. The composition of these oxides in glass making is of prime interest to the glass technologist or engineer.

It is therefore of interest to study the chemical compositions of raw materials for the glass industry, most importantly the percentages of silica contents as these are the main ingredients for glass making. Other oxides such as iron oxide (Fe_2O_3), aluminum oxide (Al_2O_3), calcium oxide (CaO), sodium oxide (Na_2O) also, have to be studied to know their suitability for glass making.

It is well known that commercial glasses are based on varying percentage of silica in structures [4]. These are made of the same SiO_4 tetrahedra on which the crystalline silicates are based (Figure 1), but these are less ordered. In such glasses, the tetrahedra link at the corners to give a random (rather than a periodic) network. Pure silica forms a glass with a high softening temperature (about 1200°C). Its strength and stability, coupled with its low thermal expansion, make it useful for special applications, but it is hard to work with because its viscosity is high [4]. This problem is overcome in commercial glasses by introducing network modifiers to reduce the viscosity. They are metal oxides, usually Na_2O and CaO, which add positive ions to the structure, and break up the network (see Fig. 1c). Adding one molecule of Na_2O, for instance, introduces two Na ions, each of which attaches to an oxygen of a tetrahedron, making it non-bridging. This reduction in cross-linking softens the glass, reducing its glass temperature, Tg (the temperature at which the viscosity reaches such a high value that the glass is a solid [4]).

Glass Modifiers

Different modifiers are used to produce different types of glass with special characteristics required for their eventual use, as shown in Table 1. Modifiers in this case are oxides which enhance or impart other desired properties to the glass product [5]. it has been estimated that there are over 50,000 glass formulae [6].

TABLE 1: ***Metal oxides and their functions In glass making***

Property required	Metal Oxides	Chemical Formula
Green colour	Iron (III) oxide	Fe_2O_3
Blue/Green colour	Copper (II) oxide	CuO
Red colour	Copper (I) oxide	Cu_2O
Opaque white colour	Tin (II) oxide	SnO_2
Purple colour	Manganese (II) oxide	M_nO_2
Blue colour	Cobalt (II) oxide	CoO
Dark brown colour	Titanium (II) oxide	TiO_2
Fluxing agent	Sodium (II) oxide	Na_2O
Stabilizing agent	Calcium (II) oxide	CaO
High refractive Index	Lead (II) oxide	PbO
Low thermal expansion		
Improve mechanical strength	Boron (III) oxide	B_2O_3
	Aluminium (III) oxide	Al_2O_3

Oxides are added to the batch formula to provide different colours and unique properties for particular application [2].

Objectives

The aims of this work, are to study the chemical composition of sands from the arid zone of North-Eastern and to know the suitability of using them in glass industry. This would entail the determination of the percentage (chemical) composition of sand samples taken from the area.

Materials and Methods

The sand samples used in this work were collected at the river banks of Kopchi, Biu, Dapchi, Gwoza and Ngala towns (see figures 2 and 3). The sand samples were first cleaned, coned and quartered to obtain the representative fractions. Conning and quartering mean to pour the sample on a flat surface so as to form a cone. A straight edge was used to separate the cone into four quarters. Then the two alternate quarters were mixed to form another cone. This process continues until the desired sample size is obtained according to Carver, [7]. The representative fractions of each sample were later crushed and ground separately to produce 120 mesh (B.S). These were used in carrying out the chemical analysis to determine the percentages by weight of SiO_2 and other oxides of the sand samples.

Laboratory Procedure

The procedures to obtain the silica content (SiO_2) and some of the oxides of the samples are described below.

One gram of each crushed sand sample was weighed and mixed with anhydrous sodium carbonate (Na_2CO_3) in a platinum crucible. The addition of Na_2CO_3 to the samples was to act as a catalyst during fussioning process. The samples were burnt in a muffler furnace for one hour at 1000°C. Each of the samples became solid in the crucible after cooling.

Dilute hydrochloric acid (30%, 10 ml HCl) was latter poured into each of the sample crucible and the mixtures were left over night. The samples were dried using ultra-violet drier. The essence of drying the samples was to dehydrate silica and test for dryness. This was achieved by dipping glass rod in ammonia solution and bringing it over each of the samples until no fume was observed over the samples. HCl 50%, 50% water were added to the dry samples and warmed for three hours at a constant temperature of 50°C.

The sample solutions were separated by filtering through ashless 541 filter papers into 150 ml clean beaker. The individual filtrates were yellow in colour while the residues were white in colour.

The residues on the filter paper made up of silica content and were put in the oven to dry for 12 hours. The solutions were kept separately for further tests.

Five silica crucibles were weighed and numbered according to the town where the samples were collected i.e. 1,2,3 up to 5. Then each of the dried filter paper was placed in the crucibles according to their number and burnt in a furnace at 1000°C. These were later weighed after cooling.

Test for Percentage of Calcium (II) Oxide CaO)

The filtrates (150 ml) obtained during silica content test, were heated to evaporation until they were each reduced to about 100ml. To these solutions, 5ml of ammonium hydroxide was added. The solutions were filtered separately through ashless 542 filter paper in a 100 ml volumetric flask. Distilled water was added to the sample solution to the mark. Then 10 ml sample solutions were pipetted into three different beakers from each sample. Then to each of the samples 40 ml of distilled water, 10 ml of potassium hydroxide solution and 3 ml of ammonium chloride were added one after the other. 3 drops of KCN (Potassium cyanide) were added. Then the solutions were titrated with 0.1M (Ethylene diamine tetra acetic acid solution) EDTA.

Preparation of Ammonia Group Solution (R_2O_3)

Iron oxide, manganese oxide, titanium oxide, phosphorus oxide and aluminium oxide were determined using the following solution. The ashless 542 filter paper containing the ammonia group substituting for the oxide from testing for the percentage of calcium oxide (CaO) were kept in an oven for drying. It was later removed from the oven and placed in a platinum crucible. The samples were burnt in a muffle furnace to about 1000°C and were later weighed after cooling them in a desiccator.

Potassium pyrosulphate crystals were added to the sample and burnt on a silica triangle until all the pyrosulphate was melted. The heating continued for an hour. The crucibles were transferred into a 150 ml beaker and to each of the samples after cooling 5 ml of HCl solution was added which were placed on a hot plate to dissolve the fused cake. The sample solutions were transferred into 100 ml volumetric flask and distilled water was added to make up to the mark with constant shaking. These solutions are the R_2O_3 group solutions.

Three different 10 ml solutions of R_2O_3 were pipetted from each sample and run through silver reductor in three separate 250 ml conical flasks. The silver reductor was washed with 150 ml portion of 0.5 dilute HCl after pouring and running of each sample.

To each of the filtered solutions from ammonium group solution 20ml of H_2O_4 was added, and titrated against 0.1N potassium dichromat using Barium chloride indicator.

Test for percentage Aluminum (III) oxide (Al_2O_3):

The ammonia group of oxides (R_2O_3 solutions) prepared consists of Fe_2O_3, MnO, TiO_2 P_2O_5 and Al_2O_3. After determining the other, oxides the Aluminum oxide would be Al_2O_3. R_2O_3. (Fe_2O_3 + MnO + TiO_2 + P_2O_5).

Flame test for percentage of sodium and potassium oxides (N_2O and K_2O):

For sodium, persistent golden yellow flame, invisible through blue glass was observed and for potassium, lilac flame this was visible through blue glass. The percentages were measured by using photometer.

Loss on Ignition at 1000°C Test

This is called the fusion loss and is the difference between 100% and percentage oxides in (chemical composition of the sand). According to Leford [5], the ignition loss is I_s = 100-O_t, where O_t is the total percentage of oxides in the sand.

Results and Discussion

Tables 2 to 12 show the results of the chemical analysis described above. In order to comment sensibly on the suitability of the sands studied as raw materials for the glass industry, one needs to know the characteristics of different types of glasses and then compare with the ones obtained in this study.

Comparing the results of the percentage chemical compositions obtained in the five sand samples with the standard chemical compositions for the various types of glasses shown in table 13 one can say, that the percentage of silica contents of the samples obtained are adequate for glass making. The percentages obtained in samples one and four (see Table 2) are suitable for borosilicate glasses which require about 81% by weight of silica for glass making. The percentage silica content in sample two is sufficient for soda lime glasses and lead glasses. The standard percentage needed for such type of glasses ranges between 70 and 75% by weight of silica.

However, samples three and five contain much higher percentage of silica, thus they are the most efficient glass formers.

They can be used for colourless and window glasses where the percentage needed lies between 92 and 95% by weight of silica, [8].

Looking at the percentage by weight of CaO and MgO obtained in the samples shown in (Tables 3 and 4) they are very low for glass making when compared with standard compositions needed. Higher percentages up to 4 to 5% are needed for manufacturing of soda lime and lead glasses or even more for fiber and alumino silicate glasses.

Although, the percentages of CaO and MgO are adequate for window and colourless glasses in which they require about 0.5% by weight. Hence, these percentages can be increased to a convenient percentage needed by the glass technologist or engineer, depending on the standard percentage needed and the type of glass to be manufactured.

The percentage by weight of the ammonia group of oxides (R_2O_3) determines the percentage composition of these oxides. The results as shown in Table 5 are a function of percentage composition of silica present in each sample. The higher the percentage by weight of silica in the sample the lower would be the percentage composition of the R_2O_3.

This reflects in samples three and five in which the percentage silica contents are 93.67 and 92.46% by weight while the percentage R_2O_3 are 3.62 and 4.24% by weight respectively.

The percentage by weight of Iron oxide obtained in samples three, four and five as shown in Table 6 are used in making coloured and amber glasses. The percentage needed for such types of glasses ranges between 2 and 3% by weight [8]. However, the percentage obtained in samples one and two are much higher. It is therefore not desirable for glass making.

The small amount of manganese oxide, titanium oxide and phosphorous oxides found, in the samples, would not have any effect in glass formulation (see Tables 7-9). Infact, higher percentage of these oxides are needed for glass formation. For instance, as much as, 4.8% by weight of titanium oxide is needed in glass ceramic formulation as stated by Bever [9] and as low as 0.1 for window and colourless glasses [8]. they are, therefore, viable for glass making, only that the percentages can be increased to reach the standard requirements needed for a special and desired glass.

The percentage compositions of aluminum oxide for samples one, three and five are adequate for soda lime, borosilicate and colourless glasses. Even though, sample three appeared to have a little bit higher amount. This would not have much effect on the glass, this is because the higher percentage adds to the chemical durability of the glass and hence improves the mechanical strength of the glass [5]. However, in samples two and four their percentage compositions are higher. These samples can be used for alumino silicate, fiber, and ceramic glasses. This is because the glasses of such type require 12-17% by weight of aluminum oxides.

The percentage compositions of sodium and potassium oxides obtained in the samples are shown in (Table 11) which are considerably low when compared with the standard percentage needed for various glass formulation.

Glasses such as borosilicate, lead, fiber and to some extent alumino silicate glasses require about 2-9% by weight of Na_2O and K_2O depending on the type of glass to be manufactured. According to Chanda [10], up to 15% by weight of Na_2O is needed for soda lime glasses. However, the percentage can therefore be increased to reach the standard percentage needed.

The loss on ignition is the portion of raw material loss in the melting process which involves gas or water vapour, such as CO_2 and SO_2 being the major volatile substances. The results of these material lost during the melting process would not have much effect on the glass, because these are negligible amounts.

Conclusion

The results show that sand from the Arid Zone of North-Eastern Nigeria can be used in glass making. The major glass forming oxide which is silica has been determined to be high between 74 and 94%. However, only samples three (Dapchi) and five (Ngala) are suitable for all glass making. The high percentage of iron oxide content, would not have any effect on the glasses, it is advisable to use these samples for coloured glasses and amber glasses. In the chemical analysis, the deleterious heavy minerals, were not detected, which also make the samples suitable for glass making. It is recommended that glass making industries be set up in the Arid Zone area of North-Eastern Nigeria to make use of the abundant sand for different types of glass. Table 14 lists out the types of glasses which each sample is suitable for.

REFERENCES

(1) Oliver D.S., (1995): The use of glass in engineering 1st Edition, Oxford University Press London pp. (8-13).

(2) Tooley F.V., (1969): Hand book of glass manufacturing, volume 2, Ogden Press, New York pp (5-109).

(3) Burgman J.A., (1970): Journal of Engineering material Vol. Open University Press Keynes pp. 3.

(4) Ashby Michael F. and Jones David R.H. (1986): Engineering materials, Vol. 2. An introduction to Microstructure, Processing and Design (International Series on Materials Science and Technology Vol. 39), Pergamon press Oxford pp. (158-159).

(5) Leford Stanley J., (1975): Industrial Minerals and Rocks, 4th Edition. American Institute of Mining Offuma block Well Press, New York. pp. (327 33).

(6) Brandy George S. and Clauser Henry R. (1986): Materials Hand Book, 12th Edition, McGraw Hill press New York pp. (714 - 716) and (737 - 714).

(7) Carver R.E., (1971): Procedure in Sedimentary Petrology, 1st Edition, John Wiley and Sons Inc. New-York, pp. (117-119).

(8) Wandby Smith J.E., (1964): A summary of the known deposits of glass sand in Nigeria (unpublished).

(9) Bever Michael B., (1986): Material Science and Engineering, 1st Edition Pergamon Press. New York pp. (1952-2024).

(10) Chanda M., (1979) Science of Engineering Materials, Vol. 2. Macmillan Company Publication India, pp. (1985-221).

Table 2: PERCENTAGE OF SILICA COMPOSITION (SiO_2) BY WEIGHT

S/No.	TOWN	WEIGHT OF SILICA CRUCIBLE Mc (g)	WEIGHT OF SILICA CRUCIBLE AND SAMPLE Ma(g)	%SiO_2=(Ma-Mc)x100
1	Kopchi	12.01021	12.8935	88.33
2	Biu	12.1300	12.9701	74.01
3.	Dapchi	12.0315	12.9682	93.76
4	Gwoza	12.1352	12.9593	82.41

S/No.	TOWN	WEIGHT OF SILICA CRUCIBLE Mc (g)	WEIGHT OF SILICA CRUCIBLE AND SAMPLE Ma(g)	%SiO_2=(Ma-Mc)x100
5	Ngala	12.0504	12.9750	92.46

TABLE 3: PERCENTAGE OF CALCIUM OXIDE COMPOSITION (CaO) BY WEIGHT

	TOWN	COMPOSITION BY WEIGHT			AVERAGE % COMPOSITION BY WEIGHT
		1	2	3	
1	Kopchi	1.14	1.13	1.09	1.12
2	Biu	2.92	2.94	2.95	2.94
3	Dapchi	0.56	0.57	0.54	0.56
4	Gwoza	1.13	1.14	1.10	1.12
5	Ngala	1.13	1.12	1.11	1.12

TABLE 4: PERCENTAGE OF MAGNESIUM OXIDE COMPOSITION (MgO) BY WEIGHT

S/N	TOWN	COMPOSITION BY WEIGHT			AVERAGE % COMPOSITION BY WEIGHT
		1	2	3	
1	Kopchi	0.41	0.42	0.37	0.40
2	Biu	0.93	0.89	0.89	0.90
3	Dapchi	0.22	0.20	0.19	0.20
4	Gwoza	ND	ND	ND	ND
5	Ngala	0.40	0.39	0.41	0.40

Table 5: PERCENTAGE OF AMMONIA GROUP OF OXIDES (R_2O_3) BY WEIGHT

S/No.	TOWN	WEIGHT OF PLATINUM CRUCIBLE Mb(G)	WEIGHT OF PLATINUM CRUCIBLE AND SAMPLE Mp(g)	R_2O_3=(Mp-Mb)
1	Kopchi	14.367	26.287	11.92
2	Biu	14.125	32.665	18.54
3	Dapchi	14.519	18.139	3.62
4	Gwoza	14.298	28.346	14.05
5	Ngala	14.455	18.695	4.24

TABLE 6: PERCENTAGE OF IRON OXIDE COMPOSITION (Fe_2O_3) BY WEIGHT

S/N	TOWN	% COMPOSITION BY WEIGHT			AVERAGE % COMPOSITION BY WEIGHT
		1	2	3	
1	Kopchi	3.99	4.0	3.98	3.99
2	Biu	4.80	4.78	4.79	4.79
3	Dapchi	1.59	1.60	1.57	1.59
4	Gwoza	0.85	0.73	0.81	0.80
5	Ngala	1.24	1.18	1.19	1.20

TABLE 7: PERCENTAGE OF MANGANESE OXIDE COMPOSITION (MnO) BY WEIGHT

S/N	TOWN	COMPOSITION BY WEIGHT			AVERAGE % COMPOSITION BY WEIGHT
		1	2	3	
1	Kopchi	0.02	0.25	0.23	0.23
2	Biu	0.26	0.25	0.23	0.25
3	Dapchi	ND	ND	ND	ND
4	Gwoza	0.19	0.20	0.21	0.20
5	Ngala	0.02	0.01	0.02	0.02

TABLE 8: PERCENTAGE OF TITANIUM OXIDE COMPOSITION (TiO_2) BY WEIGHT

S/N	TOWN	COMPOSITION BY WEIGHT			AVERAGE % COMPOSITION BY WEIGHT
		1	2	3	
1	Kopchi	0.02	0.03	0.04	0.03
2	Biu	0.02	0.009	0.01	0.01
3	Dapchi	0.01	0.01	0.02	0.01
4	Gwoza	0.009	0.02	0.01	0.01
5	Ngala	0.01	0.008	0.02	0.01

TABLE 9: PERCENTAGE OF PHOSPHOROUS OXIDE COMPOSITION (P_2O_5) BY WEIGHT

S/N	TOWN	% COMPOSITION BY WEIGHT			AVERAGE % COMPOSITION BY WEIGHT
		1	2	3	
1	Kopchi	0.01	0.007	0.02	0.01
2	Biu	0.03	0.02	0.03	0.02
3	Dapchi	ND	ND	ND	ND
4	Gwoza	ND	ND	ND	ND
5	Ngala	0.02	0.03	0.01	0.02

TABLE 10: PERCENTAGE OF ALUMINIUM OXIDE COMPOSITION (Al_2O_3) BY WEIGHT

S/N	TOWN	% BY WEIGHT OF R_2O_3	% BY WEIGHT OF (Fe_2O_3+MnO+TiO_2+P_2O_5)	WEIGHT OF AL_2O_3
1	Kopchi	11.92	8.25	3.67
2	Biu	18.54	5.12	13.42
3	Dapchi	3.64	1.62	2.02
4	Gwoza	14.05	0.97	13.08
5	Ngala	4.24	1.25	2.99

TABLE 11: PERCENTAGE OF COMPOSITION OF Na_2O AND K_2O

S/N	TOWN	% COMPOSITION OF Na_2O	% COMPOSITION OF K_2O
1	Kopchi	0.60	0.60
2	Biu	0.60	0.48
3	Dapchi	0.45	0.50
4	Gwoza	0.75	0.60
5	Ngala	0.45	0.50

TABLE 12: PERCENTAGE IGNITION LOSS

S/N	TOWN	% COMPOSITION OF TOTAL OXIDES O_T	$100-O_T$
1	Kopchi	98.98	1.02
2	Biu	97.43	2.57
3	Dapchi	99.00	1.00
4	Gwoza	98.97	1.03
5	Ngala	99.17	0.83

TABLE 13: MAIN TYPES OF GLASSES

No.	Types of Glass	Main Features
1.	Soda lime glass	70% SiO_2, 15% Na_2O_3, 10% CaO+MgO) and 5% other oxide [9].
2.	Fused silica glass	99.6 to 99.% SiO_2, without modifiers, very viscous and supplied as Lumps [10].
3.	Borosilicate glass	Soda lime glass in which other basic oxides are substituted by boron oxide and aluminium oxide [2].
4.	96% silica glass	06% SiO_2 produced from sodium boron silicate glass containing 75% SiO_2, 20% B_2O_3 and 5% Na_2O [10].
5.	Glass Ceramics	68.5 to 79.3% SiO_2 1.1%; 1.2% Al_2O_3 low thermal expansion glasses [9].
6.	Glass Fiber	52 to 65% SiO_2, 12 to 16% Al_2O_3 16 to 25% caO. Drawn into fine filaments [2, 3, 9].

TABLE 14 SUITABILITY OF SANDS STUDIED FOR THE GLASS INDUSTRY

S/No.	Sample Town	Types of Glass that can be made from it
1	Kopchi	Borosilicate
2	Biu	Soda lime and lead
3	Dapchi	Colourless and Window
4	Gwoza	Borosilicate
5	Ngala	Colourless and window.

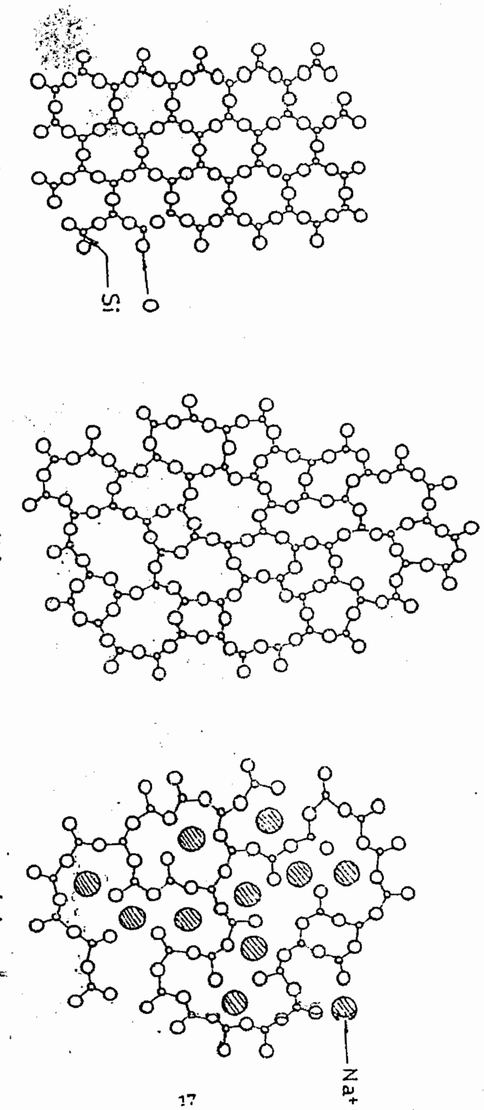

Fig. 1. Glass formation. A 3-co-ordinated crystalline network is shown at (a). But the bonding requirements are still satisfied if a random (or glassy) network forms, as shown at (b). The network is broken up by adding network modifiers, like Na_2O, which interrupt the netwok as shown at (c).

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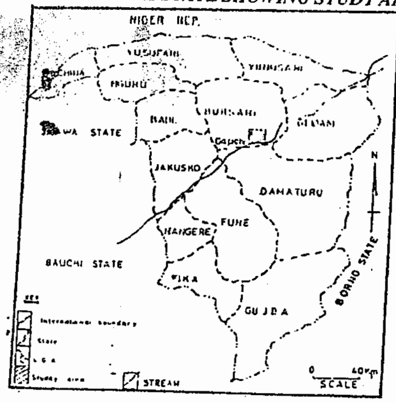
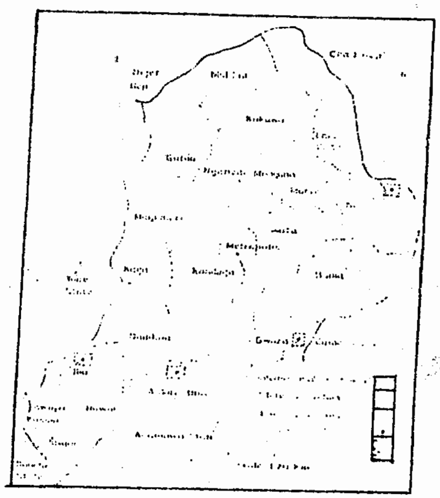
MAP OF YOBE STATE SHOWING STUDY AREA





Figs. 2 ang 3 showing the study towns