

GEOCHEMICAL, MINERALOGICAL AND INDUSTRIAL POTENTIALS OF SHALE AT OKIGWE AREA, SOUTHEASTERN NIGERIA

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ABSTRACT

Geochemical and mineralogical characteristics of shale, in Okigwe area, southeastern Nigeria were investigated using samples obtained from Ihube and Leru locations as representative samples for Nsukka and Mamu formations respectively. Calorimetric method and Atomic Absorption Spectrophotometer were used in the geochemical studies whereas X-ray diffraction method was employed in the mineralogical analysis. The intent of the study was to ascertain the industrial potentials of the deposits. The results of the chemical analysis show predominance of silica (SiO_2) and aluminum oxide (Al_2O_3). This clearly defines the shale as alumino-silicate. Chemical impurities in the shale include iron (II) oxide (Fe_2O_3), calcium oxide (CaO), sodium oxide (Na_2O) and magnesium oxide (MgO). X-ray analysis of the shale samples showed prominent quartz, kaolinite, smectite, siderite and mixed layer peaks. The chemical and mineralogical characteristics suggest that the deposits could be exploited for brick clay whereas specifically, the deposit at Leru would have more industrial applications which include serving as raw material in rubber, paper, textile and plastic manufacturing. The presence of strontium (Sr) and lead (Pb) in the samples indicates that the shale deposits are radioactive. The small amount of smectite in the shale deposits could constitute a problem because of its swelling effect on shale. However, the quality can be improved through processing and beneficiation.

Keywords: Geochemistry, Mineralogy, Formation, Shale, Oxide, Potential.

INTRODUCTION

Shale is a fine-grained, clastic sedimentary rock composed of mud that is a mixture of flakes of clay minerals and tiny fragments of other minerals especially quartz and calcite. Shale is characterized by breaks along thin laminae or parallel layering or bedding less than one centimeter in thickness, called fissility (Blatt & Robert, 1996). As noted by Makoju and Srivastava (1985), shale is essentially earth, but characterized by very fine particles that are tenacious and impervious. Mudstones, on the other hand, are similar in composition but do not show fissility and lamination.

Shale is formed as a result of the compaction and cementation of materials that weathered from pre-existing rocks. It is used all over the world for various purposes which include serving as major raw material in the ceramic, paper, refractory and pharmaceutical industries. It can also be used in the manufacturing of plastics, fertilizers and insecticides.

In Nigeria's manufacturing and construction industries, there has been an increasing demand for shale products. In that the mineralogical and geochemical characteristics of shale determine its end-use or market value, evaluations of these properties have always formed the basis for the determination of its potentials and stability for use in the industry. Thus, aspects of the mineralogy and geochemistry of shale at Ihube and Leru in Okigwe area, southeastern Nigeria, were investigated with an intent to ascertain the industrial potentials of the shale deposits. The results of this research as presented would be very useful in maximizing the potentials of these deposits and consequently reduce the foreign exchange of local industries in the area that depend on imported shale products as raw materials.

The Study Area

The outcrop at Ihube lies on longitude $05^{\circ} 51' 52''$ N and latitude $007^{\circ} 21' 28.5''$ E, with an elevation of 736ft above mean sea level whereas that of Leru is located on longitude $05^{\circ} 54' 59.5''$ N and latitude $007^{\circ} 21' 31.8''$ E, with an elevation of 481ft above mean sea level.

The study area comprises of Ihube and Leru in Okigwe Local Government Area of Imo State, southeastern Nigeria. At the Ihube and Leru locations, outcrops appear due to the road cuts at the Enugu-Port Harcourt expressway, which also served as access road for the study.

Geology and Physiography

Geologically, Okigwe lies within the Anambra Basin. The basin constitutes a major depocentre of clastic sediments in the southern portion of the Benue Trough (Nwajide, 2005). The outcropping geologic formations in the area are Ajali, Mamu and Nsukka formations. Soils in the area are derived from the false bedded sandstones or Ajali formation. Nsukka and Mamu formations are paralic, that is, consists of sand and shale sequences. Table 1 is a generalized stratigraphic sequence of sedimentary rocks in the area.

Table 1: Generalized stratigraphic sequence in Okigwe area (modified from Reyment, 1965, Mode 2004 and Ofoegbu, 1985).

Age	Formation	Lithological Characteristics
Paleocene (55-65 m.y.)	Imo Formation (Imo Shale)	Blue to dark grey shales and subordinate sandstone member (Umuna and Ebenebe sandstone).
Maastrichtian (65-68 m.y.)	Nsukka Formation	Alternating sequence of sandstone and shale with coal seams.
Maastrichtian (65-68 m.y.)	Ajali Formation	Friable sandstone with cross bedding. Alternating sequence of sandstone, siltstone, shale and claystone with coal seams.
Campanian (68-78 m.y.)	Mamu Formation Nkporo Formation (Enugu Shale)	Shale and mudstone with sandstone lenses.

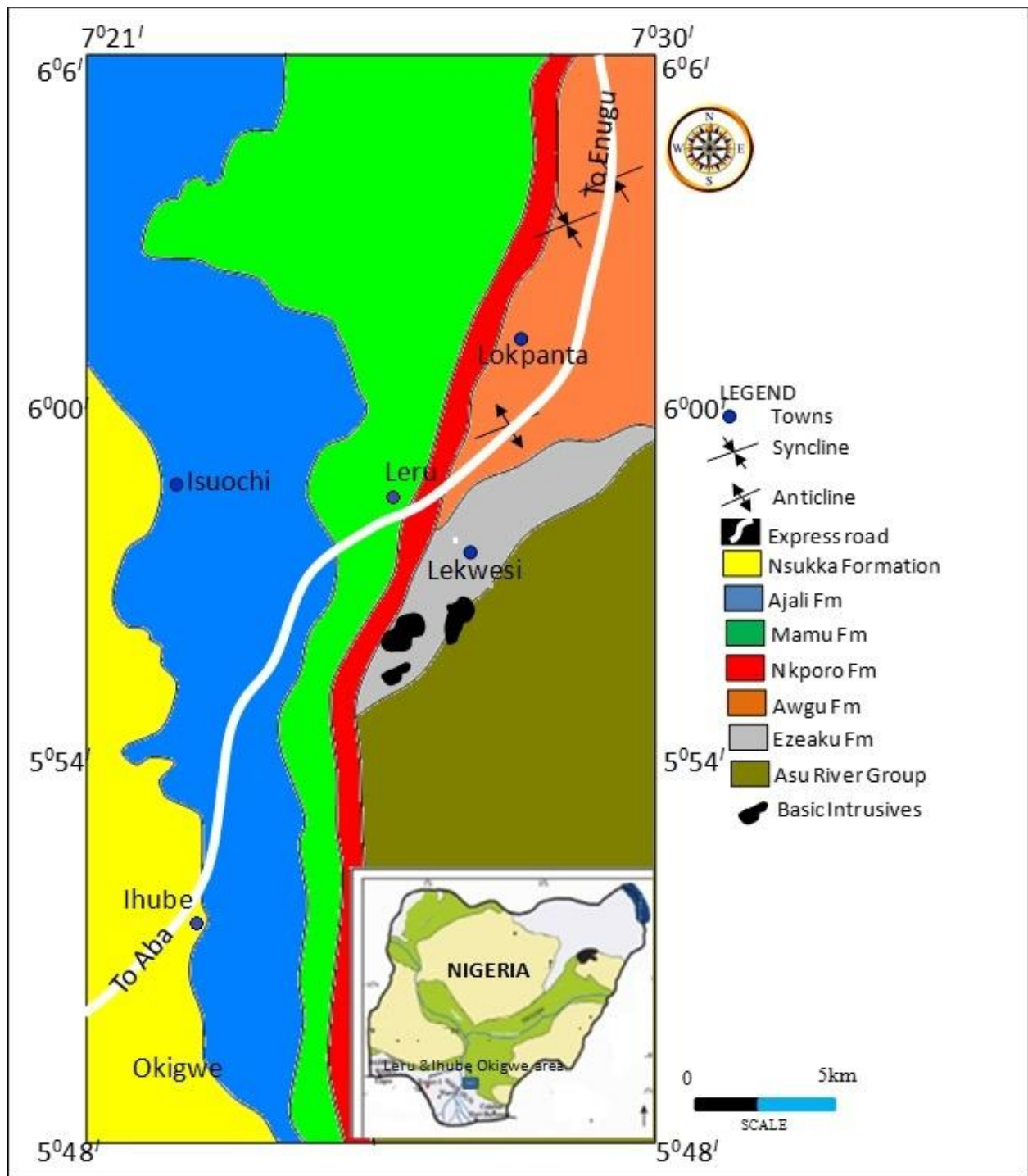


Figure 1: Geologic map of the study area (adapted from Dikeogu et al., 2018)

The area is characterized by undulating topography. As a result of differential weathering and erosion arising from resistant variations of the underlying rocks, the area and its environs are

dotted by escarpments, cuesta, and asymmetrical ridges. The area is largely drained by Imo River, with drainage patterns that are dendritic and radial.

The area has a tropical climate composed of two alternating seasons-rainy and dry seasons. The rainy season emanates from the Atlantic Ocean whereas the dry season with its dusty wind originates from the Sahara desert. The mean annual rainfall in the area is about 2000mm per year whereas the relative humidity is approximately 70%.

In the area where the Mamu shale outcrops, the vegetation is made up of trees, grasses and shrubs. In places where sandstones overlie the shales, the vegetation is thicker than it is in those areas where the shales are directly exposed.

MATERIALS AND METHODS

Field Study and Sample Collection

Field study was undertaken so as to provide adequate information on the geology of the area. Two (2) fresh outcrop samples were collected from different locations (Ihube and Leru) within the area. The samples were collected from the inner part of the outcrop in order to ensure that they are fresh. Precautions were also taken to prevent contamination and other exogenic transformations. The samples were labeled and packed into polyethene bags to prevent loss of moisture and thereafter, were taken to the laboratory for various tests and analysis.

Geochemical analysis

Geochemical studies of the shale samples were carried out at the Nigeria Geological Survey Agency (NGSA), Kaduna, using Perkin Elmer Atomic Absorption Spectrophotometer (AAS). The equipment was used for the determination of the major oxides and trace elements. Calorimetric method was used in the determination of P_2O_5 and TiO_2 . The loss on ignition was calculated from the weight difference between the dried and fired pellets. The firing was done in a furnace at a temperature of $1000^{\circ}C$ for 15 hours.

Mineralogical analysis

Mineralogical studies of the samples were also carried out at the NGSA, Kaduna, using X-ray diffraction (XRD) method, as well as Phillips P.W. diffractometer. The interpretation of the diffractogram for the shale samples was carried out by comparing the peaks obtained with those of standard minerals as presented by Carol (1971) and the Joint Committee on Powder Diffraction Standards (JCPDS, 1980).

RESULTS AND DISCUSSION

Major and Minor Oxides Geochemistry

The results of chemical analysis of the samples obtained from outcrops are presented in table2.

Table 2: Chemical composition of shale from Geologic formations in Okigwe area.

Parameter	Formation/Location	
	Nsukka Formation (Ihube)	Mamu Formation (Leru)
Major Oxides (%)		
SiO ₂	40.90	44.80
Al ₂ O ₃	14.40	15.10
Fe ₂ O ₃	4.32	6.07
K ₂ O	1.94	1.90
Na ₂ O	3.56	3.08
MgO	2.58	2.32
MnO	0.09	0.03
CaO	8.84	7.02
TiO ₂	0.83	0.85
P ₂ O ₅	0.06	0.04
Trace Elements (ppm)		
V	10	18
Cr	15	5
Ni	240	181
Cu	44	29
Zn	720	630
Sr	400	360
Zr	15	16
Pb	502	487

The results indicate that the dominant oxides present in the shale samples are the oxides of silicon and aluminium. As can be deduced from the table, the sample from Ihube contains 40.90% and 14.40% of SiO₂ and Al₂O₃ respectively. The sample from Leru has 44.80% SiO₃ and 15.10% Al₂O₃. Apart from the dominant oxides, the percentage differences in composition of other oxides found in the samples are negligible.

A wide range of trace elements were also identified in the samples and these include radioactive elements such as strontium (Sr) and lead (Pb) which occurred in relatively high amounts.

Mineralogical Characteristics

The X-ray diffraction results of the shale samples are presented in figures 2 and 3. The diffractograms showed prominent quartz, kaolinite and mixed layer peaks. The prominent basal reflections of the mixed layer clay minerals; kaolinite, smectite, siderite, and quartz for Leru and kaolinite, smectite and quartz for Ihube as indicated by strong and sharp peaks are indications of moderately or highly crystalline mineral components. The strong and sharp peaks are in line with

Amajor and Jubril (1991) wherein, it is noted that poorly crystalline and disordered minerals are characterized by blunt peaks.

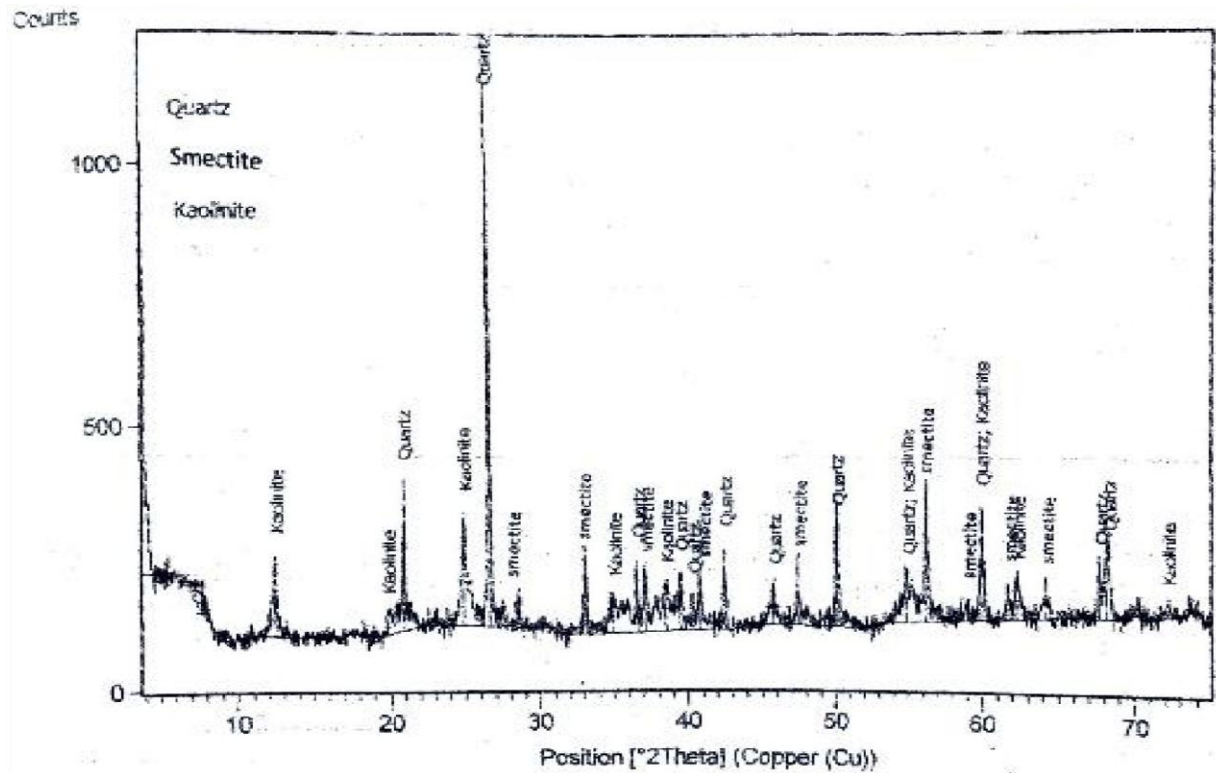


Figure 2: X-ray diffraction result for Leru-Okigwe shale in Mamu Formation (adapted from Oyedele et al., 2018)

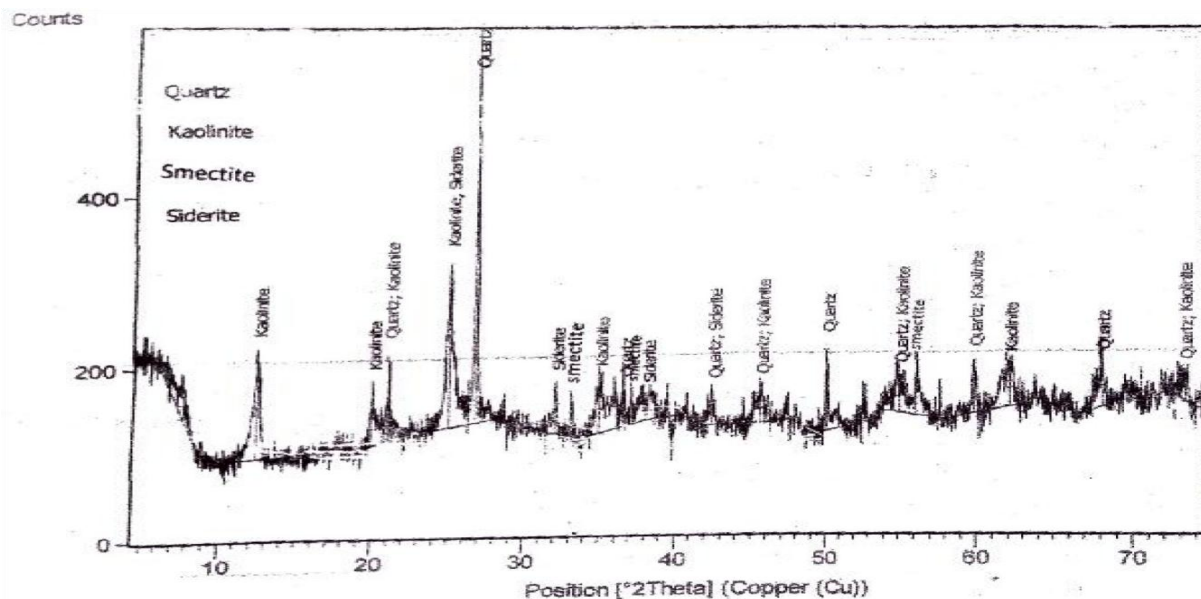


Figure 3: X-ray diffraction result for Ihube-Okigwe shale in Nsukka Formation (adapted from Oyedele et al., 2018)

Discussion

The predominance of SiO_2 and Al_2O_3 in the samples clearly defines the deposits as hydrated alumino-silicate contaminated by free silty quartz.

Chemical specifications of some industrial shales are presented in table 3 and that formed the basis for the assessment of the industrial potentials of the shale deposits.

Taking into account, the SiO_2 and Al_2O_3 contents of the samples and in reference to the chemical specification of some industrial shales as presented in table 3, the Ihube and Leru shale deposits are very good raw materials for brick clay. It is also inferred from the chemical specifications (see table 3) that the Leru shale would have more industrial applications. Thus, it will serve as a good raw material in paper, rubber, plastic and textile industries and as a catalyst in the cracking of hydrocarbons. However, some of these applications may require that on the basis of chemical composition, the shale be subjected to some processing or blending with appropriate materials to improve its quality. The presence of smectite on the deposits would constitute a problem consequent upon its swelling effect on shale. However, the swelling effect can be minimized through processing. In conditions where the aluminium oxide content of the shales is below the specification for a particular purpose, the deficit may be increased through admixture of pure aluminium or clay of high alumina content.

Table 2: Chemical specification of some industrial clays/shales (adapted from Okeke et al., 2001)

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)	(xi)
SiO ₂	47.0	45.78-47.90	45.78	44.90	45.90	45.80-45.90	45.00	67.50	51.00-70.00	38.00	46.07
Al ₂ O ₃	40.0	37.90-38.40	36.46	38.35	32.35	33.50-36.10	38.10	26.50	25.44	9.45	38.07
Fe ₂ O ₃	-	13.40-13.80	0.28	0.43	0.43	0.30-0.60	0.60	0.50-1.20	0.50-2.40	2.70	0.33
TiO ₂	-	1.35-1.75	-	1.80	1.80	0.00-1.70	1.70	1.10-1.0	1.0-2.8	-	0.50
Na ₂ O	-	0.20-0.30	0.25	0.14	0.14	0.00-1.60	-	0.20-1.50	0.80-3.50	2.76	0.27
K ₂ O	-	0.10-0.40	0.25	0.28	0.28	0.00-1.60	-	1.10-0.10	-	2.76	0.43
CaO	-	0.25-0.30	0.50	tr.	tr.	0.00-0.50	-	0.18-0.30	0.10-0.20	15.85	0.38
MgO	-	0.20-0.30	0.04	tr.	tr.	-	0.10-0.19	0.20-0.70			
H ₂ O+	13.0	-	13.40	14.20	14.20	12.00-14.70	14.70	12.00	-	3.04	13.47

(i) Pharmaceuticals (Todd, 1973)

(ii) Paints (Paynes, 1965)

(iii) Plastics (Frados, 1965)

(iv) Cracking catalyst (Keller, 1964)

(v) Rubber (Keller, 1964)

(vi) Paper (Keller, 1964)

(vii) Textiles (Keller, 1964)

(viii) Ceramics (Singer and Sonia, 1971)

(ix) Refractory Bricks (Parker, 1967)

(x) Bricks Clay (Murray, 1960)

(xi) Fertilizer (NAFCON, 1985)

The high level of Sr and Pb in the samples indicates that the shales are highly radioactive and calls for caution in the course of utilization. However, the shale at Ihube is more radioactive than that of Leru as indicated by the high values (see table 2). The Sr and Pb could be extracted for use as power source for radioisotope thermostatic generators (RTGS). Its chloride is sometimes used for the manufacture of toothpastes for sensitive teeth whereas Pb can be used in building construction, lead acid accumulators, bullets and shots, asphalt of solders, pewters, fusible alloys and as electrode in the process of electrolysis. It should however, be noted that Pb is a highly poisonous metal that affects almost every organ in the body when inhaled or swallowed.

The results of the chemical analysis for trace elements (see table 2) also show that the shales contain high amount of nickel (Ni) and zinc (Zn) and these metals could be extracted from the shales for industrial uses.

SUMMARY AND CONCLUSION

The results of the analysis indicate that the shales in Ihube and Leru in Okgwe area have industrial potentials and meet the specifications for the construction of brick clay. The Leru shale has a wider range of applications. Thus, it will serve as raw material in paper, rubber, plastic and textile industries and also as catalyst in the cracking of hydrocarbons. However, in conditions where the shales do not have the specifications for certain industrial uses, the quality may be improved through processing and beneficiation.

Mineralogical studies showed presence of quartz, smectite, siderite, and kaolinite in the shale deposits. The smectite may constitute a challenge in the utilization of the shales for certain industrial purposes as a result of its swelling effect. However, subjecting the shales to certain processes that would improve their quality is all that is required to overcome the problem.

The results of the geochemical analysis show that the shales are highly radioactive as a result of the presence of strontium (Sr) and lead (Pb). These radioactive metals can also be extracted for some industrial purposes.

Proper utilization of these shales by local industries in the area will greatly enhance production. Although, the cost of processing the shales in order to meet the requirements or specifications for certain industrial uses may be high, it will save the country some foreign exchange earnings if these abundant resources can be harnessed by local industries as raw materials.

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