SSRG International Journal of Geo-informatics and Geological Science
ISSN: 2393 – 9206 / https://doi.org/10.14445/23939206/IJGGS-V9I1P102

Volume 9 Issue 1, 13-20, Jan-April 2022

Original Article

Geochemical and Hydrogeochemical Characterization of Limestone Deposits of Okeluse Area, Southwestern Nigeria

Thompson Henry Tolulope Ogunribido[1], Mercy Modupe Ogungbamila[2]

[1]*Senior Lecturer, Department of Earth Sciences, Adekunle Ajasin University, Akungba – Akoko, Ondo State, Nigeria.*
[2]*Graduate student, Department of Earth Sciences, Adekunle Ajasin University, Akungba – Akoko, Ondo State, Nigeria.*

Received Date: 01 January 2022
Revised Date: 01 February 2022
Accepted Date: 10 February 2022

Abstract - *The geochemical and hydrogeochemical studies were carried out to determine the suitability of Okeluse limestone for cement production and the potability of natural waters in that area. Five limestone samples were collected and subjected to X-Ray fluorescence analysis to determine major oxides and their percentages. Six water samples were collected and were tested for pH, temperature, turbidity, electrical conductivity, TDS, TSS, total hardness, calcium hardness as $CaCO_3$, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, HCO_3^{2-}, SO_4^{2-}, PO_4^{3-}, NO_3^-, Fe^{3+}, Pb^{2+}, Cr^{6+}, Mn^{2+}, Cd^{2+}, Ni^{3+}, Zn^{2+}, Cu^{2+}, As^{2+}, and Co^{2+}. Results for major oxides revealed that CaO content ranged from 46.46% - 52.22%, SiO_2 from 1.52% - 5.1%. MgO, Fe_2O_3, and Al_2O_3 contents were 1.564%, 2.408% and 0.968%, respectively, while MnO, P_2O_5, K_2O, Na_2O and SO_3 are very low in concentration. CaO shows an inverse relation to SiO_2 and MgO, indicating a high degree of purity of the limestone. The limestone here is the magnesian type which is suitable for cement production. Hydrogeochemistry showed that the dissolved constituents originated from the weathering of rocks. The hydrogeochemical facies revealed Na-Cl and K-H-CO_3 wat types. Water samples were contaminated by K^+, Fe^{2+} and $Cd^{2+;}$ therefore, water is not potable. It has to be treated before use.*

Keywords - *Hydrogeochemistry, Limestone, Okeluse, Polluted, Sedimentary.*

I. INTRODUCTION

Limestone is a sedimentary rock composed by weight of at least 50% of calcium carbonate in the form of calcite and rarely as aragonite. Limestone is composed predominantly of carbonates of calcium or carbonate of calcium and magnesium in the case of dolomitic limestone and sometimes may contain a variable amount of feldspars, quartz, pyrites, siderites and clay minerals. Limestone has a hardness of 3 on Mohr's scale of hardness with a specific gravity ranging from 2.6 – 2.8. All limestone readily dissolve in cold dilute acids giving off bubbles of carbonic acids. Limestone in its purest form is white or milky in colour, but the presence of impurities such as clay, organic remains, iron oxides causes limestone to exhibit different colours, especially when weathered.

Limestone occurs in low energy, shallow and warm marine water. This sort of environment is dominated by organisms, such as foraminifera, corals, coccoliths and molluscs that can secrete calcium carbonate by extracting the needed nutrients from the ocean water. Upon death, their shells and skeletons accumulate as sediment at the seafloor and are lithified to form limestone. Limestone formed from this type of sediment is biological limestone (Nichols, 2009; Tucker and Wright, 1990). Limestone can also be formed by the direct precipitation of calcium carbonate from marine or freshwater. Limestone formed this way are chemical limestone, and they are less abundant than biological limestone (Tucker and Wright, 1990). They can also form through evaporation. Stalactite, stalagmite, and other cave formations often called speleotherms are examples of limestone that are formed through evaporation

The interaction of natural waters in Okeluse limestone left much to be the desire for the hydrogeochemistry of the environment. The hydrogeochemical processes help to get an insight into the contributions of rock-water interaction on groundwater quality. These geochemical processes were responsible for the seasonal and spatial variations in groundwater chemistry (Gurugnanam *et al.*, 2009; Nwankwoala and Udom, 2011; Senthiikumar and Elango, 2013, Vikas *et al.*, 2011). Groundwater chemically evolves by interacting with aquifer minerals or internal mixing among different groundwater along flow-paths in the subsurface (Senthiikumar and Elango, 2013). Nitrate is a common contaminant of drinking water, fertilizers yield nitrogen that is taken up by plants, and it is leached into the soil in the form of nitrate. Nitrate (NO_3^-) ion is not harmful in the human body except when it loses an oxygen atom reducing it to nitrite (NO_2^-), which is harmful to the body. Nitrate in drinking water is dangerous to infants and small children as their immature digestive system facilitates the reduction of nitrate to nitrites. Contamination of surface water can be caused by oil spills, solid and liquid waste from industries disposed into rivers, streams and runoff carrying mineral contaminants from mining sites and dumpsites. Surface water can also be polluted by sewage discharge and animal droppings containing pathogenic bacteria such as E-coli or coliforms

II. LOCATION, PHYSIOGRAPHY AND GEOLOGY OF THE STUDY AREA

Okeluse, the study area, is a town in Ose Local Government Area of Ondo State, Southwestern Nigeria. It is located at the easternmost part of the Dahomey Basin. The study area is about 5km south of Ifon. The study area lies within longitude 5°33′ E and 5°37′ E of the Greenwich meridian and latitude 6°46′ N - 6°48′ N of the equator (Fig 1). Okeluse has a tropical climate. The two main seasons of importance are the wet and dry seasons. The wet season starts in March and ends in October, while the dry season starts in November and ends in February. Temperature ranges from 24.8℃ in August to 28.2℃ in March, with an average annual temperature of 26.6℃. The study area has relatively high humidity and an average annual rainfall of about 166 mm. Although limestone does not support thick vegetation, the thickness of the overburdened material supports the abundance of evergreen vegetation. Okeluse has a low relief compared to the basement complex surrounding it, with an elevation range of 50- 80 meters. Okeluse is well drained by rivers and stream such as Omi Alayo and Omi Ovianegdon that discharges into the Ogbese River.

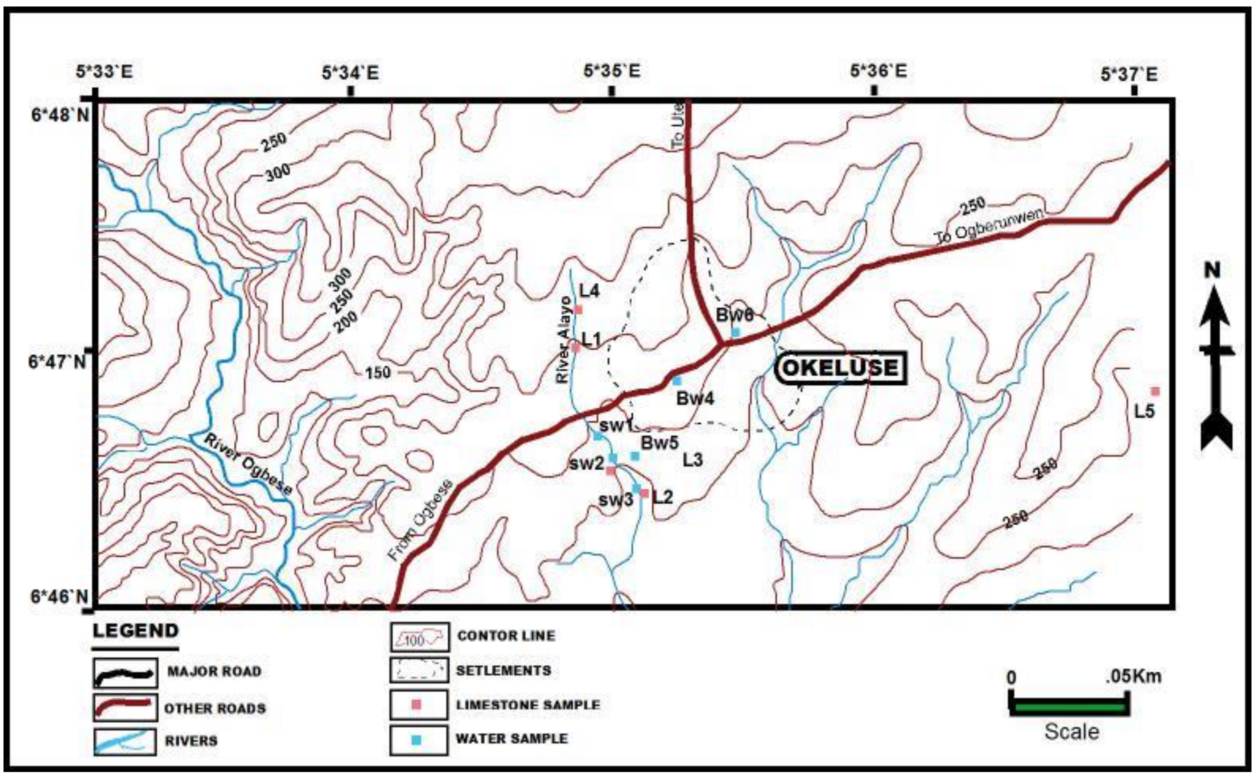

Fig. 1 Map of the study area and sampling points

The study area is underlain by the Cretaceous sediments of the Araromi Formation of the Abeokuta Group (Figure 2). The study area has mainly three lithologic units; the clay/ lateritic topsoil, brown fossiliferous limestone and the fissile grey shale at the base, but in some areas, we have the clay/ lateritic topsoil, saturated clay overlying the brown fossiliferous limestone and the grey shale at the base (Ehinola et al., 2012, Omotshola & Adegoke, 1981, adeniran & Adegoke, 1987, Adekoge, 1970, Elueze & Nton, 2004, Bilman, 1992).

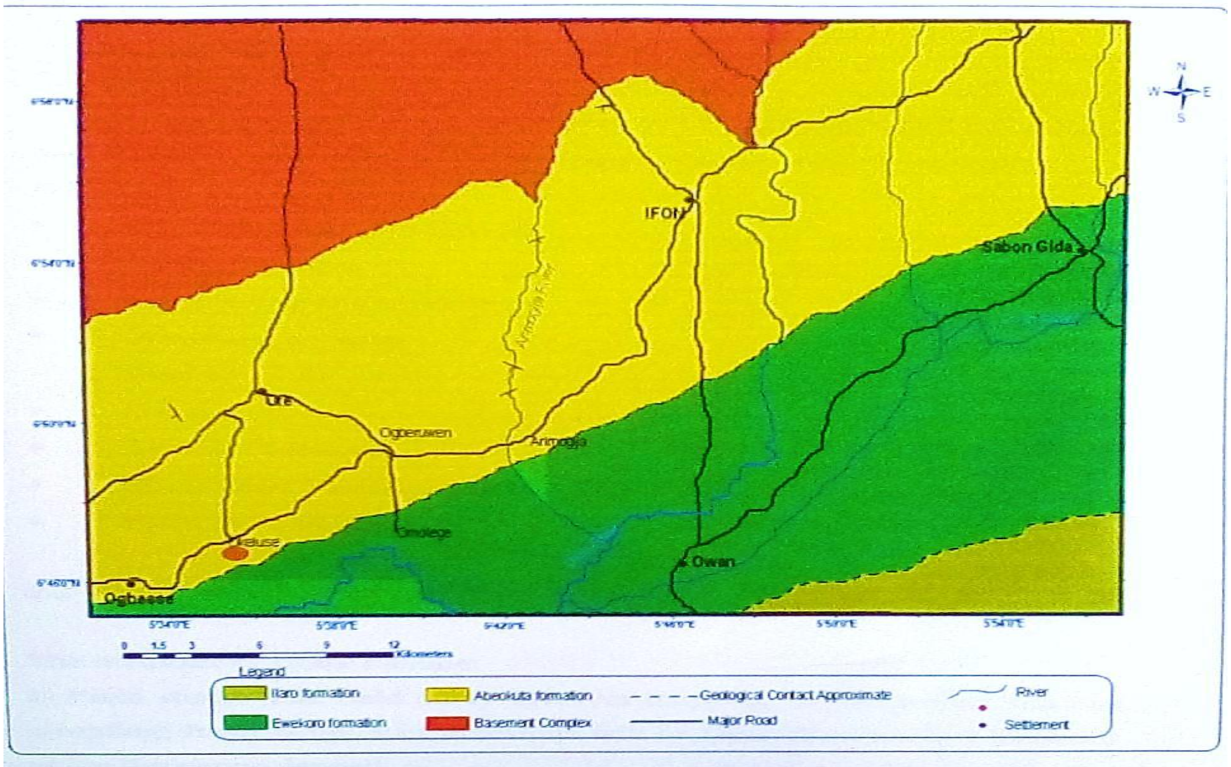

Fig. 2 Geological Map of the study area (Source- Ehinola et al., 2012)

III. MATERIALS AND METHOD

Five limestone samples and six water samples composed of 3 samples from boreholes and 3 samples from the stream were collected for analyses in this study. X-ray fluorescence (XRF) analytical technique was used to determine the geochemical composition of the limestone rock through the interaction of the limestone material with X-ray radiation. The concentration of the following oxides was determined: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, MnO, P_2O_5, K_2O, Na_2O and SO_3. Thirty-two parameters were tested for in the laboratory in each of the six water samples collected from the study area using prescribed standard methods (Ademoroti, 1992, Ogunribido, 2017). Parameters tested for were: Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Manganese (Mn^{2+}), Cadmium (Cd^{2+}), Lead (Pb^{2+}), Iron (Fe^{2+}), Nickel (Ni^{3+}), Copper (Cu^{2+}), Arsenic (As^{3+}), zinc (Zn^{2+}), Cobalt (Co^{2+}) were analyzed using Atomic Absorption Spectrophotometer. Sodium (Na^{+}), and Potassium (K^{+}) by flame photometer, Chloride (Cl^{-}), Bicarbonate (HCO_3^{2-}), Sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}), Nitrate (NO_3) and total hardness by titrations and physical parameters like pH value, turbidity, electrical conductivity, total dissolved solids and temperature were measured through handheld pH meter

IV. RESULT AND DISCUSSIONS

The results of the x-ray fluorescence analysis of Okeluse limestone samples are presented in Table 1 and hydrogeochemistry in Tables 4 and 5. Table 4.2 shows Todd's classification of carbonate rocks, while Table 4.3 shows the chemical classification of Okeluse limestone using Todd's classification. Figure 4.1 – 4.6 shows the graphical representation of the major oxides concentration of Okeluse limestone samples. Figure 4.7 shows the bar chart comparison of CaO and SiO_2 concentration in Okeluse limestone samples. Figure 4.8 shows the bar chart comparison of CaO and MgO.

Table 1. Concentration (%) of major oxides in the okeluse limestone samples

		Major oxides (%)									
S/N	Sample ID	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	SO_3
1	OK1	3.42	0.83	2.78	49.33	0.77	0.05	0.45	0.13	0.69	0.07
2	OK2	5.1	1.62	3.12	46.54	1.55	0.06	0.43	0.15	0.55	0.06
3	OK3	3.51	0.89	3.51	46.46	3.52	0.04	0.47	0.17	0.37	0.05
4	OK4	2.54	0.63	1.38	52.22	1.42	0.07	0.51	0.13	0.02	0.07
5	OK5	1.52	0.87	1.25	50.81	0.56	0.05	0.42	0.23	0.05	0.05
	Mean	3.218	0.968	2.408	49.072	1.564	0.054	0.456	0.162	0.336	0.06

Table 2. Todd's (1966) chemical classification of limestone

Descriptive Term	Standard Ratio Ca/Mg	Reciprocal Ratio Mg/Ca
Dolomitic Limestone	12.30- 1.41	0.08- 0.18
Magnesian Limestone	39.00- 12.30	0.03-0.08
Pure Limestone	100.00- 39.00	0.00- 0.18

Table 3. Chemical classification of okeluse limestone using Todd's classification of limestone

Sample ID	CaO (%)	MgO (%)	Ca/Mg	Mg/Ca	Remarks
OK1	49.33	0.77	64.065	0.0156	Pure
OK2	46.54	1.55	30.026	0.0333	Magnesian
OK3	46.46	3.52	13.199	0.0758	Magnesian
OK4	52.22	1.42	36.775	0.0272	Magnesian
OK5	50.81	0.56	90.732	0.0110	Pure
Mean	49.072	1.564	31.376	0.0319	Magnesian

Table 4. Results of physical analysis of stream and groundwater samples

S/N	Physical Parameters	W1 (USTR)	W2 (MSTR)	W3 (DSTR)	W4 (BH)	W5 (BH)	W6 (BH)	WHO (2017)
1	pH	7.59	7.71	7.91	7.35	7.49	7.09	6.5 -8.5
2	Electrical Conductivity (µs/cm)	43.3	52.2	59.8	17.00	19.90	15.00	1000
3	Temperature (ºC)	30.4	30.7	30.8	30.8	30.8	30.8	
4	Turbidity (NTU)	0.082	0.099	0.077	0.082	0.109	0.120	25
5	Total Dissolved Solid (ppm)	0.018	0.016	0.014	0.353	0.035	0.041	1000
6	Total Suspended Solid (ppm)	0.193	0.207	0.188	0.179	0.194	0.199	
7	Total Solid (ppm)	0.211	0.223	0.202	0.532	0.229	0.240	

Table 5. Results of chemical analysis of stream and groundwater samples

S/N	Chemical Parameter (in ppm)	W1 (USTR)	W2 (MSTR)	W3 (DSTR)	W4 (BH)	W5 (BH)	W6 (BH)	WHO (2017)
1	Calcium (Ca^{2+})	10.02	7.62	1.60	23.35	8.82	22.44	200
2	Calcium Hardness as $CaCO_3$	25.00	19.00	4.00	58.00	22.00	56.00	
3	Total Hardness	44.72	33.18	15.32	107.74	44.43	83.79	
4	Magnesium (Mg^{2+})	9.72	6.56	9.72	26.49	13.61	5.35	150
5	Bicarbonate (HCO_3^-)	42.7	42.7	42.7	36.60	30.5	42.7	200
7	Total Alkalinity as $CaCO_3$	42.7	42.7	42.7	36.60	30.5	42.7	
8	Chloride (Cl^-)	28.36	31.91	31.91	74.45	31.91	17.73	500
9	Phosphate (PO_4^{3-})	0.18	0.09	0.12	0.10	0.32	0.14	
10	Sulphate (SO_4^{2-})	0.26	0.25	0.24	0.35	0.29	0.25	400
11	Nitrate (NO_3^-)	0.07	0.06	0.06	0.04	0.12	0.05	50
12	Potassium (K^+)	80.300	104.500	53.100	112.600	60.400	65.900	50
13	Sodium (Na^+)	56.100	72.500	21.800	66.500	38.800	41.300	200
14	Iron (Fe^{2+})	0.371	0.259	1.044	0.720	1.153	0.844	0.3
15	Lead (Pb^{2+})	0.026	0.015	0.035	0.010	0.011	0.021	0.01
16	Chromium (Cr^{6+})	0.002	0.002	0.001	0.002	0.001	0.001	0.05
17	Manganese (Mn^{2+})	0.010	0.001	0.002	0.007	0.004	0.002	0.2
18	Cadmium (Cd^{2+})	0.016	0.010	0.001	0.002	0.003	0.014	0.003
19	Nickel (Ni)	0.020	0.001	0.002	0.002	0.002	0.020	0.07
20	Zinc (Zn^{2+})	0.004	0.007	0.001	0.006	0.002	0.005	3.0
21	Copper (Cu^{2+})	0.001	0.001	0.004	0.002	0.001	0.001	2.0
22	Arsenic As^{3+})	0.007	0.012	0.003	0.001	0.002	0.004	0.01
23	Cobalt (Co^{2+})	0.002	0.010	0.008	0.009	0.007	0.002	0.003

A. Geochemical analyses

a) XRF Analysis of Okeluse Limestone Samples

The X-ray fluorescence result of the major oxides showed that the concentration of CaO ranges from 46.46 - 52.22% with a mean value of 49.072%, the calcium oxide concentration is most prevalent. The SiO_2 content varied from 1.52% - 5.1% with a mean value of 3.218% while Fe_2O_3 content ranges from 1.25% - 2.78% with an average of 2.408%. The MgO concentration ranged from 0.56% - 3.52% with a mean of 1.564% and Al_2O_3 varies from 0.63% - 0.83% and a mean value of 0.968%. The remaining oxides; MnO, P_2O_5, K_2O, Na_2O and SO_3 were very low in concentration (less than 0.5%) with average concentration of 0.054%, 0.456%, 0.162%, 0.336% and 0.06% respectively
.

b) Calcium Oxide (CaO), Silica (SiO_2) and Magnesium Oxide (MgO)

From Table 1, CaO shows an inverse relation with SiO_2 (that is, the concentration of silica reduces as the concentration of calcium oxide increases). MgO concentration is relatively low compared to CaO, indicating that the limestone is not dolomitic. Comparison of the high concentration of CaO and the low concentration of SiO_2 and MgO indicates the high degree of purity of the limestone, which makes it suitable for cement production.

The CaO concentration of Okeluse limestone compares satisfactorily with that of Olade (1988), but the concentration of CaO is low (average 49. 1%) when compared with the CaO concentration of Sagamu (89.2 %,), Ewekoro (80.3%) and Ibeshe (75.7%) (Akinmosun et al., 2005).

The SiO_2 concentration of Okeluse limestone (average of 3.218%) is relatively low compared to Sagamu (5.7%), Ewekoro (8.7%), Ibeshe (14.8%), Igunmale (13.9%) and Sokoto (11.3%) (Olade, 1988; Akinmosun *et al*., 2005, Durhan, 1962, Edema & Owonipa, 2016, Obaje, 2009, Odeyemi *et al*., 2000). This, however, established that Okeluse limestone is a low silica limestone; hence it is of high grade

c) Classification of Okeluse limestone

Todd (1966) employed the standard ratio, Ca/Mg ratio, and its reciprocal ratio: Mg/Ca, as a parameter for the chemical classification of limestone. He grouped limestone samples based on Ca/Mg ratios as “dolomitic limestone”, “magnesian limestone”, and “pure limestone” (Table 3). This study showed that the Ca/Mg ratio of Okeluse limestone ranges from 13.199% to 90.732%, while the reciprocal Mg/Ca ratio ranges from 0.011 to 0.0758. Samples OK2, OK3, and OK4 have a Ca/Mg ratio range of 13.19- 36.38 and Mg/Ca ratio range of 0.0272- 0.0758, while sample OK1 and OK5 have Ca/Mg ratio of 64.065 and 90.732 and Mg/Ca ratio of 0.0110- 0.0156. The values of OK2, OK3, and OK4 revealed that Okeluse limestone is a magnesian limestone type (Table 3).

B. Hydrogeochemical Analyses

a) pH

The pH is the measure of acidity or basicity of the water, with a scale of 1 to 14. The pH value 1 to 6 is considered acidic, while 7 is neutral, and 7 to 14 is considered to be basic. The pH values of the stream and groundwater samples of the study area increase in the order W6< W4< W5< W1< W2< W3, with a range of 7.09 – 7.91 and a mean of 7.52. The pH of the water samples falls within the WHO (2017) drinking water standard of 6.5 – 8.5.

b) Electrical Conductivity

The conductivity of stream and groundwater samples increases in the order of W6< W4< W5< W1< W2< W3, with a range of 17.00 µs/cm – 59.8 µs/cm and a mean of 34.53 µs/cm. The conductivity of Omi Alayo stream W1, W2 and W3 were higher than that of the groundwater. The conductivity values are lower than the maximum conductivity value of 1000 µs/cm stated by WHO (2017) for drinking water. The low conductivity values make the water suitable for irrigation purposes as the values were less than 200 µs/cm (Wilcox, 1985)

c) Turbidity

The turbidity values of water samples increases in the order of W3< W1= W4< W2< W5< W6, with a range of 0.077 NTU – 0.120 NTU and a mean of 0.095 NTU. WHO's maximum permissibility limit for turbidity is 5.0 NTU, which indicates that Okeluse stream and groundwater is free from suspended and colloidal particles.

d) Total Dissolved Solids (TDS).

The TDS values of the water samples ranged from 0.014 ppm – 0.353 ppm and an average of 0.079 ppm. The values increase in the order W3< W2< W1< W5< W6< W2, Omi Alayo stream, W1, W2, and W3 have lower TDS values of 0.018 ppm, 0.016 ppm, 0.014 ppm, respectively. The WHO (2017) standard is 1000 ppm, thus indicating that the water is fresh (Davis and De Wiest, 1966).

e) Total Hardness

Hardness in water results from the presence of Ca^{2+} and Mg^{2+} contained minerals. The range of total hardness was 15.32 ppm – 107.74 ppm, with an average of 54.86 ppm. The values of total hardness increase in the order of W3< W2< W5< W1< W6< W4. Weathering of limestone in the study area serves as the source of calcium and magnesium in water. The maximum permissible limit for total hardness is 500 ppm (WHO, 2017).

f) Calcium

Calcium is essential for strong bones and teeth. The range of the value of calcium in the water sample was 1.60 ppm – 23.35ppm. The values increases in the order of W3< W2< W5< W1< W6< W4. The calcium content of the water was far below the WHO permissible standard of 200ppm. The presence of calcium ion in the water is most likely from the dissolution of the limestone.

g) Magnesium

The values of magnesium in the water increases in the order of W6< W2< W1= W3< W5< W4, and the range was 5.35 ppm – 26.49 ppm. The range of the magnesium contents of the water samples was below the WHO Magnesium permissible standard of 150ppm.

h) Sodium and Potassium

Sodium content ranged from 21.80 ppm – to 72.50 ppm. The concentration of sodium ion in the study area is relatively low compared to the WHO (2017) permissible standard for sodium of 200 ppm. The sodium concentration determines if the water can be used for irrigation because it reacts with the soil to reduce permeability. Potassium contents were higher than WHO's (2017) permissible standard of 50 ppm, and the range was 53.10ppm – 112.60ppm

.

i) Chloride

The concentrations of chloride ion range from 17.73ppm – 74.45ppm. The concentration is relatively low compared to the WHO (2017) chloride permissible standard of 200 ppm. A low concentration of chloride in the area indicates the absence of saltwater intrusion.

j) Sulphate

Sulphate concentrations ranged from 0.24ppm – 0.35ppm. The sulphate concentration is lower than the WHO (2017) limit of 400ppm. The low concentration of sulphate is an indication of the absence of saltwater intrusion in the study area.

k) Nitrate

The concentration of nitrate ranged from 0.04ppm – 0.12ppm. However, the nitrate concentration in the water samples from the study area is relatively lower than the WHO (2017) permissible standard of 50ppm. Nitrates in water are derived mainly from agricultural chemicals. The consumption of water containing nitrates in excess by infants below six months could cause serious illness and eventually death.

l) Bicarbonate

Bicarbonate concentrations in water samples increased in the order of W5< W4< W1= W2= W3= W6, bicarbonate concentrations in all locations were lower than the WHO (2017) limit of 200ppm. The source of bicarbonate is mainly from carbon dioxide in the atmosphere and partly due to the activities of biota in the soil (Udom et al., 2002).

m) Heavy metals

Iron (Fe^{2+}) has the highest concentrations which ranged from 0.259ppm – 1.153ppm and a mean of 0.732ppm. WHO (2017) recommended maximum iron concentration is 0.3ppm which showed that iron concentrations in some of the water samples are higher than the recommended drinking limit.. Water types Cadmium contents in the water samples were higher than WHO (2017) recommended limit of 0.003ppm., since cadmium concentration ranged from 0.001ppm – 0.016ppm and a mean of 0.008ppm. Lead, chromium, manganese, nickel, zinc, copper and arsenic concentrations were all lower to WHO (2017) recommended limits of 0.01ppm, 0.05ppm, 0.2ppm, 0.07ppm, 3.0ppm, 2.0ppm and 0.01ppm respectively. Lead ranged from 0.01ppm – 0.035ppm, chromium from 0.001ppm – 0.002ppm, manganese from 0.001ppm – 0.01ppm, nickel from 0.001ppm – 0.02ppm, zinc from 0.001ppm – 0.007ppm, copper from 0.001ppm – 0.004ppm and arsenic from 0.001ppm – 0.012ppm. The concentrations of the heavy metal were either below or within the limits of WHO (2017) recommended standard. . The general trends of ions is decreasing order of magnitude $K^+ > Na^+ > HCO_3^- > Cl^- > Ca^{2+} > Mg^{2+} > SO_4^{2-} > NO_3^- > PO_4^{3-}$.

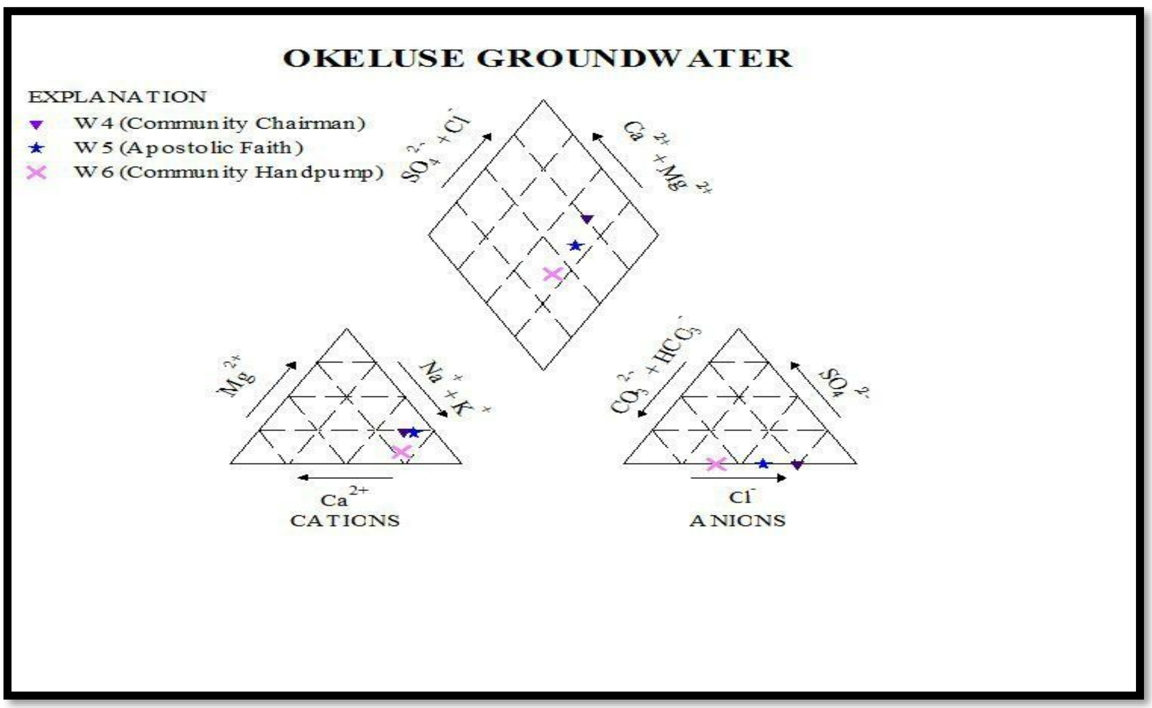

Fig. 3 Piper- diagrams

C. Suitability of natural waters in the study area for irrigation purposes

The suitability of water for irrigation purposes depends on its mineral constituents, particularly dissolved solids. Wilcox quality classification was used to determine the salinity of the groundwater in the study area and to know whether the groundwater can be used for irrigation. The general criteria for judging the suitability of groundwater for irrigation purposes are total salt ions, sodium adsorption ratio and salinity hazard. Water samples in the study area are excellently suitable for irrigation purposes

V. CONCLUSION

The geochemical analyses of limestone samples revealed the major oxides composition of the limestone, which showed its suitability for cement production. The inverse relationship between CaO and SiO_2 indicate the suitability of the limestone for cement production. The CaO concentration is higher than the concentration of SiO_2 and MgO, indicating the high purity of the limestone and its suitability for cement production, although the CaO concentration is relatively low when compared with other limestone deposits in Nigeria. Todd (1966) chemical classification revealed that Okeluse limestone is the magnesian type. The hydrogeochemical analysis of water samples showed the variability in the distribution of the different physicochemical parameters in the study area. The concentrations of Ca, Mg, Na, HCO_3, Cl, SO_4, NO_3, Pb, Cr, Mn, Ni, Zn, Cu, and As fall within the WHO (2017) recommended drinking standards while K, Fe and Cd concentrations were higher than the WHO recommended standard. Therefore, the water here should be treated before consumption or be discarded. The hydrogeochemical facies classification of stream and groundwater in the study area using Piper's (1953) diagram revealed Na-Cl and K-HCO_3 types. The dissolved constituents in the water originated from the weathering of rocks. Though the water here is suitable for irrigation, they are not safe for drinking and domestic purposes due to Fe, K and Cd contamination.

REFERENCES

[1] Adediran, S.A. and O.S. Adegoke: Evolution of the Sedimentary Basins of the Gulf of Guinea- Current Research in Africa Earth Sciences, Mathesis and Schandeimeier (Eds); Balkema, Rotterdam (1987) 283-286.

[2] Adegoke O. S.: The Eocene Stratigraphy of South-Western Nigeria Bulletin Bureau De Research Geologic Et Miners Memoirs 69 (1969) 23-48.

[3] Adegoke O. S.: Microfauna of the Ewekoro Formation Paleocene of S.W. Nigeria. Africa Geology Ibadan, (1970) 265-276.

[4] Ademoroti, C: Standard Methods for Water and Effluent Analysis.1st Edition, (1996) 32- 36

[5] Akinmosun A., Odewande A.A., and Akintola A.I: Geochemical Composition and Textural Features of Some Carbonate Rocks in Parts of South Western Nigeria. Ife Journal of Science. 7(1) (2005) 101-111.

[6] Bilman, H.G: Offshore Stratigraphy and Paleontology of the Dahomey (Benin) Embayment, West Africa. NAPE Bull. 7(2) (1992) 121-130.

[7] Davis S.N And De Weist R.J.M: Hydrogeology. New York: John Wiley and Sons. (1966) 464.

[8] Dunham, R.J: Classification of Carbonate Rocks According to Depositional Texture. In: Classification of Carbonate Rocks (Ed. Ham, W.E.). Memoir 1, American Association of Petroleum Geologists, Tulsa, OK; (1962) 108–121.

[9] Edema A. And Owonipa O.D: Geochemical Evaluation of Arimogija-Okeluse Limestones, Eastern Dahomey Basin, Southwestern Nigeria. International Letters of Natural Sciences 56 (2016) 57-64.

[10] Ehinola, O.A., Oluwajana, A. And Nwabueze, C.O.: Depositional Environment, Geophysical Mapping And Reserve Estimation of Limestone Deposit in Arimogija - Okeluse Area, Southwestern Nigeria Research Journal In Engineering and Applied Sciences. 1(1) (2012) 7-11.

[11] Elueze A.A And Nton M.E: Organic Geochemical Appraisal of Limestone and Shale in Part of Eastern Dahomey Basin, Southwestern Nigeria. Journal of Mining Geology Volume 13(1) (2004) 1-6.

[12] Gurugnanam, B., Suresh, M., Vinoth M., Prabhakaran N. and Kumaravel S.: GIS-Based Micro-Level Approach for Hydrogeochemical Studies in Upper Manimuktha Sub-Basin, Vellar, South India. Indian Journal of Science and Technology. 2(11) (2009) 6-13

[13] Obaje N.G: Geology and Mineral Resources of Nigeria. Springer Dordrecht Heidelberg London New York, (2009) 217.

[14] Nichols G.: Sedimentology and Stratigraphy. John Wiley and Sons, 2nd Ed, (2009) 411.

[15] Nwankwoala, H.O. and Udom, G.J.Hydrogeochemical Evaluation of Groundwater in Parts of Eastern Niger Delta, Nigeria. Journal of Academic and Applied Studies. 1(2) (2011) 33-58

[16] Odeyemi I.B, Oyinloye A.O, Asiwaju-Bello Y.A.B and Adegbuyi O: Geotechnical Appraisal of Limestone Deposits in Okeluse-Arimogija Areas of Ndo State: Implication of Industrial Use. Journal of Biological and Physical Science 1 (2000) 51- 60

[17] Ogunribido T.H.T: GEY 407- Hydrogeology. Unpublished Lecture Notes, (2017)

[18] Olade M.A.: Raw Materials for Cement Production after the Year 2000: Availability, Suitability and Accessibility. National Workshop on Cement and Allied Products. Abeokuta, Nigeria, (1988).

[19] Omatsola, M.E., And Adegoke, O.S: Tectonic Evolution and Cretaceous Stratigraphy of the Dahomey Basin. Journal of Mining Geology 18(1) (1981) 130-137.

[20] Piper, A.M: A Graphic Procedure in the Geochemical Interpretation of Water Analysis. United State Geological Survey (USGS) Groundwater Note 12 (1953) 506.

[21] Senthilkumar, M. and Elango L: Geochemical Processes Controlling the Groundwater Quality in Lower Palar River Basin, Southern India. Journal of Earth System Science. 122(2)(2013) 4 – 10

[22] Todd T.W Petrographic Classification of Carbonate Rocks. Journal of Sedimentary Petrology. 36 (2) (1966) 317-340

[23] Tucker E.M And Wright V.P: Carbonate Sedimentology, Blackwell Publishing Co. 7th Ed. (Reprinted In 2002) (1990) 386.

[24] Udom G.J and Accra E: Hydrogeochemical Characteristics of Groundwater in Andori Local Government Area, Rivers State. Journal for Research in Physical Sciences, 2(1) (2006) 35- 41.

[25] Vikas T., Kamra S.K., Kumar, S., Kumar, A. and Vishal, K: Hydrochemical Analysis and Evaluation of Groundwater Quality for Irrigation in Karnal District of Haryana State, India. International Journal of Environmental Sciences. 3(2) (2011)1 – 6.

[26] Wilcox L.V,): Classification and Use of Irrigation Waters. Unite D States Department of Agriculture. Circular 969. Washington D.C USA. (1955).

[27] World Health Organization: Guidelines for Drinking Water Quality. WHO Library Cataloguing-In-Publication Data. 5(2017) 518.