Evaluation of homogeneity from ore-bodied in nigeria for secondary mineral prospective

*A.I Inegbenebor *I.O. Aruwajoye and **A.O. Inegbenebor

College of Science and Technology, Covenant University, Canaan Land, Ota, Ogun-State

*Chemistry Department **Mechanical Engineering Department

Corresponding Author: *A.I. Inegbenebor*

Abstract

Samples from ore–bodied areas at different locations in Papalanto and Ifo in Ogun-State, South-West of Nigeria, where Ewekoro cement industry is situated, were analyzed so as to recover some secondary minerals of economic value. The following parameters were evaluated, conductivity, turbidity, colour, pH and other chemical parameters. Variations of Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), sulphate, nitrate, phosphate, chloride ion contents, and temperature were also studied. Mineral-forming heavy metals were in the ranges Fe: 89.0–1080 mg/l; Mg: 869–1120 mg/l; Pb: 23–80 mg/l; Zn: 180-480 mg/l. The concentration of nitrate is 20-35 mg/l; phosphate: 8-80mg/l; Dissolved Oxygen (DO): 30–45 mg/l; Total Dissolved Solids (TDS): 89-900 mg/l; pH: 6.1-8.5; Conductivity: 10-18μs/cm^3 and temperature ranged between 25-27^{o}C. Also in the tabulation are the results of the homogeneity of four geochemical explorations from other Nigerian ore-bodied environments for comparison. Correlations of some of the physical and chemical parameters have been established with the view of providing conditions for the formation of secondary minerals and the types of such minerals expected from the studied areas. The minerals may include the following groups of minerals: Adelite, Melilite, Cancrinite and Copriapite. The study apart from the present knowledge on ore-based baseline also present information on the pollution studies of the area under investigation.

Key words*: Secondary Minerals, Homogeneity. Oxide-zone and Ore*

1. Introduction

The study of minerals has led to rapid development of material technology which is a key enabling area for economic and social well being. Materials with new and improved properties, and innovative methods if processing them, give industries competitive advantage in world markets. The products lead to better medical care, enhanced safety in infrastructural projects, improved and safer transport, sporting and leisure facilities and more environmentally friendly operation. These materials are from secondary minerals. Emphasis is therefore placed on secondary minerals of economic importance in this work since mostly all of the chemical reactions that take place in oxidizing sulfide beds ores involve homogeneous or heterogeneous systems. When compounds crystallized from aqueous solutions, redox processes that occur between various dissolved species, and dissolved gases especially oxygen and carbon dioxide, play central roles in the formation of many secondary minerals in most cases.

Although, the general mode of mineral formation in the oxide zone may involve dehydration of previously crystalline oxide, or oxide derivative, other compounds formation can also occur in the process. This phenomenon has been expressed (Williams 1992) in the way Jerosite $PbFe_3(SO_4)_2(OH)_6$, and Cerrusite $Pb_3(CO_3)_2(OH)_2$ are formed from aqueous solutions, as shown in the equations below for example.

$$Pb^{2+}{}_{(aq)} + \tfrac{2}{3}CO_{2\,(g)} + \tfrac{4}{3}H_2O_{\,(l)} \rightleftharpoons \tfrac{1}{3}Pb_3(CO_3)_2(OH)_{2\,(S)} + 2H^+{}_{(aq)}$$

Hydrocerussite

$$MFe_3(SO_4)_2(OH)_{6\,(S)} + 6H^+{}_{(aq)} \rightleftharpoons M^+{}_{(aq)} + 3Fe^{3+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

Jerosite

Here, M can be H_3O, Na^+, K^+, Ag^+, NH_4^+, and 0.5 Pb^{2+}.

Ogun-State is an agrarian state, where fertilizers are frequently in use to boost the agricultural products. As a result of these activities, there is increase in acidity as well as that of level of other elements when ores are leached, some of which are toxic.

For these reasons, it is thought to examine some of the aspects of homogeneity and invariably prospective for ores so as to recover secondary minerals of economic importance. The result obtained would provide parameters of embodies baseline, especially those of heavy metals in waters of the study areas. The aim was to study the metallogenesis and other parameters in homogeneity of South Western Nigeria ore bodied environment in order to prospect for secondary minerals for industrial use.

2. Material and instrumentation

Sample Collection

To avoid inhomogeneous distribution during sample collection, spot collection was selected at Ewekoro because it is an active site for cement production, while at Papalanto and Ifo stations base-line collection was carried out. However, at Ifo samples were collected in a type of graduation. Units of oxide zone grade rock types are intercalated or mixed. Such relations indicate, that genetic conditions oscillated between extremes as they changed or possibly that materials were mixed grossly. Papalanto samples were collected by locating midpoint of particular bedrock. Notwithstanding, a unit was chosen which crop out where other components of the gradational zone are not. The top of the uppermost bed above flow is 10 ft. Samples were collected at Ewekoro, Papalanto and Ifo at close intervals along banks of the active channels.

The concept of the density flow [Wilson 1971] was applied in the collection of the sample. Here, two fluid bodied of different density were mixed together, the dense fluid tend to move above the denser one. Conversely, the denser fluids tend to flow downwards. Aqueous density flows were as a result of differences of temperature, salinity, and suspended sediment. Turbid bodies of water with large loads of suspended sediment frequently move as density flows beneath clear water.

Ten samples were collected in many series from each of the locations. Some were used for tests. Before sampling began, the homogeneity within several sections of units was tested. This is done by collecting channels chip and stratified samples of typical sections and comparing analysis made from them. Some of the homogeneous samples change appreciably when exposed for some time on the surface. The samples were put in dust-proof bag that was labeled clearly. These samples were registered in a sample book that was numbered in duplicate with sample numbers. The question then arose here whether the results of test samples were in close range. The interpretation of such was pertinent because change were compared especially at different temperatures.

The pH of the samples was determined on site by the use of an electrode pH meter (see Table 1). The temperature (^oC) of all the samples was measured in situ by the use of a graduated thermometer. Standard conductivity meter (us/cm) was used to determine the conductivity of the homogeneity while PCU was employed in detecting the colour of the water samples. Titration method was carried out for determination of alkalinity with measured volume of sample with H_2SO_4. Turbidity was measured using the graduated turbidity meter (NTU) by use of a standard solution (blank). The corresponding values of the instrument after sample was placed give the actual turbidity of the homogeneity. Elemental analyses were carried out by the use of atomic absorption spectrophotometric procedure (Thermo Corporation Model) for the determination of metals. The instrument was set at appropriate wavelength current, flame type and then calibrated by the use of standard solutions for each metal. Nitrates, sulphates and phosphates were also determined. The nitrate contents of the sample were analyzed by Brucine method. The other types of equipment used and manufacturers are recorded in Table 1.

3. RESULTS AND DISCUSSION

The amounts of the contents of major and minor elements in homogenous solution of selected geochemical environment from Ogun-State, Nigeria are listed in Tables 2 and 3, columns 1-3. The results of recent relative works carried out from other states in Nigeria, that is, Enugu, Delta, Sokoto and Abuja (columns 4-7) on the tables are included for comparison because of the climatic difference within the country.

Table 1: Equipment

EQUIPMENT	MANUFACTURERS	MODEL
TDS	Hanna microprocessor	conductivity/TDS meter HI 9835
Conductivity	Hanna microprocessor	conductivity/TDS meter HI 9835
Salinty	Hanna microprocessor	conductivity/TDS meter HI 9835
Turbidity	Hanna	fast tracker(HI 98703)
Total hardness	Hanna	Multiparameter Bench Photometer (c 99)
Colour	Hanna	Multiparameter Bench Photometer (c 99) PUC
Dissolved oxygen	Hanna	Multiparameter Bench Photometer (c 99)
COD	Hanna	Multiparameter Bench Photometer (c 99)
Acidity		Done By Titration
pH	Hanna	pH 211 microprocessor pH meter
Temperature	Hanna	Thermometer
BOD		P Selecta Incubator (Medi Low)
AAS		Thermo Corporation S series AA Spectrometer
UV	For single beam	Thermo Corporation Genesys 10 UV scanning
UV	For single beam	Thermo Scientific HELLOS ZETA UV-VIS

Table 2: Selected Physico-Chemical Properties of Ore-bodied homogeneity from some states in Nigeria

CONSTITUENTS	CONTENT IN mg/l							
	1	2	3	4	5	6	7	8
SALINITY	NA	NA	NA	NR	35	NR	NR	1
TURBIDITY	350	150	180	10	20	0.2	1.34	<500
BIOLOGICAL OXYGEN DEMAND (BOD)	50	25	30	6	3.01	NR	5.8	
CARBON OXYGEN DEMAND(COD)	500	670	650	30	821	NR	NR	
TOTAL DISOLVED SOLID(TDS)	350	900	89	NR	20	46	491	500
TOTAL HARDNESS	20	50	95	NR	NR	4.5	0.08	250
COLOUR				NR	NR	70	NR	colourless
TEMPERATURE	26	25	27	NR	26	43	26	25-26
CONDUCTIVITY				NR	0.47	NR	17.3	1000µs/m
DISSOLVED OXYGEN(DO)	35	40	45	NR	74.5	NR	NR	

Table 3: Analysis of percolating homogeneity from Ore-zones of some states in Nigeria

CONSTITUENTS	CONTENT IN mg/l							
	1	2	3	4	5	6	7	8
pH	8.5	6.1	6.5	7.5	7.8	7.8	6.43	<8.0
Cl^-	20	15	28	0.1	12	15.9	0.9	200
NO_3^-	35	20	15	40	0.18	NR	NR	10
PO_4^{3-}	8.5	45	80	3.5	0.3	NR	NR	5
SO_4^{2-}	5.5	30	18	500	481	2.1	NR	250
NH_4^+	1.5	2	1.5	2	0.2	NR	NR	
CO_3^{2-}	35	32	29	NR	24	NR	NR	100
Na	7.5	890	185	NR	1359	4.2	NR	
Ca	1120	960	950	NR	326	NR	NR	
Mg	890	1080	500	NR	51	493	NR	20
Fe	80	45	23	NR	1.51	20	NR	3.0
Pb	9.5	250	ND	NR	0.01	NR	NR	0.01
Zn	181	480	380	NR	NR	1281	NR	3.0
K	1550	120	850	NR	106	1.9	NR	

(1) Ewekoro; (2) Papalanto; (3) Ifo; (4) Enugu, (Obuzor and Nduka 2010); (5) Delta, (Umudi and Awatefe 2010); (6) Sokoto, (Uba, Gwandy, Izuwagie and Sadiq 2010); (7) Abuja, (Aremu, Ozonyia and Ikokoh 2010) (8) WHO (2004, 2007) NA=Not Analyzed; NR=Not Recorded.

The results in the tables showed varying values for both physical and chemical constituents. Noticeable from the results in Table 1, is the relatively acidic pH of 6.1 and 6.5, conductivity of 18 and 13.5 at Papalanto and Ifo environments. The amount of dissociation of water depends on pH which invariably can lead to chemical reactions of waters and its dissolved solutes as well as the physical break down of the bedrock. The principal types of chemical reactions in such oxide zone in acidic medium are hydration (i.e. absorption of water), hydrolysis (chemical reaction to produce or consume H^+ or OH^- ions), oxidation and simple solution (Bartholomew et al. 1973, Garrels and Christ 1965). It is worth pointing out that pH of 8.5 (column 1) at Ewekoro may be a result of dissociation of carbonate equilibrium involving calcium carbonate or dimorph aragonite. With a high value of Pb, Mg and Fe of 80, 1120, and 890mg/l respectively at Ewekoro, it would not be surprising if secondary carbonate minerals are widely spread in this area, especially mineral containing more common base-metals such as lead, magnesium and iron which are frequently found in the oxidize zone of sulphide ore-bodies. Such may include the minerals with general formula $AB(XO_4)(OH)$; A=Ca, Pb; B=Fe^{2+}, Mg, X=P^{5+}; As^{5+},V^{5+} that is the Adelite group for example, also the Melilite, A_2BSiO_7; A=Na, Ca, B=Mg, Z=Al, Si, the Cancrinite group, A_{6-9}(Si, $Al)_{12}O_{24}(SO_4),(CO_3)$, $C_{l2}(OH)_{2-4}.nH_{2O}$, A=Ca, K, Na and the Copiapite group $A^{2+}Fe_4^{3+}(SO_4)_6(OH)_2$ $.2H_2O$ A=Ca, Fe, Mg, Zn; B^{3+}= Fe, Al. This type of observations and conclusions does not invalidate the general conditions of formation of the group of minerals based on equilibrium of the M_nO_2–SO_3–H_2O system for example in aqueous solutions, while bearing reactants and transporting products and reactants, as well as furnishing in water necessary reagent in many cases, control chemical speciation, solute components and thus the solubility of secondary mineral species.

The value of COD at Ewekoro is 500, Papalanto 670 and Ifo, 600 are high when compared with TDS of 850 at Ewekoro and 900 for Papalanto. These constituents can be affected by additional CO_2 which are introduced into the homogenous from the atmosphere via rainfall, leaching from soil and bedrock, running from agricultural land, the stream and uncultivated lands. This is however a reflection of high solubility of the bulk solutes in water and the relative geochemical abundance. It is not surprising the presences of high dissolved oxygen, carbon dioxide and humic complexes as have earlier been reported (Bartholomew et al. 1973) to greatly increase the corroding power on solids in solutions.

Similar arguments can be made to explain the high amounts of total dissolve solid (TDS), 46ppm at Sokoto while temperature is 43^{o}C. Under arid conditions chemical weathering is minimal and physical processes are dominant. For example, temperature influences the rate of chemical reaction and affects the availability of water by increasing evaporation at high temperature. However, some elements such as Si of detrimental quartz grains characteristically can occur as component of insoluble secondary minerals during chemical reaction.

There are high amounts of Na, 1359mg/l and SO_4^{2-}; 481 mg/l for example at Delta, the values of other parameters in this area are minimum compare with the zone analyzed in this present work. It should be therefore possible to explain the pollution of waters in this location and of course the formation of secondary minerals. Where major constituents are present in high amount, pollution is minimal, because the major constituents affect the dispersal of minor elements (see Table 2) in solution primarily by providing reactants, either for the precipitation of insoluble secondary minerals or for the formation of soluble complex in ions with minor elements (Wilson 1972).

Nevertheless, as rivers at the ore-bodied environ provide water for drinking, fishing and other purposes for the communities living around them, there is need to monitor periodically these parameters because of possibility of their accumulation especially the heavy metals often mineral forming.

4. CONCLUSION

Since the above explanation is consistence with the observation, therefore as a result of these studies, it is possible to delimit quickly and more or less precisely, the area of interest where to concentrate detailed exploration. The economic value of the suspected groups of minerals would be enormous, when they may be prospective for materials in industrial use, most especially in the areas of microprocessors, memories, superconductors and other systems. The study apart from the present knowledge on ore-based baseline also present information on the pollution studies of the area under investigation where WHO values are comparable. More intensive work is in progress in conjunction with the geological, geophysical and geochemical surveyors of the study location.

Acknowledgement

The authors acknowledge the contribution of T. Owoeye, Technologist, Chemistry Department, Covenant University.

References

Aremu, M.O., Ozonyia, G.N. and Ikokoh, P.P. (2010), Chemical Society of Nigeria, Proceeding of the 33rd Annual Conference, pages 24-27.

Bartholomew, P., Evrard, P., Katekesha, F., Lopez-Ruiz, J. and Ngogo, M. (1973), Viagenetic ore-forming processes at Komoto, Katanga, Republic of Congo. In “Ores in sediments (Amstutz G.C. and A.J. Bernard, A.J. Eds.) Springer-Verlag, Heidelberg pages 21-41.

Garrels, R.M. and Christ, L.C. (1965), Solutions, Minerals and Equilibria, pages 371-372.

Obuzor, G. U. and Nduka, J. O. (2010), Chemical Society of Nigeria, Proceeding of the 33rd Annual Conference, pages 9-12.

Uba, A. and Gwandy, A.A., Izuagie, T. and Sadiq, I.S., (2010) Chemical Society of Nigeria, Proceeding of the 33rd Annual Conference, pages 67-68.

Umudi, E.Q. and Awatefe, K. J., (2010), Chemical Society of Nigeria, Proceeding of the 33rd Annual Conference, pages 60-63.

Williams, P.A. (1992), Oxide-zone Geochemistry, Ellis Harwood Inorganic Chemistry.

Wilson, I.J. (1972), Relian bed forms, their development and origins Sedimentry, Vol.19, pages 173-210.

Wilson, I.G. (1971). Desert sand flow basins and a model for the development of Ergs., Geogrl. J. 137, pages180-199.

World Health Organization (2004), Guide lines for for Drinking Water Quality, International Standard, 3rd Edition, Geneva, Vol. 1.

World Health Organization, (2007), Water for Pharmaceutical Use In: Quality Assurance of Pharmaceutical. A compendium of Guidelines and related Materials. 2nd Update Edn. World Health Organization Geneva, pages 170-187.

Prospero, J.M. and Carlson, T.N. (1972), Vertical and areal distribution of Saharan dust over the Western Equatorial North Atlantic Ocean, J. geophys. Res. 77, pages 5255-5265.