Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2016, 3(3):477-481**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Effects of Trace Elements in Nigeria Crude Oil

Kenneth K Dagde, Saviour A James

Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology Port Harcourt, Nigeria

Abstract Some metals in trace quantities have deleterious effects on certain processes in petroleum industry. It therefore, becomes very imperative to determine the concentration of these metals prior to refinery operations. This is particularly necessary for Nigeria crude where well-head crude analysis is scanty. In this research, five different well-head petroleum crude were quantitatively analyzed for nine metallic elements using frame atomic absorption spectroscopic method. Unicam Atormic Absorption spectrometer 939 (for vanadium) and Instrumentation laboratories Spectrometer 451 were used. These results were compared. All the crude studied showed higher vanadium concentration than nickel Yorla, Brass blend and gulf/shell crude have the highest vanadium/nickel ratio, while Bonny L2 and Bonny L1 have the least vanadium/Nickel ratio..

Keywords Oil spillage, gas flaring, metals concentration, photometric analysis, environmental pollution, atomic absorption spectrometer and crude oil exploration.

Introduction

Trace elements on crude oil are the linked between its formation from basin and its refinement into final products. These metal present in crude oil are known to be harmful in that they can be dangerous to the environment and also increase production costs. Crude oil consist mainly carbon and hydrogen. Moreover, some metallic elements/compounds present in traces, these trace metals present in Nigeria crude oil are Zinc, Vanadium, Nickel, Tin, Lead, Copper, Iron, Uranium, Strontium, Chromium, Barium, Gold, Cobalt, Magnesium Molybdenum, Neodymium, Beryllium Manganese, Aluminum Lanthanum, Cerium, Calcium, Arsenic, Potassium, Sodium, Titanium, Zirconium and Gallium [1]. The absence of sulphur among the elements present make Nigeria crude oil "sweetened "and of highest demand in the world market. However, Jones [2] in his own analysis of crude oil proved that apart from these common and bulk elements listed above, iron, nickel, aluminum, calcium, magnesium and vanadium existed in appreciable amount but then vanadium and nickel are the only metallic elements present significantly above one part per million (ppm) level [3-4]. These metals present in crude oil readily form oxides and as a result can cause environmental pollution andcorrosion of industrial equipment [5-6]. Crude oil and its product are ubiquitous, their recovering, processing, drilling, transportation and production are all fraught with hazard to human health and the earth's ecology. Occupational exposure to metals (direct or indirect content) contain in Nigeria crude oil should be restricted to 'safe' levels, defined as the threshold limit value for exposure for eight hours per day [7-9]. These levels are intended to provide a margin in safety between maximum exposure and minimum level that will produce illness. One major way in which these metals in Nigeria crude oil came in contact with environment is via oil spillage.

In Nigeria, quite substantial amount of crude oil is spilled annually. Nwankwo [10] reported 2,000 oil spillages in Nigeria between 1976 and 1988. According to Deyong [11], during this period about 2 x 10^6 barrels of crude oil were discharged to the environment. Between the year 2000 and 2014, more than 5,000 cases of oil spillage have been reported in the Niger-Delta region of the country where oil exploration is carried out intensely, resulting in a loss of 355.69 metric tons of petroleum products [12]. Crude oil spillage on soil makes it unsatisfactory for plant growth. This is due to insufficient aeration of the soil because of displacement of air from the spaces between the soil particles by crude oil [4]. The Shell Petroleum Development Company (SPDC), Port Harcourt which has the largest, operation in the Niger Delta recorded more than 200 barrels of

crude oil spillage within their operational zone. Equipment failure, corrosion, sabotage and drilling operations have recorded the highest sources of crude oil spill [13-14].

Another most important source of direct contact with the metals is gas flaring. The flaring of crude oil gases has become the bane of Nigeria government for the past 20 years with no immediate solution to curtail the menace [13]. Amidst the failed legislation to stop the flaring by the companies operating in the Niger Delta region, the flaring goes on unabated thereby exposing the people in that region to untold risk. They inhaled the poisoned air, drank the acid rain and felt completely the effect of global warming as a result of the gas flaring with no remedy.

This research ascertains the effects of metals present in Nigeria crude oil on the environment and the refinery operations, with emphasis on the environment because of the various effects of metals on the environment. The environment was divided into two parts, bio-geophysical and human part. The crude oil samples were collected from Bonny light crude, Yorla flow station in Ogoni Kingdom, Brass blend and Ughelli Quality Control Center (UQCC); Atomic Absorption spectrometer method was adopted for the analysis, which has advantage of detecting almost every metallic elements present in the crude oil samples including the concentrations of Nickel, Aluminum, Copper, Manganese, Magnesium Vanadium, Iron, Barium and Zinc.

Materials and methods

Materials

The materials used in this research were crude oil samples from five different well-heads in the Niger Delta region of Nigeria. They includes sample A = Yorla, Sample B = Bonny Light 1, Sample C = Gulf/She from Ughelli, Sample D = Brass blend and E = Bonny light 2.

The following apparatuses were used during the experiment.

1) Evaporating dish or Crucible made of Platinum, Porcelain or Silica of 90 to 120 ml capacity.

2) Electric muffle furnace – capable of maintaining a temperature of 550 $\pm$ 10^{o}C.

3) Atomic Absorption Spectrometer: A suitable instrument would comprise: hallow cathode lamps or other sources of resonance radiation of metals, nickel, aluminium, copper, manganese, magnesium, vanadium, iron, barium, and zinc. The instruments should be capable of measuring absorbance of up to 570nm and equipped with provision of the aspiration of organic liquid into the flame, a mono-chromator, for selecting the desired spectral line and a light detector and measuring system capable of scale expansion. Secondary air supply was used to enable air supply to the flame increased without increasing sample uptake rate. The read out system was digital controlled for various concentration values to be read. The instrument was suitable for use with organic solvents, even as it was recommended that only water was left in the drain tube overnight.

4) Volumetric flask
5) Wash bottle
6) Funnels and filter Papers
7) Beaker of capacity up to 600 ml
8) Crucible tongs made with platinum tips
9) Desiccators
10) Thermometer
11) Stands
12) Reagents

Reagents

i) Hydrochloric Acid – Weight per ml about 1.19g
ii) Trioxonitrate (v) acid – concentrated weight per ml. 1.42g
iii) Water-distilled water (not ionized) was used throughout.

Methods

Determination of trace metals in crude oil: Crude Oil sample contained in the crucible was ignited and allowed to burn until only ash and carbon remains. The carbonaceous residue was reduced to ash by heating in a muffle furnace at a temperature of 500 – 550^{o}C. The ash obtained was dissolved in Hydrochloric acid, HCl, oxidized in Trioxonitrate(V) acid (HNO_3), and then filtered. The filtered solution was then aspirated into the flame of an atomic absorption spectrometer, and the absorption of the visible or ultra-violet resonance radiation of the particular element being analyzed was measured. Depending on which metal was analyzed, the particular flame was applied. Calibration was done by spectrometric equipment with standard set of numbers according to the manufacturer's instruction.

Procedure

1. 50 grams of crude Oil sample was weighed and placed in a platinum crucible.
2. The evaporating dish or crucible was placed on plate and heated strongly over a gas burner for up to 20 minutes or more until the contents could be ignited with flame. A temperature range was maintained such that the sample continuously burned at a uniform and moderate rate leaving only ash and carbon white.

3. The crucible which contains the residue was transferred using a platinum tipped crucible tong into the flour of the electric furnace at a temperature of 550 ± 25°C. During the initial injection, the muffle furnace door was opened slightly and the opening was adjusted carefully so that air flow into the muffle was not excessive. The door was closed and ignition continued until no carbon was visible.
4. The crucible was removed from the furnace while taking care that no ash was lost when opening the muffle door and removing the crucible from the furnace, as the ash was usually light and fluffy. Also proper care was taken in order to avoid contamination of the sample from the particles of the furnace roof, wall and door.
5. The dish was cooled to room temperature in desiccators that did not contain any form of desiccating agent.

Photometric Analysis

1. The ash was treated with 0.5 ml of HCl. and digested on a water bath or hot plate to effect solution and then evaporated to dryness 5ml of a 1:1 ratio of HCl and water was further added to the ash content and heated on a water bath for five minutes.
2. After heating, it was then filtered using a glass filter into a volumetric flask and the crucible was washed with water from a fine yet until filtrate and washing together made up 100ml. the flask and its contents, was then cooled.
   N/B: The procedure above, 2:5:1 to 2:6:2 was carried out for the five different crude oil samples and each sample was ashed and made up to solution of 100ml each were aspirated into the flame for the analysis of the different metals.
3. The sample solution obtained was aspirated and it absorbance determined.

The procedure in 2.2.1 and 2.2.2 was repeated for determination of the various trace elements with little modification based on the different elements. For nickel, an air/acetylene flame, nickel hollow cathode lamp and an analytical line of 232.0nm was applied for the determination of nickel. For Aluminum, a nitrous oxide flame, aluminium hollow cathode lamp and an analytical line of 309.3nm was used for the determination of aluminium concentration in the crude oil. For Copper, a hallow lamp, an air/acetylenes flame and an analytical line of 324.7nm was used to determine its concentration. For Manganese, a manganese hollow lamp, an analytical line of 279.5nm and an air/acetylene flame was used. For Magnesium, a magnesium hollow lamp, an analytical line of 285.2nm and an air/acetylene flame was used. For Vanadium, the solution was aspirated into the flame and the absorbance of vanadium was determined. A vanadium hollow cathode lamp was used with a nitrous oxide flame and an analytical line of 315.5nm. For Iron, an air/acetylene flame, an air iron hollow lamp, and an analytical line of 248.3nm was used. For Barium, a barium hollow lamp, a nitrous oxide flame and an analytical line of 553.5nm was used. For Zinc, a zinc hollow lamp, an air/acetylene flame and an analytical line of 213.9nm was used. The concentrations were calculated as discussed in 2.2.3.

Calculations

The concentration of metals (ppm) was measured, read from the digital readout device and then recorded. This was designated as C, which is the concentration of the metal in diluted solution.

The metal content of the oil in micrograms per gram was calculated for as:

$$Metal\ \left(^{\mu g}/_{g}\right) = \frac{VC}{W} \quad (1)$$

where W is the weight of sample (g),V is the volume of solution that contains the above weight of oil (ml), and C is the Concentration of the metal in instrument (ppm)

Results and Discussion

Results

Table 1 shows the model prediction of the concentration of metals present in 100ml of crude oil in the five samples as calculated using equation (1).

Relative Abundance of Elements

From Table 1, it was obvious that Bonny L_2 has the highest metal content (30.2096), followed by Bonny L_1 (18.4011), Yorla (15.6766), Gulf/Shell (8.9892) and Brass blend (6.5911) respectively (All values are in ppm). Ni ranges between 0.072 – 1.852, averaging 0.962, V, 3.880- 23.1600, averaging 13.52; Fe 1.750 – 2.432, averaging 2.091; Zn, 0.112 – 1.998, averaging 1.055; Mg 0.052 – 0.634, averaging 0.343; Cu 0.002 = 0.172, averaging 0.087. However, the concentration of Al, Mn and Ba, were negligible.

From the results, large proportion of these metals consist of vanadium V , and Iron, (Fe), little being made up of Ni, Zn, and Mg, the least being Al, Mn and Ba, which were actually negligible.

Table 1: Concentration of Metals in the Sample (ppm)

S/No	**Elements**	**Yorla**	**Bonny L_1**	**Gulf/Shell**	**Brass Bland**	**Bonny L_2**
1	Ni	0.1638	1.8220	0.1504	0.0720	1;8520
2	Al	0.0002	0.006	0.0004	0.0003	0.0002
3	Cu	0.0520	0.0020	0.1500	0.1320	0.1720
4	Mn	0.0002	0.0002	0.0002	0.0002	0.0002
5	Mg	0.0520	0.3300	0.6340	0.6440	0.5940
6	V	13.2600	14.0200	6.0200	3.8800	23.1600
7	Fe	1.9520	2.0020	1.8720	1.7500	2.4320
8	Ba	0.0004	0.0003	0.0002	0.0006	0.0002
9	Zn	0.1960	0.2240	0.1620	0.1120	1.9980
Total	Metal Content	15.6766	18.4011	8.9892	6.5911	30.2096
	V/Ni Ratio	80.95	7.69	40.03	53.89	12.51

Vanadium and Nickel Concentration

Vanadium/Nickel ratio and rock type: The sequence V > Ni was completely consistent with all the crude oils. The ratio had been suggested to increase with the age of the reservoir rock. Consequently, considering he V/Ni ratio from this research, it was suggested that the rock type from which the oil were derived was fairly similar for sample having close V/Ni ratios and different for sample with either relatively low or high value of this ratio. For example, the rock of Bonny L_1 and Bonny L_2 appear to be formed at almost the same geological age (V/Ni = 7.69 and 12.51 respectively). Similarly, the type of Brass blend would appear closer to Gulf/Shell (V/Ni ratio of 53.89 and 40.03 respectively) than Yorla with a V/Ni ratio of 80.95. This followed the fact that the amount of metals in oil depends on the soil and rocks of the earth's crust associated with it and differences may be due to different rock types [15-16].

Vanadium and Corrosion

The Vanadium content of the oils in Table 1 suggested that there would be vanadium corrosion of the turbine in all the wells from where this oil were obtained as the levels for vanadium was high[2].

Bonny L_2 well-head crude would be most notorious in-terms of boiler corrosion (23.16) followed by Bonny L_1 (14.02), Yorla (13.26), Gulf/Shell (6.02) and Brass blend (3.88) respectively.

Catalyst Poisoning

From the results, the most dangerous elements were Cu, Zn, Ni and V. They poison catalyst with attendant reduced gasoline yield. Catalytic cracking operation suffers rather severe defects due to catalysts deactivation, mainly attributed to traces of these metallic poisons introduced into the units with the feed-stocks [15]. The loss is capable of running into millions of dollars a year. In terms of catalysts poisoning/deactivation, Bonny L_2 and Bonny L_1 well-heads crude would be expected to be most notorious, followed by Yorla, Gulf/Shell, and Brass blend.

Iron

Iron as the second most abundant element, averaging 2.09 ppm. It could be inferred that there was corrosion in the production system in the wells where the oils were derived. Naphthenic acids in oils are known to attack iron materials [14]. Corrosion might be considered high in Bonny L2 (2.43 ppm) followed by Bonny L1 (2.00 ppm), Yorla (1.95 ppm), Gulf/Shell (1.87 ppm) and Brass blend (1.75 ppm) respectively.

Conclusion

Nigeria crude contains about twenty-eight metals, with sulphur negligible (sweetened crude), the presence of nine has been established in this research, their adverse effect to both environment and refining process equipment has been determined. The spillage of these crude and flaring of their gases not only polluted the environment but caused great hazard to human life, aquatic life and the eco-system at large. Because of the corrosive effect of metals on crackers and reformers, and the large expenses involved in replacing or regenerating poisoned catalysts, as well as the metals being environmentally unacceptable, it is important that the refineries analyzes and remove these metals in crude oils, charge stocks, and residual fuels so that adequate precautions might be taken. The implication of data obtained on rock type, corrosion of materials of construction and poisoning were highlighted, where Ni, V, Cu, Mg, Fe, Zn and the V/Ni ratio were quantified. The research is recommended for both Environmental pollution control and refinery operations efficiency and profit maximization. In order to monitor the effectiveness of clean up after spillage a base line data of heavy

metal can be put in place in order to ascertain the quality of the clean-up exercise carried out and the refining industries should further identify other metals responsible for the poisoning of catalyst.

References

[1]. Reeves, A. L., Robert L. and Vauk, G. F. (1986) *Handbook on the toxicity of metals*, Vol. 2, 2nd Edition. Elsevier Scientific Publication, Amsterdam, pp. 84 – 94.

[2]. Jones, P. (1975) *Traces metals and other element in crude oil*, 2nd Edition, Sunbuy, London, pp. 1 – 40.

[3]. Alfrey, A. C. J. M Mishell, J. Birks, S. R. Rudolph, I. T. Lewis and Holmes, J. H. (1972) Syndrome of dyspraz and Multi-focal Seizures associated with chronic hem dialysis, *Trans-American society Artiff Interim Organization*,(**1**): 257 – 261

[4]. Rowell, M. J. (1977), "Effect of Crude oil spills on soils: A review of literature. In: Toogood, J. A. Ed. The Reclamation of Agricultural Soil after oil Spills Part 1: *Research, Alberta Institute of Penology, Canada*, 1 – 33.

[5]. Pinta, M. (1968)*The inorganic analysis of petroleum*, 2nd Edition, Macmillan, New York,pp. 10 – 40.

[6]. Aniefiok, E. Ite, Udo J. Ibok, Margaret, U. Ite; and Sunday W. Peters (2013); Petroleum exploration and production: Past and Present Environmental Issues in Nigeria; Niger Delta, *American Journal of Environmental Protection***1(4)**: 78 – 90.

[7]. Werning, R. and Kirsch, V. (1988) *Toxicity of inorganic compound*, 4thEdition,Mercel Dekker, New York, pp. 748 – 758.

[8]. Browning, E. (1969) *Toxicity of Industrial Metals*, 2nd edition, Butterwork Publ. New York, pp. 40 – 58.

[9]. Khuhawar, M. Y.; Aslam Mirza M. and Jahangir, T. M. (2012), "Determination of Metal ions in crude oils, crude oil emulsion, composition stability and characterization." Prof. Manar El-sayed Abdul Raouf (ed.) ISB. 978-953-51-0220-5.

[10]. Nwanwo, J. N. (1989) Critical analysis incidents in Nigerian Petroleum Industry. *Publication of Nigerian National Petroleum Corporation (NNPC)*, 12.

[11]. Deyong, E. (1980) "The Effect of a crude oil Spill on Cereals"*Environmental Pollution Series*, **22(3)**: 187-196.

[12]. Okereke, R. (2015), "The reality of Nigeria's dwindling crude oil Fortunes". *The Nigerian Guardian Newspapers*, September, 18, 2015.

[13]. Ite, A. E. and Ibok, U. J. (2013) "Gas Flaring and Venting Associated with Petroleum Exploration and Production in the Nigeria's Niger Delta", *American Journal of Environment Protection* 1 (4): 70 – 77.

[14]. Nwadinigwe, C. A. and Nwaorgu, O. N. (1999); "Metal contamination in some Nigeria well-head crude: Comparative Analysis" *Journal of Chemical Society of Nigeria*, **24**: 118-121.

[15]. Sainbayar J., A. Estetjan, T. Tugsuu, G. Sukhdorj and G. Monkhoobor, (2009); "Vanadium and Nickel in oil Tamsagbulag by Spectroscopy". *Proceeding of the Mongolian Academy of Science*, **2**: 37 – 45.

[16]. Gojik, P. F., Kraushkin, V. A., Klochko, . P., Guseva, E. E. and Morozova, R. M. (2007), "Vanadium and Nickel in Natural oil Asia, Africa, the Europe, Northern and South America, Ukraine *National Academy***6 (3)** : 137-141.