132/158

Proceedings of the 28th Annual International Conference, Maiduguri, Nigeria
Copyright © 2005 Chemical Society of Nigeria
Printed in Nigeria. All rights of reproduction in any form reserved

CHEMICAL SOCIETY OF NIGERIA

Environmental Effect of Petroleum Products on Discharge in Environments at Maiduguri and Port Harcourt Depot of Nigeria

***A. I. INEGBENEBOR**
Department of Chemistry, University of Maiduguri, Maiduguri, Nigeria
artemis1806@yahoo.com

ABSTRACT

Naturally occurring waters at the Maiduguri depot and Port-Harcourt refinery in Nigeria have been collected to study the effect on discharge of petroleum product in the environments. The solutions were analysed for the elemental contents. The values have been used in computer programme, to calculate the distribution of the species. The results show Zn and Pb ratio of 4.1 in Maiduguri sample and average of 1.54 to 2.75 in Portharcourt. Chemical compounds and subsequently secondary minerals are possibly able to crystallize from the solution with the higher ratio.

Keywords:

Introduction

In petroleum depot/refinery the activities of loading and offloading lead to discharge of effluent into the environments. These effluents from refineries usually contains oils which may be separable, emulsified or dissolved chemical including acids, alkalis, sulphides, mercaptans, ammonia, phenols, suspended solids and wastes. The wastes may originate in process of cooling the equipments, leaks and spillages, condensate from stream stripping operations. Also wash water from crude oil desalting and products treating. The releases during shutdown or start up of equipments, drawn off from storage tanks, equipment cleaning water, cooling tower blowdown, water condition plant wastes and miscellaneous sources such as areas of equipment is washdown, pump gland cooling water fire filler and sanitary may result to wastes.

All these products consist primarily of hydrogen and carbon compounds, with variable amounts of nitrogen, oxygen, phosphorous, sulphur together with traces of elements such as vanadium and nickel [1].

Generally, hydrocarbons occur in solid, liquid and gaseous states. Solid hydrocarbons are variously known as asphalt, pitch and gilstonite. Liquid hydrocarbons are termed crude oils or simply 'crude'. Gaseous hydrocarbons are loosely referred to as natural gas ignoring inorganic natural gas such as those of volcanic origin [1_2] .

These makings of petroleum products may also cause aqueous pollution by spillages or other losses during transportation and by minor looses at bulk stations (depots) and individual retailers moving the products from the depots. The latter are even difficult to control because of their small size compared with the huge depot. As a result of their distributions they discharge the effluents into the municipal sewage systems as they moved around the town and are not easily observed.

It has already pointed out [2] that water table in discharge environments should be deep enough to permit waste burial to occur entirely in the unsaturated zone. The contents of groundwater may result in greater mobility of dissolved materials. The damages cause by excess of these elements and radicals are of significant concern. Petroleum refinery effluent can cause many serious hazards to human as well as land, water and atmosphere which might lead to other undesirable consequences.

In view of these the aim of this work was to access the effluents discharge in petroleum depot /refinery ground water in Nigeria in the environs for their suitabilities in the area of domestic and the industrial uses. Subsequently, the objective is know the effect of the effluents on the landfills materials, subsurface gas migration from sources and the interactions of various factors that may influence ore production.

Materials and Methods

Solution samples together with the sediments were obtained from Nigerian National Petroleum Cooperation (NNPC) depot Maiduguri and Port Harcourt refinery (PHR).

---

*Author for correspondence

Individual solution was freed mechanically from all contaminating materials. It has been pointed out [1] that aqueous solution from the same source may have different compositions.

Therefore samples were collected from upstream, downstream and land fills. Each of the flasks (100ml) containing the solution samples were equilibrated in a thermostated water bath at $25^0 \pm 0.1^0$, with the exclusion of any gaseous phase, over two weeks with occasional stirriring. These flasks were then opened in a CO_2-free atmosphere. The pH of the solutions were measured using an orion 407A pH meter and the aqueous phases filtered through pre_washed whatman GF/F fibre glass filter papers to remove all particles grealer than 0.7m µ in size.

The solutions were immediately analysed for Pb and Zn by AAS techniques using Varian AA6 spectrometer employing a carbon rod attachment after dissolution of any solid particles in Analar HCl (0.05mol dm^{-3}). The total elemental species on solution for each sample were calculated using computer programs comics. Due to the very low levels of solubility of the precipitants, it was not possible to determine $[CO_{2\,aq}]_{TOT}$ by an independent chemical method.

The method as described by AOAC (1991) [3] and Zhang (1994) [4] were employed. The phenol contents in the samples were determined by spectrophotometric methods at 510 nm. In this techniques [3_4] the sample solution, (100 ml) was poured in a conical flask. Methyl red (1 ml) was added followed by the addition of phosphoric acid (1 ml) to make the solution permanent red. Copper sulphate (1 ml) was added drop-wise with shaking. Distilled water, (10 m l) was also added to this mixture. The resulting solution was tightly covered and heated on a bunsen flame for 20 minutes in clamps and condensed.

The distillate was collected under the condenser into a measuring cylinder (100 ml). The distillated (90 ml) was then transferred into a sample bottle (100 ml), Ammonium chloride (3 ml), 4 amino antipyrine (2 ml) and potassium ferrocyanide (2 ml) were added to the solution. This was allowed to cool for 10 minutes. UV measurement was carried out using 10 mm cell. The concentration result was obtained by direct reading of the UV in parts per million.

The total hydrocarbons (THC) were also obtained by first monitoring and controlling the formation of surface films on the effluents. Pre-wash beaker with CCl_4 was dried in the oven at 100^0C for an hour. The beaker was cooled in a desiccator with desiccant for 1 hour. Analytical beaker (250 ml) was weighed. Carbon tetrachloride (40 ml) and HCl, (5 ml) were added to the sample (200 ml) in beaker. This mixture was shaken vigorously and allows to stand for 30 minutes. Separating funnel was used to separate the CCl_4 layer. The resulting solution was heated to dryness. The sample was allowed to cool in a desiccator and the final weight was recorded from the following calculation.

Total hydrocarbons = (Final wt – Initial wt) of effluent/Vol of the sample used.

The aliquot was dissolved in a mixture of 10 ml hydrochloric acid and 5 ml nitric acid to determine the level of iron in form of ferric. The resulting solution was diluted with 200 ml of water, Ammonium hydroxide (1:1) was added until the precipitate were dissolve, and the solution turned deep blue. After boiling for a few minutes, the solution was allowed to settle and filtered in a close textured paper, wash with dilute ammonium hydroxide (1:50) and hot water. The precipitate was filtered off, washed with dilute ammonium acetate (2%) and the resulting solution was boiled until hydrogen sulphide was expelled. A few drops of nitric acid was added to oxidize the iron, followed by 5 gm of ammonium chloride and the solution again heated to boiling. Dilute ammonium hydroxide (1:1) was added until the solution was ammoniacal, and the precipitate formed is filtered. This filterate was analysed for the iron content.

The aliquot (200 cm^3) was withdrawn by a pipette for the analysis of phosphate by the following method. Nitric acid (10 cm^3) and 1 gm of ammonium nitrate were added to the aliquot. The solution was heated to 50^0c and 50 cm^3 of ammonium nitro molybdate solution. The flask was shaken and after standing for 25_30 mins, the precipitate was filtered off and phosphorus in it was determined by spectrephotometric method. The aluminum content was determined by diluting the filtrate (50 cm^3) with water (100 cm^3). The resulting solution was analysed for Al electrolytically.

Result and Discussion

Table 1 represents the selected analysis and calculated results for the effluent solution samples from Maiduguri depot (NNPC/PPMC) and Port Harcourt Refinery (PHR). Columns A, and C, are the values for the upstream in Maiduguri and Port Harcourt respectively. Letters B and D, stand for the outfall in the study areas. The values allowed for domestic used by WHO, NAFDAC and NPDWR in column E. The last column F stands as the standard (i.e, environment with little or no activity due to petroleum product). The amount for surface water in Maiduguri were listed in the table for comparism. These data when compared with the environs with little or no activities due to petroleum product see Table 1)) samples F, show that quite extreme conditions with respect to solute concentrations are obtained in the petroleum product deposit.

It is noted in Table 1 that aside from biologically ligand, BOD such as thiocyanate and oxalate as high as 324 ppm in Maiduguri depot and 204 ppm in Port Harcourt refinery, there are other organic complexation in form of cyanide for example that are important for metals in ore formation. The amount of Total Hydrocarbon, THC is also as high as 885 ppm in all the samples studied. While there is a great variety of organic donors in solutions. Perhaps, the most important of these are the "ill_defined" humic and fulvic acids

TABLE 1 Selected analysis and calculated result of the effluent solution from Nigeria petroleum cooperation sites

	Maiduguri		Port Harcourt			
	A	B	C	D	E	F
pH	5.10	5.15	5.50	4.30	6.97	7.02
Phenol	40.50	30.10	129	100.2	2.31	1.70
BOD	320	324	128	203.80	7.80	80
THC	720	765	885	510	_	35.10
TOC	1580	21,727	832	1000	_	4.8
NH_3	30.70	20.22	48.80	17.10	25.20	_
$S0_42\_$	397.90	172.50	137.60	97.90	198	2.75
$PO_43\_$	6.05	5.51	4.70	4.32	6.55	3.54
SiO_2	33	39.40	25.90	26.60	1.61	_
Mn	3.06	9.20	5.20	6.22	_	0.05
Pb	37.20	19.32	12.80	14.12	0.25	14.20
Fe	52.50	45.30	35	29.40	0.08	15.20
Zn	150	88.90	28.80	0.14	_	10.10
Ca^{2+}	2351	1570	890	910	_	5.20
Mg^{2+}	150	125	90	94	_	1.80
Na^+	1880	1530	2750	_	_	4.50
Al3+	485	410	512	390	_	1.31
Temp ^0C	27.0	25.07	29.80	26.80	25.70	28.3

A and C = Upstream in Maiduguri and Port_Harcourt; B and D = Outfall in Maiduguri and Port Harcourt ; E = Allowed for domestic used by WHO NAFDAC or NPDWR; F =Standard (see text); TDS= Total Dissolved solids,; THC = Total Hydrocarbon; BDD = biologically ligand

The humic and fulvic acids make up the bulk of organic matters containing reduced carbon in natural waters and in the crust [5]. The condensed forms may occur in form of coals, lignites etc, but a good deal exist in solution or can be extracted into solution from soils and sediments. The molecular weight vary from perhaps 2000 to 300,000 and an arbitrary scheme for extraction assigns the lower molecular weight fraction to the fulvic acids [6]. Humic and fulvic acids are modified lignins and display many properties similar to oxidized lignins. The lignins themselves are complex polyphenols, and are made up of phenylpropane units, cross linked and substituted. The oxidation gives the legating grouping such as carboxylic acids, phenols, salicylic acids and guinones.

The amount of phenols are up to 41 ppm in Maiduguri depot and 129 ppm at Port Harcourt refinery (see Table 1). The other functionalities such as amino groups, (up to 41.82 ppm in this present work) may have been introduced as degradation of lignin and condensation with amino groups proceeds. Further degradation in soils leads to the release of monomers including benzoic and hydroxy benzoic acids, which may readily be extracted and characterized. It is not surprising that these groups may be elaborately substituted, especially by alkane and alkoxy groups. Previous works on fulvic acids [5] has shown that about 40% of the carbon is contained in aromatic ring (benzene and naphthalene) and about 25% in carboxylic acid groups.

Since humic and fulvic materials are ubiquitous in these areas studied, this account for levels of metals such as Fe, Zn up to 52.5 ppm and 150 ppm. Silica, $Si0_2$ has a value as low as 25.9 ppm. It seems inescapable that they will play some parts in metal ion transport in these petroleum product effluent areas. Such is indeed the case as many metal ions (Ca^{2+}, Mg^{2+}, Na^+, Al^{3+}) are recorded in Table 1.

Other metals capable of forming even stronger complexes are Fe(III), Mn and aluminum Table 1. These metals will compete for coordination site [8]. It is also possible that humic and fulvic acids thus assist in the decomposition of silicate minerals via complexation of these metals. In fact it has been observed [9_10] that these organic acids have been involved in supergene processes such as the breakdown of silicates and the crystallization of aluminum and iron oxyhydroxides in the oxidized zone. Pigotite is an Al(III) mineral of a humic acid and sogrenite is another mineral containing considerable quantities of fulvic complexed uranyl ion

135 / 15

[11]. An Al(III) mineral of the hexacarboxytate of benzene is known as mellute and tricalcum dicitrate tertrahyydrate is the mineral earlandite.

However it is worthy to note that both galena and sphalerite are attacked by humic and fulvic acid at much higher rates than by rain and other near_surface water [12].

The Zn and Pb ratio in NNPC Maiduguri is 4.1, Portharcourt samples have average ratio in the 1.54 to 2.75 range. The Zn and Pb ratio of the sample from location is 0.71. Wide variations in the ratio are known for other element details are listed in Table 1. It has been considered [13] that a A/B metal ration in a bedrock above 0.23 would indicate the presence of metal A containing mineral and below 0.07 metal B containing mineral.

Conclusion

From the foregoing discussion, it should be obvious that the compositions of effluents in the NNPC/PPMC Maiduguri depot and PHR Port Harcourt are complex and the attainable chemistry/mineralogy there in extremely varied. For these reasons, among many others different compounds are able to crystallize in the oxidized zones in these areas, especially those to do with the formation of Mn, Fe, Al complex with organic acid. In addition, relative metal mobilities and solubilities when large quantities of organics, such as in Nigeria National petroleum depot and refineries are available in solution and effluent would probably bear reassessment for secondary mineral recovery.

Reference

1. Jambor J.L. and Mac Gregor I.O. (1974), Geol. Surv. Can. Paper 74_IB, 172 .
2. Buckely, D.C. and Cranston R.C. (1971) Atomic absorption analysis of 18 elements from a single decomposition of alumino_silicate. Chem. Geol, 7. 273_84.
3. AOAC (1991). "Official methods of analysis Association of official analytical chemistry, 15th edn. Washington D.C.
4. Zhang H. 1994. Technique for adjusting background values in stream sediments geochemistry Econs. Geol., 65, 156_165.
5. Wilkenson G. Gillard R.D. and Cleverly J.A. (1985) comprehensive coordination Chemistry Pergamon, Oxford, 7 volumes.
6. Christman R.F. and Gjessirig E. (1983) Aquatic and torrentiral Humic Materials, Ann Arbor Science, Ann Arbor.
7. Wilson M.A. Barron P.F. and Gillam A.H. (1981), Geochem. Cosmochim, Acta,
8. Kerndoff H. and M. Sehnitzer (1980), Geachim Cosmochim, Acta.44, 1701
9. Bek, K.C., Reuter J. H. and Perdue E.M. (1974) Geochim Cosmochim. Acta, 38, 34.
10. Perdue E.M. Beck K.C. and Reuter J.H. (1976) Nature (London), 260, 418.
11. Fleischer M, (1967 Amer. Mineral, 43,67.
12. Baker W.E. (1973) Geochim Cosmochim, Acta, 37, 279
13. Warren H.V. Delavault R.E and Irish R.I (1952) Biogeocehimcal investigations in the Pacific Northwest, Geol. Soc. , Am. Bult., 63, 435-484