

## Chemical Evaluation of Drilling Effluents and the Recovery of Secondary Ores at Petroleum Discharge and Drilling Sites in Gubio, Borno State

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### Abstract

Samples drawn within the composition field covered petroleum discharge and drilling sites in seven locations have been analysed. Gubio drilling site labeled C was compared with the bulk of the data from previous locations and subjected to statistical clustering. It was observed that the bulk solid dissolved in the water samples are phenol, Ca, Al<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup>, concentration analyst found 100, 48.5, 16.6 and 7.6 mol/dm<sup>3</sup> respectively. These data permit a range on the speculation of dissolve ore forming species in the study area. Accordingly secondary minerals such as diaspare, gibbsite, sapphire and corundum may be abundant in these locations. The geology bedrock drawing from Port-Harcourt to Gubio might be identical geochemically.

### Introduction

A redox boundary as reported in the literature is usually encountered next to the water table [1-3]. There also is the zone of secondary ore enrichment especially for elements such as copper, silver, aluminum and iron. Aqueous solutions of ions and compounds which are capable of interaction while bearing reactant and transporting products of reactions can now furnish the water. This is a necessary reagent in many cases for the control of chemical speciation of solute components and thus solubilities of secondary mineral species in it.

Although some of this interrelationship is complex in the oxide zone, a general pattern of mineral formation had been reported to emerge [3]. Hence the level of the water table is higher in the wet seasons and lower in the dry [4]. These fluctuations complicate the chemistry of the reaction which can always take place near to the water table. Several mineralogical suites may be superimposed on top of another. It has been reported that the water table in the petroleum discharge and drilling sites should be deep enough to permit waste burial to occur in entirely unsaturated zone [5]. In extreme cases this may extend up to 1000m. However, for most parts the depth of the oxidize zone ranges from about 20-300m.

This study examine the broader aspects of ground water model for the evaluation of the formation and recovery of the oxidized zones minerals in the petroleum discharge and drilling sites of North East Nigeria. As a result of pollutants in these areas the oxidize zone may extend to greater depths in these areas. Therefore the objective of this work is to evaluate the compositions of drilling effluents in selected petrochemical sites in respect of formation and recovery of secondary ores.

### Materials and Methods

The sample solutions were collected from Wadi 1-drilling sites of Gubio, Borno State and the landfill of NNPC Maiduguri and Portharcourt petroleum depot (PHR). The samples were freed mechanically from all contaminating material. It has been pointed out [6-7] that solutions from different localities at the same site may have different compositions. Therefore duplicate analysis gave an average for the sample used in subsequent studies.

The sample solution (100cm<sup>3</sup>) was placed together with a Teflon covered magnetic follower in flasks, for one week to obtain homogenous solutions. The pH of the sample solutions were measured using an Orion 407A pH meter and the solutions filtered through pre-washed Whatman GFF Fibreglass filter papers to remove all particles greater than 0.7µm in size.

These solutions were immediately analysed for Ca, Zn, Fe, Pb, Al and Mg by AAS techniques [5] employing a carbon rod attachment using Varian AA6 spectrometer. The total hydrocarbons (THC) was determined by addition of carbonyl tetrocholonde (50ml) and HCl (5ml) to the effluent (150ml). The mixture was shaken for one hour with magnetic stirrer. The CCl<sub>4</sub> layer was separated with separating funnel. The difference between the initial weight and the final weight was taken. This value was divided by the volume of the sample used. The method described by AOAC [8] and Zhang [9] were used to obtain total phenol. The calculations for other species in solution were carried out using the computer programme of Perrin and Sayce [10] and refinement of species carried out. Estimation of individual ionic activity coefficients were made using the extended Debye-Huckel equation [6-7].

Analytical and calculated Results for the solution from selected Petrochemical products sites.

Table 1a:

Site	Amount (in Mol/dm <sup>3</sup> )			
	pH	THC	Phenol	SiO <sub>2</sub>
A <sup>a</sup>	2.20	7.65	32.10	0.65
B <sup>a</sup>	4.30	510	100.20	0.45
C <sup>a</sup>	5.20	740	70.00	0.50
Tuma <sup>b</sup>	5.78	-	-	-
Herwa <sup>b</sup>	5.34	-	-	-
Bulta <sup>b</sup>	6.01	-	-	-
Lassa <sup>b</sup>	7.20	-	-	-

Table 1b

Site	Amount (in Mol/dm <sup>3</sup> )									
	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	Al <sup>3+</sup>	Ca	Zn	Fe	Pb	Mg	Cu	Ni
A <sup>a</sup>	1.79	0.40	15.20	39.30	1.35	0.81	0.90	5.20	-	-
B <sup>a</sup>	1.02	0.50	14.60	22.95	0.56	0.53	0.60	3.90	-	-
C <sup>a</sup>	2.96	0.70	16.60	48.50	1.80	0.88	0.14	5.50	-	-
Tuma <sup>b</sup>	7.60	-	-	6.11	5.58	4.59	2.84	3.79	2.32	-
Herwa <sup>b</sup>	5.70	-	-	5.81	4.66	4.17	4.50	4.90	1.98	-
Bulta <sup>b</sup>	5.80	-	-	5.99	4.78	6.03	5.47	1.99	5.97	-
Lassa <sup>b</sup>	-	-	-	14.40	0.42	7.35	0.60	0.90	0.92	0.50

A and B represent samples at landfill areas at Nigerian National petroleum cooperation (NNPC) depot Maidguri and Portharcourt (PHR) in that order. C is Wadi-1 on Gubio drilling site Maidguri. Total Hydrocarbon (THC) and Phenol are recorded in ppm. Letters 'a' and 'b' denote analyses in this present work and those obtained in ref [11] respectively

## Results and Discussion

The total concentration of aqueous species from Tuma, Herwa, Bulta and Lassa [11] were calculated assuming that most of these species were in aqueous phase. On the basis of these results, the results of this present work were recalculated to give the amounts in moldm<sup>-3</sup>. Tables 1a and 1b also contain the concentration of the Lassa, a non-petrochemical locality for comparison.

From the solution activity data in Table 1b, it was observed that in some cases (e.g PO<sub>4</sub><sup>3-</sup>, SiO<sub>2</sub>, Al<sup>3+</sup>, Ni) much less dissolved species is present, although pronounced variation of solution composition is noteworthy. It has been pointed [6] that in Arid zone (as the case in Borno State of Nigeria) during cycles of wetting and drying, reacting systems may not be fully immersed or inundated in water in order to effect chemical change. Compound can crystallize from aqueous solution, redox processes occur between dissolve species and dissolved gases especially, O<sub>2</sub> and CO<sub>2</sub>.

The bulk of the solids dissolved in these samples phases consist of dissociated ion principally SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>2-</sup>, and Al<sup>3+</sup> (Table 1b). To these added soluble but undissociated, SiO<sub>2</sub>, and some hydrocarbons (Table 1a). The variations in these major constituents affects the dispersion of the minor elements in the solution by providing reactants, either for the precipitation of insoluble minerals or for the formation of soluble complex ions with the minor elements [12].

Perhaps the most important is the relationship between the concentrations of hydrogen ions in the solution, expressed as the pH for the samples (in Table 1a). The pH for the precipitation of alkali and alkali earth element containing minerals are however, between 7-10. The presence of high amounts of aluminium in this present work, denoted by letters A, B and C (Table 1b) is noteworthy. The concentration of this metal in A is 15.20, B, 14.60 and C, 16.6 moldm<sup>-3</sup>. Aluminium oxides and hydroxides therefore worth separate mention. The mineral corundum, Al<sub>2</sub>O<sub>3</sub> and some of its gem varieties including sapphire and ruby, are extremely resistant towards chemical attack and can persist in supergene zone more or less indefinitely at a wide range of pH of the solution [1,13]. Diaspore and gibbsite, Al(OH)<sub>3</sub> (dimorphous) are other minerals which are thermodynamically stable and inhibit the formation of gibbsite from solution [14].

**Conclusion**

These available data can permit a range of dissolved species to be evaluated since the compositions of water are useful in pollution evaluation.

The reduction of high amounts of metals and ionic concentration are possible through organic and inorganic species complexation in the study sites. Accordingly this process may result mainly in the formation of silicate containing phosphate, aluminum ore for example. The geology bedrock drawing from Port-Harcourt to Gubio might be identical geochemically.

**References**

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