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## A Comparative Study of Environmental Impact of Mine Drainage from Enugu Coal Mines, Southeastern Nigeria

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## ABSTRACT

This research carried out a comparative study of the impact of acid mine drainage from the abandoned Enugu coal mines, southeastern Nigeria. Surface water samples were collected from Onyeama, Ribadu, Okpara coal mines and Ekulu River draining the Onyeama coal mine. A total of twelve water samples were collected across the Enugu coal mines: four surface water samples from Onyeama coal mine, three samples from Ribadu coal mine, Ekulu River at confluence of Onyeama and Ribadu coal mines and three water samples from Okpara coal mine. The source of sample collection was: springs, mine ponds, streams and river. Physicochemical parameters such as temperature, pH, turbidity, total dissolved solids (TDS), electrical conductivity (EC), total hardness, Biological oxygen demand (BOD), and dissolved oxygen (DO) were measured from the water samples. Anions such as  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{F}^-$  including major cations such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  were also analysed using standard laboratory procedures such as titration and chromatography. Heavy metals (Fe, Mn and Al) were analysed using atomic absorption spectrometer (AAS). Comparison of the results with World Standards such as WHO, USEPA and SON for potable water shows that levels of pH, turbidity,  $\text{F}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  exceeded these standards in some locations. The heavy metals concentrations were above the limits for potable water in all the mines. The average abundance of major anions was in this order:  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$ . The major cationic average abundance was in the order:  $\text{Mg}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+}$ . Classification of water samples based on total hardness shows that the water ranged from soft to moderately soft. Based on BOD values, some of the water samples contain high amounts of organic wastes. There was low dissolution of oxygen in the water samples leading to moderately acidic waters. Levels of Fe, Al and Mn were above permissible limits for potable water and show a trend of  $\text{Fe} > \text{Al} > \text{Mn}$ . Results also showed that Onyeama and Okpara coal mines have more acid mine drainage conditions than other mine locations. Acid mine drainage causes high acidity, which corrodes metals in borehole installation, devegetation, and decrease in biodiversity among aquatic biota. Bioreactors can be used in remedying acid mine drainage sites.

## 1. Introduction

The mining industry is noted to be a major producer of acidic sulphur rich waste waters which drain active and most especially abandoned mines. These mine wastes are often acidic or very acidic in some instances. Such mine wastes constitute an additional environmental hazard due to their elevated levels of heavy metals such as Fe, Al and Mn [1]. The major contaminant in Enugu coal mine sites is shales of the Mamu formation, which contain pyrite ( $\text{FeS}$ ), associated with toxic heavy metals such as As, Cr, Cd, Ni, Pb, Cu, Zn, Al, and Mn [2]. When the pyrites are oxidized, the water forms a soluble hydrous iron sulphate, which shows whitish, reddish or yellowish salt crust on weathered rock surfaces. These heavy metals found in pyrite, because of their toxicity are harmful to human health. These acidic waters which are sulphur rich are generated in both active and abandoned mines on a continuous basis and discharged into existing water sources used for human consumption such as drinking, irrigation and other domestic uses. Acid mine drainage caused by mining activities is the major problem facing the inhabitants in terms of potable water supply in Enugu and environs [3].

Enugu has an estimated population of 915,025. The discovery of coal in Enugu in 1909 led to the development of coal mines in Enugu such as Ogbete, Onyeama, Okpara, Ribadu, Iva and Asata which constitute what is today referred to as Enugu coal field [4]. Enugu is faced with water supply shortages as a major problem with the inhabitants. Enugu area is also faced with acid mine drainage pollution from underground coal mines and mine spoil scattered around the mines [5, 6]. Research has proven that acid mine drainage production results from both mining processes and

after the land has been reclaimed. Acidity is stored in acid salts if it is not flushed as generated. Salts produced during mining operation can dissolve and contribute to acid mine drainage long after mining has ceased and the area has been reclaimed. When a percentages of 0.11%, 10% and 100% of the total pyrite is oxidized, it takes 1.2 years, 108 years and 1,080 respectively, to flushed out acid generated by pyrite oxidation [7]. Equations showing pyrite oxidation can be found in [3, 6]. Previous works on the hydrochemistry and mine drainage in some of the Enugu coal mines can be found in [2-4, 6, 8]. In most cases, these mine drainage assessment was on individual mine basis, rather than a composite evaluation of mine drainage from the Enugu coal mines for comparison. Since the research on Enugu coals by Ezeigbo and Ezeanyim [8], subsequent works have not brought their investigations in the different mines to determine the level of mine drainage in these mines currently.

The ultimate goal of this paper is to examine the level of mine drainage in the abandoned Enugu coal fields on a comparative basis and determine the environmental impact. To achieve this end the paper will assess the level of acidity caused by relative degree of pyritization in the Enugu coal mines. Evaluate the water quality in the different coal mines with the view of identifying the most contaminated and suggest remedial measures. Also, to compare the extent of mine drainage by previous workers and determine the extent of water degradation in the coal mines. The water that refills the mines dissolves any acidic salts that built up on the pore spaces of exposed walls and ceilings of underground chambers. This initial drainage water is potentially polluting [1].

## 2. Experimental Methods

## 2.1 Study Area Description

The study area which consist of Onyeama, Ribadu, Ekulu River and Okpara mines is delimited by latitudes  $6^\circ 28' 18.72''$  to  $6^\circ 24' 94''$  N and

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longitudes 7° 26' 47.52" to 7° 27' 11" E (Fig. 1). Onyeama mine is located about 6.5 km northwest of Enugu metropolis. The coal field is surrounded on the northeastern side by Ribadu mine. The mine is a catchment of Ekulu River. Okpara mine is situated in the present day Enugu West. It is located about 6.5 km from Enugu Port Harcourt express way. In terms of relief the highest elevation of about 350 m above sea level was measured at a location in Ekulu River, while the lowest of 202 m was obtained at Onyeama mine site location. The valleys in the study area are characterized by gorges and ravines.

The study area is characterized by a hot and humid climate with an annual temperature in the range 25 °C to 30 °C. The climate is of the typical rainforest type with an average annual precipitation of 1895 mm and total evaporation of around 724 mm/year. The rains are usually heavy during the rainy season, which last from March to October. The heavy rains precipitate flows which affects the mine and the rivers or stream surrounding them. The mines are often flooded during the rainy season [4].

The drainage in the study area is dendritic. Major rivers draining the Enugu coal mines are: Ekulu, Ogbette, Asata and Nyaba Rivers (Fig. 1). Ephemeral streams rise from about 300 m amsl as springs and flow through deep V-Shaped valleys incised in soil materials and the Ajali sandstone, but more perennial streams rise from the middle level of the escarpment near the base of the Ajali sandstone. The area is properly drained. The streams or rivers some of which are fracture controlled in the flow path give rise to dendritic drainage pattern [8].

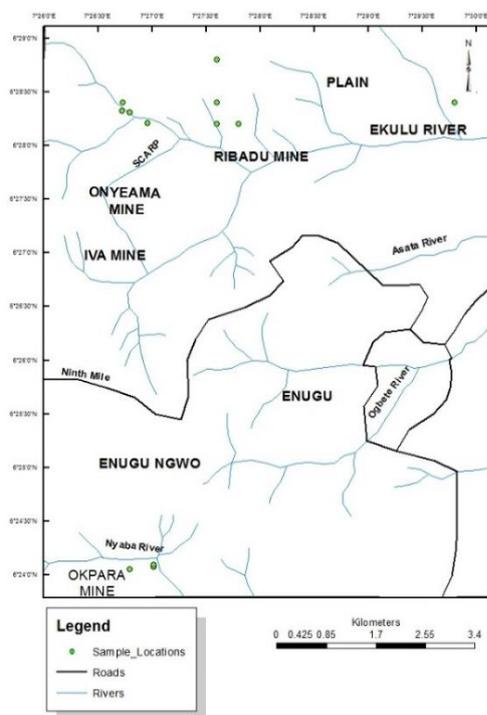


Fig. 1 Drainage map of study area showing sample locations

## 2.2 Geology and Hydrogeology

Enugu coal mines is underlain by the Enugu shale formation which consist of soft to dark gray shale mudstone and intercalation of sandstone and sandy shale. It is underlain by the Mamu formation and Ajali Sandstones. The Ajali Sandstone overlies the Mamu formation which in turn overlies the Enugu shale (Fig. 2). The Mamu formation is the most important geologic formation with respect to coal formation, occurrence and mining [3]. The Mamu formation underlies the Ajali sandstone, but are generally affected by late cretaceous tectonism, leading to faulting, folding and fracturing of the rock materials. The faults and fractures encountered in the mine tunnels continue through the Ajali sandstone to the surface providing a conduit for perennial flow at almost all of the sides of the hill cuts. Enugu shale was deposited under shallow marine environment. It consist of light to dark grey shale, mudstone intercalations of sand stone sandy shale. The Mamu formation was deposited under paralic conditions [9].

The Mamu formation exhibit cyclic sequence with heterogeneous lithology ranging from bottom to top by shale, or sandy shale/ shaly coal at the top, carbonaceous shale passing down into shale sandstone / shale or sandy shale. Among the five coal seams in Enugu, with the Mamu formation the third seam with a workable thickness of more than 1.5 m is exploited. The Mamu formation is highly fractured about 395 m thick [8].

The Mamu formation has a dip of which is the dip of the coal seam of 2° SW [10]. Coal in Onyeama Mine occurs with coal flakes [11]. Offodile, [12] reported a higher dip up to 25°, this could be traceable to faulting (Fig. 2).

The Mamu formation contributes nearly all the water entering the Enugu coalmine. The source of recharge is by precipitation [8, 12]. The Mamu Sandstone unit has a hydraulic conductivity of  $9.2 \times 10^{-3}$  cm/s and a specific discharge of 14.5 m<sup>3</sup>/year [8]. The Ajali formation constitute the main aquiferous unit with thick friable poorly sorted cross bedded sandstones, whitish with occasional iron stains. The sandstones are overlain with lateritic red earth deposit. The Ajali formation is a prolific aquifer that is unconfined at the Onyeama coal mine area, but confined in areas west of Enugu [2]. The lateritic aquifer is thinly bedded and discontinuous with a depth of 0.7 m, hydraulic conductivity (K)  $9.2 \times 10^{-3}$  cm/s and specific discharge (v) 1.75 m<sup>3</sup>/year [8]. At Onyeama mine, Agbo and Onuoha [13] evaluated the average value of hydraulic conductivity in the mine area to range from  $6.95 \times 10^{-5}$  to  $2.6 \times 10^{-3}$  m/s, while Offodile, [14], computed the average value of specific capacity to be 161.2 m<sup>2</sup>/day in the area where the aquifer is confined.

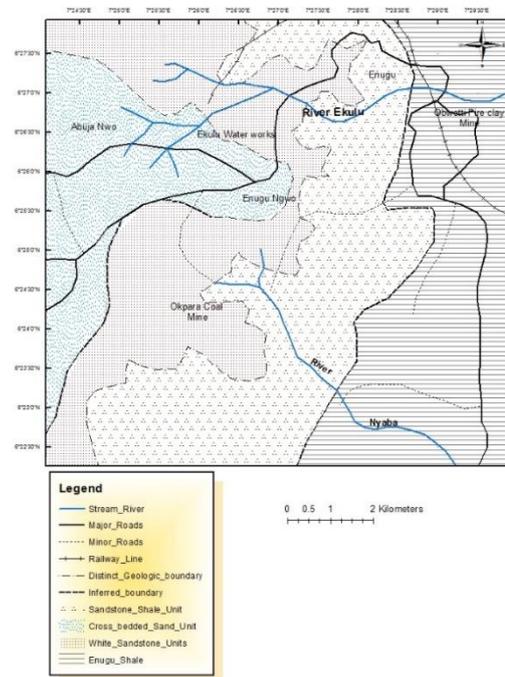


Fig. 2 Geological map of the study area

## 2.3 Sample Collection

A total of twelve water samples were collected across Enugu coal field: Onyeama, Ribadu, Okpara mines and Ekulu River. Details of the locations of the water samples are given in Fig. 1. The water samples were collected from the mines at sedimentation ponds, stream channels, stream confluence, springs, tributaries and shallow hand dug well. Field equipment such as global positioning system (GPS), for measuring coordinates and elevations, plastic water sample bottles, conductivity meter, pH meter, spectrophotometers for TDS and turbidity measurement, clinical thermometer and concentrated HNO<sub>3</sub> were used for the field work. The water sample bottles were rinsed with water to be sampled three times before sample collection. Two drops of concentrated HNO<sub>3</sub> were added to each water sample bottle to avoid loss of ions before analysis. Parameters such as temperature, pH, conductivity, turbidity and TDS were measured insitu using standard field kits listed above. The water samples were labeled using marker tape and stored in a cool refrigerator and then transported to the laboratory for analysis the following day.

## 2.4 Analytical Procedures

Measurable physical properties notably, pH, temperature, electrical conductivity, turbidity and total dissolved solids (TDS) were evaluated in the field using standard field kits digital Mv Redox pH meter to measure pH, mercury-in-glass thermometer was used to measure temperature. Electrical conductivity and turbidity were measured with conductivity meter WA 3000 and spectrophotometer Dr 3000 respectively. Chemical parameters such as major ions were analyzed using ion chromatography and titration. Major cations and heavy metals (Fe, Mn and Al) were analyzed using atomic absorption spectrophotometer (AAS) all the chemical analysis were performed at the cross river water board limited, world bank assisted at Calabar Southeastern Nigeria.

### 3. Results and Discussion

#### 3.1 Water Quality

The physicochemical characteristics and concentrations of inorganic ions/salts in the shallow groundwater samples from abandoned Enugu coal mines are presented in Table 1 together with the maximum permissible limits contained in Nigerian standards for drinking water quality [15], world health organization [16] and United States environmental agency [17].

**Table 1** Detailed results of physicochemical parameters in water samples

Parameters	1	2	3	4	5	6	7	8	9	10	11	12
Temp (°C)	23.4	24.2	24.2	24.2	24.3	24.5	24.3	24.2	24.4	27.3	28.8	28.7
pH	4.25	5.10	5.52	5.85	4.0	5.36	5.85	5.70	4.97	4.31	4.35	4.50
Conductivity (µS/cm)	68	55.0	25.9	33.3	11.29	38.6	32.1	138.4	44.5	4.36	1.99	3.03
Turbidity(NTU)	148	27.1	31.16	28.92	17.0	22.16	6.76	5.06	5.14	120	18	5
TDS (mg/L)	401	330	150	191	461	230	159	283	326	2834	1294	1970
Total Hardness (mg/L)	34	68	42	34	78	78	96	86.3	79.1	65.07	25.02	50.02
BOD (mg/L)	6.75	4.03	4.44	7.04	7.66	5.18	7.50	7.03	7.44	-	-	-
DO "	2.0	2.8	2.1	1.6	1.8	2.1	2.2	2.4	3.6	-	-	-
SO <sub>4</sub> "	320	330	380	366	60	58	59	52	48	130	125	115
NO <sub>3</sub> "	1.5	0.89	1.02	1.25	1.4	1.3	1.8	1.62	1.7	792	304	480
Cl "	5.0	508	5.20	509	7.2	7.00	6.90	7.06	9.20	150	100	70
F "	0.6	0.62	0.66	6.59	0.9	0.81	0.88	0.77	0.55	0.01	0.11	0.05
Ca "	4.80	4.52	4.0	4.30	6.41	5.58	5.56	4.40	4.90	10.40	9.12	11.42
Na "	6.95	7.64	7.61	7.60	7.69	7.39	7.60	7.58	9.60	12.10	9.89	11.41
Mg "	900	895	908	134	141	106	69	131	105	12.14	10.61	11.69
K "	10.1	9.46	9.85	10.02	8.46	10.05	8.65	9.38	6.02	16.61	17.12	16.56
Al "	1.24	0.812	0.416	0.842	1.63	0.052	2.63	0.31	0.17	1.69	1.45	1.46
Fe "	9.65	5.7	5.1	4.7	0.71	0.41	7.2	3.00	5.3	8.74	11.95	0.106
Mn "	1.05	0.5	0.6	1.01	0.8	0.66	0.15	1.01	1.16	2.93	2.914	2.861

**Table 2** Statistical summary of physicochemical characteristics in water samples

Parameter	Mean	Stdev	Min	Max	Median	WHO	USEPA	SON
Temp. °C	25.21	1.90	23.40	28.8	24.3		na	na
pH	4.98	0.68	4	5.89	5.04	6.5-8.5	na	6.5-8.5
Ec (µS/cm)	22.26	334.78	11.29	974	49.75	1400	na	1000
Turbidity (NTU)	27.19	39.25	5	148	17.5	5	5	na
TDS (mg/L)	719	862	150	2834	328	500	500	500
Total Hard. "	61.29	23.49	25.02	96	66.54	500	na	na
BOD "	6.34	1.40	4.03	7.66	7.03	6	na	na
Dissolved O <sub>2</sub> "	2.28	0.60	1.6	3.6	2.1	4-6	na	na
SO <sub>4</sub> <sup>2+</sup> "	170.25	135.86	48	380	120	250	250	100
NO <sub>3</sub> <sup>-</sup> "	3.68	4.19	0.89	11.47	1.56	50	10	50
Cl <sup>-</sup> "	31.48	48.52	5	150	7.03	250	5	250
F <sup>-</sup> "	1.05	1.77	0.04	6.59	0.64	1.5	4	1.5
Ca "	6.72	5.09	2.09	20.02	4.85	75	na	na
Na "	8.59	1.73	6.95	12.1	7.63	12	na	200
Mg "	285	374	10.61	908	118	10-150	na	0.2
K "	11.02	3.64	6.02	17.12	9.94	12	na	na
Al "	1.08	0.78	0.05	2.63	1.04	0.05-0.2	0.05-0.2	0.2
Fe "	5.53	3.45	0.41	11.95	5.2	0.2	0.2	0.3
Mn "	1.30	1.00	0.15	2.93	1.01	0.4	0.4	0.2

As presented in Tables 1 and 2, almost all the water sampled in Enugu coal mines exhibited a constant temperature range of 24.2 °C except in Okpara mine locations 10, 11 and 12 where the temperature range from 27.3 °C to 28.8 °C. This temperature reflects air temperature since the surface water is directly contacted with solar rays. This air temperature always differ from groundwater temperature because, ground water temperature is due to the heat retained by the aquiferous layers. The water temperature in the study area ranged from 23.4 °C to 28.8 °C with a mean of 25.2 °C and a standard deviation of 1.90 with a median value of 24.3 °C. Temperature affects organisms as well as physical and chemical characteristics of water [18]. The temperature seems to have no substantial impact on water quality. Generally, rules of reactions to form acid mine drainage increases with increasing temperature. Acid mine drainage is formed faster at warmed pyritic material [19].

The pH values of the water samples ranged from 4 to 5.89, which is acidic condition. The mean pH level is 4.98 with a standard deviation of 0.68 and a median of 5.04. Low pH value is evidence of acid mine drainage due to the oxidation of pyrite (FeS) in abundance. This shows that the degree of acidity is more at Ribadu mine next to Okpara mine followed by Onyeama mine. Ezeigbo and Ezeanyim [8], established pH values of 2.8 and 2.3 in Onyeama and Okpara mines respectively. Utom, et al., [5] discovered a pH range from 2.6 to 6.7 and a mean of 4.17 in Okpara mine. Temperature and pH are some of the various factors responsible for acid mine generation at reaction sites [19]. Temperature and pH also affects the solubility of heavy metals and hence their mobility and dispersion [20]. Acid mine drainage is characterized by low pH. A study of fish distribution in Pennsylvania streams affected by acid mine drainage revealed severe impact on fish at pH from 4.5 to 5. Ten species showed tolerance to acid

conditions at pH 5.5 and below and 38 species were found living in waters with pH values ranging from 5.6 to 6.4, while 68 species were only at pH levels greater than 6.4. There was complete loss of fish in 90% of streams with waters of pH 4.5 and total acidity of 15 mg/L [21]. Jamal, et al., [22] found in Churcha coal mine that pH values ranged from 2.62 to 3.80 and temperature range from 29.8 °C to 34 °C. Temperature of acid mine waters should not be 50 °C above the receiving water temperature to attain tolerance level by aquatic biota [22].

Electrical conductivity is indicative of heavy metal level of dissolution and desorption [23]. The conductivity of most fresh waters ranged from 10 to 1000 µS/cm, but may exceed 1000 µS/cm in polluted waters or those receiving large quantities of land runoff or acid mine drainage runoff [24]. Ezeigbo and Ezeanyim, [8] reported values of 700 µS/cm and 1550 µS/cm at Onyeama and Okpara mine respectively. Utom, et al., [5] found EC range of 28 to 1,053 µS/cm in Okpara mine. In this study, all the locations have EC values below 1000 µS/cm prescribed by Standard Organization of Nigeria [25]. The total dissolved solid (TDS) which gives a good indication of salinity ranged from 150.54 to 283 mg/L. The Standard Organization of Nigeria [25], stipulated an acceptable limit of TDS for potable water at 50 mg/L. The mean level of TDS of this study of 719.19 mg/L falls above acceptable limits for potable water. Total dissolved solids in Okpara mine were found to be above acceptable levels for potable water, while TDS levels in Onyeama, Ribadu and Ekulu River were below acceptable limit of 500 mg/L for potable water. The low TDS values recorded in Onyeama, Ribadu mines and Ekulu River could be due to low dissolution of sulphides, presence of buffers such as calcium carbonates and bicarbonates or dilution [26]. Ezeigbo and Ezeanyim, [8] reported TDS values of 330 mg/L and 785 mg/L for Onyeama and Okpara mines respectively.

#### 3.2 Total Hardness

Hardness is a measure of the occurrence and abundance of divalent cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>). When hardness values are very high in potential acid drainage waters indicates that the water differs from the more common type hard waters, to the extent that sulphate with no bicarbonate is the dominant anion [5]. The hardness values recorded in this study are below permissible limits of 500 mg/L for potable water (Table 3). The mean hardness value is 61.29 mg/L and ranged from 25.02 to 96 mg/L. All the coal mines reported in this study recorded low total hardness values. Such waters can be classified as Ca-Mg sulphate type, such waters are classified as soft to moderately hard [27]. Utom, et al., [5], established total hardness range from 8 to 621 mg/L in Okpara mine. Ezeigbo and Ezeanyim, [8] reported average values of 100 mg/L and 100mg/L for Onyeama and Okpara coal mines respectively.

**Table 3** Classification of water samples based on total hardness [27]

Hardness (mg/LCaCO3)	Water classification
0-75	soft
75-150	Moderately hard
150-300	Hard
>300	Very hard

#### 3.3 Biological Oxygen Demand (BOD) and Dissolved Oxygen (DO)

Atmospheric oxygen is prerequisite for direct oxidation of pyrite and for regeneration of Fe<sup>3+</sup>. Thus, if air and oxygenated or Fe<sup>3+</sup> rich waters can be excluded from pyritic material, pyrite oxidation can be inhibited and little or no acid will be regenerated [19]. Dissolved oxygen had a mean of 2.28±0.60 and ranged from 1.6 to 3.6 mg/L and a median of 2.1 mg/L. Ekulu River and the confluence of Ribadu and Onyeama mine had a high dissolved oxygen of 22 mg/L and Onyeama mine had lower dissolved oxygen. Oxygen is a key reactant in forming acid mine drainage and has low solubility in water. 10 mg/L of dissolved oxygen will produce acidic water with pH of 3.2 [19]. There is low dissolved oxygen in this study, hence there is moderate acidity due to insufficient pyritization. The permissible level of DO by WHO [16] is 4-6 ppm for potable water. None of the DO values recorded in this study area locations is up to this standard.

The BOD permissible limit is 6.0 ppm, from the samples, most locations recorded levels of BOD above 6 ppm, so we can deduce that most samples contain high amounts of organic wastes, as such are highly polluted with organic matter. Low dissolved oxygen and high BOD are some of the biological parameters that characterized the degradation of water quality [28].

#### 3.4 Anions

The water samples from the Enugu coal mines attained sulphate concentrations ranging from 48 to 380 mg/L, with a mean and standard deviation of 170.25±135.86 and a median of 120 mg/L. Sulphate levels in sample locations at Onyeama mine were found to be above 250 mg/L,

which is the permissible standard by WHO [16] for potable water (Table 1). Concentrations of sulphate in Ribadu mine and Ekulu River were below this permissible level. High concentration of sulphate is mainly due to the presence of iron sulphide in coal and rocks and its reaction with water and oxygen [28]. Sulphate levels of 310 mg/L and 420 mg/L were established by Ezeigbo and Ezeanyim, [8] in Onyeama and Okpara coal mines respectively. Water samples from acid mine drainage discharges generally has high concentration of acidity, Fe, Mn and Al [29]. Ezemokwe et al., [30] established sulphate range from <20-700 mg/L, and a mean of 226.03 mg/L in Onyeama mine.

Chloride concentrations in the sampled waters from Enugu coal mines ranged from 5 to 150 mg/L with a mean and standard deviation of 31.48±48.52 with a median of 7.03 mg/L. The levels of chloride in all the mines studied are below the permissible limit of 250 mg/L for potable water recommended by USEPA. Ezeigbo and Ezeanyim, [8] reported chloride values from 10.42-1.99 mg/L in Onyeama and Okpara mines respectively. Ezemokwe, et al., [31] discovered chloride values ranging from 27.90-160.30 mg/L with a mean of 83.44 mg/L in Onyeama mine. Also, Utom, et al., [5] established chloride mean values of 5.6 and range from 1.65-26.3 mg/L in Okpara mine. All these preceding findings were within permissible standard for potable water. In this study, Okpara mine recorded the highest chloride values than other mines. Onwuka, et al., [32], reported chloride mean value of 230 mg/L in groundwater in Enugu town. High chloride causes salty taste in water.

Nitrate levels in this study recorded a mean and standard deviation of 93.39±236.52 with a range of 89-792 mg/L and a median of 1.56 mg/L. Okpara coal mine recorded the highest level of nitrate among the mines investigated. Nitrate levels in this mine exceeded permissible level of 50 mg/L for potable water prescribed by SON [25]. High nitrate levels renders the water prone to potential risk, most especially expectant mothers and infants [33, 34]. Elevated nitrate in water causes cyanosis in infants [35]. The source of nitrate is mostly from nitrate fertilizers [20].

Fluoride concentration in Enugu coal mine recorded a mean of 1.05±1.77 and ranged from 0.04 to 6.59 mg/L and a median of 0.64 mg/L. Fluoride levels were below permissible level of 1.5 mg/L set for potable water by SON [25], except in Onyeama mine where the value of 6.59 mg/L exceeded the level prescribed for potable water. Excess fluoride causes teeth mottling and at concentration above 4-6 ppm reduces the prevalence of osteoporosis and collapse vertebra [36]. Deficiency of fluoride in human body causes pains and tenderness of bones [36]. Anion levels in water of this study show a trend of  $SO_4^{2-} > Cl^- > NO_3^- > F^-$ .

### 3.5 Major Cations

With respect to the major dissolved cations, the general trend of the mean values in water samples shows  $Mg^{2+} > K^+ > Na^+ > Ca^{2+}$ . Magnesium content which is the most abundant vary between 10.61-908 mg/L, with a mean and standard deviation of 285.2±374.36. The highest magnesium value of 908 mg/L was recorded in a location at Onyeama mine. The least magnesium value of 10.61 mg/L was obtained at Okpara coal mine. Ezeigbo and Ezeanyim, [8] recorded Mg values of 185.08 mg/L and 85.12 mg/L in Onyeama and Okpara mines respectively. Utom, et al., [5] achieved Mg range of 1.2-102 mg/L and a mean value of 19.5 mg/L in Okpara coal mine. Magnesium values ranging from 1.45-63.8 mg/L were obtained in surface water samples in a coal mine drainage from in Brazil by Campaner, et al., [37]. The source of Mg may be from magnesium carbonates. Next on the line is potassium, a biophilous element with low geochemical mobility [23]. Potassium ranged in this study from 6.02-17.12 mg/L with a mean value of 11.02±3.64. Potassium values obtained from Okpara coal mine were above a permissible limit of 12 mg/L recommended by WHO [16] for potable water. Potassium values at Onyeama, Ribadu coal mines and Ekulu river were below this standard. Sodium and potassium are mostly from dissolution of feldspars from adjoining basement areas. Calcium and Magnesium are responsible for temporary hardness in water. Sodium levels ranged from 6.95-12.1 mg/L with a mean and standard deviation of 8.59±1.73. Calcium recorded a mean of 6.72±5.09 and ranged from 2.09-20.02 mg/L. Both calcium and sodium levels were low compared to WHO [16] and SON [25] values of 12 mg/L and 75 mg/L recommended for potable water. Both sodium and calcium exhibit low level of metal pollution according to Ezemokwe, et al., [31].

### 3.6 Heavy Metal Contamination

Rock and earth layers above the coal removed during mining commonly contain traces of iron, manganese and aluminum and also contain other heavy metals. Such metals can be toxic to fish and other aquatic organisms when present in highly dissolved concentrations [28]. Iron concentrations in this study ranged from 0.41-11.95 mg/L, with a mean and standard deviation of 5.53±3.45. This mean value is above the permissible level of 0.2 mg/L for potable water by WHO [16] standard. The highest level of Fe

was obtained at the Onyeama coal mine. Iron concentrations in all the locations were above allowable limit for potable water. Ezeigbo and Ezeanyim, [8] obtained Fe levels of 8.40 mg/L and 25.76 mg/L in Onyeama and Okpara coal mines respectively, which exceed the values obtained in this study. Utom, et al., [5] recorded a mean value of 1.6 mg/L for Fe in Okpara coal mine. Ezemokwe, et al., [30] recorded iron range of 0.35-0.96 mg/L in water samples at Okpara mine. The mean levels of Al (1.08 mg/L) and Mn (1.30±1.00) obtained in this study also exceeded the standards stipulated by SON [25] and WHO [16] of 0.05-0.2 and 0.4 respectively for potable water. Aluminum levels ranged from 0.05-2.63 and a median of 1.04 ppm. Manganese concentrations in this study range from 0.15-2.93 with a median of 1.01 mg/L. This group of heavy metals are commonly associated with coal mine drainage [38, 19]. The three metals (Fe, Mn and Al) exceeded permissible levels for potable water in all the locations examined in this study. The trend of relative abundance of these heavy metals in the study are in the order: Fe>Al>Mn. At elevated levels Al is toxic to plants and animals. Excessive Mn ingestion causes reduction in haemoglobin synthesis and delay in reproductive maturation and elevated Fe causes reddish colour and odour in water. Bioreactors can be used in remediation and attenuation of high concentrations of these elements due to acid mine drainage.

## 4. Conclusion

Acid mine drainage can be generated from both active and abandoned coal mines. Acid mine drainage is caused by the oxidation of pyrite. Low sulphate content at mine sites is evidence of insufficient pyritization. Acid mine drainage is characterized by acidic to moderately acid condition of acid mine waters. This study considered BOD and mobilization of heavy metals such as Fe, Mn, Al and other heavy metals that characterized acid mine drainage conditions. Temperature and pH are essential for heavy metal mobilization. Warm temperatures are amenable for acid mine generation. Temperatures at Okpara mine are warmer than, Onyeama, Ribadu coal mines and Ekulu River. The degree of acidity is moderate in all the examined mines, but fell outside the range prescribed by WHO for potable water in all the coal mines. The water samples can be described as soft to moderately soft based on the total hardness values obtained in this study. High sulphate levels above world standards for potable water was obtained at Onyeama coal mine. Higher nitrates and chloride concentrations were recorded at Okpara coal mine than other mines suggesting probable sources from nitrogenous fertilizers and coal vitrains respectively. Fluoride levels were below world standards for potable waters except in one location at Onyeama mine that is above this standard. The average abundance of major cations is in the trend:  $SO_4^{2-} > Cl^- > NO_3^- > F^-$ .

Major cations; Ca was lower than World Standards in all the mines. Potassium and Na levels at Onyeama, Ribadu coal mines and Ekulu river were lower than prescribed standards by SON/WHO for potable water, except at Okpara coal mine where K and Na levels were found to be above this standard. Magnesium concentrations were found to be above SON/WHO permissible level for potable water at Onyeama coal mine, but fell below this standard at Ribadu, Okpara coal mines and Ekulu river. The average abundance of major cations in this study was in this order:  $Mg^{2+} > K^+ > Na^+ > Ca^{2+}$ . The average abundance of heavy metals cations in this study was in the trend: Fe>Mn>Al. The three metals recorded concentrations above permissible levels for potable water recommended by WHO/SON /USEPA. It is established that these heavy metals are commonly associated with acid mine drainage at coal mines. It can be concluded from this study that acid mine drainage generated at Enugu coal mines in decreasing order: Onyeama coal mine>Okpara coal mine > Ribadu coal mine>Ekulu River.

Acid mine drainage is harmful to aquatic life such as decrease in fish population, devegetation, heavy metal contamination such as potentially toxic metals which causes various degrees of cancer in humans through soil and water pollution.

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