

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF SCIENCE

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

**ASSESSMENT OF THE IMPACT OF THE SUBRISO EAST ROCK DUMP ON
GROUND AND SURFACE WATER QUALITY AT GOLDEN STAR WASSA
LIMITED**

BY

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B.Sc. ENVIRONMENTAL SCIENCE

**A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL & APPLIED
BIOLOGY, COLLEGE OF SCIENCE, KWAME NKRUMAH UNIVERSITY OF
SCIENCE & TECHNOLOGY, KUMASI IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN
ENVIRONMENTAL SCIENCE**

DECEMBER, 2013

DECLARATION

I hereby declared that this thesis is the outcome of the original research work undertaken by the author, any assistance obtained has been duly acknowledged. It is neither in part nor whole been presented for another degree elsewhere.

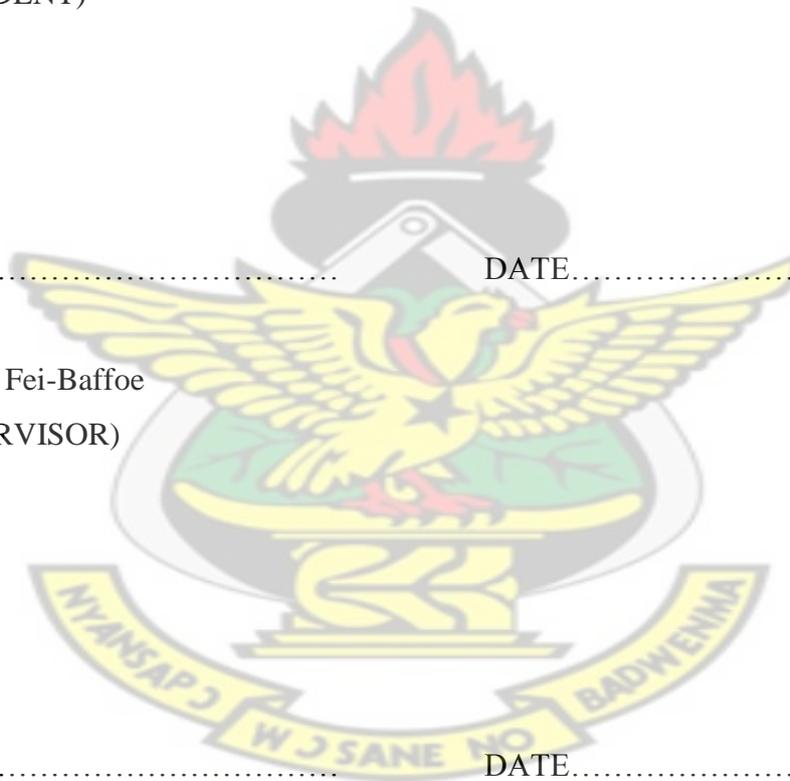
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DEDICATION

This research is dedicated to God Almighty, Mr. and Mrs. Dawohoso, Geoffrey, Akosua Addae, Eugenia and Eugene Dawohoso.

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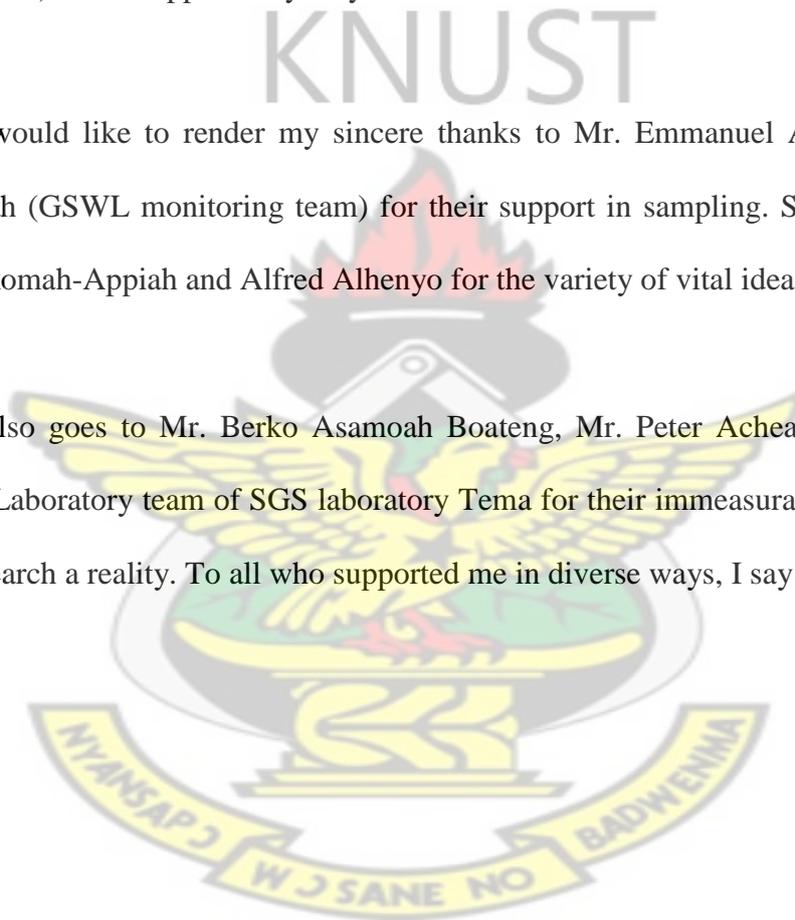
ACKNOWLEDGEMENT

First and foremost, I would like to offer my utmost gratitude to the Lord Almighty, who has been my constant guide and support in completing this research.

A special word of thanks goes to my supervisor; Dr. Fei-Baffoe (KNUST) for the guidance. My gratitude also goes Mr. Sefa Francis and Madam Charlotte FaFa Tay (Golden Star Wassa Mines, Akyempim) for the opportunity they offered.

In addition, I would like to render my sincere thanks to Mr. Emmanuel Acquah and Mr. Daniel Nkrumah (GSWL monitoring team) for their support in sampling. Special thanks to Emmanuel Ankomah-Appiah and Alfred Alhenyo for the variety of vital ideas they provided.

My gratitude also goes to Mr. Berko Asamoah Boateng, Mr. Peter Acheampong Sarpong (SGS) and the Laboratory team of SGS laboratory Tema for their immeasurable assistance in making the research a reality. To all who supported me in diverse ways, I say God bless you.



ABSTRACT

Acid rock drainage (ARD) has emerged as one of the greatest environmental threats facing the mining industry owing to its characteristic low pH, high acidity and elevated concentrations of metals and sulphate content. The aim of this study was to assess the impacts of the Subriso East Rock Dump on ground and surface water quality at GSWL. Water samples were collected from deep and shallow monitoring boreholes and surface water within the immediate environs of the rock dump and analysed. Overall, surface water sampled was slightly acidic most especially the upstream point. For groundwater, the majority of the shallow monitoring boreholes were also slightly acidic. The deep monitoring boreholes were near neutral and within WHO (2006)/GSB (2009) acceptable range for drinking water. EC, CaCO₃, TDS, and SO₄ for the deep, shallow and surface water within the study area were below their respective WHO (2006)/GSB (2009) permissible limits. Statistically, there was no significant difference between the deep monitoring boreholes around the waste rock dump and the reference point (BRMB-01A). The same trend was depicted by the shallow monitoring boreholes. However, there was significant variation between the upstream point (SW-SE-07) and downstream points (TS-SE-01 and TS-SE-02) for EC, CaCO₃, TDS, and SO₄. Heavy metal concentrations in surface, deep and shallow monitoring boreholes were generally very low and below their respective WHO (2006)/GSB (2009) permissible limits. SEMB-02B and SEMB-03B (shallow boreholes) and all the surface water samples had Mn and Fe concentrations above the WHO (2006)/GSB (2009). All the deep boreholes also had Mn concentrations exceeding the above standards. Nonetheless, statistically, there were not significant differences amongst the various sampling points and their respective reference points. Cd, Pb and Ag were not detected. Although high concentrations of Fe and Mn were recorded in some sampling points, the differences were not significant ($p \geq 0.05$). In brief, it can be concluded that, no significant impacts existed that could be attributed to the SE rock dump.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the study

The minerals industry is fundamental to modern life in both developed and developing countries. Several products are manufactured from over 90 mined substances/minerals around the world. Mining has the potential to lead to the growth of the economic system of any country from taxes paid by mining companies that lead to socioeconomic development within the field where the mine is sited; directly and indirectly create employment prospects in the mines or via service rendered to the mines; increase human capital through teaching and health services; improve on foreign exchange returns; improve infrastructure such as water supply and roads; and as well create other economic actions to defend the mines rather than import all materials from overseas. Conversely, the supply of minerals and metals comes with environmental and social challenges. Substandard mining and mineral processing practices could result in poisoning of water resources, soils and the air (International Organization of Supreme Audit Institutions, 2010).

The accompanying environmental effects of mining operations commence from exploration and continuing through extraction, processing of ore deposits, and may even persist after closure of the mine. The type and magnitude of effects can vary at each stage of the project during implementation. Mining is known to have a wide range of adverse environmental impacts on the ecosystem. This study, however, focuses on Acid Rock Drainage (ARD) which, according to Gaikwad and Gupta (2008) is amongst the significant environmental challenges confronting the industry globally. This agrees with Ezeigbo and Ezeanyim (2006) that ARD constitutes a serious problem in numerous active and abandoned mines in developing and developed economies.

Acid Rock Drainage (ARD) refers to acid formation that occurs when Potentially Acid Generating (PAG) materials with acid generating sulphide minerals in excess of neutralizing minerals (primarily carbonates) become oxidized when exposed to oxygen and water in the environment, eventually leading to the discharge of acidic water harmful to the environment (World Bank Group, 2007). ARD may also be known as or Acid Mine Drainage (AMD). Even though the phenomenon is often linked to mining activities, it can occur everywhere sulphide minerals are naturally weathered. For mining operations, the exposure of sulphide minerals, for example pyrite (FeS_2) and pyrrhotite (FeS), and the absence of significant acid neutralizing capacity for example dolomite and limestone, can generate acidic drainage from several different sources including surface run-off from open mines; drainage from underground workings; seepage and as well as run-off from rock waste dumps at mines; tailings impoundments; and or stockpiles and abandoned heap leach piles (Marchant and Lawrence, 2008).

ARD occurs when waste rock containing sulphide comes into contact with air and water, these minerals are oxidized, releasing sulphuric acid. An acid-generating mine can become a 'perpetual pollution machine' depending on the bulk composition of the waste rock present (Peppas *et al.*, 2000). Sprynskyy *et al.*, (2006) explained that the ARD process is aggravated by bacteria, such as *Thiobacillus ferrooxidans* that obtain energy from the oxidation reaction for growth. The discharge of acid into ground and surface water resources can cause the pH to become very low (as low as 2). Under such acidic conditions, the concentrations of heavy metal concentrations increase owing to the dissolution of these metal elements from waste rock. The heavy metals which include Cu^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} pose serious health threat to humans, animals and ecological systems. They cannot be biodegraded, hence bioaccumulate in living organisms, causing various diseases and disorders (Sprynskyy *et al.*,

2006). After ARD formation starts, the reactions can speed up and become very difficult to arrest. Treatment is essential, however, if ignored; AMD could persist for several years until the source of the pyritic sulphur is exhausted (Gandy *et al.*, 2009). According to Harding and Boothroyd (2004), the phenomenon can have a great deal of adverse effects on freshwater environments and communities varying from lethal effects from metal toxicity through to interfering with ecosystem processes. The effects are even more pronounced in vertebrate life such as fish than on the plant and unicellular life (McGinness, 1999). AMD is a problem of great concern due to the fact that a vast majority of living organisms live and survive at, or near, pH 7 (Mallo, 2011).

Todd and Redick (1997) reported that ARD problems are present in West Virginia, Maryland, Kentucky, Pennsylvania, Ohio, Oklahoma, Indiana, Missouri, Illinois, Iowa, Kansas, Tennessee, Virginia, Georgia and Alabama. Todd and Redick (1997) also emphasized that Northern West Virginia and Pennsylvania are the most mined states in Appalachia, however, lack limestone formations, and as a result experience severe acid drainage pollution. Numerous cases of ARD have transpired throughout Canada, where the metal from mines combined with the acid from pyrite, causing destruction to aquatic habitats. Acid drainage has been acknowledged as the utmost environmental liability being confronted by the Canadian mining industry, and the public through the abandoned mine sites to a minor extent (Tremblay and Hogan, 2000). Tremblay and Hogan (2000) as well emphasized that the liability is estimated to vary between two billion and five billion Canadian dollars depending on the complexity of the treatment and control technology. Similarly, examples of mine drainage are related to coal mines in Donbas (Russia), Ruhr coalfields (West Germany), and in Australia, India and Canada with predominant Shortwall mining. In India the coal mines are facing serious problems due to acid mine drainage, particularly in the lower Gondwana

coal of the Barakar formation, and the Tertiary coal of Assam (Jamal *et al.*, 1991). AMD is equally causing environmental problems in the Cornwall coal fields of England following centuries of coal mining.

Ghana is second to South Africa in the whole of Africa in terms of gold production, the third largest of aluminium and manganese and a major producer of diamond and bauxite. Presently, out of about fifty (50) mining companies in the country, twenty five (25) are large mining companies and operate on a large scale (Armstrong, 2008). Due to the extensive mining activities arriving and on-going in the country, proactive measures need to be developed and implemented to arrest significant mining challenges such as ARD which happen to be a prominent problem confronting mining countries worldwide.

A previous study by Ankomah-Appiah (2011) to assess the impact of ARD of dissolved trace metals that are leached into underground and surface water in some selected communities within the Hwini-Butre and Benso (HBB) mine sites reported Fe, Cu, Mn, Zn, Cd, Pb, and As concentrations were below their respective Ghanaian EPA permissible limits. Since ARD is a persistent problem and takes time to impact mine catchment communities, which are quite distant from the mine operational areas, it is imperative to assess the quality of water resources within the immediate environs of potentially acid generating rock waste dumps.

1.2 Problem statement

The Subriso East Waste Rock Dump (SEWRD) is made up of overburden mined from the Subriso East Pit. Waste rock from this pit comprises Non-Acid Generating (NAG) and Potential Acid Generating (PAG) material. During the emergence of acidic discharges from SEWRD, pH reported was as low as 2.5.

However, discharges were treated and dump subsequently encapsulated and rehabilitated to prevent air-water interaction with the PAG material. Nonetheless, oxide or laterite may gradually be eroded, making way for water to percolate into the dump resulting into the formation and discharge of acidic water into creeks and groundwater. The study site is in the wet semi-equatorial climatic zone of Ghana that is characterized by an annual double maxima rainfall pattern occurring in the months of April to July and from September to November. Thirty year data (1979 to 2009) for the project areas reported a mean annual rainfall of 1,745.5 mm (GSWL, 2009). This affirms the presence of conditions (water and air) that promote acid drainage and possible pollution of water resources in the area.

According to Oelofse (2008), an aggravating characteristic of ARD/AMD is its persistence. Impacts linked to AMD are not limited to pollution of surface and groundwater, but is also accountable for the degradation of soil quality, aquatic habitats, and dissolution and seepage of heavy metals into the environment (Adler and Rascher, 2007). These metals may cause poisoning leading to the damage of mental and central nervous systems, damage to the composition of blood, and all vital organs. Metal accumulation in the body results in progressive muscle and neurological degenerative diseases. Low concentrations of heavy metals can pose serious health effects. It is therefore important to understand their source, mode of bio-availability and ingestion pathways (Chapman, 2011). ARD is a problem because the vast majority of living organisms live and survive either at or near pH 7. The discharges acidifies the waterways and either kill or impedes the growth of the river ecology, with the effects more pronounced on vertebrate life than on plant and unicellular life (McGinness, 1999).

Ground and surface water are the main sources of drinking water and water for domestic purposes for the mine catchment communities. Given the persistent nature of ARD/AMD and also the close proximity of the major river (Subri River) to the SEWRD dump, it is imperative to investigate the quality of water resource within the immediate environs of the dump. This will help detect pollution cases proactively, and the appropriate remediation measures implemented to address the problem.

1.3 Objective of the study

The general objective of this study was to assess the impact of the Subriso East Waste Rock Dump on ground and surface water quality within the immediate environs of the dump. The specific objectives were:

- i. to assess the acidity, sulphate, total dissolved solids (TDS) and electrical conductivity levels of ground and surface water within the study area;
- ii. to determine metal concentrations (i.e. Fe, As, Cd, Cu, Mn, Ag, Pb and Zn) of ground and surface water in the immediate environs of the Subriso East Rock Waste Dump;
- iii. to determine the effectiveness of the encapsulation by comparing results from monitoring boreholes around the acid rock dump with results from reference bores.

1.4 Research Questions

To meet the objectives detailed above, answers would be sought for the following research questions:

- i. What are the concentrations of metals (ARD indicators) in ground and surface water in the study area?
- ii. Do concentrations of the various indicators reported pose health and environmental quality problems?
- iii. Was the encapsulation for PAG material effective and meeting the intended purpose?



CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Description of acid mine drainage phenomenon

Acidic Mine Drainage (AMD) is a sternly corrosive waste stream linked with mining of gold, coal and other sulphide containing ore. Excavation of the ground for such mineral deposits exposes these sulphur bearing compounds to favourable conditions, including water and atmospheric influences which comprises oxygen and oxidizing bacterial e.g. *Thiobacillus Ferrooxidans* (Johnson and Hallberg, 2003). These conditions undergo chemical reaction with the sulphur bearing minerals, yielding AMD (Johnson and Hallberg, 2003). Evangelou and Zhang (1995), characterised AMD as extremely acidic discharge or seepage with low pH (i.e. as low as 2), due to oxidation of pyrite and other iron sulphides (FeS_2) in mining wastes, tailing dumps, and overburdens associated with mining processes enriched with soluble iron, manganese (Mn), aluminium (Al), sulphate (SO_4), and heavy metals for example lead (Pb), mercury (Hg), Boron (B), etc.

Even though AMD is generally identified with distinctly acidic nature, it can nonetheless have a near neutral or slightly alkaline pH depending on the geology of the rock and metal sulphide composition. This is because the presences of calcareous minerals such as calcite and dolomite have the potential to “buffer” the pH of the mine water, but whether neutral or acidic, the drainage/seepage from many mining operations has high concentrations of dissolved solids, ranging approximately from 200 mgL^{-1} to $10,000 \text{ mgL}^{-1}$. Consequently, in virtually all cases of AMD, the discharges have highly polluting effects on receiving water resources (Burkea and Banwart, 2002).

The chemical environment leading to the formation of AMD can be described in terms of two parameters, namely; oxidation potential (Eh) and acidity (pH) within which the solid phases

of iron, carbon, and sulphur are of the greatest importance in terms of reactions relating to the generation and the neutralization of acidic waters (Mack and Skousen, 2007).

2.2 Generation of Acid Rock Drainage (ARD) and Metal Leaching (ML)

Acid Rock Drainage (ARD) arise once sulphide-rich minerals, for example pyrite (FeS_2), are exposed to atmospheric air and water (Lacelle *et al.*, 2007). Pyrite oxidation is a complicated process that involves a series of redox reactions, hydrolysis, and complex ion formations that fluctuate as a function of pH. ARD generation can be observed as a three-stage process well-defined by the pH of water interacting with the sulphide minerals (Egiebor and Oni, 2007).

Figure 1 shows the three stages.

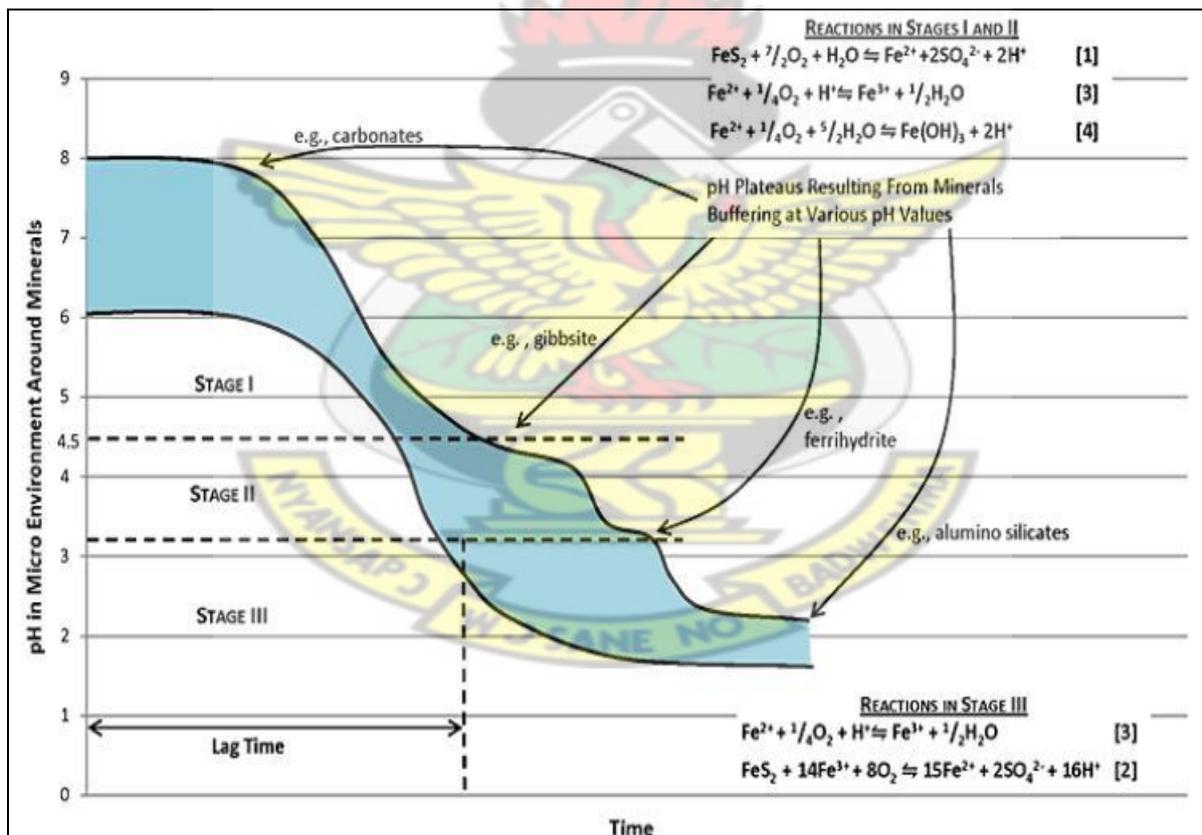


Figure 1: Stages in the formation of acid rock drainage (Walls, 2010).

In stage 1, pyrite undergoes chemical reaction (i.e. oxidation) with water and oxygen to form sulphuric acid at near-neutral pH. The chemical equation for this step is shown below:

→

Microbial oxidation of sulphide can also be catalysed by acidophilic bacteria like *Thiobacillus ferrooxidans* (Egiebor and Oni, 2007).

Stage 2 occurs under weakly acidic pH conditions. Ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which precipitates as ferric hydroxide, $\text{Fe}(\text{OH})_3$, and releases more acidity in the form of hydrogen ions (H^+), thus further lowering the pH. This stage is shown in the two equations below:

→

→

While the pH value drops to below 3.5, a number of ferric iron remains in solution and oxidizes supplementary pyrite directly, in accordance to the below equation:

→

Under the acidic conditions of stage 3, *T. ferrooxidans* speedily catalyses the process via further oxidation ferrous iron to ferric iron. This increases the overall rate of acid production through numerous orders of magnitude. A rapid cyclic process ensues, which yields large quantities of acid and corresponding release of heavy metals into solution (Egiebor and Oni 2007).

Metal leaching (ML) is elevated by ARD owing to the high solubility of most metals under acidic conditions. Nonetheless, environmental impacts could happen from ML under neutral or alkaline drainage conditions. This is the illustration principally for geological materials with elevated levels of arsenic, molybdenum, selenium, or zinc (British Columbia Ministry of

Water, Land and Air Protection, 2002). The precise metals established in ARD/ML flows differ depending on the geological factors. Research has been largely concentrated on mining-related ARD since the mining industry presents the greatest source of ARD/ML. In Canada, it was determined that 155 acid-generating mines exists (Feasby and Jones, 1994). According to Feasby *et al.*, 1997, approximately 200 million tonnes of acid-generating tailings and 420 million tonnes of acid-generating waste rock were reported in BC in 1997. However, these are increasing at a rate of 25 million tonnes per year.

2.3.0 Factors influencing acid drainage from sulphides

A mine's potential to produce acid and leach metals or other related contaminants is highly dependent on numerous factors and is site-specific. Akcil and Koldas (2006), categorized these site-specific factors into generation factors, control factors and physical factors. Akcil and Koldas (2006), also reported that the primary factors that regulate the rate of acid generation comprises pH, oxygen content of the gas phase, temperature oxygen concentration in the water phase, , chemical activity of Fe^{3+} , degree of saturation with water , surface area of exposed metal sulphide, bacterial activity, and chemical activation energy required to initiate acid generation.

2.3.1 Generation Factors

Generation factors regulate the capacity of the material to yield acid. Water and oxygen are basic necessities to generate acid drainage; some bacteria augment acid generation. Water serves as a medium for bacteria and a transport medium for oxidation products and additionally as reactant. Availability of atmospheric oxygen is essential to drive the oxidation reaction. Oxygen is predominantly significant in keeping the rapid oxidation catalysed by bacteria at pH values below 3.5. The sulphides oxidation is considerably reduced when the

concentration of oxygen in the pocket of air spaces of mining waste units is below 1 or 2 percent. Different bacteria adapt well to different pH levels and physical factors. For example, for bacteria to survive or thrive well, environmental conditions need to be favourable. For instance, *A. ferrooxidans* is most active in water environment with a pH of less than 3.2. However, in unfavourable conditions, the bacterial influence on acid generation is minimal. This obvious significance of environmental conditions, clarifies the contradiction in reported experimentation that showed that bacterial influence varies from major to negligible. In circumstances where bacterial acceleration is significant, there are other factors that determine the degree of bacterial activity relating to the rate of acid generation. The bacterial type and population sizes change as growth conditions are improved (Rosner, 1999).

2.3.2 Chemical Control Factors

Chemical control factors regulate the oxidation reaction products. These factors take account of the ability of the generation rock or receiving water to neutralize the acid or to change the effluent features through addition of metal ions mobilized by residual acid. Alkalinity released when acid reacts with carbonate minerals is a vital means of diminishing acid production and is capable of delaying the onset of acid production for extended periods or indefinitely.

The very common neutralizing minerals include calcite and dolomite. Products of the oxidation reaction including hydrogen ions and metal ions can react with other non-neutralizing components. Potential reactions embrace ion exchange on clay particles, gypsum precipitation, and dissolution of minerals. The dissolution of other minerals adds to the contaminant load in the acid discharges or drainage. Instances of metals occurring in the dissolved form include manganese, lead, zinc, aluminium, copper, and others (Rosner, 1999).

2.3.3 Physical Factors

Physical factors influencing acid drainage from sulphides include the physical features of the waste, and the local hydrology and the order of arrangement of acid generating and neutralizing materials. The physical properties of the material, such as permeability, particle size, and physical weathering characteristics, are vital to the acid generation potential. Although tough to weigh, all these factors influence the potential for acid generation. It is therefore an important consideration for waste management long term. The particle sizes are a major concern since it affects the surface area exposed to weathering and oxidation (i.e. surface area is inversely proportional to particle size). Coarse grain material found in waste rock dumps, for example, exposes less surface area. Nonetheless, this could allow air and water to infiltrate deeper into the unit, thus exposing more material to oxidation and eventually produce more acid. Circulation of air in coarse material is supported by the wind, and changes in barometric pressure (Rosner, 1999).

2.4.0 Environmental consequences of ARD

ARD is amongst the most challenging types of water pollution owing to its serious contaminating nature, intricate solution techniques, and remediation difficulties (Grande *et al.*, 2004). The acidity and mobilization of heavy metals related to the dissolution of pyrite has several adverse effects on both aquatic ecosystems as well as human communities.

Contamination caused by ARD may render aquatic ecosystems becoming absolutely sterile. The bottom-dwelling communities (benthic organisms) in streams are principally vulnerable to metal precipitation ensuing from lowered metal solubility once the ARD gets to more alkaline streams (DeNicola and Stapleton, 2002). Metal precipitates together with solid ferric hydroxide formed become heavy sedimentation that covers or blankets the stream. The

stream becomes discoloured by the "blanket" and covers up flora and/or prey on which higher aquatic organisms depend. In addition to covering food, the "blanket" also blocks out sunlight required for photosynthesis by producers (e.g. plants). After the plants dead, the remaining aquatic cycle is distressed and eventually the stream becomes unproductive (Mallo, 2011). Chemical stresses can destroy the biodiversity and ecological integrity of the algae and invertebrates of bottom dwellers (benthic communities).

Aquatic organisms feeding on the benthic organisms, algae and other invertebrates may well lack the resilience required to endure ARD conditions. A study of the Loyalhanna River, Westmoreland County established that cold-water fisheries degraded at pH values less than 6 and warm-water fish was unable to survive in streams that had pH values averaging below 5.5 (McGill, 1972). Fish and other organisms are as well sensitive to aluminium levels above 0.2 mg/L (DeWalle *et al.*, 1995). Heavy metals may as well bioaccumulated within the fatty tissues of organisms (Grande *et al.*, 2004). Whilst the persistent heavy metals accrue and build up the food chain in the process of bio-magnification, the fatty tissues of fish and other larger aquatic organisms turn out to be more concentrated with toxic heavy metals in comparative to the surface water.

Damage to the aquatic ecosystem inevitably impacts human communities as many local fishers certainly will like catching and consuming fish from surrounding creeks (Joseph, 2004). Eating fish in creeks with possibly toxic levels of heavy metals can result in acute and chronic health effects (Grande *et al.*, 2004). "Yellow boy" precipitation similarly degrades the aesthetic qualities of the creek (Hill and MacDougall, 2005).

ARD additionally impacts public health by threatening the safety of drinking water supplies and imposing huge financial burdens. Sulphate concentrations above the secondary maximum contaminant level may yield laxative effects in humans and infant diarrhoea (USEPA and USCDC, 1999). Sulphate and dissolved heavy metals in water supplies can result into several health concerns. High levels of aluminium in drinking water lead to concentration in infant bones and cause health defects and an increase in the risk of developing Alzheimer's disease later on in life. Iron, though an essential nutrient for humans, it can be lethal in very high doses (World Health Organization, 2003). A major challenge faced in the supply of potable water to Enugu is the acid mine drainage phenomenon caused by coal mining undertakings in the area (Mallo, 2011). The AMD water has high values of sulphate, iron ions, and very low pH. Mallo (2011) reported in a study pH of 2.08 at Onyeama Mines, 6.1 at the Iva Valley Coal Mine, 2.3 at the Okpara Mine and 6.3 at the active Obwetti fireclay mine. Sulphate concentrations are known to be high in mine waters. Mallo (2011) reported as well sulphate values of 310 mg/l, 420 mg/l, 58 mg/l, and 178mg/l for the Onyeama, Okpara, Iva Valley and Obwetti Mines correspondingly. The mine water is therefore acidic and corrodes mining and plumbing equipment. The water has as well high total dissolved solids (TDS) levels and also moderately hard (Ezeigbo and Ezeanyim, 2006). Over 60% of the mine drainage compositions from three mine pits were slightly acidic in Ishiagu Lead and Zinc (Pb/Zn) mine. The mean pH values ranged from 6.7 to 8.1 in wet season and 6.1 to 7.3 in dry season (Aroh, 2003). Eze and Uko (2003) recorded a much lower mine pH of 5.6 and 5.1 for wet and dry season respectively in a separate study.

2.5.0 Health effects of heavy metals

Metals have beneficial or harmful biological effects (Caussy *et al.*, 2003). Heavy metals are well-known for their toxicity in humans, aquatic life and the environment. Therefore, heavy metals in water have been a major concern for several years due to the fact that they cannot be degraded biologically comparative organic pollutants. Heavy metals in drinking water present public health problems due to their absorption and accumulation in organisms (Chiron *et al.*, 2003). Although, certain heavy metals such as Fe, Cu, Co, Mn, Zn and Cr are essential elements for humans, and their deficiency could induce illness including clinical abnormalities. Conversely, at high doses, essential elements can as well cause toxic effects. Lead (Pb), mercury (Hg), cadmium (Cd) and arsenic (As) are not renowned essentials for neither animal nor humans (Caussy *et al.*, 2003).

ARD mobilizes heavy metals into solution increasing concentration to levels harmful to aquatic ecosystems, riparian communities and probably human health. Once acid drainage is generated, metals are leached into the surrounding environment, and become readily accessible to biological organisms (Murphy *et al.*, 1997). Animals can accumulate metals by consuming plants, or drinking water with high metal concentrations. However, they are unable to excrete the metals but rather accumulate mostly in their organs as well as the bones, skin, and hair. Fish also accumulate metals from the water in which they live and organisms they eat. Bottom feeders are predominantly vulnerable to metals bioaccumulation since they can ingest metal laden sediments (Murphy *et al.*, 1997).

2.5.1 Cadmium (Cd)

According to Bernard (2008), cadmium is an element which is naturally occurring and the most abundant. Cadmium is highly carcinogenic for living beings. It occurs in nature in mineral form and extracted from cadmium ore known as greenockite (Agency for Toxic Substances and Disease Registry, 1999a).

Cadmium compounds are very toxic to plants, animals and humans (Senthil *et al.*, 2010). The liver, placenta, kidneys, lungs, brain and bones have been identified as target organs for Cd toxicity (Sobha *et al.*, 2007). Cadmium is known to have no physiological function within the human body. Once absorbed, Cd accumulates in the body throughout the life of the organism (Bernard, 2008). Low concentration of Cd, can adversely affect the metabolic processes in animal body (Bernard, 2004; Nordberg *et al.*, 2007). Cadmium intoxication can lead to kidney, bone and pulmonary damages (Godt *et al.*, 2006). Kocak and Akc (2006) indicated that cadmium toxicity affects numerous organs including the testis, liver, lung, and hematopoietic system in animals. Wright *et al.*, (1997), also detailed that excessive intake of Cd in cattle can lead to, poor growth, loss of appetite, anaemia, abortions and teratogenicity effects. Additionally, excessive intake of Cd alters the metabolism of Zn and Cu in animals (Wright *et al.*, 1997).

Besides the aforementioned findings, other evidence indicated that mitochondrial dysfunction results due to cytotoxicity of cadmium (Sokolova, 2004). Acute toxicity in humans can occur at levels of 1,500 to 8,900 mg or 20 to 30 mg/kg which leads to human fatalities (Agency for Toxic Substances and Disease Registry, 1989b). Furthermore, high doses of Cd are acknowledged to cause gastric annoyance that result in abdominal pain, vomiting, and diarrhoea (Agency for Toxic Substances and Disease Registry, 1989b). Abdominal and

muscular cramps, overtiredness headache, shock and ultimately death are examples of acute toxicity symptom (USAF, 1990).

It has been established also that significant quantities of Cd can be absorbed from cigarette smoke which causes toxic effects on human health. The deleterious effects are particularly on the liver, kidneys, and vascular systems, however, most detrimental effects have been noticed on reproductive tissues and developing embryos (Thompson and Bannigan, 2008). Thompson and Bannigan (2008) detailed that studies on Cd toxicity in humans and animals are well documented. Krajnc *et al.*, (1983) reported that Cd contamination in animals ensue through forage, feed and water consumption whilst in humans Cd contamination occur through the consumption of dairy products such as meat and milk. Another study concentrated on the relationship between Cd concentration in organs of cattle and Cd contents in soil and reported that contamination in cattle organs was due the consumption of forage growing on contaminated lands/soils (Staniskien and Garalevicien, 2004).

The International Agency for Research on Cancer classified Cd and its associated compounds in group 2B but limited proof of carcinogenicity in animals. The drinking water standard and daily intake into human body for Cd is 5 µg/l and 0.28µg/kg respectively (Navrátil and Minařík, 2002).

2.5.2 Arsenic (As)

Arsenic is amid the most toxic metals known in the environment. As has three valence states: As (0), As (III) and As (VI) (Agency for Toxic Substances and Disease Registry, 2000). Inorganic As is much more toxic than organic form. It is ubiquitous metal present in water, soil and air (Matschullat, 2000). Arsenic enters air through the burning of materials contaminated with As, for example wood, metal alloys, coal, and arsenic wastes (Agency for

Toxic Substances and Disease Registry, 1989). Arsine gas, generated from microelectronics industries, metallurgical and mining processes is a highly dangerous source of poison.

Chronic As poisoning leads to weight loss and loss of appetite. This is accompanied by gastrointestinal disorders similar to gastroenteritis. Acute As poisoning in humans is characterized by central nervous system effects, resulting into coma and eventual death. Inorganic As^{3+} methylate in the liver of most mammals, while As^{5+} is reduced in the blood before methylation in the liver. Arsenic species present in human urine disclose metabolism to decrease toxicity, and the nature of the contaminating source. The International Agency for Research in Cancer classifies As in group 1; however, there is inadequate evidence for carcinogenicity in animals and sufficient carcinogenicity evidence in humans (Navrátil and Minaóík, 2002). According to Martin and Griswold (2009), ingestion of very high levels can possibly result in death. Daily intake into the human body is 0.7 micrograms of As per kg of body weight (Navrátil and Minaóík, 2002).

The Occupational Safety and Health Administration (OSHA) has established a permissible limit of $10 \mu\text{g}/\text{m}^3$ for As in air. The Environmental Protection Agency of the United State (USEPA) has specified the maximum contaminant level for arsenic in drinking water to be 10ppb.

2.5.3 Silver (Ag)

Silver is a naturally occurring element in the environment in addition to other elements such as chloride, sulphide, and nitrate. Ag is often obtained as a by-product during the recovery of copper, zinc, lead, and gold ores.

Human activities including cement manufacturing, processing of ores, and the burning of fossil fuel could release Ag into the air (Agency for Toxic Substances and Disease Registry, 2011).

Long term exposure to high levels of Ag may result in a condition known as argyria (a blue-gray discoloration of the skin and other body tissues). Short term exposures to Ag may as well cause Ag to be deposited in the skin and other parts of the body but this is not known to be harmful. Argyria is a permanent effect, and more of a cosmetic problem and not harmful to health. Breathing problems, lung and throat irritation, and stomach pains have resulted due to exposures to high levels of Ag in air, lung and throat irritation, and stomach pains. Direct contact of the skin with Ag can cause mild allergic reactions including rash, swelling, and inflammation in some people. Animal studies uncovered that swallowing Ag results in the deposit of Ag in the skin. Additionally, a study using mice established that the animals exposed to Ag in drinking water were less active than unexposed ones (Agency for Toxic Substances and Disease Registry, 2011).

2.5.4 Lead (Pb)

Lead naturally occurs as bluish-grey metal in small amounts in the earth's crust (Agency for Toxic Substances and Disease Registry, 1993). Pb is a ubiquitous element found in rocks, soil, plants, animals and humans. However, it occurs naturally in quite low level (Griffith, 2002).

Lead is moderately toxic to animals and plants but its toxicity is greater than that of chromium, manganese, barium, and zinc but lower than that of mercury, cadmium, and

copper. On the other hand, tetraethyl lead is more toxic than either the methylated derivatives or inorganic compounds.

Pb is physiological and neurological toxicant to humans. Short term (acute) Pb poisoning may results in a dysfunction in the kidney, reproduction system, liver and the brain causing sickness and death (Odum, 2000). At extremely low concentrations, Pb exerts great threat (Kazemipour *et al.*, 2008). A particularly serious effect of lead toxicity is its teratogenic effect. Lead poisoning as well causes inhibition of the synthesis of haemoglobin; cardiovascular system and acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS). Anaemia, fatigue, gastrointestinal problems and anoxia are other chronic effects of Pb poisoning. Lead can also cause high blood pressure, muscle and joint pains, and pregnancy difficulties (Odum, 2000). Pb is also known to affect the intelligence quotient and can lead to loss of hearing (Goyer, 1996; Ryan *et al.*, 2000). Centers for Disease Control and Prevention (CDC) also reported that a person with blood Pb level of 10 $\mu\text{g}/\text{dL}$ or beyond is a matter of great concern. Pb also impairs the development of children even at blood Pb level below 10 $\mu\text{g}/\text{dL}$ (Agency for Toxic Substances and Disease Registry, 2007).

According to Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH) and American Conference of Governmental Industrial Hygienists (ACGIH), the permissible limit for Pb in the air of workplace is $50\mu\text{g}/\text{m}^3$ (OSHA, 2003; ACGIH, 2007). While in accordance with FDA calculations, the permissible limit regarding Pb exposure that a person can consume without being ill is $0.5\mu\text{g}/\text{mL}$ (FDA, 1994; FDA 1995).

2.5.5 Manganese (Mn)

Manganese is also one of the most abundant elements in the earth's crust and is extensively dispersed in soils, sediments, rocks, water, and biological materials. It is an essential trace element for all known living organisms. Mn (II) ions work as cofactors for a number of enzymes in higher organisms. Mn is required for the creation of connective tissue and bone, for growth, embryonic development, and reproductive functions. The chief sources of man-made environmental Mn pollution ascend from mining operations and steel manufacturing. According to World Health Organization data, the daily intake of airborne Mn by the general population in areas without Mn-emitting industries is lower than 2µg/day. Contrarily, in areas with major foundry facilities, intake could increase to 4–6 µg/day, and in areas related to ferro- or silico-manganese industries, Mn could be as high as 10µg/day, with peak values exceeding 200 µg/day (Ykateryna *et al.*, 2011).

Chronic Mn poisoning is a recognized health hazard linked with the mining and processing of Mn ores. Even though the principal source of human exposure to Mn is through water and food, other exposure could occur through air adulterated with Mn emissions. Mn poisoning has been associated to impaired motor skills, metabolic processes and cognitive disorders. Environmental Mn pollution and its long-term effect on the health of the pediatric population living in Mn-mining areas is a major concern (Ykateryna *et al.*, 2011).

2.5.6 Aluminium (Al)

Al is a very reactive element and does not exist as free metal in nature. It combines with other elements, mostly with oxygen, fluorine and silicon. These chemical compounds are normally found in soil, minerals, rocks (principally igneous rocks), and clays. Mining and processing of aluminium ores or the production of aluminium metal, alloys, and compounds produces

high levels of Al in the environment. The concentration of Al in natural waters is generally below 0.1ppm unless the water is very acidic (Agency for Toxic Substances and Disease Registry, 2008).

2.5.7 Copper (Cu)

Cu is a vital element in mammalian nutrition as a component of metalloenzymes in which it functions as an electron donor or acceptor. Exposure to high levels of Cu can cause several adverse health effects. Human exposure to Cu happens primarily from the consumption of food and drinking water. Acute Cu toxicity is commonly linked with accidental ingestion but some members of the population may be more susceptible to the adverse effects of high Cu intake owing to genetic predisposition or disease (Stern *et al.*, 2007). Excessive human consumption of Cu could lead to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression. Serious gastrointestinal irritation and likely necrotic changes in the liver and kidney can also ensue (Argun *et al.*, 2007). Cu is present in normal human serum (i.e. the liquid part of blood) at concentrations of 120-140 μ g/L. Signs of toxicity is seen whenever the Cu concentration rises significantly above aforementioned range (Bradl, 2005; Wright and Welbourn, 2002).

2.5.8 Iron (Fe)

Fe is the fourth most profound element in the earth's crust, and essential for both animal and plant life. Fe rusts in damp air and dissolves readily in dilute acids. It is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous compounds and the trivalent iron (III), or ferric compounds (MDH, 2006). Ferrous and ferric Fe are soluble in water, nonetheless ferrous Fe is easily oxidized to ferric hydroxide (Essortment,

2002). Fe in animal products is absorbed faster into the human body than Fe in plant products. Fe is a vital part of haemoglobin, the red colouring agent of the blood that transports oxygen through our bodies (Young, 2005c). Ingestion accounts for most of the toxic effects of Fe since it is absorbed rapidly in the gastrointestinal tract. The corrosive nature of Fe further increases the absorption. Target organs are usually the liver, kidneys and cardiovascular system. It results in elevated blood pressure; cognitive and neurobehavioral effects in children & adults. Lead exposure *in utero*, in infancy and childhood may result in low birth rate, anaemia, neurological impairment, IQ deficits, renal alterations, colic, growth retardation or impaired metabolism of vitamin D

(<https://noshipatavoca.s3.amazonaws.com/NoShipFactsheetHeavyMetals.pdf>).

2.5.9 Zinc (Zn)

Zinc is amongst the most common elements in the earth's crust. It is as well an essential element for all living things. Pure zinc is a bluish-white, shiny metal. Zn in the powdered state is very explosive and could burst into flames if stored in a damp place. Zn however does not degrade nor can it be destroyed (Argonne National Laboratory, 2007). Zn, though an essential element in our diet, too little or too much can be harmful. Without adequate dietary consumption, people could experience a loss of appetite, reduced sense of taste and as well as smell, decreased immune function, slow healing of wounds, and skin sores. Lack or too little zinc could as well result in poorly developed sex organs and also result in retarded growth in young men. Additionally, lack of adequate Zn in pregnant women could result retarded growth in babies. Contrarily, too much Zn has harmful effects and generally begins at levels from 10 to 15 times greater than the commended dietary allowances of 5 mg per day for infants, 12mg per day for women, and 15 mg per day for men. Consuming large quantities of Zn could result in stomach cramps, nausea, and vomiting. However, for extended periods, Zn

can cause anaemia, lower the levels of high-density lipoprotein cholesterol and damage to the pancreas. Inhaling dust or fumes with large amounts of Zn can cause acute metal fume fever. Acute metal fume fever is an immune response upsetting the lungs and body temperature. No known health effects from inhaling lower levels of Zn over long periods of time has been established. Like wisely, it is also not known whether high levels of Zn affect reproduction or cause birth defects in humans. Conversely, low birth weight, infertility, and skin irritation have been reported in laboratory animals including guinea pigs, rats, mice, and rabbits given high doses of Zn (Argonne National Laboratory, 2007).

2.6.0 Control of acid mine drainage

ARD generation may be prevented or significantly reduced through exclusion of one or more of the principal components involved in the sulphide oxidation process. Waste containing reactive sulphides, oxygen, and water are the principal components that facilitate the process. Practically, the initial stage of the oxidation reaction cannot ensue, thus no acid generation would occur in the absence of these components. Additionally, bacterial activity, pH, temperature, and the presence of buffer or alkaline minerals are factors that influence acid generation in terms of the rate of production.

Generation of acid can as well be reduced through the control of the environment at source in order to impede and retard the rate of production to an insignificant level. Where sulphides minerals in rock waste cannot be isolated, deprivation of oxygen and water and control of pH become the principal approaches of controlling or suppressing ARD generation (MEND, 1997).

Acid mine drainage control could be carried out where AMD is in existence or predicted. Source control approaches involves the direct treatment of the acid-producing rock to cease or retard the production of acidity, while treatment approaches induce chemicals directly to acidic water discharges from rock mass. Certain control approaches/methods are suitable for abandoned mines while others are only practically on active operations. Some techniques yielded less than 100% controls of acidity produced on-site, and are therefore considered failures according to some people. Getting rid of substantial amount of the acid or metal loads in a watershed through a control strategy could improve the health of a stream to the extent of re-introducing certain fish species or regenerating some designated uses of the stream. On the other hand, a method could as well be combined with another partial control system to achieve effluent limits. Partial control methods are mostly less costly; using a combination of such techniques is hence financially attractive (Skousen, 1996).

2.6.1 Alkaline Amendment to Active Mines

Some alkaline alterations can control AMD from spoil and refuse (Rose *et al.*, 1995). All alkaline alterations or amendment schemes rely on Acid Base Accounting (ABA) or kinetic tests to determine the requisite alkalinity for neutralization of pyritic materials. Special handling of overburden pursues blending acid producing and neutralizing rocks in the mining process to create a neutral rock mass. Acid producing materials can be compacted or encapsulated within the spoil (Meek, 1994). Insufficient alkalinity availability in the spoil or waste will therefore require external sources of alkalinity to avert potential impacts (Skousen and Larew, 1994). Limestone is regarded the least costly and most the readily accessible source of alkalinity. Limestone has neutralization potential varying between 75 and 100% and safe to handle. Conversely, it has no cementing properties and thus cannot be used as a barrier. Fluidized Bed Combustion (FBC) ashes commonly have neutralization potential of

between 20 and 40%, and tend to stabilize in cement when wet (Skousen *et al.*, 1997). Additional power-generation ashes, such as flue gas desulfurization products and scrubber sludge, could as well have significant neutralization potential, thus makes them suitable alkaline amendment materials (Stehouwer *et al.*, 1995). Kiln dust from lime and cement kilns contain related levels of CaO, thus between 15 to 30% as FBC ash, but also contains 50 to 70% unreacted limestone. Kiln dust absorbs moisture and hardens when wet (Rich and Hutchison, 1994), thus widely used in stabilization and as barrier material. Additionally, lime mud, grit, and dregs from pulp and paper industries also serve as neutralizing products. When fresh, steel slags have neutralizing potential varying from 45 to 90% and could be used as an alkaline amendment and also as a medium for alkaline recharge trenches. Slags are produced from a number of processes; care is thus required to ensure that slags are not prone to leaching metal ions including Cr, Mn, and Ni. Some studies detailed the use of phosphate rock in controlling AMD. The phosphate reacts with Fe released during pyrite oxidation to form insoluble coatings (Evangelou, 1995). However, phosphate costs more than other calcium-based amendments and it is well required in almost the same quantity (Ziemkiewicz and Meek, 1994).

2.6.2 Land Reclamation

Backfilling coupled with re-vegetation are effective approaches to reduce acid loads from an active mining operation or abandoned mine lands. Backfilling alone is capable of substantially reducing the acid load and improving water quality to meeting effluent limits (Faulkner and Skousen, 1995). Flow of water from seepages could be reduced through diversion and reclamation, and in some cases on sites where flow may not be reduced, the quality of water can change from acid to alkaline. Channelling or diverting surface water to control volume, direction and contact duration could be used to minimize the effects of

AMD. Surface diversion involves construction of drainage ditches to direct surface water rapidly from the site before infiltration or by providing impermeable channels for existing streams to carry water across the disturbed area (Skousen, 1996).

Water flow was reduced on 12 out of the 16 sites in West Virginia where reclamation was accomplished on bond-forfeited and unreclaimed areas (Faulkner and Skousen, 1995). On those sites where flow was not reduced, water quality changed from acidic to alkaline. In only two out of 16 cases was the acidity increased in water, but flows were reduced dramatically causing 45% decrease in total acid load. Vegetation establishment greatly reduced the occurrence and amount of runoff compared to a barren tailings area in Montana. Runoff water from the vegetated area had a higher pH (6.2 vs 4.0), metal loadings of As, Cu, and Zn were also more than four orders of magnitude lower than the unvegetated area (Skousen *et al.*, 1998).

2.6.3 Dry Barriers

Dry barriers decrease the flow of water and oxygen into areas containing acid producing rock. These water control technologies (Skousen *et al.*, 1998) comprise impervious membranes, dry seals, grout walls and hydraulic mine seals. Surface barriers can accomplish substantial reduction in water flow through piles, however, it does not control AMD completely. Grouts could be used to segregate acid producing rock and groundwater. Injection of grout barriers can as well significantly reduce the volume of groundwater moving through waste stockpiles. Gabr *et al.*, (1994) reported that a 1.5-m-thick grout wall, installed by pumping a mixture of class F fly ash and Portland cement grout into vertical boreholes near the high wall, reduced groundwater inflow from the high wall to the spoil by 80%, resulting the drying up of some seepages while others reduced substantially in flow. At the

Heath Steele Metal Mine in New Brunswick, a soil cover was designed to exclude oxygen and water from a tailings pile (Bell *et al.*, 1994). It entailed a 10cm gravel layer for erosion control, 30cm gravel or sand layer as an evaporation barrier, 60cm compacted till of conductivity 10^{-6} cm/sec, 30cm sand, and pyritic waste rock. This barrier excluded 98% of precipitation, and oxygen concentrations in rock stockpile dropped from 20% to approximately 1%. In Upshur Mining Complex in West Virginia, Meek, (1994) reported reduction in acid loads by 70% when a 20 hectare waste rock stockpile was covered with a 39mil PVC liner.

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2.6.4 Alkaline Recharge Trenches

Alkaline recharge structures are surface structures designed to collect and divert infiltrating water through porous alkaline zones thus inducing water into the reclaimed. In several instances, recharge zones can be known from surface depressions and the construction of structures, whether trenches, funnels or pits, will provide an avenue for alkalinity. Infiltrating alkaline waters provide an alkaline front that migrates through the backfill, neutralizing alkaline acidity and increasing pH. The alkalinity can affect bacteria activity and cause the acid producing reaction to be decelerated or total ceased (Skousen *et al.*, 1998).

Alkaline recharge trenches were created onto an eight hectare, acid producing coal waste disposal site, and three years afterwards, the drainage water displayed 25 to 90% reduction in acidity with 70 to 95% Fe and SO₄ reductions (Nawrot *et al.*, 1994). Pumping water into alkaline trenches significantly increased the movement of alkalinity into the backfill and can change acid seepages to become alkaline (Ziemkiewicz *et al.*, 2000).

2.6.5.0 Chemical Treatment of Acid Mine Drainage

AMD generation from active and inactive mine sites often not in compliance with the water quality standards which are re-requisite for the safe discharge into the environment, it is therefore imperative to first treat to meet these standards. These polluting creeks are enriched with several undesirable species, including soluble iron (i.e. present as Fe^{2+} or Fe^{3+}), Mn^{2+} , Al^{3+} , SO_4^{2-} , Cl^- , PO_4^{2-} , as well as other heavy metals, such as Pb, Hg, and oxyanions (e.g. CrO_4^{2-} , AsO_3^- etc.), thus conventional and present treatment technologies comprises a series of integrated steps, either used repeatedly or in combination to augment each other, which are founded on several key methods (Kommatsias *et al.*, 2004). Each AMD discharge has a tendency to to be highly variable since AMD contains multiple combinations of acidity and metals, as such requires tailored treatment. The best option amongst the present treatment technologies depends on both technical and economic factors. The technical factors consist of the effluent volume, acidity levels, type and concentration of contaminants present, and preferred final water quality. The the economic factors are centred on the prices of reagents, labour, machinery and equipment, the duration needed for treatment, and risk factors.

Present and conventional approaches for treatment of AMD, involves neutralization by adding alkaline chemicals. Other chemicals such as flocculants and coagulants, aeration combined with oxidants (effectively used to enhance particle settling efficiency) are used sparingly in AMD treatment (Hendricks, 2005).

2.6.5.1 Active neutralization processes of acid mine drainage

Conventional active AMD treatment requires the installation of actively working plants, principally constituting precipitators, agitated reactors, clarifiers and thickeners, etc. This is a relatively costly operation owing to the cost of operation, maintenance, reagents, labour and

disposal of metal laden sludge (Gasea *et al.*, 1996). Alkaline materials used to neutralize AMD includes limestone, hydrated lime, pebble quick lime and dolomitic lime, sodium hydroxide (caustic soda), sodium carbonate (soda ash), ammonia potassium hydroxide, and magnesium hydroxide. However, the most common traditional method of AMD neutralization is founded on limestone and/or lime treatment (Gasea *et al.*, 1996; Evangelou and Zhang, 1995).

2.6.5.2 AMD treatment with limestone

Conventionally, limestone is seemingly one of the most suitable materials utilized in the neutralization of acid mine drainage due to its related advantages (Kommatsias *et al.*, 2004). Amongst the advantages is its ready availability in large quantities, cost advantage over other alkaline substitutes, its addition does not add harmful constituents to the water, and also for the fact that these carbonate-rich rocks require no preparation other than sizing. The limestone is transported to the source of the AMD and then added to the mine effluent in crushed form. Alternatively, the acidic water may be pumped into nearby wells containing the carbonate rocks. Once contact is established between limestone and the acidic water, Ca^{2+} ions are released, thus adding alkalinity to the system with subsequent rise in pH. The ultimate effect of the added alkalinity is the neutralization of acidic water from the AMD. Irrespective of the several advantages associated with the use of limestone, it does portray certain disadvantages which significantly affect its neutralizing capacity (Evangelou and Zhang, 1995). They include:

- The primary disadvantage of limestone application is that, the acid water is neutralized at the expense of added hardness (i.e. resulting effluent becomes saline)
- When the Fe rich AMD comes in contact with carbonate rocks, the limestone's reacting surfaces is rapidly coated by the precipitation of insoluble ferric hydroxide, a

process term as armouing. The outcome is that the rate of dissolution of the coated limestone is inhibited and its neutralizing capacity is consequently lessened. The armouing problem could be addressed by grinding the limestone into fine particles and higher sheering rates during agitation; however this process quite expensive.

- Due to the limited solubility of limestone and depending on the rate of flow of the water being treated, reaction between the acid and solid may not be complete. Even high quality limestone has need of long reaction periods, which makes the process very tedious and more expensive.

2.6.5.3 AMD treatment with lime

Lime neutralization is considered as one of the oldest methods used in AMD wastewater treatment. There are three basic lime treatment process utilized and they include pebble quick lime, hydrated lime and dolomitic lime (Zink and Aube, 2000).

However, preference is given to the use of hydrated lime and/or pebble quick lime due to the fact that dolomitic lime has the disadvantage of producing undesirable quantities of magnesium salts, precisely $MgSO_4$ (Epsom salts) dissolved in the water (Zink and Aube, 2000). These dissolved salts may complicate treatment of the formed effluent (secondary process waters), since magnesium is more difficult to remove than calcium.

The preparation of hydrated lime involves the addition of varying proportions of water and quicklime (CaO), a process called slaking. This yields hydrated lime slurry, which is then thoroughly mixed with the metal bearing wastewater. Pebble quicklime may also be used as treatment chemical on its own (Zink and Aube, 2000). Upon lime dosing of the acid mine waters, the derived alkalinity from the lime functions as a pH buffer and neutralizes the AMD, while concurrently precipitating the pertinent contaminants (metals, etc.).

As known of all AMD treatment technologies, the efficiency of the lime process is undesirably affected by some disadvantages, according to Chih-Huang and Huang (2004) includes:

- The cost related to lime treatment plants is extremely high, since there is the need to construct a lime treatment plant. Since the minimum solubility for the different metals often found in the polluted water occur at different pH values and the fact that the hydroxide precipitates are amphoteric in nature, maximum removal efficiency is not attainable at a single precipitation pH level. Lime precipitation is thus a limited process.
- Because the process often requires the aid of supplementary chemical reagents, such as oxidants and coagulants/flocculants to support particle settling, the cost those chemicals adds to the expenditure of the process.
- A major disadvantage of lime treatment borders the formation of voluminous metal hydroxide and gypsum sludge, which has large land requirements when being disposed of and can give rise to secondary wastes.

2.6.6.0 Passive treatment systems for AMD

For the fact that AMD will continue for decades after the decommissioning of the mine, other low-cost treatment schemes, known as passive systems have been developed as well (Gasea *et al.*, 1996). These systems typically require less operation and maintenance, since the treatment scheme makes use of naturally occurring geochemical and biological processes in order to improve the quality of the influent water. Three principle types of passive technologies have been developed for the treatment of AMD (Gasea *et al.*, 1996).

2.6.6.1 Aerobic wetlands

Aerobic wetlands consist of wetland vegetation in shallow (<30 cm), relatively impermeable sediments comprised of soil, clay or mine spoil. In aerobic wetlands, oxidation reactions results in the precipitation of metals as hydroxides and oxyhydroxides. According to Skousen *et al.* (2000), metals are retained within wetlands by the formation of metal oxides and oxyhydroxides; formation of metal sulphides; organic complexation reaction; exchange with other cations on negatively-charged sites; direct uptake by living plants; and metals can also be retained by filtration and adsorption/exchange metals onto algal mats. Additional beneficial reactions in wetlands include generation of alkalinity due to microbial mineralization of dead organic matter, microbial dissimilatory reduction of Fe oxyhydroxides and SO_4 , and dissolution of carbonates.

Aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe, Al, and Mn oxyhydroxides. The success of metal removal is dependent on dissolved metal concentrations, dissolved oxygen content, pH and net acidity of the mine water, the presence of active microbial biomass, and detention time of the water in the wetland. The pH and net acidity/alkalinity of the water are mostly important because pH influences both the solubility of metal hydroxide precipitates and the kinetics of metal oxidation and hydrolysis. Therefore, aerobic wetlands are best used in combination with water that contains net alkalinity to neutralize metal acidity (Skousen, 1996).

Analysis of 73 sites in Pennsylvania suggested that constructed wetlands are the best available technology for many post-mining ground water seeps, particularly those of moderate pH (Hellier *et al.*, 1996). However, those sites with net acidic discharges have much lower successful treatment efficiency. For example, the Rougeux #1 site has a flow of 5.2gpm and influent chemistry of 2.9 pH, 445 mg/L acidity as CaCO_3 , Fe 45 mg/L, Mn 70

mg/L, and Al 24 mg/L. After flowing through a two-celled aerobic wetland, pH increased to 3.2, acidity was decreased by 43%, Fe by 50%, Mn by 17%, and Al by 83%. The wetland cost about \$15/m² to build in 1992 and was severely undersized. Although there is improvement in the water, the wetland effluent did not conform to effluent limits. Two other wetlands constructed on the site show similar results (Hellier, 1996).

2.6.6.2 Anoxic Limestone Drains

Anoxic limestone drains (ALDs) can also be used to treat acidic waters. ALDs are limestone filled trenches through which acidic water is directed so the limestone can produce bicarbonate alkalinity via dissolution. ALDs are encapsulated with clay or compacted soil to avert AMD contact with oxygen. The effluent is held in a settling pond to allow pH adjustment and metal precipitation prior to being discharged to natural water courses. Where water quality is suitable for an ALD, it could be used to pre-treat the AMD prior to forcing the waters through subsequent passive treatment units (Zipper *et al.*, 1998).

When working as intended, ALDs can renovate acidic waters more cost effectively than wetland-based systems. ALDs, however, are not capable of treating all AMD waters. Significant concentrations of O₂, Al or Fe³⁺ in the water will cause an ALD to clog with metal hydroxides once a pH of 4.5 or above is reached. When excess Fe³⁺ is present in the AMD or is allowed to form from Fe²⁺ due to the presence of O₂, solid-phase Fe can precipitate within the ALD, while Al precipitation can occur as pH increases even when O₂ is excluded. If significant metal precipitation occurs within the ALD, the precipitant floc (a gel comprised of hydrolysed solid-phase metal precipitants) clogs the ALD's pores, hindering the waters from moving through the system and impairing its function. Once an ALD becomes

clogged with precipitants, it becomes non-functional and must be replaced, repaired, or abandoned.

Faulkner and Skousen (1995) reported both successes and failures among 11 ALDs with water pH being raised in all cases. However, three of the sites had pH values <5.0, indicating that the ALD was not fully functioning (pH in ALDs rise to 6.0). Water acidity decreased 50 to 80%, but ferric iron and Al will precipitate as hydroxides at this pH. With observed Fe and Al decreases in outflow water, some coating of limestone is probably occurring inside the ALD.

To maximize the probability that an ALD will not clog, Fe^{3+} , Al, and dissolved O_2 concentrations of the influent waters should all be below 1 mg/L. However, Skousen *et al.*, (2000) recommend that ALDs can be used successfully for AMD with dissolved O_2 concentrations of up to 2 mg/L and Al concentrations of up to 25 mg/L, when less than 10 percent of total Fe in the Fe^{3+} form. Although such ALDs can be expected to clog eventually, they can still offer cost-effective water treatment compared to other passive system processes during their time of operation. ALDs are far less costly to construct than anaerobic or vertical flow wetland treatment systems and can render less costly treatment on a lifecycle basis, even if periodic but infrequent repair and replacement is required (Zipper *et al.*, 1998).

2.6.6.3 Anaerobic/Compost wetlands

Anaerobic (or anoxic) wetlands add alkalinity, raise pH, and promote removal of metals. They appear similar to aerobic wetlands but have a thick, permeable, organic substrate that is either mixed with limestone or placed over a limestone bed. Compost wetlands promote anaerobic bacterial activity, resulting in sulphate reduction and the subsequent precipitation

of metal sulphides, as well as the generation of alkalinity. The combination of the organic substrate and limestone removes metals and adds alkalinity. The organic substrate keeps the water moving through the system free of oxygen so that the metal ions in the acid mine drainage remain in a reduced state. This prevents the coating or armouring of limestone. Chemical mechanisms that occur in-situ include metal exchanges, formation and precipitation of metal sulphides, microbial generated alkalinity, and formation of carbonate alkalinity (due to limestone dissolution). Since anaerobic wetlands produce alkalinity, they can be used in net acidic and high dissolved oxygen (>2 mg/L) AMD. Microbial mechanisms of alkalinity production are critical to long-term AMD treatment. Under high acid loads (>300 mg/L), pH sensitive microbial activities are eventually overwhelmed. At present, the sizing value for Fe removal in these wetlands is 10 grams per day per meter squared (Hedin and Nairn, 1994).

A constructed wetland was tested for its efficiency in treating acid mine drainage entering Slippery Rock Creek (Pennsylvania, USA) (Brenner, 2001). It was estimated that since the initial wetland construction in 1995, 39% of the acidity in the mine drainage was removed and approximately 192 kg of alkalinity was added. Sikora *et al.*, (2001) developed design criteria for removing manganese using subsurface wetlands. The authors reported that manganese removal was higher in limestone than gravel and was likely influenced by the higher pH in the limestone system (6.9) compared to the gravel system (5.5). Oxygen levels between 3 to 5 mg/L were required for favorable manganese removal. Lead and zinc removal (90% and 72%, respectively) from neutralized mine effluent was reported in a laboratory-scale constructed wetland system (Song *et al.*, 2001). Whole effluent toxicity tests using undiluted wetland effluent with fathead minnows and *Daphnia magna* (Goulet and Pick, 2001a) resulted in 100% survival of both types of organisms. A seasonal study was conducted to measure the retention and transformation of both dissolved and particulate iron

and manganese in a constructed wetland (Goulet *et al.*, 2001a). Results indicated that the wetland mediated transformation of dissolved iron and manganese to particulate species from spring to fall; however, during the winter, dissolved iron and manganese were released. Diel changes in iron concentration in a subsurface wetland were measured, with the lowest iron concentrations measured during the day and higher concentrations at night (Goulet and Pick, 2001b). As a result of these variable conditions, the authors suggest that wetland performance can be overestimated when based solely on samples collected during the day. The presence of cattails (*Typha latifolia*) was found to have no significant effect on the accumulation and partitioning of metals in the surficial sediments of a subsurface flow constructed wetland (Goulet and Pick, 2001c). Metal retention in a constructed wetland was evaluated by measuring metal content of a common pond snail (*Helisoma trivolvis*) (Goulet *et al.*, 2001a). The authors report that in general, metal concentrations in snails at the downstream end of the wetland were higher than those near the inlet and suggested that the higher concentration of metal particulates at downstream locations facilitated metal uptake from the metal precipitates. A comparison of heavy metal accumulation in a natural and constructed wetland receiving acid mine drainage indicated that loading rates and removal efficiencies for most metals were generally higher in constructed wetlands than natural systems (Mays and Edwards, 2001).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1.0 Study area

The study was conducted at Golden Star Wassa Limited (GSWL), a gold mining company in the Mpohor Wassa East District of the Western Region of Ghana. The Wassa East District occupies the mid-southern part of the Western region of Ghana with Tarkwa as its administrative capital. The population of the district is approximately 236, 000 and is mainly composed of the indigenous Wassa tribe, but all tribal entities in Ghana are well represented. Subsistence farming is the main occupation of the people, although rubber, oil palm and cocoa are also produced. Mining is the main industrial activity in the area (Avotri *et al.*, 2002). The area lies within the main gold belt of Ghana that stretches from Axim in the southwest, to Konongo in the northeast (Kortatsi, 2004).

The study was conducted specifically at the Hwini-Butre and Benso (HBB) concession of GSWL within the Western Region, about 35 km NNW of the Port of Takoradi and about 20 km SE of Tarkwa. The key communities within and outside the concession are Subriso, Ningo, Akyakrom, and Awonakrom. The Benso Township is approximately 5 km from the Benso mine site to the south and the Mpohor Township is approximately 2 km west of the Hwini Butre mining site. The project areas are close to well-developed infrastructure. The southern cluster of deposits is only about 15 km to the WNW of Takoradi, which has a major port and railway facility. The northern cluster is about 35 km NW of the port. Location of the HBB mine site is shown in Figure 2.



Figure 2: Map of Ghana showing GSWL operational areas (GSWL, 2009)

GSWL Operations are in the wet semi-equatorial climatic zone of Ghana that is characterized by an annual double maxima rainfall pattern. The first and largest peak occurs in June, whilst the second and smaller peak occurs in October. Around 53% of all rain in the region falls between March and July. The mean annual rainfall is approximately 1874 mm with maximum and minimum values of 1449 mm and 2608 mm, respectively (Kortatsi, 2004). The mean annual rainfall varies widely from year to year. Rain water in the area during 2000-2001 had a pH of 6.07 (Kortatsi, 2004). The area is very humid and warm with temperatures between 26-30°C (Dickson and Benneh, 1980).

3.1.1 Topography and Drainage

Around the HBB mine sites, the area between Mpohor and Subriso falls mainly within the catchment areas of the Butre River to the west and the Hwini River to the east. The topography is quite variable and results from the erosion of extensive peneplain (old weathered) surfaces. Around Mpohor, the topography is quite subdued. The broad valley bottoms of the main rivers (Hwini and Butre) are close to 10 m above sea level (ASL) and gain elevation gradually to the north to about 20 m. Progressing north from Hwini-Butre towards Benso, the hills become more prominent, mostly due to the resistant volcanic bedrock. The sharp, narrow valley bottoms are mainly at elevations in the range 50 m to 70 m ASL, whereas the flat, elongate ridges and hills have elevations mostly in the range 160 m to 170 m ASL.

3.1.2 Hydrogeology

The Benso project lies within the vicinity of the Ben and Subri Tuntum Rivers, which are tributaries of the Bonsa River. The Hwini Butre project is within a catchment area of the

Butre River; there are no permanent water courses close to the project. Therefore, the main mining area is comprised of headwaters for these tributaries.

The hydrogeology of the GSWL operational area is characterised by two main lithological units. An upper, oxidised zone and lower, fresh rock zone, both of which are considered hydro-geologically distinct. Both units have low permeability, but this is increased by up to two orders of magnitude with the presence of faulting and quartz. The upper aquifer is the oxidised zone. It is generally phreatic and the principal groundwater flow occurs where the vein quartz occurs more abundantly. The water in this aquifer generally has low mineralization; it is therefore, likely to have been recently recharged to the aquifer. The upper saprolite (<10 m) has a moderately low permeability. The permeability will decrease with depth through the saprolite. The lower aquifer is within the un-oxidised bedrock. It is unconfined in topographically elevated areas and semi-confined in the valleys where there is a vertical head gradient. The recharge area for this aquifer is on the topographic ridges local to the area where a downward vertical head gradient exists.

3.1.3 Vegetation

There are two forest reserves around the project namely; the Bonsa and Subri River forest reserves. Forests dominate the steep slopes and areas found unsuitable for agriculture within both of the concessions and serve as a source of timber, domestic fuel wood, and wood for buildings. The HBB project site falls within the Moist Evergreen (ME) vegetation zone of Ghana. The structure of the vegetation is a mosaic of intensively-cultivated farmlands, fallows, and secondary forest. Major recognizable vegetation cover types within the overall area are Moist Evergreen Forest, Forb Regrowth, Thickets and Secondary forests. The Subri River Forest Reserve covers the watershed between the Pra River in the east and the Bonsa

River in the west. Their tributaries cut up the area, which generally undulates, with extensive areas of swamp. A 2,590 ha of research area (Research Working Circle) has been established in the southwest 'arm' of the reserve along the Benso to Amantin road, where Tropical Shelter wood System ('TSS') treatments has been carried out (GSWL, 2009).

3.2.0 The Subriso East waste dump

The Subriso East dump constitutes waste rock material (material of less economic value) mined from the Subriso East pit and covers an area of 19.93 hectares. Based on the composition of the waste rock, two types are generated, namely; potentially acid generating (PAG) and non-acid generating (NAG) wastes. Rock waste was cut from the crest as well as from the slopes and pushed to fill toe and allowable spaces of the dump to achieve a slope of 22°. A safety berm 5 -10 m was constructed to stabilise the slopes and to control runoff from one level to the other. The surface profile shaping and levelling was graded in decreasing order to prevent ponding. To prevent the generation of acidic drainage, the shaped dump was capped with oxide 2 m thick. This was completed in lifts of not more than 0.5 m and each lift was compacted with roller. The lifts were compacted to 95% Proctor before the next lift was applied. The material was of suitable size fraction to prevent the penetration of oxygen and no rocks or boulders were included in the layers. Upon completion, a rooting layer of 0.6 m of competent subsoil, to allow the establishment of vegetation, was applied followed by 0.2 m of topsoil to allow the establishment of vegetation for the final forest cover. See Plate 1.



Plate 1: View of encapsulation and aerial view after re-vegetation of the SE rock dump

3.3.0 Sampling points

Water samples were collected from twin monitoring boreholes installed around the toe of the Subriso East rock dump, reference boreholes located approximately 500 m from the dump and surface water from the Subri River which lies about 50 m from the dump on monthly basis for six months (i.e. August, 2012 - February, 2013). Each pair of twin boreholes is 60 m and 30 m deep, approximately 1.2 m apart and 46 m from the nearest pair of boreholes. The diameter of the bores is 10 cm. Samples from the Subri River were taken from both upstream and downstream of the river. In all, water was sampled from fourteen sampling sites. Map of the Benso mine site showing the sampling points is shown in Figure 3.

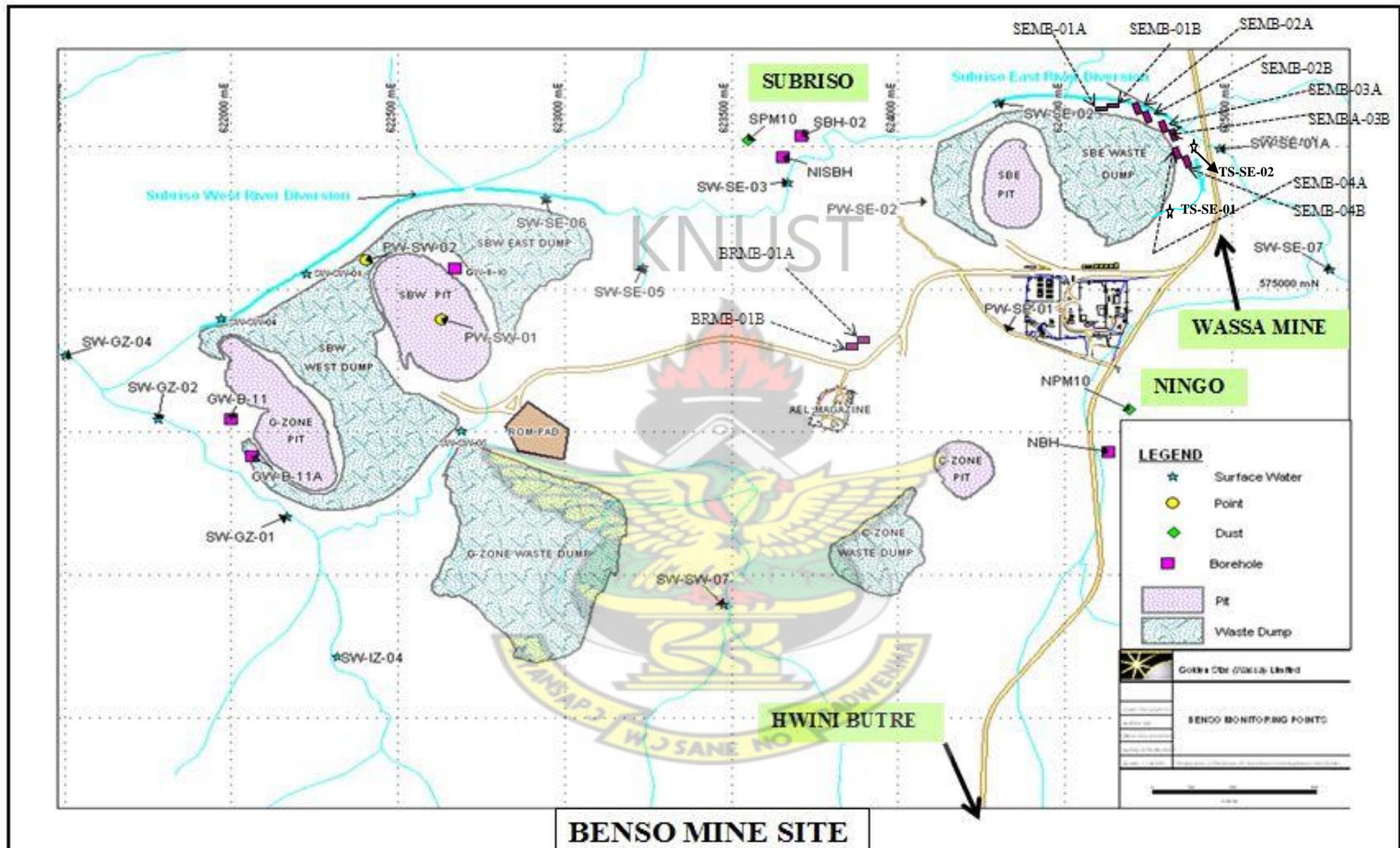


Figure 3: Map of the Benso mine site showing the sampling sites (GSWL, 2009)

3.3.1 Geographical Positioning System (GPS) coordinates for sampling points

GPSMAP® 76 chart plotting receiver was used to determine the coordinates (Latitudes and Longitudes) for each sampling point. Coordinates picked are shown in Table 1.

Table 1: GPS coordinates Universal Transverse Mercator (UTM) of sampling sites.

SRL No.	ID for sampling	Description	Northings/ Longitudes (UTM)	Eastings/ Latitudes (UTM)
1.	SEMB-01A	Monitoring borehole-Deep	624791	575152
2.	SEMB-01B	Monitoring borehole-Shallow	624790	575149
3.	SEMB-02A	Monitoring borehole-Deep	624846	575516
4.	SEMB-02B	Monitoring borehole-Shallow	624850	575514
5.	SEMB-03A	Monitoring borehole-Deep	624673	575600
6.	SEMB-03B	Monitoring borehole-Shallow	624680	575596
7.	SEMB-04A	Monitoring borehole-Deep	624387	575624
8.	SEMB-04B	Monitoring borehole-Shallow	624395	575632
9.	BRMB-01A	Monitoring borehole-Deep	624071	575014
10.	BRMB-02B	Monitoring borehole-Shallow	624070	575020
11.	SW-SE-01A	Subri at diversion Channel	624940	575254
12.	SW-SE-02	Subri down South East Pit	624310	575632
13.	SW-SE-03	Subri on bridge to Subriso	623753	575374
14.	TS-SE-01	Toe sump at south eastern section of SE waste dump	624726	575048
15.	TS-SE-02	Toe sump at south eastern section of SE waste dump	624732	575057
16.	SW-SE-07	Subri Further upstream before project impact	624940	575254

3.4.0 Sampling

Water samples were taken in duplicates from ten boreholes at the toe of the SE dump and four surface water sampling points (Upstream and downstream) from August, 2012 to February, 2013. With nitrile gloves on, water samples were collected into 500 ml plastic bottles, which were thoroughly rinsed with distilled water. A Bailer was used in drawing water from the boreholes (Plate 2). Surface water samples were collected by directly fetching from river using well rinsed 500 ml bottles. Each bottle was immersed below the water surface. The pH and conductivity of each water sample was determined on site using Orin 5 star multi-parameter analyzer. Total suspended solid was also determined using Insite IG 3150 meter. Each sampling bottle was eligibly labeled indicating the ID, time and date of sampling. The samples were transported to the laboratory in a cool box over ice for analysis. Water samples collected for metal analysis were acidified with 50% HNO_3 to attain a pH of 2 in order to keep the metal ions in the dissolved state, as well as to prevent microbial activities (APHA *et al.*, 2005).



Plate 2: Sampling from monitoring boreholes

3.5.0 Laboratory analysis

Each surface and ground water sample was analyzed for the following: pH, electrical conductivity, sulphate, alkalinity Arsenic (As), Manganese (Mn), Iron (Fe), Zinc (Zn), Copper (Cu), Cadmium (Cd), Mercury (Hg) and lead (Pb).

3.5.1 Determination of pH, and electrical conductivity

pH, and electrical conductivity parameters were determined using the Orin 5 Star multi-parameter analyzer. The instrument was first calibrated for pH using solutions of pH 4 and pH 10 buffers. For electrical conductivity, the electrodes were immersed in the solution of 0.1M KCl of conductivity 1413.0 $\mu\text{s}/\text{cm}$ and appropriately calibrated. Readings were taken by dipping the probe into the water sample and the readings recorded at every sampling site (Standard Methods, 1992).

3.5.2 Sulphate determination

The HACH DR 4000 spectrophotometer was used in the determination of sulphate in the water samples. 10 ml of sample was filtered using a 0.45 μm membrane filter into a sample cell (bottle). The content of one SulfaVer 4 Reagent Powder pillow was added to the samples. The sample cell was stopped and shaken for 30 seconds. An additional 30 seconds was observed while the sample is undisturbed. The blank, standard samples were read at a wavelength of 450 nm.

3.5.3 Alkalinity determination

To determine alkalinity, 100 ml of the water sample was measured into 250 ml flask. The pH of the sample was measured and recorded. Three drops of Bromocresol green indicator were then added, after which the sample was titrated with 0.02 N H₂SO₄ until the color changed from blue to yellow (i.e. endpoint was reached-pH 4.5). The total volume of acid used in order to obtain the endpoint was recorded. The total alkalinity was computed as detailed below:

$$\text{Alkalinity (mg CaCO}_3\text{/L)} = A \times N \times 50,000 / \text{ml Sample}$$

“A” represents the total volume (mL) of the standard acid used.

“N” represents the normality of the standard acid used.

“50, 000” is a conversion factor to change the normality into units CaCO₃/L (Standard Methods, 1992).

3.5.4 Metal Analysis

The concentrations of Arsenic, Manganese, Iron, Zinc, Copper and Cadmium were determined using Varian 220 Spectra AA model of Atomic Absorption Spectrometer (AAS). The AAS was calibrated using standard solutions of the different metals under investigation. Concentrations of dissolved metals were determined at the following wavelengths: As = 193.7 nm, Mn = 279.3 nm, Fe = 284.3 nm, Zn = 213.9 nm, Cu = 324.8 nm and. Cd = 228 nm. About 100 ml of the water sample was measured into the sample bottle. The bottle was rinsed three times with the sample before actual sample was put in the sample bottle. 1 ml of concentrated HNO₃ was added to the sample using the calibrated dispenser. The sample was shaken and allowed to stand for about an hour in order for digestion to take place. Filtration was done using a 0.45µm membrane filter.

Sample was then analysed using the Varian 220 Spectra AA model of Atomic Absorption Spectrometer (AAS).

3.5.5 Statistical Analysis

One-way analysis of variance (ANOVA) was used to test for data variation between variables (i.e. each sampling point and the corresponding reference point). The data obtained from the laboratory analysis were tested at 95% confidence level. The statistical tool used was Excel Analysis toolpak 2010.



CHAPTER FOUR

4.0 RESULTS

4.1 Physico-chemical parameters in surface water

The mean values for pH, CaCO₃, EC, TDS and SO₄²⁻ determined in surface water samples collected from the Subri River which lies approximately 50 m from the Subriso East Rock Dump (SERD) is shown in Table 2.

Table 2: Mean (± S. D) of physico-chemical parameters in surface water from August, 2012 to February, 2013.

Parameter		SW-SE-01A	SW-SE-02	TS-SE-01	TS-SE-02	SW-SE-07
pH	Mean	5.47	5.73	6.38	6.17	5.48
	St.Dev.	±0.23	±0.12	±0.19	±0.21	±0.12
Alkalinity (mg/L)	Mean	14.00	14.33	107.5	93.17	14.67
	St.Dev.	±7.18	±7.61	±55.49	±70.27	±8.57
EC (µS/cm)	Mean	6.65	6.88	59.08	44.68	6.73
	St.Dev.	±0.88	±0.81	±16.95	±10.10	±1.06
TDS (mg/L)	Mean	57.0	57.2	362.0	250.0	47.0
	St.Dev.	±7.64	±13.76	±155.43	±33.15	±4.86
SO₄ (mg/L)	Mean	1.67	5.00	130.83	72.00	7.00
	St.Dev.	±0.58	±2.16	±95.09	±29.15	±1.42

The mean pH values of surface water sampled ranged from 5.47 ± 0.23 to 6.38 ± 0.19 . SW-SE-07 (upstream point) and SW-SE-02 (downstream point) reported mean pH values of 5.48 ± 0.21 and 5.73 ± 0.12 respectively. Samples collected close to the dump reported mean pH of 6.38 ± 0.19 for TS-SE-01, 6.17 ± 0.12 for TS-SE-02 and 5.47 ± 0.23 for SW-SE-01A. Mean pH values for the samples were generally slightly acidic and above the value at the upstream point. pH values determined for all the samples were below the and the Ghana Standard Board (GSB-2009)/WHO (2006) permissible range of 6.5-8.5. Statistically, variation in pH between SW-SE-07

and SW-SE-01A was not significant. Contrarily, the variation between the upstream point, SW-SE-07 and each of the other sampling points (TS-SE-01, TS-SE-02 and SW-SE-02) was significant ($p \leq 0.05$). Appendix 1 shows the details of statistical analysis between the variables.

Mean alkalinity of surface water ranged from 14.00 ± 7.18 mg/L to 107.5 ± 55.49 mg/L. The upstream (SW-SE-07) and downstream (SW-SE-02) points reported mean CaCO_3 values of 14.67 ± 8.57 and 14.33 ± 7.61 mg/L respectively. At sampling points close to the dump (i.e. TS-SE-01, TS-SE-02 and SW-SE-01A), mean CaCO_3 levels were 107.5 ± 55.49 mg/l, 93.17 ± 70.27 mg/l and 14.00 ± 7.183 mg/l respectively. The maximum and minimum values were reported at sampling points around the dump. Most of the samples had CaCO_3 levels well above the upstream sample (SW-SE-07), except SW-SE-02 and SW-SE-01A which had relatively low CaCO_3 levels. However, CaCO_3 levels of all the samples were well below GSB (2009) permissible limit of 500 mg/l. The CaCO_3 variations between the upstream point (SW-SE-07) and SW-SE-02 and SW-SE-01A were not statistically significant. Nonetheless, there was significant variation between SW-SE-07 and TS-SE-01; and SW-SE-07 and TS-SE-02 ($p \leq 0.05$). Appendix 2 shows the details of statistical analysis between the variables.

The mean EC values in surface water samples ranged from 6.65 ± 0.88 $\mu\text{S}/\text{cm}$ to 59.08 ± 16.95 $\mu\text{S}/\text{cm}$. Samples collected around the SERD; TS-SE-01, TS-SE-02 and SW-SE-01A had mean EC values of 59.08 ± 16.95 $\mu\text{S}/\text{cm}$, 44.68 ± 10.10 $\mu\text{S}/\text{cm}$ and 6.65 ± 0.88 $\mu\text{S}/\text{cm}$ respectively. The mean EC level of the upstream sample (SW-SE-07) was 6.73 ± 1.06 $\mu\text{S}/\text{cm}$ and the downstream sample (SW-SE-02) was 6.88 ± 0.81 $\mu\text{S}/\text{cm}$. EC levels of all the samples were above the upstream sample, except SW-SE-01A which was relatively. Nonetheless, EC levels of all samples

collected and analyzed were well below the WHO (2006) permissible limit of 1500 $\mu\text{S}/\text{cm}$. The EC variations between the upstream point (SW-SE-07) and SW-SE-02 and SW-SE-01A were not statistically significant. However, there was significant variation between SW-SE-07 and TS-SE-01; and SW-SE-07 and TS-SE-02. Appendix 3 shows the details of statistical analysis between the variables.

The range for Total Dissolved Solids (TDS) in the surface water samples was from 47.0 ± 4.86 mg/l to 362.0 ± 155.43 mg/l. The sampling points close to the dump, TS-SE-01, TS-SE-02 and SW-SE-01A had mean TDS levels of 362.0 ± 155.43 , 250.0 ± 33.15 and 57.0 ± 7.642 respectively. The upstream point, SW-SE-07 had mean TDS of 47.0 ± 4.86 mg/l and the downstream point had 57.2 ± 13.76 mg/l. The upstream point reported a lower TDS value than all the other sampling points. The mean TDS determined for all the water samples were below the limit (1000 mg/l) permitted by WHO (2006)/GSB (2009) in drinking water. Statistically, there was a significant difference between SW-SE-07 and each of the other sampling points, TS-SE-01, TS-SE-02, SW-SE-01A and SW-SE-02 (i.e. $p \leq 0.05$) (Appendix 4).

Mean sulphate (SO_4^{2-}) concentration in surface water sampled varied between 1.67 ± 0.577 mg/l and 130.83 ± 95.09 mg/l. SW-SE-07 (Upstream point) and SW-SE-02 (Downstream point) reported mean sulphate concentration of 5.0 ± 2.16 mg/l and 7.0 ± 1.42 mg/l respectively. TS-SE-01, TS-SE-02 and SW-SE-01A (samples taken close to the dump) had 1.67 ± 0.577 mg/l, 130.83 ± 95.09 mg/l, and 72.0 ± 29.15 mg/l respectively. The upstream sample had SO_4^{2-} concentration well below that reported by all the other samples except SW-SE-01A. Nonetheless, SO_4^{2-} concentrations of all the samples were below the GSB allowable limit of 250 mg/l in drinking

water. Statistically, the difference between SW-SE-07, SW-SE-01A and SW-SE-02 was not significant. On the other hand, the difference between SW-SE-07 and TS-SE-01 and between SW-SE-07 and TS-SE-02 were statistically significant ($p \leq 0.05$). Appendix 5 shows the details of statistical analysis between the variables.

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4.2 Physico-chemical parameters in samples collected from deep monitoring boreholes

The mean pH values, CaCO₃, EC, TDS and SO₄²⁻ concentrations determined in groundwater samples collected from deep (60m in depth) monitoring boreholes in the study area is shown in Table 3.

Table 3: Mean (± S. D) for physico-chemical parameters determined for deep monitoring boreholes from August, 2012 to February, 2013

Parameter		SEMB-01A	SEMB-02A	SEMB-03A	BRMB-01A
pH	Mean	6.90	6.88	6.95	6.73
	St.Dev.	±0.28	±0.20	±0.12	±0.21
Alkalinity (mg/L)	Mean	208.80	238.00	241.67	131.50
	St.Dev.	±4.83	±18.97	±23.45	±61.69
EC (µS/m)	Mean	48.8	54.37	60.03	26.90
	St.Dev.	±4.66	±4.32	±2.86	±3.25
TSD (mg/L)	Mean	237.5	253.8	302.7	166.0
	St.Dev.	±116.34	±123.17	±174.74	±82.05
SO₄ (mg/L)	Mean	1.00	5.17	38.17	6.17
	St.Dev.	±0.00	±1.33	±6.05	±1.33

The mean pH measured in the deep monitoring borehole samples varied between 6.73 ± 0.21 and 6.95 ± 0.12. The reference borehole, BRMB-01A had the minimum mean pH of 6.73 ± 0.21 and monitoring boreholes at the toe of the dump; SEMB-01A, SEMB-02A and SEMB-03A had mean pH values of 6.90 ± 0.28, 6.88 ± 0.20 and 6.95 ± 0.28 respectively. The reference borehole gave mean pH value relatively lower than boreholes at the toe of the rock dump. Nonetheless, pH values of all the samples were within the WHO (2006)/GSB (2009) permissible limits of 6.5-8.5.

The variation of pH between BRMB-01A and each of the monitoring boreholes at the toe of the dump was not significant difference (Appendix 6).

EC determined in deep monitoring borehole samples varied between $26.90 \pm 3.25 \mu\text{S/m}$ and $60.03 \pm 2.86 \mu\text{S/m}$. The reference borehole (BRMB-01A) had mean EC value of $26.90 \pm 3.25 \mu\text{S/m}$ and monitoring boreholes at the toe of the rock dump; SEMB-01A, SEMB-02A and SEMB-03A had EC values of $48.8 \pm 4.66 \mu\text{S/m}$, $54.37 \pm 4.32 \mu\text{S/m}$ and $60.03 \pm 2.86 \mu\text{S/m}$ respectively. Mean EC of boreholes at the toe of the dump were relatively higher than the reference borehole. Comparative to the WHO (2006) standards for drinking water, EC values of the deep monitoring boreholes were within the permissible limit of $1500 \mu\text{S/cm}$. Variation between BRMB-01A and each of the deep boreholes at the toe of the dump was statistically significant. Appendix 7 shows the details of statistical analysis.

The mean alkalinity (CaCO_3) for deep monitoring boreholes sampled varied between $131.5 \pm 61.69 \text{ mg/l}$ and $241.67 \pm 23.45 \text{ mg/l}$. The reference borehole, BRMB-01A had the minimum mean CaCO_3 value. Deep monitoring boreholes at the toe of the rock dump; SEMB-01A, SEMB-02A and SEMB-03A had mean CaCO_3 value of $208.80 \pm 4.83 \text{ mg/l}$, $238.0 \pm 18.97 \text{ mg/l}$ and $241.67 \pm 23.45 \text{ mg/l}$ respectively. Boreholes at the toe of the dump had CaCO_3 levels well above that given by the reference borehole. Nonetheless, CaCO_3 levels recorded for all the samples were well below GSB permissible limit of 500 mg/l . Variation between results for the deep reference borehole and each of the deep boreholes at the toe of the dump was not statistically significant (Appendix 8).

The mean TDS measured in the deep monitoring boreholes varied between 166.0 ± 82.05 mg/l and 302.7 ± 174.74 mg/l. The reference borehole (BRMB-01A) had mean TDS of 166.0 ± 82.05 mg/l and boreholes at the toe of the dump; SEMB-01A, SEMB-02A and SEMB-03A had mean TDS of 237.5 ± 116.34 mg/l, 253.8 ± 123.17 mg/l and 302.7 ± 174.74 mg/l respectively. Mean TDS recorded in samples from boreholes at the toe of the dump were relatively higher than the reference borehole. Generally, TDS values for all the water samples were below the limit (1000 mg/l) permitted by WHO (2006)/GSB (2009) in drinking water. Statistically, there was no significant difference between (BRMB-01A) and each of the monitoring boreholes around the dump (Appendix 9).

Mean SO_4^{2-} levels measured for deep monitoring boreholes ranged from 1.0 ± 0.00 mg/l to 38.17 ± 6.05 mg/l. The reference borehole (BRMB-01A) gave mean SO_4^{2-} concentration of 6.17 ± 1.33 mg/l and the boreholes at the toe of the rock dump; SEM-01A, SEMB-02A and SEMB-03A gave mean SO_4^{2-} concentration of 1.00 ± 0.00 mg/l, 5.17 ± 1.33 mg/l and 38.17 ± 6.05 mg/l respectively. SEMB-01A and SEMB-02A reported mean SO_4^{2-} concentrations below that given by the reference borehole except SEMB-03A. SO_4^{2-} concentrations for all samples were below the WHO (2006)/GSB (2009) allowable limit of 250 mg/l in drinking water. The variation in SO_4^{2-} concentrations between BRMB-01A and each of the monitoring boreholes at the toe of the rock dump was not statistically significant (Appendix 10).

4.3 Physico-chemical parameters for samples collected from shallow monitoring boreholes

Mean pH, CaCO₃, EC, TDS and SO₄²⁻ determined in groundwater sampled from shallow (30 m in depth) monitoring boreholes in the study area is shown in Table 4.

Table 4: Mean (± S. D) of physico-chemical parameters determined for shallow monitoring bores from August, 2012 to February, 2013

Parameter		SEMB-01B	SEMB-02B	SEMB-03B	BRMB-01B
pH	Mean	6.30	6.30	6.68	6.88
	St.Dev.	±0.13	±0.17	±0.20	±0.19
Alkalinity (mg/l)	Mean	116.67	140.17	270.83	240.83
	St.Dev.	±13.37	±15.94	±34.17	±93.61
EC (µS/m)	Mean	28.48	43.87	61.03	59.57
	St.Dev.	±2.43	±3.79	±8.44	±15.30
TDS (mg/l)	Mean	196.4	245.3	292.2	295.6
	St.Dev.	±36.7	±160.06	±174.3	±173.7
SO ₄ (mg/l)	Mean	2.00	54.50	22.17	16.00
	St.Dev.	±0.00	±16.22	±4.36	±4.52

Mean pH of samples from shallow boreholes varied between 6.30 ± 0.13 and 6.88 ± 0.19 . The reference borehole (BRMB-01B) gave mean pH of 6.88 and samples from boreholes at the toe of the rock dump; SEMB-01B, SEMB-02B and SEMB-03B gave mean pH values of 6.30 ± 0.13 , 6.30 ± 0.17 and 6.68 ± 0.20 respectively. pH values of boreholes at the toe of the dump were lower than that given by the reference borehole. BRMB-01B and SEMB-03B pH values were within WHO (2006)/GSB (2009) permissible limit of 6.5-8.5 for drinking water. SEMB-01B and SEMB-02B had slightly acidic pH values. Statistically, there was significant difference between BRMB-01B and SEMB-01B and also between BRMB-01B and SEMB-02B. Conversely, the difference between BRMB-01B and SEMB-01B was not significant (Appendix 11).

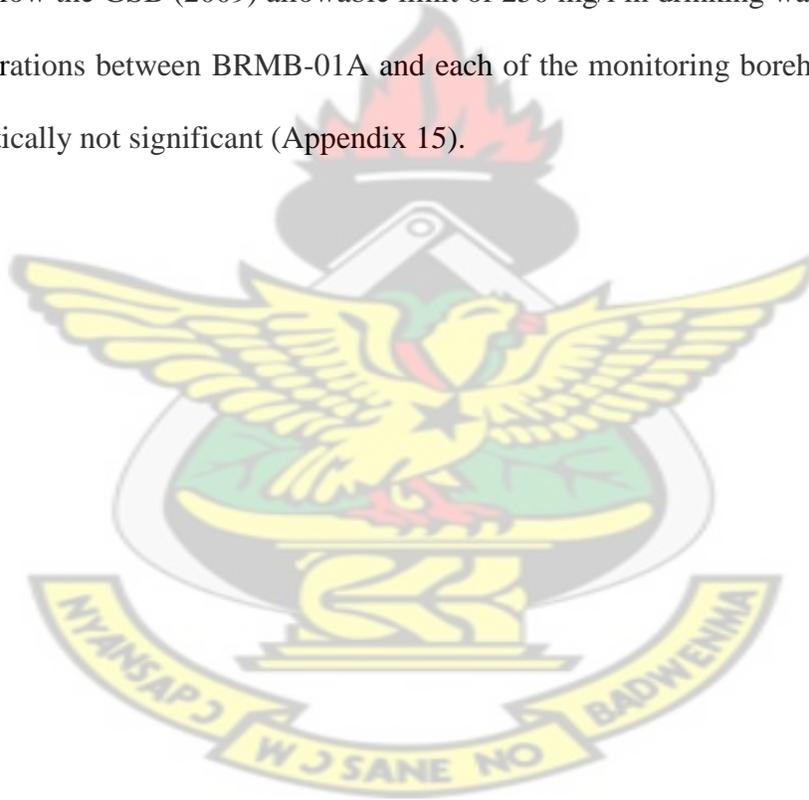
EC determined in samples from the shallow boreholes varied between $28.48 \pm 2.43 \mu\text{S/m}$ and $61.03 \pm 8.44 \mu\text{S/m}$. Mean EC reported were $59.57 \pm 15.30 \mu\text{S/m}$ for BRMB-01B (reference borehole), $28.48 \pm 2.43 \mu\text{S/m}$ for SEMB-01B, $43.87 \pm 3.79 \mu\text{S/m}$ for SEMB-02B, and $61.03 \pm 8.44 \mu\text{S/m}$ for SEMB-03B. Majority of the shallow boreholes at the toe of the rock dump had mean EC levels lower than the reference borehole. In general, the mean EC recorded for all the samples were below WHO (2006) permissible limit of $1500 \mu\text{S/cm}$ for drinking water. There was significant difference between BRMB-01B and each of the shallow boreholes at the toe of the dump, except SEMB-03B. Appendix 12 shows details of statistical analysis.

The mean alkalinity (CaCO_3) for the shallow monitoring boreholes varied between $116.67 \pm 13.37 \text{ mg/l}$ and $270.83 \pm 34.17 \text{ mg/l}$. The reference borehole, BRMB-01B had mean CaCO_3 value of $240.83 \pm 93.61 \text{ mg/l}$ which is well above $116.67 \pm 13.37 \text{ mg/l}$ reported for SEMB-01B and $140.17 \pm 1594 \text{ mg/l}$ reported for SEMB-02B. SEMB-03B, located at the toe of the dump gave the maximum mean CaCO_3 value of $270.83 \pm 34.17 \text{ mg/l}$. Nonetheless, CaCO_3 level recorded for all the samples were compliant with GSB permissible limit of 500 mg/l . The variation in CaCO_3 levels between the reference borehole (BRMB-01B) and SEMB-01B and SEMB-02B was statistically significant. Conversely, variation between BRMB-01B and SEMB-03B was not statistically significant (Appendix 13).

Water samples from SEMB-01B, SEMB-02B, SEMB-03B and BRMB-01(reference borehole) had mean TDS levels of $196.4 \pm 36.7 \text{ mg/l}$, $245.3 \pm 160.06 \text{ mg/l}$, $292.2 \pm 174.3 \text{ mg/l}$, and $295.6 \pm 173.7 \text{ mg/l}$ respectively. The reference borehole gave mean TDS level relatively higher than boreholes around the dump. Nonetheless, TDS values for all the water samples were below the limit (1000 mg/l) permitted by WHO (2006)/GSB (2009) in drinking water. Statistically,

variation between the BRMB-01 and each of the monitoring boreholes around the rock dump was not significant (Appendix 14).

Mean SO_4^{2-} concentration of 2.00 ± 0.00 mg/l, 54.50 ± 16.22 , 22.17 ± 4.36 mg/l, and 16.00 ± 4.52 mg/l were reported for SEMB-01B, SEMB-02B, SEMB-03B and BRMB-01B. Overall, water samples from boreholes at the toe of the rock dump were considerably higher in SO_4^{2-} levels than the reference borehole (BRMB-01B) except SEMB-01B. SO_4^{2-} concentrations for all samples were below the GSB (2009) allowable limit of 250 mg/l in drinking water. The variation in SO_4^{2-} concentrations between BRMB-01A and each of the monitoring boreholes at the toe of dump was statistically not significant (Appendix 15).



4.4 Metal concentration in surface water

Mean concentrations of trace metals in surface water within the immediate environs of the rock dump sampled and analyzed is shown in Table 5.

Table 5: Mean (\pm S. D) concentrations of metals in surface water sampled within the study area from August, 2012 to February, 2013

Parameter (mg/l)		SW-SE-01A	SW-SE-02	TS-SE-01	TS-SE-02	SW-SE-07
Fe	Mean	1.30	1.38	2.78	3.50	1.50
	St.Dev.	± 1.71	± 1.59	± 2.34	± 2.65	± 1.86
Cu	Mean	0.02	<0.02	0.03	<0.02	<0.02
	St.Dev.	± 0.00	± 0.00	± 0.00	± 0.00	± 0.00
Mn	Mean	0.24	0.12	0.52	0.64	0.74
	St.Dev.	± 0.32	± 0.02	± 0.32	± 0.48	± 1.11
Zn	Mean	0.34	0.14	0.2	0.45	0.06
	St.Dev.	± 0.28	± 0.01	± 0.01	± 0.18	± 0.06
Al	Mean	0.30	0.32	0.45	0.54	0.61
	St.Dev.	± 0.33	± 0.37	± 0.41	± 0.43	± 1.00
Cd	Mean	<0.002	<0.002	<0.002	<0.002	<0.002
	St.Dev.	± 0.00	± 0.00	± 0.00	± 0.00	± 0.00
Pb	Mean	<0.01	<0.01	<0.01	<0.01	<0.01
	St.Dev.	± 0.00	± 0.00	± 0.00	± 0.00	± 0.00
Ag	Mean	<0.02	<0.02	<0.02	<0.02	<0.02
	St.Dev.	± 0.00	± 0.00	± 0.00	± 0.00	± 0.00
As	Mean	<0.002	0.002	0.002	0.002	0.002
	St.Dev.	± 0.00	± 0.00	± 0.00	± 0.00	± 0.00

Iron (Fe) concentration in surface water varied between 1.30 ± 1.713 mg/l and 3.50 ± 2.65 mg/l. Mean Fe concentration of 1.30 ± 1.713 mg/l, 1.38 ± 1.59 mg/l, 1.50 ± 1.86 mg/l, 2.78 ± 2.34 mg/l and 3.50 ± 2.65 mg/l were reported for SW-SE-01A, SW-SE-02, SW-SE-07, TS-SE-01 and TS-SE-02 respectively. The upstream sampling point (SW-SE-07) had mean Fe concentration slightly higher than the downstream points, except TS-SE-01 and TS-SE-02 which exceeded the upstream value. Fe concentration of all the samples exceeded the WHO (2006)/GSB (2009) permissible limit of 0.3 mg/l for drinking water. Statistically, the variation between Fe concentration of the upstream point and each of the downstream sampling points was not significant (Appendix 16).

Mean Mn concentrations determined were 0.24 ± 0.321 mg/l, 0.21 ± 0.02 mg/l, 0.74 ± 1.11 mg/l, 0.52 ± 0.32 and 0.64 ± 0.48 mg/l were reported for SW-SE-01A, SW-SE-02, SW-SE-07, TS-SE-01 and TS-SE-02. Overall, downstream sampling points reported Mn concentrations marginally below the upstream point (SW-SE-07). Comparative to WHO (2006)/GSB (2009) standards, all the samples exceeded Mn permissible limit of 0.1 mg/l in drinking water. Statistical analyses showed variation between Mn concentration measured in the upstream point and each of the downstream points (SW-SE-01A, SW-SE-02, TS-SE-01 and TS-SE-02) was not significant (Appendix 17).

Copper (Cu) concentration determined in samples from SW-SE-01A and TS-SE-01 reported mean values of 0.002 mg/l and 0.003 mg/ respectively. The upstream sampling point (SW-SE-07), SW-SE-02, and TS-SE-02 were below the minimum detection limit of 0.002 mg/l. In

summary, all the surface water sampling points were below the GSB permissible limit of 1.0 mg/l for drinking water.

Zn concentrations of 0.34 ± 0.276 mg/l, 0.14 ± 0.01 mg/l, 0.2 ± 0.01 mg/l, 0.45 ± 0.18 mg/l and 0.06 ± 0.06 mg/l was reported for SW-SE-01A, SW-SE-02, TS-SE-01, TS-SE-02 and SW-SE-07 respectively. In general, the downstream samples reported mean Zn concentrations greater than the upstream point (SW-SE-07). Nonetheless, Zn concentrations for all samples were below WHO (2006)/GSB (2009) allowable limit of 3.0 mg/l. Statistical analyses showed variation in Zn concentration between the upstream sample and each of the downstream samples was not significant (Appendix 18).

Mean Al concentration measured ranged between 0.3 ± 0.331 mg/l and 0.61 ± 1.00 mg/l. Mean Al concentration of 0.3 ± 0.331 mg/l, 0.32 ± 0.37 mg/l, 0.54 ± 0.42 mg/l, 0.45 ± 0.43 and 0.61 ± 1.00 mg/l were reported for SW-SE-01A, SW-SE-02, TS-SE-01, TS-SE-02 and SW-SE-07 respectively. Overall, the Al concentration of the upstream point (SW-SE-07) determined was slightly above the concentration of the downstream points. The results reported for all samples analysed were above WHO (2006)/GSB permissible limit of 0.2 mg/l. Statistically, there was no significant difference between SW-SE-07 sample and each of the downstream samples (Appendix 19).

As concentration determined for all surface water samples reported a common mean concentration of 0.002 mg/l except SW-SE-01A which was below the minimum detection limit. The upstream point (SW-SE-07) had As concentration same as downstream point (SW-SE-02).

As concentrations recorded for all the samples were within WHO (2006) /GSB (2009) permissible limit of 0.01 mg/l for As in drinking water. There was no significant difference amongst the variables (Appendix 20).

Cd, Pb and Ag determined for all surface water samples were below their respective minimum detection limits.

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4.5 Metal concentration in water sampled from deep monitoring boreholes

Table 6 shows mean concentrations of metals in water sampled from deep monitoring bores within the study area.

Table 6: Mean (\pm S. D) concentrations of metals in water sampled from deep monitoring bores in the study area from August, 2012 to February, 2013.

Parameter (Dissolved) mg/L		SEMB-01A	SEMB-02A	SEMB-03A	BRMB-01A
Fe	Mean	0.10	0.10	<0.01	0.06
	St.Dev.	± 0.00	± 0.00	-	± 0.06
Cu	Mean	<0.02	<0.02	0.03	<0.02
	St.Dev.	-	-	± 0.00	-
Mn	Mean	0.10	0.27	0.33	<0.02
	St.Dev.	± 0.13	± 0.20	± 0.16	-
Zn	Mean	<0.05	<0.05	<0.05	<0.05
	St.Dev.	-	-	-	-
Al	Mean	<0.03	<0.03	<0.03	0.10
	St.Dev.	-	-	-	± 0.06
Cd	Mean	<0.002	<0.002	<0.002	<0.002
	St.Dev.	-	-	-	-
Pb	Mean	<0.01	<0.01	<0.01	<0.01
	St.Dev.	-	-	-	-
Ag	Mean	<0.02	<0.02	<0.02	<0.02
	St.Dev.	-	-	-	-
As	Mean	0.005	0.003	0.002	0.002
	St.Dev.	± 0.001	± 0.001	± 0.00	± 0.00

Mean Fe concentration of 0.10 mg/l, 0.10 mg/l, and 0.06 ± 0.06 mg/l was reported for SEMB-01A, SEMB-02A, and BRMB-01A respectively. SEMB-03A was below the minimum detection limit. Monitoring boreholes at the toe of the dump had mean concentrations marginally above that reported by the reference borehole (BRMB-01A). Fe concentrations of all the samples were within the WHO (2006)/GSB (2009) permissible limit of 0.3 mg/l for drinking water. Statistically, the variation between Fe concentration of the deep reference borehole and each of the deep boreholes at the toe of the dump was not significant (Appendix 21).

Mean Mn concentrations determined were 0.10 ± 0.13 mg/l, 0.27 ± 0.20 mg/l and 0.33 ± 0.16 mg/l for SEMB-01A, SEMB-02A and SEMB-03A respectively. The reference monitoring borehole was below the minimum detection limit. Mn concentrations of all the samples exceeded the WHO (2006)/GSB (2009) permissible limit of 0.1 mg/l for drinking water except SEMB-01A.

Water sampled from the deep monitoring boreholes and analysed for Cu concentrations were all below the minimum detection limit of 0.02 mg/l except SEMB-03A which had Cu concentration of 0.03 ± 0.00 mg/l. This value is well below the GSB (2009) permissible limit of 1.0 mg/l.

Zn, Cd, Pb and Ag concentrations were all below their respective detection limits for all the samples collected from the various deep monitoring boreholes. Al concentration for the various deep monitoring boreholes were also below the minimum detective limit except the reference borehole which reported mean Al concentration of 0.10 ± 0.06 mg/l which is within WHO (2006)/GSB (2009) permissible limit of 0.2 mg/l.

As concentration measured for water samples from the deep monitoring boreholes varied between 0.002 and 0.005 mg/l. SEMB-01A, SEMB-02A, SEMB-03A and BRMB-01A had mean As concentration of 0.005 ± 0.001 mg/l, 0.003 ± 0.001 mg/l, 0.002 mg/l and 0.002 mg/l respectively. As concentration for SEMB-01A and SEMB-02A were marginally above the reference borehole (BRMB-01A). Overall, As concentrations recorded for all the samples were within WHO (2006)/GSB (2009) permissible limit of 0.01 mg/l for As in drinking water. Variation between the BRMB-01A and each of the deep boreholes at the toe of the dump was statistically not significant ($p \geq 0.05$) (Appendix 22).



4.6 Metal concentrations in water sampled from shallow boreholes

Table 7 shows mean concentrations of metals in water sampled from shallow monitoring boreholes at the study area.

Table 7: Mean (\pm S. D) concentrations of metals in water sampled from shallow monitoring boreholes in the study area from August 2012 to February 2014

Parameter (Dissolved) mg/l		SEMB-01B	SEMB-02B	SEMB-03B	BRMB-01B
Fe	Mean	<0.01	1.00	1.00	0.20
	St.Dev.	-	± 0.00	± 0.00	± 0.00
Cu	Mean	<0.02	<0.02	<0.02	0.03
	St.Dev.	-	-	-	± 0.00
Mn	Mean	0.06	2.01	0.21	0.04
	St.Dev.	± 0.00	± 0.38	± 0.15	± 0.00
Zn	Mean	<0.05	<0.05	<0.05	<0.05
	St.Dev.	-	-	-	-
Al	Mean	0.03	0.11	0.04	0.06
	St.Dev.	± 0.01	± 0.00	± 0.02	± 0.00
Cd	Mean	<0.002	<0.002	<0.002	<0.002
	St.Dev.	-	-	-	-
Pb	Mean	<0.01	<0.01	<0.01	<0.01
	St.Dev.	-	-	-	-
Ag	Mean	<0.02	<0.02	<0.02	<0.02
	St.Dev.	-	-	-	-
As	Mean	0.002	0.002	0.002	0.003
	St.Dev.	± 0.00	± 0.00	± 0.001	± 0.001

Mean Fe concentration for water sampled and analysed varied between 0.2 ± 0.00 mg/l and 1.0 ± 0.00 mg/l. SEMB-02B, SEMB-03B and BRMB-01B had mean Fe concentration of 1.0 ± 0.00 mg/l, 1.0 mg/l and 0.2 mg/l respectively. Fe concentration for SEMB-01B was below the minimum detection limit. The mean Fe concentration of SEMB-02B and SEMB-03B were above the reference borehole and also exceeded the WHO (2006)/GSB (2009) permissible limit of 0.3 mg/l for drinking water. Statistically, the variation between Fe concentration of the reference borehole (BRMB-01B) and each of the shallow bores at the toe of the dump was not significant (Appendix 23).

The mean Mn concentration for the shallow monitoring boreholes varied between 0.04 ± 0.38 mg/l and 2.01 ± 0.38 mg/l. Mean Mn concentration of 0.06 mg/l, 2.01 ± 0.38 mg/l, and 0.21 ± 0.15 mg/l and 0.04 mg/l was reported for SEMB-01B, SEMB-02B, SEMB-03B, and BRMB-01B respectively. The shallow boreholes around the dump reported mean Mn concentrations above the reference borehole (BRMB-01B). SEMB-02B and SEMB-03B exceeded the WHO (2006)/GSB (2009) permissible limit of 0.1 mg/l for Mn in drinking water. Statistically, the variation between Mn concentration of the shallow reference borehole and SEMB-01B and SEMB-03B was not significant. Contrarily, there was significant variation between BRMB-01B and SEMB-02B ($p \leq 0.05$). Appendix 24 shows details of statistical analysis.

Mean Al concentration for the shallow boreholes varied between 0.03 ± 0.01 mg/l and 0.06 mg/l. The reference borehole (BRMB-01B) had mean Al concentration of 0.06 mg/l which was slightly above that reported for boreholes at the toe of the dump which reported mean Al concentrations of 0.03 ± 0.01 mg/l and 0.04 ± 0.02 mg/l for SEMB-01B and SEMB-03B

respectively. SEMB-02B had Al concentration (0.11 mg/l) exceeding that of the reference borehole. In general, all samples had Al concentrations well below WHO (2006)/GSB permissible limit of 0.2 mg/l. There was no significant difference in Al concentration between BRMB-01B and each borehole around the dump (Appendix 25).

SEMB-01B, SEMB-02B and SEMB-03B gave a common mean As concentration of 0.002 mg/l. This is below the mean As concentration of 0.003 ± 0.001 mg/l reported for BRMB-01B (reference borehole). Overall, As concentrations recorded for all samples from the shallow boreholes were within WHO (2006)/GSB (2009) permissible limit of 0.01 mg/l for As in drinking water. There was no significant difference ($p \geq 0$) in As concentration between BRMB-01B and each borehole around the dump (Appendix 26).

Concentrations for Zn, Cd, Pb and Ag were all below their respective minimum detection limit for all the samples collected from the various shallow monitoring boreholes. Cu concentration of all the shallow monitoring boreholes were also below the minimum detection limit except the BRMB-01B which reported mean Cu concentration of 0.003 ± 0.00 mg/l and falls within GSB (2009) allowable limit of 1.0 mg/l.

Deductively, the overall variations in the quality of surface and ground water samples and their respective reference points were insignificant. Based on the results of the study, it can be reasoned that the encapsulation for PAG material has achieved the primary purpose for which it was constructed, it is hence effective with opportunity for improvement owing to eroded sections of the dump for which maintenance has not be carried out for.

CHAPTER FIVE

5.0 DISCUSSION

Results shown in Table 1 indicate that all surface water sampled were slightly acidic most especially the upstream point (SW-SE-07) and SW-SE-01A. The slightly acidic nature of water from creeks in the study area conforms to the baseline assessment conducted prior to commencement of the HBB mine operations. The trend of pH in surface water could be attributed to the high levels of decomposing organic matter that end up in the Subri River, owing to runoff or direct shedding of riparian vegetation leaves into the water course. This supports Langmuir (1997) assertion that the slightly acidic nature of natural waters may be due to the presence of dissolved carbon dioxide and organic acids (fulvic and humic acids), which are plagiatic from the decay and following leaching of plant materials. On the other hand, acidity of water at downstream points close to the rock dump could be evidence of low pH seepage from the dump. Eroded portions of the encapsulated dump allow percolation of rainwater which promotes acidic drainage from the rock dump. pH of water from the deep monitoring boreholes (60 m) were within WHO (2006)/GSB (2009) permissible limits. Though the reference monitoring bore (BRMB-01A) recorded the minimum pH of 6.73, there was no significant variation amongst the various deep boreholes. This could be evidence that the quality of underground water at this depth has not been impeded by the SE rock dump. The shallow monitoring boreholes were also in compliance with WHO (2006)/GSB (2009) permissible limit except SEMB-01B and SEMB-02B which were slightly acidic. This deviation could be credited to possible leachate of low pH water from the SE rock dump into underground water. This agrees with Acid Base Accounting (ABA) feasibility test conducted for the study area which showed that most of the rock types tested had the potential to generate acid (i.e. sulphide containing

compounds). According to Brady *et al.* (1990), upon exposure, sulphide minerals oxidize in the presence of water and oxygen to form highly acidic, sulphate-rich drainage.

Alkalinity (CaCO_3) of surface water sampled in general was very low (varied between 14.0 mg/l and 107.5 mg/l) and below GSB permissible limit. There was no significant variation between the upstream and downstream sampling points. Toe sumps, TS-SE-01 and TS-SE-02 recorded alkalinity levels well above the upstream point (SW-SE-07). This could be attributed to decomposition of dead vegetation which pre-existed in the area prior to pooling/stagnation of water. This agrees with Skousen *et al.* (2000), that an example of beneficial reaction in wetlands comprise the generation of alkalinity resulting from microbial mineralization of dead organic matter. Alternatively, this could be due to dissolution of limestone material in the waste dump. The deep monitoring boreholes recorded low alkalinity levels and were below the WHO permissible limit. Boreholes at the toe of the dump recorded alkalinity levels well above the reference borehole (BRMB-01A). For the shallow monitoring boreholes, the reference borehole (BRMB-01B) recorded relatively higher alkalinity level than those at the toe of the dump except for SEMB-03B which recorded distinctively high alkalinity level of 270.83 mg/l. Nonetheless, alkalinity levels for all the samples were below WHO (2006)/GSB (2009) permissible limit. The trend of alkalinity levels in both shallow and underground water could be attributed to the dissolution of limestone deposits within the study area which produces calcium trioxocarbonate.

Electrical conductivity (EC) for surface water were generally low and well below WHO (2006)/GSB (2009) permissible limit. The upstream and downstream sampling points gave EC much lower than sumps close to the dump.

EC of water from the deep monitoring boreholes were generally low and well below WHO (2006)/GSB (2009) permissible limit. EC was relatively higher water from boreholes around the toe of the SE rock dump than the reference borehole. Contrarily, for the shallow monitoring boreholes, the reference borehole (BRMB-01B) recorded EC higher than boreholes at the toe of the dump except SEMB-03B which recorded the peak EC level of 61.03 mg/l. Nonetheless, EC recorded was within WHO (2006)/GSB (2009) permissible limit. The low conductivity levels in the study area confirm low amounts of dissolved minerals (ions) in surface and underground water. According to Raghunath *et al.*, (2001) low EC values signify the anoxic condition of groundwater.

TDS recorded for all surface water sampled were below WHO (2006)/GSB (2009)) allowable limit of 1000 gm/l. The downstream points and sumps at toe of the dump reported lower TDS comparative to the upstream point (SW-SE-07) except TS-SE-01 which recorded distinctively high TDS value. This could be attributed to runoff containing high level of fertilizer constituents due to frequent application of fertilizer to boost nutritional content of topsoil to support plant growth (i.e. reclamation of the SE rock dump). According to Murphy (2007), fertilizer can dissolve in storm water and be carried to surface water during storms, and contribute to TDS. Variation in TDS between the surface water sampling points was not statistically significant. TDS in deep monitoring boreholes was well below WHO (2006) /GSB (2009) permissible limit. The deep boreholes at the toe of the dump were relatively higher in TDS compared to the reference borehole. On the contrary, TDS of water from the reference shallow monitoring boreholes was higher compared to shallow boreholes at the toe of the dump. Despite this trend, TDS recorded were below WHO (2006)/GSB (2009) permissible limit. Variation in TDS levels

amongst the monitoring bores was not statistically significant. This supports Butler et al., (2002) study which reported substantially high TDS in some shallow wells (7.3 m deep) than deep wells (17.7 m deep) and attributed the variation in TDS to more mineralization of ground water at lower depths water.

Sulphate concentrations at downstream sampling points were generally lower than the upstream point (SW-SE-07) except TS-SE-01 which reported a distinctively high concentration of 130.83 mg/l. In general, the sulphate concentration recorded for all the surface water samples were within WHO (2006) /GSB (2009) permissible limit. Sulphate concentration in deep monitoring boreholes was generally very low and compliant with GSB permissible limit. Additionally, sulphate concentrations of boreholes at the toe of the dump were below that of the reference borehole except SEMB-03A which gave distinctively high concentration of 38.17 mg/l. The shallow monitoring boreholes also recorded low sulphate concentrations and were in compliance with the WHO (2006)/GSB (2009) permissible limit. The sulphate concentration in SEMB-02B and SEMB-03B were distinctively above that of the reference borehole. The isolated cases of sulphate concentration exceeding reference points (controls) could be attributed to gradual dissolution of sulphide minerals from the rock dump into surface and underground water. This occurrence is facilitated by heavy down pour (rainfall) during the sampling period in the study area. Jung (2001) also attributed high concentration of sulphate in stream water in the Au – Ag mine in Korea to the oxidation of pyrite. In a similar study, Nganje *et al.*, (2010) reported high sulphate concentration above the WHO (2006) maximum permissible level in the wet season.

5.1 Metal concentrations in surface and groundwater

Surface water recorded iron (Fe) concentration exceeding the WHO/GSB permissible limit of 0.3 mg/l. Toe sumps close to the dump; TS-SE-01 and TS-SE-02 recorded distinctively high Fe concentrations above that of the upstream point. Fe concentration in surface water is extremely variable, reflecting difference in underlying bedrock, erosion to a lesser degree, and industrial and municipal discharges (Smith, 1981). The deep monitoring boreholes recorded Fe concentration below WHO (2006)/GSB (2009) permissible limit. The toe boreholes recorded Fe concentrations marginally above that of the reference borehole. The shallow monitoring boreholes at the toe of the dump recorded Fe concentrations above that reported for the reference boreholes except SEMB-01B. SEMB-02B and SEMB-03B gave Fe concentrations exceeding WHO permissible limit. It is evident that the deep boreholes had lower Fe concentrations than the shallow boreholes. The high concentration of Fe in the shallow monitoring boreholes is evidence of richness in naturally occurring Fe in the study area which through dissolution and infiltration gets into underground water. Also, the concentration of Fe in groundwater could be higher under more reducing conditions due to bacteriological degradation of organic matter which leads to the formation of various humic and fluvic compounds (White *et al.*, 1991). Under reducing condition, the Fe from biotite mica and laterites are leached into solution in ferrous state. According to Singhal and Gupta (1999), Fe content in groundwater is mainly due to the dissolution of Fe oxides.

Surface water recorded manganese (Mn) concentrations exceeding the WHO (2006)/GSB (2009) permissible limit. The upstream sampling point (SW-SE-07) recorded the maximum Mn concentration.

Downstream samples and toe sumps close to the SE rock dump were marginally below the upstream concentration. According to Howe *et al.* (2005), dissolved Mn concentrations in natural surface waters rarely exceed 1 mg/l and are usually less than 0.2 mg/l. Mn does not occur naturally as a base metal but is a component of more than 100 minerals, including various sulfides, oxides, carbonates, silicates, phosphates, and borates (NAS, 1989). Surface freshwater data suggest that higher Mn concentrations occur during periods of higher stream flow, such as spring runoff, and lower concentrations tend to occur downstream of lakes that act as settling areas for sediment (Howe *et al.*, 2005). While the deep reference monitoring borehole was below the minimum detection limit, boreholes at the toe of the SE rock dump recorded distinctively high Mn concentrations above the WHO (2006)/GSB (2009) permissible limit except SEMB-01A. For the shallow monitoring boreholes, SEMB-02B and SEMB-03B, which were located at the toe of the SE rock dump recorded Mn concentration exceeding that of the reference borehole and WHO (2006)/GSB (2009) permissible limit. The trend of Mn concentration in surface and groundwater in the study area slightly contradicts previous study by Ankomah-Appiah (2011), which reported low Mn concentrations in the study area. Filipek *et al.*, (1987) reported in a study that in waters receiving acid mine drainage, dissolved Mn concentrations were <0.04 mg/l with pH above 5.5; however, below pH 3, dissolved Mn concentrations ranged from 0.25 to 4.4 mg/l. High Mn concentration in the study area could be attributed to Mn dissolution influenced by acid mine drainage. Stokes *et al.*, (1988) also established other important sources of dissolved Mn to be anaerobic environments where particulate Mn oxides are reduced and the direct reduction of particulate Mn oxides in aerobic environments by organics, with or without ultraviolet light. Copper (Cu) concentration in the study area was generally very low.

Surface water samples from points close to the dump (TS-SE-01 and SW-SE-01A) were the only points that reported the presence of Cu. The concentrations recorded were below GSB permissible limit. Most of the monitoring boreholes were below the detection limit except SEMB-03A (deep monitoring borehole) and BRMB-01B (reference shallow borehole) which reported low Cu concentrations. Both boreholes reported concentration of 0.03 mg/l which is below GSB (2009) permissible limit. Ankomah-Appiah (2011), also confirmed the presence of low Cu concentration in water resources in the study area.

Zinc (Zn) concentrations in surface water analysed were in general below the GSB tolerable limit. However, the downstream point (SW-SE-02) and toe sumps close to the dump recorded high Zn concentrations exceeding that of the upstream point (SW-SE-07). This could be due to mobilization of Zn in seepage from the dump, which was facilitated by high rainfall over the sampling period. Nonetheless, variation between the upstream point and each surface water sampling points was not statistically significant. It was noted in previous studies (Ankomah-Appiah, 2011) that Zn concentration in the study area was low and no detrimental effects are linked to the use of water in the study area. For all the various deep and shallow monitoring boreholes, Zn concentrations were below the detection limit. This confirms the absence of Zn mobilization into groundwater.

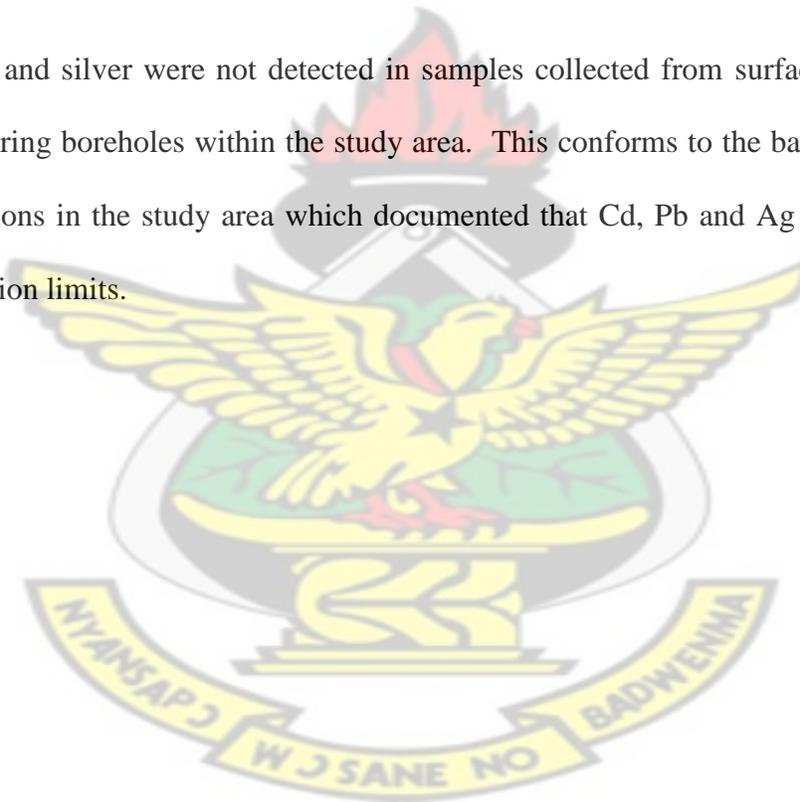
Aluminium (Al) concentration recorded in the downstream point was lower than that of the upstream sampling point. Nonetheless, Al concentrations recorded for all the surface water samples exceeded the WHO (2006)/GSB (2009) permissible limit. Variation in Al concentration between the upstream point and each of the other surface water sampling points was not

statistically significant. Al concentrations for the shallow boreholes at the toe of the dump were all below that recorded for the reference borehole (BRMB-01B) except SEMB-02B. Nonetheless, Al concentration of all the samples exceeded the WHO (2006)/GSB (2009) permissible limit. All the deep monitoring boreholes were below the Al detection limit except the reference borehole (BRMB-01B) which recorded concentration below WHO (2006)/GSB (2009) tolerable limit. Al in surface and ground waters nearly entirely come from mineral weathering. In the pH range of most natural waters, Al is not mobile. However, in acidic waters ($\text{pH} < 4$) Al can be mobilized by dissolution of gibbsite and the accelerated weathering of both clay minerals (e.g. kaolinite) and rock-forming minerals. However, Al concentrations are still very low in natural waters due to the extreme low solubility of Al-bearing minerals. Concentrations in groundwater are strongly pH dependent (Nordstrom, 2011). The presence of dissolved Al in groundwater is indicative of acidic conditions (acid mine drainage/rainfall acidity).

Surface water in the study area was generally low in arsenic (As) concentration and was within the GSB permissible limit. All the surface water samples recorded As concentration of 0.002 mg/l except SW-SE-01A which was below the minimum detection limit. Baseline concentrations of As in rivers vary according to the composition of the surface recharge, base flow and the bedrock lithology. Rivers containing low concentrations of As drain As poor bedrock (Kaye, 2005). According Younger *et al.* (2002), As becomes more soluble in water at higher pH. As concentrations of both shallow and deep monitoring boreholes within the study area were generally low and within the WHO (2006)/GSB (2009) permissible limit. Shallow boreholes at the toe of the dump gave As concentration marginally below the corresponding reference borehole. SEMB-01A and SEMB-02A (deep boreholes) reported As concentration marginally

above that of the reference borehole. Overall, As concentrations was slightly higher in groundwater. Variation in As concentration between the respective reference points and each of the corresponding sampling points was not statistically significant. According to Smedley *et al.* (2002), under natural conditions the greatest range and highest concentrations of As are found in groundwater as a result of the favourable conditions for As mobilisation and accumulation. Smedley *et al.* (2002) asserts that dissolved As is rapidly removed in acid mine waters as Fe is oxidised and precipitated and the As scavenged through adsorption mechanisms.

Cadmium, Lead and silver were not detected in samples collected from surface water, shallow and deep monitoring boreholes within the study area. This conforms to the baseline assessment (EIS) for operations in the study area which documented that Cd, Pb and Ag were below their respective detection limits.



CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

The study revealed that water sampled from surface and ground waters (i.e. specifically the shallow monitoring boreholes) were slightly acidic. The deep monitoring boreholes were near neutral and within WHO (2006)/GSB (2009) permissible limit for drinking water. EC, CaCO₃, TDS, and SO₄ determined for surface and ground water (deep and shallow monitoring boreholes) within the study area were below their respective WHO/GSB permissible limits. There was significant variation between the upstream point (SW-SE-07), TS-SE-01 and TS-SE-02 for pH, EC, CaCO₃, TDS, and SO₄. Variations in water quality of the upstream and downstream samples were generally not significant. Concentrations of the various metals for surface and ground water were generally low. Cadmium, lead and silver were not detected in any of the samples. However, Fe, Mn and Al concentrations exceeded the WHO (2006)/GSB (2009) allowable limits for drinking water for a number of the sampling points.

Fe concentrations were highest in surface water sampling points (TS-SE-01 and TS-SE-02) closest to the dump. The shallow monitoring boreholes, SEMB-02B and SEMB-03B, located at the toe of the SE rock dump reported Fe and Mn concentrations above both the reference borehole and the WHO (2006)/GSB (2009) allowable limits. A few of deep monitoring boreholes at the toe of the SE rock dump reported Fe and Mn concentration above the reference borehole but compliant with WHO/GSB allowable limits.

In brief, it can be concluded that, no significant impacts exist that could be attributed to the SE rock dump.

6.1 RECOMMENDATION

Depending on the sloping of waste rock dumps containing acid-generating or potentially acid generating material, high precipitation pattern as in the case of GSWL promotes erosion and facilitates infiltration of water in rock dump leading to subsequent discharge of acidic water harmful to the environment. It is therefore recommended that;

- ❖ Stone pitch be constructed for pockets of already eroded surface of the dump to avert possible infiltration and pathway for runoff. Other appropriate mechanisms for erosion control should be considered.
- ❖ Continuous monitoring of water resources within the immediate environs of the SE rock dump and all other dumps must be enforced to ensure appropriate actions are determined timely and implemented during alarming changing trends in both physico-chemical and metal concentrations.
- ❖ Subsequent study should consider investigating metal concentration in aquatic organisms in the Subri River to establish possible bioaccumulation and potential health impacts and advise accordingly.

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APPENDICES

APPENDIX 1: ANOVA analysis for pH of surface water samples

SW-SE-07 & SW-SE-06)						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.0533333	1	0.05333333	1.92771	0.195158	4.9646027
Within Groups	0.2766667	10	0.02766667			
Total	0.33	11				
SW-SE-07 & TS-SE-01						
Between Groups	2.43	1	2.43	58.32	1.76E-05	4.9646027
Within Groups	0.4166667	10	0.04166667			
Total	2.8466667	11				
SW-SE-07 & TS-SE-02						
Between Groups	1.4008333	1	1.40083333	46.4365	4.66E-05	4.9646027
Within Groups	0.3016667	10	0.03016667			
Total	1.7025	11				
SW-SE-07 & SW-SE-02						
Between Groups	0.1875	1	0.1875	6.21547	0.031822	4.9646027
Within Groups	0.3016667	10	0.03016667			
Total	0.4891667	11				
SW-SE-07 & SW-SE-01A						
Between Groups	0.0008333	1	0.00083333	0.0173	0.897962	4.9646027
Within Groups	0.4816667	10	0.04816667			
Total	0.4825	11				



APPENDIX 2: ANOVA analysis for EC of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.9075	1	0.9075	0.44833265	0.51829	4.964603
Within Groups	20.24166667	10	2.02417			
Total	21.14916667	11				
SW-SE-07 & TS-SE-01						
Between Groups	8221.5675	1	8221.568	56.98335184	1.95E-05	4.96460274
Within Groups	1442.801667	10	144.2802			
Total	9664.369167	11				
SW-SE-07 & TS-SE-02						
Between Groups	4320.6075	1	4320.608	83.78114284	3.55E-06	4.96460274
Within Groups	515.7016667	10	51.57017			
Total	4836.309167	11				
SW-SE-07 & SW-SE-01A						
Between Groups	0.020833333	1	0.02083	0.0219106	0.88527	4.964603
Within Groups	9.508333333	10	0.95083			
Total	9.529166667	11				
SW-SE-07 & SW-SE-02						
Between Groups	0.0675	1	0.0675	0.07565851	0.78887	4.964603
Within Groups	8.921666667	10	0.89217			
Total	8.989166667	11				

APPENDIX 3: ANOVA analysis for CaCO₃ of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.083333333	1	0.08333	0.00096432	0.97584	4.964603
Within Groups	864.1666667	10	86.4167			
Total	864.25	11				
SW-SE-07 & TS-SE-01						
Between Groups	25854.08333	1	25854.1	16.4019265	0.00232	4.964603
Within Groups	15762.83333	10	1576.28			
Total	41616.91667	11				
SW-SE-07 & TS-SE-02						

Between Groups	18486.75	1	18486.8	7.37694615	0.02171	4.964603
Within Groups	25060.16667	10	2506.02			
Total	43546.91667	11				
SW-SE-07 & SW-SE-01A						
Between Groups	1.333333333	1	1.33333	0.02132196	0.88681	4.964603
Within Groups	625.3333333	10	62.5333			
Total	626.6666667	11				
SW-SE-07 & SW-SE-02						
Between Groups	0.333333333	1	0.33333	0.00507614	0.94461	4.964603
Within Groups	656.6666667	10	65.6667			
Total	657	11				

APPENDIX 4: ANOVA analysis for TDS of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	120.3333333	1	120.333	3.68367347	0.08391	4.964603
Within Groups	326.6666667	10	32.6667			
Total	447	11				
SW-SE-07 & TS-SE-01						
Between Groups	49536.75	1	49536.8	10.9405379	0.00791	4.964603
Within Groups	45278.16667	10	4527.82			
Total	94814.91667	11				
SW-SE-07 & TS-SE-02						
Between Groups	14560.33333	1	14560.3	33.7252934	0.00017	4.964603
Within Groups	4317.333333	10	431.733			
Total	18877.66667	11				
SW-SE-07 & SW-SE-01A						
Between Groups	6.75	1	6.75	0.93533487	0.35629	4.964603
Within Groups	72.16666667	10	7.21667			
Total	78.91666667	11				
SW-SE-07 & SW-SE-02						
Between Groups	3	1	3	0.26162791	0.62011	4.964603
Within Groups	114.6666667	10	11.4667			
Total	117.6666667	11				

APPENDIX 5: ANOVA analysis for SO₄ of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	10.08333333	1	10.0833	0.02674033	0.87336	4.964603
Within Groups	3770.833333	10	377.083			
Total	3780.916667	11				
SW-SE-07 & TS-SE-01						
Between Groups	297675	1	297675	24.6179229	0.00057	4.964603
Within Groups	120918	10	12091.8			
Total	418593	11				
SW-SE-07 & TS-SE-02						
Between Groups	123627	1	123627	220.21197	3.8768E-08	4.964603
Within Groups	5614	10	561.4			
Total	129241	11				
SW-SE-07 & SW-SE-01A						
Between Groups	300	1	300	7.31707317	0.02212233	4.964603
Within Groups	410	10	41			
Total	710	11				
SW-SE-07 & SW-SE-02						
Between Groups	310.0833333	1	310.083	2.91203631	0.1187291	4.964603
Within Groups	1064.833333	10	106.483			
Total	1374.916667	11				

APPENDIX 6: ANOVA analysis for pH of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.05333	1	0.05333	0.87912	0.37054	4.9646
Within Groups	0.60667	10	0.06067			
Total	0.66	11				
BRMB-01A & SEMB-02A						
Between Groups	0.0675	1	0.0675	1.60079	0.23448	4.9646
Within Groups	0.42167	10	0.04217			
Total	0.48917	11				
BRMB-01A & SEMB-03A						
Between Groups	0.14083	1	0.14083	4.88439	0.05155	4.9646

Within Groups	0.28833	10	0.02883			
Total	0.42917	11				

APPENDIX 7: ANOVA analysis for EC of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1441.02	1	1441.02	89.3112	2.66183E-06	4.9646
Within Groups	161.348	10	16.1348			
Total	1602.37	11				
BRMB-01A & SEMB-02A						
Between Groups	2263.25	1	2263.25	155.046	2.06226E-07	4.9646
Within Groups	145.973	10	14.5973			
Total	2409.23	11				
BRMB-01A & SEMB-03A						
Between Groups	3330	1	3330	356.118	3.7844E-09	4.9646
Within Groups	93.5083	10	9.35083			
Total	3423.51	11				

APPENDIX 8: ANOVA analysis for CaCO₃ of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	50583.1	1	50583.1	26.5802	0.00043	4.9646
Within Groups	19030.4	10	1903.04			
Total	69613.4	11				
BRMB-01A & SEMB-02A						
Between Groups	50103.8	1	50103.8	26.3273	0.00044	4.9646
Within Groups	19031.1	10	1903.11			
Total	69134.8	11				
BRMB-01A & SEMB-03A						
Between Groups	36410.1	1	36410.1	16.7181	0.00218	4.9646
Within Groups	21778.8	10	2177.88			
Total	58188.9	11				

APPENDIX 9: ANOVA analysis for TDS of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	15336.8	1	15336.8	1.5134	0.24677	4.9646
Within Groups	101340	10	10134			
Total	116676	11				
BRMB-01A & SEMB-02A						
Between Groups	23144.1	1	23144.1	2.11329	0.17668	4.9646
Within Groups	109517	10	10951.7			
Total	132661	11				
BRMB-01A & SEMB-03A						
Between Groups	56033.3	1	56033.3	3.92376	0.07577	4.9646
Within Groups	142805	10	14280.5			
Total	198839	11				

APPENDIX 10: ANOVA analysis for SO₄ of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	19.8147	1	19.8147	1.43044	0.25928	4.9646
Within Groups	138.521	10	13.8521			
Total	158.336	11				
BRMB-01A & SEMB-02A						
Between Groups	0.80083	1	0.80083	0.74348	0.40875	4.9646
Within Groups	10.7714	10	1.07714			
Total	11.5723	11				
BRMB-01A & SEMB-03A						
Between Groups	4.70001	1	4.70001	0.72788	0.41354	4.9646
Within Groups	64.5711	10	6.45711			
Total	69.2711	11				

APPENDIX 11: ANOVA analysis for pH of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.02083	1	1.02083	38.0435	0.00011	4.9646
Within Groups	0.26833	10	0.02683			
Total	1.28917	11				
BRMB-01B & SEMB-02B						
Between Groups	1.02083	1	1.02083	31.0914	0.00024	4.9646
Within Groups	0.32833	10	0.03283			
Total	1.34917	11				
BRMB-01B & SEMB-03B						
Between Groups	0.12	1	0.12	3.02521	0.11261	4.9646
Within Groups	0.39667	10	0.03967			
Total	0.51667	11				

APPENDIX 12: ANOVA analysis for EC of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2898.52	1	2898.52	24.166	0.00061	4.9646
Within Groups	1199.42	10	119.942			
Total	4097.94	11				
BRMB-01B & SEMB-02B						
Between Groups	739.47	1	739.47	5.95402	0.03484	4.9646
Within Groups	1241.97	10	124.197			
Total	1981.44	11				
BRMB-01B & SEMB-03B						
Between Groups	6.45333	1	6.45333	0.04228	0.84121	4.9646
Within Groups	1526.19	10	152.619			
Total	1532.64	11				

APPENDIX 13: ANOVA analysis for CaCO₃ of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	171913	1	171913	39.2395	9.33218E-05	4.9646
Within Groups	43811.3	10	4381.13			
Total	215724	11				
BRMB-01B & SEMB-02B						
Between Groups	30401.3	1	30401.3	6.74361	0.026635215	4.9646
Within Groups	45081.7	10	4508.17			
Total	75483	11				
BRMB-01B & SEMB-03B						
Between Groups	2700	1	2700	0.54383	0.47779563	4.9646
Within Groups	49647.7	10	4964.77			
Total	52347.7	11				

APPENDIX 14: ANOVA analysis for TDS of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	48768.8	1	48768.8	3.07084	0.11026	4.9646
Within Groups	158812	10	15881.2			
Total	207581	11				
BRMB-01B & SEMB-02B						
Between Groups	6302.08	1	6302.08	0.25272	0.62605	4.9646
Within Groups	249374	10	24937.4			
Total	255676	11				
BRMB-01B & SEMB-03B						
Between Groups	3	1	3	0.00013	0.99111	4.9646
Within Groups	229762	10	22976.2			
Total	229765	11				

APPENDIX 15: ANOVA analysis for SO₄ of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.59407	1	0.59407	0.50484	0.49362	4.9646
Within Groups	11.7676	10	1.17676			
Total	12.3616	11				
BRMB-01B & SEMB-02B						
Between Groups	0.63941	1	0.63941	0.55562	0.47319	4.9646
Within Groups	11.5081	10	1.15081			
Total	12.1475	11				
BRMB-01B & SEMB-03B						
Between Groups	23.2408	1	23.2408	2.6004	0.13791	4.9646
Within Groups	89.3741	10	8.93741			
Total	112.615	11				

APPENDIX 16: ANOVA analysis for Fe concentration of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.27	1	0.27	0.08687259	0.77422	4.964603
Within Groups	31.08	10	3.108			
Total	31.35	11				
SW-SE-07 & TS-SE-01						
Between Groups	0.3675	1	0.3675	0.08334278	0.77871	4.964603
Within Groups	44.095	10	4.4095			
Total	44.4625	11				
SW-SE-07 & TS-SE-02						
Between Groups	6.02083	1	6.02083	1.08233214	0.32268	4.964603
Within Groups	55.6283	10	5.56283			
Total	61.6492	11				
SW-SE-07 & SW-SE-01A						
Between Groups	0.52083	1	0.52083	0.17060654	0.68829	4.964603
Within Groups	30.5283	10	3.05283			
Total	31.0492	11				
SW-SE-07 & SW-SE-02						
Between Groups	0.3675	1	0.3675	0.12631036	0.72967	4.964603
Within Groups	29.095	10	2.9095			
Total	29.4625	11				

APPENDIX 16: ANOVA analysis for Cu concentration of surface water samples

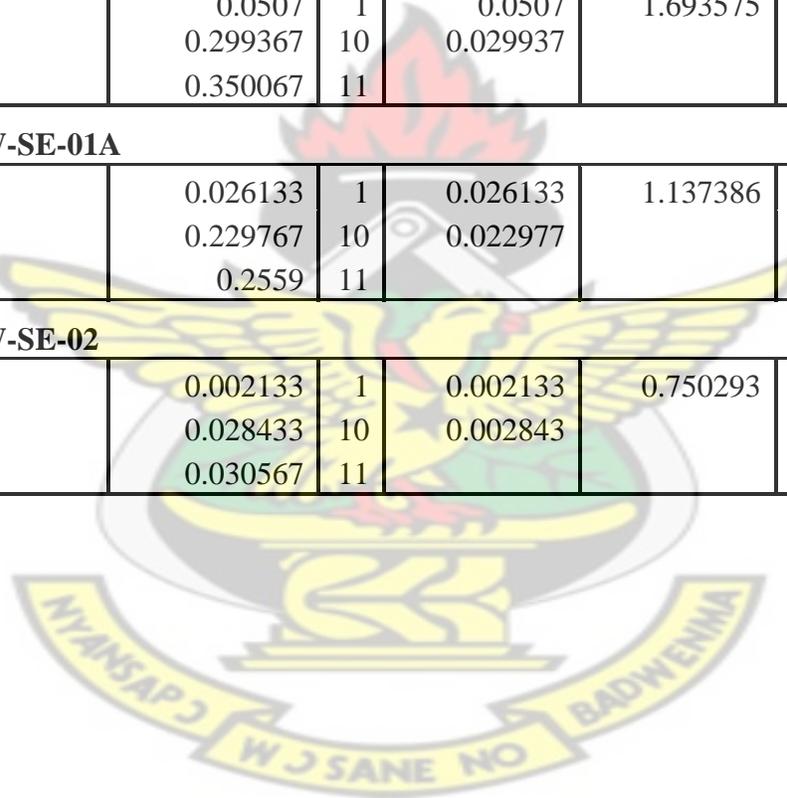
ANOVA (SW-SE-07 & TS-SE-01)						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	7.5E-05	1	0.000075	1	0.34089	4.964603
Within Groups	0.00075	10	0.000075			
Total	0.00083	11				
SW-SE-07 & SW-SE-01A						
Between Groups	3.3333E-05	1	3.3333E-05	1	0.34089	4.964603
Within Groups	0.00033333	10	3.3333E-05			
Total	0.00036667	11				

APPENDIX 17: ANOVA analysis for Mn concentration of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.033075	1	0.033075	0.05214	0.823978	4.96460274
Within Groups	6.343216667	10	0.634321667			
Total	6.376291667	11				
SW-SE-07 & TS-SE-01						
Between Groups	0.06600833	1	0.066008333	0.12870	0.72724	4.964603
Within Groups	5.12868333	10	0.512868333			
Total	5.19469167	11				
SW-SE-07 & TS-SE-02						
Between Groups	0.06163333	1	0.061633333	0.10993	0.74706	4.964603
Within Groups	5.60646667	10	0.560646667			
Total	5.6681	11				
SW-SE-07 & SW-SE-01A						
Between Groups	0.33000833	1	0.330008333	0.68135	0.42837	4.964603
Within Groups	4.84341667	10	0.484341667			
Total	5.173425	11				
SW-SE-07 & SW-SE-02						
Between Groups	0.51253333	1	0.512533333	1.14508	0.30973	4.964603
Within Groups	4.47593333	10	0.447593333			
Total	4.98846667	11				

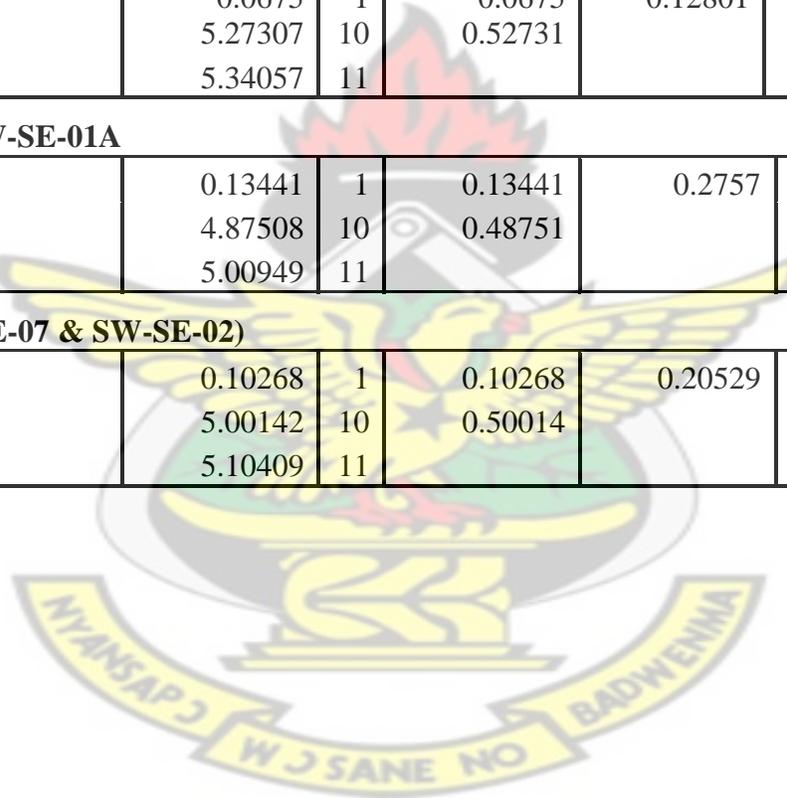
APPENDIX 18: ANOVA analysis for Zn concentration of surface water samples

SW-SE-07 & SW-SE-06						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.003675	1	0.003675	0.588785	0.46062	4.9646
Within Groups	0.062417	10	0.006242			
Total	0.066092	11				
SW-SE-07 & TS-SE-01						
Between Groups	0.006533	1	0.006533	1.191489	0.30062	4.9646
Within Groups	0.054833	10	0.005483			
Total	0.061367	11				
SW-SE-07 & TS-SE-02						
Between Groups	0.0507	1	0.0507	1.693575	0.22231	4.9646
Within Groups	0.299367	10	0.029937			
Total	0.350067	11				
SW-SE-07 & SW-SE-01A						
Between Groups	0.026133	1	0.026133	1.137386	0.31127	4.9646
Within Groups	0.229767	10	0.022977			
Total	0.2559	11				
SW-SE-07 & SW-SE-02						
Between Groups	0.002133	1	0.002133	0.750293	0.4066	4.9646
Within Groups	0.028433	10	0.002843			
Total	0.030567	11				



APPENDIX 19: ANOVA analysis for Al concentration of surface water samples

ANOVA (SW-SE-07 & SW-SE-06)						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.22413	1	0.22413	0.47051	0.50834	4.9646
Within Groups	4.76367	10	0.47637			
Total	4.9878	11				
SW-SE-07 & TS-SE-01						
Between Groups	0.1323	1	0.1323	0.26004	0.62116	4.9646
Within Groups	5.08767	10	0.50877			
Total	5.21997	11				
SW-SE-07 & TS-SE-02						
Between Groups	0.0675	1	0.0675	0.12801	0.72794	4.9646
Within Groups	5.27307	10	0.52731			
Total	5.34057	11				
SW-SE-07 & SW-SE-01A						
Between Groups	0.13441	1	0.13441	0.2757	0.61097	4.9646
Within Groups	4.87508	10	0.48751			
Total	5.00949	11				
ANOVA (SW-SE-07 & SW-SE-02)						
Between Groups	0.10268	1	0.10268	0.20529	0.66016	4.9646
Within Groups	5.00142	10	0.50014			
Total	5.10409	11				



APPENDIX 20: ANOVA analysis for As concentration of surface water samples

ANOVA (SW-SE-07 & SW-SE-06)						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0	1	0	0	1	4.9646
Within Groups	1.06667E-05	10	1.06667E-06			
Total	1.06667E-05	11				
SW-SE-07 & TS-SE-01						
Between Groups	0	1	0	0	1	4.9646
Within Groups	1.06667E-05	10	1.06667E-06			
Total	1.06667E-05	11				
SW-SE-07 & TS-SE-02						
Between Groups	3.33333E-07	1	3.33333E-07	0.29412	0.59947	4.9646
Within Groups	1.13333E-05	10	1.13333E-06			
Total	1.16667E-05	11				
SW-SE-07 & SW-SE-02						
Between Groups	3.33333E-07	1	3.33333E-07	0.38462	0.54901	4.9646
Within Groups	8.66667E-06	10	8.66667E-07			
Total	0.000009	11				

APPENDIX 12: ANOVA analysis for pH of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.05333	1	0.05333	0.87912	0.37054	4.9646
Within Groups	0.60667	10	0.06067			
Total	0.66	11				
BRMB-01A & SEMB-02A						
Between Groups	0.0675	1	0.0675	1.60079	0.23448	4.9646
Within Groups	0.42167	10	0.04217			
Total	0.48917	11				
BRMB-01A & SEMB-03A						
Between Groups	0.14083	1	0.14083	4.88439	0.05155	4.9646
Within Groups	0.28833	10	0.02883			
Total	0.42917	11				

APPENDIX 21: ANOVA analysis for Fe concentration of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0	1	0	0	1	4.9646
Within Groups	0.02667	10	0.00267			
Total	0.02667	11				

APPENDIX 22: ANOVA analysis for As concentration of the deep monitoring boreholes

BRMB-01A & SEMB-01A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.000012	1	0.000012	3.103448	0.108611	4.964603
Within Groups	3.87E-05	10	3.87E-06			
Total	5.07E-05	11				
BRMB-01A & SEMB-02A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.14963	1	0.14963	6.73619	0.0267	4.9646
Within Groups	0.22213	10	0.02221			
Total	0.37177	11				
BRMB-01A & SEMB-03A						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1.3E-06	1	1.3E-06	1.42857	0.25957	4.9646
Within Groups	9.3E-06	10	9.3E-07			
Total	1.1E-05	11				

APPENDIX 23: ANOVA analysis for Fe concentration of the shallow monitoring boreholes

BRMB-01B & SEMB-02B						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.05333	1	0.05333	0.61538	0.45095	4.9646
Within Groups	0.86667	10	0.08667			
Total	0.92	11				
BRMB-01B & SEMB-03B						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.05333	1	0.05333	0.61538	0.45095	4.9646
Within Groups	0.86667	10	0.08667			
Total	0.92	11				

APPENDIX 24: ANOVA analysis for Mn concentration of the shallow monitoring boreholes

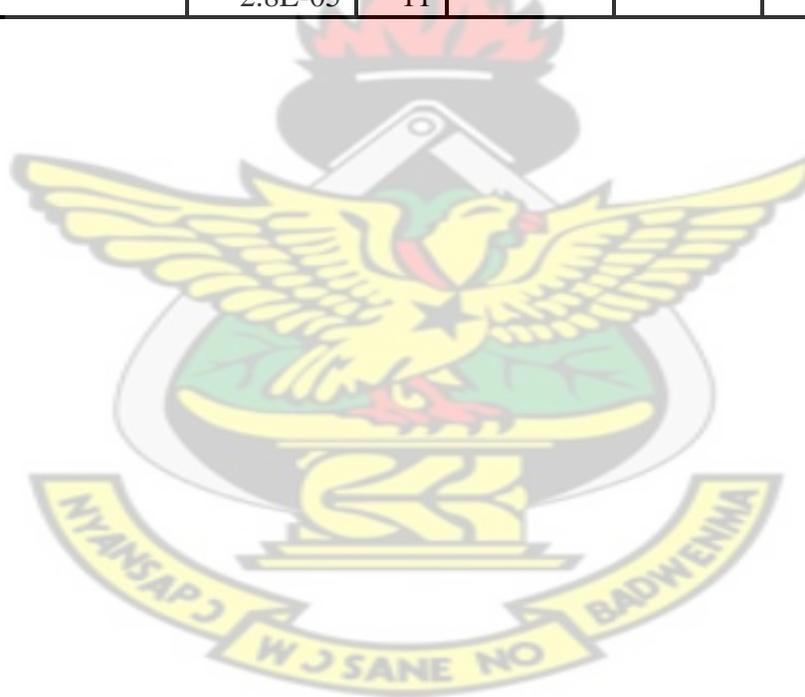
BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.3E-05	1	3.3E-05	0.07692	0.78716	4.9646
Within Groups	0.00433	10	0.00043			
Total	0.00437	11				
BRMB-01B & SEMB-02B						
Between Groups	12.0801	1	12.0801	166.286	1.48094E-07	4.9646
Within Groups	0.72647	10	0.07265			
Total	12.8066	11				
BRMB-01B & SEMB-03B						
Between Groups	0.03	1	0.03	2.61172	0.1371489	4.9646
Within Groups	0.11487	10	0.01149			
Total	0.14487	11				

APPENDIX 25: ANOVA analysis for Al concentration of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00013	1	0.00013	0.28169	0.60718	4.9646
Within Groups	0.00473	10	0.00047			
Total	0.00487	11				
BRMB-01B & SEMB-02B						
Between Groups	0.00021	1	0.00021	0.15924	0.69825	4.9646
Within Groups	0.01308	10	0.00131			
Total	0.01329	11				
BRMB-01B & SEMB-03B						
Between Groups	0.0003	1	0.0003	0.5	0.49565	4.9646
Within Groups	0.006	10	0.0006			
Total	0.0063	11				

APPENDIX 26: ANOVA analysis for As concentration of the shallow monitoring boreholes

BRMB-01B & SEM-01B						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3E-06	1	3E-06	1.8	0.20938	4.9646
Within Groups	1.7E-05	10	1.7E-06			
Total	2E-05	11				
BRMB-01B & SEMB-02B						
Between Groups	1.33E-06	1	1.33E-06	0.769231	0.401034	4.964603
Within Groups	1.73E-05	10	1.73E-06			
Total	1.87E-05	11				
BRMB-01B & SEMB-03B						
Between Groups	3.3E-07	1	3.3E-07	0.12195	0.73417	4.9646
Within Groups	2.7E-05	10	2.7E-06			
Total	2.8E-05	11				



APPENDIX 30: World Health Organization (WHO) guideline and Ghana Standards Authority (GSB) water quality standards

PARAMETER	UNIT	WHO GUIDELINE VALUES	GSB STANDARDS
		2006	2009
pH	-	6.5-8.5	6.5-8.5
Conductivity	µS/cm	< 1500	1000
Total Dissolved Solids	mg/L	1000	1000
Alkalinity	mg/L	-	-
Sulphate (SO ₄)	mg/L	250	0-250
Cadmium (Cd)	mg/L	0.003	0-0.05
Lead (Pb)	mg/L	0.01	0.01
Arsenic (As)	mg/L	0.01	0.01
Zinc (Zn)	mg/L	3	0-3.0
Iron (Fe)	mg/L	0.3	0-0.3
Manganese (Mn)	mg/L	0.1	0-0.1/0.04
Copper (Cu)	mg/L	1.0	1.0
Aluminium (Al)	mg/L	0.2	0.2
Silver (Ag)	mg/L	-	0.3

Nasrullah *et al.* (2006); Urushotham *et al.* (2013); Ghana Standards Board limits for Drinking water (GS 175-1:2009 3rd Edition).

