# An Evaluation of the Effects of Historical Coal Mining Activities on Water Quality in the Elitheni Colliery, Eastern Cape Province, South Africa

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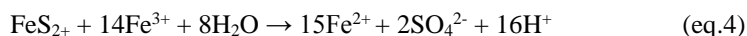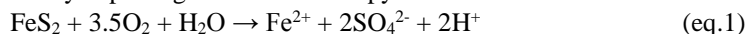Department of Environmental Sciences, University of South Africa
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**ABSTRACT—** *The study reported on here was conducted to assess the impacts of historic coal mining activities at Elitheni Colliery in South Africa. Five boreholes and five water ponds were sampled during the summer of 2010 and winter of 2011. Physical characteristics (pH, EC, TDS) and hydrochemical characteristics ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $Cl^-$, $SO_4^{2-}$, $F^-$, Pb and Fe) of the water were determined. To assess the suitability of the water for irrigation purposes, parameters such as total hardness, sodium absorption ratio (SAR), percentage sodium (% Na), residual sodium carbonate (RSC), permeability index (PI) and Mg ratio were calculated. The pH of the water ranged from 6.87 to 8.91, and electrical conductivity (EC) was between 4.5 and 94 mS/m. Total dissolved solids (TDS) ranged from 178 to 470 mg/L; spatial variations in TDS attest to variations in lithological composition, activities and prevailing hydrological regimes. $HCO_3^-$ and $SO_4^{2-}$ were the dominant anions, while $Na^+$ was the dominant cation. $Na$-$K$-$SO_4$ and $Na$-$HCO_3$ were the dominant hydrochemical facies. Fe content was high in borehole water due to the oxidation of pyrite. On the basis of the calculated SAR, % Na, RSC, Mg ratio and salt content, it was concluded that the water can be used for irrigation purposes. The water quality analysis provided no conclusive evidence that historical mining activities have had any significant impact on the acidification of water resources in Elitheni Colliery. However, further studies are required to ascertain the ability of the aquatic environment and surrounding rocks to buffer any acid generated.*

**Keywords—** Molteno-Indwe Coalfield, Acid mine drainage, Geochemical characteristics, Water quality

## 1. INTRODUCTION

Coal mining is one of the major causes of acid mine drainage (AMD), which affects fresh water systems and resources both in South Africa[1] and worldwide[2]. AMD arises from the oxidation of sulphide minerals, especially pyrite and marcasite ($FeS_2$), which are found mainly in coal deposits[3,4]. Reactions responsible for AMD genesis are best illustrated by exploring the oxidation of pyrite:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \text{(eq.1)}$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \qquad \text{(eq.2)}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 \text{ (S)} + 3H^+ \qquad \text{(eq.3)}$$

$$FeS_{2+} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{(eq.4)}$$

Iron sulphide is oxidised into dissolved iron (eq. 1), sulphate and hydrogen, therefore increasing the total dissolved solids (TDS) content and acidity of water which, unless neutralised, causes a decrease in pH. When the surrounding environment is sufficiently oxidising, the resultant ferrous iron is oxidised to ferric iron (eq.2). Ferric iron is hydrolysed, and at a pH between 2.3 and 3.5, ferric iron precipitates as $Fe(OH)_3$ and jarosite, leaving little $Fe^{3+}$ in solution while simultaneously lowering pH (eq.3). The remaining $Fe^{3+}$ from eq.2 that does not precipitate from solution through eq.3 may be used to oxidise additional pyrite (eq.4)[5,6]. Except for eqs. (2) and (3), the equations presented above assume that the oxidised mineral is pyrite and the oxidant is oxygen.

The rate at which AMD is generated depends on pH, temperature, amount of oxygen of both the gaseous and water phase, degree of saturation with water, activities of $Fe^{3+}$, surface area of the exposed sulphide mineral, the chemical activation energy necessary to induce generation of acid and bacterial activity[5,7]. However, the biogeochemical processes involved in the formation of AMD are complex and involve several reactants and products under various conditions[8,9,10]. Oxidation of sulphide minerals proceeds spontaneously and the reactions are catalysed by the action of Fe-oxidising chemolithoautotrophs such as the bacteria *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*[4,10]. In general, the aerial extent and composition of AMD are a function of depositional

environments, rock composition, mineralogy, geochemistry, and climatic and hydrological characteristics of the site of deposit[11,12].

Oxidation of sulphide minerals and the subsequent dissolution of carbonate, oxide and aluminosilicate minerals by acidic water along the pathway generally accounts for elevated concentrations of $SO_4$, Fe, Al, Mn, associated metals and metalloids[8,13-17]. The above-mentioned parameters influence the pH, composition and mineralogy of downstream precipitates and water[18]. Precipitated phases include poorly ordered iron III oxyhydroxide hydrates and iron III hydroxyl-sulphates complexes, which are effective sorbents of trace metals and oxyanions[10,19].

However, the stability of these iron precipitates and their likely associated contaminants are cause for concern due to poorly ordered minerals like ferrihydrite ($HFe_5O_8.4H_2O$) and schwertmannite [$Fe_8O_8(OH)_6SO_4$]. These transform rapidly to stable minerals such as goethite [$FeO(OH)$], which is a weaker sorbent of contaminants[20]. Moreover, development of a pH or redox gradient can accelerate the transformation processes, hence facilitating the dissolution of iron precipitates or desorption of metals with a resultant latent source of pollution[21]. Desorption of metals presents a potential danger, especially when they accumulate in water systems[22]. Therefore, AMD pollutes receiving streams and aquifers, thereby having a negative effect on the quality, quantity and potential uses of water resources[23,24].

AMD is not restricted to the source area, but may cover a large area if the acid water is allowed to discharge into the main streams[25]. In addition, AMD is a long-term environmental problem, as oxidation processes may continue for decades or even centuries[26]. In South Africa, the threat of AMD to the water systems has reached acute levels in recent years[27-29]. Both operational and abandoned coal mines generate AMD in South Africa[30].

In the Eastern Cape Province of South Africa, commercial coal mining at the Molteno-Indwe Coalfield ceased in 1948, after the operations were considered not to be economically viable, as the coal was of low grade. Informal mining nevertheless continued over the 100 years or so[31], and following the introduction of circulating fluidised bed (CFB) technology, Elitheni Colliery was established in 2008[32]. The study reported on here was conducted to ascertain the impact of historical coal mining activities on surface and ground water as well as the buffering capacity of the water resources.

## 2. GEOLOGY, SURFACE, GROUNDWATER HYDROLOGY, AND CLIMATIC CONDITIONS OF THE STUDY AREA

Molteno-Indwe Coalfield (Figure 1B) is located in the Eastern Cape province in South Africa and extends in an arc from Aliwal North in the west through Molteno, Dordrecht, Indwe and Elliot to Maclear in the east[33]. The coalfield covers an area of ca. 13 000 km$^2$ [33], and is found within the Main Karoo Basin of South Africa (Figure 1A).

The Main Karoo Basin is interpreted as a retroarc foreland basin underlain by stable bedrocks of the Kaapvaal Craton in the northwest and the Namaqua-Natal Metamorphic Belt in the south. It is bounded along its southern margin by the Cape Fold Belt[34]. Basin development was related to the Late Palaeozoic to Early Mesozoic subduction episode of the Paleo-Pacific Plate under the Gondwana Plate[35]. The Karoo Basin contains an extensive stratigraphy succession of the Karoo Supergroup that is well exposed with a continuous sedimentological record of Permian–Triassic times[35]. Lithostratigraphically, the Karoo Supergroup has been subdivided into five recognised groups (in ascending order), namely the Dwyka, Ecca, Beaufort, Stormberg and Drakensberg Groups[35-37]. These rocks are reflective of changing depositional environments which included glacial, deep marine, deltaic, fluvial and Aeolian[37].

Most of the coal deposits in the Molteno-Indwe Coalfield are hosted within the Molteno Formation (Carnian–Norian: [36, 38] Figure 1C) of the Stormberg Group, which unconformably overlies the Beaufort Group[36]. A major stratigraphical gap corresponding to the Late Anisian–Ladinian interval separates the Stormberg Group from the underlying Tarkastad Formation and older sequences[36]. Stratigraphically, the Stormberg Group consists of (in ascending order) the Molteno, Elliot and Clarens Formations. The Molteno Formation is of Late Triassic age[33,39], and unconformably rests on top of the Burgersdorp Formation[39]. The Molteno Formation, the focus of our study, attains a maximum of ca. 600 m in thickness and forms a northerly thinning intracratonic clastic wedge[33,40,41].

The Bomboesberg and Indwe Sandstone Member form the sequence of the Molteno Formation, with Transitional Member finning the upper sequence[40]. Yellowish grey or brown, bluish and light grey sandstone with ordinate dark or olive grey, dark reddish brown, dusky red siltstone, mudstones and coal characterise the formation[37]. Most sandstones are medium- to coarse-grained tabular sheets. Laterally continuous sheet sandstones were deposited by braided streams on a flood brandplain. Provenance studies of the Molteno sandstones conducted so far point to the

Dwyka, Ecca and Beaufort rocks as sources of sediments[33,42,43]. Siltsone, mudstone, and coal are less abundant and are interpreted as fills of abandoned channel tracts and within ponded bodies of water on the brandplain[40].

"The Bomboesberg Member predominantly consists of olive grey fine to medium grained sandstone, internally structured equally by horizontal and trough cross stratification"[35]. The overlying Indwe Sandstone Member is characterised by sandstone internally structured by trough cross classification[33, 35, 40]. The Transitional Member coarsens upwards, and is overlaid by the Elliot Formation. In general, the Molteno Formation represents deposition in a terrestrial environment[37].

The study area falls within a catchment area whose uplands are due to the gently undulating Msenge plateau. Most of the streams and river valleys are unnamed and ephemeral. Gully erosion is a common feature associated with the alluvial fans at the bottom of the stepper slopes. Gully erosion is mainly due to mining of mud from river banks for brick making by the local communities. The unnamed tributary of the Nomaguwana River, later becomes the Little Guba River and then the Guba River, with a seep zone (wetland) on the northern bank of the river. The Guba River conflux the Indwe River 5km downstream of the dam wall of the Doringrivier Dam, and the Lubisi Dam to the south with a full storage capacity of 158 million cubic meters. Downstream of the Lubisi Dam, the Indwe River has its confluence with the White Kei River, which is one of the larger river systems of the Eastern Cape[32].

With regards to groundwater, the groundwater is main associated with the fractured intrusive dolerite contacts and, to a lesser extent, with fractured Karoo Sequence lithology. The aquifers are unconfined to semi-confined secondary hardrock aquifers (44). The groundwater is mainly hosted in voids, fractures, bedding planes and joints.

The study area is characterized by a subtropical highlands climate, with warm summers and chilly, dry winters. The mean annual precipitation received ranges between 500 - 650mm, with rainfall occurring mainly during summer. The average annual temperature is 13.3 °C and the average annual minimum temperature is 6.0 °C [32].

## 3. MATERIALS AND METHODOLOGIES

Water samples were collected twice, during the summer of 2010 and winter of 2011, from 5 boreholes, 2 rivers and 5 ponds of water respectively. The depths of the boreholes (BH), numbered 1, 2, 3, 4 and 5, were 24.25 m, 13.85 m, 14.90 m, 8.77 m and 13 m respectively. The boreholes are open to the Molteno Formation. The rock chips generated from the drill indicated the presence of shale and sandstone. Water from the boreholes was collected by lowering a one-litre polypropylene bottle tied to a bailer inside each borehole. Prior to each field trip, the polyethylene bottles were washed in the laboratory with dilute hydrochloric acid and then rinsed twice with double-distilled water. The initial water samples collected were used to rinse two polypropylene bottles, after which the two bottles were filled to capacity and capped immediately afterwards to prevent oxidation and other chemical changes before laboratory tests. The exercise was repeated for each borehole.

The streams sampled are small and the water was well mixed. Therefore, a single grab sample was taken from each, using a polypropylene bottle rinsed with the water from that particular stream. Water samples were collected by dipping the polypropylene bottle in the stream at a single location, with the bottle being moved up and down to sample the entire vertical column of water. The sampler stood downstream from the sampling point so as to avoid stirring up any sediment that could alter the chemical analysis of the water sample.

pH and EC were measured in situ, with pH measured using a WTW pH 526 meter, while EC was read on a WTW 330i conductivity meter. Once in the laboratory, the samples were filtered through 0.45 μm membranes to remove most of the suspended solids, microorganisms, and large colloidal particles. The samples were analysed for water quality parameters such as major cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$), major anions ($SO_4^{2-}$, $HCO_3^-$, $Cl^-$, $NO_3^-$ and $F^-$) and trace metals (Fe and Pb) following standard methods. The bicarbonate content was determined by titration with 0.1 N HCl using the colour turning method with methyl orange indicator. Na and K were analysed using a flame photometer, while Mg, Ca and TH as $CaCO_3^-$ were determined by volumetric method. Anions were determined in the laboratory using a calibrated ion-specific electrode combined with a Metrohm 654 voltage meter. $SO_4^{2-}$ was determined photometrically. During sample collection, (handling and preservation) standard procedures recommended by the Department of Water and Forestry[45] were followed to ensure data quality and consistency. The analysis of the water chemistry was conducted at Amatole Water Laboratory in East London, Eastern Cape, South Africa.

Water types were identified by plotting the water chemical data obtained on a Piper diagram using Geochemistry software AqQA version AQC10664[46]. Further, suitability of water for irrigation purposes was evaluated using parameters such as sodium adsorption ratio (SAR), sodium percentage (Na %), permeability index (PI), residual sodium carbonate (RSC) and magnesium ratio.
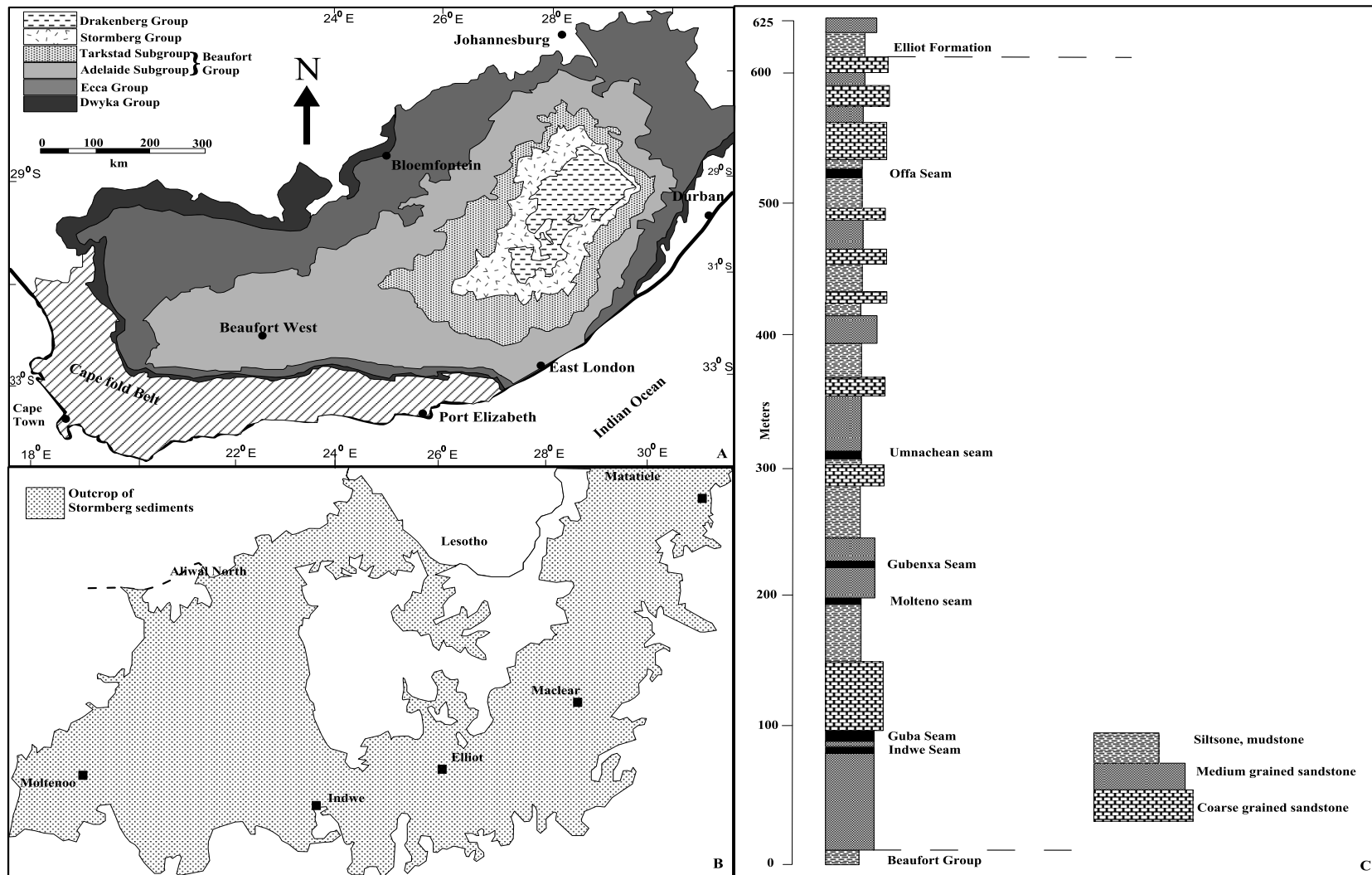
**Figure 1: A-** Geological map of the Main Karoo Basin showing the study area and indicating the main lithostratigraphic units of the Karoo Supergroup[47] **B-** The Molteno-Indwe Coalfield[48] **C** -Stratigraphy of the Molteno-Indwe Coalfield[48]

# 4. RESULT AND DISCUSSION

## 4.1 pH, EC, and TDS

The water samples studied had a pH in the range of 6.87 to 8.91, with an average of 7.62. These differences in pH are related to a variation in the soil $CO_2$ and bicarbonate concentration. The pH was within the WHO[49] admissible limit (6.5–9.2) for drinking water quality. The electrical conductivity (EC) of the water ranged between 4.5 and 94 mS/m, with an average of 37.33 mS/m. TDS is a measure of the amount of material dissolved in water[50]. This material can include carbonate, bicarbonate, chloride, sulphate, phosphate, nitrate, calcium, magnesium and sodium ions, in addition to organic ions[51]. The concentration of TDS in mine and groundwater is a function of lithology, the nature of geochemical reactions and the solubility of interactive rocks. The TDS readings were between 178 and 470 mg/L, with an average of 300.85 mg/L (Table 1).
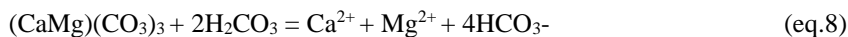
## 4.2 Major anion chemistry

$HCO_3^-$ was the dominant anion, with a concentration in the range of 39 to 276 mg/L. $HCO_3^-$ contributed 55% to the total anionic balance. $HCO_3-$ is derived mainly from the $CO_2$ in the soil zone and dissolution of carbonates or from the reaction of silicates with carbonic acid. The soil zone in the sub-surface environment contains elevated $CO_2$ pressure, which in turn combines with rain water to form bicarbonate by the following reaction:
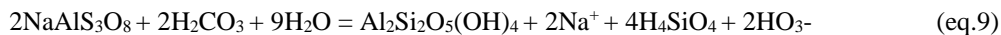
$$CO_2 + H_2O = H_2CO_3 \tag{eq.5}$$

$$HCO_3- = H^+ + HCO_3- \tag{eq.6}$$

Bicarbonate may also be derived from the dissolution of carbonates and/or silicate minerals by the carbonic acid from the reactions:

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3- \tag{eq.7}$$

(limestone)

$$(CaMg)(CO_3)_3 + 2H_2CO_3 = Ca^{2+} + Mg^{2+} + 4HCO_3- \tag{eq.8}$$

(dolomite)

$$2NaAlS_3O_8 + 2H_2CO_3 + 9H_2O = Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HO_3- \tag{eq.9}$$

(albite)　　　　　　　　　　(kaolinite)

The concentration of $SO_4^{2-}$ was between 5.3 and 144 mg/L, and accounted for 33% of the total anionic balance. $NO_3-$ ranged from 0.02 to 32 mg/L, while $Cl^-$ content was between 4 and 46, and $F^-$ content was between 0.09 and 36 mg/L (Table 1). All the water samples exhibited a higher $SO_4^{2-}$ concentration than $Cl^-$. The concentration of $SO_4^{2-}$ is associated with the oxidative weathering of sulphide-bearing minerals like pyrite or the dissolution of gypsum or anhydrite exposed to water through mining. In the Gondwana coals and associated sediments, pyrite occurs as a secondary mineral[50]. $NO_3-$, $Cl^-$ and $F^-$ contributed 7, 4 and 1% respectively to the total anionic balance (Figure 2).

## 4.3 Major cation chemistry

$Na^+$ was the dominant cation in the water samples studied. The $Na^+$ content was between 2.3 and 181 mg/L, while that of $K^+$ was between 0.9 and 3.1 mg/L. In aquatic systems, $Na^+$ is derived mainly from atmospheric deposition, evaporite dissolution, and silicate weathering[52]. In this case $Na^+$ in water samples probably indicated weathering of Na silicate minerals such as albite[53,54]. The concentration of $Ca^{2+}$ varied from 4.2 to 41 mg/L, while $Mg^{2+}$ ranged from 0.64 to 20 mg/L. The $Na^+$ content of the water was greater than the $K^+$ content, while the $Ca^{2+}$ content was greater than the $Mg^{2+}$ content. $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ accounted for 73%, 2%, 17% and 8% respectively of the total cations ($TZ^+$) (Figure 2).
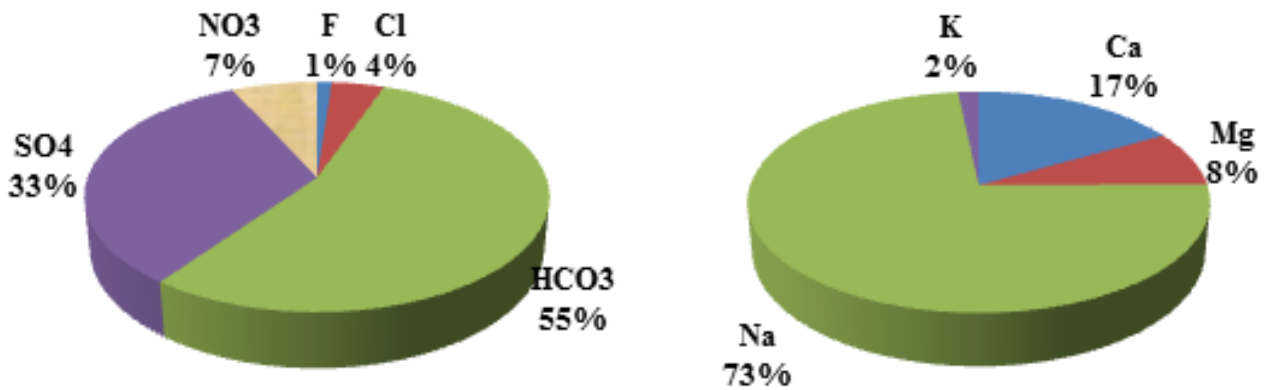
**Figure 2:** Contribution of individual ions towards the total (a) anionic and (b) cationic mass balance in the Indwe-Molteno Coalfield water

### 4.4 Trace element chemistry

The analysed trace metal values of the water were compared with relevant water quality criteria, such as those set by the WHO[49]. Trace elements analysed in this case were Fe and Pb, which are associated with sulphide minerals in coal environments. Fe concentrations in water from the boreholes sampled during the summer season of 2010 exceeded the maximum desirable limit for drinking water stipulated by the WHO[49]. The Fe content ranged from 0.4 to 2835 µg/L, whereas the Pb content was between 0.1 and 1.8 µg/L (Table 1). Known primary sources of Fe are silicates and aluminosilicates, which characterise igneous rocks[55]. Pyrite is another common source of Fe. Fe is mobilised and redistributed largely during the chemical weathering of rocks.

### 4.5 Geochemical classification and hydrogeochemical facies

To further classify the chemical composition of the water, the data was plotted on a Piper trilinear diagram (Figure 3)[56]. The plotted data of borehole water sampled in the summer season of 2010 falls in regions 2 and 4, signifying the dominance of alkalis (Na + K) over alkaline earth metals (Ca + Mg) and of strong acids ($SO_4^{2-}$ + $Cl^-$) over weak acids ($HCO_3^-$). The water is sulphate type. However, the data of borehole water sampled during the winter season of 2011 falls in regions 2 and 3, signifying the dominance of alkalis (Na + K) over earth alkaline (Ca + Mg) and of weak acids ($HCO_3^-$) over strong acids ($SO_4^{2-}$ + $Cl^-$). Water data from the ponds also falls in regions 2 and 3, indicating the dominance of alkalis (Na + K) over earth alkaline (Ca + Mg) and of weak acids ($HCO_3^-$) over strong acids ($SO_4^{2-}$ + $Cl^-$) (Figure 3). The hydrochemical facies observed in this study were Na-K-$SO_4$ and Na-$HCO_3$, and reflect the weathering of K-feldspars and albite, and oxidation of sulphide minerals[52].
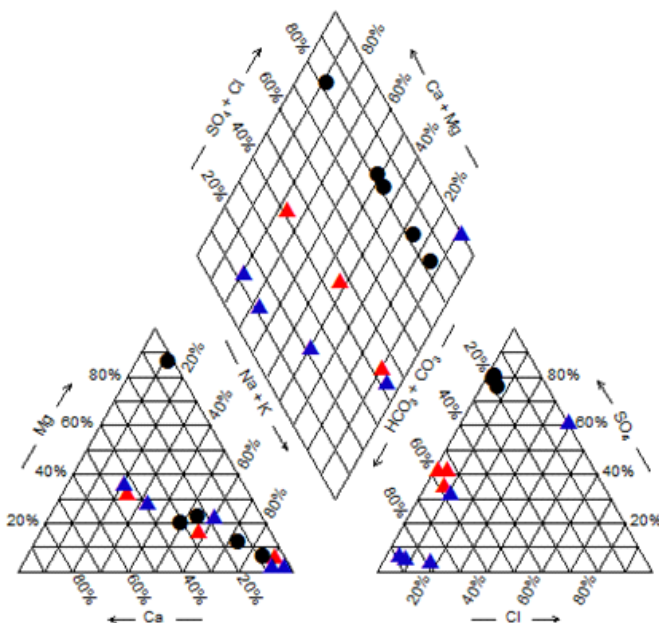


**Figure 3:** Piper's trilinear diagram of borehole and pond water

**Table 1:** Major ion chemistry of water from the Molteno-Indwe Coalfield

| Site | pH | EC (mS/m) | TDS (mg/L) | F$^-$ | Cl$^-$ | HCO$_3$- | SO$_4$$^{2-}$ (mg/L) | NO$_3$- mg/L | Ca$^{2+}$ (mg/L) | Mg$^{2+}$ (mg/L) | Na$^+$ (mg/L) | K$^+$ (mg/L) | TH (mg/L) | Fe ( µg/L) | Pb ( µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Water samples collected during the summer season of 2010** | | | | | | | | | | | | | | | |
| BH1 | 6.9 | 52 | 260 | 0.5 | 7.3 | 168 | 5.3 | 15 | 41 | 20 | 22 | 1.8 | 184.5 | 298 | 0.1 |
| BH2 | 6.9 | 47 | 236 | 0.3 | 4.8 | 158 | 6.4 | 22 | 33 | 14 | 32 | 2.3 | 139.9 | 2835 | 0.1 |
| BH3 | 7.5 | 53 | 266 | 0.3 | 4.3 | 197 | 8.9 | 28 | 7.2 | 64 | 110 | 1.1 | 280 | 1786 | 1.4 |
| BH4 | 7.2 | 94 | 470 | 0.7 | 25 | 239 | 88 | 0.02 | 4.2 | 12 | 181 | 2.7 | 59.7 | 303 | 0.6 |
| BH5 | 8.5 | 67 | 336 | 0.6 | 46 | 276 | 10 | 15 | 25 | 18 | 97 | 2.6 | 136.3 | 310 | 0.1 |
| **Water samples collected during the winter season  of 2011** | | | | | | | | | | | | | | | |
| BH1 | 7.3 | 35.5 | 253 | 0.5 | 10 | 185 | 100 | 11 | 24 | 8.5 | 60 | 0.9 | 253 | 500 | 0.1 |
| BH3 | 8.5 | 50.9 | 236 | 0.2 | 4 | 157 | 90 | 16 | 6.9 | 4.8 | 173 | 2 | 236 | 100 | 0.1 |
| BH4 | 8.9 | 4.6 | 446 | 0.5 | 18 | 228 | 110 | 32 | 4.5 | 1.9 | 2.3 | 1 | 446 | 57 | 1.8 |
| Pond 1 | 7.1 | 11.4 | 178 | 36 | 4 | 43 | 135 | 6.6 | 6.9 | 3.1 | 46.3 | 3.1 | 30 | 0.51 | 0.2 |
| Pond 2 | 7 | 6.7 | 257 | 0.2 | 4 | 44 | 130 | 15 | 13 | 6.9 | 80 | 1.6 | 257 | 0.53 | 1.3 |
| Pond 3 | 7.5 | 8.1 | 222 | 0.3 | 4 | 39 | 140 | 25 | 7.7 | 3.9 | 100 | 1.4 | 222 | 0.6 | 0. 7 |
| Pond 4 | 8 | 4.3 | 370 | 0.1 | 4 | 42 | 144 | 23 | 34 | 20 | 90 | 1.8 | 370 | 0.4 | 0.1 |
| Pond 5 | 7.8 | 50.9 | 381 | 0.1 | 7.4 | 40 | 129 | 24 | 33 | 13 | 60 | 1.6 | 381 | 0.51 | 0.1 |
| WHO (1997) (max. desirable) | 7.0 – 8.5 | 750 | 500 | - | 250 | 200 | 200 | 50 | 200 | 150 | 200 | 200 | 500 | 300 | 10 |
| WHO (1997) (highest permissible) | 6.5-9.2 | 1500 | 1500 | 1.5 | 600 | 600 | 600 | 50 | 200 | 150 | 200 | 200 | 500 | 1000 | - |

# 5.  WATER QUALITY ASSESSMENT

## 5.1 Drinking purposes and general uses

The limits suggested by the WHO[49] were used to assess the suitability of the water for drinking and public health use (Table 1). The suitability of the water for drinking purposes was assessed based on TDS. TDS refers to the sum of the major ion constituents of water, which includes major cations (dissolved $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$), major anions (dissolved carbonate species, $Cl^-$, $Fl^-$ and $SO_4^{2-}$) and non-ionic silica[57]. Four classes of water based  on the TDS, namely: fresh (< 1000 mg $L^{-1}$), brackish (1000–10 000 mg $L^{-1}$), saline (10 000–100 000 mg $L^{-1}$) and brine (> 100 000 mg $L^{-1}$) had been proposed[58]. Based on these criteria, all the water samples studied were fresh water, and their TDS reading was below the desirable limit of 500 mg $L^{-1}$ recommended by the WHO[49].

The water samples were further classified based on total hardness (TH). Water can be classified as soft (< 75 mg $L^{-1}$), moderately hard (75–150 mg $L^{-1}$), hard (150–300 mg $L^{-1}$) and very hard (> 300 mg $L^{-1}$)[59]. The total hardness of the water was between 30 and 446 mg $L^{-1}$, soft to very hard. The hardness of water is a property attributed to the presence of alkaline earths metals $Ca^{2+}$ and $Mg^{2+}$, [50]. Hard water is not a health hazard, but it is unsuitable for domestic use, especially laundry and drinking[60].

$Na^+$ and $SO_4^{2-}$ contents were also used to evaluate the quality of water. The recommended limits for $Na^+$ and $SO_4^{2-}$ in drinking water are 200 and 600 mg $L^{-1}$ respectively. Both $Na^+$ and $SO_4^{2-}$ were below the WHO (49) recommended limit.

The Fe content of the water from the boreholes sampled during the summer season of 2010 was above the maximum desirable limit for drinking water stipulated by the WHO[49].

## 5.2 Irrigation purposes

The water was further evaluated to determine its suitability for irrigation purposes. Based on the total concentration of salts, the EC of water for irrigation purposes can be classified as low (EC = 250 µS/cm), medium (EC = 250–750 µS/cm), high (EC = 750–2250 µS/cm) or very high (EC = 2250–5000 µS/cm)[61]. Based on the EC, the water studied had a low to medium concentration of salts, with the exception of water from BH4 sampled during the summer season of 2010, which had a high concentration of salts. Elevated concentrations of salts in water result in poor plant growth and low soil microbial activity due to osmotic stress and toxic ions. Salts affect soil structure, permeability and aeration, and plant growth. Salinity over time leads to sodicity[62,63]. Excessive salt in the root zone prevents plant roots from withdrawing water from surrounding soil**.**

## 5.3 Sodium adsorption ratio

The relative Na, Ca and Mg contents determine the quality of water for irrigation purposes. Both Ca and Mg are crucial for maintaining the structure of clay soils. When water with a high Na content and low Ca and Mg content is frequently used to irrigate soil, Na tends to displace Ca and Mg on clay particles, resulting in the breakdown of structure, precipitation of organic matter and reduction of soil permeability[64]. The sodium absorption ratio (SAR) is used to access the relative Na, Ca and Mg content in irrigation water and provide a useful indicator of the potential damaging effects of water on soil structure and permeability[65,66]. In this study, SAR was calculated based on laboratory results for discrete constituents and was calculated with the analytical results of $Ca^{2+}$, $Mg^{2+}$ and $Na^+$ using the following equation[67,68]:

$$SAR = Na^+ / \sqrt{[(Ca^{2+}+Mg^{2+})/2]} \qquad (eq.10)$$

Where $Ca^{2+}$, $Mg^{2+}$ and $Na^+$ represent concentrations expressed in milliequivalents per litre for each constituent.

Irrigation water is divided into the following four classes based on alkali content; low (0–10), medium (10–18), high (18–26) and very high (> 26)[61]. The calculated SAR of the water was between 0.75 and 34.42, with an average of 10.18, thus low to very high. High SAR values were observed in water from pond 3 and BH4 sampled during the summer season of 2010. The water was further plotted on a US salinity diagram, with SAR representing the alkalinity hazard and EC representing the salinity hazard. Most of the water studied fell within the C2SI class, indicating medium salinity and low Na (Figure 4). Only one water sample (BH4) fell within the C3S4 class, indicating high salinity hazard and high Na. Water characterised by low salinity and low Na can be used for irrigation in all soil types without soil developing harmful levels of exchangeable Na. Water characterised by high salinity is not recommended for soils with restricted drainage.
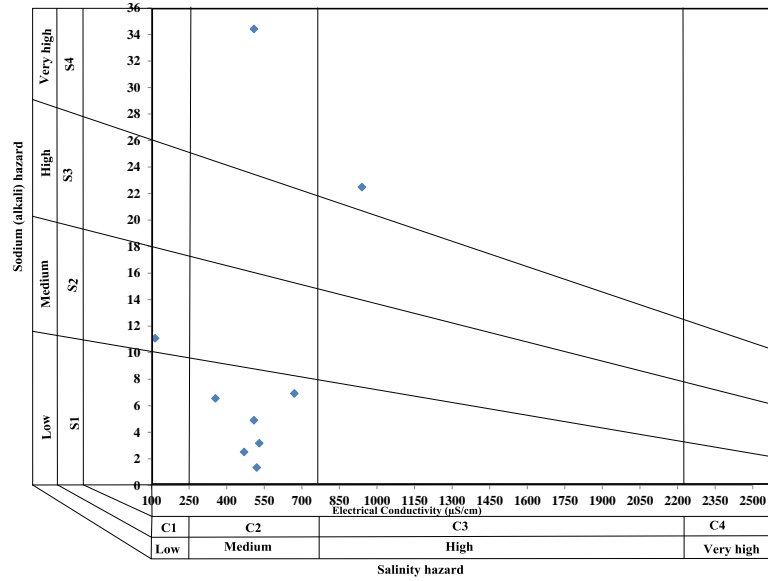
**Figure 4:** US salinity diagram for classification of irrigation water[61]

## 5.4 Percentage sodium (% Na)

Percentage sodium (% Na) is another parameter that was used to assess the suitability of the water for irrigation purposes[69]. A high concentration of Na in irrigation water reduces soil permeability and leads to poor soil drainage. Soils with poor drainage have restricted water and air circulation during wet periods and are unusually hard during the dry period[70,71]. The % Na was calculated using the following equation[72]:

$$Na \% = [(Na^+ + K^+)/(Ca^{2+} + Mg^{2+} + Na^+ + K^+)] *100 \qquad (eq.11)$$

Where $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ represent concentrations expressed in milliequivalents per litre for each constituent. The WHO[49] recommended a maximum % Na of 60% for irrigation water. The % Na of the water studied ranged from 21.36 to 91.11%, with an average of 58.88%. The data was further plotted on the Wilcox diagram (Figure 5)[69]. Most of the water samples fell in the excellent to good zones, and two fell in the permissible to doubtful zones, indicating that the water can be used for irrigation purposes.
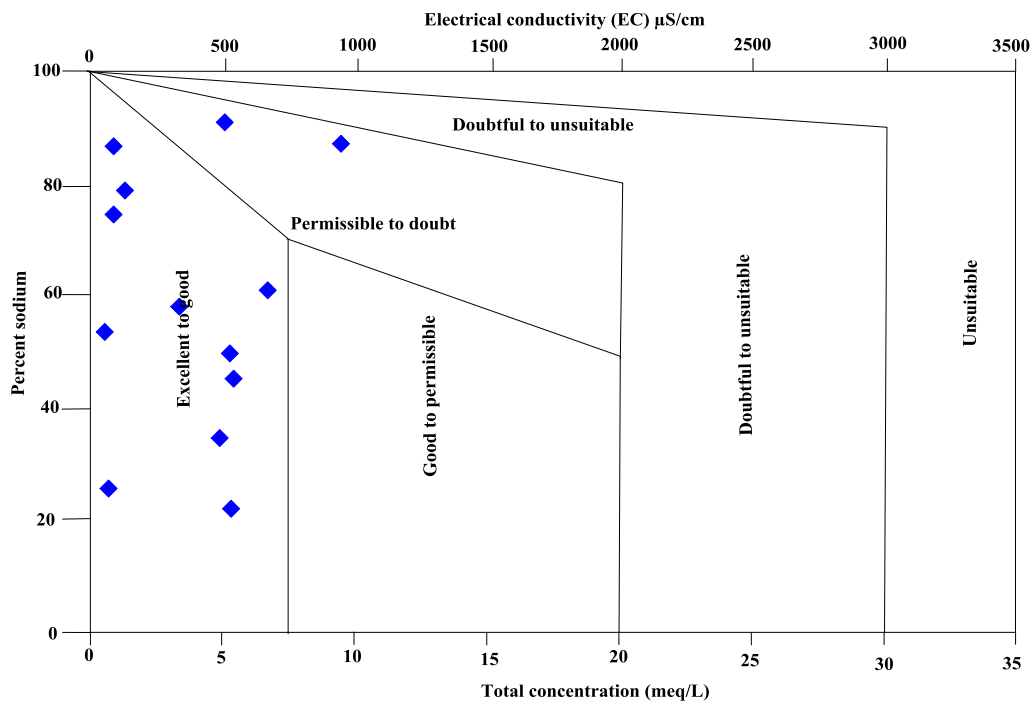


**Figure 5:** Plot of sodium percentage versus electrical conductivity[69]

### 5.5 Residual sodium carbonate (RSC)

Residual sodium carbonate (RSC) is another parameter that was used for assessing the sodium permeability hazard. RSC takes into account the bicarbonate, carbonate and Ca and Mg content of irrigation water. High concentrations of $CO_3^{2-}$ and $HCO_3^-$ compared with the contents of alkaline earths $Ca^{2+}$ and $Mg^{2+}$ may cause $Ca^{2+}$ and $Mg^{2+}$ to precipitate as a carbonate[73]. Residual sodium carbonate (RSC) is calculated as:

$$RSC = (CO_3 + HCO_3) - (Ca + Mg), \quad (eq.12)$$

Where $Ca^{2+}$, $Mg^{2+}$, $CO_3$ and $HCO_3$ represent concentrations expressed in milliequivalents per litre for each constituent. Water with RSC values of less than 1.25 meq/L is safe for irrigation; water with RSC values of 1.25 to 2.5 is marginal, and water with RSC values above 2.5 meq/L is considered unsuitable for irrigation. Based on the calculated RSC most of the water samples, except for those from BH 1, 2 and 3, were not suitable for irrigation purposes.

### 5.6 Permeability index (PI)

The permeability of soil is affected by the $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $HCO_3-$ content. The suitability of water for irrigation was further assessed based on the permeability index (PI)[74]:

$$PI = \frac{Na \pm \sqrt{HCO3}}{Ca+Mg+Na} \times 100 \quad (eq.13)$$

Where $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $HCO_3-$ represent concentrations expressed in milliequivalents per litre for each constituent.

Based on the PI, water is classified into three classes: classes I and II are suitable for irrigation purposes, while class III is unsuitable for irrigation. The PI values of the water samples when plotted on Doneen's chart revealed that most of the water samples fell within class I and class II, meaning that the water was suitable for irrigation purposes. The exception was the water from BH4 (Figure 5).

### 5.7 Magnesium ratio

The magnesium ratio is expressed as:

$$Mg\ ratio = \frac{Mg \times 100}{Ca+Mg}L. \quad (eq.14)$$

Where $Ca^{2+}$ and $Mg^{2+}$ represent concentrations expressed in milliequivalents per litre for each constituent.

Excessive Mg in water affects soil quality, and results in poor crop yield[75]. Water with a Mg ratio greater than 50% is not suitable for irrigation purposes. The calculated Mg ratio of the water studied ranged from 6.39 to 63.13, with an average of 48.39. Based on the Mg ratio water from the ponds, the water from BH1 and 2 was not suitable for irrigation purposes.
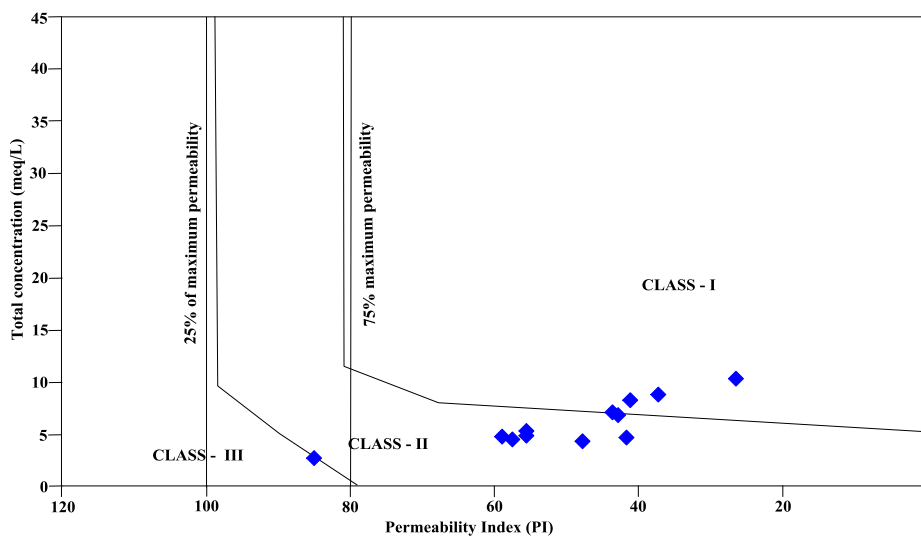


**Figure 6:** Classification of irrigation water based on the permeability index[74]

## 6. CONCLUSIONS

The quality of water from selected boreholes and ponds was evaluated so as to determine the impacts of historical coal mining activities on water quality. Further, the suitability of the water for irrigation purposes was ascertained. The water was neutral to alkaline, with $Na^+$ being the dominant cation and $HCO_3$ the dominant anion. The $Na$-$K$-$SO_4$ and $Na$-$HCO_3$ were the dominant hydrochemical facies observed. Distribution of anions and cations, and the occurrence of different hydrochemical facies suggest that the composition of water is influenced by water–rock interaction. The water quality assessment showed that the water was fresh, and ranged from soft to hard with low to medium salt contents. However, borehole water had high concentrations of Fe, and this was ascribed to the oxidation of pyrite. Domestic use would require treatment and disinfection, as the water is unsafe for drinking.

High SAR values were observed in water from pond 3 and BH4 sampled during the summer season of 2010. According to the US salinity diagram, most of the water studied fell within the C2SI class, indicating medium salinity and low Na. However, one water sample (BH4) fell within the C3S4 class, indicating a high salinity hazard and high Na. With regard to % Na, most samples fell within the excellent to good zones, with two water samples within the permissible to doubtful zones on the Wilcox diagram. The results of physio-chemical analyses (TDS, pH, EC and major ions) and the calculated water quality parameters (SAR, RSC, Mg ratio, total hardness and permeability index) indicated that most of the water samples were good and suitable for irrigation purposes. However, based on the Mg ratio water from the ponds, BH1 and 2 were not suitable for irrigation purposes.

In this study, there was no conclusive evidence from the water quality analysis that historical mining activities have had any significant impact on the acidification of water resources in the Molteno-Indwe Coalfield. However, water from BH4 should be used with caution, and not used on poorly draining soils. In general, the naturally alkaline conditions prevalent in the water resources represent a buffering capacity. The extent to which the aquatic environment and surrounding rocks would be able to buffer any acid produced is a subject for further study in order to identify possible acid buffering measures.

## 7. ACKNOWLEDGEMENT

## 8. REFERENCES

[1] Bester, M., Vermeulen, P. D., Investigation of potential water quality and quantity impacts associated with mining of the shallow waterberg coal reserves, west of the daarby fault, limpopo province, south africa. WaterSA, vol. 36, no. 5, pp. 531-542, 2010.

[2] Mallo, S. J., Mining costs analysis: various costs categories and methods of estimation. NIMG-NEITI Training Seminar on Economic evaluation of Mining Investment, Nasarawa State, Nigeria, August 2-4, 2011.

[3] Pinetown, K.L., Ward, C.R., van der Westhuizen, W.A., Quantitative evaluation of minerals in coal deposits in the witbank and highveld coalfield, and the potential impact on acid mine drainage. Interntional Journal of Coal Geology, vol. 70, no. 19, pp. 166-183, 2007.

[4] Hubbard, C. G., Black, S., Coleman, M.L., Aqueous geochemistry and oxygen isotope compositions of acid mine drainage from the río tinto, sw spain, highlight inconsistencies in current models. Chemical Geology, vol. 265, no. 3-4, pp. 321-334, 2009.

[5] Akcil, A., Koldas, S., Acid mine drainage (amd): Causes, treatment and case studies. Journal of Cleaner Production, vol. 14, no. 12-13, pp. 1139-1145, 2006.

[6] Kalin, M., Fyson, A., Wheeler, W.N., The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. Science of the Total Environment, vol. 366, no. 2-3, pp. 395-408, 2006.

[7] Cravota, C. A III., "Relations among sulfate, metals, sediments, and stream flow data for a stream draining a coal-mined watershed in east-central pennsylvania", In Proceedings of the 5th International Conference on Acid Rock Drainage (ICARD), pp 401–410, 2000.

[8] Benner, S.G., Blowes, D.W., Gould, R., Herbert, R.B.J., Ptacek, C.J., Geochemistry of a permeable reactive barrier for metals and acid mine drainage. Environment Science and Technology, vol. 33, pp. 2793-2799, 1999.

[9] Cravotta, C. A III., Suzanne J. Ward, S.J., Hammarstrom, J.M., Downflow limestone beds for treatment of net acidic, oxic, iron-laden drainage from flooded anthracite mine, pennsylvania, USA-2. Laboratory evaluation. Mine Water and the Environment, vol. 27, no. 1, pp. 86-99, 2008.

[10] Nordstrom DK, B.D.a.P.C. Hydrogeochemistry and microbiology of mine drainage: An update. Applied Geochemistry, vol. 57, pp. 3-16, 2015.

[11] Hammarstrom JM, Seal, R.R II., Meier, A.L., Kornfeld, J. M., Secondary sulfate minerals associated with acid drainage in the eastern us: Recycling of metals and acidity in surficial environments. Chemical Geology, vol. 215, no. 1, pp. 407-431, 2005.

[12] Balistrieri, L. S., Seal, R. R., Piatal, N. M., Paul, B., Assessing the concentration, speciation, and toxicity of dissolved metals during mixing of acid-mine drainage and ambient river water downstream of the elizabeth copper mine, vermont, USA. Applied Geochemistry, vol. 22, no. 5, pp. 930-952, 2007.

[13] Cravotta, C. A III., Trahan, M. K., Limestone drains to increase ph and remove dissolved metals from acidic mine drainage. Applied Geochemistry, vol. 14, pp. 581-606, 1999.

[14] Gammons, C. H., Duaime, T. E., Parker, S. R., Poulson, S. R., Kennelly, P., Geochemistry and stable isotope investigation of acid mine drainage associated with abandoned coal mines in central montana, USA. Chemical Geology, vol. 269, no. 1, pp. 563-570, 2002.

[15] Cravotta, C. A II., Effects of abandoned coal-mine drainage on streamflow and water quality in the mahanoy creek basin, schuylkill, columbia, and northumberland counties, pennsylvania, 2001. U.S. Geological Survey, USA, 2005.

[16] Perez-Lopez, R., Nieto, J. M., de Almodovar, G. R., Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste: Column experiments. Chemosphere, vol. 67, no. 8, pp. 1637-1646, 2007.

[17] Nordstrom, D. K., Acid rock drainage and climate change. Journal of Geochemical Exploration, vol. 100, no. pp. 97-104, 2009.

[18] Williams, D. J., Bigham, J.M., Cravota, C. A III., Traina, S. J., Andersen, J. E., Lyon, J. G., Assessing mine drainage ph from colour and spectral reflectance of chemical precipitates. Applied Geochemistry, vol. 17, no. 10, pp. 1273-1286, 2002.

[19] McCubbin, F. M., Tosca, N. J., Smirnov, A., Nekvasil, H., Steele, A., Fries, M., Lindsley, D. H., Hydrothermal jarosite and hematite in a pyroxene-hosted melt inclusion in martian meteorite miller range (mil) 03346: Implications for magmatic hydrothermal fluids on mars. Geochimica et Cosmochimica Acta, vol. 73, no. 16, pp. 4907-4917, 2009.

[20] Rose, S., Ghazi, A. M., Release of sorbed sulfate from iron oxyhydroxides precipitated from acid mine drainage associated with coal mining. Environmental Science and Technology, vol. 31, no. 7, pp. 2136-2140, 1997.

[21] Karathanasis, A., Thomspn, Y., Mineralogy of iron precipitates in a constructed acid mine drainage wetland. American Journal of soil Science, vol. 59, no. 6, pp. 1773-17781, 1995.

[22] Fajtl, J., Kabrna, K. M., Tichy R and Ledvina R Environmental risk associated with aeration of freshwater sediment exposed to mine drainage water. Environmental Geology, vol. 41, no. 5, pp. 563-570, 2002.

[23] Wolkersdorfer, C., Bowelle, R. J., Contemporary reviews of mine water studies in europe, part 1. Mine Water and the Environment, vol. 23, no. 4, pp. 162-182, 2004.

[24] Derakhshani, R., Alipour, M., Remediation of acid mine drainage by using tailings decant water as a neutralization agent in sarcheshmeh copper mine. Research Journal of Environmental Science, vol. 4, no. 3, pp. 250-260, 2010.

[25] Jamal, A., Yadav, H. L., Pandey, S. S., Heavy metals from acid mine drainage in coal mines – a case study. European Journal of Advances in Engineering and Technology, vol. 2, no. pp. 16-20, 2015.

[26] Christensen, B., Laake, M., Lien, T., Treatment of acid mine water by sulfate-reducing bacteria: Results from a bench scale experiment. Water Resources, vol. 30, no. 7, pp. 1617-1624, 1996.

[27] Naiker, K., Cukrowska, E., McCarthy, T. S., Acid mine drainage arising from gold mining activity in johannesburg, south africa, and environs. Environmental Pollution, vol. 122, pp. 29-40, 2003.

[28] Ewart, T. I., Acid mine drainage in the gauteng province of south africa – a phenomenological study on the degree of alignment between stakeholders concerning a sustainable solution to acid mine drainage. University of Stellenbosch, South Africa, 2011.

[29] Tandlich, R., Bioremediation challenges originating from mining and related activities in south africa. Journal of Bioremediation & Biodegradation, vol. 3, no. pp. 3, 2012.

[30] McCarthy, T. S., Impact of acid mine drainage in south africa. South African Journal of Science, vol. 107, no. May/June 2011, pp. 1-7, 2011.

[31] Peatfield, D., Coal and coal preparation in south africa – a 2002 review. Journal of the South African Institute of Mining and Metallurgy, vol. July/August 2003, no. pp. 335-375, 2002.

[32] Cobban, D. A., Rossouw, J. N., Versfeld, K., Nel, D., "Water quality consideration for open cast mining of the molteno coalfield, indwe, Eastern Cape", IN Proceedings of the the International Mine Water Conference, pp 222-232, 2009.

[33] Christie, A. D. M., Stratigraphy and sedimentology of the molteno formation in the elliot and indwe area, M.Sc. Thesis, University of Natal, South Africa, 1981.

[34] Cadle, A. B., Cairncross, B., Christie, A. D. M., Roberts, D. L., The karoo basin of south africa: Type basin for the coal-bearing deposits of southern africa. International Journal of Coal Geology, vol. 23, no. 1-4, pp. 117-157, 1993.

[35] Catuneanu, O., Hancox, P. J., Rubidge, B. S., Reciprocal flexural behavior and contrasting stratigraphies: A new basin development model for the karoo retroarc foreland system, south africa. Basin research, vol. 10, no. 4, pp. 417-439, 1998.

[36] SACS (South African Committee for Stratigraphy)., Stratigraphy of South Africa, Part 1: Lithostratigraphy of the Republic of South Africa, South West Africa/Namibia, and the Republic of Bophuthatswana, Transkei and Venda, Handbook 8, Geological Survey of South Africa, South Africa, 1980.

[37] Smith, R. M. H., A review of stratigraphy and sedimentary environments in the karoo basin of south africa. Journal of African Earth Sciences, vol. 10, no. 1, pp. 117-137, 1990.

[38] Anderson, J. M., Anderson, H. M., Paleoflora of southern africa molteno formation (triassic) vol II. A.A. Balkema, UK, 1983.

[39] Hancox, P. J., The continental triassic of South Africa. Neues Jahrbuch für Geologie und Paläontologie, vol. 1998, no. pp. 1285-1324, 2000.

[40] Turner, B. R., The stratigraphy and sedimentary history of the molteno formation in the main karoo basin of south africa and lesotho, University of the Witwatersrand, South Africa, 1975.

[41] Cairncross, B., A geological overview of the coal-bearing strata in south africa and the potential for coalbed methane. Geological Society of South Africa, South Africa, 1995.

[42] Eriksson, P. G., A palaeoenvironmental analysis of the molteno formation in the natal drakensberg. South African Journal of Geology, vol. 87, pp. 237-244, 1984.

[43] Hancox, P. J., A stratigraphic, sedimentological and palaeoenvironmental synthesis of the beaufort-molteno contact in the karoo basin, PhD thesis, University of the Witwatersrand, South Africa, 1998.

[44] Labuschagne, P. (2008) Hydrogeological assessment report elitheni coal mine phase 1, Rivonia, South Africa.

[45] Department of Water Affairs. Sampling protocol for inorganic chemical analysis, South Africa, 2004.

[46] Rockware AqQA Software., Version aqc10664, 2011, http://www.rockware.com. 2016.

[47] Rubidge, B. S., Re-uniting lost continents – fossil reptiles from the ancient karoo and their wanderlust. South African Journal of Geology, vol. 108, pp. 135-172, 2005.

[48] Christie, A.D.M. Molteno coalfield. In:. Anhauser C. R, (Eds.), Geological Society of South Africa, Johannesburg, South Africa, 1986.

[49] ), W.H.O. (World Health Organisation)., Guidelines for drinking water quality, Word Health Organisation, Swirterland, 1997.

[50] Singh, A. K., Mahato, M. K., Neogi, B., Singh, K. K., Quality assessment of mine water in the ranijanj coalfield area, india. Mine Water and the Environment, vol. 29, no. 4, pp. 248-262, 2010.

[51] Haddon, M., Mines and misdemeanours, Water Bulletin, 1994.

[52] Berner, E. K., Berner, R. A., The global water cycle: Geochemistry and environment, Prentice-Hall, New Jersey, 1987.

[53] Zhao, B., Usher, B. H., Yibas, B., Pulles, W., Evaluation and validation of geochemical prediction techniques for underground coal mines in the witbank/vryheid regions, Water Research Commission, South Africa, 2010.

[54] Malaza, N., Zhao, B., Origin of sodium and its applications to water quality prediction in the south african coal mine environment, Water Research Commision, South Africa, 2011.

[55] Deer, W. A., Howie, R. A., Zussman, J., An introduction to the rock forming minerals 2$^{edn}$, Longman Scientific & Technical, UK, 1992.

[56] Piper, A. M., A graphical procedure in the geochemical interpretation of water analysis. Transactions, American Geophysical Union, vol. 25, no. 6, pp. 914-928, 1944.

[57] Hem, J. D., Study and interpretation of the chemical characteristics of natural waters. United States Geological Survey, United States, 1985.

[58] Carroll, D., Rainwater as a chemical agent of geologic processes – a review. U.S. Geological Survey Oak Ridge, Tennessee, 1962.

[59] Sawyer, C.N., McCarty, P. L., Chemistry for sanitary engineers, McGraw-Hill series in Sanitary Science and Water Resources Engineering, McGraw-Hill, Canada, 1967.

[60] Agrawal, V., Jagetia, M., "Hydrogeochemical assessment of groundwater quality in udaipur city, rajasthan, india", In Proceedings of National Conference on Dimension of Environmental Stress in India, Baroda, pp 151-154, 1997.

[61] Richards, L. A., Diagnosis and improvement of saline and alkali soil, U.S.D.A Handbook, US Department of Agriculture, USA, 1954.

[62] Rashidi, M., Seilsepour, M., Modeling of soil cation exchange capacity based on some soil physical and chemical properties. ARPN Journal of Agricultural and Biological Science, vol. 3, no. 4, pp. 6-13, 2008.

[63] Seilsepour, M., Rashidi, M., Prediction of soil cation exchange capacity based on some soil physical and chemical properties. World Applied Sciences Journal, vol. 3, pp. 200-205, 2008.

[64] Mengel, K., Kirkby, E. A., Principles of plant nutrition, International Potash Institute, Berb, Swirtzerland, 1982.

[65] Emerson, W. W., Bakker, A. C., The comparative effects of exchangeable calcium, magnesium and sodium on some physical properties of red-brown earth sub-soils. II. The spontaneous dispersion of aggregates in water. Australian Journal of Soil Research vol. 11, no. 2, pp. 151-157, 1973.

[66] Page, A. L., Miller, R. H., Keeney, D. R., Method in soil analysis: Part 2. Chemical and microbial properties, American Society of Agronomy, USA, 1982.

[67] Sumner, M. E., Sodic soils: New perspectives. Australian Journal of Soil Research, vol. 31, no. 6, pp. 683-750, 1993.

[68] Quirk, J. P., The significance of the threshold and turbidity concentrations in relation to sodicity and microstructure. Australian Journal of Soil Resaerch, vol. 39, no. 6, pp. 1185-1217, 2001.

[69] Wilcox, L. V., Classification and use of irrigation waters, USDA circular 969, USDA, Washington DC, 1955.

[70] Collins, R., Jenkins, A., The impact of agricultural land use on stream chemistry in the middle hills of the himalayas, nepal. Journal of Hydrology, vol. 185, no. 1, pp. 71-86, 1996.

[71] Saleh, A., Al-Ruwaih, F., Shehata, M., Hydrogeochemical processes operating within the main aquifers of kuwait. Journal of Arid Enviroments, vol. 42, no. 3, pp. 195-209, 1999.

[72] Raghunath, H. M., Groundwater, Wiley Eastern Limited, New Delhi, 1987.

[73] Karanth, K. R., Ground water assessment development and management, Tata McGraw-Hill Education, India, 1989.

[74] Doneen, L. D., Notes on water quality in agriculture, Water science and engineering paper 4001, University of California, USA, 1964.

[75] Szabolcs, I., Darab, C., "The influence of irrigation water of high sodium carbonate content of soils", In the Proceeding of the 8th International Congress Soil Science Sodics Soils, pp 803–812, 1964.