Journal of African Earth Sciences 92 (2014) 68–75

Contents lists available at ScienceDirect

Journal of African Earth Sciences

journal homepage: www.elsevier.com/locate/jafrearsci

Hydrogeochemical characteristics of a flooded underground coal mine groundwater system

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ARTICLE INFO

Article history:
Received 23 July 2013
Received in revised form 7 January 2014
Accepted 27 January 2014
Available online 4 February 2014

Keywords:
Acid mine drainage
Acid buffering
Carbonates
Flooded underground coal mine
Groundwater quality
Hydrogeochemical processes

ABSTRACT

Hydrogeochemical processes have an important influence on evolution of the groundwater chemistry and its quality. An investigation was conducted to assess the hydrogeochemical processes in a flooded underground coal mine located in a typical Karoo Basin of Southern Africa. The study utilises scatter plots, PHREEQC hydrogeochemical model and the expanded Durov diagram as complimentary tools to analyse the groundwater chemistry. 144 Samples were collected from 16 piezometers drilled into the flooded underground coal mine during a three year monitoring period (2000–2002). Field results indicate that the groundwater system is characterised by a Ca-SO_4 main hydrochemical groundwater type that evolved from acid mine drainage (AMD) buffering by calcite and dolomite carbonate minerals. The carbonate AMD buffering process is hindering the leaching of metals into the flooded mine groundwater system. Hardness in at least 85% of the samples exceeded 1200 mg/L as $CaCO_3$ and the groundwater was classified as excessively hard. Modelling results using PHREEQC suggests that increase of Ca^{2+} and SO_4^{2-} concentration that evolve from carbonate AMD buffering process can only occur up to certain point until which the aqueous solubility of these ions becomes indirectly limited by gypsum saturation.

1. Introduction

Coal is an important energy resource in South Africa. South Africa is rated as the sixth and fifth largest producer and exporter of coal respectively in the world (International Energy Agency, 2010). It is mainly used for electricity generation and fuel production. Although coal is an important strategic energy resource, its mining activities are also associated with a number of environmental problems.

It is widely accepted that acid mine drainage (AMD) and its potential impact on groundwater resources is one of the most serious environmental concern associated with coal mining (Brady et al., 1997; Rose and Cravotta, 1998; Bell et al., 2001; Vermeulen and Usher, 2009). However, during AMD a number of hydrogeochemical processes can occur as the mine water evolves through various stages towards a particular hydrochemical type and quality. A good understanding of such hydrogeochemical processes is very important for investigating the groundwater quality characteristics. Typical hydrogeochemical processes that can occur during AMD include; acid neutralisation/buffering, chemical precipitation, attenuation or dissolution of metals (Blowes and Ptacek, 1994). It is clear that a number hydrogeochemical process that occurs during AMD can potentially contribute to evolving hydrochemical groundwater type. The main task of a hydrogeochemical study is to identify the process responsible for the evolution of measured groundwater chemistry. Considering that different hydrogeochemical processes can result in the same hydrochemical groundwater type, identification of the responsible processes can be mainly achieved with the assistance of a diagnostic approach (Gomo et al., 2012). It is upon such a background that this study was aimed at investigating the hydrogeochemical characteristics of a flooded underground coal mine and its contribution to the overall groundwater quality. The study utilises a diagnostic approach through the application of scatter plots, USGS geochemical code PHREEQC (Parkhurst and Appelo, 1999) and expanded Durov diagram as complimentary tools to analyse the groundwater chemistry data collected from a flooded underground coal mine over a three year period (2000–2002).

2. Methods and materials

2.1. Study area description

The flooded underground mine is located in the Witbank coal fields in Mpumalanga Province of South Africa (Fig. 1). The mine

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http://dx.doi.org/10.1016/j.jafrearsci.2014.01.014

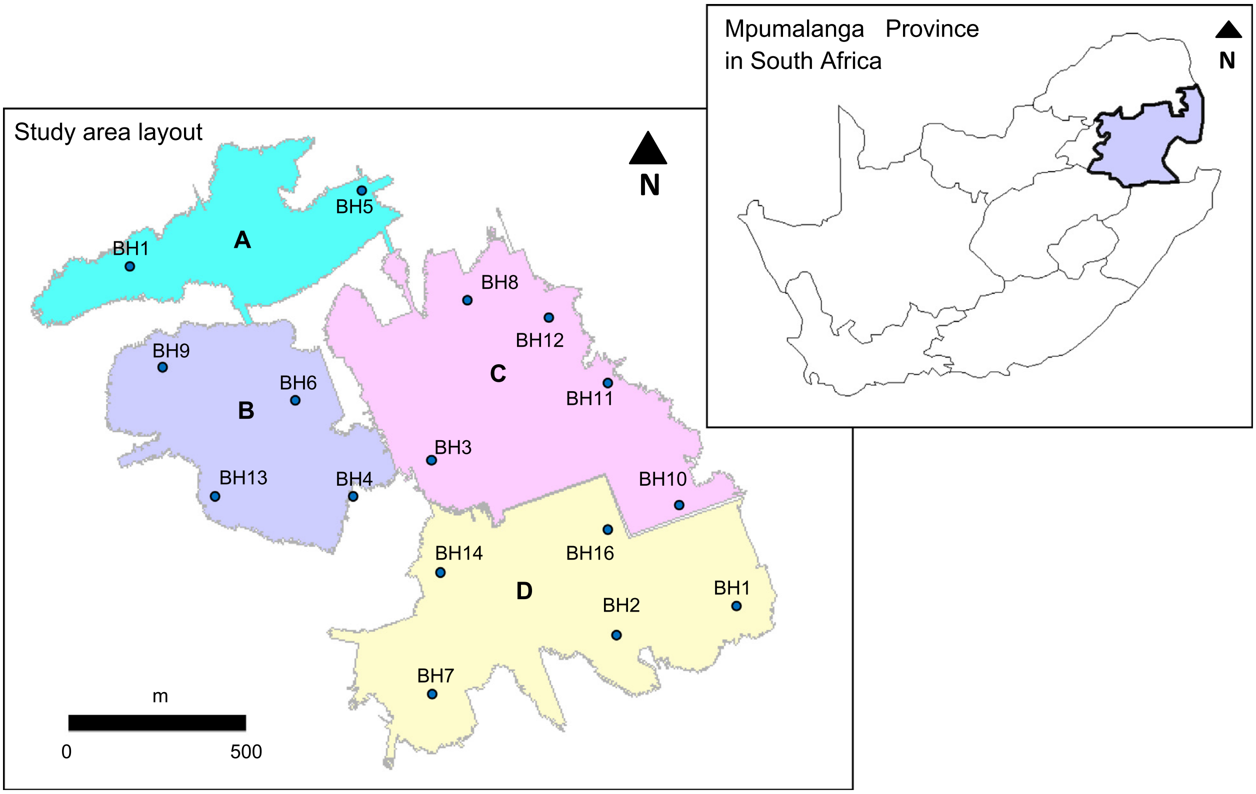

Fig. 1. Location of monitoring piezometers across the underground mine compartments at the study area; the insert map shows the location of Mpumalanga Province in South Africa where the site is located.

consist of four main compartments lettered A–D. In total, an area of about 235 ha has been mined. The mined depth ranges from 13.2 to 77.6 meters below ground level (mbgl). It is understood that active mining at the site stopped in 1975 when the compartments started filling with water. Unpublished mine reports at the mine indicate that the mine compartments were completely flooded when groundwater quality monitoring for this study started in 2000.

On average the area receives about 698 mm of rainfall per annum. The mean annual evaporation (MAE) for the area is in the order of 1600 mm. The land above the mine is used for agriculture crop production through the aid of irrigation.

2.2. Geology

General geology of the study area consists of weathered regolith that is underlined by alternating layers of siltstone, sandstone and carbonaceous shale of the Karoo Basin. The main Karoo Basin overlies the central and eastern parts of South Africa. Dolerite dykes and sill intrusions are also common features throughout the study area.

Coal seams generally occur in between the alternating layered sedimentary formations. The seams are contained within a 70 m succession and parting thickness between the seams is reasonably constant across the field (Smith and Whittaker, 1986). Pyrite is a common mineral in the Witbank coal (Azzie, 2002; Pinetown and Boer, 2006) and its AMD related problems in the environment are widely known. Other studies in the Witbank coalfields have also shown the existence of acid buffering minerals such as calcite and dolomite that occurs together with pyrite within the coal seams (Van Vuuren and Cole, 1979; Gaigher, 1980; Van der Spuy and Willis, 1991; Usher et al., 2001; Azzie, 2002; Pinetown and Boer, 2006). Mineral phases detected in the geological samples collected from the mined depth indicate the presence of pyrite, calcite and dolomite minerals (Table 1).

2.3. Hydrogeology

General hydrogeology of the study area consists of weathered shallow aquifer overlying the fractured groundwater system. The shallow weathered aquifer generally extends to depths of 10 mbgl. The grains in the fresh rock below the weathered zone are well cemented and have low permeability. Most groundwater movement therefore occurs and moves along secondary structures, such as fractures, cracks and joints in the rock. These secondary groundwater storage and flow features are best developed in the sandstone thus leading to improved water-yielding properties of the underlying fractured aquifer system. The underlying dolerite sills and dykes are generally impermeable to water movement unless they have been altered by weathering and or fracturing.

A total of 16 piezometers (Fig. 1) were installed to monitor groundwater levels and quality. Each piezometer has a diameter of 140 mm and the depth of penetration varies depending on mined depth. To allow interaction with the flooded mine water, the piezometers were perforated along the section corresponding to the mined thickness. Groundwater level measured in the boreholes across the mine compartments during the monitoring period ranges from 1528.91 to 1585.27 meters above mean sea level (mamsl). The huge differences in groundwater level can be probably attributed to changes in hydraulic flow properties brought about by the subsurface mining disturbances.

It was however beyond the scope of this research to determine the hydraulic patterns and groundwater interflow between the compartments and the surroundings of the mine. The main focus of the study was to assess the hydrogeochemical characteristics of the flooded underground mine and not the potential offsite migration

Table 1
X-ray diffractometry (XRD) results showing the major minerals detected in the geology samples collected from each compartment.

Sample no.	Mineral phases						
	Quartz	Kaolinite	Illite	Pyrite	Calcite	Siderite	Dolomite
A	XX[a]	X[b]	<x[d]	x	x	<x	x
B	XX	X	x	xx[c]	xx	x	<x
C	XX	xx	<x	x	x	<x	<x
D	XX	X	<x	x	x	<x	x

[a] Dominant (>40% per volume).
[b] Major (10–40% per volume).
[c] Minor (2–10% per volume).
[d] Accessory (1–2% per volume).

of mine water into the surrounding aquifers and surface water resources. It was assumed that interflow between mine compartments will have limited effect on the resultant hydrochemical groundwater type of the flooded underground mine as compared to AMD-calcite and dolomite buffering hydrogeochemical processes.

2.4. Groundwater sampling

144 samples were collected from piezometers drilled into the flooded underground mine groundwater system during the three year monitoring period (2000–2002). Three sampling periods in a year were designed to represent summer, autumn and winter seasons.

Groundwater samples were obtained from the flooded underground mine using a low flow pump at a discharge rate of 0.3 l/s. Temperature and electrical conductivity (EC) were continuously measured and monitored in the purged water. Samples were only collected after stabilisation of the temperature and EC. This was done to ensure that samples were collected from the groundwater that comes from flooded mine and not the standing water in the piezometer. Samples were collected into clean 500 ml polyethylene bottles. Prior to sample collection, bottles were rinsed with hydrochloric acid at a pH of 2 to remove leachable material. All samples were filtered using 0.45 μm Millipore membrane filters. After sampling, the bottles were tightly closed to protect from atmospheric gases, labelled, stored (<4 °C) and delivered to the laboratory within 24 h.

2.5. Chemical analysis and calculations

Chemical analysis was conducted by the Institute of Groundwater Studies (IGS) laboratory of the Free University in South Africa. Groundwater samples were analysed for heavy metals, major and minor ions. Analysis for cations and heavy metals was done using a PerkinElmer Optima 3000 DV Inductively Coupled Plasma (ICP) and a Dionex DX-120 Ion Chromatograph (IC) was used for the anions. Alkalinity measurements were made using a TW alpha plus titration kit. All the analyses were conducted based on the guidelines provided in the Standard Methods for the Examination of Water and Wastewater (American Public Health Association et al., 2005). Calculated ionic balance error for the analyses ranged between ±7.6% to ±15.4%. Saturation indices (SI) for mineral phases were calculated using PHREEQC hydrogeochemical model (Parkhurst and Appelo, 1999). Scatter diagrams and Pearson Product Moment (PPM) correlation coefficients between chemical ion concentrations were plotted and calculated respectively using spreadsheets of Microsoft Office Excel 2007.

3. Results and discussion

Table 2 shows the descriptive statistics of the major ions detected in the flooded underground coal mine groundwater system during the monitoring period. Major ions concentration in the groundwater were detected in the following order; $SO_4^{2-} > Ca^{2+} > Mg^{2+} > HCO_3^- > Na^+ > Cl^- > K^+ > NO_3^- > F^-$. The pH measured in the groundwater samples during the monitoring period ranges from 5.48 to 9.40 (Fig. 2). Expanded Durov diagram (Burdon and Malzoum, 1958) (Fig. 3) shows that the groundwater system is characterised by a Ca-SO_4 (A). as the main hydrochemical groundwater type. A few of the samples (<12%) plot as Mg-SO_4 (B), Na + K-SO_4 (C), Na + K-HCO_3 (D), Mg-HCO_3 (E) and Ca-HCO_3 (F) minor hydrochemical types (Fig. 3). Minor hydrochemical groundwater types are probably a reflection of the mixing processes that occur as the groundwater evolves to the main Ca-SO_4 main hydrochemical type.

3.1. Hydrogeochemical processes

There are various rock-mineral and water reactions that can result in the same hydrochemical groundwater type. A good understanding of site geology, mineralogy and hydrogeology is important to develop a sound hydrogeochemical conceptual model. It is also imperative to assess the validity of each hypothetically identified potential reaction based on the measured chemical data.

3.1.1. Initial hydrogeochemical conceptual model

It is expected that when sulphide minerals such as iron pyrite that have been shown to be abundant in the Witbank coal seams (Azzie, 2000; Pinetown and Boer, 2006) are exposed to oxygen and moisture, the pyrite will be oxidised producing AMD. The overall process of pyrite oxidation is described by the reaction presented in Eq. (1) (Lowson, 1982; Nordstrom, 1982; Pons et al., 1982). According to Stumm and Morgan (1996), pyrite weathering can be generally regarded as the strongest acid-producing process of all oxidation mechanism known to occur in the natural environment. Based on stoichiometry, the overall pyrite oxidation reaction will produce 4 mol of H^+ for each mole of pyrite oxidised and 2 mol of SO_4^{2-}.

$$FeS_2 + 3.75O_{2(aq)} + 1.5H_2O_{(aq)} \leftrightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ \qquad (1)$$

On the other hand, extensive studies in the Witbank coal fields of Southern Africa (Van Vuuren and Cole, 1979; Gaigher, 1980; Van der Spuy and Willis, 1991; Usher et al., 2001; Azzie, 2002; Pinetown and Boer, 2006) have shown the existence of acid buffering minerals such as calcite and dolomite that occur together with pyrite within the coal seams.

According to Usher (2003) when conducting investigations on the AMD aspects in South African coalmines it is important to understand the co-existence of acid generating and carbonate buffering minerals. In another study, Azzie (2002) revealed that calcite was more abundant in the coal samples. Studies have shown that weathering and dissolution rates for rocks that contain carbonate minerals can be in the same order as the AMD generation redox reactions in sulphide mining environments (Sherlock et al., 1995;

Table 2
Descriptive statistics of the major ions detected in the flooded underground coal mine groundwater system during the monitoring period; also shown in the table is the SANS (2006) and WHO (2011) drinking water quality guidelines.

Parameter (mg/L)	n^e	Minimum (mg/L)	Maximum (mg/L)	Arithmetic Mean (mg/L)	Std deviation (mg/L)	SANS (2006) Target (mg/L)	WHO (2011) Guideline (mg/L)
Ca	144	2.50	727.2	298.07	225.84	⩽32	–[b]
Mg	144	1.42	115.30	52.10	36.98	⩽30	–[b]
Na	144	6.2	44.51	25.95	11.01	⩽100	–[b]
K	144	1.3	59.00	6.98	7.03	⩽50	–[b]
HCO_3	144	2	284	115.44	100.27	–[b]	–[b]
Cl	144	5.80	25	11.03	3.92	⩽100	–[b]
SO_4	144	1.50	1915	879.1	639.4	⩽200	–[b]
F	144	0.08	2.83	0.32	0.37	⩽1	1.5

[e] Number of samples above the detection limit.

[b] No established guideline value.

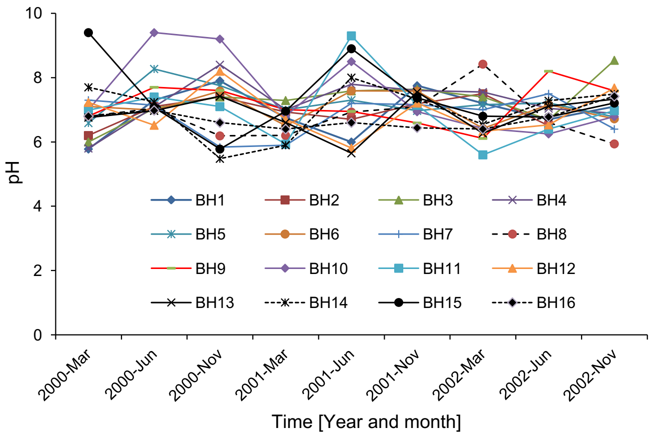

Fig. 2. pH measured in the samples collected from underground mine groundwater system during the monitoring period.

Stumm and Morgan, 1996). It was therefore hypothesised that the carbonates would neutralise AMD from pyrite oxidation at the study site.

3.1.2. Calcite and dolomite AMD buffering

It has long been known that calcite and dolomite buffering processes are dominant in the pH range of 6.5–7.5 (Blowes et al., 1994 and Geller et al., 2000). Measured pH in 95% of the 144 analysed groundwater samples is within the 6.5–7.5 range (Fig. 2). Based on this measured pH range it can be inferred that under the current hydrogeochemical conditions, calcite and dolomite minerals are buffering AMD.

The AMD produced in the form of $4H^+$ (Eq. (1)) is buffered by calcite and dolomite carbonates as described by the reactions shown in Eqs. (2) and (3) (Stumm and Morgan, 1981). Eq. (2) indicates that 2 mol of calcite are required to neutralise 4 mol of acid (H^+) while Eq. (3) shows that 1 mol of dolomite is required to neutralise 4 mol of acid (H^+). In an open system, the majority produced CO_2 is expected to exsolve into the atmosphere.

$$2CaCO_3 + 4H^+ \leftrightarrow 2Ca^{2+} + 2H_2O + 2CO_2 \tag{2}$$

$$CaMg(CO_3)_2 + 4H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2H_2O + 2CO_2 \tag{3}$$

Considering that pyrite oxidation and carbonate AMD buffering reactions occurs simultaneously then Eqs. (2) and (3) can be thermodynamically combined with Eq. (1) and be represented with reactions shown in the following equations.

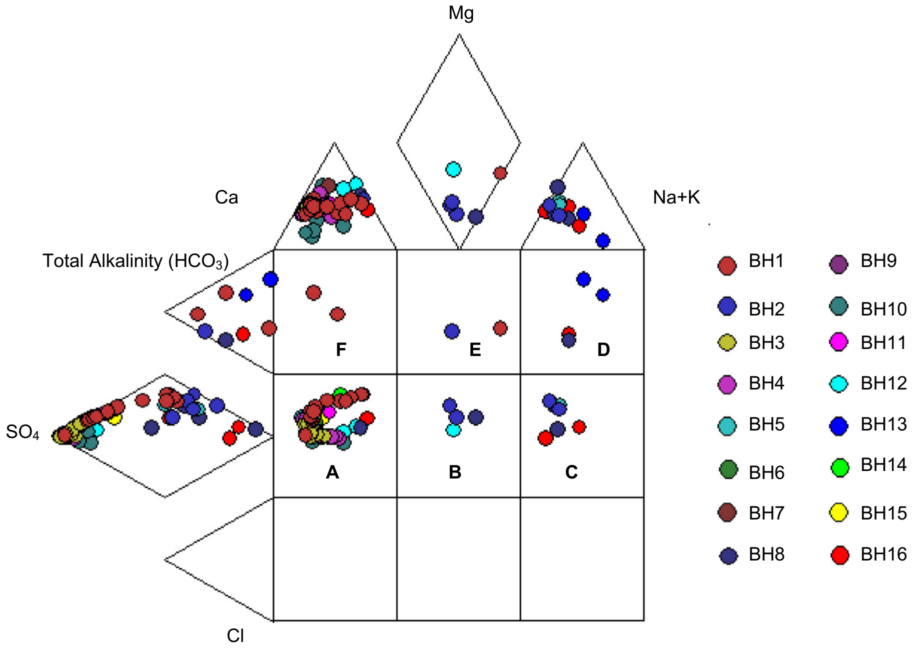

Fig. 3. Durov diagram showing the hydrochemical groundwater types (A–F) of the study area; A is the main hydrochemical groundwater type while B–F is minor hydrochemical groundwater types.

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \leftrightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2 \quad (4)$$

$$FeS_2 + CaMg(CO_3)_2 + 3.75O_2 + 1.5H_2O \leftrightarrow Fe(OH)_3 + 2SO_4^{2-} + Ca^{2+} + Mg^{2+} + 2CO_2 \quad (5)$$

Eq. (4) shows that the acid produced from 1 mol of FeS_2 is neutralised by 2 mol of $CaCO_3$. From this reaction for every 1 mol of FeS_2 neutralised by 2 mol of $CaCO_3$, 2 mol of SO_4^{2-} and 2 mol of Ca^{2+} will be released into the solution. The reaction in Eq. (5) shows that the acid produced from 1 mol of FeS_2 is neutralised by 1 of mole of $CaMg(CO_3)_2$. This reaction releases 2 mol of SO_4^{2-}, 1 mol of Ca^{2+} and 1 mol Mg^{2+} into the solution for every 1 mol of FeS_2 that is neutralised by 1 mol of $CaMg(CO_3)_2$.

The reactions in Eqs. (4) and (5) are occurring simultaneously and their combined stoichiometry predicts that the SO_4^{2-} concentration in the mine groundwater should increase with both concentration of Ca^{2+} and Mg^{2+}. On the other hand, Ca^{2+} and Mg^{2+} will also have to increase proportionally in the solution as they evolve from the same process.

Fig. 4 shows a scatter plot of SO_4^{2-} against Ca^{2+} and Mg^{2+} concentrations that were measured in the groundwater system. SO_4^{2-} is highly correlated to Ca^{2+} and Mg^{2+} with positive PPM correlation coefficients of 0.97 and 0.96 respectively. This shows that the three ions are linearly increasing at the same time in the groundwater system.

Based on stoichiometry, the combined overall effect of the two reactions (Eqs. (4) and (5)) would effectively release 4 mol of SO_4^{2-}, 3 mol of Ca^{2+} and 1 mol Mg^{2+} in the mine groundwater system. In a groundwater system controlled by the reactions shown in Eqs. (4) and (5), the molar ratio of SO_4^{2-} to Ca^{2+} and Mg^{2+} should be 4:3 and 4:1 respectively. This implies that a plot of SO_4^{2-} against Ca^{2+} and SO_4^{2-} against Mg^{2+} will have slopes of 1.3 and 4 respectively. Field data (Fig. 4) shows that the plot of SO_4^{2-} against Ca^{2+} and Mg^{2+} is characterised by slopes of 1.2 and 4.2 respectively which is very close to the stoichiometry prediction.

It has been shown that the overall reactions of calcite and dolomite AMD buffering result in 3 mol of Ca^{2+} and 1 mol Mg^{2+} in the groundwater system (Eqs. (4) and (5)). In such a groundwater system, Ca^{2+} to Mg^{2+} molar ratio would be 3:1 giving a slope of 3 for a scatter plot of Ca^{2+} against Mg^{2+}. A scatter plot showing a high positive relationship between Ca^{2+} and Mg^{2+} concentrations measured in the mine groundwater system during the monitoring period is presented in Fig. 5. The plot is characterised by a slope of 3.5 which is close to the stoichiometry perdition value of 0.3.

The authors could not identify any other possible hydrogeochemical processes that can result in the simultaneous increase of SO_4^{2-} with increase of Ca^{2+} and Mg^{2+} concentrations and also the increase of Ca^{2+} with increase of in Mg^{2+} concentration other than the calcite and dolomite AMD buffering reactions. Taking SO_4^{2-} to represent the total acid produced and Ca^{2+}+Mg^{2+} to be the produced alkalinity, then if AMD has been buffered by carbonates (Eqs. (4) and (5)) the molar ratio of SO_4^{2-} to Ca^{2+}+Mg^{2+} in the groundwater system will be 1:1. This will imply that 4 mol of SO_4^{2-} released into the groundwater system from the produced acid should be equal to 3 mol Ca^{2+} plus 1 mol Mg^{2+} for total alkalinity produced. Leached metals were detected in very low concentrations (Table 3) and the contribution on produced residual acidity of the groundwater system was thus assumed to be negligible.

Fig. 6 shows a scatter plot of Ca^{2+}+Mg^{2+} against SO_4^{2-} concentrations measured in the groundwater system. Samples plot very close to the 1:1 equiline indicating a balance between the acid and alkalinity produced during the carbonate AMD buffering process. This is evidence to show that all AMD produced from oxidation of pyrite minerals was buffered by the carbonate minerals known to exist within the coal seams.

The interpretation used for this discussion assumes that all carbon dioxide produced from reactions in Eqs. (4) and (5) will exsolve into the atmosphere. However, under field conditions there will be probably some that dissolves in the water to give rise to carbonic acid as described in the following equation.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (6)$$

Carbonic acid produced in Eq. (6) is buffered by calcite and dolomite carbonates as described by reactions presented in Eqs. (7) and (8) respectively. These reaction result in the further release Ca^{2+} and Mg^{2+} ions and some bicarbonate residual alkalinity. If most of the carbon dioxide exsolve into the atmosphere, then the bicarbonate residual alkalinity can be regarded as very small in comparison to the total alkalinity produced to buffer AMD. The slight shift of the samples from the 1:1 equiline plot (Fig. 6) can therefore be attributed to additional Ca^{2+} and Mg^{2+} ions added from the bicarbonate dissolution as part of residual alkalinity.

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (7)$$

$$2H_2CO_3 + CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (8)$$

3.1.3. Saturation state

Using PHREEQC hydrogeochemical model (Parkhurst and Appelo, 1999), SI for calcite, dolomite and gypsum were calculated. Calculations were made using the thermodynamic data contained

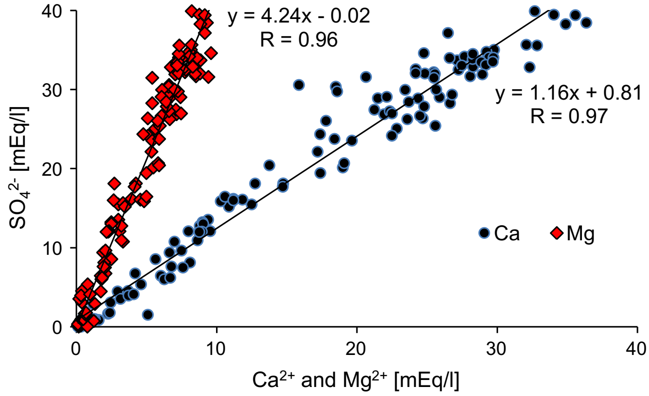

Fig. 4. Scatter plot showing SO_4^{2-} against Ca^{2+} and Mg^{2+} concentrations that was measured in the mine groundwater system during the monitoring period.

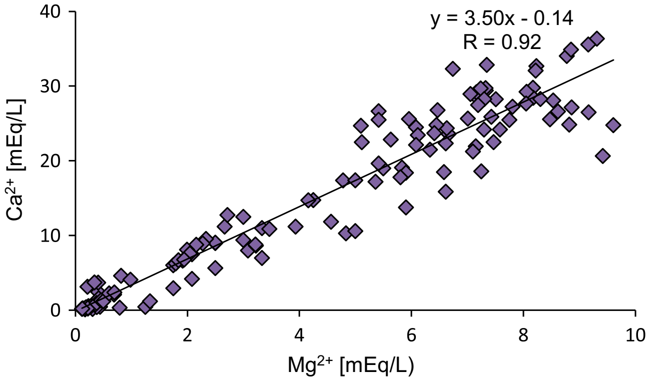

Fig. 5. Scatter plot showing the positive relationship between Mg^{2+} and Ca^{2+} ions measured in the mine groundwater system during the monitoring period.

Table 3
Descriptive statistics of the metal concentration detected in the flooded underground mine ground water during the monitoring; also shown in the table is the SANS (2006) and WHO (2011) drinking water quality guidelines.

Parameter (mg/L)	*n*[e]	Minimum (mg/L)	Maximum (mg/L)	Arithmetic Mean (mg/L)	Std deviation (mg/L)	SANS (2006) Target (mg/L)	WHO (2011) Guideline (mg/L)
Cd	88	0.006	0.009	0.004	0.004	⩽0.02	0.003
Cr (total)	88	0.0008	0.01	0.009	0.002	<0.5	0.05[c]
Co	1	0.005	0.005	0	0	⩽1	–[b]
B	88	0.009	0.803	0.115	0.126	–[b]	2.4
Ba	99	0.001	0.163	0.039	0.040	–[b]	0.7
Be	87	0.002	0.010	0.004	0.003	–[b]	–[b]
Cu	106	0.0002	0.07	0.012	0.015	⩽1	2
Fe (total)	84	0.009	105	4.93	15.81	⩽0.1	–[b]
Pb	85	0	2.05	0.027	0.042	⩽10	0.01[c]
Hg	96	0.009	0.009	0	0	–[b]	0.006
Ni	91	0.0008	0.19	0.014	0.035	–[b]	0.07
Zn	105	0.06	1.82	0.164	0.287	–[b]	–[b]
Li	96	0.0023	0.15	0.024	0.022	–[b]	–[b]
Mn	141	0.0028	5	0.86	1.02	⩽0.05	–[b]
Mo	90	0.0011	0.009	0.003	0.002	–[b]	–[b]
Sr	105	0.028	9.614	3.708	2.604	–[b]	–[b]
V	88	0.009	0.244	0.122	0.090	–[b]	–[b]

[e] Number of samples above the detection limit.
[b] No established guideline value.
[c] Provisional guideline.

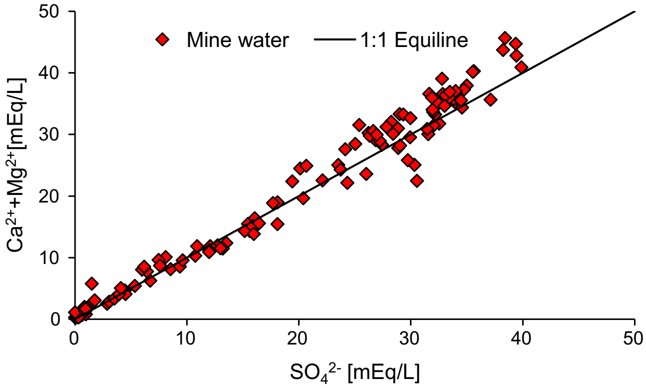

Fig. 6. Scatter plot of $Mg^{2+} + Ca^{2+}$ against SO_4^{2-} ions measured in the mine groundwater system during the monitoring period; 1:1 equiline shows where the samples should plot when the total acid and total alkalinity produced during the carbonate-AMD buffering process are equal.

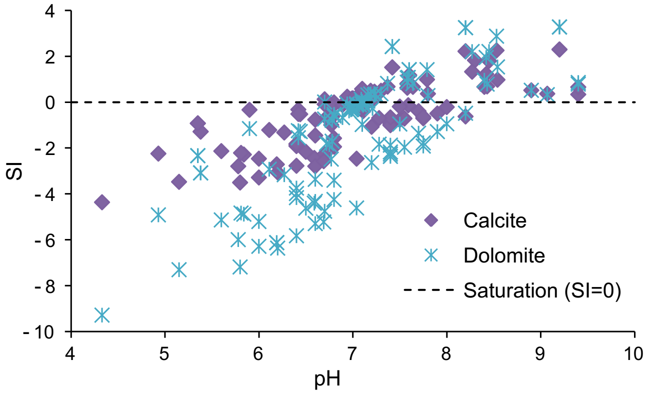

Fig. 7. Scatter plot of dolomite and calcite SI against pH.

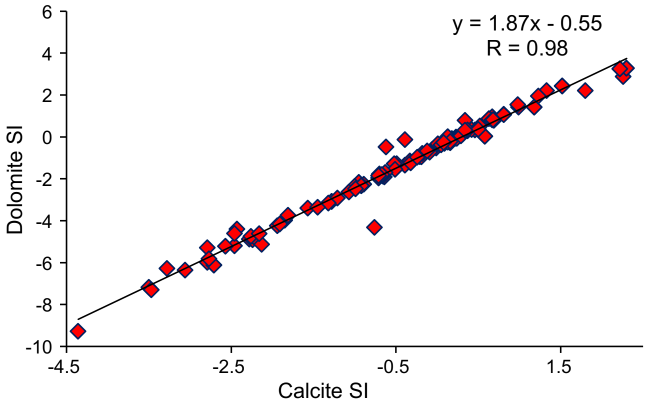

Fig. 8. Scatter plot of dolomite SI against calcite SI.

in the database of the PHREEQC for Windows software. Zero SI indicates solubility equilibrium of the solution composition with respect to the mineral phase. Negative SI indicates undersaturation while positive values reflect supersaturation hydrogeochemical conditions. Undersaturation implies that the mineral phase can dissolve in the solution while the opposite is true for supersaturation. It was hypothesised that the mineral phases of calcite, dolomite and gypsum are controlling the hydrogeochemistry of the flooded mine groundwater system. Field results have already shown that calcite and dolomite carbonate minerals are buffering AMD and hence understanding their saturation levels was important. Gypsum precipitates has been observed in some of the Witbank underground coal mines (Vermeulen, 2003; Usher, 2003).

Saturation indices of calcite and dolomite consistently increase with pH (Fig. 7). The increase in pH is due to the alkalinity produced during the neutralisation of AMD by calcite and dolomite carbonates. However for pH-values below 6.5, the mine groundwater is under saturated with respect to dolomite and calcite. Calcite and dolomite SI are following a positive linear trend that is characterised by a correlation coefficient of 0.98 (Fig. 8). High positive correlation shows that the mineral phases are changing in a similar trend which is further evidence to show that the reactions of the two mineral are controlled by similar hydrogeochemical process (AMD-calcite and dolomite buffering).

The plot of gypsum SI against measured concentrations of Ca^{2+}, and SO_4^{2-} (Fig. 9) shows that at the concentration of 32.32 mEq/L and 32.81 mEq/L for Ca^{2+} and SO_4^{2-} respectively the mine groundwater becomes saturated with respect to gypsum. Saturation can

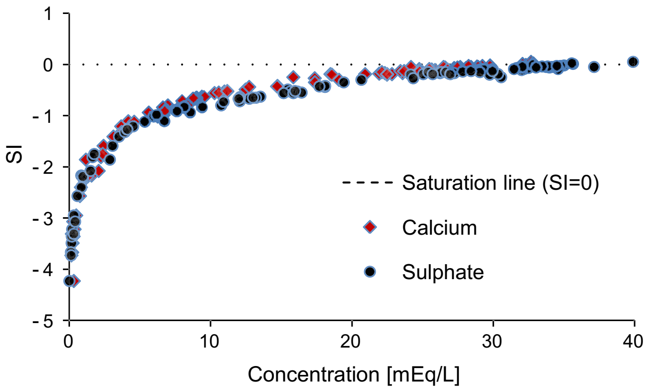

Fig. 9. Scatter plot of gypsum SI against Ca^{2+} and SO_4^{2-}.

prompt the precipitation of gypsum leading to reduction of Ca^{2+}, and SO_4^{2-} ions measured in the groundwater system. The trend suggests that an increase Ca^{2+} and SO_4^{2-} in the groundwater system would only occur up to certain point until which the aqueous solubility of these ions becomes indirectly limited by the saturation of gypsum. Formation of gypsum as secondary mineral of carbonate AMD buffering has been shown to have an important influence on the groundwater hydrogeochemistry of Witbank coal mines (Usher, 2003). It is therefore important to evaluate the saturation state of gypsum and its potential influence on the measured Ca^{2+} and SO_4^{2-} concentrations in such a groundwater system.

On the other hand, it is also possible to have a similar relationship like the one shown in Fig. 9 when gypsum dissolution is the source of Ca^{2+} and SO_4^{2-}. To prove that carbonate AMD neutralisation reactions are the source of Ca^{2+} and SO_4^{2-} and not gypsum dissolution a plot of gypsum SI against Mg^{2+} is used. Fig. 10 shows that a similar trend exists between gypsum SI and Mg^{2+} just as it with Ca^{2+} and SO_4^{2-}. This is simply because Mg^{2+} concentrations in the groundwater were changing in a similar trend with Ca^{2+} and SO_4^{2-} as controlled by the calcite and dolomite AMD buffering and not gypsum dissolution. It is another evidence to prove that these three major ions evolve from the same process reactions (dolomite and calcite carbonate AMD buffering).

3.2. Groundwater quality

The principal reaction of the oxidation of sulphide minerals during acid mine drainage releases acid sulphate and metals into the groundwater system and these can affect the resultant groundwater quality. On the other hand, carbonate acid neutralization processes can also release elevated cations into the groundwater system and these can also contribute to the evolving groundwater quality.

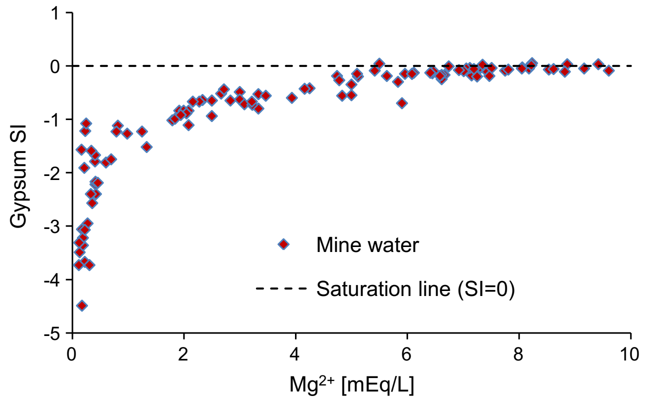

Fig. 10. Scatter plot of gypsum SI against Mg^{2+}.

3.2.1. Metals

Pyrite, iron disulphide is the most common mineral in metal sulphide and coal deposits (Banks et al., 1997). According to Spears et al. (1994), pyrite often occurs in potential association with other chalcophile metals such as; Bi, Cd, Co, Cu, Ga, In, Hg, Mo, Pb, Re, Sn and Zn. Under acidic conditions which can develop during AMD, some metal chalcophile elements can be leached into the groundwater system. Elevated concentrations of metals pose a potential threat of contaminating groundwater. It is therefore important to measure and assess the levels of metal concentrations in a groundwater system that might have hydrogeochemically evolved through AMD.

Table 3 shows the descriptive statistics of metals that were detected in the flooded mine groundwater system. Measured metals concentration were compared to SANS (2006) and WHO (2011) drinking water quality guidelines. The major concern is Fe and Mn that exceeded the SANS (2006) drinking water quality target concentration in 19% and 34% of the samples respectively. However it is difficult to directly infer the presence of elevated Fe and Mn species in some of the groundwater samples to the effect of AMD metal leaching process due to the absence of background data prior to mining.

With the exception of Fe and Mn, the rest of the detected metals are generally in low concentrations that are all below the SANS (2006) and WHO (2011) drinking water quality guidelines. In hydrogeochemical conditions where AMD occurs, metals are leached out of the surrounding lithology and these can contaminate groundwater resources (Blowes and Ptacek, 1994; Rose and Cravotta, 1998). However at the study site, the acid buffering capacity offered by the calcite and dolomite carbonate minerals has great potential to hinder the leaching of metals. Under the reported hydrogeochemical conditions it can therefore be concluded that the calcite and dolomite minerals in the coal seams are buffering the AMD thus hindering the leaching of metals into the flooded mine groundwater system.

3.2.2. Total dissolved solids (TDS)

Table 4 shows the groundwater quality classification for the flooded underground mine based on TDS levels (WHO, 2003). More than 53% of the groundwater samples have TDS greater than 1200 mg/l and are classified as unacceptable for drinking purposes. High TDS in the groundwater is due to elevated SO_4^{2-}, Ca^{2+} and Mg^{2+} ions released during the carbonate AMD buffering process. Although the carbonates are buffering AMD which prevent the leaching of metals, SO_4^{2-}, Ca^{2+} and Mg^{2+} ions released during the process can still lead to elevated TDS. About 38% of the groundwater samples are classified to have excellent and good groundwater quality (Table 4). However these are also characterised by a Ca-SO_4 hydrochemical groundwater type indicating that they evolved from the AMD buffering process just like the rest.

Table 4
Groundwater quality classification of the site based on TDS WHO (2003).

Quality	TDS (mg/L) number of samples	
Excellent	<300	30
Good	300–600	24
Fair	600–900	3
Poor	900–1200	10
Unacceptable	>1200	77

Table 5
Groundwater hardness classification McGowan (2000).

Hardness class	Total hardness as $CaCO_3$ (mg/L)	Number of samples
Soft	<60	12
Moderately hard	60–120	15
Hard	120–180	8
Very hard	>180	109

3.2.3. Hardness

Table 5 shows the hardness classification for the groundwater in the flooded underground mine that was calculated based on the index by McGowan (2000). Results showed that at least 85% of the samples collected during the monitoring period are characterised by very hard conditions (total hardness as $CaCO_3 > 1200$ mg/L). The hardness of the groundwater is mainly driven by elevated Ca^{2+} and Mg^{2+} concentrations released from the calcite and dolomite AMD buffering process. Although the calcite and dolomite buffering mechanisms are important for reducing the AMD levels and minimizing the potential leaching of metals into the mine groundwater system they also presents the problem of hardness.

4. Conclusions

The investigation identifies and describes the dominant hydrogeochemical processes contributing to the evolution of the main hydrochemical groundwater type and quality of the flooded underground coal mine. Study findings shows that the flooded underground mine is characterised by a Ca-SO_4 hydrochemical groundwater type. The Ca-SO_4 hydrochemical groundwater type evolves from the buffering of AMD by calcite and dolomite carbonate minerals.

Results further shows that the majority of the groundwater samples are characterised by elevated hardness which is mainly driven by the release of Ca^{2+} and Mg^{2+} ions during the buffering of AMD by calcite and dolomite minerals. Calculated SI indicate that an increase in Ca^{2+} and SO_4^{2-} ions in this flooded underground mine groundwater system can only occur up to certain point from which the aqueous solubility of these two ions becomes indirectly limited by the saturation of gypsum. Although the calcite and dolomite buffering mechanisms are important for reducing the AMD levels and minimizing the potential leaching of metals into the mine groundwater system they also presents the problem of hardness and elevated TDS.

References

American Water Works Association and Water Environment Federation, 2005. Standard Methods for the Examination of Water and Wastewater. Washington, DC 20001-3710.

Azzie, B.A., 2002. Coal mine waters in South Africa: their geochemistry quality and classification. PhD thesis, University of Cape Town, South Africa.

Banks, D., Younger, P.L., Arnesen, R.-T., Iversen, E.R., Banks, S.B., 1997. Mine-water 506 chemistry: the good, the bad and the ugly. Environ. Geol. 32 (3), 157–174.

Bell, F.G., Bullock, S.E.T., Hälbich, T.F.J., Lindsay, P., 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. Int. J. Coal Geol. 45, 195–216.

Blowes, D.W., Ptacek, C.J., 1994. Acid-neutralization mechanisms in inactive mine tailings. In: Jambor, J.L., Blowes, D.W. (Eds.), The Environmental Geochemistry of Sulphide Mine-Wastes, vol. 22. Mineralogical Association of Canada, Nepean, pp. 271–292.

Blowes, D.W., Ptacek, C.L., Frind, E.O., Johnson, R.H., Robertson, W.D., Molson, J.W., 1994. Acid-neutralization reactions in inactive mine tailings impoundments and their effect on the transport of dissolved metals. Proc. Int. Land Reclam. Mine Drain. Conf. Pitt. 1, 429–438.

Brady, K.B.C., Rose, A.W., Cravotta, C.A., Hellier, W.W., 1997. Bimodal distribution of pH in coal mine drainage (abst.). Geological Society of America, GSA Abstracts with Programs, 29 (1), pp. 32.

Burdon, D.J., Malzoum, J., 1958. Some chemical types of groundwater from Syria. In: Proceedings of the UNESCO Symposium, Teheran, pp. 73–90.

Gaigher, J.L., 1980. The mineral matter in some South African coal. M.Sc thesis, University of Pretoria, South Africa.

Geller, W., Friese, K., Herzsprung, P., Kringel, R., Schultze, M., 2000. Limnology of sulphur-acidic mining lakes. II Chemical properties: the main constituents and buffering systems. Verhandlungen des Internationally Verein Limnologie 27, 2475–2479.

Gomo, M., van Tonder, J.G., Steyl, G., 2012. Investigation of the hydrogeochemical processes in an alluvial channel aquifer located in a typical Karoo Basin of Southern Africa. Environ. Earth Sci.. http://dx.doi.org/10.1007/s12665-012-2118-9.

International Energy Agency, 2010. Coal Information. OECD, Paris.

Lowson, R.T., 1982. Aqueous oxidation of pyrite by molecular oxygen. Chem. Rev. 82, 461–497.

McGowan, W., 2000. Water Processing: Residential, Commercial, Light-Industrial, 3rd ed. Water Quality Association, Lisle, Illinois, USA.

Nordstrom, D.K., 1982. Aqueous pyrite oxidation and the consequent formation of secondary ion minerals. In: Nordstrom, D.K. (Eds.), Acid Sulphate Weathering. Soil Science Society of America, Special Publication No. 10, pp. 37–56.

Parkhurst, D.L., Appelo, C.A.J., 1999. PHREEQC for windows version 1.4.07. A hydrogeochemical transport model. US Geological Survey Software. Washington.

Pinetown, K.L., Boer, R.H., 2006. A quantitative evaluation of the modal distribution of minerals in coal deposits in the Highveld area and the associated impact on the generation of acid and neutral mine drainage. Water Research Commission (WRC), Report No. 1264/1/06. Pretoria, South Africa.

Pons, L.J., van Breeman, N., Driessen, P.M., 1982. Physiography of coastal sediments and development of potential soil acidity. In: Acid Sulfate Weathering. Soil Science Society of America, Special Publication No. 10, pp. 1–18.

Rose, A.W., Cravotta III, C.A., 1998. Geochemistry of coal mine drainage. In: Brady, K.B.C., Smith, M.W., Schueck, J. (Eds.), Coal Mine Drainage Prediction and Pollution in Pennsylvania. Bureau of Mining and Reclamation, Pennsylvania Department of Environmental Protection, Harrisburg.

SANS, 2006. South African National Standard: Drinking Water, sixth ed. The South African Bureau of Standards, ISBN 0-626-18876-8. Pretoria, South Africa.

Sherlock, E.J.R., Lawrence, W., Poulin, R., 1995. On the neutralization of acid rock drainage by carbonate and silicate minerals. Environ. Geol. 25, 43–54.

Smith, D.A.M., Whittaker, R.R.L.G., 1986. The Springs-Witbank coalfield, 1969–1984. In: Anhaeusser, C.R., Maske, S. (Eds.), Mineral Deposits of Southern Africa. Geological Society of South Africa 1, pp. 1020.

Spears, D.A., Tarazona, M.R.M., Lee, S., 1994. Pyrite in U.K. coals: its environmental significance. Fuel 73, 1051–1055.

Stumm, W., Morgan, J.J., 1981. Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters, second ed. John Wiley & Sons, New York.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry – Chemical Equilibria and Rates in Natural Waters, third ed. Wiley & Sons, New York.

Usher, B.H., 2003. The evaluation and development of hydrogeochemical prediction techniques for long-term water chemistry in South African coalmines. PhD thesis, University of the Free State, South Africa.

Usher, B.H., Cruywagen, L., de Necker, E., Hodgson, F.D.I., 2001. On-site and laboratory investigations spoil in opencast collieries and the development of acid-base accounting procedures. Water Research Commission (WRC), Report Number: 1055/1/03. Pretoria, South Africa.

Van der Spuy, D., Willis, J.P., 1991. The occurrence of aragonite in carbonate lenses in coal from the Witbank area. S. Afr. J. Geol. 94 (2/3), 178–180.

Van Vuuren, C.J., Cole, D.I., 1979. The stratigraphy and depositional environments of the Ecca Group in the northern part of the Karoo Basin. In: Anderson, A.M., van Biljon, W.J. (Eds.), Some sedimentary basins and associated ore deposits of South Africa. Geological Society of South Africa, Special Publication 6, pp. 103–111.

Vermeulen, P.D., 2003. Investigation of decant water from the underground collieries in Mpumalanga. MSc thesis, University of the Free State, South Africa.

Vermeulen, D., Usher, B., 2009. Operation and monitoring guidelines and the development of a screening tool for irrigating with coal mine water in Mpumalanga Province, South Africa. Water SA 35 (4), 379–386.

WHO, 2003. Total dissolved solids in drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality. WHO/SDE/WSH/03.04/16. Geneva, Switzerland.

WHO, 2011. Guidelines for Drinking-water Quality (fourth ed.). ISBN 978 92 4 154815 1. Geneva, Switzerland.