

AMD formation and dispersion of inorganic pollutants along the main stream in a mining area

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Abstract

The highveld coalfields area in Mpumalanga Province of South Africa is well known for the intensive mining activities focusing mostly on coal processing. The imminent impact of these activities on the water systems has been addressed by the mining companies over the years but the potential threat to the degradation of surface and ground waters quality has resurfaced (BFAP, 2012). This study aimed to quantitatively evaluate the level of mine pollution indicators in the surface water around the mining areas and particularly the implication efflorescent salt iron phase on the acidification of water. Water and efflorescent salts samples were collected along the stream from the mining areas in summer. These samples were analysed for their geochemical properties, anions and metal concentrations. High level of potentially toxic elements such as As, Cd, Co, Cu, Fe, Ni, Pb, U and Zn were detected in the main stream from mining areas that was very acidic ($\text{pH} < 4$) with high level of sulphate (2000 to 9000 mg/L). The efflorescent salts formed from acidic water were characterized using XRD and Mossbauer. Mikasaite, romerite, greigeite, cesanite, merwinite, maghemite, magnetite, nickelhexahydrite and thernardite were the dominant minerals in the salt samples. These results are indicative of acid mine drainage resulting from mining activities in the region. The formation of efflorescent salts near the stream with the potential to further acidify water and release metal pollutants was further indication of the presence of permanent threat to the degradation of water quality.

This study highlights the potential of formation and the characteristics of a typical acid mine drainage as well as the impact of mine wastes on the quality of environmental water in the neighborhood of mining activities.

Key words: Acid mine drainage, efflorescent salts, pollution, Mössbauer

Introduction

Coal is known to be the primary source of energy in South Africa; apart from contributing to 96% of the country's electricity generated in coal fired power plant, coal is also used as feedstock for the production of considerable fraction of the country's liquid fuels (Hancox and Gotz 2014). The country is among the largest producer of coal in the world and will certainly rely on coal for energy generation for several decades.

The highveld coalfields area in Mpumalanga Province of South Africa is well known for the intensive mining activities focusing mostly on coal processing. Coal mining and processing has significant environmental impact in the form of noxious gases generated during combustion and exposure of acid generating rocks which contribute to acidification of underground and surface waters. In the later case poor management of deposits accumulated over several years has resulted in the oxidation of pyrite and other sulphide minerals which further acidify rain water which percolates through the tailing dumps leading to the mobility of toxic metals and pollution of surrounding aquifer (Marsden 1986; Naicker et al. 2003). Iron sulphide minerals are reported to be the main source of sulphide oxidation products present in coal beds or strata overlying and underlying the coal exposed to oxygen and water (Qureshi et al. 2016; INAP 2009; Lottermoser 2007; Montero et al. 2005; Jennings et al. 2000). The formation of acid mine drainage (AMD) from mining areas expending to the farming and residential areas through rivers and streams has constituted a serious threat for the water reserve, farm development and conservation of touristic sites in the country during the past few decades. The

imminent impact of these activities on the water systems has been addressed by the mining companies over the years but the potential threat to the degradation of surface and ground waters quality has resurfaced (BFAP 2012). Some of the methods implemented include: limiting oxygen ingress into closed mine workings, acid neutralization, water purification, controlled release and soil protection. However, most of these techniques have been abandoned because ineffective or too costly (McCarthy and Pretorius 2009). With such inconsistency in the management of coal wastes, monitoring of the environmental impact of AMD in the area becomes a necessity to evaluate the performance of remediation strategy. Understanding of the impact of effluents from mine requires geochemical studies that predict dispersion of key pollutants such as acidity and metals along the river basin; this also implies consideration of salt crusts which have a storage potential of pollutants and are susceptible to negatively impact the quality of receiving water depending on the solubility of the minerals in the crust. The Mossbauer technique is recognized to determine various phases of iron which impacts on the solubility of iron sulphide minerals.

This study aims at determining the pollution potential of acid mine effluents around the mining areas in the highveld coalfield and predict the persistence of pollution impact downstream and overtime.

Methods

Water sampling and analysis

Sampling strategy consisted to follow the flow of the effluents from mining area to the different paths in the surrounding community, such as to establish the extent of pollutants dispersion in the surface water system.

The samples were collected close to the surface inside the pounds in the premises of the mine, in the dams at the vicinity of the mine and along the effluents network on a distance of approximately 5 Km, using previously rinsed 500 mL plastic bottles. The following physico-chemical parameters were measured in-situ using a pH combined electrode with integrated temperature probe (portable Lovibond SensoDirect 150 multi-parameter water quality meter): Temperature (°C), pH, Electrical conductivity EC (mS/cm), Dissolved oxygen DO (mg/L), and Redox potential Eh (mV). The pH-meter was calibrated before analysis in the field, using reference buffer solutions. (...). The samples were then stored in the cooler bag containing ice packs until taken to the laboratory for analysis. The concentrations of sulphate (SO_4^{2-}), nitrate (NO_3^-) and cyanide (CN^-) were measured using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA).

The metal ions in the samples were measured using the inductively coupled plasma optical emission spectrometer (ICP Expert II, Agilent Technologies 720 ICP-OES).

Efflorescent crust sampling

Efflorescent crust (salt) was carefully collected at the top 5 cm of the deposit along the stream bank in the vicinity of the mine. Samples were collected in the polypropylene clean plastic bag and transported to the laboratory. The samples were spread at the flat surface in the lamina flow hood and air dried for 72 hours. The dried samples were screened using a 150 μm mesh sieve size to remove large debris and stones. Screened samples were then analyzed using XRD and Mossbauer.

X-Ray Diffractometer (XRD) analysis

The efflorescent crust samples were dried at 50°C overnight in the oven and ground in a mortar; for the determination of the mineralogical phase, they were subjected to X-ray diffraction (XRD) analysis using the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017°. The proportion of elements in the suspended solids was determined by X-ray fluorescence (XRF) using the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland); a rhodium(Rh) anode was used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

Mössbauer analysis

The Mössbauer analyses were conducted on the powdered samples with the aid of a Halder Mossbauer Spectrometer as described by Waanders et al. (2014). The samples were placed between perplex plates and then irradiated with γ -rays from a 50 mCi⁵⁷Co(Rh) radioactive source to obtain a

room temperature Mossbauer spectrum. The Mossbauer spectrometer was calibrated using α -Fe as the reference and the product species were identified as the basis of their quadrupole and isomer shifts with reference to the values available in the literature.

Results and discussion

Spatial distribution of pollutants from mine effluent

Water samples collected along the drainage from the coal mine were analyzed to determine the nature and the spatial distribution of pollutants. The physicochemical qualities of the mine effluent from the upstream to the downstream points are recorded in Table 1. There was consistency in the level of pH at the proximity of the mine, in the dams and downstream in the residential area; it was characterized by acidic pH in the range of 2.24 – 3.35 which is typical of acid mine drainage (Gray 1998). The EC level was generally high (2.41 – 11.85 mS/cm) at all the sampling points; the EC being an estimate of the total dissolved solid (TDS), it could therefore signify that the water was highly polluted. This corroborated with very high concentrations of SO₄²⁻, CN⁻, Cl⁻, Al, Ca, Fe, Mg, Mn and Na which reached maximum concentrations of 18090 mg/L, 671 mg/L, 700 mg/L, 433 mg/L, 719 mg/L, 3145.8 mg/L, 1362 mg/L and 532.7 mg/L, respectively. Overall, the trend of pollution seems to be increasing from the mine till the mid points and then decrease downstream; the lowest concentration of pollutants were recorded at the farthest point from the mine in the residential area, indicating that the pollutants tend to precipitate along the stream. While the lowest pH and highest EC were recorded inside the dam (point ID) which also coincided with higher concentration of Fe and SO₄²⁻, implying that the acidification probably resulted from the oxidation of pyritic particles in the dam; similar results were reported in our previous work (Fosso-Kankeu et al. 2015). However, it was also observed that at the highest pH (3.35), a significant drop of the concentration of Fe which was due to precipitation; it is known that iron is less soluble at pH value close to 4.

Table 1 Measured values of major pollutants in the water samples

Samples ID	In-situ variables			Major anions				Major cations						
	pH	Ec	Eh	SO ₄ ²⁻	NO ₃ ⁻	CN ⁻	Cl ⁻	Al	Ca	Fe	K	Mg	Mn	Na
		mS/cm	mV	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
UDB	2.55	8.42	215	7550	0	286	466.7	257.0	584.4	2516.7	17.9	451.8	104.9	149.7
NDB	2.64	8.46	212	18090	0	264	333.3	252.5	583.3	2495.4	17.3	443.5	103.4	153.9
NDA	2.65	8.58	210	18090	0	363	466.7	253.7	581.1	2608.9	16.3	446.2	103.8	150.0
ID	2.24	11.85	230	17085	0	671	666.7	358.6	531.1	3145.8	5.7	662.0	160.6	174.9
IAD	3.35	9.59	175	15075	74.8	88	700.0	433.1	699.7	7.7	68.8	1362.8	532.7	457.3
IAD2	2.55	6.55	216	7035	123.2	242	400.0	212.7	691.5	1402.6	12.1	426.1	95.6	149.0
FD	2.5	6.71	219	14070	262.5	440	666.7	218.5	715.9	1450.6	12.3	444.9	95.6	155.9
DDU	2.46	6.65	221	5285	4.5	264	600.0	213.4	719.2	1415.8	142.1	438.4	94.2	239.4
DU	2.64	2.41	220	2265	23.1	11	366.7	35.2	175.6	45.3	12.8	88.6	13.0	104.5

The most problematic pollutants as far as water quality is concerned, mostly occurred in trace amount (Table 2). Metals such as U, As, Ni and Pb were the dominant trace elements which were randomly distributed along the drainage; noticeable high concentrations of uranium (4.57 mg/L) in the dam and arsenic (67.14 mg/L) at point NDB compared to other points were recorded. Although the overall concentrations of trace metals decreased at the farthest point downstream (sampling site DU); U, As, Ni and Pb were still present at non-permissible levels based on the drinking water recommendation by the South African Bureau of Standard (SABS 2005). The spatial distribution of pollutants along the drainage shows that the pattern varies depending of the pollutants; while some of the concentrations of some of the pollutants may decrease moving downstream from the mine, it is not the case with other pollutants for which the concentrations increase along the drainage. It is therefore likely that dissolution of minerals may take place simultaneously with precipitation. Efflorescent salts deposited on the bank of the river were therefore analyzed to better understand their contribution to the contamination of water.

Table 2 Measured values of trace metals in water samples

Sampling sites	Concentration of minor cations in water (mg/L)							
	Ag	U	As	Cd	Cu	Ni	Pb	Zn
UDB	0	2.4	0	0.45	0	13.06	43.57	8.82
NDB	0.42	1.89	67.14	1.66	0.77	5.61	8.34	12.44
NDA	0	1.69	14.57	0	0.5	24.57	60.04	5.51
ID	0.38	4.57	0	0.79	0.18	30.38	38.68	12.41
IAD	0.08	1.85	31.64	0	0.19	8.47	10.89	11.44
IAD2	0.41	1.82	8.39	0	0	37.36	53.92	4.36
FD	0.02	1.76	9.51	0.99	0	20.43	33.93	5.22
DDU	0	1.44	0	0.79	2.64	22.21	0	13.64
DU	0	1.59	6.42	0.18	0	33.8	29.7	1.53

Mineralogical composition of efflorescent salts

Specific sampling sites were selected before and after the dam to better understand the influence of efflorescent salts (shown in Figure 1) on the pollution upstream and downstream.



Figure 1 Efflorescent crust at the bank of the acid mine drainage

The mineralogical composition of efflorescent salts was determined using the XRD analysis. The results in Table 3 show that Goethite and hematite were found in salts at all the sampling points, while SO₄²⁻, Fe, Mg and Mn were predominant in salts at all the sampling points; this confirms the results obtained from the analysis of water as these were among the major elements occurring in the drainage. It could be suggested that the salts are likely to contribute to the pollution of water; it was reported in previous study that electrical conductivity could increase while pH decreases following dissolution of efflorescent crust (Tutu et al. 2011).

Table 3 XRD results of efflorescent salts at sampling sites

Minerals	Formula	Samples			
		ND	NDBB	NDAB	IAD
Apjohnite	Mn Al ₂ (SO ₄) ₄ (H ₂ O) ₂₂	X	X		
Goethite; Goethite, syn	FeO (OH)	X	X	X	X
Mikasaite, syn	Fe ₂ (SO ₄) ₃	X			
Hematite, syn	Fe ₂ O ₃	X	X	X	X
Kaolinite	Al ₄ (OH) ₈ (Si ₄ O ₁₀)		X	X	
Magnesium sulfate hexahydrate	MgSO ₄ (H ₂ O) ₆		X		X
iron(III) sulfate	Fe ₂ (SO ₄) ₃			X	
Pickeringite	(Mg _{0.93} Mn _{0.07}) Al ₂ (SO ₄) ₄ (H ₂ O) ₂₂				X

Fe-components in efflorescent salts

From the XRD analysis all the samples contain some hematite which was not detected in the Mössbauer experimental runs. According to the XRD results samples 3 and 4 should contain 10% and 16% hematite respectively and should have been seen in a Mössbauer spectrum run at 10 mm/s, which was however not detected. Both samples contain similar amounts of goethite, which was detected in the Mössbauer experiments (Table 4). Since the hematite has a hyperfine magnetic field in a Mössbauer spectrum the samples 3 and 4 were run at 10 mm/s but only the doublet was observed and to ensure a better resolution of the doublets all samples were run at 4 mm/s velocity to ensure a better resolution between the doublets and the parameters found for the goethite fall well in to known literature values (Stevens et al. 2005). In addition sample 3 had an iron sulphate species present as was also observed in the XRD spectrum

It should be noticed that the mineral Mikasaite is rare on earth and was detected on Mars (Nomura et al. 2005; Dyar et al. 2013) and thus doubtful that they are in the samples originating from a dam or stream. Mikasaite was found in sample 1 in the XRD spectrum and not observed in the Mössbauer spectrum.

Table 4 Hyperfine interaction Mössbauer parameters of Fe-components found in this investigation

Sample	Component	IS	QS	H	Relative intensity
		mms ⁻¹	mms ⁻¹	Tesla	(%)
		(±0.02)	(±0.02)	(±0.3)	
Sample 1 ND	Doublet goethite	0.337	0.771		100
Sample 2 NDBB	Doublet goethite	0.36	0.726		100
Sample 3 NDAB	Doublet goethite	0.34	0.74		40
	Doublet iron sulphate	1.58	2.85		60
Sample 4 IAD	Doublet goethite	0.371	0.858		100

Note: IS = Isomer shift relative to α-Fe, QS = Quadrupole splitting
H = Hyperfine magnetic field strength

Conclusions

The physicochemical analysis of mine effluent considered in this study showed that it was typical of acid mine drainage containing very high load of pollutants which were distributed all along the stream moving down to the residential area. There is concern with the very acidic pH and the high concentrations of heavy metals in leached from the mining sites and sustain by the progressive dissolution of salts at the bank of the stream. The Mössbauer and XRD results have confirmed the occurrence of goethite in all the salts which is much likely to be involved in the oxidation or dissolution process and contribution of high level of Fe in water. The impact of the AMD formation on the stream downstream in the residential area was quite pronounced as the levels of pollutants especially heavy metals were above the permissible values recommended by the national guideline for drinking water. There is therefore an obvious risk of destabilization of the aquatic ecosystem, intoxication of farm animals and human relying on that stream.

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