Hydrochemical Characteristics of Open-Pit Groundwater from a Closed Metalliferous Mine in O'kiep, Namaqualand Region, South Africa

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***Abstract*—** O'kiep, a small town located in the arid to semi-arid Namaqualand region of South Africa is dependent on the Lower Orange River for its water needs, i.e. for domestic and agricultural use. The protection of groundwater resources in this region is important due to water shortages with no peripheral rivers. The town is characterised by an environment with a high proportion of mine tailings and dumps containing sulfidic ores, which can facilitate groundwater contamination. As such, open-pit groundwater (OPGW) samples were collected downstream from a closed metalliferous mine and analysed for physicochemical properties, to evaluate the fitness of OPGW for any potential use. A charge balance error (%CBE) of ±5% was used to interpret the hydrochemical properties of the OPGW, with results indicating that the water is mildly acidic, with a high concentration of SO42-, which suggested sulphide oxidation and weathering of the exposed rocks. Overall, the OPGW was under saturated in terms of metallic species such as Sb, AS, Cd, Cr, Co, Hg, Ni, Se, V and Zn. Furthermore, when the hydrochemical determinants were compared to national drinking water guidelines, it was determined that the OPGW is not suitable for drinking nor irrigation thus requires treatment prior to utilisation.

***Keywords*—**Arid and semi-arid, Copper, Hydrochemical characteristics, Metalliferous mine, O'kiep, Open-pit groundwater.

I. Introduction

South Africa (SA) has more than 55.6 million population [1], with the majority of the population using surface water resources. Due to surface water shortages and effects of climate change, implementation of water resource management strategies is becoming important for sustainable economic growth [2]. The pollution of surface water sources by mining activities, is a major problem globally [3] including in SA. Locally, Acid Mine Drainage (AMD) is largely associated with coal and gold mining operations which currently affects the water quality of the Olifants and Vaal Rivers, including their tributaries [4]. Hypothetically, the Olifants and Vaal water management areas, cannot be the only region in SA affected by mining activities, with local conditions at O'kiep being identified to have the potential to facilitate AMD formation, due to the copper bearing mineral deposits in the area.

Since copper deposits are mostly excavated in open-pits, these operations tend to produce a large quantity of oxidisable waste and tailing. Oxidation of sulphide minerals and geochemical weathering in mine waste dumps and tailings generates a long-term risk which is largely influenced by chemical characteristics and hydrology of the area, which has a direct influence on the transportation and fate of the contaminants [5-10]. A variety of species, in their numerous forms, can thus become bioavailable, which can further toxify the soil, further inhibiting the biodegradation of other organic pollutants. An outcome, which further exacerbates hazardous conditions in the ecosystems which further impacts on humans through contact with polluted soil or indirect ingestion, drinking of polluted groundwater, reduction in land usability for agricultural purposes which further causes food insecurity [11]. Sulphidic species are mobilised under oxidative conditions, whereas their derivitised oxides are solubilised in acidic solutions, with acidophilic bacteria, such as Thiobacillus ferrooxidans playing a crucial role in the ferrous-sulphate and sulphur oxidation processes, by modifying the surroundings to facilitate mineral leaching [12,13]. Such oxidation processes, are conducive to oxidation of metal sulphide in ores, such as pyrite and copper sulphides to produce sulphuric acid and the release of some heavy metals from the ore into the environment [14-23], further contributing to the pollution in the environment [24]. The key objective of this study was to characterise the hydrochemical composition of open-pit groundwater (OPGW) and its suitability for use for domestic and irrigation purposes.

II. Procedure for Paper Submission

Authorisation was obtained from the Namakhoi Municipality and O'okiep Copper Company (OCC) for the purposes of this

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study. The OPGW samples (n=5) were collected in April 2017 (Fig. 1), a dry season with an average temperature up to 37°C and no rainfall [25]. Multi-parameter instruments and sensors were calibrated prior to field use according to national field water measurements standards [26], with polypropylene sample bottles (500 mL and 100 mL) being used for sample collection. The sampling bottles were thoroughly cleaned and rinsed in dilute 0.5 M HCL, then subsequently rinsed with deionized water.

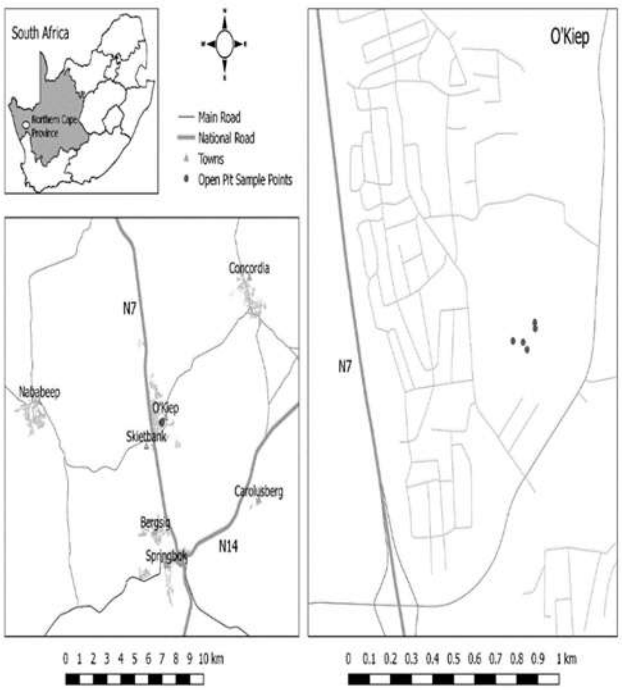

Fig. 1: Geographic information system (GIS) map of the study area in the Northern Cape of South Africa

The bottles were air dried, and stored closed to prevent pollution prior to sample collection. Samples were collected in duplicate at a depth between 1 and 9.5 m using a HydraSleeveTM "No-Purge" groundwater sampler [27], with GPS coordinates being recorded. Subsequent collection of samples, the following physical determinants were quantified on-site, i.e. pH, temperature, electrical conductivity (EC), salinity, redox potential (Eh) and total dissolved solids (TDS), using an EXSTIK II® EC500 and an EXSTIK II® CA895, for dissolved oxygen (DO). The instruments were calibrated prior to sampling using standard procedures, for which pH 4 and 7 including the EC 1413 mS/m standards being used to validate the calibrations. Temperature was measured in-situ, to minimise atmospheric variations [28]. Samples were also filtered through a 0.45-µm pore-size cellulose membrane filter using a hand-vacuum pump into a 100 mL polypropylene sampling bottles [29, 30]. The unfiltered samples were digested with technical grade nitric acid (0.2 M) at pH < 2. Unless otherwise stated, all reagents used were of analytical grade (ACS), while standardised methods were used [31]. All samples were stored in cooler boxes with ice to ensure preservation during transportation to the laboratory where further analyses were performed. Analyses performed included anions, cations, heavy elements, and chemical oxygen demand, using High-performance liquid chromatography (HPLC), UV-Vis spectrophotometer, inductively coupled plasma coupled either with an optical emission spectrometer (ICP-OES) or with a mass spectrometer (ICP-MS) at an external South African National Accredited laboratory. The samples were analysed without dilution. Fig. 1, indicates the sampling area.

III. Data Treatment

Multivariate statistical methods were performed using Microsoft Excel (2016); the results were reported as the mean, minimum and maximum concentrations of the analytes. The quality assurance of the major ion analyses was ensured through the estimation of charge balance error (%CBE) which was calculated post analyses to assess the accuracy of measurement for each sample [32]. The *%CBE* within ±5 % was deemed an appropriate variation for the hydrochemical analyses performed with all anions and cations being expressed in milli-equivalents. Similarly, as numerous methods were reported for an evaluation to determine the suitability of water for irrigation, total salinity (TS) was used as a representation of the (un)suitability of the samples for irrigation, an evaluation associated with sodium sulphate and sodium chloride concentration in the samples, thus its toxicity potential to crops and soils.

IV. Results And Discussion

Hydrochemical characteristics of the OPGW are the main factors determining its suitability for numerous uses [33]. The physico-chemical parameters of the chemical components of the water from the OPGW were compared to those listed in the South African National Standards (SANS 241) and the World Health Organization (WHO) drinking water standards. The results for the physical parameters measured in the OPGW are presented in Table I.

TABLE I: Physical Determinands Of The Open-Pit Groundwater (OPGW) And Maximum Limits In Drinking water

Sample Numbers	pH	Temperature	EC	TDS	DO	Salinity	Eh
	-	°C	mS/m	mg/L	mg/L	ppt	mV
OP1	5,2	24,7	8215	5720	1,0	4,0	109,9
OP2	4,9	23,8	9000	6283	1,1	4,5	122,5
OP3	5,0	24,2	8013	5583	1,1	3,9	125,7
OP4	4,8	23,2	8403	5855	1,2	4,1	130,1
OP5	4,5	19,2	7380	5145	0,4	3,7	127,3
Minimum	4,5	19,2	7380	5145	0,4	3,7	109,9
Maximum	5,2	24,7	9000	6283	1,2	4,5	130,1
Average	4,9	23,0	8202	5717	0,9	4,1	123,1
SANS241-1:2015	5-9,7	-	≤170	≤1200	-	-	-
WHO:2011	6,5-9.5	-	100	500	5	-	-

The pH level range was 4.5 to 5.2 with an average of 4.9, suggesting that the groundwater in the study area is slightly acidic. Similarly, DO values were determined to be low, with concentrations between 0.4 and 1.2 mg/L. Generally, low DO values indicate that the open-pit contains water with an elevated quantity of dissolved metalloids, a process facilitated by a low pH between 2 and 4, which suggested a microbially controlled geochemical process related to mineral oxidation, under anoxic conditions [34], thus the potential to form AMD.

For oxidative processes to take place, a suitable EC is required, which is highly influenced by the TDS in the water being studied [35]. The concentration of TDS was 5145 to 6283 mg/L, with a mean value of 5717 mg/L, which is the indication of brackish water characteristics with the OPGW salinity being up to 4.5 g/L (ppt). Overall, the speciation of ions becomes increasingly significant as the salinity of the solution increases, an attribute that suggested that elevated TDS might be due to metalloid leaching from the surroundings into the open-pit, as it is surrounded by tailings, dumps and closed O'kiep Copper Mine (COCM). For effective monitoring of the source point pollution plume, both EC and Eh are required, particularly since the Eh is not only an indication of organic matter degradation activity but also because it can be used to quantify redox active components within the OPGW.

For the OPGW, the Eh was 109.9 to 130.1 mV with a mean of 123 mV implying oxidative conditions [36], with metallic species, Na^+ and K^+ , being one of the components with concentrations averaging 493 and 35 mg/L, respectively. The abundance of cations was determined to be $Mg^{2+} > Na^+ > K^+ > NH^{3+}$, which included dominant associate anions, i.e. SO_4^{2-} and Cl^-, thus an assertion that oxidation of sulphide minerals is taking place, which is the primary indicator of AMD formation from sulphidic ores. The concentration range was determined to be 4020 to 6 020 mg/L for cations and 607 to 759 mg/L for anions with averages of 4020 and 607 mg/L, respectively. The dominance of Cl^- and Na^+ ions in the OPGW further provided evidence of percolation into the open pit from an external saline source [37]. Other anions observed in the OPGW were F^- and PO_4^{3-}, although at a low concentration of 5.4 to 9.6 mg/L and 3.51 to 3.77 mg/L, respectively. The abundance of anions was in the order $SO_4^{2-} > Cl^- > F^- > PO_4^{3-}$, another indicator of AMD pollution [38]. The presence of Al, Cd, Co, Cr, Cu, Mn, Ni, and Zn in the OPGW can be associated with copper rich sulphides ores, a result of leaching of minerals (especially oxides and sulphides) into the open-pit, as observed by the higher concentrations of heavy metals, Cu > Mn > Al > Fe > Ni > Co > CN > Cr > Cd > Zn > V. Due to the mildly acidic pH, ore dissolution increases, facilitating the solubilisation of numerous elements in the ore-body including copper [39]. Since, heavy metals have the potential to form inorganic complexes, particularly at slightly elevated temperatures due to a semi-arid climate, the potential to form complexes of zinc, copper, nickel, manganese, cadmium, lead and mercury is high [40]. Furthermore, since the concentrations of Cu, Al and Fe were significantly higher than most metal species identified in the OPGW, implies that a significant quantity of the metals was of a geologic weathering source rather than being from anthropogenic activities associated with COCM activities [41]. Additionally, the solubility of copper can significantly increase at pH of ~5.5 [42] or as a result of longer exposure to the OPGW, which can culminate from periodic ore fragmentation or due to direct oxidation of the sulphidic ore, facilitating metal atom/ion transfer into the water. Additionally, the observations also suggested possible oxidation of tailing residue derived from chalcopyrite and digenite [43]. Tailing-moisture interactions causes pollutant dispersion both by solid transport mechanisms, geological weathering and dissolution; with all these processes leading to an increase in heavy metal concentrations in groundwater thus groundwater contamination [41].

Assessment of the OPGW characteristics is a prerequisite quantification of its suitability for drinking and/or agricultural use. Overall, water quality parameters are evaluated by comparative analyses with national guidelines [35-44]. The hydrochemical parameters of the OPGW were compared to SANS and WHO drinking water guidelines., with the OPGW having a relatively high turbidity values between 502 and 556 NTU, a significant parameter indicative of the unsuitability of the OPGW for drinking [45]. Similarly, high concentration of Mn (544 mg/L) and Fe (64 mg/L) exceeded the recommended drinking water limits; although Sb, AS, Cd, Cr, Co, Hg, Ni, Se, V, Zn and CN were determined to be lower than the guideline limits. The total salinity (TS) of the OPGW was examined using anion and cation concentrations quantified (Cl^-, SO_4^{2-}, Na^+), with high levels of EC and TDS including slightly acidic pH and a high chorine concentration (759 mg/L). High TS, EC and TDS is indicative of the unsuitability of the OPGW for irrigation purposes.

V. Conclusion

The depth of samples collected had an insignificant effect on the OPGW hydrochemical characterisation analyses undertaken. The pollutants in the OPGW were identified as Mg^{2+}, Na^+, K^+, NH^{3+}, SO_4^{2-}, Cl^-, F^-, PO_4^{3-} and heavy metals such as Cu, Mn, Al, Fe, Ni, Co, CN, Cr, Cd, Zn and V, which was attributed to AMD formation potential. Currently, AMD formation is one of the most important environmental concerns at O'kiep, due to water shortages. Additionally, the presence of mine dumps, tailing dams and polluted sediment in the area, is a concern for the local community [46-51]. All studied hydrochemical parameters for samples collected exceeded the guideline limits, indicative of the unsuitability of the OPGW for both drinking and irrigation purposes. Considering community developmental activities presently pursued in this region, it is prudent to continue this monitoring programme for future environmental impact assessments. From this study, it is prudent to develop monitoring remedial measures for implementation to improve the quality of the OPGW.

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