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Chemical Speciation and Characterization of Coal Fly Ash and Soil Samples Sourced from Hendrina Power Station

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Abstract:This study aimed at characterizing the composition and performing chemical speciation modelling to determine species that are abundant in the coal fly ash (CFA) and sol samples sourced from Hendrina Power station located in Mpumalanga Province. All CFA samples were alkaline in nature with pH values ranging between 8.11 ± 0.07 and 8.60 ± 0.03 with an electrical conductivity (EC) ranging between 301.70 and 1515.00 µS/cm while EC of control soil was 103.10 µS/cm. The control soil pH was found to be 6.24 ± 0.13 and total organic carbon values ranged between 2.68 and 85.82 mg/kg and some percentage organic carbon values of CFAs were found to be greater than 8%, which is above the permissible limits of hazardous waste dumping. Oxidation-reduction potential values were negative in all CFA samples and positive in soil. The speciation modelling showed that the potential for a trace metal to have hazardous effects in soil systems depends on its concentration, specific form and interactions with other constituents in CFA. The slow release of metals from CFA to soil was assessed by looking at how a given metal is distributed throughout its several possible chemical forms. The presence of divalent cations (Pb^{2+}, Cu^{2+}, Zn^{2+}, etc.) in CFAs might pose a threat to soil quality. In the competition for binding sites on ferric hydroxides, dissolved metal ions faced off against other metals. Protons (H^+) were seen to be in competition with Pb, Cu and Zn for the ability to bind to hydroxyl (OH^-) groups and this is due to chemical precipitation and surface complexation.

Keywords: coal fly ash; metals; hendrina power station; total organic carbon; speciation modelling

1. Introduction

Coal fly ash (CFA) is one of the most challenging and voluminous waste that the world is currently facing. It is a fine powder and hazardous material containing both organic and inorganic pollutants generated from coal fired-power plants (C-FPPs) after generating electricity (Assi et al., 2020). It is mainly formed by amorphous spherical particles due to the heating on high temperature and cooling of fluid that resulted from melting minerals available in the feed coal. Its quality highly depends on several factors such as combustion technique, chemical composition of the feed coal, and degree of pulverization. CFA has several value-added minerals like oxides of silica, alumina, iron, calcium, sodium, potassium, and magnesium. It contains sulphur, carbon, metals, trace amounts of heavy metals, and small amounts of radioactive elements such as ^{226}Ra, ^{232}Th and ^{40}K (Kursun Unver, & Terzi, 2018). CFA also has several natural micro- to nano-structured materials such as cenospheres, unburned soot, spherical ferrous-rich particles, carbon nanomaterials, and plerospheres (Yadav et al., 2023). CFA is classified into two main classes, F and C (Alterary, & Marei, 2021). Class F CFA is generated from burning bituminous or anthracite coal, usually with a low lime content (under 15%), and this is the most used one in South African C-FTPs (Musyoka, 2009; Alegbe et al., 2018). It consists of a significant mix of alumina, silica and iron (over 70%) compared to class C CFA (Wardhono, 2018; Panda et al., 2021; Kelechi et al., 2022). Class C CFA is generated from sub-bituminous coal or lignite and has a high content of sulphate and alkali (Wardhono, 2018; Kelechi et al., 2022). Currently, most of C-FPPs are running out of disposal areas due to the huge amount of generated CFA while its global

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reusability rate is not proportional to its production (Yadav et al., 2023). In South Africa, the cement, construction and geopolymer industries are the ones reusing a small fraction of the generated CFA (Kelechi et al., 2022). The widespread distribution of trace metals in the environment due to intense anthropogenic activities and technical applications has sparked worries about their possible consequences on the environment and public health. Their toxicity is highly dependent on several variables including chemical species, dose and mode of exposure, in addition to the age, gender, genetics, and nutritional state of those who are exposed. Moreover, people living in the vicinity of C-FPPs suffer from lung diseases and cancers, eye problems and other dust-related side effects. However, Pb, Cu, As, Cr, Cd, Hg, and Zn have been listed as priority metals of public health concern due to their high degree of toxicity (Krishna, & Ahuja, 2023). Agricultural lands and water reservoirs are also suffering from the leachate of this CFA due to weathering processes. Due to high concentration levels of inorganic pollutants in the CFA, this by-product material can be an alternative potential source of trace elements, precious metals and radioactive elements (Kursun Unver, & Terzi, 2018). It can also be used as an adsorbent or for the synthesis of other different nanoparticles for heavy metal adsorption from wastewater (Alegbe et al., 2018; Munyengabe et al., 2024). Total organic carbon (TOC) is amongst the main indicators of complete or incomplete burned coal and there is a strong correlation between TOC and organic pollutant content where high concentration of TOC in CFA implies high concentration of organic pollutants (Ruwei, Jiamei, Jingjing & Liu, 2013). Moreover, the organic matter content has a strong influence on buffer capacity, cation exchange capacity and the retention of heavy metals (Rosselli et al., 2003). Metals present in organic-rich soil are less mobile and less bioavailable than metals present in mineral-rich soil (Olaniran et al., 2013; Banda et al., 2021). In view of the importance of CFA in environmental issues, we need to study the CFA in terms of the heavy metal content related to it to evaluate the potential risks. But knowledge of total metal content alone does not provide information about the actual risk posed by CFA to the biota as it does not tell us about the available fraction. No work has been done to determine the amount of metal content in CFA collected from Hendrina power station. The only available research investigated the mineralogical, chemical and morphological of this CFA (Alegbe et al., 2018). Therefore, PH REdox EQuilibrium in C language (PHREEQC) was applied to investigate the chemical speciation of trace metals and major elements, determine metal toxicity and mobility in CFA and soil samples collected from Hendrina power station located in Mpumalanga Province. Concentrations of trace and major elements were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES).

2. Materials and Methods

2.1. Sample Collection

CFA samples were collected from six random sampling sites (assigned Dam 3B, Dam 3C, Dam 4B, Dam 4C, Dam 5A, and Dam 5C) and one for control soils from the Hendrina power station CFA dams located in Mpumalanga Province, South Africa. The CFA samples were sealed in plastic bags tightly closed to prevent ingress and absorption of air to minimize the reaction of calcium oxide with carbon dioxide to form calcite, which could reduce the calcium oxide content. A small fraction from each bag was crushed and sieved to make a homogeneous sample ad stored in glass bottles for further analysis.

2.2. Methodology and Instrumentation

Sample treatment and characterization method of CFA, soil and certified reference material (CRM) was adopted from Banda et al. (2021) with some modification. For electrical conductivity (EC), oxidation-reduction potential (ORP) and pH measurements, 5.00 g in triplicate of each sample were transferred into 15 mL centrifuge tubes and 10 mL of deionized water was added to each tube and the mixture was shaken overnight using a mechanic shaker (Laboratory Marketing Services CC, Maraisburg, South Africa) and then centrifuged using a centrifuge (Nuvefuge CN180, Akyurt, Turkey) for 15 minutes at 4000 rotation per minute. The EC, ORP and pH of all samples were

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measured using a conductivity-pH combimeter (Orion Star Series Meter Thermo Fischer Scientific Inc., Beverly, USA). The TOC content was determined using a Shimdzu TOC-LCPH analyzer. Accurately 0.05 g of each sample was weighed and then transferred into 50 mL centrifuge tubes in triplicate. Hydrochloric acid (HCl) (0.22 mol/L, 30% purity) was also prepared in 1000 mL volumetric flask. 50 mL of HCl was mixed with each of the above masses and the mixtures were shaken using a mechanic shaker for 2 h then after the tubes were placed straight up for easily settling down. The supernatant liquids were siphoned and transferred into clean tubes. Before running the samples, the instrument (Shimdzu, TOC-LCPH analyzer) was calibrated by injecting 1000 mg/L of total carbon (TC) and inorganic carbon (IC) and the instrument automatically diluted it to the standard solutions from 0, 10, 20, 40, 80, and 100 mg/L. The un-spiked and spiked CRMs of CFA were run to check if there is any other matrix interfering and if the instrument is giving accurate results. Ultrapure water was also run on the instrument to flush it and samples were then run in a single dilution by injecting 50 microliters.

2.3. Digestion of CFA, CRM and Soil Prior to ICP-OES Analysis

All samples were subjected to acid digestion prior metal analysis. CFA, soil and CRM were accurately weighed (0.25 g) into digestion vessels and digested using a two-stage method in 5 mL HNO_3 (65%) using a MARS 1 Xpress microwave digestor (CEM Cooperation, Smith Farm, USA) for 30 min at 1200 W. A blank, consisting of 5 mL of HNO_3 (65% w/w), was digested along with the samples, and the resulting digests were cooled and subsequently diluted to 25.00 mL with Millipore® water. The CRM (sediment SRM 1944) of CFA was used for method validation. ICP-OES was used to determine the concentrations of metals in soil and CFA as well as in the CRMs for chemical speciation purpose. The instrument was calibrated using standards prepared by diluting a 1000 mg/L ICP grade standard stock solution of each element to the required working concentrations (1, 3, 5, 7, and 10 mg/L). The instrument operating parameters were set as follows: plasma power (1500 W), sample uptake rate (1.6 mL/min), auxiliary gas flow rate (1 L/min), plasma gas flow rate (15 L/min), and nebulizer flow rate (0.8 L/min).

3. Results and Discussion

3.1. Physical and Chemical Properties of Soil and CFA Samples

Physical and chemical properties (pH, ORP, EC, and TOC) of CFA presented in Table 1 and soil samples were determined to facilitate the modelling process.

Table 1. Physical and chemical properties of CFA and soil samples.

Sampling sites	pH	ORP (mV)	EC (µS/cm) @ 25ºC	TOC (mg/kg)
Dam 3B	8.17 ± 0.13	-47.7±2.2	1027.30	84.37±0.80
Dam 3C	8.40 ± 0.06	-45.9±11.3	632.70	2.68±2.68
Dam 4A	8.60 ± 0.03	-57.5±1.6	301.70	83.74±
Dam 4B	8.11 ± 0.07	-46.9±2.5	757.70	2.22±0.98
Dam 5A	8.20 ± 0.16	-41.8±3.9	1159.00	85.02±1.42
Dam 5C	8.23 ± 0.07	-37.1±4.1	1515.00	2.46±0.28
Control Soil	6.24 ± 0.13	44.3±15.8	103.10	85.82±0.60
Un-spiked CRM	-	-	-	2.50±0.54
Spiked CRM	-	-	-	27.14±0.31

From Table 1, all pH values of CFA samples were alkaline in nature (> 8.00) except for the control soil which was 6.24 ± 0.13. The pH of the CFA usually ranges between 4.50 and 12.00 and depends on the particle size distribution of the ash and the concentration levels of trace metals and major elements contained in the CFA (Haider et al., 2016; Kelechi et al., 2021). The higher the fineness of CFA, the higher the dissolution of metals and good pH measurements, that is why the CFA has alkaline pH

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values than the soil due to its high fineness. The EC values of CFA ranged from 301 to 1515.00 µS/cm at 25 ºC, which is greater than one of the control soil, indicating higher concentrations of metal ions in CFA. ORP is normally used to determine if reducing or oxidizing conditions are prevalent in soil or water, and to predict the states of different chemical species available in environmental matrix such as dissolved metals and their leaching behavior (Duffy, 2011). Figure 1 shows the relationship between pH and ORP of CFA and control soil samples, where ORP of control soil is positive while ORPs of CFA samples in alkaline conditions are negative and decrease almost linearly with increasing pH values. There is a strong correlation between pH and ORP values as well as chemical speciation modelling of metals (Komonweeraket et al., 2015). According to the measured ORPs, metals in the leachates should mostly exist in an oxidized form under acidic conditions (pH < 7.00). In environmental situation, it is common to have complex non-equilibrium conditions between a large number of species, so it is usual to obtain an approximate value and define the conditions as being in the reducing or oxidizing regime. However, high pH environmental matrix has more reducing agents (negative ORPs) while low pH environmental matrix has more oxidizing agents (positive ORPs) (Komonweeraket et al., 2015; Zhang et al., 2016).

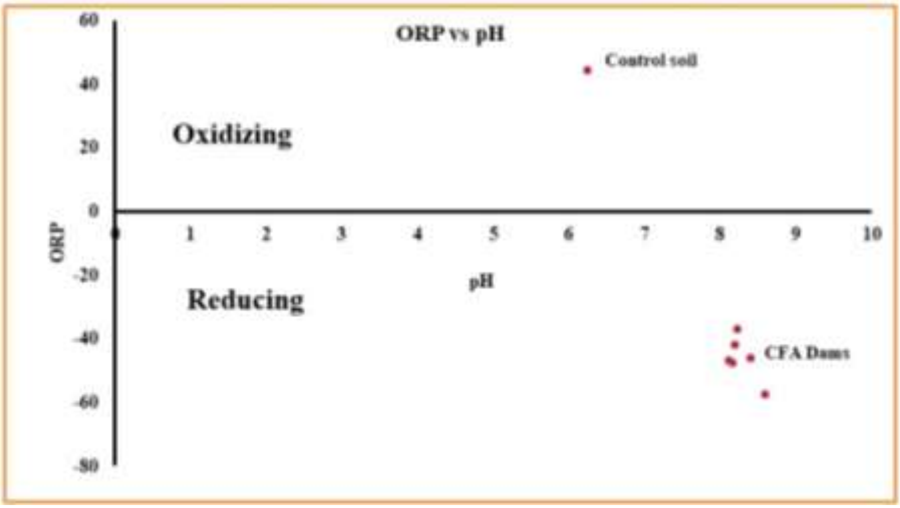

Figure 1. ORP values as a function of pH for CFA and control soil.

TOC is another important property of CFA that consists of both unburned carbon (UC) and volatile carbonaceous matter, which reflects the combustion efficiency of the power plant and leads to different effects on ecosystem due to ash improper disposal or utilization (Cheng et al., 2020). The TOC of all samples ranged between 2.22 ± 0.98 and 85.26 ± 0.93 mg/kg and for control soil was 85.82 ± 0.60 mg/kg, and values below 10000 mg/kg suggest the unrestricted mobility of metals (Baran et al., 2019). This mean that metals present in organic-rich soil are less mobile and less bioavailable than metals present in mineral-rich soil (Olaniran et al., 2013). According to the European Union Council (2003), CFA with TOC (in the form of percentage organic carbon) concentrations higher than 6% is considered hazardous while < 5% is nonhazardous waste, and < 3% for inert waste with pH greater than 6 (EU Council decision, 2003). The percentage organic carbon values calculated from TOC values of all CFA samples ranged from 0.22 to 8.50 wt%. According to the above EU Council decision taken in 2003 about the coal usage and utilization, the samples collected from Dams 3C, 4B, 5A and 5C as well as the control soil were only above 8 which are above the permissible limit of 5 wt% recommended by EU Council decision (Cheng et al., 2020). This can indicate that the CFA disposal in this area has contaminated even the surrounding areas in Mpumalanga Province. Moreover, the TOC results were also in the range of un-spiked and spiked CRMs values.

3.2. Trace Metal and Major Element Analysis

The elements analyzed and subjected to speciation modelling process are presented in Table 2. Only CFA sample collected from Dam 3B was modelled as other samples showed similarities to it.

The CRM was used to validate data obtained for Ag, Al, B, Ba, Mn, Cr, Pb, Fe, Ni, Mg, Ca, Ca, Co, Cu, Zn, Na, and K in CFAs and control soil. No significant differences ($p \leq 0.05$) were observed between the measured and the certified values for all elements.

Table 2. Concentration levels of trace and major elements (mg/kg) in all samples.

Sample ID	Ag	Al	B	Ba	Mn	Cr	Pb	Fe	Ni	Mg	Ca	Co	Cu	Zn	Na	K
CFA 3B	1.15±0.07	493.92±0.01	3.07±0.00	12.27±0.01	5.17±0.01	2.04±0.01	0.05±0.28	375.37±0.00	0.30±0.00	158.50±0.00	432.80±0.00	0.06±0.01	0.41±0.00	1.21±0.01	18.47±0.01	71.14±0.01
CFA 3C	0.97±0.12	347.92±0.00	3.34±0.01	13.37±0.01	4.62±0.00	1.58±0.01	0.13±0.07	285.98±0.01	0.25±0.01	13.40±0.00	543.14±0.00	0.08±0.02	0.45±0.00	1.31±0.01	0.51±0.16	70.38±0.02
CFA 4B	2.56±0.24	1178.59±0.00	4.94±0.00	16.85±0.00	8.45±0.00	4.93±0.00	0.20±0.03	939.81±0.00	0.95±0.00	211.91±0.00	599.76±0.00	0.03±0.00	0.01±0.00	ND	0.17±0.00	346.02±0.00
CFA 5A	1.25±0.34	481.23±0.01	1.77±0.00	9.62±0.03	5.30±0.01	2.20±0.00	0.04±0.16	376.25±0.00	0.40±0.03	137.90±0.00	362.62±0.00	0.10±0.02	0.40±0.00	0.46±0.00	8.73±0.00	234.30±0.00
CFA 5C	1.20±0.27	359.47±0.00	3.12±0.00	12.77±0.01	5.27±0.00	1.82±0.00	0.03±0.40	354.81±0.00	0.33±0.01	162.37±0.00	476.02±0.00	0.08±0.01	0.40±0.00	1.36±0.00	20.63±0.00	242.97±0.01
CRM	1.95±0.12	500.47±0.01	10.83±0.01	6.94±0.00	4.46±0.01	2.98±0.00	0.62±0.05	856.50±0.01	0.61±0.00	13.35±0.00	384.33±0.00	0.20±0.02	1.12±0.00	0.31±0.00	0.16±0.00	118.90±0.00
SOIL	2.70±0.21	407.04±0.00	2.90±0.17	2.12±0.01	10.48±0.01	6.20±0.00	0.12±0.16	952.82±0.00	0.74±0.01	175.65±0.00	486.88±0.00	0.24±0.00	0.86±0.01	1.12±0.00	2.85±0.00	233.36±0.00

ND: Not detected!

From Table 2, metal concentrations in all samples including control soil ranged from 0.97±0.12 to 2.56±0.24 mg/kg (**Ag**), 347.92±0.00 to 1178.59±0.00 mg/kg (**Al**), 1.77±0.00 to 4.94±0.00 mg/kg (**B**), 2.12±0.01 to 16.85±0.00 mg/kg (**Ba**), 4.62±0.00 to 10.48±0.01 mg/kg (**Mn**), 1.58±0.01 to 6.20±0.00 mg/kg (**Cr**), 0.03±0.40 to 0.20±0.03 mg/kg (**Pb**), 285.98±0.01 to 952.82±0.00 mg/kg (**Fe**), 0.25±0.01 to 0.95±0.00 mg/kg (**Ni**), 13.40±0.00 to 175.65±0.00 mg/kg (**Mg**), 362.62±0.00 to 599.76±0.00 mg/kg (**Ca**), 0.10±0.02 to 0.24±0.00 mg/kg (**Co**), 0.01±0.00 to 0.86±0.01 mg/kg (**Cu**), ND to 1.36±0.00 mg/kg (**Zn**), 0.17±0.00 to 20.63±0.00 mg/kg (**Na**), and 70.38±0.02 to 346.02±0.00 mg/kg (**K**). Al, Fe, Ca, Mg, Na, and K presented high concentrations in all samples as these are major elements while trace metals were in low concentrations. Comparing with the literature, these results were similar but lower than to those obtained in CFA sampled from Kangal lignite-firing thermal power plant, Turkey by Altıkulaç et al. (2022), which were 35211.00 ± 4328.40 mg/kg (**Fe**), 367.60 ± 95.20 mg/kg (**Zn**), 40.30 ± 14.70 mg/kg (**Pb**), 155.40 ± 22.40 mg/kg (**Ni**), 272.80 ± 33.00 mg/kg (**Mn**), and 189.20 ± 23.70 mg/kg (**Cr**). In another study, the concentrations of heavy metals in CFA sampled from Parichha thermal power plant, Jhansi, India were 34.809 mg/kg (**Pb**), 51.609 mg/kg (**Ni**), 2635 mg/kg (**Fe**), 64.772 mg/kg (**Cr**), and 286.205 mg/kg (**Mn**) (Verma, Madan, & Hussain, 2016).

3.3. Chemical Speciation Modelling

Understanding the chemical speciation of the trace metals in CFA is essential for evaluating the environmental behaviour of CFA disposed of in a landfill. The PHREEQC geochemical modelling

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code was utilized to accomplish this speciation modelling. The CFA samples had numerous species of each trace metal, as revealed by our results. This is significant because it helps anticipate environmental mobility and bioavailability under the variety of geochemical conditions observed in terrestrial and aquatic environment. To predict the states of different chemical species in the CFA dissolved metals and determine if oxidizing or reducing conditions are typical in CFA, one can utilize the ORP values. Furthermore, one of the most important factors influencing the behaviour of trace metal leaching is ORP. Table 1 shows the relationship between pH and ORP for the CFA samples from the pH-dependent leaching studies. In alkaline conditions (pH 8.17± 0.13) the ORP readings for all CFA samples were negative and decrease almost linearly with increasing pH. In CFA samples linear connections have also been noted. The determined ORP indicated that under acidic to slightly acidic conditions (pH 6.24 ± 0.13), trace metals in the leachates should primarily exist in oxidized forms. It is typical to acquire an approximate value and classify the conditions as being in the oxidizing or reducing regime in environmental situations where complicated non-equilibrium conditions between several species are widespread. The results revealed that CFA with higher pH typically contains more reducing agents (ORP). The pH had a major impact on the trace metal leaching concentrations. It was observed that the leaching of metals occurred at neutral pH with little concentration and increased concentration at acidic and basic pH conditions. Redox potential was found to have a major impact on the leaching of metals. Very little metal leached at a lower ORP, although the leaching of metals rose dramatically under highly oxidizing circumstances. The results demonstrated that CFA has high pH and EC, and this is due to alkaline conditions with high salinity. Environmental system processes can be simulated using the scientific PHREEQC geochemical modeling code. Environmental processes depend on several parameters, such as pH, the redox potential of the medium, and the makeup of the system (Arias-Arce et al., 2023). Trace metal speciation within the soil matrix has a major effect on soil quality (Li et al., 2022). The foundation of it is equilibrium chemistry and chemical kinetics. The functions of PHREEQC modeling are numerous; however, the ones that pertain to speciation modeling are summarized in this paper. To shed light on the heavy metal speciation and bioavailability in CFA and soil, speciation modeling was carried out. The total concentrations of metals found in CFA collected from Dam 3B were utilized as input data for the model to replicate the conditions of the real environment (Table 3). The pH and Eh values obtained during lab analysis were also employed and the distribution of species in the CFA sample.

The simulation demonstrated that most of the heavy metals discovered through chemical analysis were in the reduced oxidation states, for instance of Fe^{2+} and Cu^{+}. Redox active transition metals such as iron and copper exist in two oxidation states (Fe^{2+} and Fe^{3+}/Cu^{+} and Cu^{2+}) (Nikolić et al., 2023). Their capacity to alter their oxidation states enables them to take part in a variety of crucial metabolic activities (Nikolić et al., 2023). According to the PHREEQC model, $Cr(OH)^{2+}$ was the main Cr^{3+} species that contributed to the total Cr^{3+} concentration under all conditions simulated in this work. The highest concentration of Cr (2.04 ± 0.01 mg/kg) was observed in sample CFA collected from Dam 3B. CFA contains potentially harmful and bioavailable heavy metal species, according to the model's observed in species distribution. Chromium is a polyvalent element that can exist in many distinct oxidation states; however, only trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) chromium are commonly encountered in the natural environment. Because it acts as an oxidizing agent and generates free radicals when Cr^{6+} is reduced to Cr^{3+} in the environment, Cr^{6+} is very dangerous. The finding of Pb, Cu, Zn and Cr species in CFA also raises the possibility of a major ecological concern because these species have the potential to contaminate surface and ground waters, increasing their bioavailability to humans and other animals. The monitoring of levels of metals in different seasons would be critical to prevent environmental and health impacts.

Based on the speciation modelling, CFA was found to be important for iron speciation because the samples of CFA predominantly leached Fe^{3+} rather than bioavailable Fe^{2+}. The mineral phases that the PHREEQC input data anticipated supported this. Precipitations projected to be predominant included mineral phases such as magnetite, hematite, and goethite. The iron precipitates that are generated show signs of integrated copper. This is a blatant sign that if iron precipitates from CFA

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with a high iron concentration could serve as sorption sites for dissolved copper species. The amount of bioavailable metals in natural waterways can be lowered by precipitation that occurs at pH 8.17 ± 0.13. The simulation indicated that precipitates of lead and cobalt, in addition to iron, could occur at pH 8.17 ± 0.13. When Pb and Cu concentration increases, they precipitate in a form of oxyhydroxides. They exist as co-precipitate and adsorb to other metal oxide and hydroxide minerals such as hematite and goethite.

Table 3. Distribution of species in CFA 3B sample at pH 8.17 ± 0.13.

Species	Molality	Activity	Molality	Activity	Gamma
Al 7.648e-03					
Al(OH)4-	7.622e-03	4.112e-03	-2.118	-2.386	-0.268
Al(OH)3	2.467e-05	2.467e-05	-4.608	-4.608	0.000
Al(OH)2+	1.593e-06	9.337e-07	-5.798	-6.030	-0.232
AlOH+2	7.521e-09	8.878e-10	-8.124	-9.052	-0.928
Al+3	2.570e-17	6.705e-13	-16.590	-12.174	4.417
Ca 2.772e+00					
Ca+2	2.761e+00	2.535e+02	0.441	2.404	1.963
CaOH+	1.093e-02	6.696e-03	-1.961	-2.174	-0.213
CaH2BO3+	1.261e-04	4.914e-05	-3.899	-4.309	-0.409
Co(2) 4.717e-07					
Co+2	4.717e-07	7.392e-12	-6.326	-11.131	-4.805
CoOH+	3.104e-12	1.953e-13	-11.508	-12.709	-1.201
Co(OH)2	2.054e-14	2.054e-14	-13.687	-13.687	0.000
Co2OH+3	4.682e-15	7.235e-26	-14.330	-25.141	-10.811
Co(OH)3-	8.624e-18	5.426e-19	-17.064	-18.265	-1.201
CoOOH-	2.271e-18	1.429e-19	-17.644	-18.845	-1.201
Co(OH)4-2	7.266e-21	1.139e-25	-20.139	-24.944	-4.805
Co4(OH)4+4	4.811e-24	0.000e+00	-23.318	-42.537	-19.219
Co(3) 1.263e-32					
CoOH+2	1.263e-32	1.980e-37	-31.898	-36.703	-4.805
Co+3	0.000e+00	0.000e+00	-47.948	-43.531	4.417
Cr(2) 3.996e-18					
Cr+2	3.996e-18	6.263e-23	-17.398	-22.203	-4.805
Cr(3) 1.747e-05					
Cr+3	1.696e-05	2.622e-16	-4.770	-15.581	-10.811
Cr(OH)+2	4.846e-07	7.595e-12	-6.315	-11.119	-4.805
Cr(OH)2+	1.945e-08	1.224e-09	-7.711	-8.912	-1.201
CrO2-	6.656e-10	4.188e-11	-9.177	-10.378	-1.201
Cr(OH)3	6.086e-10	6.086e-10	-9.216	-9.216	0.000
Cr(OH)4-	5.099e-10	3.208e-11	-9.293	-10.494	-1.201
Cr(6) 1.695e-28					
HCrO4-	1.204e-28	7.576e-30	-27.919	-29.121	-1.201
NaCrO4-	2.824e-29	1.777e-30	-28.549	-29.750	-1.201
KCrO4-	1.737e-29	1.093e-30	-28.760	-29.961	-1.201

CrO4-2	3.520e-30	3.232e-28	-29.453	-27.491	1.963
H2CrO4	4.449e-38	4.449e-38	-37.352	-37.352	0.000
Cr2O7-2	0.000e+00	0.000e+00	-51.875	-56.680	-4.805
Cu(1) 2.893e-06					
Cu+	2.893e-06	1.820e-07	-5.539	-6.740	-1.201
Cu(2) 1.126e-08					
Cu2(OH)2+2	3.882e-09	6.084e-14	-8.411	-13.216	-4.805
CuOH+	3.058e-09	1.556e-09	-8.515	-8.808	-0.293
Cu(OH)2	4.111e-10	4.111e-10	-9.386	-9.386	0.000
Cu(OH)3-	1.775e-11	1.117e-12	-10.751	-11.952	-1.201
Cu+2	4.048e-12	3.717e-10	-11.393	-9.430	1.963
Cu(OH)4-2	7.425e-13	1.164e-17	-12.129	-16.934	-4.805
Fe(2) 2.951e-03					
Fe+2	2.951e-03	4.625e-08	-2.530	-7.335	-4.805
FeOH+	4.303e-09	2.438e-09	-8.366	-8.613	-0.247
Fe(OH)2	2.564e-12	2.564e-12	-11.591	-11.591	0.000
Fe(OH)3-	1.895e-12	1.074e-12	-11.722	-11.969	-0.247
Fe(3) 3.933e-05					
Fe3(OH)4+5	1.310e-05	1.222e-35	-4.883	-34.913	-30.030
Fe2(OH)2+4	7.405e-09	4.467e-28	-8.130	-27.350	-19.219
Fe(OH)2+	3.228e-09	1.892e-09	-8.491	-8.723	-0.232
Fe(OH)3	2.691e-09	2.691e-09	-8.570	-8.570	0.000
Fe(OH)4-	5.659e-10	3.317e-10	-9.247	-9.479	-0.232
FeOH+2	3.564e-14	3.673e-15	-13.448	-14.435	-0.987
Fe+3	1.647e-25	4.296e-21	-24.783	-20.367	4.417
Mg 1.931e-03					
Mg+2	1.794e-03	1.647e-01	-2.746	-0.783	1.963
MgOH+	1.373e-04	8.680e-05	-3.862	-4.061	-0.199
MgH2BO3+	4.938e-08	1.924e-08	-7.306	-7.716	-0.409
Ni 2.217e-06					
NiOH+	2.115e-06	1.331e-07	-5.675	-6.876	-1.201
Ni+2	8.697e-08	7.984e-06	-7.061	-5.098	1.963
Ni(OH)2	1.400e-08	1.400e-08	-7.854	-7.854	0.000
Ni(OH)3-	2.946e-10	1.853e-11	-9.531	-10.732	-1.201
Pb 1.127e-07					
Pb2OH+3	3.969e-08	6.134e-19	-7.401	-18.212	-10.811
Pb4(OH)4+4	6.898e-09	4.162e-28	-8.161	-27.381	-19.219
PbOH+	5.702e-09	3.588e-10	-8.244	-9.445	-1.201
Pb(OH)2	1.502e-11	1.502e-11	-10.823	-10.823	0.000
Pb+2	1.175e-12	1.079e-10	-11.930	-9.967	1.963
Pb(OH)4-2	4.115e-13	6.450e-18	-12.386	-17.190	-4.805
Pb(OH)3-	3.161e-13	1.989e-14	-12.500	-13.701	-1.201
Pb3(OH)4+2	3.099e-17	4.857e-22	-16.509	-21.314	-4.805

Zn 8.230e-06					
ZnOH+	8.068e-06	5.076e-07	-5.093	-6.294	-1.201
Zn(OH)2	1.065e-07	1.065e-07	-6.973	-6.973	0.000
Zn+2	4.176e-08	3.834e-06	-7.379	-5.416	1.963
Zn(OH)3-	1.124e-08	7.069e-10	-7.949	-9.151	-1.201
Zn(OH)4-2	2.378e-09	3.726e-14	-8.624	-13.429	-4.805

In the environment, iron mobilization through proton-promoted dissolution was seen in CFA samples. Furthermore, investigations were conducted on pH dependency. There was diversity in the dissolution facilitated by protonation. As a result of variable Fe compounds forming and multiple valence states of Fe existing in Fe oxides, the concentration of Fe oxides increased in CFA. While Cu in Fe oxidation state also had the higher proportion, it is possible that Fe, Al, and other amorphous oxides had a greater influence on Cu adsorption (Table 4). As in CFA, which primarily existed in Fe oxidation state, this was primarily because Cu in residual state can interact with Fe compounds to form stable $CuFe_2O_4$.

Table 4. Saturation indices in CFA 3B sample at pH 8.17.

Phase	I**	log IAP	log K	(298 K,1 atm)
Al(OH)3(am)	1.38	12.18	10.80	Al(OH)3
Al2O3	4.78	24.43	19.65	Al2O3
Boehmite	3.63	12.20	8.58	AlOOH
CoFe2O4	16.70	13.17	-3.53	CoFe2O4
Cupricferrite	8.88	14.87	5.99	CuFe2O4
Cuprite	4.19	2.78	-1.41	Cu2O
Cuprousferrite	14.33	5.41	-8.92	CuFeO2
Diaspore	5.33	12.20	6.87	AlOOH
FeCr2O4	0.20	7.40	7.20	FeCr2O4
Ferrihydrite	0.80	3.99	3.19	Fe(OH)3
Gibbsite	3.89	12.18	8.29	Al(OH)3
Goethite	3.52	4.01	0.49	FeOOH
Hematite	9.46	8.04	-1.42	Fe2O3
Maghemite	1.66	8.04	6.39	Fe2O3
Magnesioferrite	6.66	23.52	16.86	Fe2MgO4
Magnetite	13.56	16.97	3.40	Fe3O4

Certain trace elements in CFA, including as Cu, Pb and Zn, whose concentrations were inversely related to particle size, also displayed concentration increasing variation rules with decreasing particle size. This could be because CFA with smaller particle sizes has a higher specific surface area, which boosts Cu, Pb and Zn adsorption capability. For several elements in CFA, such Cr and Cu, there were no discernible relationships between concentration and particle size. It could be because Cr is an oxyphilic element, which means that only a small number of its oxides can be adsorbed by CFA and that their oxides have a higher boiling point and are more difficult to evaporate.

4. Conclusions

CFA is by-product of burning coal to generate power and it may make leaching of trace metals into the environment. The aim of the study was to identify the species that are prevalent in CFA and soil samples collected from the Hendrina Power Station, Mpumalanga Province. The CFAs were characterized to investigate the composition of trace metals. The chemical speciation modelling was applied to determine the distribution of metal species. The CFA samples at pH ranging between 8.11

± 0.07 and 8.60 ± 0.03 in saturation indices indicated that oxyhydroxides were dominant. Certain CFA samples were discovered to have TOC values greater than 8%, which is above the allowable limits and may indicate that adjacent communities are exposed to toxicants. Based on its concentration, particular form, and interactions with other CFA constituents, trace metals including Pb, Cu, Zn, and Cr were found to be hazardous in soil systems. The speciation of a trace metal is crucial to comprehending its behaviour in soil and its level of toxicity. The oxidation state of each trace metal was taken into consideration. The slow release of metal ions into soil from CFA may occur during windy and rainy seasons. What was also observed was that various metals compete with dissolved metal ions for binding sites on ferric hydroxides ($Fe(OH)_3$). Due to chemical precipitation and surface complexation, protons (H^+) were observed to be in competition with Pb^{2+}, Cu^{2+} and Zn^{2+} for the capacity to attach to hydroxyl (OH^-) groups. Authors recommend the determination of persistent organic pollutant content (e.g.: polycyclic aromatic hydrocarbons which result from incomplete combustion of organic matter) in these CFA dams as they contain a high amount of organic carbon.

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