Journal of Ghana Science Association, Volume 23(2)
Date of Publication: 11th March 2026
ISSN: 2737-713X

GEOCHEMICAL CHARACTERIZATION OF AN ABANDONED MINE TAILINGS AND ITS METAL LEACHING POTENTIAL

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Abstract

Abandoned mine tailings pose significant environmental risks due to their potential to release toxic metals through the production of Acid Mine Drainage. These tailings are remnants of ore processing and often contain heavy metals and other contaminants that can leach into surrounding water bodies and soils. Geochemical characterization is essential to assess their stability and potential for contaminant release over time. This study evaluates the acid-generating capacity and metal leaching potential of the Kototeasua tailings dam at Obuasi. A total of thirty (30) tailing samples were collected from different sections of the tailings dam. The samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to determine their elemental composition. X-ray Diffraction (XRD) analysis was conducted to assess their mineralogical characteristics. The Acid Base Accounting (ABA) test was performed to estimate the potential for AMD generation. Column leaching test was conducted over a 20-week period. Leachates were collected weekly, and their physicochemical parameters, along with chemical composition, were analyzed. Correlation analysis was conducted to identify key factors influencing contaminant release. The XRD results showed that the samples contained quartz, muscovite, albite, chlorite and dolomite minerals with quartz been dominant in composition both before and after the leaching test. The mean concentration of Fe was high in the samples and in the leachates. Elevated As and Fe levels were observed under circumneutral pH conditions, with carbonate buffering dominating geochemical control, suggesting that near-neutral pH does not eliminate the potential for metal mobility and environmental risk. The findings are directly relevant to tailings management in Ghana, indicating that near-neutral drainage does not preclude As and Fe release, and thus continuous groundwater protection and monitoring measures are required.

Keywords
Acid mine drainage, column leaching test, acid-base accounting test, potential acid forming, heavy metals.

Introduction

Mining and mineral processing wastes present major environmental and long-term health risks globally. These wastes typically occur as either waste rocks or tailings. Annually, it was estimated that 5 to 7 billion tonnes of mine tailings are generated worldwide (Araujo et al., 2022). Mine tailings are fine-grained residues (ranging from 1 to 600 μm) left behind after extracting valuable minerals from ore. Their small particle size makes them highly reactive. The physical and chemical characteristics of tailings vary based on the type of ore processed and the specific mineral processing techniques employed. Tailings often contain elevated levels of metals such as Fe, Cu, Ni and Zn, generally ranging from 0.5% to 3%. They may also carry trace amounts of precious metals like gold and silver, as well as toxic elements such as arsenic, which can reach concentrations up to 100 mg/kg (Balali-Mood et al., 2021).

Ghana has a long history of artisanal mining, with large-scale mining gaining prominence in the 1980s through foreign investment (Pijpers, 2020). The country was Africa's second-largest gold producer and also extracts manganese, bauxite, and diamonds (Pijpers, 2020). In 2018, metallic mineral production accounted for 8.5% of Ghana's Gross Domestic Product (GDP) (Besada and Golla, 2023). As of 2021, Ghana has 16 major operating mines (Adjei et al., 2024). Additionally, approximately one million people are engaged in artisanal mining and the large scale mining which both contribute mine waste into the environment (McQuilken and Hilson, 2016). Ghana has 21 reported tailings storage facilities, with risk ratings ranging from "not applicable" to "extreme consequences". Approximately half of these dams use an upstream construction design, while the rest are built using downstream, upstream-downstream hybrid, or centerline construction designs (Islam and Murakami, 2021). Concentrator tailings and waste rocks in Ghana have been left in vast quantities without any environmental or security safeguards. Metal sulphides, primarily pyrite and pyrrhotite, are frequently abundant in waste materials pertaining to base and precious metals. When exposed to air and water, pyrite and pyrrhotite undergo oxidation, generating acidity that enhances the dissolution of toxic metals in mine waste (tailings). This process, known as acid mine drainage, poses significant environmental risks. The oxidation of sulphides can persist for decades to centuries (Benner et al., 1997; Lapakko, 2002; Moncur et al., 2005; Schippers et al., 2010). Bacteria frequently act as catalysts for this process. Although the focus of extraction was on ore minerals, low-pH fluids are mostly caused by pyrite and pyrrhotite, which are typical accessory minerals in many types of ore deposits. But once an acid environment was created, other sulphide, oxide, silicate, and carbonate minerals dissolve and release metals like Cu, Zn, Pb, Ni, Cd, Co, Hg, Al, Mn, and U, as well as metalloids like As, Sb, and Se, depending on the type of ore deposit (Nordstrom et al., 2015).

While acid drainage was widely studied, mine waste drainage can also be circumneutral or even alkaline yet still contain harmful concentrations of metals and metalloids. The accelerated weathering of certain minerals, with or without acid generation, can lead to the release of toxic metal concentrations into the environment. Many metals have low solubility at neutral pH and tend to adsorb onto iron oxyhydroxides and other substrates, weakly hydrolyzing metals such as Ni, Cd, and Zn may require a higher pH (8.5 or above) to effectively reduce their mobility in the environment. Additionally, elements of concern under neutral drainage conditions, such as As, Sb, Mo, and Se, often form anionic complexes that are less effectively adsorbed at neutral to high pH levels, increasing their potential for environmental contamination.

Because it was far more expensive to restore sites that contain AMD-producing mine wastes, it was crucial to accurately forecast the potential for acid formation before these tailings are deposited and abandoned in the environment. There are other predictive techniques that can be applied, including as mathematical models, kinetic testing, and static tests (Benzaazoua et al., 2004; Jambor et al., 2007; Lapakko, 2002; Plante et al., 2020). The study assessed the potential for acid production from mine wastes connected to the abandoned tailings at Kototeasua, a suburb in the mining town of Obuasi. Despite numerous studies on acid mine drainage and metal leaching from mine wastes such as tailings, limited information was available on the geochemical behaviour in tropical mining environments such as Ghana. Few studies have combined column leaching and acid base accounting test (ABC) experiments with multivariate statistical analysis to elucidate the controlling processes and temporal trends in metal release. This study addresses this gap by investigating the leaching behaviour and geochemical controls of major ions and heavy metals from tailings using column tests and principal component analysis. The specific objectives were to (i) evaluate temporal variations in pH, electrical conductivity, and major ion chemistry, (ii) assess the mobility of heavy metals, and (iii) identify the mineralogical composition of the tailings.

Materials and Methods

Area of Study

This study was conducted in Obuasi, located in the Ashanti Region of Ghana. The municipality was well known for its intensive gold mining operations with Gold Fields Mining Company and now AngloGold Ashanti as the main mining company, that have been in the municipal over the past five decades. Activities of the mining company have left several mine wastes within the municipality. Kototeasua tailings dam is one of the abandoned tailing dams within the municipality with lots of farming activities around it. Figure 1 shows the map of the research site and the sample collection location while Figure 2 shows a cross-section of the Kototeasua tailings dam.

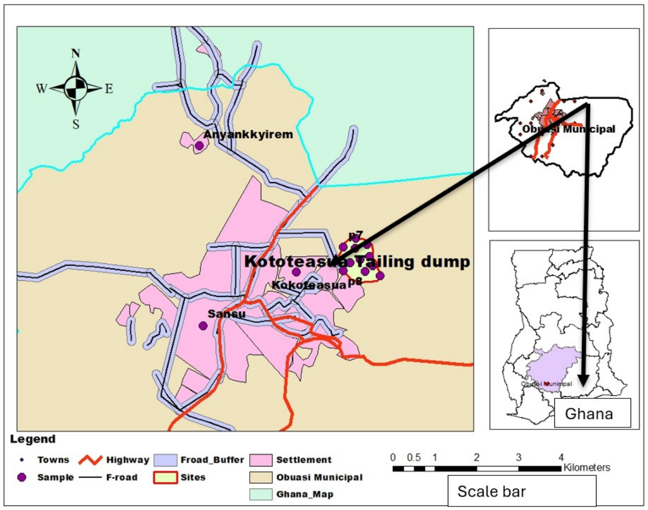

Figure 1. A map of the study area showing the sampling locations.

Figure 2. A field photograph of a section of Kototeasua tailing dam.

Obuasi, located in Ghana’s Ashanti Region, lies approximately 64 km south of Kumasi. Obuasi is situated in the latitude range of 6° 12’ and 21.67’ N and longitude -1° 39’ and 42.88’ W in a belt of tropical evergreen rain forests. It has an approximate area of 162.4 km^2 (Asabere and Bempah, 2013). Double rainfall maxima, with a primary dry season from December to March and a double rainy season from April to June and October to November, are what define the region. About 1480 mm of rain falls on average each year (Asabere and Bempah, 2013). Obuasi’s terrain is composed of undulating hills with noticeable ridges. The tallest hills are found in the Moinsi and Kusa ranges, which rise to a height of 290 meters above sea level.

Situated in the Ashanti belt, which extends from Axim to beyond Konongo, is the AngloGold Ashanti Obuasi Mine. Approximately 250 km long and 40 km wide, it is a component of a conspicuous belt of Precambrian volcano sedimentary and igneous rocks that run north-east to south-west (Leaders et al., 2018). The Tarkwaian, Upper Birimian, and Lower

Birimian formations make up the belt. The Birimian which is intruded by granitoids, was unconformably overlain by the synclinal Tarkwaian rocks in this section of the belt, with superficial deposits overlaying it (Kesse, 1985).

Sampling

Thirty (30) tailing samples from the Kototeasua tailings dam were collected at 20-meter intervals from different sites and placed in sample bags. The Garmin global positioning system (GPS) was used to capture the sampling locations' geographic coordinates. A plastic hand trowel was used for the collection of the tailings to a depth of about 5-10 cm which were kept in Ziploc bags and labelled KT01 to KT30. The samples were then transported to the laboratory.

Acid-Base Accounting (ABA) Test

The ABA test used in this study includes the total carbon and sulphur levels, paste pH, and electrical conductivity (EC). Deionized water was used to equilibrate the pulverized samples in order to assess the paste's pH and EC. Usually, the sample-to-water ratio is 1:2 by mass, and the equilibration time is between 12 and 16 h. According to (Plante et al., 2021), this is a reflection of the waste material's natural acidity and alkalinity upon initial exposure in a waste emplacement region. As part of the ABA test, results were obtained for maximum potential acidity (MPA), acid neutralization capacity (ANC), often referred to as neutralization potential (NP), and net acid generating pH (NAGpH).

Multiplying the total sulphur content by 30.6 yields the MPA produced by a sample. The complete oxidation of pyrrhotite and pyrite by O_2 to generate $Fe(OH)_3$ and H_2SO_4 is represented by this factor, which signifies the stoichiometric relationship. The computation was predicated on the idea that pyrite (FeS_2) contained the sulphur concentration, and that pyrite reacted with oxidizing substances to produce acid, as shown in Equation 1.

$$\mathrm{FeS_2} + \frac{15}{4}\mathrm{O_2} + \frac{7}{2}\mathrm{H_2O} \longrightarrow \mathrm{Fe(OH)_3} + 2\,\mathrm{H_2SO_4} \tag{1}$$

The reaction indicates that the MPA of a sample with 1% S as pyrite yields 30.6 kilogram of H_2SO_4 per tonne of material (kg H_2SO_4/t). The MPA of each sample was therefore calculated by multiplying the total sulphur content by 30.6, as demonstrated by Equation 2.

$$\mathrm{MPA}\left(\frac{\mathrm{kg\ H_2SO_4}}{\mathrm{t}}\right) = (\text{Total Sulphur, \% S}) \times 30.6 \tag{2}$$

Acid Neutralization Capacity (ANC) was determined by acid titration following standard static test procedures. Briefly, a known mass of finely ground sample was reacted with an excess of standardized hydrochloric acid (HCl), and the suspension was back-titrated to a fixed endpoint pH (typically pH 7.0 or 4.5) using standardized sodium hydroxide (NaOH). The ANC was calculated from the net acid consumed by the sample according to Equation 3:

$$\mathrm{ANC} = \frac{(\mathrm{N_{HCl}} \times \mathrm{V_{HCl}}) - (\mathrm{N_{NaOH}} \times \mathrm{V_{NaOH}} \times 50)}{m} \tag{3}$$

- V_{HCl}: the volume of HCl added (mL)
- N_{HCl}: the normality of HCl
- V_{NaOH}: the volume of NaOH used for back-titration (mL)
- N_{NaOH}: the normality of NaOH
- 50: the conversion factor from equivalents to kg H_2SO_4
- m: the mass of sample (g)

A fizz test was used to calculate the volume and concentration of acid required for the titration to assess the ANC.

The Net Acid Producing Potential (NAPP) was calculated as the difference between the Maximum Potential Acidity (MPA) and ANC, as shown in Equation 4:

$$\mathrm{NAPP} = \mathrm{MPA} - \mathrm{ANC} \tag{4}$$

Elemental Analysis

Heavy metal concentrations were determined using a Perkin Elmer NexION 2000 Inductively Coupled Plasma–Mass Spectrophotometer (ICP-MS), while major element concentrations were measured with a Perkin Elmer Avio 500 Inductively Coupled Plasma–Atomic Emission Spectrophotometer (ICP-AES), both from Perkin Elmer (USA). A 2.0 g of the pulverized samples were subjected to acid digestion using aqua regia (3:1 mixture of HCl and HNO_3). The combination was heated to 120 °C for 30 minutes, and then it was left to cool to room temperature. After being digested, the sample was filtered and mixed with deionized water. The filtrate was used for the heavy metals and elemental analysis.

Mineralogy and XRD Analysis

Portions of the pulverized samples were sent to the Regional Water and Environmental Sanitation Centre, Kumasi (RWESCK), KNUST, for X-ray Diffraction (XRD) analysis (Kusi et al., 2024). The powdered samples were placed in a sample holder, with their flat surfaces oriented towards the incident X-ray beam. Diffraction patterns were obtained, and the positions and intensities of the peaks were compared with mineral reference standards in a database to identify the mineral phases present (Wallace et al., 2023).

Mineralogical analysis was performed using an XRD-D2 PHASER (BRUKER AXS, Germany) equipped with a Lynxeye detector and a copper (Cu) anode as the radiation source (Kusi et al., 2024). The instrument operated at glancing angles (2θ) ranging from 4.998° to 79.996°, with a scanning step size of 0.02°/min. The diffraction data were processed and analyzed using Diffrac.EVA software (BRUKER), with phase identification carried out by comparison against the ICDD PDF2 and PDF4 reference databases.

After calibration and setting the parameters of the instrument, 2.0 g of the pulverized dried samples each was placed in the sample holder which is a 20 mm × 20 mm corning glass. A microscope glass slide was used to flatten the surface in a circular motion into a disc form that was 15 mm in diameter and 1 mm in thickness. This ensured a consistent diffraction pattern. The sample holder with its content was inserted into the equipment. The scan button was pressed to begin the process. After scanning the software and the detector displayed the diffraction data with identification of the minerals and quantifications in the sample. The same parameters and preparation technique were used for all samples.

Column Leaching Test

To replicate field circumstances, the samples were subjected to the column leaching experiment test. All the tailing samples from Kototeasua tailing dam were composited to represent the site. PVC pipes, measuring 304.8 cm in height and 10.16 cm in width, were supported by a wooden structure (Kusi et al., 2024). This was used for the leaching column test. The tailings were milled and therefore they were used in that state. 12 kg was weighed and packed into the columns (and two duplicates). There was a blank test, where the PVC pipe was filled with washed, dried sand. An initial 4.0 L of the buffered deionized water of pH 6.5 (average annual rainfall pH of the study area) was added into the columns for wetting. This was repeated every week. The columns were eluted with buffered deionized water and the leachates collected at weekly intervals. In all 20 leachates samples were collected representing 20 weeks of elution.

The caps used at the pipe ends were sealed and perforated at both ends to allow the outflow of leachates.

Unsaturated flow conditions were maintained using weekly pulse additions of 4.0 L of leaching solution, resulting in temporary saturation during dosing and predominantly unsaturated conditions during the remainder of the experiment. Leachates were collected weekly, and their physicochemical parameters were measured. Additionally, samples were analyzed for heavy metal concentrations as well as sulphates and carbonates concentrations.

Quality Control

Quality control for ICP-MS and ICP-AES analyses included multi-point external calibration using matrix-matched standard solutions. Calibration curves showed coefficients of determination (R^{o}) ≥ 0.999 for all analyzed elements. Instrument performance was verified using continuing calibration verification (CCV) standards after every 10 samples, and recalibration was performed when recoveries fell outside ±10% of expected values. Analytical precision was assessed by duplicate analysis of selected samples, with relative standard deviations (RSDs) generally less than 5% for major elements and less than 10% for trace elements.

Method detection limits (MDLs) were determined as three times the standard deviation of procedural blanks, while limits of quantification (LOQs) were defined as ten times the standard deviation of blanks. The MDLs ranged from 0.01 to 1.00 µg/L for heavy metals and from 0.01 to 0.10mg/L for major ions/major elements. Certified reference materials (CRMs) appropriate for water and leachate matrices were analyzed with each batch of samples. Recoveries for CRMs ranged between 90% and 110%, indicating acceptable analytical accuracy.

X-ray diffraction (XRD) instrument performance was verified using a standard reference material (NIST silicon/corundum) to confirm peak position accuracy and instrument alignment. Phase identification was carried out using standard reference databases (ICDD PDF-4), and duplicate scans were performed on selected samples to assess reproducibility. Peak positions were reproducible within $\pm 0.02^{o}$ 2θ. Quality control during the column leaching experiment included the use of reagent-grade leaching water and periodic analysis of influent (blank) water to confirm the absence of target metals and major ions above detection limits.

Results and Discussion

Acid-base Accounting (ABA) Test

All of the tailing samples that were collected at different places around the research area are shown in Table 1 together with the results of their geochemical classifications and ABA test. At the study site, the geochemical classification as shown in Table 1 showed that nineteen (19) of the samples analysed, were non-acid producing (NAF) due their negative values obtained from NAPP and high NAG pH values, seven (7) samples had negative values for the NAPP but had NAG pH values below 4.5 and therefore classified as uncertain (UC). Only four (4) of the samples analysed possessed NAGpH readings below 4.5 and positive NAPP values, which led to their classification as potential acid forming (PAF). Figure 3 displays the relationship between NAGpH and NAPP which also shows the geochemical classifications of the samples.

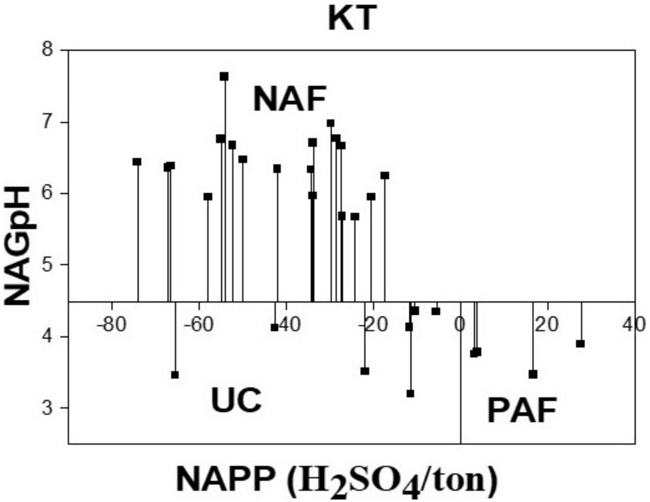

Figure 3. Shows the relation between NAGpH and NAPP at the study site.

The pH values were higher on average, indicating a more neutral to slightly alkaline environment as shown in Figure 4. The EC values at this site have a smaller range, suggesting less variability in ionic concentration. Higher paste pH values at this site correlate with moderate EC values, which may be that fewer soluble ions are available due to potential precipitation

Table 1. ABA test results at Kototeasua tailings dam

SAMPLE ID	% S	% C	Paste pH	Paste EC (µS/cm)	MPA	ANC	NAPP	NAG pH	Geochem Class
KT01	0.89	1.94	8.01	346	27.23	10.71	16.53	3.47	PAF
KT02	0.34	1.93	8.04	1064	10.40	39.00	-28.60	6.77	NAF
KT03	0.02	1.41	8.07	726	0.61	35.00	-34.40	6.33	NAF
KT04	0.45	2.05	8.12	567	13.77	63.75	-49.98	6.47	NAF
KT05	0.58	2.31	8.16	534	17.75	85.00	-67.25	6.36	NAF
KT06	0.44	1.90	8.14	492	13.46	80.00	-66.54	6.38	NAF
KT07	0.35	2.29	8.10	1231	10.71	38.00	-27.29	5.68	NAF
KT08	0.28	1.83	7.76	479	8.57	42.50	-33.93	6.71	NAF
KT09	0.23	2.17	8.04	426	7.07	34.50	-27.43	6.66	NAF
KT010	0.43	2.32	8.13	638	13.16	23.75	-10.59	4.36	UC
KT011	0.36	2.13	8.24	435	11.02	53.75	-42.75	4.12	UC
KT012	0.41	2.20	8.08	619	12.55	30.00	-17.45	6.25	NAF
KT013	0.45	2.22	7.87	327	13.77	35.75	-21.98	3.51	UC
KT014	0.80	2.07	8.10	573	24.48	21.50	2.98	3.76	PAF
KT015	0.35	1.99	7.77	1512	10.71	68.75	-58.04	5.95	NAF
KT016	0.38	2.26	7.93	745	11.63	41.50	-29.87	6.98	NAF
KT017	0.43	2.39	7.95	413	13.16	25.00	-11.84	4.13	UC
KT018	0.39	2.11	8.23	1150	11.93	32.50	-20.57	5.95	NAF
KT019	0.38	2.09	8.14	714	11.63	36.00	-24.37	5.67	NAF
KT020	0.27	1.95	8.34	613	8.26	62.50	-54.24	7.63	NAF
KT021	0.44	2.04	8.24	402	13.46	25.00	-11.54	3.20	UC
KT022	1.39	2.24	7.95	349	42.53	15.00	27.53	3.90	PAF
KT023	0.55	2.39	8.03	1206	16.83	22.50	-5.67	4.35	UC
KT024	0.78	2.27	8.01	924	23.87	20.25	3.62	3.78	PAF
KT025	0.08	1.58	8.30	541	2.45	57.50	-55.05	6.76	NAF
KT026	0.03	1.54	8.44	367	0.92	35.00	-34.10	5.97	NAF
KT027	0.34	1.95	8.08	1041	10.40	52.50	-42.10	6.34	NAF
KT028	0.33	1.84	8.14	745	10.10	62.50	-52.40	6.67	NAF
KT029	0.39	1.93	7.94	1024	11.93	77.50	-65.57	3.46	UC
KT030	0.27	2.14	8.13	450	8.26	82.50	-74.24	6.44	NAF

Maximum Potential Acid (MPA) = 30.6% × Total Sulfur (S); Net Acid Potential Production (NAPP) = MPA – ANC; MPA, ANC, NAPP in kg H_2SO_4/ton. Classification: NAF: NAG pH ≥ 4.5; NAPP ≤ 0;
PAF: NAG pH < 4.5; NAPP > 0; UC: NAGpH < 4.5; NAPP < 0.

or adsorption processes occurring in a higher pH environment.

Mineralogical Studies

The tailings samples mineralogical analysis from Kototeasua tailings dam using XRD method was conducted. The analysis was performed to identify the phases and percentages of minerals in the samples. The XRD test was performed twice. Thus, before and after the column leaching experiment. Table 2 shows the mineral composition and percentages in the samples before and after the column leaching test.

The XRD results in Table 2 showed that the samples were all mainly composed of quartz and aluminosilicates minerals (muscovite, albite and chlorite). Quartz (low) with reference COD 1011176 was the dominant mineral in the samples, followed by chlorite, albite, muscovite and dolomite with reference COD 9010166, COD 9002202, COD 9014748 and COD 9003519 respectively. Goethite, lavenite and datolite with references COD 9011412, COD 9015426 and COD 9016512 respectively were the least dominant minerals in the samples as presented in Table 2. No sulphidic or pyritic minerals were detected. However, the presence of goethite, which is a secondary mineral show that pyrites were among the minerals in the tailings dam and have undergone oxidation over the years and had led to the goethite formation. The detection of goethite also signifies the long period that the tailings have been kept there. Dolomite formation has been found to occur under anaerobic conditions (Lusunzi et al., 2023; Mehmood et al., 2018; Xu et al., 2020) the compact nature of the tailings dam might have left to its formation. Although primary dolomite precipitation has been reported in rare modern and microbially mediated environments, most dolomite is interpreted to be of secondary diagenetic origin formed by replacement of precursor calcite, and thus the dolomite identified in this study is more likely secondary rather than primary (Kesse, 1985; Mueller et al., 2020; Wenzhi et al.,

Table 2. XRD analysis before and after the column leaching test

MINERAL	FORMULA	Percentage (%)
	Before Column Test	
Quartz low	SiO_2	62.0
Muscovite	$Al_{2.8}Ba_{0.01}Fe_{0.08}H_2K_{0.9}Mg_{0.04}Na_{0.07}O_{12}Si_{3.04}Ti_{0.04}$	7.2
Albite	$AlNaO_8Si_3$	10.1
Chlorite	$Al_{0.865}Fe_{0.255}H_4Mg_{2.292}O_9Si_{1.588}$	10.8
Goethite	$FeHO_2$	1.5
Dolomite	$CCa_{0.5}Mg_{0.5}O_3$	6.1
Datolite	$BCaHO_5Si$	1.0
Lavenite	$Ca_{0.99}FFe_{0.31}Mn_{0.33}Na_{1.25}Nb_{0.09}O_8Si_2Ti_{0.26}Zr_{0.73}$	1.3
	After Column Test	
Quartz	SiO_2	25.4
Muscovite	$Al_{2.8}Ba_{0.01}Fe_{0.08}H_2K_{0.9}Mg_{0.04}Na_{0.07}O_{12}Si_{3.04}Ti_{0.04}$	10.7
Albite	$AlNaO_8Si_3$	18.6
Chlorite	$Al_{0.865}Fe_{0.255}H_4Mg_{2.292}O_9Si_{1.588}$	22.2
Goethite	$FeHO_2$	4.6
Dolomite	$CCa_{0.5}Mg_{0.5}O_3$	16.6
Datolite	$BCaHO_5Si$	1.9

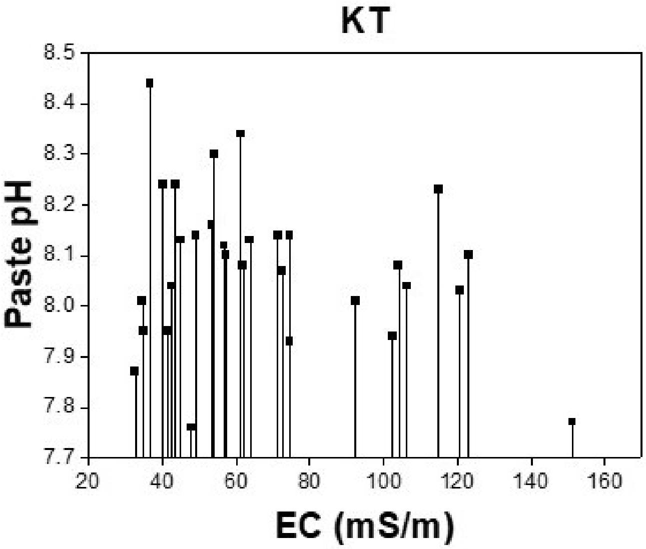

Figure 4. Relationship between paste pH and EC.

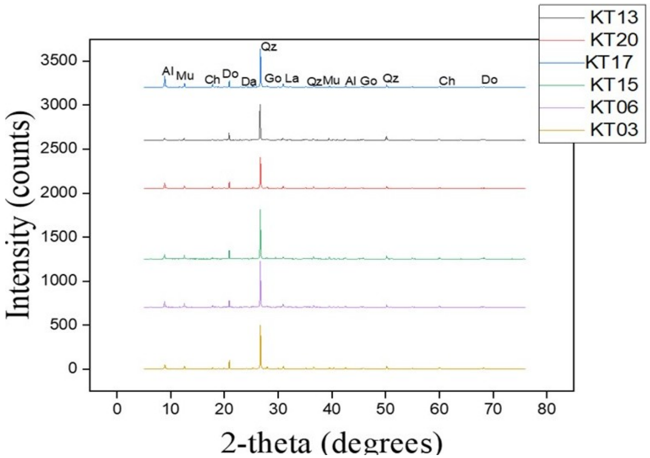

Figure 5. XRD patterns of samples before the column leaching test.

2018). Phyllite and schist are predominant rocks in the study area and they could have been attributed to the formation of chlorite (Worden et al., 2020). There was a significant decrease in the percentage composition of quartz after the column leaching test as shown in Table 2 however, quartz remained the dominant mineral with the rest of the minerals showing increases in their percentage compositions. Given the high resistance of quartz to dissolution under circumneutral conditions, the apparent decrease in quartz abundance is more likely due to preferential dissolution of more reactive minerals and normalization effects in semi-quantitative XRD, rather than true quartz dissolution. The increase in the chlorite could be attributed to the more compact nature of the tailings in the PVC pipes during column leaching which created the anaerobic condition for its formation.

Figure 5 and Figure 6 present the XRD patterns of the analysed samples before and after the column leaching test. Similar XRD peak patterns among the samples show consistent mineralogy within the location.

Elemental Analysis

Table 3 and Table 4 show the descriptive statistics of the levels of heavy metals and major elements at Kototeasua site respectively.

Table 3 showed that Fe had the highest concentration with a mean value of 3684.87 ± 1196.83 mg/kg followed by As with a mean value of 1461.10 ± 332.69 mg/kg. The high concentration of Fe could be due to the abundance of Fe and as a major element found in the earth's crust. High Fe concentrations also indicate the likely formation of secondary Fe

Table 3. Concentrations (mg/kg) of heavy metals in tailings samples at the site

Element	Min	Max	Mean ± SD	CV (%)	WHO limits
As	802.77	2005.10	1461.17±332.69	23	15 – 20
Sr	67.87	135.30	95.86±17.61	18	
Mo	0.92	2.43	1.35±0.30	22	
Ag	0.35	0.36	0.67±0.23	34	
Cd	0.18	0.48	0.26±0.07	27	0.80 – 3.00
Sn	0.22	1.28	0.41±0.19	46	
Hg	0.07	0.43	0.23±0.10	43	
Pb	16.26	67.62	31.21±9.33	30	60 – 85
Ti	4.24	7.72	5.75±0.96	17	
V	4.21	10.54	6.75±1.48	22	
Cr	11.15	38.59	23.31±6.52	28	100
Mn	748.74	1529.83	1067.00±199.60	19	2000
Fe	0.02	6117.23	3684.87±1196.83	32	
Co	8.36	19.03	12.77±2.63	21	50
Ni	22.69	75.00	33.67±10.19	30	35 – 50
Cu	29.50	92.96	49.24±12.30	25	36 – 100
Zn	47.94	100.79	73.57±14.35	20	50 – 300

*WHO limits for agriculture soil

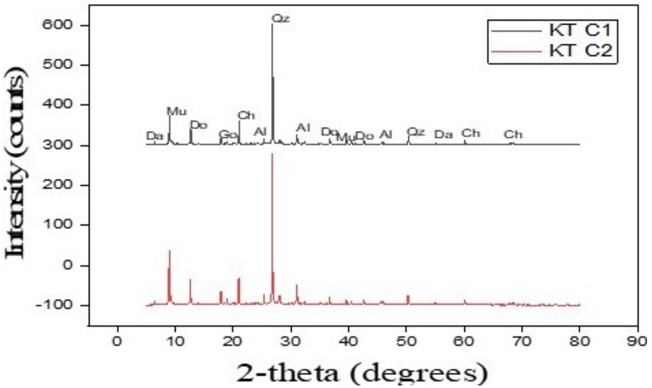

Figure 6. XRD patterns of samples after the column leaching test.

oxyhydroxides such as ferrihydrite and Fe sulphate phases such as schwertmannite, in the tailings which can strongly adsorb As and other trace metals. These phases may temporarily attenuate metal mobility but also represent potential sources of remobilization under changing geochemical conditions. The high concentration of As could be attributed to the arsenopyrite ore which bears gold. After the extraction of the gold from the ore through the grinding and milling processes, As form part of the waste in the tailings. Strontium (Sr), Sn, Ag, Cd and Hg had low concentration levels of the metals with mean levels of 95.86 ± 17.61 mg/kg, 0.41 ± 0.19 mg/kg, 0.67±0.23 mg/kg, 0.26 ± 0.07 mg/kg and 0.23 ± 0.10 mg/kg respectively.

The high levels of As can pose a potential environmental risk, especially considering its toxicity. Arsenic could leach into the surrounding environment, contaminating water sources and posing health risks to local ecosystems and communities. The relatively low concentrations of Sr, Sn, Ag, Cd, and Hg suggest that while they are present, they may not pose an immediate environmental concern. However, the presence of toxic metals like Cd and Hg, even at low levels, could represent a long-term risk due to bioaccumulation in ecosystems when released.

The concentration of the major elements present in the analysed samples is presented in Table 4. Sulphur showed a high mean concentration of 1088.10±412.40 mg/kg with a CV of 38%, which indicates relatively consistent distribution. Calcium and Mg were among the most abundant elements in the tailings, with mean concentrations of 1828.09±601.98 mg/kg and 1020.83±403.53 mg/kg respectively. Their relatively lower CVs (33% and 40%) suggest that these elements are more uniformly distributed in the samples. Moderate concentrations of Al, K and Na were recorded with mean concentrations of 389.32±154.20 mg/kg, 25.25±11.85 mg/kg and 6.45±3.29 mg/kg respectively.

Calcium, Mg and S were the dominant major elements in the tailings, suggesting the presence of carbonate and sulphide minerals. The high sulfur content may pose a risk of AMD, but the predominance of Ca and Mg can buffer the effect of acid that may be generated. Bismuth showed the highest variability, indicating its irregular distribution in the samples and may occur in localized deposits or phases.

Column Leaching Test

The column leaching test provides kinetic information regarding reaction rates, time lag to acid onset and metal loads. The physiochemical parameters (pH, EC, TDS), sulphates levels, carbonates levels, heavy metals and major elements concentrations of the leachates were measured on week basis for a period of twenty weeks.

Table 4. Concentrations (mg/kg) of major elements in tailings samples at the site

Element	Min	Max	Mean ± SD	CV (%)
Al	0.55	660.20	389.32±154.20	40
Bi	BDL	0.63	0.17±0.18	106
Ca	BDL	3010.83	1828.09±601.98	33
K	BDL	46.40	25.25±11.85	47
Mg	0.67	1780.65	1020.83±403.53	40
Na	BDL	13.81	6.45±3.29	51
P	0.21	53.86	35.27±12.85	36
S	3.92	1716.57	1088.10±412.40	38
Si	BDL	96.53	70.82±25.57	26

Table 5. Descriptive statistics of the physicochemical parameters of the leachates.

Parameter	Min	Max	Mean ± SD
pH	7.25	7.93	7.66 ± 0.19
EC (mS/m)	0.13	7.93	1.35 ± 1.87
TDS (ppt)	0.09	3.96	0.69 ± 0.92
Vol of leachate (L)	2.36	4.30	3.50 ± 0.49

pH, EC and TDS in Leachates at Kototeasua

During the test, the pH of the leachates remained relatively stable, fluctuating only slightly between 7.25 and 7.97, as indicated in Table 5, suggesting that there is little acid production and that the leachates are neutral to slightly alkaline. This could be possibly due to limited oxidation of sulphide minerals or effective neutralization by buffering minerals. The pH was circumneutral which could be attributed to the nature of the minerals, which were mostly Mg and Ca bearings such as chlorite and dolomite. These minerals have alkalinity properties and tend to raise the pH. The EC and TDS were high at the first week and decreased significantly in the second week then decreased steadily till the end of the 20th week as shown in Figure 7. This suggests that there was a high dissolution rate at the beginning of the test and a gradual decrease as the weeks passed by.

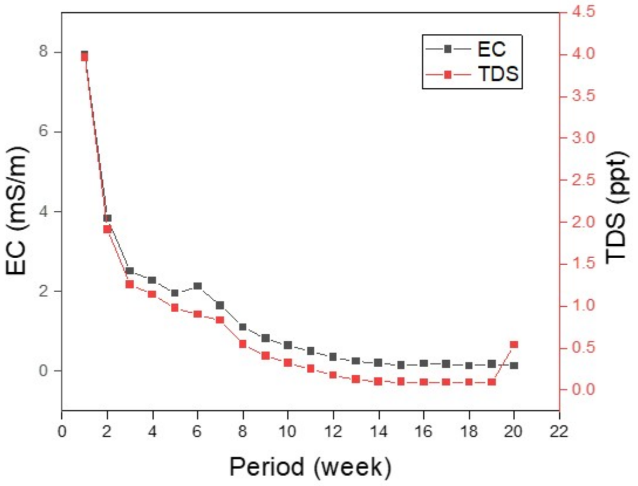

Figure 7. The relationship between the weekly leachates of EC and TDS.

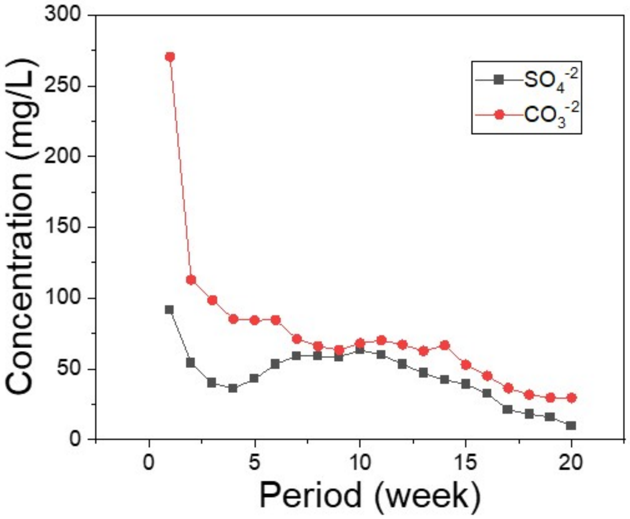

Figure 8. The relationship between the weekly leachates of EC and TDS.

Sulphates and Carbonates Concentrations in Leachates

Although the sulphate concentrations were not very high, it decreased as the testing experiment progressed. Sulphates are the direct products of the oxidation of iron sulphides, they can also combine with some elements such as (Mg, Ca, K) to form precipitate. Due to the long-abandoned nature of the tailings, sulphates that were formed from pyrite oxidation might have also precipitated in the tailings. The high concentration of sulphates that leached during the first week could result from dissolution of these soluble sulphate precipitates (Hakkou et al., 2005). The sulphates tended to disappear gradually over time as shown in Figure 8 probably due to the depletion of the neutralizing effect of the silicate minerals and the formation of precipitation of secondary minerals such as goethite which saw an increase in percentage as presented in Table 2.
Similarly, the initial high concentration of carbonates in the first week of the column leaching test as shown in Figure 8, were likely due to the rapid dissolution of readily soluble carbonate minerals and the flushing of pre-existing weathered carbonates within the tailings. The subsequent decline in concentrations can be attributed to several factors, including the depletion of easily soluble carbonates, a reduced dissolution rate as the system approaches saturation and equilibrium, shifts in leaching dynamics such as changes in flow rate, and the potential precipitation of secondary carbonate minerals. Magnesium and Ca contribute to carbonate levels in acid mine systems. When Mg and Ca dissolve from minerals such as muscovite, chlorite and dolomite, they are likely to play a key role in generating significant levels of carbonates, surpassing the contributions from sulphates as presented in Figure 8. This indicates that carbonate minerals in the system have a more prominent influence on neutralizing acidity than sulphate minerals.

Table 6. Descriptive statistics of heavy metals concentration (mg/L) in leachates.

Element	Min	Max	Mean ± SD
As	0.30	0.76	0.54 ± 0.13
Cr	BDL	0.12	0.03 ± 0.04
Cu	0.005	0.05	0.01 ± 0.01
Mn	0.03	0.85	0.27 ± 0.23
Ni	0.002	0.03	0.007 ± 0.008
Pb	BDL	BDL	
Sr	0.07	3.60	0.79 ± 0.99
Zn	0.002	0.03	0.008 ± 0.008
Fe	1.16	6.85	2.36 ± 1.26
Sn	0.02	0.12	0.03 ± 0.02
Se	0.003	0.04	0.006 ± 0.008

*BDL (below detection limit) < 0.0001 mg/L

Table 7. Descriptive statistics of major elements concentrations (mg/L) in leachates.

Element	Min	Max	Mean ± SD
As	0.30	0.76	0.54 ± 0.13
Cr	BDL	0.12	0.03 ± 0.04
Cu	0.005	0.05	0.01 ± 0.01
Mn	0.03	0.85	0.27 ± 0.23
Ni	0.002	0.03	0.007 ± 0.008
Pb	BDL	BDL	
Sr	0.07	3.60	0.79 ± 0.99
Zn	0.002	0.03	0.008 ± 0.008
Fe	1.16	6.85	2.36 ± 1.26
Sn	0.02	0.12	0.03 ± 0.02
Se	0.003	0.04	0.006 ± 0.008

*BDL (below detection limit) < 0.0001 mg/L

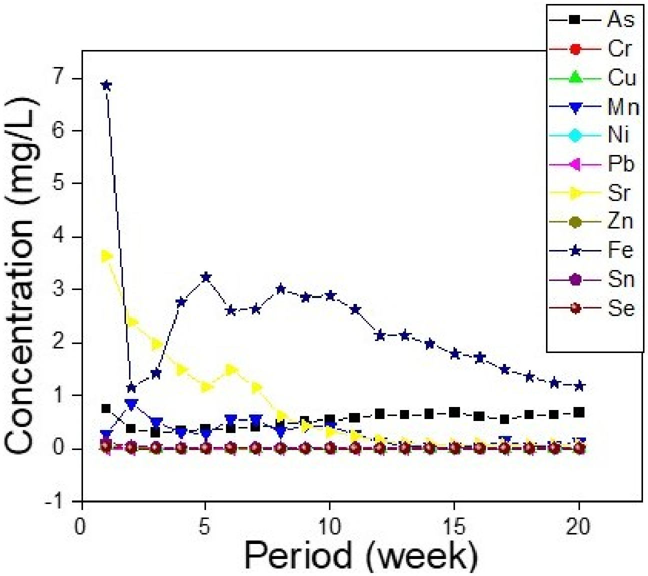

Figure 9. Concentration of heavy metals leached.

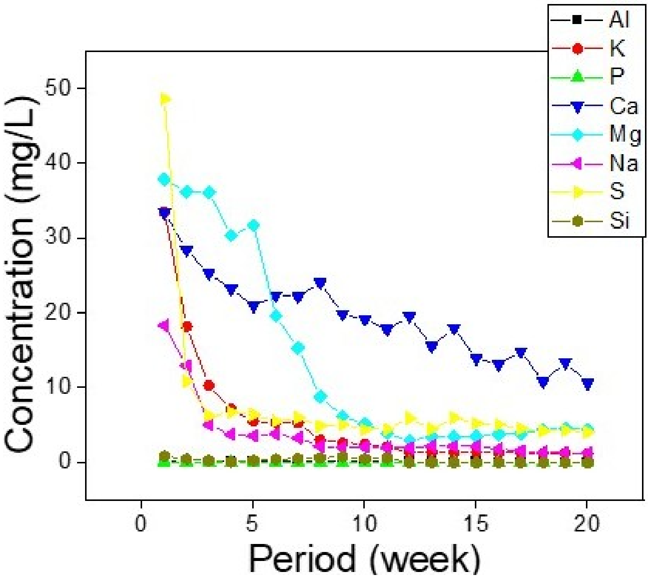

Figure 10. Concentration of major elements leached.

Again, the observed decline in sulphate and carbonate concentrations is consistent with progressive approach to the saturation and precipitation of secondary sulphate and carbonate minerals, such as schwertmannite and dolomite respectively, which would buffer dissolved concentrations and reduce aqueous sulphates and carbonates over time.

Heavy Metals and Major Elements Concentrations of Leachates from the study site

Table 6 and Table 7 show the descriptive statistics of the heavy metals and major elements that leached during the test.

The results from Table 6 showed that Fe, Sr, Mn and As recorded high concentrations in the leachates from the columns with mean concentration of 2.36 ± 1.26 mg/L, 0.79 ± 0.99 mg/L 0.27 ± 0.23 mg/L and 0.54 ± 0.13 mg/L respectively. However, Cr, Cu, Ni, Zn and Sn recorded low levels with mean concentrations of 0.028 ± 0.044 mg/L, 0.013 ± 0.01 mg/L 0.007 ± 0.008 mg/L and 0.0076 ± 0.008 mg/L respectively as presented in Table 6. Dissolution of minerals such muscovite, chlorite and lavenite could have resulted in high levels of Fe as shown in Figure 9. The weekly concentrations of Pb in the leachates were below detection limit (< 0.0001 mg/L). The low concentration of metals in the leachates could be attributed to the slightly alkaline nature of the leachates as presented in Table 5. In slightly alkaline (neutral to basic) conditions, hydrogen ion concentration is low, reducing the dissolution of metal-bearing minerals and increasing the precipitation of metal hydroxides and carbonates.

Correlation Analysis

One way to assess the degree of association and relationship between two variables is through correlation. Such association is likely to lead to reasoning about the relationship between the variables. Two variables are perfectly positively correlated when their correlation is +1. When two variables have a correlation of -1, it means that their changes are inverse. When the correlation coefficient is zero, it means that the two variables

Table 8. Pearson's correlation matrix of physicochemical parameters and heavy metals from the leachates.

	pH	EC	TDS	SO_4^{2-}	CO_3^{2-}	As	Cu	Mn	Ni	Pb	Fe	Cr	Zn	Ca	Mg	K
pH	1															
EC	-0.482*	1														
TDS	-0.455*	0.993**	1													
SO_4^{2-}	-0.288	0.563**	0.512*	1												
CO_3^{2-}	-0.322	0.959**	0.947**	0.669**	1											
As	0.733**	-0.148	-0.110	-0.157	0.026	1										
Cu	-0.202	0.898**	0.901**	0.642**	0.927**	0.090	1									
Mn	-0.669**	0.494*	0.470*	0.511*	0.348	-0.737**	0.354	1								
Ni	-0.542*	0.984**	0.974**	0.510*	0.913**	-0.257	0.833**	0.577**	1							
Pb	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.						
Fe	-0.204	0.739**	0.722**	0.739**	0.840**	0.145	0.852**	0.128	0.621**	0.	1					
Cr	-0.005	0.793**	0.799**	0.436	0.882**	0.447*	0.844**	-0.059	0.703**	0.	0.810**	1				
Zn	-0.073	0.525*	0.521*	0.503*	0.577**	0.086	0.652**	0.283	0.477*	0.	0.584**	0.511*	1			
Ca	-0.576**	0.869**	0.835**	0.755**	0.841**	-0.430	0.773**	0.699**	0.885**	0.	0.652**	0.525*	0.460*	1		
Mg	-0.693**	0.835**	0.825**	0.341	0.708**	-0.582**	0.599**	0.634**	0.890**	0.	0.411	0.389	0.318	0.810**	1	
K	-0.369	0.984**	0.984**	0.503*	0.950**	-0.047	0.901**	0.447*	0.972**	0.	0.680**	0.822**	0.532*	0.822**	0.789**	1

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

are unrelated (Mishra and Kapil, 2017). A correlation study was carried out to find the plausible associations of heavy metals pH, EC, TDS and major elements in the leachates.

Table 8 shows a strong positive correlation between TDS, SO_4^{2-}, and CO_3^{2-}, with correlation coefficients (r values) of 0.51 for TDS and SO_4^{2-}, 0.67 for CO_3^{2-} and SO_4^{2-}, and 0.95 for TDS and CO_3^{2-}. This suggests that these parameters are likely influenced by similar sources or processes. The presence of sulphates and carbonates played a role in affecting the solubility and mobility of other ions, which in turn impacted TDS levels.

Additionally, as shown in Table 8, Fe exhibited positive correlations with Zn (r = 0.58) and Cr (r = 0.81). However, Mg-As and Mn-As showed negative correlations, with r values of -0.58 and -0.74, respectively. These negative correlations indicate an inverse relationship, where lower concentrations of As in the leachates corresponded with higher concentrations of Mg and Mn.

Arsenic showed a positive correlation with pH (r = 0.73), while Mn and Ni exhibited negative correlations with pH, with r values of -0.669 and -0.542, respectively. The positive correlation between As and pH suggests that as pH increases, As concentrations in the leachates also tend to rise. This is likely due to the increased solubility of certain As species, such as arsenate (AsO_4^{3-}), at higher pH levels, allowing for greater release from mineral sources, particularly under neutral to alkaline conditions. The positive As–pH correlation also reflects increased mobility of As(V) at higher pH due to reduced sorption to Fe oxyhydroxides. In addition, localized reducing conditions within the column may promote partial reduction of As(V) to the more mobile As(III), further enhancing arsenic release. Thus, both pH-dependent desorption and redox-controlled speciation likely influence arsenic behaviour in the system.

Conversely, the negative correlations of Mn and Ni with pH indicate that these metals tend to form hydroxide precipitates at circumneutral pH. Specifically, Mn and Ni commonly precipitate as $Mn(OH)_2$ and $Ni(OH)_2$ when pH levels rise, reducing their solubility in the aqueous phase. As a result, their concentrations in leachates decrease as pH increases.

Conclusion

The study employed both the ABA test and the kinetic column leaching test to characterize the tailings and assess the potential for AMD formation over time. It specifically examined the release of sulphates, the neutralization effects of carbonates/silicates and the mobilization of heavy metals and major elements. The ABA test and the geochemical assessment showed that majority of the samples had high paste pH, negative values for NAPP and NAG pH values above 4.5. Thus, making majority of the samples been classified as non-acid forming (NAF) and the rest as uncertain (UC) and potential acid forming (PAF). The column leaching test results also affirm the ABA test. The results revealed that the site was not acid producing. This was due to the high pH values; high concentrations of carbonates and low concentrations of sulphates found in the leachates. Significant concentrations of the major elements leached out than the heavy metals during the column leaching test due to the nature of the minerals (dolomite, muscovite, chlorite).

Although carbonate buffering and secondary Fe mineral formation limited acid generation and partially attenuated metal mobility, the continued release of As indicates a persistent environmental risk. These findings highlight the need for long-term monitoring and proactive management of mine tailings to protect groundwater and surrounding ecosystems. Management strategies should include routine monitoring of As in leachates and nearby surroundings. In addition, maintaining or enhancing alkaline buffering capacity within tailings facilities may help to limit long-term metal mobility and environmental impacts. For tailings facilities in Ghana, these results support the need for routine As monitoring and management practices that maintain alkaline conditions to reduce long-term contamination risks.

Acknowledgement

This research was carried out at the Department of Chemistry, Kwame Nkrumah University of Science and Technology.

Statements and Declarations

Ethics approval and consent to participate not applicable

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors declare that they have no competing interests.

Funding

This research did not receive specific grants from public, private or funding agencies.

Authors' contribution

All authors made substantial contributions to the writing of the manuscript. All authors read and approved the final manuscript.

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