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Geochemical behaviour of heavy metals in sludge effluents and solid deposits on the Zambian Copperbelt: Implication for effluent treatment and sludge reuse

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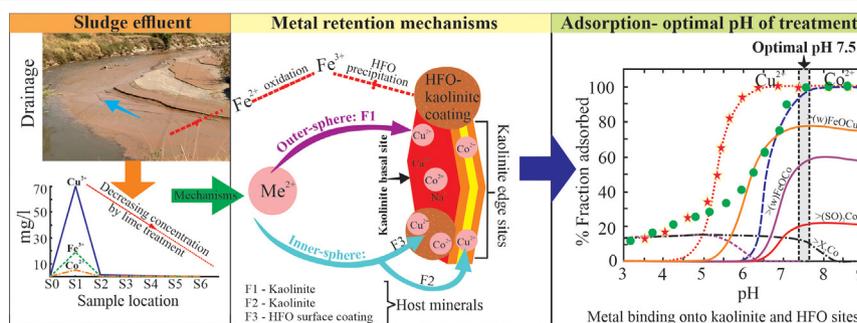
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HIGHLIGHTS

- Formation of hydrous ferric oxide from biotite weathering
- Interpretation of sequential extraction from modeling predictions
- Adsorption behaviours of copper and cobalt onto mixture of kaolinite and Fe oxide

GRAPHICAL ABSTRACT



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ABSTRACT

Sludge effluents and solid deposits generated from the conventional lime treatment processes on the Zambian Copperbelt have led to reports of copper (Cu) and cobalt (Co) contamination into the nearby water bodies. To better understand the behaviour of the metals; partitioning, adsorption and their specific binding forms were studied through sequential extraction, batch adsorption experiments and surface complexation modeling (SCM). Results of mineral composition analyses indicated that micas, kaolinite, quartz and feldspar are abundant with hydrous ferric oxide (HFO) precipitates that formed as a result of the weathering of biotite grains existing as grain surface coating. Sequential extraction revealed that Cu and Co metals are partitioned in the order of: exchangeable (F1: 600–1500 mg/kg Cu; 100–200 mg/kg Co), acid-soluble (F2: 2200–5500 mg/kg Cu; 190–220 mg/kg Co) and reducible fraction (F3: 2200–5500 mg/kg Cu; 260–300 mg/kg Co). Metals in F1 are hosted by kaolinite, F2 by both kaolinite and HFO whereas in F3 by dominantly HFO. Equal Cu concentration between F2 and F3 is due to both the limited amount of HFO (i.e. 5–10 g/kg) and desorption of loosely adsorbed Cu and Co metals to HFO surfaces. Batch adsorption experiments revealed adsorption as the dominant metal retention mechanism. According to modeling predictions, HFO sites are the dominant metal adsorption sites. At HFO site; $>(s)FeOCo+$, Co showed adsorption decrease from 40% in single system to 25% in binary system between pH 7–7.5 due to metal competition for adsorption sites. The high Cu concentration (i.e. 0.5–1.1% Cu) displaced low Co (i.e. 0.03–0.07% Co) concentration from the adsorption sites present in sludge, thus rendering Co mobile into the environment. To keep the adsorbed metals stable from release, optimal pH of 7.5 is suggested during

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treatment with lime. At this optimal pH, metals are decreased to below the regulation standard values and with less generation of voluminous sludge. Adsorbed Cu and Co can be recoverable from sludge through acid treatment at pH <3 based on sequential extraction results. The resultant metal-free sludge material has potential of been used as aggregate in construction.

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1. Introduction

The Zambian Copperbelt is famous for copper (Cu) and cobalt (Co) sulphide ore deposits of Central Africa. During the ore beneficiation and metal recovery processes, low pH sludge effluents are generated and lime-treated before their deposition in ponds and impoundments. During periods of heavy rainfall, sludge erosion causes stream and river siltation resulting in subsequent non-compliance metal concentration discharge into the nearby surrounding environments (Pettersson and Ingri, 2001; Sracek et al., 2012). Therefore, sludges have the potential to become of negative legacy in Zambia. To avoid secondary contamination from the sludges and to optimise effluent treatment, understanding of metal partitioning, adsorption mechanisms, specific binding surfaces and stability conditions are unambiguously important. Previous studies on the Zambian Copperbelt by Sracek et al. (2010, 2012) reported on partitioning and concentrations of metals in stream sediments and sludge by sequential extraction method. They reported that a high percentage of Cu and Co is present in the exchangeable/acid-soluble fraction, hence the potential for their dissolution and remobilisation is high. However, their works did not fully envisage the host minerals in exchangeable/acid-soluble fractions except for the metals partitioned to hydrous ferric oxide (HFO). Furthermore, Sracek et al. (2010) and Sracek (2015) illustrated the geochemical and mineralogical capacities of sludges and tailings, the formation of iron ochre and secondary hematite and attenuation of contaminants through the oxidative dissolution of pyrite and chalcopyrite. However, at some of the mine sites on the Copperbelt, no iron ochre has been reported or observed in the vicinity of the drainages and storage sites. This geochemical condition is completely different from the ordinary acid mine drainage (AMD) treatment sites in which secondary minerals play important roles in the metal removal. Therefore, there is still limited information regarding the metal behaviours and stability conditions in sludge effluents and solid deposits.

In soils, sediments and surface water, clay minerals and metal oxides are the dominant solid phases controlling the trace metal distribution and mobilities (Zhang et al., 2014). Studies on clay minerals (Sposito, 1984; Schindler et al., 1987; Stumm and Morgan, 1995) and metal oxides (Jenne, 1998; Smith, 1999) have indicated that the geochemical conditions of the host material including pH have profound effects on trace metal partitioning. Metal partitioning is currently studied through sequential extraction methods. Sequential extraction, despite its limitations and experimental uncertainties reviewed by many authors (Tack and Verloo, 1995; Bacon and Davidson, 2008), is still regarded as a powerful tool in assessing the distribution and mobility of trace metals with the solid phase and predicting their behaviours under changing environmental conditions. In general, sequential extraction uses the partitioning phases to determine the metal-binding behaviours with the solid surface. Metal-binding is particularly of greater significance in areas affected by anthropogenic metal mining activities because greater amounts of metals are associated with less stable geochemical phases. Therefore, to fully understand metal partitioning and specific binding forms to solid phases, some geochemical models have been developed. Surface complexation modeling (SCM) (Weng et al., 2001; Gustafsson and Pechova, 2003; Pan et al., 2017) has so far proved to have the ability to provide excellent modeling predictions to the laboratory experimental adsorption data under varying geochemical conditions related to the natural environments (Pan et al., 2017). The commonly used SCM is the component additivity (CA) approach

(Davis et al., 1998; Dong and Wan, 2014). The CA-SCM approach describes the metal adsorption onto mineral assemblages through the summation of different contributions of submodel descriptions characterising the sample (Gustafsson and Pechova, 2003). The advantages of CA-SCM are that (i) surface adsorption models and parameters can be developed from reference materials or obtained from previous literature; (ii) the model parameters are transferable from one field site to another and (iii) the model results can be useful for understanding the relative contributions of each mineral component for the overall adsorption (Dong and Wan, 2014). To adequately determine the partitioning and adsorption behaviour of the metals bound to multiple sites (e.g. clay minerals and HFO) in natural conditions, the integration of experimental and modeling results is necessary. In this paper, our overall objectives are to evaluate: (a) metal partitioning in solid sludge through sequential extraction, and (b) metal adsorption behaviours and specific binding forms through batch experiment and SCM prediction. We attempted to complement our objectives through further investigations of the physio-chemical and geochemical characteristics at the solid-liquid interface so as to gain more insight into the factors controlling metal partitioning. Our results are expected to provide information on effluent treatment, metal stability and metal recovery conditions.

1.1. Site description

The studied site is located on the Zambian Copperbelt (Fig. 1a), north of Chingola town (Fig. 1b). Details of the regional geology have been described by Rainaud et al. (2005) and McGowan et al. (2006). The dominant Cu and Co sulphide ore minerals are chalcocite (Cu_2S) and carollite (CuCo_2S_4). Other mineable ores include metal oxides known as refractory ores which constitute 14% of the total extractable ores (Whyte et al., 2001). Several drainage channels traverse the mine site, and transport spillages of metal-laden effluents emanating from the metal processing plant. The currently studied drainage is labelled S0 to S6 (Fig. 1b). S0 represents the background water from catchment sources unaffected by anthropogenic mining-related activities. S1 represents the anthropogenic source from the metal processing at the concentrator prior to mixing with the nearby receiving drainage (Fig. 1c). After mixing, the diluted effluent (i.e. S2–S6) is transported downstream to the storage ponds (Fig. 1d). To decrease the metal concentrations and maintain a neutral pH condition, lime treatment (Fig. 1e) is conducted at designated points labelled L, however, the treatment method seems to lack control and optimisation to achieve better treatment results.

2. Materials and methods

2.1. Field sampling

A total of 36 sludge effluent samples were collected in 2018 and 2019 under contrasting weather conditions of dry and wet season. Temperature, pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were measured using a multi-probe (model W-22XD, Horiba Ltd. Kyoto, Japan). Measured ORP values were converted into measured Eh values for thermodynamic calculations. The effluent samples were filtered with 0.2 and 0.45 μm (ADVANTEC-cellulose-acetate) disposable membrane filters. The 0.2 μm filtrates were split into two subsample sets, one acidified with 100 μl of 1% analytical grade nitric acid (HNO_3) for analyses of dissolved major and minor cations and

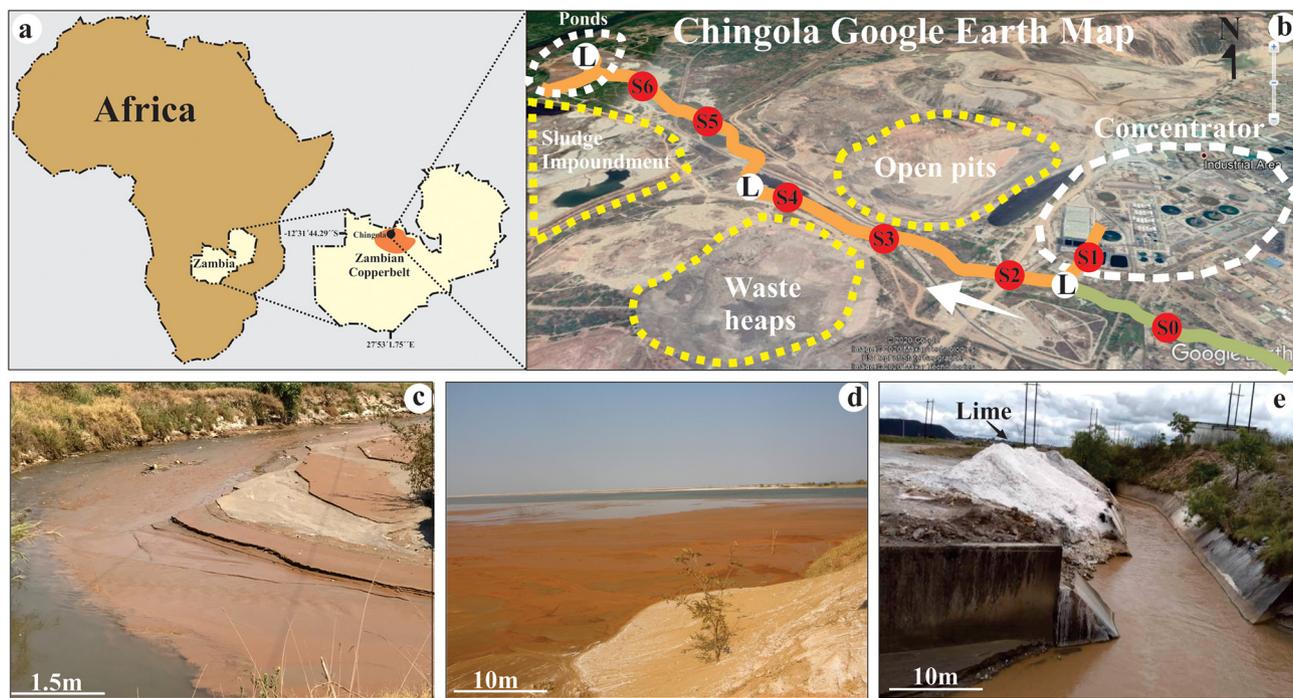


Fig. 1. (a) Regional geographical location of the studied area; (b) Sampling sites location in the study area; (c) Drainage siltation from sludge effluents; (d) Sludge storage ponds and impoundments; (e) Lime drainage treatment.

another set of the non-acidified sample was analysed for the major anions. The $0.45 \mu\text{m}$ filtrate was measured for the alkalinity conditions through titration with $100 \mu\text{l}$ of 1% analytical grade HNO_3 . Solid materials were collected alongside effluent samples along the drainage and at storage ponds using the steel shovels. In the dry season, white precipitates (i.e. efflorescent salts) were collected on surfaces of the drainage and storage ponds. All solid samples were stored in clear and clean plastic bags prior to shipment for laboratory analyses.

2.2. Analytical methods

2.2.1. Water sample

Details of equipment, sample preparations and analytical procedures are similar to those outlined by Ito et al. (2017). The dissolved major and minor cation concentrations were measured from the $0.2 \mu\text{m}$ acidified filtrates using inductively coupled plasma-atomic emission (ICP-AES; ICPE-9000, Shimadzu) with ICP multi-element standard solution IV (1000 mg/l) of Certipur® from Merck-chemicals of Germany. Working standard solution of 10 mg/l was prepared from stock solution using Milli-Q water (18 M Ω) added with 1% of ultrapure grade of HNO_3 . Samples were diluted between 10 and 10,000 times. The non-acidified water samples were analysed for the major anions using ion chromatography (IC; IC861, Metrohm) with a multi-anion standard solution (FUJIFILM Wako analytical grade). The measured major anions are chloride (Cl^-) and sulphate (SO_4^{2-}) at stock solution concentrations of 20 mg/l and 100 mg/l respectively. Bicarbonate (HCO_3^-) ion concentration was estimated from the alkalinity measurement data using the Gran function plot method suggested by Rounds (2015). Limit of detection (LOD) was calculated by average and standard deviations from 5 blank water (18 M Ω) samples acidified with 1% ultrapure HNO_3 . In the calculation of the LOD, the 3 s/b equation was taken into consideration, where s is the standard deviation of absorbance of the blank samples and b is the slope of the calibration curve for each element. The correlation coefficients (r) of the calibration curves were greater than 0.998 for all elements studied. The LOD values for cations varied from 0.01–0.09 mg/l and for anions from 0.01–0.5 mg/l.

2.2.2. Sludge solids

Sludge solids were air-dried at room temperature, homogenised and sieved to bulk (i.e. $<53 \mu\text{m}$) particle sizes. To obtain the clay-sized (i.e. $<2 \mu\text{m}$) particles, a series of continuous shaking and centrifugation in polyethylene bottles with deionized water were conducted following the procedures outlined by Arroyo et al. (2005). X-ray diffraction (XRD; RINT 1200, Rigaku) equipped with $\text{CuK}\alpha$ was used to analyse solid samples at fixed working conditions of 30 kV and 20 mA and 2 θ -scanning rate of 0.02 $^\circ$ /min. Quantitative estimation of mineral composition was achieved by PANalytical X'pert HighScore Plus software (Malvern Panalytical, UK). Scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometry (JSM-6500F; JSM-IT200, JEOL) was used to analyse the morphology and chemical composition. SEM sample preparations involved adding sample particles on a carbon tape attached to aluminum specimen tub, coated with graphite and analysed at 15–20 keV conditions. An optical microscope (Olympus, U-LH100) was used to analyse both thin and polished section samples. A transmission electron microscope (TEM- JEM-2010, JEOL) was used to observe the surface morphology and check the chemical composition of the mineral particles. White precipitates were dissolved in deionized water, pH measured, filtered with $0.2 \mu\text{m}$ membranes and split into acidified and non-acidified samples for ICP-AES and IC analyses.

2.2.3. Sequential extraction

The study adopted the modified eight (8) operationally defined procedures and protocols suggested by Horowitz (1985) and Filgueiras et al. (2002) shown in Table 1. The protocol defines clearly (i) the exchangeable and acid-soluble fractions and (ii) the three (3) leaching stages (i.e. easily, moderately and strongly) of the reducible fraction. Trace metals partitioned in the exchangeable fraction are associated with clay minerals (Stumm and Morgan, 1995), in acid-soluble fraction with carbonates (Tessier et al., 1979) and in reducible fraction with HFO (Tessier et al., 1979; Rauret et al., 1999), thus the behaviours of the metals with the host mineral in each fraction can easily be studied. The choice of the leaching reagent was based on the reagent chemical

Table 1
Sequential extraction protocols (Modified after Horowitz (1985) and Filgueiras et al. (2002)).

1 g of sludge sample		
Fraction	Procedure and conditions	Reference
Exchangeable (1)	1 M ammonium acetate (NH ₄ OAc; Pure analytical grade) at pH 7, shaking at room temperature and pressure (RTP) in darkness for 10 h at 200 rpm	1
Acid soluble (2)	1 M NH ₄ OAc/acetic acid (HOAc) at pH 5, shake at RTP in darkness for 10 h	2
Weakly reducible (3)	0.25 M Hydroxylamine hydrochloride (NH ₄ OHCl) + 0.25 M hydrochloric acid (HCl) at pH 2.5, water bath heating at 80 °C for 2 h and shaking for 2 h at 25 °C	3
Moderate reducible (4)	0.1 M ammonium oxalate (NH ₄ Ox; Pure chemicals analytical grade) + 0.1 M oxalic acid (HOx) at pH 3, water bath heating at 80 °C for 2 h and shaking for 2 h at 25 °C	3
Strongly (Crystalline) reducible (5)	1 M Sodium dithionite (Na ₂ S ₂ O ₄ ; Pure analytical grade) + Trisodium citrate (Na ₃ C ₆ H ₅ O ₇ ; Pure analytical) + sodium bicarbonate (NaHCO ₃ ; Wako Pure Chemicals) shake overnight at RTP	4
Organic Matter (6)	35% hydrogen peroxide (H ₂ O ₂) water bath heating for 1 h	5
Sulphide (7)	7 mg Potassium chlorate (KClO ₃ ; Pure analytical grade) + HCl + nitric acid (HNO ₃), water bath heating for 1 h	1
Residual (8)	Microwave digestion (Ethos Advance microwave Lab station, milestone Inc., Sorisole, Italy) in Teflon beakers at 200 °C for 55 min, HNO ₃ + HCl + Perchloric acid (HClO ₄) at (6:3:1) acid ratios	3

¹Thomas, 1982; ²Hass and Fine (2010); ³Chao and Zhou (1983); ⁴Mehra (2013); ⁵Tessier et al. (1979).

properties and leaching efficacy as recommended by the cited literature. For example, in step 1 and 2 (Table 1), ammonium acetate (NH₄OAc) inhibits the possible precipitation of metals after leaching (Hass and Fine, 2010; Leermakers et al., 2019) especially that the studied sludge samples contained some considerable amount of metals that might easily precipitate with other anionic complexes in solution. Acidified hydroxylammonium chloride (NH₂OH·HCl) is effective in dissolving the easily or weakly adsorbed metals associated with amorphous Fe oxides (Qin et al., 2020). Similarly, NH₂OH·HCl cannot liberate metals that are moderately bound to Fe oxides (Hass and Fine, 2010). Instead, acidified ammonium oxalate (NH₄Ox·HOx) liberates metals moderately adsorbed or incorporated with Fe oxides (Chao and Zhou, 1983). Therefore, the 3 leaching stages involving NH₂OH·HCl and NH₄Ox·HOx of the reducible fraction provides a better understanding of metal partitioning in reducible fraction.

2.2.4. Batch experiment

Two types of sludge materials were prepared and used in batch experiments. Sludge; (i) with HFO coating and (ii) without HFO coating. For sludge without HFO coating, the removal of HFO coating followed chemical extraction protocols and procedures outlined by Chao and Zhou (1983) using acidified ammonium oxalate (NH₄Ox). To ensure the total removal of HFO coating, additional chemical treatment steps outlined by Mehra (2013) were conducted. The batch adsorption experiments were performed in both single and binary metal systems as described below.

2.2.4.1. Sludges with and without HFO coating. Sodium nitrate (NaNO₃) from FUJIFILM Wako Pure analytical grade was used to prepare 100 ml of 0.05 M electrolyte in a 250 ml volume of polyethylene plastic bottles. Each of the 1 g solid of <2 µm clay-size particles (i.e. sludge with and without HFO) was added to each of the separately prepared electrolytes and the initial pH adjusted to pH 3 by HNO₃. The solution was

equilibrated by end-over-end shaking at speed of 200 rpm for 24 h. In single metal system experiments, 1.10 mM copper (II) nitrate trihydrate (Cu (NO₃)₂·3H₂O from FUJIFILM Wako Pure analytical grade) and 0.11 mM cobalt nitrate hexahydrate (Co (NO₃)₂·6H₂O from FUJIFILM Wako Pure analytical grade) were added to each of the prepared electrolytes. In binary metal system experiments, 1.10 mM Cu and 0.11 mM Co were simultaneously added to each of the prepared electrolytes. The aliquots were equilibrated for 24 h by an end-over-end shaker at a shaking speed of 100 rpm. Batch adsorption experiment involved titrating aliquot volume with 0.05 M HNO₃ and 0.05 M sodium hydroxide (NaOH; FUJIFILM Wako Pure analytical grade) to desired pH 3–9 under the magnetic stirring bar. After equilibration to the desired pH conditions, the mixture was again placed on an end-over-end shaker at 100 rpm for 24 h after which pH re-measured, centrifuged and filtered with 0.2 µm membranes. The filtrates were acidified by pure grade HNO₃ and analysed by ICP-AES.

2.2.4.2. Reference kaolinite. Reference kaolinite sample (JCSS-1101) was obtained from the Clay Science Society of Japan. The sample was acid washed in 0.1 M HCl solution, and oven-dried at 90° for 24 h and analysed by XRD. XRD results showed characteristic peaks of kaolinite with no other mineral components detected. The surface area was measured by the Brunauer-Emmett-Teller (BET) method by protocols outline by Brame and Griggs (2016) using a Quantachrome analyser (NOVA touch LX³ NT3LX-1). The measured value was 18.34 m²/g. Two sets of adsorption experiments were conducted by adding 1 g kaolinite to 100 ml of 0.05 M NaNO₃ electrolyte in a single metal system. A 0.25 mM Cu and 0.0163 mM Co were each prepared and added to each of the prepared 100 ml volumes of electrolytes. The aliquot solutions were varied from pH 3–9 through titration with 0.1 M HNO₃ and 0.1 M NaOH solutions at 0.25-pH unit increment and equilibrated for 24 h. The aliquot pH-re-measured, centrifuged, filtered through 0.2 µm filters and analysed by ICP-AES.

2.2.5. Metal solubility and surface complexation modeling

Geochemist's Workbench® (GWB ver.14, Bethke, 2008) with the Lawrence Livermore National Laboratory database (thermo.tdat) and ACT2 module was used to obtain metal solubility diagrams using laboratory measurement analyses of field wastewater data for checking the saturation state of secondary precipitates. The CA-SCM prediction was adopted. HFO sites were modeled with the FeOH+.sdat dataset in GWB package from the diffuse double layer (DDL) of Dzombak and Morel (1990) database by assuming strong sites >(s)FeOMe+ and weak sites >(w)FeOMe+ where Me²⁺ represents the metal adsorbed. The concentrations of Fe used in modeling were estimated from the chemical extraction treatment of HFO coating from sludge with NH₄Ox following sequential extraction protocols outlined in Table 1. Kaolinite modeling was made possible through SCM constants and equilibria obtained from the previously published papers cited in Table 2. SCM constants and equilibria from previous papers were used due to

Table 2
Input parameters for the surface complexation modeling of kaolinite obtained from previous published literature.

Surface reactions	log K		
	H	Cu	Co
Surface reactions			
>SOH + H ⁺ = >SOH ₂ ⁺	3.24 ^a		
>SOH = >SO ⁻ + H ⁺	-7.15 ^a		
>X ⁻ .Na ⁺ + H ⁺ = >X ⁻ .H + Na ⁺	-2.88 ^a		
>SOH + Me ²⁺ = >(SO) ₂ Me ⁺ + H ⁺		-4.58 ^b	-6.87 ^a
2>X ⁻ .Na ⁺ + Me ²⁺ = >X ₂ ⁻ .Me ²⁺ + 2Na ⁺		3.31 ^b	3.02 ^b
Other parameters			
Surface area (m ² /g)	25.7 ^c		
Site density X ⁻ (mol/kg)	0.05 ^d		
Site density SOH (mol/kg)	0.05 ^d		

^aAngove et al. (1999); ^bIkhsan et al. (1999); ^cLandry et al. (2009); ^dFan et al. (2019).

the lack of a thermodynamic database of micas. Therefore, kaolinite was assumed to be the dominant host surface. For kaolinite adsorption, two sites, $>X_2Me$ at low pH and $>(SO)_2Me$ at high pH were selected based on their reasonably better model fit to the experimental data. Both model simulations were constructed using the REACT module of GWB package software.

3. Results and discussion

3.1. Chemistry of effluents

Trends in the hydrochemical characteristics of the drainage effluents are given in Fig. 2 and Table S1. Generally, the overall pH (Fig. 2a) ranges

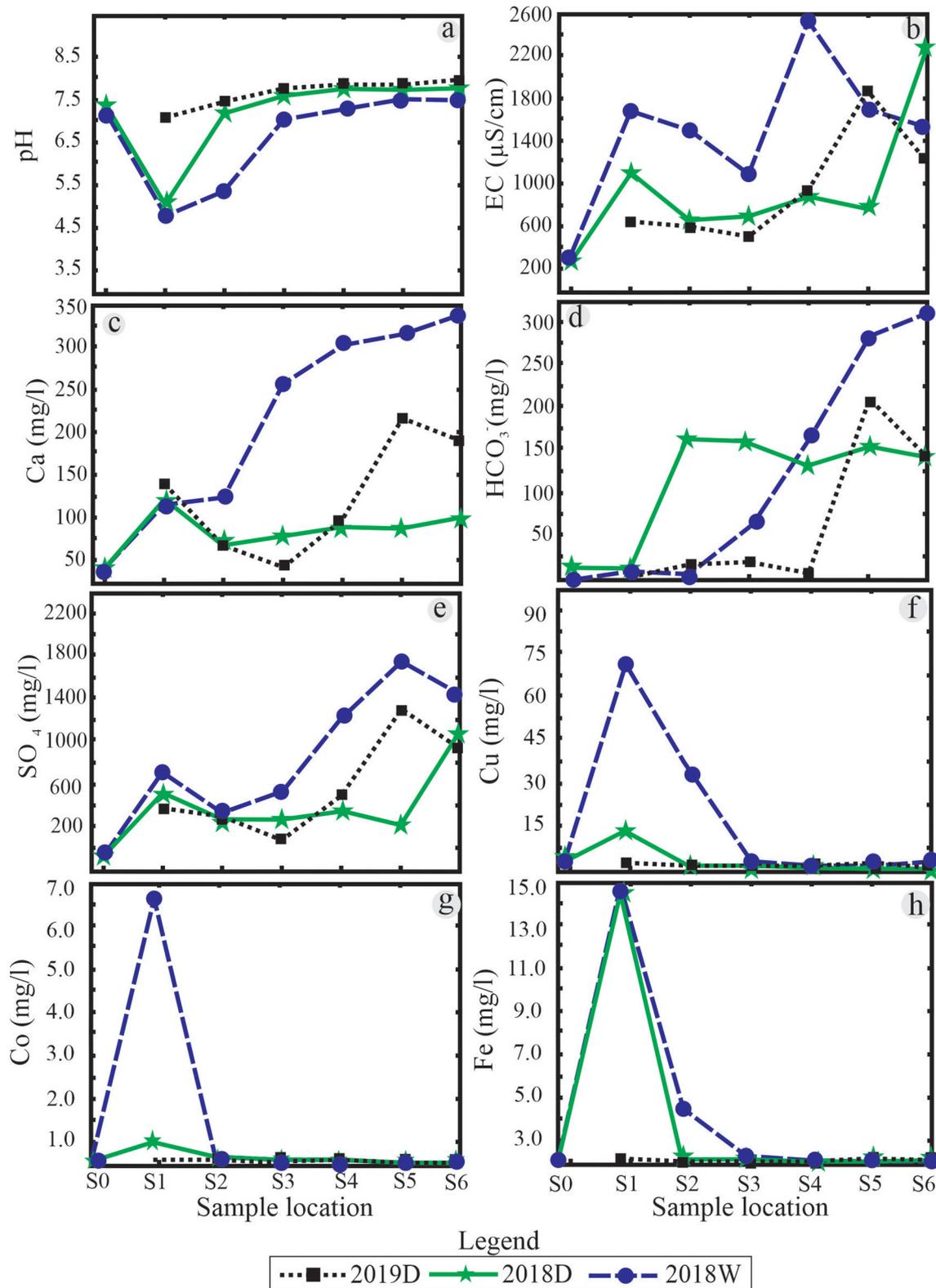


Fig. 2. Hydrogeochemical data of sludge effluents; (a) pH; (b) EC; (c) Ca; (d) HCO_3^- ; (e) SO_4^{2-} ; (f) Cu^{2+} ; (g) Co^{2+} ; (h) Fe^{2+} . Abbreviations: 2019D, 2018D, 2018W are sampling dates (i.e. years) and seasons (W-wet season) and (D-dry season). S1-S6 are drainage sample location (refer to Fig. 1b).

from acidic (pH 4.66) to neutral (pH 7.50) conditions. In background water (S0), pH was consistently neutral. At S1, low pH values were often recorded. For instance, the low pH values recorded in 2018 W (pH 4.66) and 2018D (pH 5.14) were probably caused by acidic effluents at the concentrator (Fig. 1b) during the ore beneficiation process. However, reasons for the neutral pH recorded in 2019D (pH 7.09) are unclear, though this may be due to either the absence of low pH effluent or lime treatment at the time of sampling. The observed variations in the pH values at S1 suggest that there is a high potential for metal remobilisation along the drainage as evidenced by the decrease in pH at S2 in 2018 W (pH 5.49). The increasing trends in EC values towards the downstream (Fig. 2b) are positively correlated with the increase in dissolved major ions concentrations such as calcium (Ca^{2+}), HCO_3^- and SO_4^{2-} (Fig. 2c, d, e). The increase in Ca^{2+} and HCO_3^- concentrations is a presumably good indication for the activity of continuous dissolution of lime. The SO_4^{2-} ion concentrations also showed increasing trends towards the downstream flow path (Fig. 2e), suggesting the possibilities of other drainage effluent inputs, especially between S3–S5. The dissolved concentrations of trace elements (i.e. Cu^{2+} and Co^{2+}) were high at S1 (Fig. 2f, g) owing to the prevailing acidic condition. Cu has had the highest concentration of 70 mg/l which is above the maximum contamination levels (MCL) of 1.3 mg/l recommended by the environmental protection agency (EPA, 2017). The highest Co concentration was 6.75 mg/l, 10 times lower than Cu but above the standard guideline of $\sim 50 \mu\text{g/l}$ recommended by the world health organization (WHO, 2006). The highest dissolved iron (Fe) (probably Fe^{2+}) concentration measured at S1 (i.e. 15 mg/l) (Fig. 2h) is much lower compared to areas affected by Fe-sulphide oxidations (Sanchez Espana, 2008) indicating that ordinary acid mine drainage (AMD) conditions are not the ultimate source of Fe in sludge effluents. Although other contaminant sources are expected between S3 – S5 from external drainage sources according to SO_4^{2-} concentration, the dissolved metals kept their decreasing concentrations, probably due to the lime neutralisation of the effluents. Therefore, the decrease in the dissolved metal concentrations from S2–S6 shows that lime treatment is effective, though the geochemical processes responsible for decreasing trends and keeping low concentrations still needed to be addressed.

In lime treatment systems, the reaction of lime with the atmospheric conditions (i.e. carbon dioxide) is reported to promote the precipitation of carbonate minerals (Shih et al., 1999). To check the possibility of metal carbonate precipitation at the studied site, metal solubility diagrams were constructed through geochemical modeling and results are as shown in Fig. 3. In Fig. 3a, Cu showed undersaturation to near-

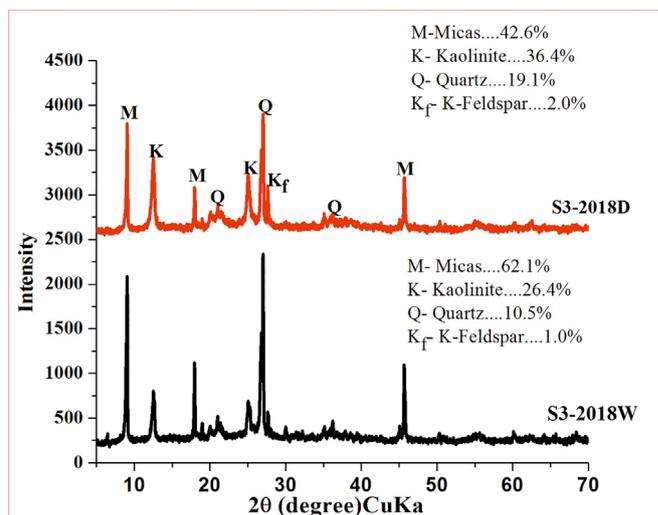


Fig. 4. (a) XRD patterns of sludge.

saturation with respect to malachite whereas Co metal (Fig. 3b) showed under-saturation with respect to Co carbonate complex. Both metals exhibited the lowest metal solubility characteristics and based on the thermodynamic modeling results, the removal of metals in effluents may not be expected by the metal carbonate precipitation process. Instead, the major solute compositions of effluents are consistent with several processes occurring within the drainages including the dissolution of lime and possible weathering of the component minerals.

3.2. Mineral composition of sludge

XRD patterns of sludge are shown in Fig. 4. The dominant mineral components are micas (i.e. biotite and muscovite), kaolinite, quartz and k-feldspar. Quantitative percentage estimation by Rietveld refinement analyses showed micas (40–70%), kaolinite (20–40%), quartz (8–20%) and k-feldspar (<2%). No significant variations in mineral compositions were observed in different sampling dates suggesting that the supply sources may be uniform.

In SEM analyses, some notable weathering features of biotite surfaces such as (i) the exfoliated layers and rugged erosion surfaces (Fig. 5a) and (ii) the etched pits (Fig. 5b) were revealed. These features indicate the tendency of biotite to undergo layered and edge

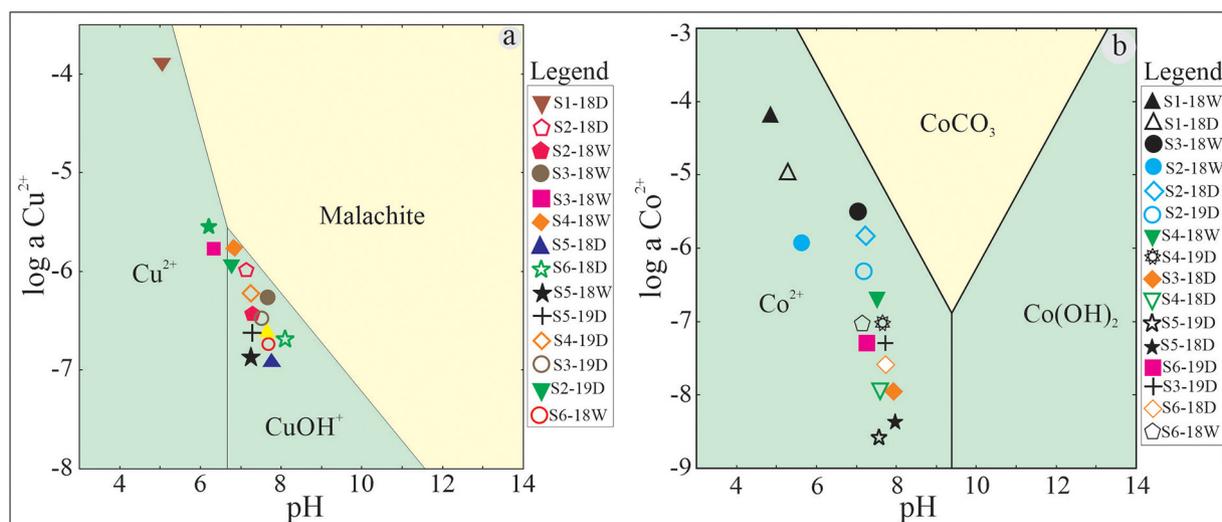


Fig. 3. Metals solubility diagrams plotted as a function of pH at 25 °C of: (a) Cu and (b) Co. Abbreviation of symbols; S1–S6 are sampled location (refer to Fig. 1b); 18 W, D and 19D are sampling dates (i.e. years) and seasons (e.g. W-wet season) and (e.g. D-dry season).

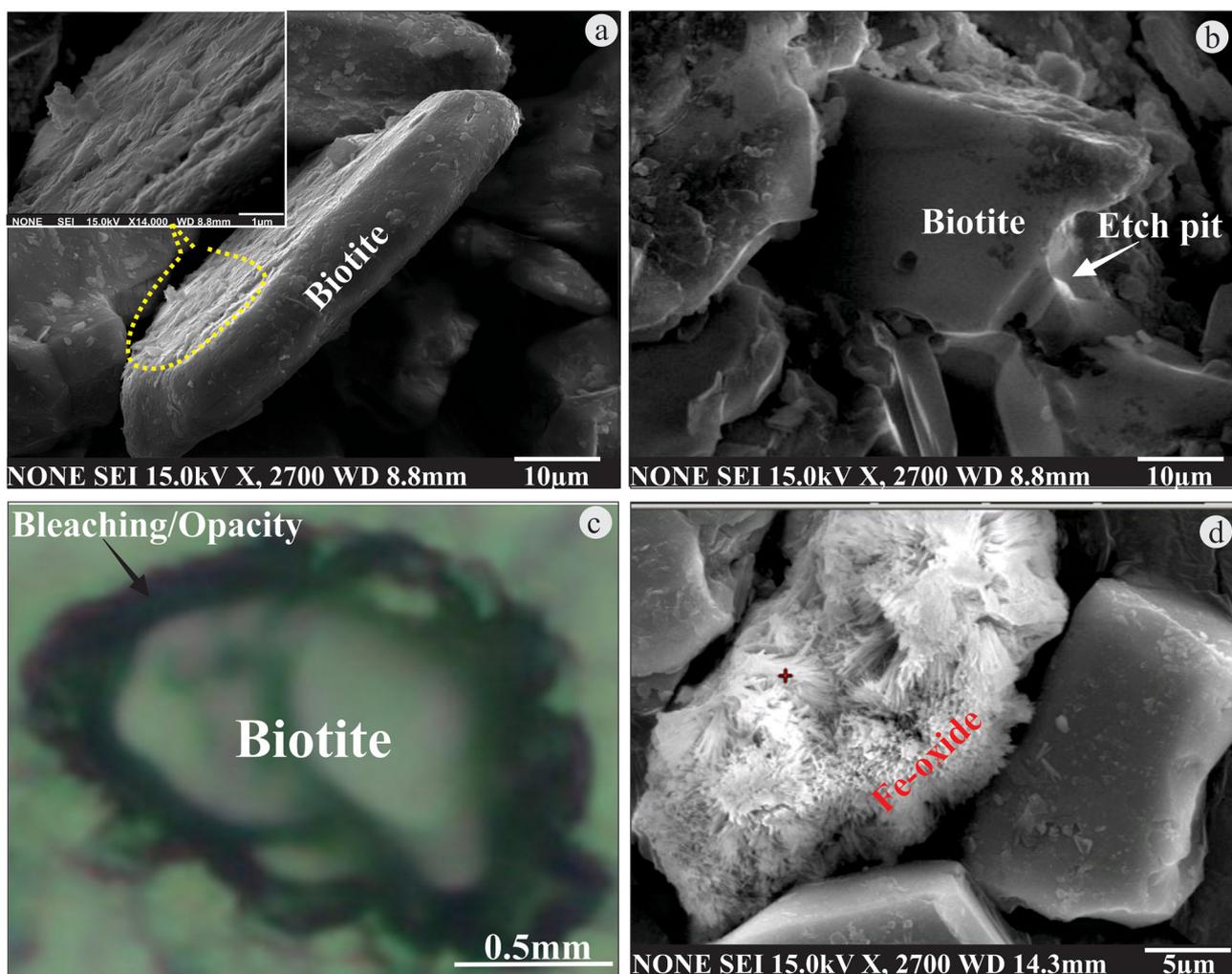


Fig. 5. (a) Exfoliation layers formed by the layered weathering of biotite grains, (b) Etched pits formed by edge weathering of biotite grains, (c) Bleaching and opacity of biotite grain surfaces due to coatings with non-crystalline material (i.e. HFO) during and after biotite weathering, (d) HFO precipitate formation by oxidations of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions released from biotite weathering. Abbreviations: HFO-hydrous ferric oxide.

weathering mechanisms consistent with the studies conducted by Ghabru et al. (1987) and Wilson (2004). Edge weathering (i.e. etched pits) are reported by Wilson (2004) to cause mineral deformations, easy disintegration and rapid fracturing of minerals along certain crystallographic orientations. Specific to biotite, Davis and Hayes (1986) indicated that such structural deformations tend to cause the release of the octahedral ferrous (Fe^{2+}) ion which oxidises to ferric (Fe^{3+}) ion forming Fe oxides (i.e. HFO). The evidence of Fe^{2+} to Fe^{3+} oxidation is bleaching and opacity of biotite surface grains (Fig. 5c) consistent with the earlier findings by Bisdom et al. (1982). With ageing, more discrete forms of HFO are evidenced by SEM (Fig. 5d). According to Chakraborty et al. (2011), Fe (III) oxyhydroxides are a potential sink of heavy metals and are expected to control the mobility of metals in oxidising conditions.

3.3. Grain surface coating

Freshly precipitated HFO has been found to occur as a surface coating on suspended sediments, carrying several adsorbed metals during transport (Singh et al., 1984). In the studied sludge, the existence of HFO coating was indirectly recognized by XRD pattern (Fig. S1). Before chemical treatment, low peak intensities of micas, kaolinite and quartz were determined. After treatment with NH_4Ox solution, the signal/noise ratio of the peak increased suggesting that the X-ray amorphous materials are removed. The estimated amount of chemically extracted

HFO coating is in the ranges of 5–10 g/kg (Table S2). This measured amount of HFO is low and consistent with the limited proportion of the released Fe ion from biotite weathering rather than from the known Fe-rich sulphide oxidations common in AMD conditions (Blowes et al., 2003). The interactions of HFO with other component minerals were commonly observed with the kaolinite surface by SEM-EDS (Fig. 6a). HFO – kaolinite association has been reported by Carroll (1959) and Jenne (1998) to especially modify the metal adsorption behaviour and affinity characteristics of kaolinite surface. Such modification has been studied with models by Lund et al. (2008) and Landry et al. (2009) and their results confirm that both minerals display capacities to control heavy metal mobilities. It is, therefore, to be expected that kaolinite – HFO associations in the studied sludge are to a greater extent controlling the retention and transport of the heavy metals. In TEM-EDS analyses (Fig. 6b), another type of surface coating resembling “microencapsulation” was observed around a micaceous grain which according to Quispe et al. (2013) is attributed to the rapid precipitation of HFO under neutral to alkaline conditions. Microencapsulation is likened to the formations of hardpans and cemented layers commonly observed in tailings surfaces (Graupner et al., 2007) and widely investigated especially for their potential in minimizing the discharge of metal contaminants (McGregor and Blowes, 2002; Gilbert et al., 2003) either by adsorption or precipitation (Jenne, 1998). The processes (i.e. dissolution of primary mineral phases, transport processes, and precipitation of secondary phases) leading to the formation of hardpans have been

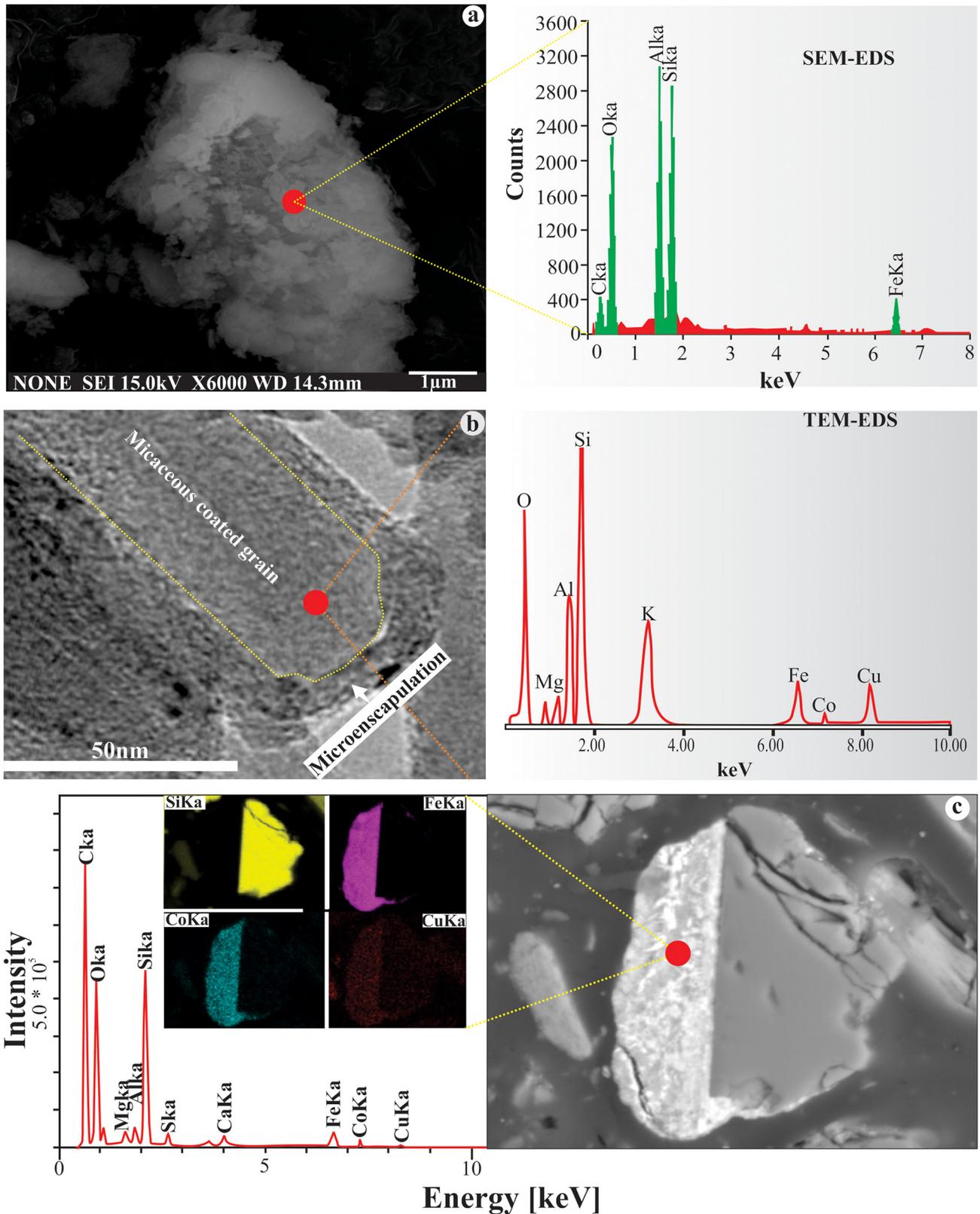


Fig. 6. (a) Freshly HFO precipitates adhering and coatings kaolinite surfaces, (b) Layered (cemented) surface coating onto micaceous grains resembling microencapsulation or hardpans (c) SEM elemental mapping of grain surfaces showing HFO coating onto silica/quartz grain and their subsequent adsorbed metals (i.e. Co adsorption onto HFO).

reported by Graupner et al. (2007) and appear to parallel the conditions under study. The significance of these layers in environmental studies is that they can temporarily act as a potential sink of metal thereby limiting the metal mobility. In the studied sludge, this condition has the ability to enhance metal-stability conditions, though maybe in a short-term

condition due to the observed variations in the low pHs in drainage effluents (Fig. 2: Table S1). Under SEM-EDS elemental surface mapping (Fig. 6c), HFO coating was observed onto the surface of sand grains. Quartz sands are relatively abundant in sludge and their capacities to adsorb metals are relatively unclear. However, based on these results,

the grains are seemingly potential transporting mediums of heavy through grain surface coating. Quartz surface coating is reportedly similar to iron oxide-coated sands (IOCS) that are currently studied and applied in the pretreatment of wastewater (Hansen et al., 2001).

3.4. Sludge surfaces precipitates

During the dry season, white precipitates of efflorescent salts were common along the drainage (Fig. S2-a) and storage ponds (Fig. S2-b, c). XRD analyses revealed that their composition comprised mainly of

gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) (Fig. S3). Due to their high solubility, the salts dissolve during the rainy season and mix with river water during the flow. At the laboratory scale, dissolving the salts in deionized water and analysing their elemental concentrations showed Cu and Co concentrations to be below the detection limit. The absence of Cu and Co in the efflorescent salts indicates that the salts are not the potential hosts or sinks of metals in both short-term and long-term conditions. This condition is unique because heavy metals (i.e. Cu, Zn, Mn) are commonly found to undergo isomorphic substitution with AMD salts such melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

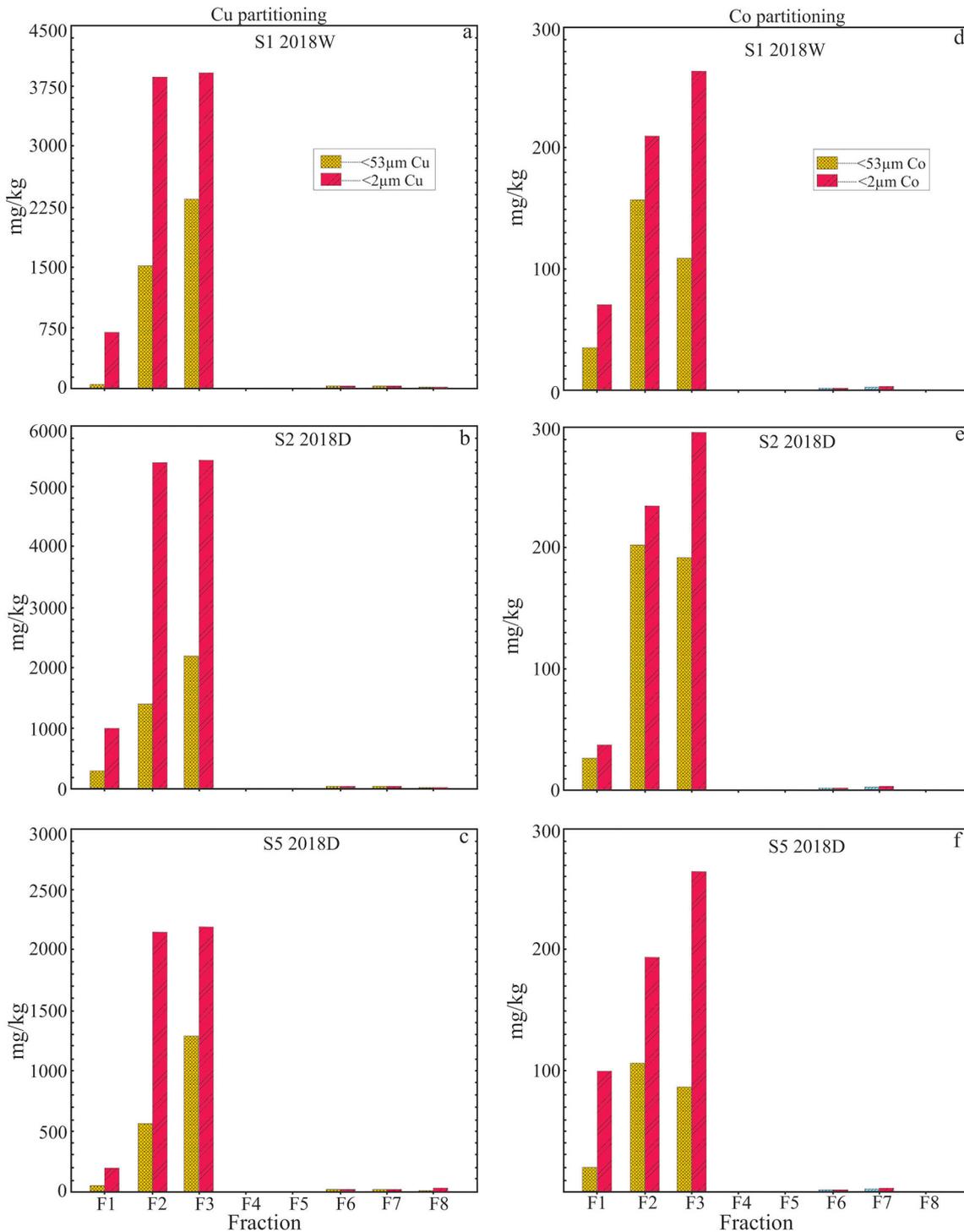


Fig. 7. Sequential extraction results of solid sludge. For individual fraction phases, refer to Table 1 and for sample location, refer to Fig. 1 and Table S1.

forming alpersite ($\text{Cu, Zn, Mn, Mg, Fe} \text{ SO}_4 \cdot 7\text{H}_2\text{O}$) in typical AMD conditions (Nordstrom and Alpers, 1999; Peterson et al., 2006). This observation suggest that some metal retention mechanisms are likely to be taking place in sludge. Another form of surface precipitate observed along the drainage surface is greenish malachite (Fig. S2-d). Its formation may be linked to drying up or evaporation of aqueous CuCO_3 bearing solutions because the effluents collected from drainage are undersaturated with respect to malachite (Fig. 3a). From the results of some previous studies by Bourg (1988), Prusty et al. (1994) and Solomons (1995), detrital and non-detrital carbonate minerals were reported to enhance heavy metal complex formation on surfaces of primary minerals, a condition which parallels the studied site. Thus, the observed malachite is possibly authigenic in origin due to the abundant Cu concentration adsorbed by the detrital and non-detrital carbonate and primary minerals. The presence of malachite precipitates is also evidence that its formation acts as a sink and hosts the Cu in dry seasons, but not during rainy seasons.

3.5. Metal partitioning by sequential extraction

Fig. 7 shows the results of metal partitioning analysed in the bulk-sized and clay-sized particles. In both particle sizes, metals are partitioned into; exchangeable (F1), acid-soluble (F2) and reducible (F3) fractions. Overall, the differences in the metal concentration between bulk and clay-sized particle is largely a function of surface area. For instance, in F1, Cu and Co concentrations in the bulk-sized and clay-sized particles were in the ranges of; 50–350 mg/kg Cu; 20–30 mg/kg Co and 200–1000 mg/kg Cu; 30–100 mg/kg Co respectively. As earlier indicated (Section 2.2.3), clay minerals (Stumm and Morgan, 1995) are the host minerals in F1, hence kaolinite present in sludge based on the mineralogical composition analyses by XRD (Fig. 4) is the potential host of metals. Furthermore, the observed variations in Cu and Co concentration in F1 according to Appel and Ma (2002) commonly occur as a result of the presence of high concentrations and selectivity adsorption characteristics of the metals. This

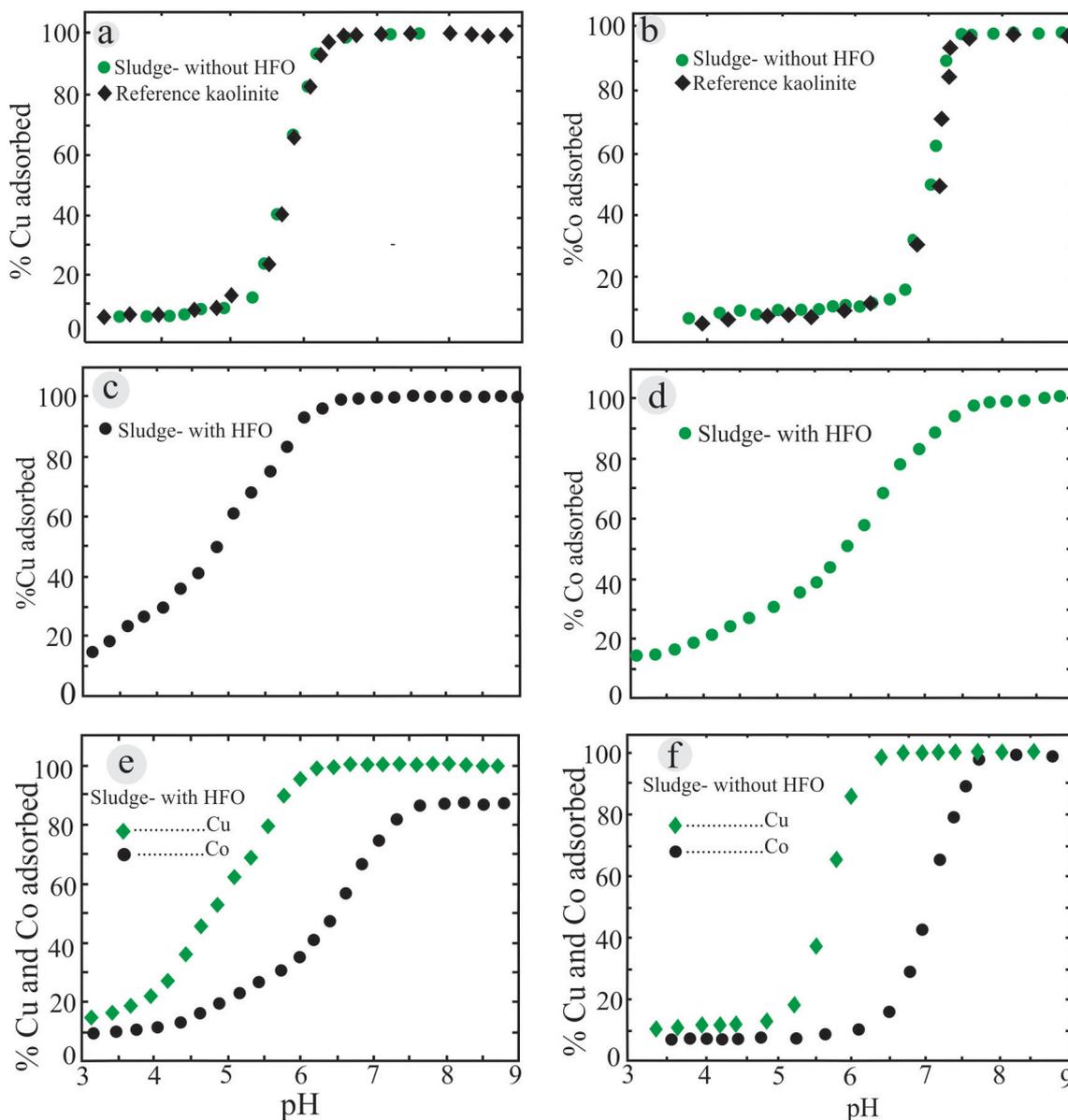


Fig. 8. Characteristics of adsorption of: (a) Cu onto sludge without HFO coating in a single system batch experiment at 1.10 mM and 0.25 mM (b) Co onto sludge without HFO coating in a single system batch experiment at 0.11 mM and 0.0163 mM, (c) Cu onto sludge with HFO coating in a single system batch experiment at 1.10 mM, (d) Co onto sludge with HFO in a single system batch experiment at 0.11 mM, (e) Cu and Co adsorption onto sludge with HFO coating in a binary system at 1.10 mM and 0.11 mM; (f) Cu and Co adsorption onto sludge without HFO in a binary system at 1.10 mM and 0.11 mM. For all experimental conditions, 0.05 M ionic strength is used.

condition reflects the (i) relatively affinity of the metal to the host minerals and (ii) competition for adsorption sites.

In F2 fraction, Cu and Co metal concentrations are associated with carbonate minerals (Tessier et al., 1979). However, XRD and SEM analyses revealed that the carbonates are absent in the studied sludge. The measured Cu and Co concentrations in bulk and clay-sized particles for each metal were in the ranges of 600–1500 mg/kg Cu; 100–200 mg/kg Co and 2200–5500 mg/kg Cu; 120–260 mg/kg Co. In the absence of carbonate minerals (i.e. acid-soluble fraction), it remains unclear whether kaolinite or HFO host the metals. Therefore, to assess the role of kaolinite in hosting the metals, batch adsorption experiments were conducted (Section 3.6).

In F3 fraction, Cu and Co metal concentrations in bulk and clay-sized particles for each metal were in the ranges of 1300–2300 mg/kg Cu; 80–200 mg/kg Co and 2200–5500 mg/kg Cu; 260–290 mg/kg Co. Cu concentration is equally distributed between F2 and F3. However, by default, metal concentrations associated with F3 fraction are expected to be of a much greater proportion than F2 fraction due to the metal partitioning characteristics associated with the HFO surfaces (Lindsay et al., 2015). The high proportions of metals in F2 especially Cu is suggested to be a contribution from some loosely or weakly bound metals associated with the HFO surfaces, including HFO coating onto the bulk size grains (Fig. 6c) and clay-size particles. This observation is consistent with results of the previous study conducted by Essen and El Bassam (1981) which indicated that Fe oxides dissolve and release weakly adsorbed metals into solution at treatment conditions of pH <6. Thus, acid-soluble fraction treatment at pH 5 (Table 1) likely results in, some desorption of weakly adsorbed metals associated with HFO sites. Other sequential extraction steps (i.e. F4, F5, F6, F7 and F8) revealed very low concentrations to the below detection limit.

3.6. Batch experiments

Fig. 8 shows the result of metal behaviours towards the kaolinite and HFO surfaces. In single system experiment shown in Fig. 8a–b, two (2) adsorption stages are revealed onto kaolinite. The initial stage occurs at low pH condition as outer-sphere complexation at exchange sites and the second stage at high pH conditions as inner-sphere complexation at pH-dependent variable charge sites (Ikhsan et al., 1999; Srivastava et al., 2005; Gu and Evans, 2008) Adsorption at the exchange sites (i.e., F1 shown in Fig. 7) is pH-independent and our batch adsorption experiment results show relatively low percentages (<10% adsorption) of the adsorbed metals (i.e. Cu and Co) consistent with previous literature by Lund et al. (2008) and Landry et al. (2009). With increasing pH, pH-dependent kaolinite sites (Fig. 8a–b) associated with F2 fraction (Fig. 7) showed enhanced adsorption (i.e. 90%) for both metals. From the adsorption edge characteristics, the potential of kaolinite to hosting the metals in F2 fraction in the absence of carbonates is high. Based on the volumes of clay-size particles in sludge (Table S2), kaolinite can be the eminent host of the metals despite its known low surface area and low affinity sites consistent with studies conducted by Oakley et al. (1981) which indicated that the presence of >60% clay minerals can aptly host considerable metal concentrations in natural environments.

Adsorption behaviours of Cu and Co metals associated with the combined kaolinite – HFO surfaces are shown in Fig. 8c–d. At low pH conditions, 20% Cu and Co is adsorbed as outer-sphere complexation from pH 3–4.5 and pH 3–5.5 respectively. The adsorbed percentage for each metal is slightly high than onto uncoated kaolinite surfaces (Fig. 8a–b) suggesting that the HFO surface could be playing a pivotal role in controlling the metal transport, consistent with the findings made by Jenne (1998) suggesting both metal adsorption and coprecipitation with HFO surfaces between the low pH to circumneutral pH conditions. At increasing pH conditions, significant adsorption in form of inner-sphere complexation takes place for both metals. The major difference in adsorption behaviour between the metals is the pH_{50} (i.e. 50% adsorption) measured from the shape of the adsorption edge. The

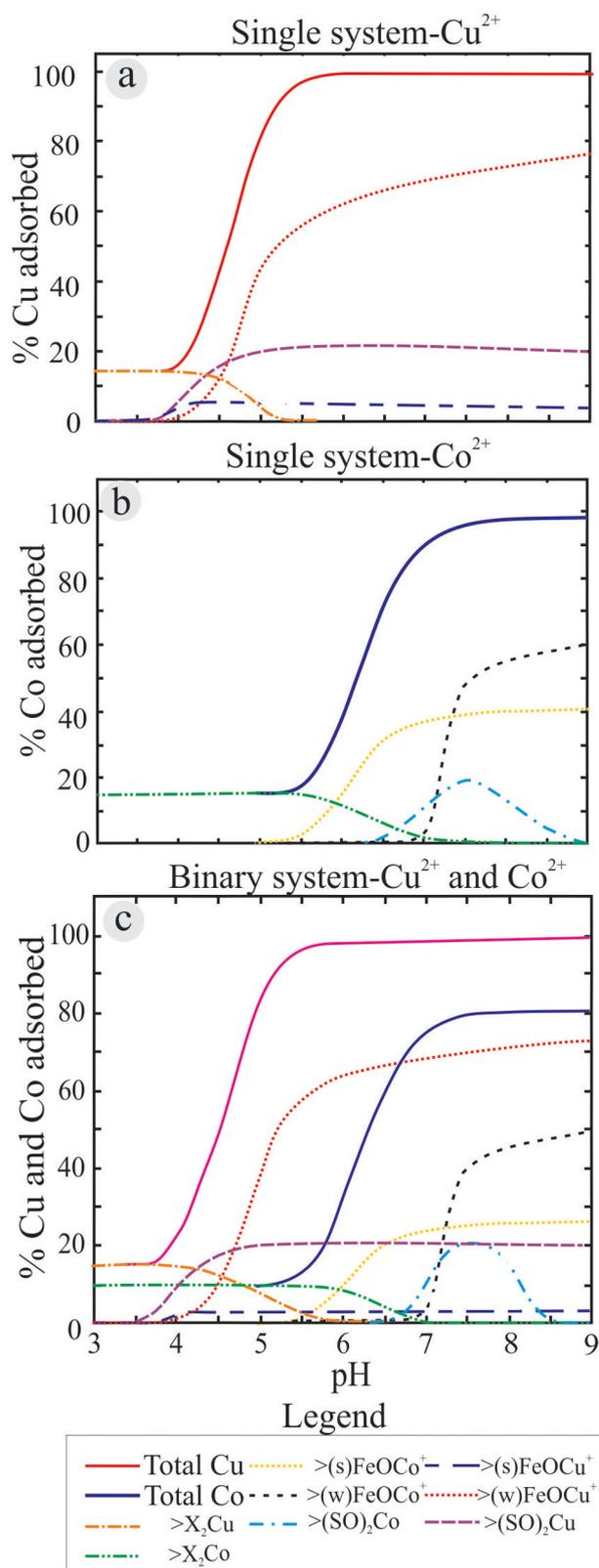


Fig. 9. Model prediction of: (a) Cu adsorption in a single system at 1.10 mM; (b) Co adsorption in a single system at 0.11 mM; (c) Cu and Co adsorption in a binary system at 1.10 mM and 0.11 mM respectively. For all experimental conditions, 0.05 M ionic strength is used. Solid, dotted and dashed lines are SCM predictions onto batch adsorption experimental data (Fig. 8c, d, e).

measured pH_{50} for Cu is pH 5 and Co is pH 6.5. According to Sposito (1984), the lower the pH_{50} , the higher the metal adsorption affinity for sites. Therefore, because of the low pH_{50} for Cu, relatively high concentrations are expected in sludge.

The results of the binary system for sludge with HFO and sludge without HFO are shown in Fig. 8e–f. Minor differences exist between the adsorption behaviours observed between single and binary systems based on the shapes of the adsorption edges. However, the observed behaviour of Co adsorption edge (Fig. 8e) is suggested to be as a result of the possible metal competition for adsorption sites. From these results, the behaviour of the metal towards the host mineral is revealed, and that both pH and the nature of the adsorbent play significant roles in influencing metal adsorption consistent with the previous findings suggested by Spark et al. (1995).

3.7. Metal-binding onto kaolinite - HFO surfaces

In the single system, (Fig. 9a–b), modeling predicts that at low pH conditions, both metals are bound by $>X_2Cu$ and $>X_2Co$ exchange site of kaolinite. The percentages adsorbed for each metal are 15% indicating that without metal competition, individual metal adsorbs equally as outer-sphere complex. With increasing pH conditions, both metals show 20% adsorption at kaolinite sites $>(SO)_2Cu$ and $>(SO)_2Co$ before attaining saturation at pH 5.5 and pH 7.5 respectively. At HFO sites, 70% Cu is adsorbed by the $>(w)FeOCu+$ site at pH 7.5 (Fig. 9a) whereas 40% Co by $>(s)FeOCO+$ and 50% Co by $>(w)FeOCO+$ sites (Fig. 9b) between pH 7–7.5 respectively. In comparison to kaolinite pH-dependent sites, it can be concluded that both metals show some high affinity for HFO sites than kaolinite sites, with Cu still exhibiting a considerably high specific adsorption than that of Co metal.

In a binary system (Fig. 9c), no significant variations in adsorption behaviour is discernible for Cu at both kaolinite and HFO sites. However, significant variation exists for Co at exchange sites and pH-dependent sites. At exchange sites, 10% Co is adsorbed in binary system, a decrease of 5% from that of the single system. At increasing pH, Co adsorption at HFO sites decreased from 40% in a single system to 25% adsorption in a binary system by $>(s)FeOCO+$ between pH 7–7.5. The observed decreases are due to metal competition consistent with other previous studies conducted by Atannasova (1995) and Serrano et al. (2009) in natural soils. From the results of the binary system, it becomes apparent that Co adsorption in the studied sludge is affected by the presence of high Cu concentrations due to the preferential and selectivity adsorption behaviour that Cu tends to exhibit in the presence of other metals with different electronegativity characteristics (Irving and Williams, 1948).

3.8. Interpretation of sequential extraction results by SCM predictions

From the results of SCM predictions (Fig. 9), sequential extraction results (Fig. 7) are interpreted.

From the results of sequential extraction, metal partitioning in F1 fraction translates to between 4 and 11% Cu and 7–13% Co. In a binary system (Fig. 9c), modeling predicts 15% Cu by $>X_2Cu$ and 10% Co by $>X_2Co$ at pH 3–5 and pH 3–6 respectively. The decrease in Co percentages is consistent with the high Cu concentrations at the exchange sites. Besides, the high Cu concentrations, also the high Ca concentrations are reported to compete favorably for exchange sites more than Co (Harter, 1992). Therefore, the presence of high Ca concentrations from the dissolution of lime is expected to also affect Co adsorption in sludge rendering Co metal highly mobile into the environment. Our results between sequential extraction and modeling predictions are well comparable, though some small difference in percentage concentrations could be due to the use of modeling parameters extracted from previous literature data.

In F2 fraction (Fig. 7), metal partitioning at pH-dependent kaolinite site translates to between 46–47% Cu and 35–41% Co respectively. SCM predicts 20% Cu adsorption by $>(SO)_2Cu$ at pH 5.5 and Co

adsorption by $>(SO)_2Co$ between pH 7–7.5 (Fig. 9c). These model predictions are consistent with kaolinite low adsorption characteristics due to the low surface area and low affinity sites (O'Day et al., 1994; Gu and Evans, 2008). The difference in percentage concentrations between the two experimental results (i.e., sequential extraction and model predictions) is suggested to be as a result of metal desorption from loosely or weakly bound HFO sites earlier reported (Fig. 7) and supported by the results of previous study by Essen and El Bassam (1981).

In F3 fraction (Fig. 7), metal partitioning at HFO sites translates to between 46–47% Cu and 35–53% Co. The model predicts 70% Cu adsorption by $>(w)FeOCu+$, and 25% and 50% Co adsorption by $>(s)FeOCO+$ and $>(w)FeOCO+$ sites between pH 7–7.5 (Fig. 9c) respectively. The difference in percentages of model prediction with sequential extraction is that the model assumes that no desorption of metals occurred during the F2 leaching stage. Comparing the results of sequential extraction and model predictions, most metals are loosely or weakly bound to kaolinite and HFO sites, and that they tend to desorb at the acid-soluble leaching stage. Therefore, the reported metal release by sludge on the Zambian Copperbelt is as a result of the dominance in metals concentrations associated with the labile fractions and weakly adsorbed metals onto HFO surfaces.

3.9. Implications for effluent treatment and sludge reuse

Sludge treatment and disposal are an important factor in sludge management practices (Nowak, 2006). Therefore, ways to reduce sludge treatment costs and/or to increase treatment efficiency are an important undertaking. The results of batch adsorption experiment and SCM, adsorption is the main mechanism for metal retention onto sludge surface. The maximum adsorption pH of Cu and Co onto sludge by lime treatment is pH 6.5 and pH 7.5 based on adsorption behaviours (Fig. 8) and SCM predictions (not shown). At optimal pH 7.5, adsorbed metals are stable from release and that the effluent metal concentrations are kept within the regulation standard limits indicated by EPA (2017) and WHO (2006). The advantages of adsorption treatment processes are; (i) relatively low costs and treatment efficiency (Wang and Peng, 2010; dos Reisa et al., 2020) and (ii) low amount of lime dosage to raise the treatment pH condition thereby generating relatively low volumes of sludge unlike the precipitation method conducted in most AMD conditions which require large amounts of lime dosage to attain the metal hydroxide precipitation.

In terms of sludge reuse, knowledge of sludge characteristics and metal partitioning are necessary factors to consider (Zinck, 2005; dos Reisa et al., 2020). In this study, sludge consists of metals adsorbed to kaolinite surface (F1 and F2) and HFO surface (F2 and F3). These host minerals of the metals have previously been studied to be soluble at $pH < 6$ (Chang et al., 1999; Zinck, 2005). From the results of sequential extraction, sludge treatment at $pH < 3$, dissolves into solution the host minerals (i.e. kaolinite and Fe oxides) including the adsorbed metals partitioned in F1, F2 and F3 fraction (Fig. S4). The dissolved metals can then be recoverable through hydrometallurgical treatment processes such as solvent extraction methods at the concentrator (Kinoshita et al., 2003; Tuncuk et al., 2012). The resultant sludge free of many of the metals of concern is thus either safely disposed of or reused. For further research findings in the area of sludge reuse, Levlin (1998) and Zinck (2005) suggested options for the utilisation of sludge as aggregate in construction materials.

4. Conclusion

This paper discussed the geochemical behaviour of heavy metals in sludge effluents on the Zambian Copperbelt. The major findings of the present study are summarized as follows:

1. Sludge effluent treatment with lime decreased the dissolved trace metals and influenced the precipitations of secondary minerals

such as HFO. HFO exists as a coating on surfaces of component minerals such as micas (i.e. biotite and muscovite), kaolinite, and quartz. The oxidations of Fe^{2+} to Fe^{3+} ions from biotite weathering and dissolution are the ultimate source of HFO precipitates.

- Trace metal distribution and partitioning are concentrated in the exchangeable, acid-soluble and reducible fraction. The host mineral in the exchangeable is kaolinite, acid-soluble fraction is both kaolinite and HFO whereas in reducible is dominantly HFO. In the absence of carbonates, this study has revealed that kaolinite show potential to host the metals associated with the acid-soluble fraction through batch adsorption experimental and SCM prediction results. Cu and Co partitioned mostly in the exchangeable and acid-soluble fraction are commonly labile due to the loose or weak binding to kaolinite and HFO sites. Model predicted that Cu show preferential and selective adsorption behaviour onto the adsorption sites more than Co and because of metal competition for limited adsorption sites, most Co is relatively mobile into the environment.
- Sludge treatment with lime is efficient in decreasing the trace metal concentrations at optimal pH 7.5. This optimal pH of treatment was derived from the observed maximum adsorption of metals in a binary system. At this pH condition, metals are stable and below the maximum contamination levels. The adsorbed metals are, however, easily leachable and recoverable after treatment with acid at pH <3. The resultant sludge can be used as a potential aggregate in the field of engineering after further treatment and purification.

CRediT authorship contribution statement

Cryton Phiri: Conceptualization, Investigation, Formal analysis, Writing – original draft. **Daiki Shimazui:** Conceptualization, Investigation, Formal analysis. **Tsubasa Otake:** Conceptualization, Investigation, Formal analysis, Writing – review & editing. **Ryosuke Kikuchi:** Conceptualization, Investigation, Formal analysis, Writing – review & editing. **Isaac Chintu:** Investigation, Formal analysis. **Meki Chirwa:** Investigation, Writing – review & editing. **Lawrence Kalaba:** Investigation, Formal analysis. **Imasiku Nyambe:** Investigation, Formal analysis, Writing – review & editing. **Tsutomu Sato:** Conceptualization, Investigation, Formal analysis, Writing – review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.144342>.

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