

Characterization and Geochemical Modeling of Cu and Zn Sorption Using Mixed Mineral Systems Injected with Iron Sulfide under Sulfidic-Anoxic Conditions I: Case Study of Cwmheidol Mine Waste Water, Wales, United Kingdom

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Abstract—This study investigates sorption of Cu and Zn contained in natural mine wastewater, using mixed mineral systems in sulfidic-anoxic condition. The mine wastewater was obtained from disused mine workings at Cwmheidol in Wales, United Kingdom. These contaminants flow into water courses. These water courses include River Rheidol. In this River fishing activities exist. In an attempt to reduce Cu-Zn levels of fish intake in the watercourses, single mineral systems and 1:1 mixed mineral systems of clay and goethite were tested with the mine waste water for copper and zinc removal at variable pH. Modelling of hydroxyl complexes was carried out using phreeqc method. Reactions using batch mode technique was conducted at room temperature. There was significant differences in the behaviour of copper and zinc removal using mixed mineral systems when compared to single mineral systems. All mixed mineral systems sorb more Cu than Zn when tested with mine wastewater.

Keywords—Cu- Zn, hydroxyl complexes, kinetics, mixed mineral systems, reactivity.

I. INTRODUCTION

COPPER and Zinc ions are major chemical sources of polluted water. These are toxic to aquatic life and are emptied in water systems by acid rock drainage [1]. The metabolism of the human body depends on copper and zinc ions as trace elements. However, excess of these metals could lead to poisoning [1], [2]. Growth reduction is caused by low amount of copper and zinc in humans [3], [4]. Where metal ions accumulate, these can impact humans [5]-[7].

Copper and zinc removal from aquatic systems using systems of minerals are provided [1], [8]. Studies that are available have attempted to characterize copper and zinc sorption related to single mineral-metal interaction [9]. Copper and Zinc sorption characterization has been studied at a limited level with limited modeling involved [1] by interacting simulated wastewater with mixed mineral systems [10], [11]. This paper explores Cu and Zn removal from natural mine wastewater using sulfidic-anoxic mixed mineral systems and

attempts to model the speciation, reactivity and kinetics involved in metal removal [1].

A. Theoretic Concept

Sediments do not fix copper and zinc ions released by various processes into water courses [1], [12]. It is widely known that copper and zinc metals are released into aquatic systems. These are taken out as free species or other forms [13]. The overall adsorption of metal ion depends on the stability of the complex formed [1], [14].

Adsorption is enhanced by ligand possessing high attachment for metal [1], [13]. A complex containing a mineral and ligand is formed when the ligand has a direct affinity that is high for the mineral system [1], [15]. The attitude of reaction sites in the reaction center determines the mineral surface reactivity [1], [16].

Clay and goethite surfaces have the ability to fix copper and zinc ions [1], [17], [18]. Process of complexation depends on the colloidal fractions of mineral systems [19].

Clay and oxide mineral surfaces consist of silanol (SiOH) and aluminol (AlOH) sites [20]. The charge distribution determines the reactivity of these sites. Furthermore, the reactivity of these sites is a function of the metal involved in the reaction process [14]. At higher pH, some of the reactive sites carry lower interaction energy sites. Therefore, mineral mixing of clay and goethite could attenuate reaction [21].

Under oxic condition, these metals are removed from solution [22]. Complex stability are in the order $Zn > Cu$.

Solution ionic species are impacted by complexes [1]. The presence of dissolved species, lowers the effective concentration of metals by precipitation [23].

The formation of complexes reduces the removal of Zn ions in solution [24], [25]. However, ligands formed by these ions are not stable [26], [27].

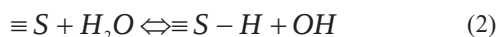
Hydrolysis is considered to be a more realistic reaction mechanism in metal removal when compared with ion exchange [28], [29]. Pyrite surface charge can be governed by protonation-deprotonation reactions of the surface S groups as provided:



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S or Fe sites of reactions are involved in decomposition of water and hydration [1], [30], leading to release of protons in solution as provided:



The main objective of this work is to characterize and model effects of mineral mixing under sulfidic-anoxic condition in the removal of Cu and Zn contained in mine wastewater.

II. STUDY SITES

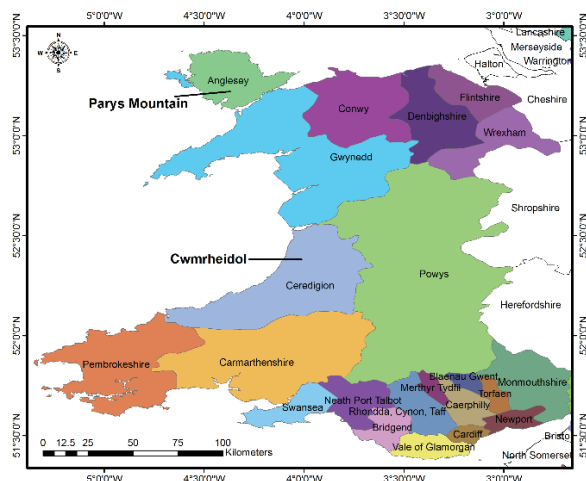


Fig. 1 Location map of study sites in Wales [1]

Mine at Parys Mountain in Wales provided the waste water used in this study. Cwmrheidol was a component source of these mine water [1] as provided in Fig. 1. Discharges of mine wastewater from both mines contain Cu and Zn. These contaminants flow into water courses such as River Rheidol in Mid Wales where commercial and local fishing activities exist. The study sites consist of Cu-Zn lode embedded in volcanic and metamorphic rock sequence. These are highly fractured rocks [31]-[34]. Mine tailings consist of residual minerals derived from these rocks [35], [36]. Sources of wastewater discharged to receiving watercourses are derived from abandoned mine workings [37].

III. MODELING OF CU AND ZN SORPTION

A. Empirical Modeling of Cu and Zn Sorption

Coefficient of distribution (Kd) formed the empirical model used in this paper [1], [11]. Kd (L/Kg) was calculated from the Freundlich model equation provided:

$$S = KdC^N \quad (4)$$

In (4), S or Q represents amount of metal removed (mg/kg), coefficient of distribution is represented by Kd (L/Kg), equilibrium amount in solution (mg/L) is represented

by C, and coefficient of chemical -specific is represented by N [1], [34]. Due to the low range of metal concentration used in this study adsorption isotherms were of the C type, resulting in linear isotherms. The empirical model as provided by [10] to address the mineral-metal interactions is given:

$$Kd_{total} = \frac{Kd_1 + Kd_2 + Kd_n}{n} \quad (5)$$

where Kd_{total} is the theoretical distribution coefficient for a 1:1 mixed system, Kd_1 is the distribution coefficient for first single mineral system, and Kd_2 is the distribution coefficient for second single mineral system, Kd_n is the distribution coefficient for n number of mineral systems and n is the number of mineral systems. Removal of copper and zinc by mixed mineral surfaces is governed by the following empirical model:

1. There is limited development of significant secondary mineral systems by the mixed mineral systems especially at alkaline pH.
2. Components of minerals in the mixed mineral systems act as individual networks and not as chemisorbed species.

B. Phreeqc Modeling of Hydroxyl Complex Speciation

TABLE I
PHREEQC MODELING INPUT FOR MINERAL SYSTEMS

Solution parameter (mmol/Kgw)	
pH	2-8
Temperature (°C)	23°C
FeS	0.00569
Cwmrheidol mine waste water	
Zn	0.0478
Cu	0.0015
SO4	0.0331

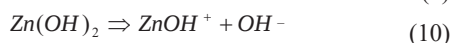
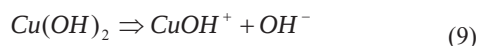
The geochemical modeling software package PHREEQC was used to simulate the mine waste water containing FeS at variable pH [38]. The PHREEQC model allows the basic mixing chemistry and secondary mineral formation as well as surface complexation reactions. In this study, only the basic mixing chemistry, dissolution of minerals and secondary mineral formations were considered as a possibly occurring reaction. Although the applied major reaction process was limited to the sorption processes, this approach may be reasonable to apply because the modeled systems are known to be essentially controlled by sorption process. The PHREEQC modeling input and chemical composition in each system is summarized in Table I. All simulations assumed equilibrium chemistry.

The degree of saturation (D_s) for the presumed complexes $Cu(OH)_2$ and $Zn(OH)_2$ is related to the Ion Activity Product (IAP) and the conditional solubility constant (K_{sp}) as:

$$IAP \equiv [M_2 + [OH]_2] \quad (6)$$

$$D_s \equiv \frac{IAP}{K_{sp}} \quad (7)$$

$$SI \approx \log IAP - \log K_{sp} \quad (8)$$



IV. MATERIALS AND METHODS

Log DS is the Saturation index (SI) where $\text{SI} < 0$ the system is under-saturated with respect to the complex; $\text{SI} = 0$, system is saturated to the complex; $\text{SI} > 0$, system is supersaturated with respect to the complex; and where M^{2+} is the metal molar concentration and H^+ is system pH [39].

A. Preparation of Sulfidic-Anoxic Iron Sulfide System

Sulfidic-anoxic conditions are characterized by depletion of dissolved oxygen. These conditions will occur if the rate of oxidation is greater than the supply of dissolved oxygen [40]. In sulfidic-anoxic environment, hydrogen sulfide occurs as a product of sulfate and sulfide reduction [41]. In this study, 1% acidified iron sulfide sulfidic-anoxic system was prepared using deoxygenated deionized water. Purified nitrogen gas was bubbled through the iron sulfide system continuously for 24 h. The content, securely sealed was stored in airtight containers in the anaerobic chamber in dark environment before use. The formation of hydrogen sulfide was prototypically characterized by a “rotten egg” odor [42]- [45].

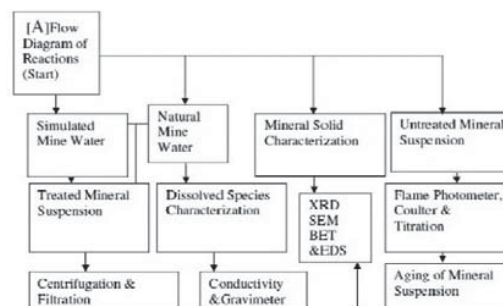


Fig. 2 Flow diagram of experimental studies.

TABLE II
CHARACTERISTICS OF NATURAL MINE WASTEWATER

Location	pH	Conductivity (ms/cm)	TDS (mg/L)	Salinity (g/L)	Cu (mg/L)	Zn (mg/L)	SO ₄ (mg/L)
Cwmheidol SN131782	3.70	1.69	970.00	0.97	4.76	156.00	159.00
Parys Mt SN443907	2.50	2.60	1526.00	1.50	76.07	165.00	1234.00

TABLE III
CHARACTERISTICS OF CLAYS, GOETHITE [5], [6] AND IRON SULFIDE

Mineral systems	Particle size (μm)	% colloid ($<1\mu\text{m}$)	pH $\pm \delta$	Specific Surface Area $\pm \delta$ (m^2/g)	Point of Zero Salt Effect $\pm \delta$
Kaolinite	20.5	3.00	6.05 ± 0.05	47.01 ± 0.24	7.01 ± 0.15
Montmorillonite	80.05	0.53	2.01 ± 0.09	10.00 ± 0.00	7.16 ± 0.20
Goethite	40.10	2.92	8.05 ± 0.06	71.05 ± 0.17	7.50 ± 0.08
Kaolinite/Montmorillonite	80.05	0.97	5.01 ± 0.02	88.05 ± 0.55	4.30 ± 0.21
Montmorillonite/Goethite	15.25	3.85	3.03 ± 0.04	147.10 ± 0.50	4.30 ± 0.04
Kaolinite/Goethite	140.35	0.73	3.05 ± 0.01	79.30 ± 0.59	4.70 ± 0.13
Iron sulfide	80.20	4.729	4.02 ± 0.03	2.00 ± 0.00	4.5 ± 0.04

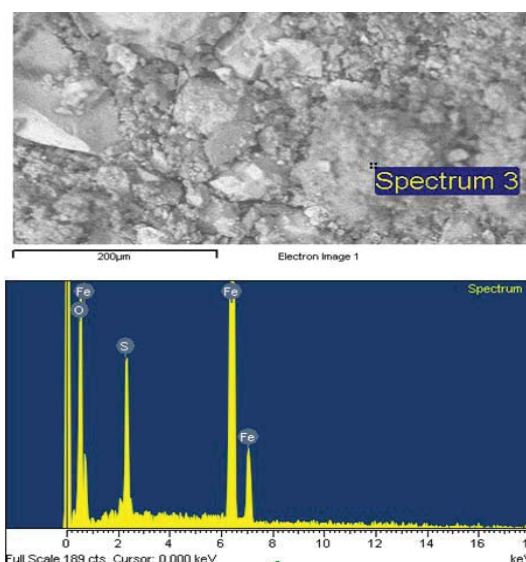


Fig. 3 Scanning electron microscopy and energy dispersive spectroscopy /of iron sulfide

TABLE IV
PROTON COEFFICIENTS (α) AND REGRESSION COEFFICIENT (R) OF CU AND ZN
SORBED ON MINERAL SYSTEMS

Sorbate	Cu			Zn		
Mineral systems	R	α	α_{total}	$\alpha - \alpha_{total}$	α	α_{total}
Iron sulfide	0.99	1.180	*	*	1.128	*
Kaolinite	0.99	1.374	*	*	1.265	*
Goethite	0.99	1.612	*	*	1.281	*
Montmorillonite	0.99	1.354	*	*	1.223	*
Kaolinite/ Montmorillonite	0.99	1.201	1.364	-0.164	1.107	3.39
Goethite/ Kaolinite	0.99	1.192	1.493	-0.302	1.120	1.27
Goethite/ Montmorillonite	0.99	1.348	1.483	-0.135	1.161	1.25

Note: * not applicable

TABLE V
CU AND ZN SORBED ON MINERAL SYSTEMS AT PH 4

Mineral systems	Cu(mmol/g)	Zn(mmol/g)
Iron sulfide	3.33	3.32
Kaolinite	9.60	9.46
Goethite/kaolinite	8.80	8.76
Kaolinite/montmorillonite	8.85	8.66
Montmorillonite	9.56	9.46
Goethite/montmorillonite	9.54	8.88
Goethite	9.51	9.36

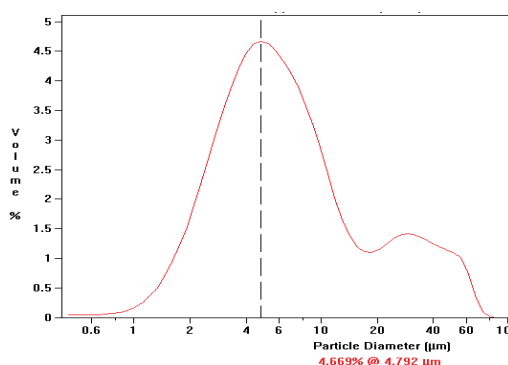


Fig. 4 Particle size distribution curve of iron sulfide

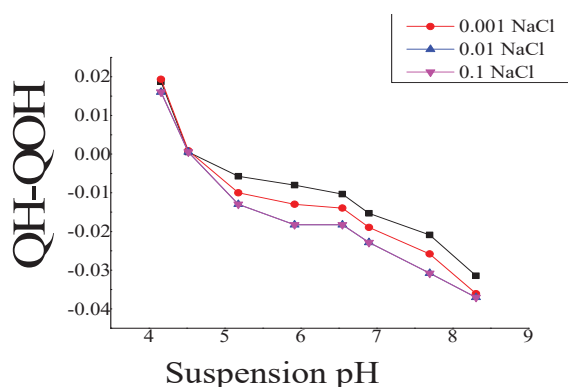


Fig. 5 Potentiometric titration curves of Iron sulfide as a function of pH at different ionic strengths. QH= concentrated acid and QOH= concentrated base [PZSE = 4.5]

B. System Characterization

Characterization and modeling are presented (Figs. 2-7) and (Tables I-VI). The batch mode reactions: experimental design for Cu and Zn sorption by mineral systems is presented in this paper (Fig. 2). Details of characterization of minerals used and experimental methods and the characteristics of the mine wastewater is provided (Figs. 2 and 4) and (Tables I-III).

All solutions were prepared using de-aerated and deionized water. This water was prepared by bubbling purified nitrogen gasthrough deionized water for at least 24 hours. Deionized water was obtained from a Millipore Milli-Q system. Then the water was purged overnight in an anaerobic chamber containing a mixture of 5% hydrogen and 95% nitrogen gases.

Clays and iron sulfide used in this study provided by the Richard Baker Harrison Company and Acros Organics Ltd and goethite provided by Iconofile Company Inc. were nitrogen flushed and stored in airtight containers in the anaerobic chamber before use to avoid oxidation. Particle sizes was determined by Coulter laser method. Curves of particle size distribution were used to determine % colloid. Jenway ion meter was used to determine pH. Surface areas was determined using Brunauer, Emmett, and Teller (BET) [1], [46], [47]. cation exchange capacity was determined using saturation methode (Table I). Scanning electron microscopy, energy dispersive spectroscopy was used to perform spectral analyses. Identification of mineral was done by X-Ray diffraction techniques [1], [10], [11], [48], [49], (g) Cu and Zn concentrations in the mineral samples were determined using ICP-OES (Table I).

C. Reactivity Experiments

Reactivity and removal kinetics were studied at room temperature (23 ± 2 °C). For reactivity studies, standard laboratory procedure [47], [48] was used to determine the proton coefficient (1) -(2). 1% sulfidic-anoxic system of iron sulfide was added to 1% single and 1:1 mixed mineral systems with no added electrolyte made up to 50 ml of mine wastewater containing 4.76 ppm Cu and 156 ppm Zn. These solutions contained zero added electrolyte. 0.1 M HNO₃ and 0.1 M NaOH were used to adjust the pH. pH was measured using a Model 3340 Jenway ion meter. This was after equilibration for 24h.

For each experiment, the amount of metal removed (S) in mgkg⁻¹ was calculated from the difference between C_i and C_e as provided [1] :

$$Q_e = (C_i - C_e) \frac{V}{W} \quad (11)$$

where S or Q represents amount of metal removed (mg/kg). This was calculated from initial metal amount in solution C_i and the amount of metal in solution after its removal C_e. V_i is the system volume and W is the mass of mineral solid. The amount of metal remaining in the filtrate was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Results were used to compare with the amount of surface reactive sites involved in sorption under similar

conditions of pH and solute concentrations (Fig. 1). Based on preliminary experiments, difference in molar concentration between Cu and Zn over the range of metal concentration (mg/L) used in this study was not sufficient to statistically (χ^2) significantly affect the distribution coefficient ($P \leq 0.01$).

For the surface charge, potentiometric titrations at zero added electrolytes with 0.001, 0.01, and 0.1 M ionic strength

were carried out using 1% by mass mineral systems and references containing 1:1 electrolyte solution. After purging and equilibration, pH differences between the references and the mineral systems were measured and the data used to construct titration curves after [10] for point of zero salt effect (PZSE).

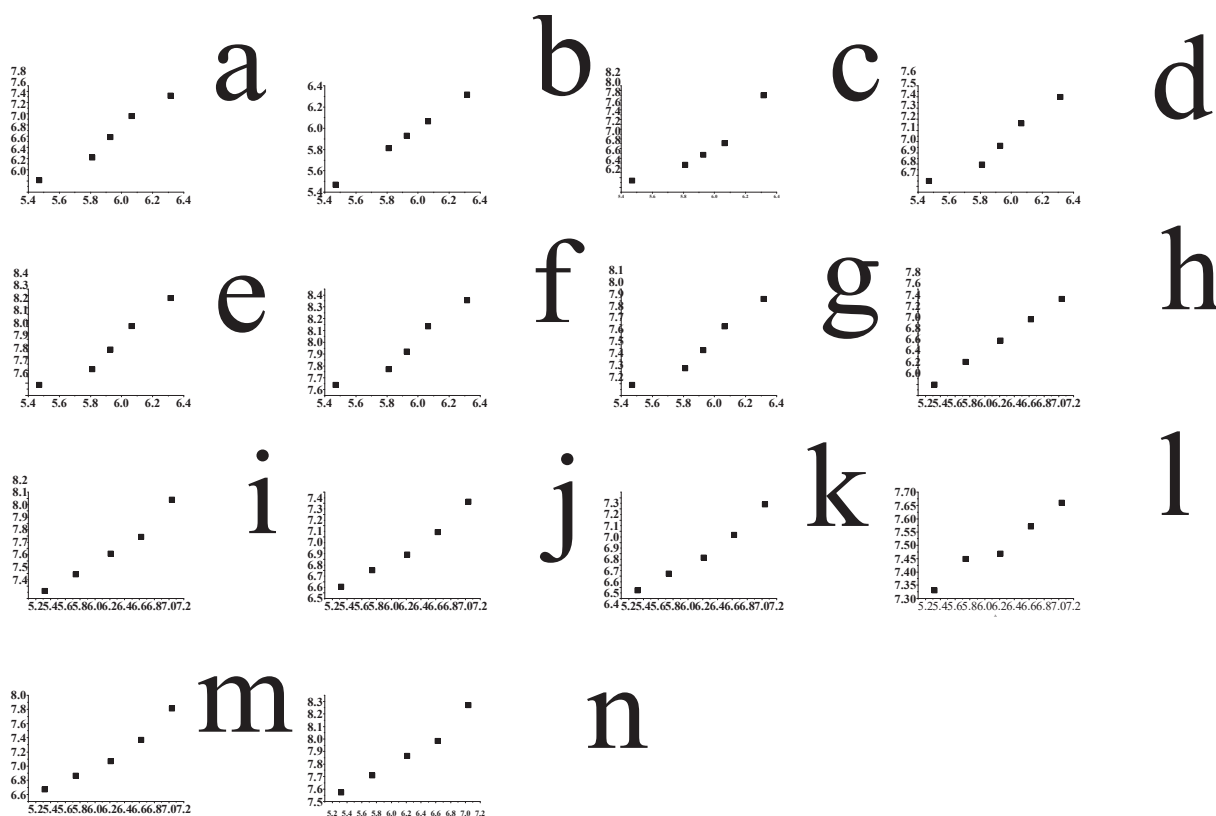


Fig. 6 Plots of $\log K_d$ versus final pH for Cu sorbed on sulfidic anoxic mineral systems x-axis representing final pH and y-axis representing $\log K_d (L/Kg)$: (a) Iron sulfide, (b) kaolinite, (c) goethite/kaolinite, (d) kaolinite/montmorillonite, (e) montmorillonite, (f) goethite/montmorillonite, (g) goethite and Zn sorbed on sulfidic-anoxic mineral systems: (h) Iron sulfide, (i) kaolinite, (j) goethite/kaolinite, (k) kaolinite/montmorillonite, (l) montmorillonite, (m) goethite/ montmorillonite/ (n) goethite

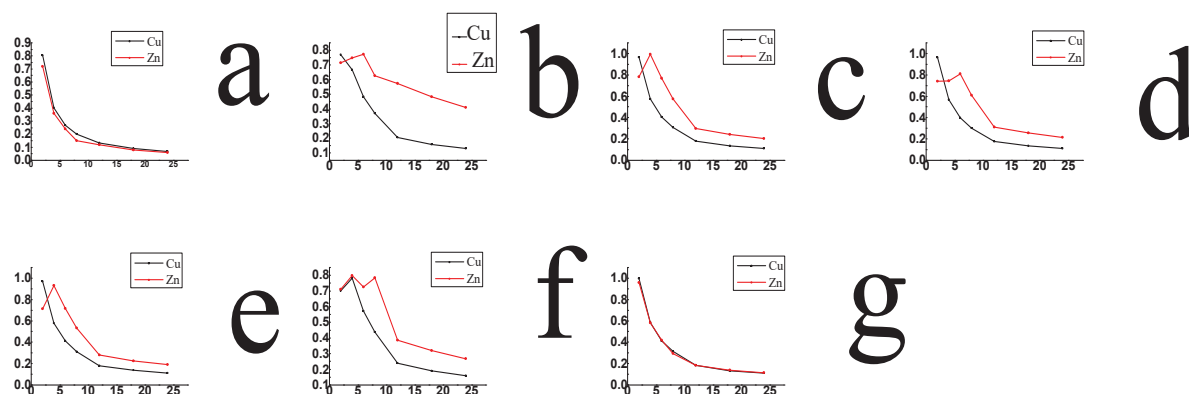


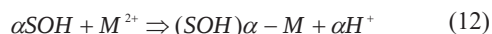
Fig. 7 Plots of C_t/C_0 (y-axis) versus residence time (Hours) [mass transfer rates] (x-axis) for Cu and Zn sorbed on: (a) kaolinite; (b) montmorillonite; (c) goethite; (d) kaolinite/goethite; (e) goethite/montmorillonite; (f) kaolinite/montmorillonite, (g) Iron sulfide mineral systems

TABLE VI
MASS TRANSFER RATES FOR MINERAL SYSTEMS

Mineral	Metal	Slope I (hr ⁻¹)	SlopeII (hr ⁻¹)	SlopeIII (hr ⁻¹)	Exposed Surface Area(cm ⁻¹)	KfI(cmhr ⁻¹)	KfII(cmhr ⁻¹)	KfIII(cmhr ⁻¹)
Iron sulfide	Cu	8.73e-4	*	*	200	4.36e-6	*	*
Iron sulfide	Zn	4.70e-4	*	*	200	2.35e-6	*	*
Kaolinite	Cu	4.32e-2	2.69e-2	2.70e-4	4700	9.19e-6	5.72e-6	5.75e-6
Kaolinite	Zn	0.0233	0.028	1.45e-4	4700	4.96e-6	5.96e-6	3.09e-8
Montmorillonite	Cu	.081	0.064	0.048	1000	2.43e-4	9.72e-5	2.02e-5
Montmorillonite	Zn	0.0790	0.067	0.0468	1000	6.7e-5	6.7e-5	4.68e-5
Goethite	Cu	2.42e-2	4.06e-3	8.40e-3	7100	3.40e-6	5.72e-7	1.18e-6
Goethite	Zn	0.0605	0.0102	0.0211	7100			
Kaolinite/Montmorillonite	Cu	3.35e-2	0.02	0.020	8800	3.81e-6	2.27e-6	2.30e-6
Kaolinite/Montmorillonite	Zn	0.075	0.049	0.0448	8800	8.52e-6	5.57e-6	5.09e-6
Kaolinite/Goethite	Cu	1.78e-2	1.35e-2	1.43e-2	7900	2.26e-6	1.71e-6	1.80e-6
Kaolinite/Goethite	Zn	0.0254	0.020	0.0204	7900			
Montmorillonite/Goethite	Cu	2.42e-2	1.46e-2	1.47e-2	14700	1.64e-6	9.92e-7	1.00e-6
Montmorillonite/Goethite	Zn	0.323	0.02044	0.195	14700	2.20e-5	1.39e-6	1.33e-5

Note: * Not applicable

Surface charges govern the sites of reactions at surfaces of minerals [49]. Sorption of Cu and Zn on mineral surfaces requires proton exchange, the stoichiometry of this reaction is described and the proton consumption function is provided:



$$\text{LogKd} = \log \text{Kp}(\text{SOH})\alpha + \alpha\text{pH} \quad (13)$$

where SOH is the mineral surface-binding site, M^{2+} is the soluble metal species, $(\text{SOH})\alpha - \text{M}$ is the surface bound metal, $\log\text{Kp}$ is the apparent equilibrium binding constant, and α is the proton coefficient, representing the number of protons displaced when one mole of metal binds to the mineral surface [50]. Proton coefficient was calculated from the slope of $\log\text{Kd}$ versus pH plot (Fig. 6).

D. Kinetic Experiments

1% sulfidic-anoxic system of iron sulfide was added to 1% single and 1:1 mixed mineral systems, reacted with mine wastewater containing 4.76 ppm Cu and 156 ppm Zn at pH 4 and variable contact time. Amounts metal remaining in solution after 2, 4, 6, 8, 12, 18, and 24 h were determined using ICP-OES. Twenty-four hours was sufficient for kinetic studies because sorption reactions occur in milliseconds or minutes [10], [11], [51]-[56].

The transport of adsorbate from external layers to the mineral surface where sorption occurs is dependent on a mass transfer constant K_f obtained from the slopes of the curve derived from plotting C_t/C_0 versus time (Fig.7).

$$\left[\frac{d(C_t/C_0)}{dt} \right]_{t=0} \cong -K_f S_s \quad (14)$$

where C_0 is initial metal concentration (mg/l) at time $t = 0$; C_t is metal concentrations (mg/l) at time t , S_s is the exposed external surface area of the sorbent, and K_f is the mass transfer coefficient [57], [58]. A higher inverse of K_f suggests greater sorption. The Freundlich isotherm was chosen to describe sorption of Cu and Zn because this is suitable for

heterogeneous surfaces over a wide range of solute concentrations [59], [60].

At the end of equilibration, systems were shaken and centrifuged at 3000 rpm for 15 min and passed through a 0.45- μm filter to remove suspended solids. The amount of metal remaining in solution was then determined. In all experiments conducted, each treatment had three replicates and the differences in replicate runs were not statistically significant ($P \leq 0.01$).

V. RESULTS AND DISCUSSION

A. Mineral Systems and H^+/M^{2+} Exchange Stoichiometry

Although the proton coefficient (α) is not characteristic of a particular mineral (Table IV) and (Fig. 7), subtle differences between the α for the single and mixed mineral phases expressed as differences between the actual α and the theoretical α (α_{total}) may be linked to differences in the availability of strongly thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and acidic reactive sites.

In previous study [10], the proton coefficient of kaolinite for Zn sorbed is slightly higher than Zn sorbed on goethite and Al-montmorillonite, being attributed to the acidic sites present on kaolinite planar surface. Significant numbers of weakly acidic edge sites in goethite and Al-montmorillonite may reduce the proton coefficient because of the limited exchange of protons for sorbing ions. In this study, proton coefficient for Cu is higher than that of Zn for all mineral systems investigated.

Theoretical proton coefficient for Cu and Zn is higher than predicted for all mixed mineral systems. This means that mineral mixing under sulfidic-anoxic condition reduces the exchange of protons for sorbing ions. The higher the acidity of sites the more protons are exchanged for Cu and Zn. Therefore, mineral mixing reduces the acidity of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and acidic reactive sites. This may be attributed to the competition for the sorbing ion by the mixed mineral surfaces as reported elsewhere [10].

The H^+/M^{2+} exchange stoichiometry of <2 for Cu and Zn sorption on both the single and mixed mineral phases agrees

with the findings of [10], [49] for divalent cations sorbed on (hydr)oxides. In this study H^+/M^{2+} exchange stoichiometry is higher and still <2 . This suggests that surface charges become increasingly positive as metal sorption takes place. Furthermore, mineral surfaces with few displaceable H^+ where the pH-dependent sorption is limited, support lower H^+/M^{2+} stoichiometry. Under sulfidic anoxic condition, sulfidic solutions are complex and multiple valence states, of sorbing ions may exist and precipitation may occur.

B. Mineral Systems and Cu-Zn Removal

Previous study reported PZSE of the single mineral systems higher than those of the mixed mineral systems [10]. In this study, iron sulfide used in the preparation of the sulfidic anoxic mineral system possesses PZSE of 4.5. The equilibrium pH (except for goethite) of the single mineral systems and the mixed mineral systems of kaolinite/goethite, and montmorillonite/goethite were below their PZSE, suggesting that they have little capacity to sorb Cu and Zn by electrostatic attraction. The lower PZSE of mixed mineral systems when compared with the single mineral systems may be attributed to the permanent and pH-dependent charges of the mixed mineral systems.

Previous study [10] showed that the amount of Cu sorbed on kaolinite and montmorillonite was (a) lower than the CEC for metal sorbed on kaolinite and montmorillonite at 0.01M ionic strength and (b) equal to the CEC for metal sorbed on kaolinite at 0.1 M ionic strength and Zn sorbed on montmorillonite at 0.1 M ionic strength. In the present study under sulfidic-anoxic condition, Cu sorbed on all mineral systems is higher than Zn (Table V).

These suggest that Cu and Zn removal involves simple ion exchange, as reported elsewhere [61]. This is based on the reasoning that where sorption involves both electrostatic and specific attraction, sorption of sorbing ions could exceed the number of net proton surface sites; otherwise, sorption could be less or near equal to the number of available reactive surface sites. This agrees with the suggestions of on surface charge effects on heavy metal sorption on soil systems [62].

C. Mineral Systems and Sorption Kinetics

In previous study, (i.e. in the absence of iron sulfide) [10] Cu sorbed on kaolinite mineral system displayed higher first order diffusion rate (K_{fI}) than Zn during the fast reaction process. The reverse was the case for goethite and montmorillonite displaying similar transfer rate patterns for both Cu during the fast and slow reaction phases. In the present study under sulfidic –anoxic condition, diffusion or mass transfer rate is in the order: montmorillonite > kaolinite > Iron > sulfide > goethite for the single mineral systems and kaolinite-montmorillonite > kaolinite-goethite > montmorillonite for the mixed mineral systems (Table VI and Fig. 8). Second mass transfer rate K_{fII} is in the order: montmorillonite > kaolinite > iron sulfide > goethite for the single mineral systems and the order: kaolinite-montmorillonite > kaolinite-goethite > montmorillonite-goethite. Third mass transfer rate is in the order: kaolinite > montmorillonite > goethite.

Theoretical mass transfer rates are in the order: $K_{fI} > K_{fIII} > K_{fII}$ for kaolinite-montmorillonite and kaolinite-goethite, and $K_{fII} > K_{fIII} > K_{fI}$.

This means that the predicted mass transfer rates are higher for mixed mineral systems of kaolinite-montmorillonite and kaolinite-goethite i.e. mineral mixing reduces metal transfer relative to the single mineral systems in all reaction phases.

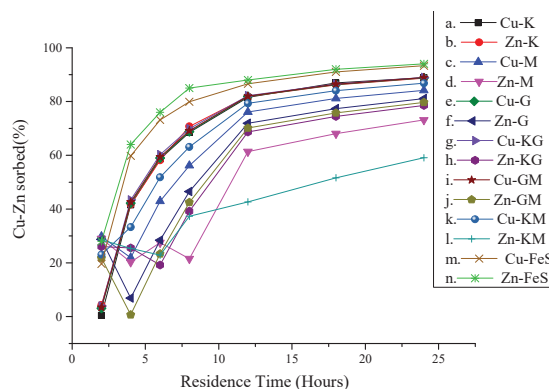


Fig. 8 Plots of Cu-Zn sorbed (%) vs. contact time (hours): (a) Cu-kaolinite, (b) Zn-kaolinite., (d) Cu-montmorillonite, (e) Cu-goethite., (f) Zn-goethite., (g) Cu-kaolinite/goethite., (h) Zn-kaolinite/goethite., (i) Cu-goethite/montmorillonite., (j) Zn-goethite/montmorillonite., (k) Cu-kaolinite/montmorillonite., (l) Zn-kaolinite/montmorillonite., (m) Cu-iron sulfide., (n) Zn-iron sulfide, sulfidic-anoxic systems

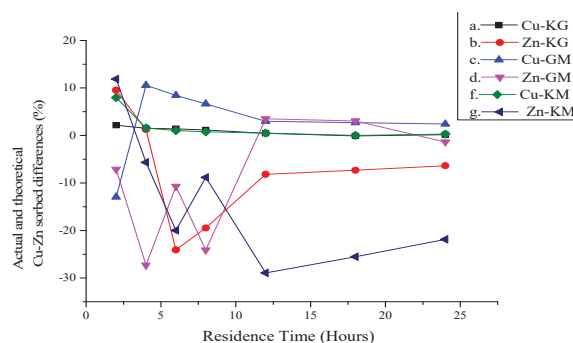


Fig. 9 Plots of actual and theoretical Cu-Zn sorbed differences (%) vs. contact time (hours): (a) kaolinite/goethite; (b) goethite/montmorillonite; (c) kaolinite/montmorillonite sulfidic-anoxic systems

Except for Zn sorbed on kaolinite-montmorillonite and montmorillonite, Cu-Zn removal increase at the onset of sorption plateauing out after 12h residence or contact time. Differences between the sorption kinetic patterns of the single and mixed mineral systems as depicted by differences between the actual and theoretical percent sorption (Fig. 9) exhibit complex relationship. Zn sorbed on kaolinite-montmorillonite and kaolinite-goethite is positive at the onset of sorption becoming negative overtime. Cu sorbed on goethite-montmorillonite was negative at the onset of sorption, becoming positive overtime. Differences in Cu sorbed on kaolinite-montmorillonite do not reflect significant change overtime. This suggests that under sulfidic anoxic condition,

sorbing ions on mixed mineral systems are different at the onset of sorption but become like those of the single mineral components over time, cross-cutting each other overtime. Differences in mass transfer rates may be attributed to differences in the external surface areas of the mixed mineral systems and the complex behavior of these metals under sulfidic-anoxic condition.

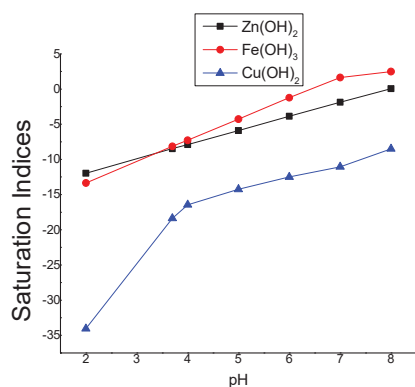


Fig. 10 Plot of saturation indices versus pH, Saturation Indices of Hydroxyl Complexes

Speciation of the mine wastewater with respect to copper hydroxide and zinc hydroxide indicated under-saturation to these hydroxide species at all pH investigated (Fig 10). Saturation indices increases with pH over the range of pH investigated. Iron hydroxide is under saturated at lower pH, becoming super-saturated between pH7-8.

Speciation for these hydroxyl complexes are in the order $\text{Fe}(\text{OH})_3 > \text{Zn}(\text{OH})_2 > \text{Cu}(\text{OH})_2$ and are pH dependent. Complexes of iron hydroxide and zinc hydroxide cross cut at pH 4 indicating similar saturation indices for these complexes. Neither Cu nor Zn appears to form stable hydroxyl complexes. An alternative explanation could be that Cu and Zn hydroxyl complexes were formed but became destabilized over time due to hydrolysis.

VI. CONCLUSION

- In this work the results of experimental characterization and modeling for Cu and Zn removal from Cwmheidol mine wastewater are presented.
- The experiments were performed in a laboratory using different mixed mineral systems injected with sulfidic-anoxic iron sulfide mineral system.
- The model isotherm used in predicting the reactions and kinetics of Cu and Zn are discussed.
- The results obtained from the modeling are compared with previous study in the absence of sulfidic-anoxic condition.
- This work demonstrates the possibility of using empirical models to characterize complicated effects of Cu and Zn interaction with mixed mineral systems under sulfidic-anoxic condition.

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