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Evaluation of the Potential for Acid Mine Drainage Formation From Pit Lake Walls and its Interaction with the Aquifer System

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Abstract: Pit lakes are water bodies that gradually accumulate in former open-pit mine excavations once mining operations have ceased, typically filled by rainfall, surface runoff, or infiltration from groundwater. Their existence can pose environmental challenges, particularly the development of “acid mine drainage (AMD)”, which is often indicated by low pH values and elevated levels of dissolved metals. This research focuses on evaluating the geochemical properties of pit wall rocks and the water quality within pit lakes in the Separi coal mining region of East Kalimantan. The objective is to determine the likelihood of AMD generation and assess whether contaminants may migrate into the surrounding groundwater system. Field sampling involved collecting materials from pit wall rock, water within the pit lake, adjacent surface water, and groundwater monitoring wells. Mineralogical analysis was performed using X-Ray Diffraction (XRD), while elemental composition was identified through X-Ray Fluorescence (XRF). Water quality parameters such as pH, total dissolved solids (TDS), electrical conductivity, and concentrations of metals—specifically iron (Fe) and manganese (Mn)—were measured using Atomic Absorption Spectroscopy (AAS) and ion chromatography techniques. The findings reveal that several rock samples fall into the Potentially Acid Forming (PAF) category, attributed to their low acid-neutralizing capacity and elevated sulfur content, especially in samples containing pyrite. The pit lake water was found to be acidic (pH 4.2–4.6), with high levels of Fe and Mn, suggesting active sulfide oxidation. Conversely, groundwater from nearby areas displayed more neutral pH values (5.4–6.4) and lower metal concentrations, although some locations still showed contamination risks. These results underscore the need for a comprehensive understanding of geochemical processes and highlight the importance of preventive strategies, such as isolating reactive materials, managing hydrological inputs, and consistently monitoring water quality for long-term environmental protection.

Keywords: AMD; Groundwater quality; Pit lake

Introduction

Pit lakes typically develop in former open-pit mine areas after mining operations have ended and the site is left unused (Padhye et al., 2023). Once mining ceases, these excavated areas begin to accumulate water from various sources, including rainfall, surface runoff, and groundwater (Ojonimi et al., 2021). The speed and volume of water filling the pit depend on several local hydrogeological factors, such as the permeability of surrounding rock layers, their connection to groundwater aquifers, and regional rainfall patterns (Rinder et al., 2020). As these lakes fill, they can form either open systems, which allow interaction and water flow with the surrounding environment (Druschel et al., 2004), or closed systems, where water collects with little

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to no exchange (Muellegger et al., 2013). These system types significantly influence the lake's water chemistry, which is further shaped by geochemical reactions within the exposed pit walls (Acharya et al., 2020). Numerous researchers have explored different elements of pit lakes, such as the geochemistry of their formation, the movement of water in and out of them, and the broader environmental implications (Sánchez-España et al., 2014). For instance, Tuheteru et al. (2021) analyzed how variations in hydrogeological settings affect both the rate of water recharge and the quality of water in pit lakes. Castendyk et al. (2015), emphasized the role of rock permeability and aquifer connections in influencing recharge dynamics and potential groundwater interactions. Marques et al. (2012) focused on how the distinction between open and closed systems can impact the water's chemical composition and the risk of contamination (Gautama et al., 2014). Additionally, Muellegger et al. (2013) warned of possible pollution from pit lakes, especially in cases where contaminated water seeps into nearby aquifers, posing a risk due to toxic metals or abnormal pH levels (Anawar, 2015).

Weathering reactions within the wall rocks of pit lakes play a significant role in shaping water chemistry by releasing various dissolved substances. The oxidation of sulfide minerals particularly pyrite (FeS_2) is a well known process that can result in "acid mine drainage (AMD)", marked by acidic conditions and elevated levels of heavy metals (Acharya et al., 2020). In contrast, the presence of carbonate minerals within the geological matrix can provide a buffering effect, mitigating acidity (González et al., 2018). As a result, the chemical profile of pit lake water is closely tied to the mineralogical composition of the surrounding rock (Banerjee, 2014). Understanding the interactions between pit lake water and nearby groundwater is critical in hydrogeochemical investigations, particularly because seepage from the lake into aquifers may lead to contamination (González et al., 2018). Key variables such as rock permeability, hydraulic gradients, and concentrations of dissolved elements in the lake water must be evaluated to assess potential environmental risks (Castendyk et al., 2015). As equilibrium develops between pit lake water and adjacent aquifers (Thomas et al., 2023), two primary flow scenarios may emerge (Trettin et al., 2007). If the hydraulic head in the lake exceeds that of the surrounding groundwater, the lake can act as a recharge source, allowing water and potentially contaminants to migrate into the aquifer (Moreno-González et al., 2022). Conversely, if the groundwater has higher hydraulic pressure, it can flow into the lake, transporting dissolved minerals that alter the lake's chemical balance (Peng et al., 2019). The direction and intensity of this exchange are governed by factors such as the permeability of geological materials, fracture networks, and differences in hydraulic head (Newman et al., 2020). In certain situations, leakage of polluted water from pit lakes particularly those with high metal concentrations or extreme pH can adversely affect nearby ecosystems (Denimal et al., 2005).

A thorough understanding of the mechanisms behind "acid mine drainage (AMD)" formation is essential for preventing environmental degradation in pit lakes. AMD arises when sulfide minerals come into contact with oxygen and water (Z. Wang et al., 2020), resulting in the generation of sulfuric acid, which subsequently mobilizes heavy metals from the surrounding rock matrix (Acharya et al., 2020). This chemical process produces a toxic mixture that poses a threat to water quality and aquatic ecosystems (Johnson et al., 2003). Consequently, investigating the pathways of sulfide oxidation is crucial for developing effective mitigation strategies aimed at minimizing its adverse effects (Okibe et al., 2004). Previous research Favas et al. (2016) has demonstrated that the oxidation of sulfides significantly contributes to the acceleration of AMD formation and leads to increased concentrations of metals in pit lake water. Findings from Fuentes-López et al. (2022) indicate that carbonate minerals can counteract acidity to some extent, though the neutralization capacity depends on the relative abundance of carbonate to sulfide minerals (Das et al., 2023). To ensure the long-term health of pit lake ecosystems and adjacent environments, an integrated management approach is necessary (Denimal et al., 2005). This includes preventive measures such as isolating reactive sulfide-bearing materials, treating acidic runoff, and implementing regular water quality monitoring to detect early indicators of AMD. Early detection allows for timely intervention before contamination spreads (Favas et al., 2016). Additionally, various remediation strategies have been proposed, ranging from the application of alkaline substances to neutralize acidity, to the use of ecological engineering techniques that promote bioremediation, and hydrological control through the management of water inflow and outflow (Trettin et al., 2007).

Continued research and the adoption of forward-looking management practices play a vital role in reducing the adverse effects of "acid mine drainage (AMD)", thereby helping to preserve the health and sustainability of aquatic ecosystems for future generations (Padhye et al., 2023). Nonetheless, several challenges persist, particularly those related to unexpected environmental events such as extreme weather or abrupt geological shifts, which can undermine the effectiveness of existing mitigation efforts (Newman et al., 2020). For instance, intense rainfall may trigger the overflow of acidic mine water from abandoned sites, overwhelming treatment infrastructure and causing severe ecological harm (Dutta et al., 2017). Although scientific efforts to better understand AMD processes and refine remediation strategies are ongoing, the unpredictable nature of environmental disturbances continues to present obstacles (Ligate et al., 2022). Even with well-designed preventive measures in place, the potential for declining water quality and biodiversity loss remains (Gautama et al., 2004). As such, implementing a flexible, adaptive management framework that can respond to environmental variability is essential for ensuring the long-term resilience of mine-affected ecosystems (Druschel et al., 2004).'

Method

The research was conducted at the Separi mine pit, located in Embalut District, Kutai Kartanegara Regency, East Kalimantan, Indonesia (Figure 1). This area lies within the Kutai Basin, which is bounded by the Barito Basin and Meratus Mountains to the south, the Schwanger Hills and Melawai Basin to the west, and the Central Kalimantan Zone to the north (Wilson et al., 1999). The study site encompasses diverse landforms, including floodplains, fluvial terraces, rolling plains, and upland hills. The underlying lithology is composed of various sedimentary units such as topsoil, swamp alluvial deposits, mudstone, siltstone, coal seams, and sandstone. The uppermost soil layer is distinguished by its brownish-yellow hue, clay-sized particles, plastic consistency, low strength, and a typical thickness of 3 to 4 meters. Below this, the swamp-derived alluvial deposits are marked by a yellowish tint, a muddy, semi-fluid texture, and an approximate thickness of 5 meters. The mudstones observed in the area exhibit a gray coloration, fine clay-like grain size, laminated and stratified textures, and range from weak to moderately hard, with plastic behavior.

Structurally, the region is characterized by a synclinal fold known as the Tenggarong Syncline, which trends in a northeast-southwest direction. The bedding planes on the limbs of the fold dip at angles between 20° and 30°, while closer to the fold axis, the inclination decreases to a range of 0° to 7°. Additionally, structural undulations and evidence of erosional features within the coal seams are identified along the syncline axis. These geological features also play a role in shaping the area's drainage system (Fuentes-López et al., 2022). A trellis drainage pattern dominates the eastern flank of the syncline, whereas a sub-dendritic pattern is more pronounced along its central axis (Qureshi et al., 2016). Groundwater levels are relatively elevated in the northeastern sector and gradually decrease toward the central and southwestern parts of the study area. The highest groundwater elevation is recorded at 55.53 meters above sea level (masl), while the lowest point reaches -18.08 masl (Koroša et al., 2022). The direction of groundwater flow generally follows the natural gradient, moving from the northeast toward the southwest in alignment with regional topography (Padhye et al., 2023). The hilly terrain in the northeastern portion, located along the limbs of the syncline, acts as a discharge zone. In contrast, the central and southwestern sections—comprising swamps, floodplains, and aquatic systems such as the Mahakam River and its tributary, the Separi River—serve as primary recharge zones (González et al., 2018).

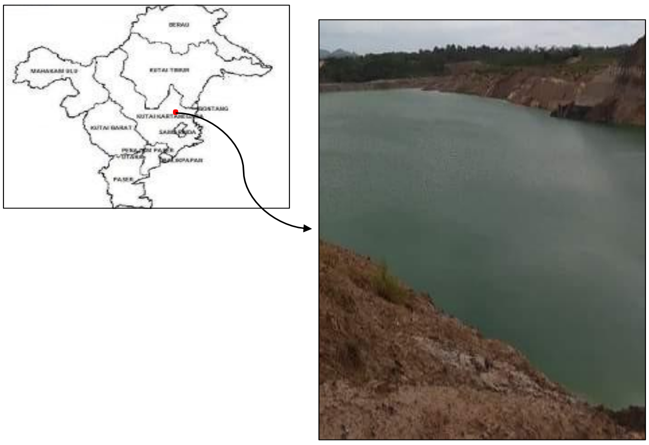

Figure 1. Research location

Sampling and Analysis of Samples

The research took place at a pit lake site formed as a result of open-pit coal mining. This specific location was chosen due to its diverse geological attributes, particularly the variation in wall rock composition, the level of connectivity with the surrounding groundwater system, and its potential influence on regional water quality. To assess the behavior of the hydrogeochemical system, the study focused on analyzing the lake's physical structure, depth profiles, and groundwater movement patterns. A total of 18 rock samples were collected from multiple sections of the pit lake wall, selected to represent different lithological compositions and degrees of weathering. In addition, water sampling involved 6 samples from the lake itself and 9 groundwater samples taken from monitoring wells around the site. Fieldwork was conducted using standard geological and hydrological tools, including hand drills, rock hammers, and water sampling containers. In the laboratory, "X-Ray Diffraction (XRD)" was used to determine the mineral composition of the rock samples, while heavy metal concentrations in water were analyzed using an "Atomic Absorption Spectrophotometer (AAS)". Other water quality parameters such as pH, electrical conductivity, major cations and anions, as well as redox indicators were assessed using Ion Chromatography (IC) and portable field instruments. The rock samples collected for this study were first air-dried, crushed, and sieved to prepare them for further examination (Castendyk et al., 2015). Mineralogical analysis using "X-Ray Diffraction (XRD)" was conducted to identify dominant mineral phases, while elemental composition was determined through X-Ray Fluorescence (XRF) (Das et al., 2023). Water samples were obtained from various points within the pit lake and nearby monitoring wells. Field measurements, including pH, temperature, electrical conductivity, total dissolved solids (TDS), and total suspended solids (TSS), were recorded in situ using portable instruments (Denimal et al., 2005). To prevent metal precipitation, water samples were stabilized with nitric acid prior to being analyzed in the laboratory (Druschel et al., 2004).

The geochemical analysis aimed to investigate the interaction between the mineral composition of pit wall rocks and the chemical characteristics of lake water. XRD results focused on identifying critical minerals such as pyrite, a key contributor to acid generation, and carbonate minerals like calcite, which can buffer acidity (Dutta et al., 2017). XRF was employed to measure the concentrations of major and trace elements, including Fe, S, Ca, and Al, within the rock matrix. Water quality assessments focused on parameters such as pH, alkalinity, major anions (SO_4^{2-}, Cl^-, HCO_3^-), and heavy metals like Fe and Mn, which were quantified using "Atomic Absorption Spectrophotometry (AAS)" and "Ion Chromatography (IC)". The relationship between the geochemical profile of the rocks and the surrounding water quality was evaluated by comparing laboratory results. These findings were further interpreted in the context of national environmental guidelines, particularly the "Indonesian Minister of Environment Regulation No. 113 of 2003", which outlines acceptable water quality thresholds in mining operations (Favas et al., 2016).

Result and Discussion

Geokimia Dinding Pit Lake

The results of the "Acid-Base Accounting (ABA)" and "Net Acid Generation (NAG)" tests presented in Table 1 illustrate a clear differentiation in acid-generating potential among the categorized samples: NAF (Non-Acid Forming), PAF-L (Potentially Acid Forming – Low Capacity), and PAF-H (Potentially Acid Forming – High Capacity). Samples classified as NAF exhibit properties that indicate minimal risk of acid generation, and in many cases, a notable capacity to neutralize acidity. This is reflected in their relatively high "Acid Neutralizing Capacity (ANC)" values, which range from 1.3 to 41.5, and consistently negative "Net Acid Producing Potential (NAPP)" values (from -41 to -5), signifying that neutralization processes dominate over acid production. Additionally, the low Total Sulfur (TS) content, ranging between 0.01 and 0.77, supports the conclusion that these samples are unlikely to contribute to acid formation. The "Maximum Potential Acidity (MPA)" values for this group are also comparatively low, falling within the range of 0.22 to 7.9. The "ANC to MPA" ratios, spanning from -38.7 to 0, further emphasize that the buffering capacity in these materials exceeds their acid-forming potential. This assessment is reinforced by the NAG test outcomes, which show elevated NAG pH values (between 7.13 and 10.2) and minimal NAG4.5 values (ranging from 0 to 1.96), indicating that the likelihood of these samples producing acidic drainage is negligible.

The PAF-L (Potentially Acid Forming – Low Capacity) group exhibits intermediate characteristics between NAF and PAF-H, with signs of possible acid generation, although not as pronounced as in the PAF-H group. "Acid Neutralizing Capacity (ANC)" values for these samples range from 6.4 to 21.9, suggesting a moderate buffering ability that is less effective than that found in NAF samples. The Total Sulfur (TS) content, ranging from 0.15 to 0.88, is slightly elevated compared to NAF, pointing to a greater possibility of acid production. The "Maximum Potential Acidity (MPA)" spans a broader range (1.1 to 46.8), indicating that certain samples within this category may present a substantial risk of acid generation. "Net Acid Producing Potential (NAPP)" values vary from -13 to 9, reflecting that while some samples remain neutral, others could contribute to acidity. ANC/MPA ratios between -6 and 0.62 further indicate a limited neutralizing capacity, with several samples having insufficient ANC relative to their acid potential. NAG test results for PAF-L samples reveal a NAG pH between 4.2 and 5.6 lower than that observed in NAF but not as acidic as PAF-H. The NAG 4.5 values (1.96 to 1.99) suggest a higher likelihood of acid formation than NAF, although still less than that of PAF-H.In contrast, the PAF-H (Potentially Acid Forming – High Capacity) category demonstrates the strongest potential for acid generation. ANC values in this group are significantly lower some even negative (ranging from -11.5 to 17.5) indicating minimal or absent neutralization ability. The TS content is notably higher (0.36 to 3.77), and MPA values are substantially elevated (4.8 to 57.6), implying a higher sulfur presence and a greater capacity for acid production. "NAPP" values, which range widely from -17 to 130, confirm that many of these samples pose a serious acidification risk. The "ANC/MPA" ratio spans from -268 to 9.4, showing that while a few samples may offer limited buffering, most are dominated by acid-forming potential. NAG test results reinforce this, with NAG pH values between 2.16 and 3.8, signaling significant acidity, and NAG 4.5 values ranging from 9.6 to 134.62, further indicating a high likelihood of acid generation within this category.

Table 1. Rock Sample Description

Acid-Base Accounting Test			
		Classification	
	NAF	PAF(Low Capacity)	PAF(High Capacity)
ANC	1.3 to 41.5	6.4 to 21.9	-11.5 to 17.5
TS	0.01 to 0.77	0.15 to 0.88	0.36 to 3.77
MPA	0.22 to 7.9	1,1 to 46.8	4.8 to 57.6
NAPP	-41 to -5	-13 to 9	-17 to 130
ANC/MPA	-38.7 to 0	-6 to 0.62	-268 to 9.4
Net Acid Generation (N AG) Test			
NAGpH	7.13 to 10.2	4.2 to 5.6	2.16 to 3.8
$NAG_{4.5}$	0 to 1.96	1.96 to 1.99	9.6 to 134.62

*"ANC (Acid Neutralizing Capacity)"; "TS (Total Sulfur)"; "MPA (Maximum Potential Acidity)"; "NAPP (Net Acid-Producing Potential); and NAG4.5 (Net Acid Generation at pH 4.5)"; **"Non-Acid Forming; low acid producing - (NAG <2 kg H_2SO_4/t); high acid producing - (NAG >10 kg H_2SO_4/t)".

The geochemical assessment and mineralogical examination of pit lake wall samples, carried out through "XRD and XRF" analyses, reveal the diversity of minerals present and their potential influence on the surrounding water systems. The identified minerals fall into several categories: (i) Sulfide minerals, including Pyrite (FeS_2), Galena (PbS), and Sphalerite (ZnS), which are prone to oxidation—this can elevate water acidity and mobilize heavy metals into the aquatic environment. (ii) Oxide and hydroxide minerals such as Ferrihydrite ($Fe(OH)_3$), Manganite (MnO(OH)), and Gibbsite ($Al(OH)_3$), which may contribute to the adsorption and precipitation of metals, thus influencing water chemistry. (iii) Carbonate minerals like Calcite ($CaCO_3$), which have a buffering capacity and can help neutralize acid generated from sulfide oxidation. (iv) Lastly, the presence of evaporite minerals, including Epsomite ($MgSO_4 \cdot 7H_2O$) and Melanterite ($FeSO_4 \cdot 7H_2O$), suggests ongoing sulfate leaching processes that can increase the ionic load in both surface and groundwater systems.

Hidrokimia Pit Lake and Groundwater

Analysis of the data presented in Table 2 reveals significant differences in water quality across the samples, which appear closely related to variations in lithological composition. Samples VD-1 through VD-6 are characterized by low pH values, ranging from 4.2 to 4.62, reflecting acidic conditions. These samples, associated with lithologies such as Sandstone, Claystone, and Carbonaceous Claystone, also exhibit elevated electrical conductivity (151–172 µg/L) and high Total Dissolved Solids (TDS), measured between 217 and 230.12 mg/L. Iron (Fe) and manganese (Mn) concentrations are notably high in this group particularly in samples VD-1 to VD-5 with Fe levels reaching up to 74.4 mg/L and Mn up to 12.37 mg/L, indicating a strong likelihood of Acid Mine Drainage (AMD) resulting from the oxidation of sulfide minerals. Interestingly, although sample VD-6 shares a similarly low pH, its iron content is substantially lower (1.39 mg/L), suggesting localized geochemical variation. Conversely, samples Grd-01A to Grd-09 demonstrate higher pH values, ranging from 5.41 to 6.48, suggesting conditions that are closer to neutral and less conducive to acid generation. These samples, associated with Sandstone, Silty Claystone, and Shale Coal, show lower conductivity (51.6–112 µg/L) and reduced TDS (48.34–92.81 mg/L). Additionally, the concentrations of Fe and Mn are considerably lower, especially in samples Grd-01A, Grd-08, and Grd-09, where Fe ranges from 3.50 to 3.81 mg/L and Mn from 0.88 to 3.63 mg/L. These findings point to more favorable water quality with a reduced presence of dissolved metals.

The results of water quality testing summarized in Table 3 highlight noticeable differences in pH levels, concentrations of cations and anions, as well as redox potential across various sampling locations. The pH values ranged between 3.8 and 6.55, with sample VD-6 exhibiting the most acidic condition, whereas Grd-01A reflected a more neutral environment. Calcium (Ca^{2+}) concentrations varied from 33.6 to 48.8 mg/L, with the highest value recorded in sample Grd-05. Dissolved iron (Fe^{2+}) was most concentrated in VD-6 at 12.6 mg/L, and least in Grd-08 at 4.4 mg/L. Manganese (Mn^{2+}) levels followed a similar trend, peaking in VD-6 at 10.2 mg/L and reaching a minimum of 5.36 mg/L in Grd-09. Among the anions, bicarbonate (HCO_3^-) levels showed substantial variation, with the highest concentration found in Grd-08 at 118 mg/L and the lowest in VD-6 at 6.7 mg/L. Chloride (Cl^-) ranged from 10.5 to 16.74 mg/L, with VD-6 again registering the highest value.

Sulfate (SO_4^{2-}), commonly linked to pollution from sulfide oxidation, was also highest in VD-6 at 563.95 mg/L, while Grd-08 had the lowest at 126.7 mg/L. In terms of redox conditions, water samples from the VD area generally showed higher oxidation-reduction potential (Eh), with VD-4 recording the peak value of 472 mV, indicating more oxidizing conditions. Conversely, the Grd site samples tended to be more reducing, with some showing negative Eh values—for instance, Grd-09 reached as low as -47.04 mV. This suggests that the Grd environment is more reductive compared to the VD area. Furthermore, dissolved oxygen (DO) levels were higher in the VD samples, ranging from 7.6 to 7.8 mg/L, whereas DO in the Grd samples was comparatively lower, between 1.2 and 5.24 mg/L.

Table 2. Metal Content in Water Sample

Sample ID	Litology	pH	Conductivity (μg/L)	TDS (mg/L)	Fe (mg/L)	Mn (mg/L)
VD-1	Sandstone	4.24	151	217	74.17	12.17
VD-2	Sandstone	4.46	152	224,6	74.36	12.34
VD-3	Claystone	4.32	168	225,2	74.29	12.37
VD-4	Carbonaceouse Claystone	4.2	157	223.78	74.4	11.96
VD-5	Sandy Siltstone	4.28	162	228.6	74.18	11.78
VD-6	Carbonaceouse claystone	4.62	172	230.12	1.39	12.06
Grd-01A	Sandstone	6.48	112	48.34	3.50	0.88
Grd-02	Sandstone	5.58	92.3	70.44	70.99	8.73
Grd-03	Clayey Silstone	5.46	51.6	74.78	68.80	9.29
Grd-03A	Silty Claystone	5.55	52.6	78.65	68.06	10.29
Grd-05	Coaly Shae	5.41	63.2	80.72	68.72	9.07
Grd-06	Silty Claystone	5.69	72.6	92.81	67.23	10.21
Grd-07	Sandy Siltstone	5.56	68.9	86.64	68.02	8.10
Grd-08	Sandstone	6.31	66.76	57.76	3.81	3.63
Grd-09	Shale Coal	6.32	68.5	58.61	3.70	3.52

*Vd; Pit Lake; *Grd; Groundwater

The results of this study align with previous research conducted by various scholars between 2021 and 2023, which have explored the hydrogeochemical characteristics of groundwater across different regions. These studies consistently highlight the influence of geological formations, redox conditions, and anthropogenic activities on groundwater quality.

For instance, Wang et al. (2020) investigated the hydrological and chemical characteristics of karst groundwater in the Xiangxi River Basin, China. Their findings revealed that the groundwater exhibited pH values ranging from 7.28 to 8.16, indicating weak alkalinity. The dominant cations were calcium (Ca^{2+}), and the primary anions were bicarbonate (HCO_3^-), reflecting the dissolution of carbonate rocks. The study also noted high dissolved oxygen levels, averaging between 9.65 and 10.79 mg/L, which is indicative of oxic conditions. These observations are consistent with the current study's findings, where variations in pH, cation and anion concentrations, and redox potential were observed across different sampling locations

Similarly, Zhang et al. (2023) conducted a comprehensive analysis of groundwater hydrochemistry in the Baiquan Basin, Northern China. They reported that the groundwater's hydrochemical composition was primarily influenced by the dissolution of carbonate and sulfate minerals, as well as cation exchange processes. The study highlighted that the molar ratios of $(Ca^{2+} + Mg^{2+})/(HCO_3^- + SO_4^{2-})$ were less than 1, suggesting that the hydrochemistry was predominantly driven by the weathering of carbonate rocks. This aligns with the current study's observation of high calcium concentrations and significant variations in bicarbonate and sulfate levels, indicating similar geochemical processes at play.

Furthermore, the study by Li et al. (2025) assessed the hydrogeochemical characteristics of karst groundwater in the Mengzi Basin, Yunnan Province, China. They found that the groundwater chemistry was largely influenced by the dissolution of carbonate rocks, with calcium and bicarbonate being the dominant ions. The study also noted that the natural source of magnesium (Mg^{2+}) in groundwater was related to the dissolution of dolomite, and that sulfate (SO_4^{2-}) and chloride (Cl^-) had geological origins, such as the dissolution of sulfate minerals. These findings corroborate the current study's results, which indicate significant variations in cation and anion concentrations due to geological factors.

In addition, the research conducted by (Berhanu et al. (2024) focused on the spatial and seasonal assessment of groundwater quality for drinking suitability using index and machine learning approaches. They observed that sulfate ion levels varied between 0 and 48 mg/L across different seasons, with all samples remaining below the World Health Organization's permissible limit. The study attributed the presence of sulfate in groundwater to the weathering of naturally available sulfate-containing rocks and the intensive application of fertilizers. This is in line with the current study's findings, where sulfate concentrations varied significantly across sampling locations, suggesting both natural and anthropogenic influences.

Table 3. Cation, Anion and Redox Content in Water

Sample Point	Cation						Anion			Redox	
	pH	Ca^{2+} (mg/L)	Mn^{2+} (mg/L)	Fe^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	Eh (mV)	DO (mg/L)
VD-1	4.4	42.3	9.82	10.83	6.9	3.5	6.9	14.46	212.24	462	7.61
VD-2	4.42	42.23	9.76	10.49	6.85	3.47	6.75	14.3	220.3	466	7.7
VD-3	4.46	42.18	9.8	10.04	6.8	3.52	6.5	14.27	213.3	464	7.69
VD-4	4.5	42.32	10.09	10.25	6.92	3.51	6.81	14.38	228.3	472	7.66
VD-5	4.47	43.02	10.06	10.3	6.88	3.49	6.76	14.44	224.6	469	7.8
VD-6	3.8	45.3	10.2	12.6	7.41	3.24	6.7	16.74	563.95	452.24	7.84
Grd-01A	6.55	35.8	4.12	5.22	7.06	2.6	114	10.5	161.2	-42.9	1.7
Grd-02	6.2	37.62	7.25	6.3	7.5	4	106.7	11.76	208.76	28.96	5.24
Grd-03	4.8	47.9	8.59	9.2	7.88	3.9	9.6	13.3	311.2	92.12	5.06
Grd-03A	4.8	47.36	8.75	9	8	3.76	9.2	13.6	308.5	114.7	4.84
Grd-05	4.55	48.8	9.35	9.5	7.63	3.35	8.6	12.9	312.64	122.64	4.12
Grd-06	5.2	44.7	9.12	8.95	7.5	3.4	9.78	11.36	274.2	78.99	2.4
Grd-07	5.26	43.6	9.04	8.75	7.2	3.18	9.2	11.14	266	74.3	2.15
Grd-08	6.4	33.6	5.88	4.4	6.9	2.15	118	10.8	126.7	-46.28	1.2
Grd-09	6.36	34.32	5.36	4.6	6.7	2.21	116.4	11.05	130.4	-47.04	1.3

Lastly, the study by Wang et al. (2024) examined the spatiotemporal variations in geochemical and hydrological controls on the release of soluble reactive phosphorus from the shallow aquifer of a riparian zone. They found that redox conditions in the upper aquifer were generally oxic to less-reducing, with oxidation-reduction potential (Eh) values ranging between 100 and 450 mV at depths less than 60 cm. These redox conditions influenced the mobility of redox-sensitive species, such as iron and manganese. The current study similarly observed variations in Eh values across different sampling locations, indicating differing redox environments that affect the chemical composition of groundwater.

Conclusion

Pit lakes resulting from open-pit mining operations display complex hydrogeochemical behavior, shaped by the lithological characteristics of the surrounding rock, mineral composition, and water-rock interactions. Geochemical testing of rock samples indicates that certain specimens contain more than 1% total sulfur and exhibit very low NAG pH values (ranging from 2.16 to 3.8), reflecting high acidity potential. Additionally, the elevated NAG 4.5 values (ranging between 9.6 and 134.62) further emphasize the strong potential for acid generation in these materials. Water quality assessments at pit lake locations such as Vd-02, Vd-04, and Vd-05 revealed low pH levels (between 3.2 and 4.5), alongside elevated concentrations of dissolved metals iron (Fe) exceeding 5 mg/L and manganese (Mn) over 2 mg/L pointing to ongoing sulfide mineral oxidation processes. In contrast, groundwater sampled from nearby locations (Grd-01 and Grd-02) exhibited neutral pH values (approximately 6.5 to 7.2) and significantly lower metal concentrations (Fe < 0.314 mg/L; Mn < 0.125 mg/L), indicating a stark difference in geochemical conditions between the pit lake and the surrounding groundwater system. Hydrogeological analysis suggests that certain portions of the pit function as discharge zones, inferred from the direction of groundwater flow and elevated piezometric levels, particularly around Grd-03 and Grd-05. This implies that the pit lake could be receiving inflows from adjacent groundwater sources, raising concerns about the potential for aquifer contamination if not properly managed. These findings highlight the need for a comprehensive environmental management approach. Strategies such as controlling surface water inflow, utilizing neutralizing agents like limestone, and conducting routine water quality monitoring are essential to reduce the long-term environmental risks posed by pit lakes . One limitation of this study lies in its spatial and temporal scope, which may not fully capture the dynamic and heterogeneous nature of hydrogeochemical processes across the broader study area. While the research successfully identifies strong acid generation potential, elevated metal concentrations, and notable contrasts between pit lake and groundwater geochemistry, the findings are primarily based on a limited number of sampling locations and time-specific data. This constraint may reduce the generalizability of the results, particularly concerning long-term trends and seasonal variations in water quality and groundwater–surface water interactions. Furthermore, while hydrogeological analyses suggest potential discharge zones and groundwater inflows into pit lakes, the study lacks detailed modeling or tracer-based validation to confirm subsurface flow pathways. Thus, further research employing high-resolution temporal monitoring and hydrogeochemical modeling is needed to better predict contaminant transport mechanisms and to refine mitigation strategies for protecting surrounding aquifer systems.

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