Hydrogeochemical and Isotope-Based Assessment of Level-Specific Mine Water and Rock Characteristics in a Recently Closed Coal Mine

Ki-Rim Lee[1], Duk-Min Kim[1], Young-Min Kim[1], Jee-Hyun Jung[1], Jae-Hyun Park[1], Da-Som Kim[1], Joon-Uk Kwon[2] and Jung-Sik Park[3]

[1]*Department of Energy, Resources, and Environmental Engineering, Sangji University, Wonju, 26393, Gangwon-do, Republic of Korea, kdukmin8@sangji.ac.kr, ORCID 0000-0002-1537-6866*

[2]*GeoMirae Engineering and Construction Co., Ltd., Seoul, 08505, Republic of Korea, kwonjoonuk@naver.com*

[3]*Korea Mine Rehabilitation and Mineral Resources Corporation (KOMIR), Wonju, 26464, Republic of Korea, parkjs@komir.or.kr*

Abstract

Hydrogeochemical characteristics, acid-generating potential of rocks, and isotopic ratios were investigated to evaluate acid mine drainage (AMD) formation in a closed coal mine. Mine water, surface water, and groundwater were sampled during dry and wet seasons. Shallow mine workings showed acidic conditions with low alkalinity, indicating pyrite oxidation and depletion of carbonates, whereas deeper zones exhibited neutral conditions due dominant influence of carbonates. Most rock samples were classified as Non-Acid Forming, although several showed localized potential for AMD generation. Water isotopes indicated two different water bodies, and sulfate isotopic ratios could be used to calculate relative contributions between Fe(III) and dissolved oxygen as oxidant for pyrite.

Introduction

In abandoned mine areas, oxidation of sulfide minerals generates AMD, which is a major source of contamination for surface water and groundwater (Yun *et al.* 2001; Cidu *et al.* 2009). The acidity produced by sulfide mineral oxidation can also be neutralized through reactions with carbonate minerals, resulting in simultaneous acid generation and neutralization processes (Toran 1987). The geochemical evolution of mine drainage has been extensively investigated in various mining environments (Nordstrom & Southam 1997). After mine closure, the rise of mine water levels changes dissolution conditions of sulfide and carbonate minerals. In coal mines, sulfide minerals such as pyrite coexist with neutralizing minerals including limestone and silicate minerals, creating a complex geochemical environment where acid-generating and neutralization reactions occur simultaneously. Long-term weathering and oxidation in shallow mine levels may promote the consumption of neutralizing minerals, whereas deeper levels that were relatively recently excavated may retain greater buffering capacity under less weathered conditions. This geological heterogeneity leads to variations in water quality among different mine workings, and in some zones, active pyrite oxidation occurs together with neutralization through dissolution of carbonate minerals. In addition, acid-generating potential assessments of rock samples have shown that certain levels contain high sulfur contents, low NAGpH values, and high Fe leaching, indicating potential risks for AMD generation. Therefore, this study aimed to investigate the hydrogeochemical and geological characteristics, together with stable isotope compositions, of mine water, surface water, and groundwater in a closed coal mine with maintained drainage conditions to elucidate the mechanisms of AMD formation, to identify hydrogeochemical differences according to mine level, and to evaluate its future occurrence potential.

Study area and hydrologic setting

The study area is a recently closed coal mine located in Korea. Mining activities have ceased; however, mine drainage pumping systems are still operating to control mine water levels (Figure 1). Therefore, the mine workings have not reached completely flooded conditions, and the investigated mine levels remain partially drained. The study area consists of the Dong Tunnels and Bokam Tunnels, Active drainage conditions are still maintained in the study area. Therefore, hydrogeochemical conditions may vary according to mine level, groundwater circulation, and oxidation environment.

Methods

Mine water, surface water, and groundwater samples were collected during both the dry season (February 2025) and the wet season (August 2025). Mine water samples were obtained from representative locations within each mine level, whereas surface water samples were collected from the midstream and downstream sections of the adjacent stream. Groundwater samples were collected from nearby monitoring wells. In the field, pH, oxidation–reduction potential (ORP), electrical conductivity (EC), dissolved oxygen (DO), and temperature were measured using a portable multi-parameter water quality meter. Alkalinity was determined by field titration and expressed in mg/L as $CaCO_3$. For hydrogeochemical analysis, samples were filtered through 0.45 µm membrane filters immediately after collection. Major cations and trace elements were analyzed using ICP-AES (Inductively Coupled Plasma–Atomic Emission Spectrometry). Major anions (e.g., SO_4^{2-} and Cl^-) were quantified using ion chromatography. For stable isotope analysis, oxygen and hydrogen isotopes of water ($\delta^{18}O_{water}$ and δ^2H_{water}) were measured using a stable isotope ratio mass spectrometer. For sulfur and oxygen isotope analysis of sulfate, filtered samples were acidified with HCl to $pH < 3$ to prevent carbonate precipitation, and $BaCl_2$ solution was added to precipitate $BaSO_4$. The precipitated $BaSO_4$ was recovered and used for $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ isotope analyses. Rock samples were collected in the field, dried, and pulverized prior to analysis. Sulfur isotopes of sulfide minerals ($\delta^{34}S_{sulfide}$) were analyzed to evaluate the origin of sulfide minerals. Net Acid Producing Potential (NAPP) and Net Acid Generation (NAG) pH tests were conducted to assess acid-generating potential, and samples were classified as Non-Acid Forming (NAF) or Potential Acid Forming (PAF). To supplement the NAPP–NAG_{pH} evaluation, sequential extraction step 3 was performed to quantify oxidized iron

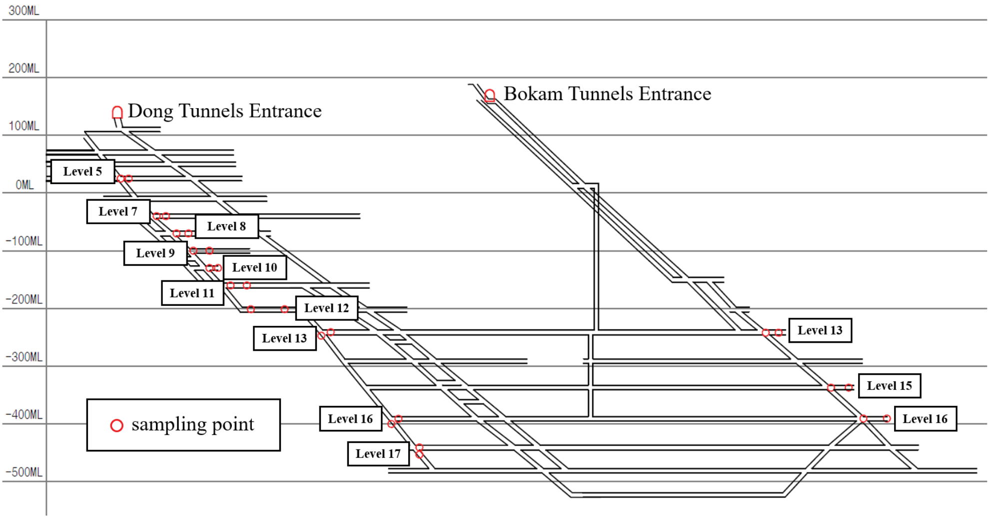

Figure 1 *Mine workings and sampling locations in the recently closed coal mine.*

(Fe(III)). The extracted Fe concentration was measured using ICP-AES and used as an indicator of the sensitivity of pyrite oxidation. Isotopic data were interpreted by comparison with the Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL) to determine water sources. In addition, sulfur isotopes of rock samples were analyzed.

Results and discussion

Hydrogeochemical results showed that mine water in the study area could be divided into two distinct groups according to mine level and oxidation environment rather than complete flooding status. Because the mine has been closed only recently and pumping systems are still operating, all investigated levels remain partially drained and are exposed to different oxidation conditions. Therefore, the observed hydrogeochemical differences are interpreted as level-specific responses rather than development of a fully flooded mine pool. The upper-levels of the Dong Tunnels (levels 5–12) exhibited slightly acidic conditions (Table 1). In particular, levels 8–11 showed low pH values of 4.7–5.5 and high ORP values exceeding 500 mV, indicating oxidizing conditions. Alkalinity in this zone ranged from 0 to 20 mg/L as $CaCO_3$, suggesting limited buffering capacity against acid generation. Consequently, Mn and Al concentrations were relatively elevated. For example, level 11 exhibited Mn concentrations of 3.9–5.6 mg/L and Al concentrations of 5.0–13.7 mg/L, indicating enhanced mobilization associated with sulfide mineral oxidation. In contrast, levels 5, 7, and 12 showed relatively higher pH values despite elevated SO_4^{2-} concentrations and higher Ca and Mg concentrations, indicating simultaneous pyrite oxidation and neutralization by carbonate or silicate minerals. Protons generated by pyrite oxidation react with carbonate and silicate minerals, releasing Ca and Mg, and this process is typically accompanied by increasing SO_4^{2-} concentrations (Drever 1997; Kim *et al.* 2017). Level 7, in particular, maintained pH values of 6.6–6.8 with high SO_4^{2-} concentrations of 748.5–789.4 mg/L, representing active oxidation with effective buffering by carbonate minerals. These results indicate that sulfide oxidation and neutralization reactions coexist within some mine levels and produce heterogeneous geochemical environments. In contrast, deeper zones including the lower Dong Tunnels (levels 13, 16, and 17) and the Bokam Tunnels showed neutral to slightly alkaline conditions. pH values ranged from 6.9–8.0, and alkalinity reached 455–483 mg/L as $CaCO_3$ in level 16 and 628–653 mg/L as $CaCO_3$ in level 17, indicating favorable conditions for metal precipitation and adsorption. Mn and Al concentrations were generally below 0.1 mg/L, clearly contrasting with the upper-levels. However, As concentrations of 43–65 μg/L were observed in level 16, likely due to limited adsorption of dissolved As onto Fe(III) hydroxide surfaces under alkaline conditions. Samples from the Bokam Tunnels also showed stable water quality with pH values of 7.7–7.9 and low Mn and Al concentrations. Major ion composition further supported these differences. Upper-level samples were mainly classified as Ca–Mg–SO_4 or Ca–SO_4 type waters, indicating dominance of sulfate derived from sulfide mineral oxidation (Figure 2). In contrast, lower levels and Bokam Tunnel samples were characterized by Ca–HCO_3 or Na–HCO_3 type water, reflecting weaker oxidation influence and stronger carbonate dissolution and deep groundwater mixing. Some deeper samples, particularly levels 13 and 17, showed relatively higher Na compared to Ca, suggesting Ca–Na ion exchange during prolonged residence or mixing with deeper groundwater (Capuano & Jones 2020). Additionally, downstream surface water showed increased SO_4^{2-} and EC values, together with detectable Mn and Al, indicating influence from treated mine water discharge.

Acid-generating potential tests indicated that most rock samples were classified as NAF, with NAG_{pH} values greater than 4.5 and negative NAPP values, suggesting limited potential for AMD generation under current conditions. However, several samples exhibited high acid-generating potential. Sample 10-1 showed total S content of 9.17%, NAG_{pH} of 2.61, and NAPP of 280.3 kg $CaCO_3$/t, representing the highest risk and was classified as PAF. Samples 10–2, 11–2, and 12–1 were also classified as PAF. These results indicate that localized AMD generation may occur where sulfide mineral content is high and neutralization capacity is limited. Sequential extraction (step 3) results supported this interpretation. High Fe(III) contents (> 500 mg/L) were observed in samples 7–1, 7–2, 10–1, and 10–2, indicating prolonged pyrite oxidation. Despite high Fe(III) release, samples from level 7 remained classified as NAF, suggesting sufficient neutralization capacity due to abundant carbonate minerals. Although AMD generation currently appears limited in most mine levels, continued rise of mine water levels following future termination of pumping systems may alter oxidation and neutralization conditions. Therefore, mine levels containing high sulfur contents and oxidation-sensitive materials may become important sources of future AMD generation.

Stable isotope results of water ($\delta^{18}O_{water}$ and $\delta^{2}H_{water}$) showed that most mine water, surface water, and groundwater samples plotted near the GMWL and LMWL, indicating meteoric origin (Craig 1961). Lower Dong Tunnel and Bokam Tunnel samples showed relatively lighter isotopic compositionsupper-level compared with upper-levels, suggesting differences in recharge conditions and water sources. In contrast, upper-level samples

Table 1 Field measurements of mine water from each level during the dry season (February 2025).

Position		pH	ORP (mV)	EC (µS/cm)	DO (mg/L)	Alkalinity (mg/L as $CaCO_3$)
Dong Tunnels	5–1	6.1	601.6	689	10.3	130
	5–2	6.2	606.2	688	10.3	128
	7–1	6.8	536.7	1327	10.3	42
	7–2	6.6	545.3	1321	10.1	52
	8–1	5.1	554.9	691	10.7	0
	8–2	5.2	544.5	688	10.5	9
	9–1	5.5	545.1	354	10.7	14
	9–2	5.5	543.2	353	10.6	20
	10–1	5.1	486.2	760	10.7	0
	10–2	5.1	474.3	743	10.7	0
	11–1	4.7	505.3	1162	11.0	1
	11–2	4.9	501.2	1403	11.1	0
	12–1	6.3	467.4	1617	10.6	208
	12–2	6.2	477.1	1608	10.6	196
	13–1	6.9	474.6	551	9.0	238
	13–2	7.0	481.2	546	9.1	224
	16–1	7.7	486.1	1094	10.7	455
	16–2	7.6	479.2	1098	10.7	483
	17–1	7.9	493.9	1595	10.0	653
	17–2	8.0	501.2	1598	10.0	628
Bokam Tunnels	13–1	7.9	486.8	283	10.6	120
	13–2	7.8	474.2	711	10.6	220
	15–1	7.7	490.1	475	8.6	187
	15–2	7.8	494.2	473	8.7	200
	16–1	7.7	408.4	1203	8.0	335
	16–2	7.8	412.5	1200	7.9	342

showed isotopic compositions similar to surface water. Wet-season samples exhibited generally lighter isotopic values compared with dry-season samples, reflecting increased recharge and dilution by isotopically depleted rainfall during the monsoon season. This tendency suggests that seasonal recharge contributes to mine water composition even under partially drained conditions.

A negative relationship was observed between $\delta^{18}O_{sulfate}$ and SO_4^{2-} concentrations, indicating isotope fractionation during pyrite oxidation (Taylor *et al.* 1984; Kim *et al.* 2019). Oxygen in sulfate is derived from both water and dissolved oxygen, and the observed $\delta^{18}O_{sulfate}$ values reflect mixing of these sources. Upper-level samples showed higher SO_4^{2-} concentrations and relatively lower $\delta^{18}O_{sulfate}$ values, indicating prolonged pyrite oxidation and higher contribution by Fe(III) as oxidant. In contrast, deeper samples showed lower SO_4^{2-} concentrations and limited variation in $\delta^{18}O_{sulfate}$, suggesting weaker oxidation influence. Additionally, differences between sulfate sulfur isotopes and sulfide sulfur isotopes ($\Delta\delta^{34}S_{sulfate–sulfide}$) were generally within ±3‰, indicating sulfate derived from the similar sulfide mineral source (Toran & Harris 1989).

Summary

Integrated analysis of hydrogeochemistry, acid-generating potential of rocks, and stable isotopes revealed distinct geochemical characteristics of mine water according to mine level and oxidation environment in the recently closed coal mine. Because pumping systems are still operating, all investigated

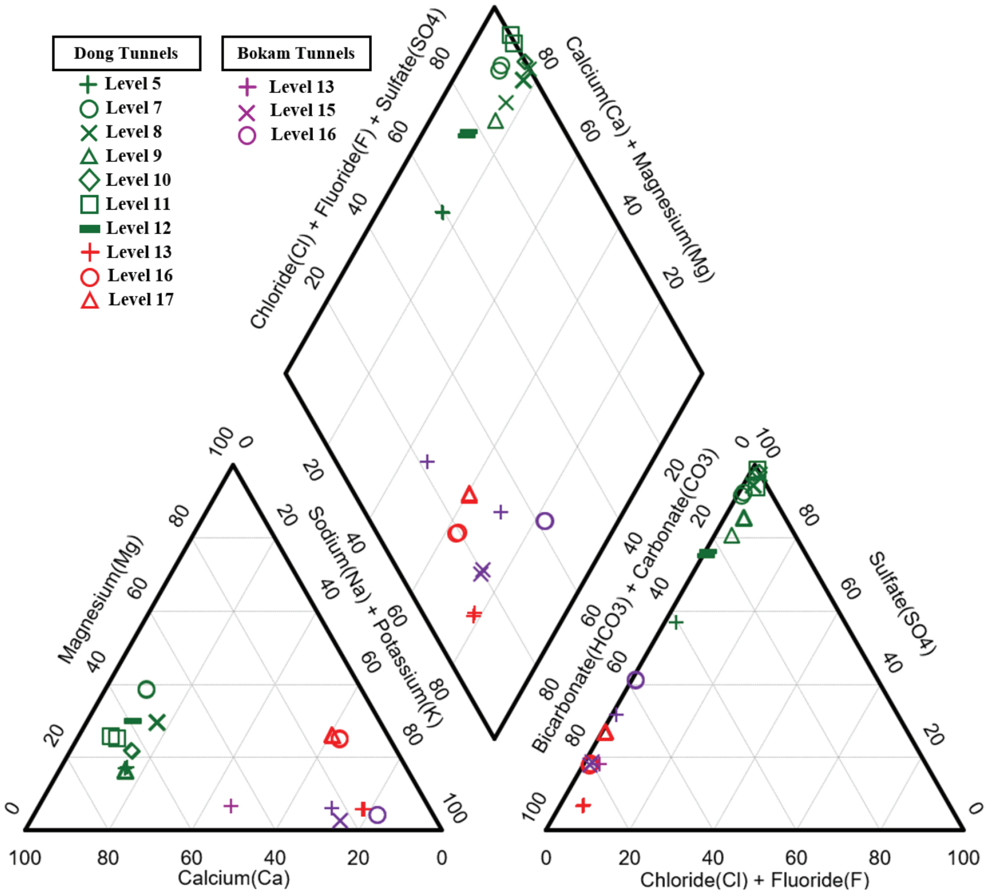

Figure 2 *Piper diagram showing hydrogeochemical facies of mine water samples.*

mine workings remain partially drained rather than completely flooded. Upper mine workings showed acidic tendencies characterized by low pH, high ORP, and low alkalinity, indicating active pyrite oxidation. In contrast, deeper workings and the Bokam Tunnels exhibited neutral conditions with high alkalinity, suggesting dominant neutralization through carbonate dissolution and mixing with deeper groundwater. Acid-generating potential tests indicated that most rock samples were classified as NAF. However, several levels showed high sulfur contents and strong oxidation sensitivity, indicating localized potential for AMD generation. Water isotope compositions indicated meteoric recharge characteristics, whereas sulfate isotopes suggested variable contributions of Fe(III) and dissolved oxygen during pyrite oxidation. Overall, the mine showed level-specific hydrogeochemical differences controlled by oxidation intensity, neutralization reactions, and lithological heterogeneity rather than development of a fully flooded mine pool. Although AMD generation is currently limited, future rise of mine water levels following termination of pumping systems may alter geochemical conditions and enhance localized AMD occurrence. Therefore, continuous monitoring is required for predicting future water quality evolution in recently closed coal mines.

Acknowledgements

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