Environ Monit Assess (2012) 184:503–513
DOI 10.1007/s10661-011-1983-0

Water quality changes of a closed underground coal mine in Korea

**Young Wook Cheong · Gil-Jae Yim ·
Sang Woo Ji · Sang Soo Kang · Jeffery Skousen**

Received: 25 May 2010 / Accepted: 24 February 2011 / Published online: 22 March 2011

Abstract The objective of this study was to assess the changes in mine water quality as an underground mine flooded from July 2005 to October 2008. The effect of air injection with a blower into the water was used to evaluate the potential to convert ferrous to ferric iron and to provide in situ treatment and precipitation. Mine flooding averaged 31 cm/day with a linear shape until November 2007, when it flattened out due to outflow. During flooding, mine water pH remained around 6, but Eh shifted from 200 to −150 mV. After the mine water level stabilized, contents of elements such as Fe and SO_4 tended to decrease as time passed. Air was injected by diffusers (150 L/min/each) at three different depths of 2, 3, and 5 m below the water level in the shaft. Dissolved oxygen eventually increased to 4 or 5 mg/L depending on the depth of the diffusers. Aeration caused conversion of ferrous iron to ferric iron and about 30 mg/l of iron was removed from the mine water. Therefore, air injection shows potential as a semi-active treatment or part of conventional treatment to precipitate iron in the mine pool.

Keywords Water quality changes · Underground coal mine · Air injection

Introduction

When below-drainage underground mines are closed, pumping of water ceases and the mine voids fill with water. The water is often contaminated with residual salts from the material left in the mine or from that which had fallen into the mine voids and is often quite poor in quality depending on the geologic conditions. Once the water fills the mine, it is anticipated that water quality will improve over time as these salts are flushed from material surfaces, but some of this water may reach the land surface and contaminate streams or wells. Therefore, pumping may be required to maintain water levels at a specific elevation to control the discharge and for treatment if needed (Johnson and Younger 2000; Demchak et al. 2004). Treatment after closure is often required for a time, and chemical and passive treatment techniques have been used to treat

---

Y. W. Cheong · G.-J. Yim (✉) · S. W. Ji · S. S. Kang
Geologic Environment Division, Korea Institute
of Geoscience and Mineral Resources,
92 Gwahang-no, Yuseong-gu, Daejeon,
305-350, South Korea
e-mail: gjyim@kigam.re.kr

J. Skousen
Division of Plant and Soil Sciences,
West Virginia University, PO Box 6108,
Morgantown, WV 26506-6108, USA

this contaminated water before discharge into streams or rivers (Younger et al. 2003; ŠŠlesárová et al. 2007). But over time, it is expected the water quality will improve and treatment will be unnecessary.

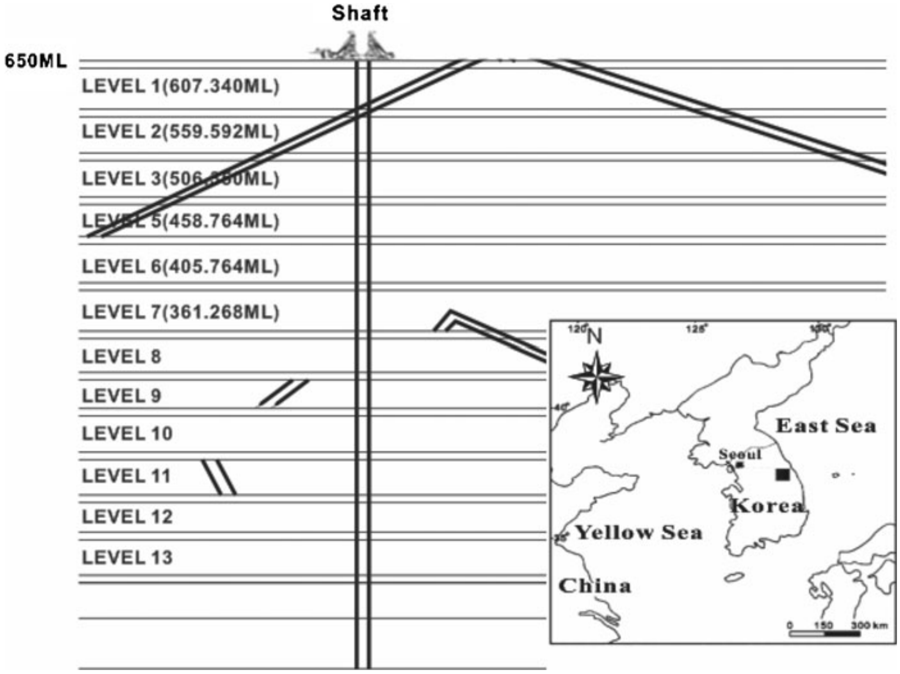
Previous studies of water quality changes from closed underground mines have shown declines in acidity or metal concentrations over time (Mack and Skousen 2008; Wood et al. 1999; Younger 2000). As described in Demchak et al. (2004), the type of underground mine (above-drainage versus below-drainage) is an important factor in the degree and rate of change in water chemistry over time and the prediction of future changes (Mack et al. 2010).

Most contaminated mine water is treated by active systems (e.g., aeration-lime addition–filtration–precipitation) and passive treatment systems (e.g., constructed wetlands) (Younger et al. 2002; PIRAMID Consortium 2003). In situ treatment has been suggested such as the addition of alkaline materials (e.g., fly ash) and organic carbon into mine voids or pools (Houston et al. 2005; Canty and Everett 2006; Wendt-Potthoff et al. 2010). Although in-situ treatment has been studied as a potential option, applications have only been done in small-scale trials (Wolkersdorfer 2006).

Over 300 of the many coal mines in Korea have been closed and abandoned during the 1980s to 1990s, and pumping of mine water from these mines has ceased. Although monitoring of chemistry after mine closure to determine proper treatment has been done on a few sites, most abandoned sites have not been monitored as to the effects of mine flooding on water chemistry and its longevity.

A very large underground mine complex was closed in Korea and the amount of water that would eventually be discharged from the mine was too high in quantity with high metal concentrations for a passive treatment system to effectively treat the water. So a different solution for cost-effective treatment was needed. The objective of this study was to determine the changes in mine water quality during and after flooding of this underground mine. In addition, direct air injection with a blower into the mine water was also carried out to evaluate the feasibility of aeration for in situ mine water treatment within a shaft.

Fig. 1 Location of the study coal mine and view of the underground workings



Site description

The Dongwon coal mine is situated in Sabuck, Kwangwon Province, South Korea (Fig. 1), which is located in the largest of the several coal fields in Korea. The mine operated from 1963 to 2004 and extracted an estimated 2 million tons of coal per year (Kang et al. 2004). The mining area reached a total of 3,593 ha. The coal deposit mainly consisted of several coal seams which are distributed at elevations of 1,150 ML (meters above sea level) to −500 ML and extended to about 13,500 m long. Average widths of the major two coal seams were 2.5 and 1.8 m, respectively, and the average slope of coal seams was 35° (Kang et al. 2004).

Before mine closure, one shaft was operating and mining activity mainly occurred in level 11 (150 ML) to level 13 (50 ML) which was vertically 550 m down from the ground surface (650 ML; Fig. 1). Water was discharged by gravity from above level 0 (higher than 650 ML) and by pumping from below 650 ML. On average, pumped and gravity discharge from the mine were 5,250 m^3/day and 3,744 m^3/day, respectively. The pumped mine water was collected at several sumps in each level and then delivered to a water treatment plant to control turbidity and iron. The raw mine water in 2004 before pumping ceased had 2 mg/L of Fe and 64.6 NTU of turbidity (Kang et al. 2004). Dewatering pumps were switched off in February 2005 at which point the mine water started to rise.

Methods

Monitoring of rebound of mine water in the shaft

Mine water levels were monitored by a CTD diver and Baro diver (Van Essen Instruments, The Netherlands) installed in the shaft from July 2006 to October 2008. July 2005 to June 2006 water levels were provided by Shinwon Co., who was in charge of the mine water treatment plant. Water parameters such as pH, dissolved oxygen (DO), conductivity, and temperature were determined in the top 200 m of the water column, approximately one third of the whole shaft, using an MP troll 9500 (In Situ Inc., USA).

Chemical analysis of mine water

Mine water samples were taken on a monthly basis from the top of the shaft from April 2006 to November 2007 when the mine was flooding. After that, samples were collected at about 3-month intervals until September 2008. All the water parameters such as pH, ORP, DO (Toa pH/ORP meter, Japan), total dissolved solids (TDS), EC, temperature, and conductivity (Orion 130 Conductivity/TDS meter, USA) were measured on site. In addition, ferrous iron and turbidity were measured by Spectrophotometer (Hach DR2800, USA) and turbidimeter (Hach 2100P, USA) on

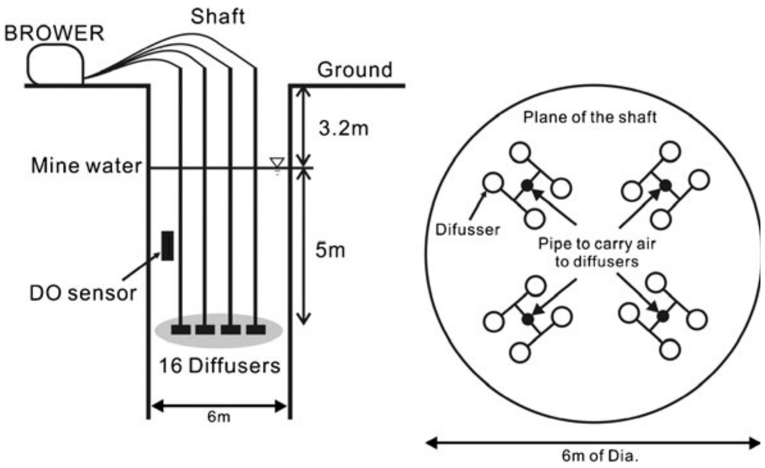


Fig. 2 Setup of a blower and 16 diffusers in the mine water in the shaft

site as well. Water samples were collected and filtered through 0.45 μm membrane filters and two aliquots, one acidified with nitric acid and one unacidified, were placed on ice. Acidified aliquots were analyzed for Fe, Al, and Mn with ICP-AES in the laboratory. Ion chromatography was applied to analyze sulfate in unacidified aliquots.

An injection of air into the mine water

In a batch experiment, air was injected into 1,000 ml of mine water at the rate of 3 mL/min per milliliter of mine water using an aquarium pump. The water before and after aeration was analyzed for pH, turbidity, Fe^{2+}, DO, and ORP. In a field experiment, air was injected into the mine water in the shaft with a ring blower (maximum capacity 2.1 m^3/min) and 16 diffusers (maximum capacity 150 L/min). The depth of diffusers was −5, −3, and −2 m below the mine water surface (Fig. 2). The water samples before, during, and after each air injection at the different depths were collected at the surface to determine Fe^{2+} and turbidity. Meanwhile, the DO had been continuously monitored by a DO sensor (MP Troll 9500, USA) which was fixed in the mine water −2 m below the water surface. Aeration experiments were carried out from September to October 2008.

Results

Relation between water qualities and rebounding of mine water in the shaft

The results of mine water levels and rainfall events from July 2005 to September 2008 are shown in Fig. 3. The rate of underground mine filling averages 31 cm/day, which was similar to 25 and 30 cm/day reported by Johnson and Younger (2000). The pattern was close to a straight linear line (Fig. 2), which indicates no losses and consistent additions. Considering the filling rate and rainfall, the rate of filling during the rainy season

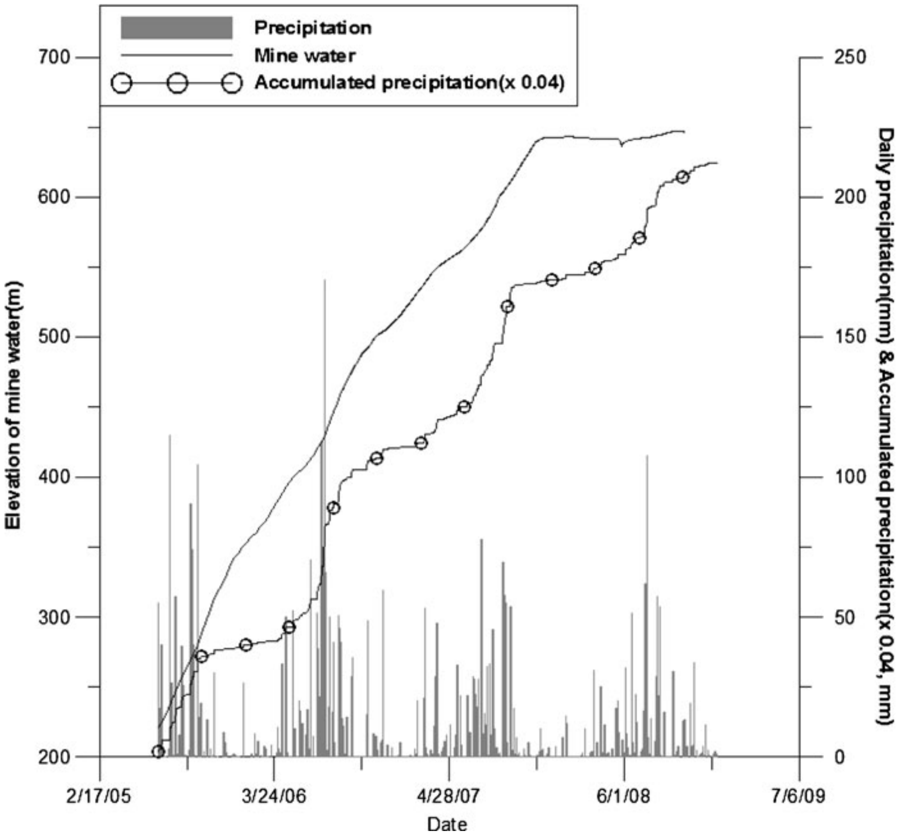


Fig. 3 Elevation of the mine water in the shaft and daily and accumulated precipitation

Table 1 Summary of water qualities of the mine water collected in the shaft

Water parameters	Min.	Max.	Mean (n)
pH	6.11	8.15	6.87(41)
ORP(mV)	−119	169	71(41)
EC(μS/cm)	1,204	5,610	2,487(41)
DO(mg/l)	2.37	9.5	4.4(38)
Al(mg/l)	0.01	0.78	0.09(37)
Fe(mg/l)	8	194	99(40)
Mn(mg/l)	3.8	9.4	6.4(37)
SO_4^{2-}(mg/l)	448	1,670	982(37)
TDS(mg/l)	539	2,930	1,195(41)

tended to be a little higher than during the dry season (Fig. 3).

Mine water was originally expected to be flowing out at ground elevation (650 ML) at the top of the shaft. However, the rise of mine water stopped at 639 ML on November 11, 2007 when the level of mine water stabilized (Fig. 3). It was later revealed that the mine water leaked where cracks occurred in the concrete lining of the shaft at that elevation.

Water parameters and chemical analysis while the mine water was rising are summarized in Table 1. According to the correlation coefficients, the levels of mine water were significantly correlated with pH and ORP negatively, and positively correlated with conductivity, Fe, and TDS. This meant that the mine water deteriorated and became more acidic with flooding. Conductivity and TDS also correlated with Fe, Mn, and SO_4 (Table 2). However, the precipitation did not correlate to the level of the mine water and other water parameters. Small rainfall events may not have reached mine voids to change water levels and big rainfall events often have lag periods before influencing water levels (Fig. 3).

Values of pH stayed circum-neutral (Table 1, Fig. 4). Meanwhile, ORP was in the range of −119 to 169 mV and shifted from an oxidized state to a reduced state as expected during flooding (Fig. 4). Iron content was as low as 2 mg/L during pumping and before closure. However, iron and sulfate contents considerably increased and reached a maximum of 194 and 1,670 mg/L, respectively, while the mine water was rising. These values tended to decline after stabilization of the mine water level (Fig. 5). Mn concentrations also increased but not to as great a degree. Al, however, remained constant at less than 1 mg/L during the monitoring period (Table 1). The low contents of Al in the water resulted from the circum-neutral pH which lowered the solubility of Al compounds.

The reason elements such as Fe and S were the major components of total dissolved solids in the water (Larsson et al. 1990; Rimstidt and Vaughan 2003) was because high levels were exchanged or adsorbed to the surfaces of the materials before flooding. A gradual decrease in dissolved solids concentrations following flooding has been reported by several authors (Banks et al. 1997; Demchak et al. 2004; Mack et al. 2010). Banks et al. (1997) explained the decline in Fe after flooding to the water coming to equilibrium in

Table 2 Correlation coefficients of some elements and water parameters

	pH	ORP	EC	Fe	Mn	SO₄	TDS	DO	Al	Rn
ORP	0.481**									
EC	−0.720**	−0.657**								
Fe	−0.569**	−0.545**	0.725**							
Mn	−0.210	0.042	0.477**	0.280						
SO₄	−0.389*	−0.098	0.630**	0.424**	0.966**					
TDS	−0.683**	−0.658**	0.992**	0.681**	0.515**	0.657**				
DO	0.302	0.194	−0.233	−0.113	0.037	−0.034	−0.214			
Al	−0.121	0.172	−0.010	0.045	0.292	0.300	−0.037	−0.290		
Rn	0.132	0.128	−0.117	−0.023	0.123	0.086	−0.126	−0.279	0.402**	
Level	−0.651**	−0.450**	0.705**	0.693**	0.129	0.280	0.662**	−0.250	0.008	0.069

EC Conductivity, *Rn* Rainfall, *Level* Min Water Level in the shaft
*Correlation is significant at the 0.05 level (2-tailed)
**Correlation is significant at the 0.01 level (2-tailed)

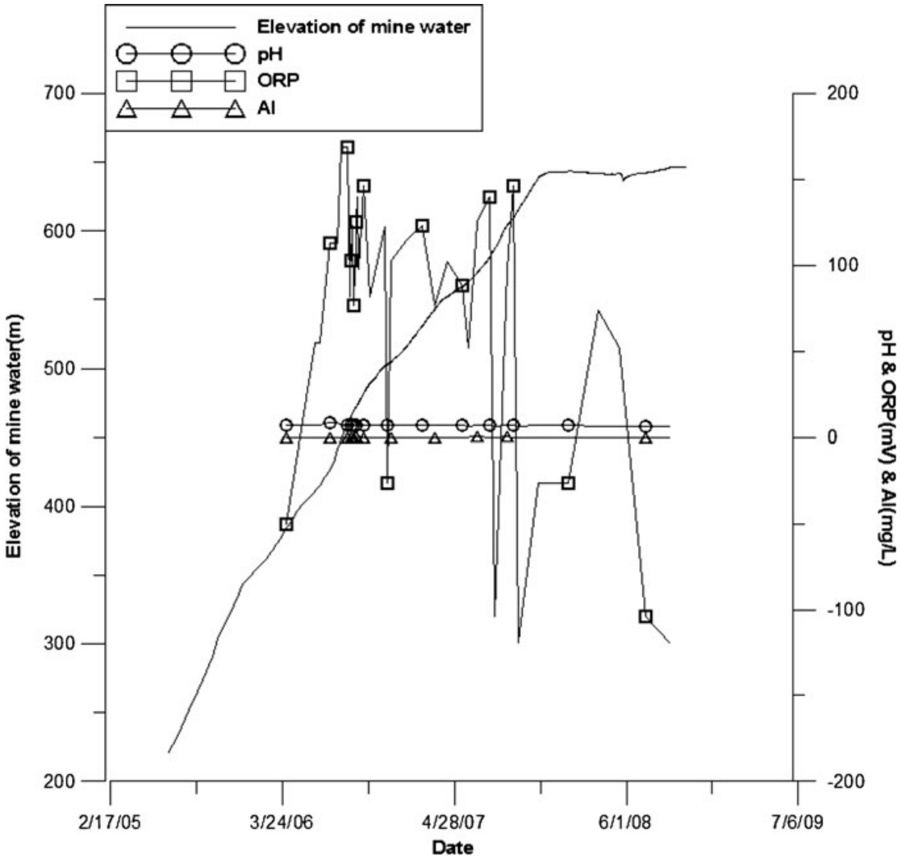


Fig. 4 Variation of pH, ORP, and Al vs. the level of mine water

the system, Fe precipitation in the mine pool, and to the gradual flushing of products of pyrite oxidation.

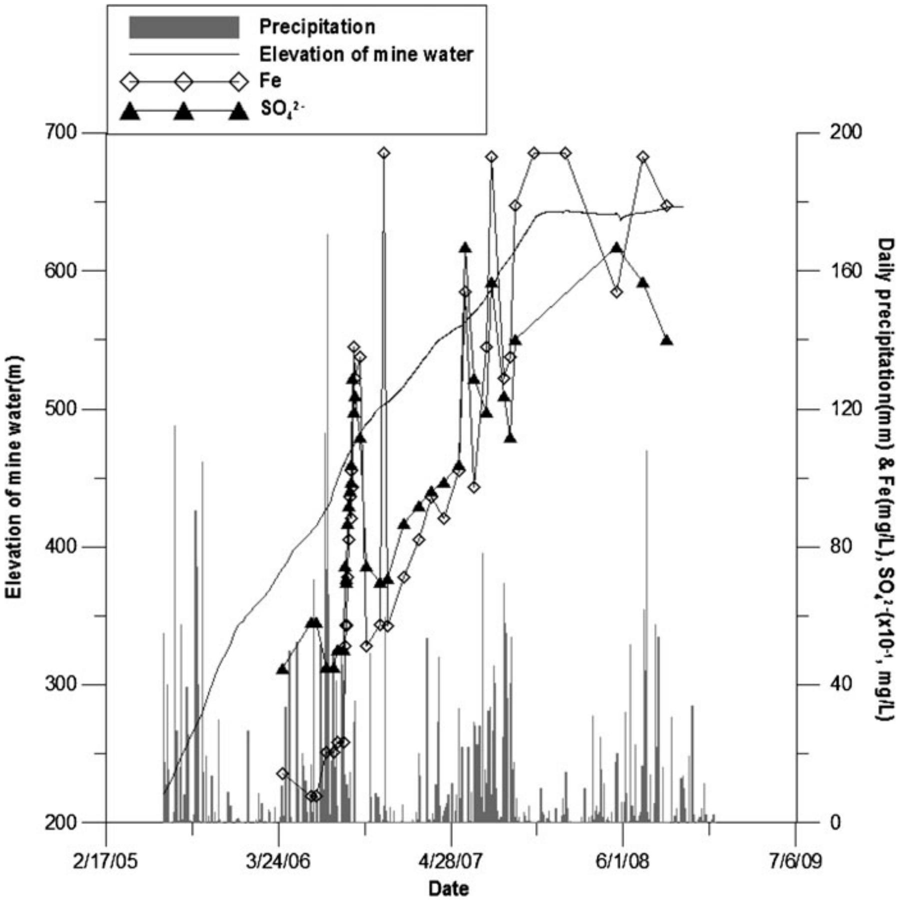
Vertical profiles of pH, EC, and temperature of the mine water body

Stratification in underground mine pools can be tracked by temperature as well as electrical conductivity changes (Wolkersdorfer 2006). According to the vertical profiles of pH, EC, and temperature at different depths, no distinct stratification, due to temperature (thermocline) or electrical conductivity (chemocline), within 200 m of the shaft were detected (Fig. 6). Water pH was relatively constant, with measured values of around 6.5. Some researchers (Banks et al. 1997; Wolkersdorfer 2006; Espana et al. 2009) reported stratification of mine water pools with poorer water quality occurring with depth. Our results implied that the mine water in the shaft was almost homogeneous and that there were no distinct quality differences among levels, implying that a thorough mixing occurred within the shaft water column.

Fe removal due to air injection

Water discharge by pumping during mining activities was 5,250 m^3/day. This rate is too high for a passive water treatment system due to limited land space and large metal loadings. Composition of dissolved solids mainly consists of ferrous iron and sulfate. Singer and Stumm (1970) explain that ferric iron hydrolysis and precipitation occurs much more rapidly than ferrous iron oxidation and precipitation, and oxidation has been identified as the rate-limiting step. Thus, if oxidation could be enhanced and conversion of ferrous iron to ferric iron could be accomplished, the treatment of this water could be achieved or enhanced in a short residence time. As abiotic iron

Fig. 5 Variation of Fe, Mn, and SO_4 vs. the level of mine water



oxidation kinetics have been explained by Stumm and Morgan (1981), decreases in ferrous iron correlate with the concentration of oxygen so that dissolved iron would be removed from water.

$$\frac{d\left[\mathrm{Fe}^{2+}\right]}{dt}=\frac{-k_1\left[\mathrm{Fe}^{2+}\right]\left[\mathrm{O}_2\right]}{\left[\mathrm{H}^{+}\right]^2}\quad(\text{for pH} > 4.0)$$

where

k_1 rate constant in moles per liter per minute
t time in minutes
[ ] aqueous concentration in moles per liter

In the batch experiment, changes in ferrous iron, DO, turbidity, and ORP in the mine water during 100 min of aeration are shown in Fig. 7. The DO in the mine water rapidly increased to 9 to 10 mg/L while ORP approached the oxidized condition as the aquarium pump was operating. The content of ferrous iron concurrently declined to below 10 mg/L from the original concentration of 160 mg/L. Removal efficiency was better with higher rates of air injection. When blowing air into the mine water in the shaft at three depths, DO concentrations increased from less than 1 mg/L to over 4 to 5 mg/L depending on the depth of the diffusers. DO increased, then decreased after 3,000 s at −2 m, 6,000 s at −3 m, and 7,000 s at −5 m. Ferrous iron reacted with the DO present in water, which is an oxygen demand process (Stumm and Lee 1961; Stumm and Morgan 1981). The reason of the increase and then decrease in DO was because of consumption of DO in the conversion of ferrous iron to ferric iron. The rate of DO increase after the depression at 3,000 to 7,000 s was faster at the −2 m depth than at deeper levels (Fig. 8) because the amount and size of air bubbles depend on water pressure. Smaller air bubble size has more surface area so that it would more effectively oxidize and precipitate metals.

Fig. 6 Variation of pH, EC, and temperature vs. depth of the water body in the shaft

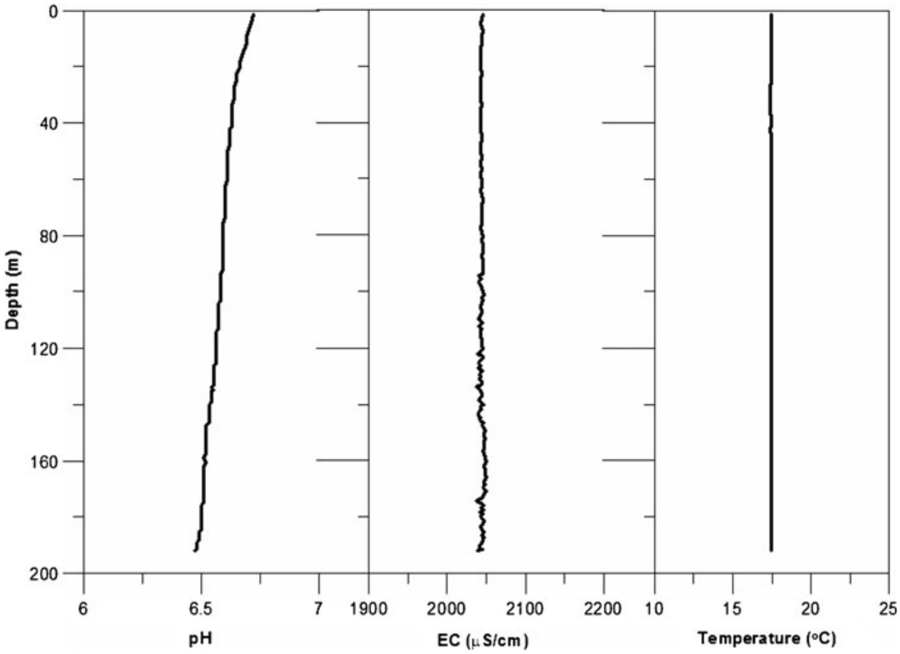


Figure 9 shows removal of ferrous iron in the mine water. A maximum amount of Fe removal was about 30 mg/L. One milligram per liter of DO can remove 7 mg/L of ferrous iron. Thus ferrous iron decreases in the water may be explained by the increase of DO (4 mg/L of DO), which caused oxidation and removal of about 30 mg/L of ferrous iron. However, comparing the bubbling at −2 m to the bubbling at −3 and −5 m, the shallow bubbling tended to make the removal of iron faster than bubbling at deeper depths (Fig. 9). If DO could be increased to 8 mg/L in mine water

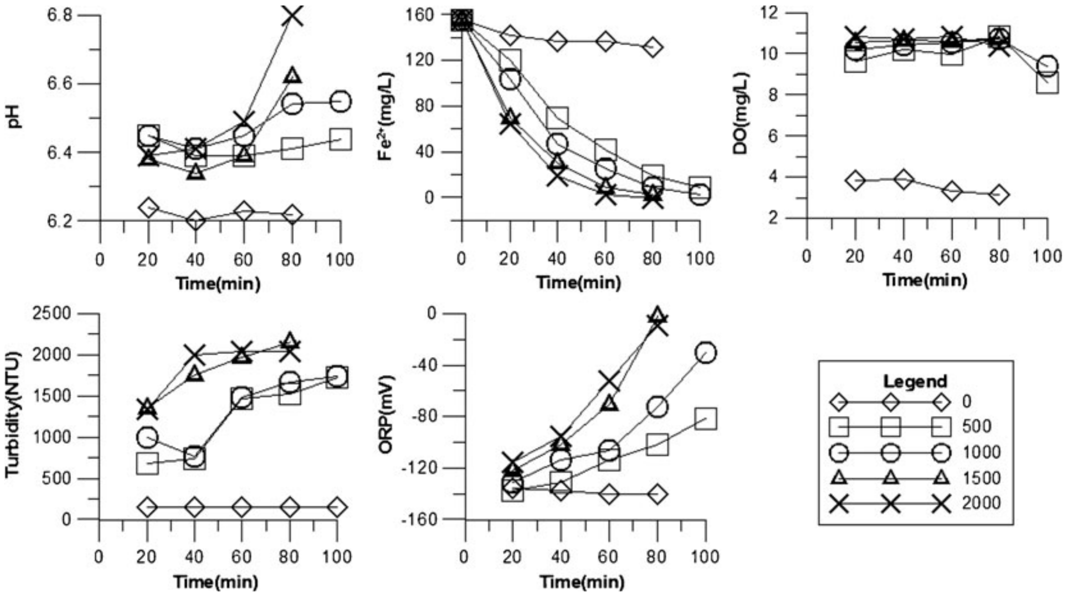


Fig. 7 Variation of water parameters over time

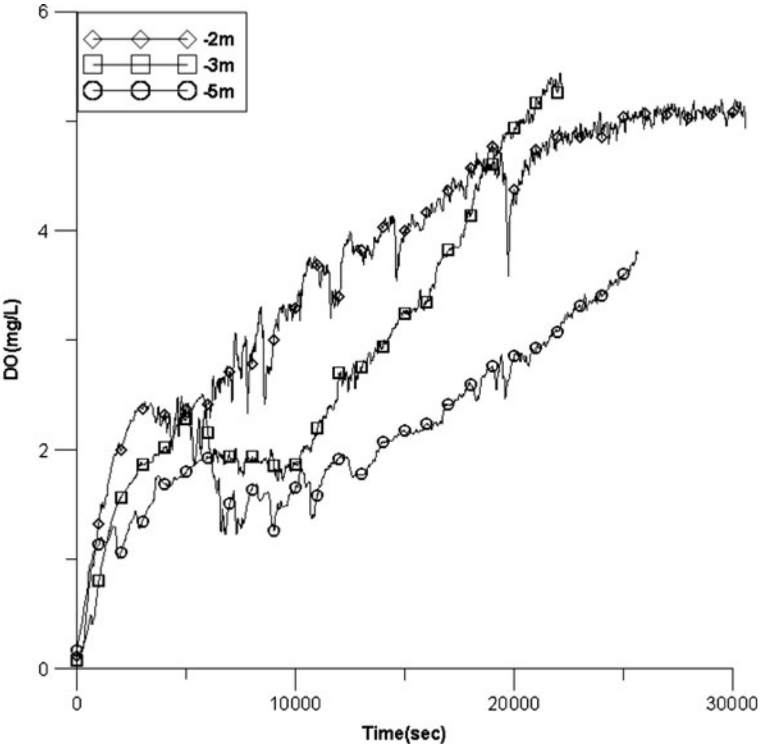


Fig. 8 Variation of DO in the mine water in the shaft over time

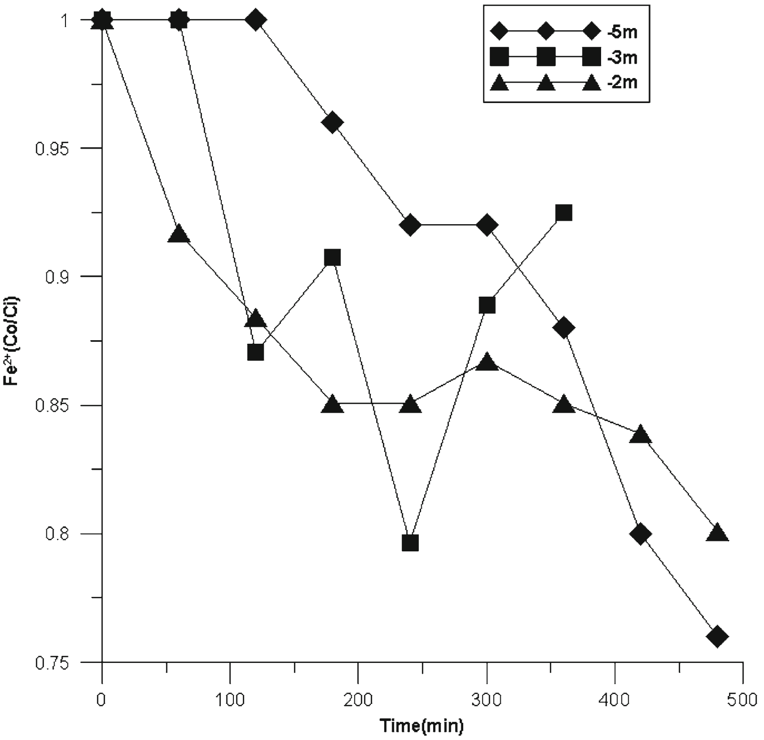


Fig. 9 Removal of ferrous iron over time vs. the depth of the diffusers

with more intensive air injection, the removal rate of ferrous iron could potentially remove 56 mg/L ferrous iron.

Conclusions

The quality of underground mine water during and after flooding was monitored in the shaft at the closed Dongwon coal mine from 2005 to 2008. After pumping ceased, mine water flooded at an average rate of 31 cm/day in a linear trend. The chemical analysis showed that Fe, Mn, and sulfate contents increased after flooding but aluminum remained less than 1 mg/L.

The thermal or chemical stratification of the water column of 200 m high was not observed as temperature, pH, and EC were relatively constant throughout the shaft. The water column of the shaft was anoxic with negative ORP values and DO was found to be lower than 1 mg/L.

When blowing air into the mine water in the shaft at three depths, DO concentrations increased from less than 1 mg/L to over 4 to 5 mg/L depending on the depth of the diffusers. Removal of Fe was about 30 mg/L. About 1 mg/L of DO removed 7 mg/L of ferrous iron. Thus, if DO could increase to 8 mg/L in mine water with more intensive air injection, removal rates of ferrous iron might reach over 50 mg/L. Mechanical aeration in the shaft would be an alternative measure to decrease Fe contents in mine drainage before other treatment methods.

Acknowledgements This paper was written as part of a sabbatical project supported by the Korea Institute of Geoscience and Mineral Resources during 2009–2010. The authors would like to acknowledge Dr. Louis McDonald of West Virginia University for his interest and support in this project. Thanks also go to graduate student Jin-Woog Jung of Chungnam National University in Korea for his help with graphs.

References

Banks, D., Younger, P. L., Arnesen, R., Iversen, E. R., & Banks, S. B. (1997). Mine-water chemistry: The good, the bad and the ugly. *Environmental Geology, 32*(3), 157–174.

Canty, G. A., & Everett, J. (2006). Alkaline injection technology: Field demonstration. *Journal of Fuel, 85*, 2545–2554.

Demchak, J., Skousen, J., & McDonald, L. M. (2004). Longevity of acid discharges from underground mines located above the regional water table. *Journal of Environmental Quality, 33*, 656–658.

Espana, J. S., Pamo, E. L., Diez, M., & Santofimia, E. (2009). Physico-chemical gradients and meromictic stratification in Cueva de la Mora and other acidic pit lakes of the Iberian Pyrite Belt. *Mine Water and the Environment, 28*, 15–29.

Houston, K. S., Milionis, P. N., Eppley, R. L., Harrington, J. M., & Harrington, J. G. (2005). Field demonstration of in-situ treatment and prevention of acid mine drainage in the abandoned Tide Mine, Indiana County, Pennsylvania. In *Proceedings, West Virginia surface mine drainage task force symposium* (Vol. 26, pp. 1–9).

Johnson, K., & Younger, P. L. (2000). *Abandonment of Frazer's grove fluorspar mine, North Pennines* (pp. 271–279). UK: Prediction and observation of water level and chemistry changes after closure, IMWA.

Kang, S. S, Cheong, Y. W., Yim, G. J., & Cho, W. J. (2004). *A study on the mine pollution control for the mine closure(III)* (pp. 24–79). KIGAM report KR-04(C)-14, in Korean.

Larsson, L., Olsson, G., Holst, O., & Karlsson, H. T. (1990). Pyrite oxidation by Thermophilic Archaebacteria. *Applied and Environmental Microbiology, 56*(3), 697–701.

Mack, B., McDonald, L. M., & Skousen, J. (2010). *Acidity decay of above-drainage underground mines in West Virginia*. doi:10.2134/jeq2009.0229.

Mack, B., & Skousen, J. (2008). Acidity decay curves of 40 above drainage mines in West Virginia. In *Proceedings, 2008 American society of mining and reclamation* (pp. 612–627).

PIRAMID Consortium (2003). *Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters* (pp. 1–151). University of Newcastle Upon Tyne, Newcastle Upon Tyne UK.

Rimstidt, J. D., & Vaughan, D. J. (2003). Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. *Geochimica et Cosmochimica Acta, 67*(5), 873–880.

Singer, P., & Stumm, W. (1970). Acidic mine drainage, the rate-determining step. *Science, 167*(3921), 1121–1123.

ŠŠlesárová, A., Zeman, J., & Kuššnierová, M. (2007). Geochemical characteristics of acid mine drainage at the smolník deposit (Slovak Republic). In R. Cidu, & F. Frau (Eds.), *IMWA symposium: Water in mining environments, 27th–31st May 2007*. Cagliari, Italy.

Stumm, W., & Lee, G. F. (1961). Oxygenation of ferrous iron. *Industrial and Engineering Chemistry, 53*, 143–146.

Stumm, W., & Morgan, J. J. (1981). *Aquatic chemistry* (2nd Ed., p. 790). New York: Wiley.

Wood, S. C., Younger, P. L., & Robins, N. S. (1999). Long-term changes in the quality of polluted minewater discharges from abandoned underground coal workings in Scotland. *Quarterly Journal of Engineering Geology, 32*, 69–79.

Wendt-Potthoff, K., Bozau, E., Frömmichen, R., Meier, J., & Koschorreck, M. (2010). Microbial iron reduction during passive in-situ remediation of an acidic mine pit lake mesocosm. *Limnologica, 40*, 175–181.

Wolkersdorfer, C. (2006). Acid mine drainage tracer tests. In *6th proceedings of ICARD* (pp. 26–30). ASMR.

Younger, P. L. (2000). Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: A first approximation. *Journal of Contaminant Hydrology, 44*, 47–69.

Younger, P. L., Banwart, S. A., & Hedin, R. S. (2002). *Mine water: Hydrology, pollution, remediation* (pp. 230–259). Dordrecht: Kluwer academic publishers.

Younger, P. L., Jarvis, A. P., & Laine, D. M. (2003). *Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters*. European Commission 5th Framework RTD Project no. EVK1-CT-1999-000021 "Passive in-situ remediation of acidic mine / industrial drainage" (PIRAMID). 164 p.