



Lab-scale study on the application of In-Adit-Sulfate-Reducing System for AMD control

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ARTICLE INFO

Article history:

Received 21 August 2006

Received in revised form 16 January 2007

Accepted 6 March 2008

Available online 20 March 2008

Keywords:

Acid mine drainage (AMD)

SAPS

In-Adit-Sulfate-Reducing System (IASRS)

ABSTRACT

In a study of the 29 operating passive systems for acid mine drainage (AMD) treatment, 19 systems showed various performance problems. Some systems showed very low efficiency even without visible leakage or overflow. Though systems show fairly good efficiency in metal removal (mainly iron) and pH control, sulfate removal rates were very low which indicates the possibility of very poor sulfate reductions by Sulfate Reducing Bacteria (SRB).

As an alternative method, In-Adit-Sulfate-Reducing System (IASRS), the method of placing the SAPS inside the adit, to have temperature constant at about 15 °C, was suggested. Lab-scale model experiments of IASRS were carried out. The models 1 and 2 were run at 15 °C and 25 °C, respectively. The model 1 contained about a half of COD in the beginning of the operation than that of model 2. Metal removal ratios were higher than 90% in both systems. Both systems showed the sulfate removal ratios of 23% and 27%, respectively, which were still considerably low, even though higher than those of presently operating systems. However, since the synthetic AMD used was very low in pH (2.8) and very high in sulfate concentration, if some suggested modifications were applied to the standard design, it is presumed that the sulfate removal ratio would have increased.

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1. Introduction

From 1989, over 98% of coal mines in Korea has been closed under the coal industry promotion program and, only 10 coal mines are currently operating [1]. About 900 metal mines were closed or suspended from activity, with only 19 mines presently operating. Since 1996 till 2002, 35 passive treatment systems in 29 mines were constructed to treat acid mine drainage (AMD). Processes like successive alkalinity producing systems (SAPS), anoxic limestone drains (ALDs), anaerobic wetland, aerobic wetland, and oxidation pond were combined and applied in the construction of passive treatment systems [2].

In an investigation study for the 29 operating passive systems for AMD treatment, 19 systems showed various problems. Some systems showed very low efficiency even without visible leakage or overflow [3]. Research and investigation on passive treatment systems in Korea was mostly focused on the removal efficiency of iron and aluminium, and pH control [4,5]. However, many systems reveal very low removal ratio or even increased concentrations of sulfate with time [2]. Though systems show fairly good efficiency in

metal removal (mainly iron) ratios and pH control, sulfate removal rates were very low which indicates the possibility of very poor sulfate reductions by SRB.

The experiments on model SAPS at various temperatures, showed that maximum sulfate removal ratio of 70% at 20 °C and 87% at 36 °C, but no sulfate removal at 1 °C [6]. Lee [6] also found SRB activity also was almost negligible at 1 °C but quite vigorous at 20 °C and 36 °C, indicating low or non-existent SRB activity during harsh winter.

Problems in SAPS include low temperature in winter, seasonal variation of AMD flux, inappropriate HRT (hydraulic retention time), sludge cake or coating on organic substrate layer, lack of space, topographical situations of mountainous area, and seasonal flooding.

The In-Adit-Sulfate-Reducing System (IASRS) was suggested as an alternative method to improve the treatment systems where SAPS are put inside the mine adit (Fig. 1). Since whole system is placed inside the mine adit, temperature would remain constant and the anoxic condition would be generally maintained even if flow rate changes; thus appropriate condition for sulfate reduction would be maintained. And the construction of treatment system inside the mine adit would minimize the site area needed, with little or no leakage or plugging that usually occurs in general SAPS. Similar treatment system was suggested and pilot

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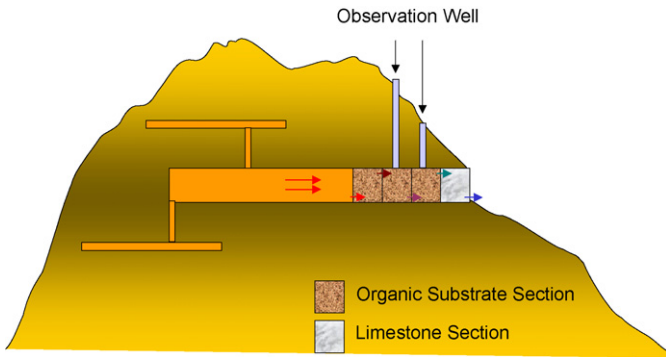


Fig. 1. Schematic diagram of the In-Adit-Sulfate-Reducing System.

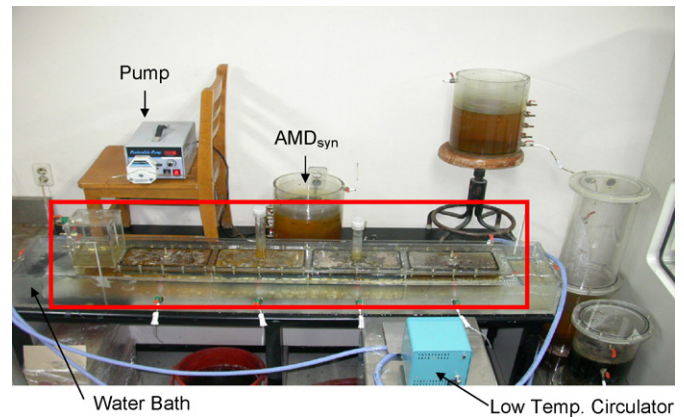


Fig. 3. Photograph of laboratory scale IASRS model.

study was carried out elsewhere [7]. But there, the researchers focused on metals removal and sulfate removal efficiency was not mentioned.

This study was carried out to examine the possibility of application of IASRS in the field. Experiments with two laboratory scale IASRS models were performed for 80 days.

2. Structure of IASRS and experiment

2.1. Structure

Two IASRS models were operated, each consisting of four reactive sections. Each section was 12 cm (H) × 12 cm (W) × 30 cm (L). Total volume of each model system was 17.28 l. The first three sections were filled with gravel and spent mushroom compost (SMC) and the last section was filled with limestone (Fig. 2). Lee [6] suggested the suitable hydraulic retention time (HRT) for sulfate reduction in the SAPS 8–12 days so in this study HRT was set to 10 days. Two observation holes were made to measure pH and Oxidation Reduction Potential (ORP).

From the observation study in adit temperature at several mines were from 12 °C to 18 °C. So in this study 15 °C was selected as an in adit temperature. The model 1 was run at about 15 °C and the model 2 was run at 25 °C. Water bath was used to maintain the temperature (Fig. 3).

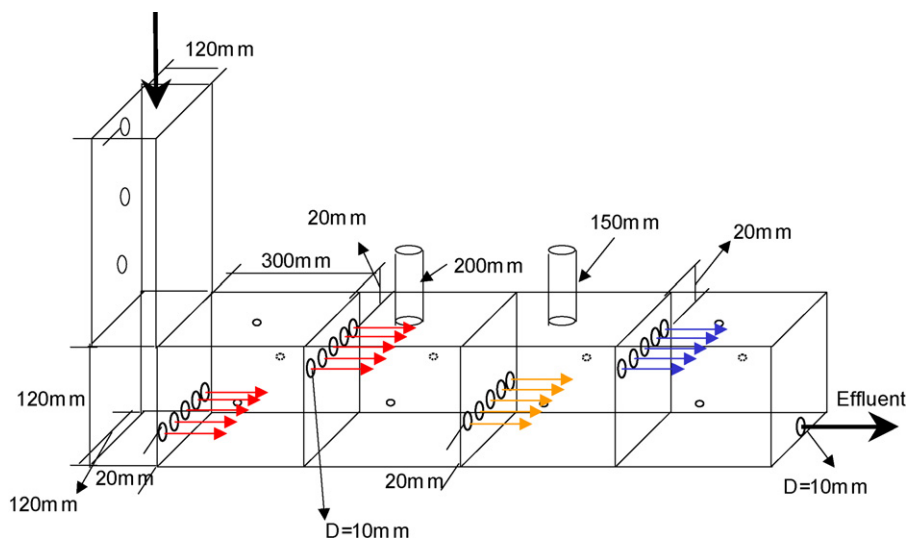


Fig. 2. Schematic sketch of laboratory scale IASRS model.

2.2. Materials used

SMC used in this study was from a mushroom farm in Buyeogun, Chungcheong-namdo. And limestone was from Danyang limestone mine in Danyang-gun Chungcheong-bukdo.

SMC and limestone were analyzed by XRF (X-ray fluorescence spectrometer—Philips PW2400) at the Pusan branch of Korea Basic Science Institute (KBSI) and EA (elemental analyzer—Flash EA 1112 series/CE Instruments) at the Seoul branch of KBSI. Table 1 shows the chemical composition of the SMC and limestone used in this study. Calculated purity with result of EA and XRF analysis of limestone and SMC were 98.3 wt.% for CaCO_3 and 56.7 wt.% for CH_2O .

Synthetic AMD was made by mixing distilled water with waste rock from the Samcheok coal mine. The properties of the synthetic AMD were a pH 2.78, total dissolved solid (TDS) 1500 mg/l, Fe_T 363.92 mg/l, Al^{3+} 262.50 mg/l, SO_4^{2-} 2362.01 mg/l at equilibrium. These properties were nearly same as Samcheok coal mine leachate.

2.3. Analytical methods

The pH and ORP of effluent were measured once in every 2 days using a portable pH/ORP meter (HI 98150; Hanna, Italy),

Table 1

Chemical compositions of the spent mushroom compost and limestone used in the experiment

	Spent mushroom compost (wt.%)	Limestone (wt.%)
C	28.37 ± 0.05	10.43 ± 0.01
H	3.85 ± 0.00	0.00 ± 0.00
O	30.27 ± 0.03	27.88 ± 0.00
N	2.33 ± 0.00	0.01 ± 0.00
S	0.08 ± 0.02	0.00 ± 0.00
SiO ₂	16.75	1.46
Al ₂ O ₃	1.26	n.d.
Fe ₂ O ₃	0.35	0.20
MnO	0.26	n.d.
CaO	4.21	55.81
MgO	0.76	n.d.
K ₂ O	1.62	n.d.
Na ₂ O	0.44	n.d.
P ₂ O ₅	0.77	n.d.
TiO ₂	n.d.	n.d.
LOI	58.10	42.02

C, H, O, N, S: analyzed by elemental analyzer. Others: analyzed by X-ray fluorescence spectrometer.

and the conductivity and TDS were measured using a conductivity/TDS meter (HI 9835; Hanna, Italy). Water samples collected for cations determination were filtered through a 0.45 mm cellulose nitrate membrane filter using a hand pump, and were immediately acidified to pH < 2.0 by adding HNO₃. Samples collected for anion determinations were filtered but not acidified. All water samples were stored in a refrigerator at 4 °C. Analysis for dissolved cations was performed using the ICP-AES (inductively coupled plasma atomic emission spectrophotometer; Jobin Yvon Co. 138 Ultrace) at the Seoul branch of KBSI. Anions were determined using the ion chromatography (Dionex series 500DX) at the Pusan branch of Korea Basic Science Institute. Chemical oxygen demand (COD) was analyzed using the spectrophotometer (HACH-DR 2010; Hach, Japan) after having the sampling reacted with the COD analyzing reagent HS-COD-M (Humas, Korea).

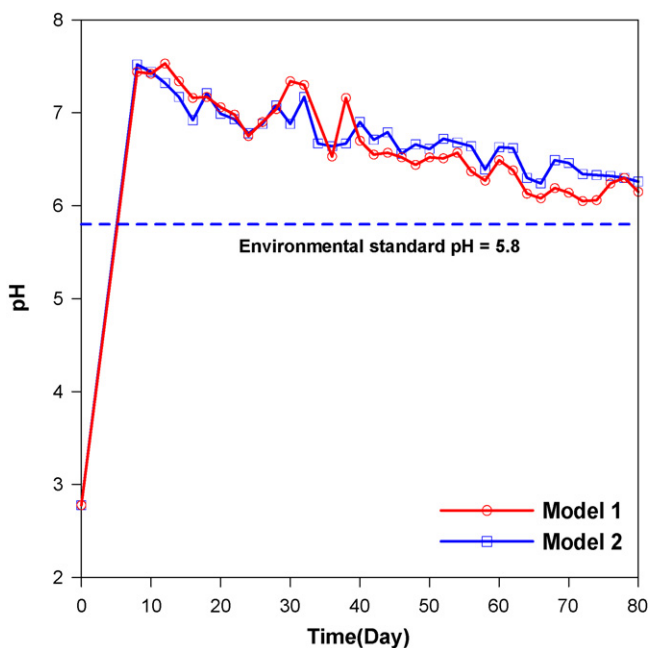


Fig. 4. The variation of pH in the effluent of each IASRS model with time.

3. Results and discussions

Black precipitates in Sections 2 and 3, and strong odor of H₂S indicated that likely sulfate reducing reaction after 5 days of observation in the model 2, and after 10 days in the model 1. After 80 days of run, pH of both models converged to about 6.3 (Fig. 4). The maximum COD values of model 1 in the beginning of the operation was 2940 mg/l at model 2. But COD values of model 2 were about double of those of model 1 (Fig. 5). It indicated that shallow underground temperature of about 15 °C might also be appropriate for the reduction of dissolved organic carbon (DOC).

Iron and aluminium removal ratios were over 90% in both models (Fig. 6(a) and (b)). Effluent manganese concentration increased from 3.69 mg/l to 39.05 mg/l after 30–40 days but was decreased

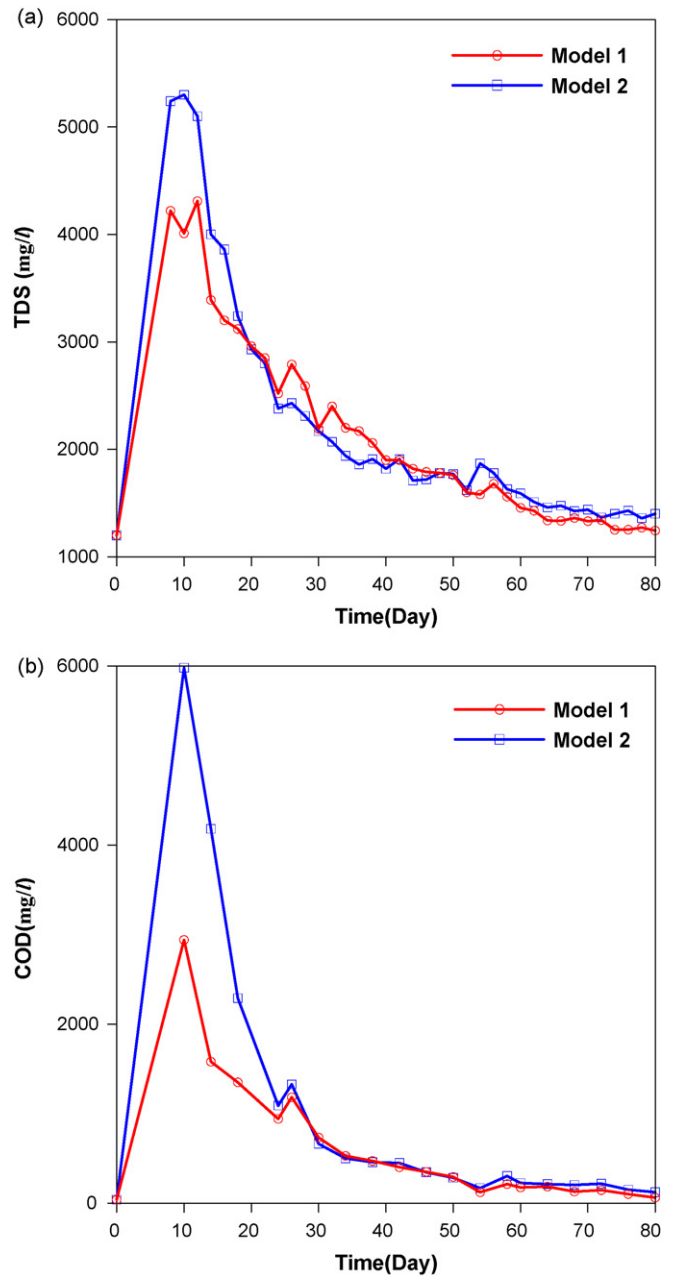


Fig. 5. The variation of (a) TDS and (b) COD in the effluent of each IASRS model with time.

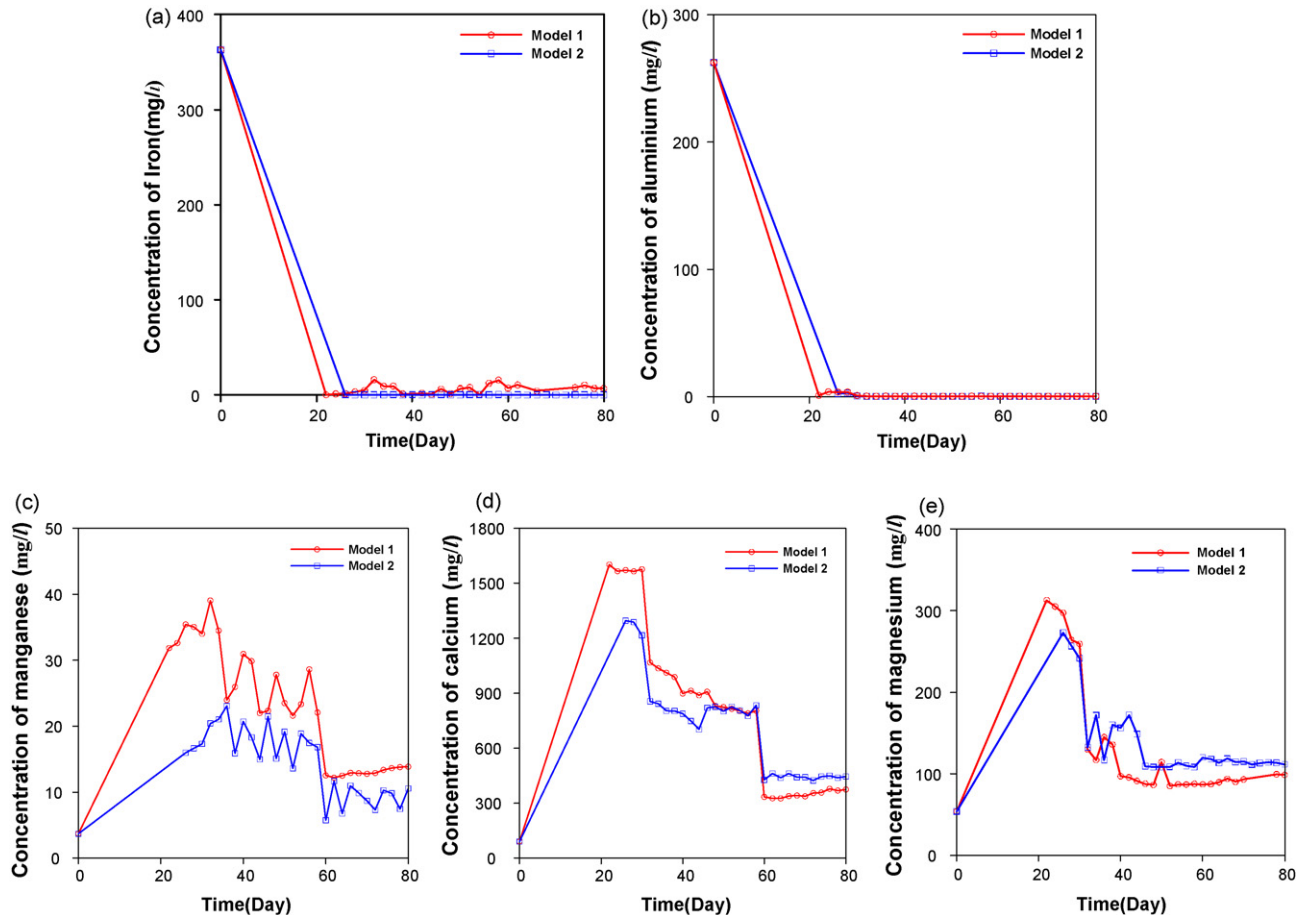


Fig. 6. The variations of (a) iron, (b) aluminium, (c) manganese, (d) calcium and (e) magnesium concentrations in each IASRS model with time.

gradually about 13 mg/l (Fig. 6(c)), similar trends were reported in studies concerning AMD with SAPS [8,9]. Dissolution of manganese might have caused from SMC as proposed by Hedin et al. [8] and Drury [10]. Calcium concentration derived from both of limestone and SMC was increased at the beginning of operation about 1600 mg/l (Fig. 6(d)) but decrease later to about 350 mg/l. Since Magnesium was not detected in the limestone used in this study (Table 1) magnesium must have been derived from SMC (Fig. 6(e)).

Sulfate concentration increased in the beginning of the operation in model 1 while that of in model 2 did not increase. Sulfate addition by leaching from SMC might be similar in both models. But more favorable temperature condition for SRB in model 2 may lead to much higher activity of SRB than in model 1. Therefore active sulfate reduction in model 2 might have decreased the sulfate concentration from the beginning of the experiment. Earlier occurrence of black precipitates in model 2 was observed. So sulfate concentration was not decreased in model 1 at the start of the experiment as compared to model 2. After about 60 days, sulfate removal rate converged to about 23% in model 1, about 4% lower than that of model 2 (Fig. 7).

The sulfate removal ratios of about 23% were higher than those of currently implemented systems (under 10%). The sulfate removal ratio might had been higher than 23% if pH of synthetic AMD used in the study was higher than 2.8.

The absence of black precipitates at Section 1 and pH of about 4 at the first observation hole (Fig. 8), perhaps indicates that SRB in Section 1 could not survive due to the very low pH of synthetic AMD.

Postgate [11] suggested that for vigorous SRB activity presence of sulfate, sufficient amount of low molecular weight carbonate compounds, pH of higher than 4, and the absence of the oxidizer such as O_2 , Fe^{3+} , Mn^{4+} are to be maintained. Elliott et al. [23], Kolmat and Johnson [24] reported the stoppage of SRB activity under pH 3 are essential. Even though in some studies it was reported that at pH around 3, SRB controlled the microenvironment very near to bacterial cells and induce sulfate reduction [12–15], that may be due to favorable factors such as high temperature (20–30 °C) and enough supply of easily decomposable carbon source like sodium lactate, etc. Such a condition however, is very different from that of the uncontrolled bulk aqueous environment. Also it is noticeable that even though they mentioned the possible condition of pH lower than 3, all of their experiments were carried out above pH 4. For example, Lyew et al. [13] showed that a down flow column reactor inoculated with SRB and operated under continuous flow condition could remove 90% of dissolved metals and 11% of sulfate from AMD and could increase pH of the solution from 4.8 to above 5. However, when AMD of pH 3.5 was introduced into the reactor, SRB activity ceased.

Also it was reported that for active growth of SRB an anaerobic environment with a ORP lower than -100 mV was needed [11,16], whereas the ORP in the first observation hole was $+100$ mV (Fig. 9).

HRT is an important factor for the bacterial sulfate reduction. In the experiment if Section 1 were to function at low pH and high ORP, the actual HRT would have been reduced to about 7 days, which again could be insufficient for the sulfate reduction.

Another likely reason is believed to be the extremely high sulfate concentration of synthetic AMD used in this study. Sulfate

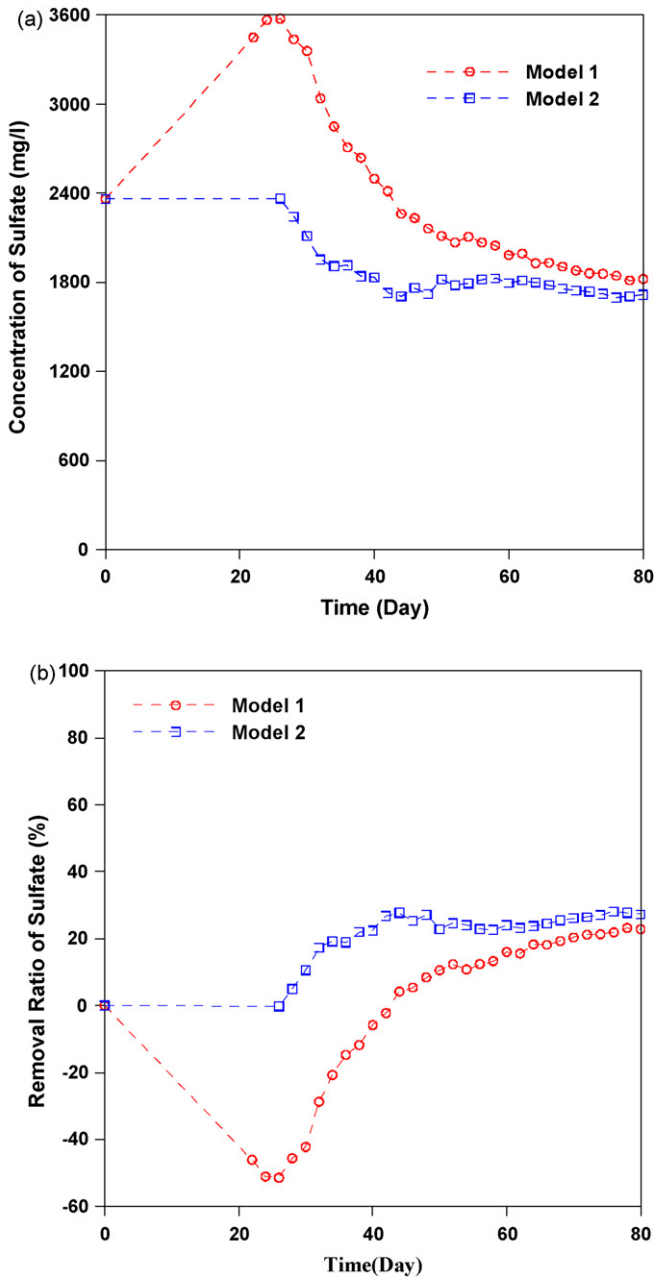


Fig. 7. The variations of sulfate (a) concentrations and (b) removal ratios in each IASRS model with time.

concentration was more than 2300 mg/l which was equal to 2.46 mol/(m³ day). Even though removal efficiency of model 1 was 23%, it meant the system treated more than 560 mmol/(m³ day). Eger and Wagner [17] reported that typical sulfate reduction in the sulfate reducing reactor ranged from 200 to 600 mmol/(m³ day). And Acid Drainage Technology Initiative (ADTI, WV, USA) also suggested that the standard efficiency of passive treatment systems is achieved between 100 and 300 mmol/(m³ day) [18]. Considering the above, sulfate removal efficiency of the model system was high.

For the actual field application, activated SRB source could be added for proper operation of the first reactive section. Mixing of limestone chips and available organic matter decompose more quickly than SMC, helping the activity of SRB in the beginning of the operation. Other activating materials substitute for SMC

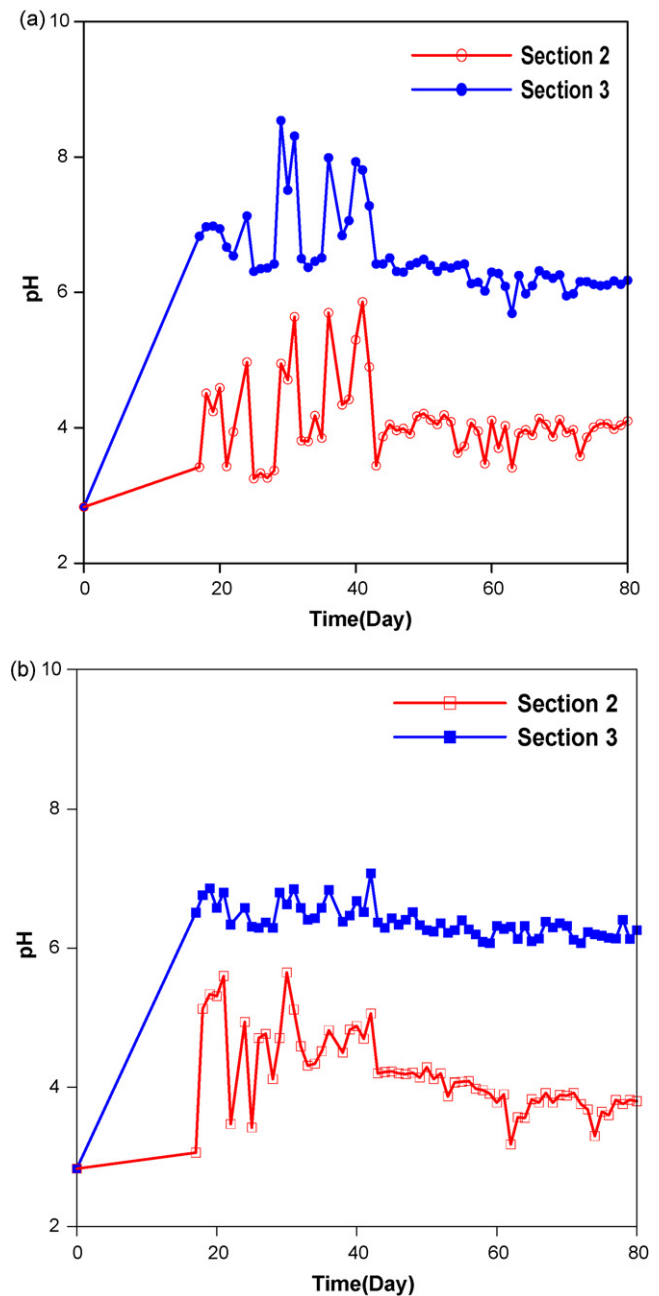


Fig. 8. pH variations with time at each observation hole of the (a) model 1 and (b) model 2.

for encourage the activity of SRB in the beginning of the operation are sewage sludge [4,19], paper mill sludge [19], and whey from cheese factory [10], etc. Also, for the long-term operation of the system, charging to organic matters less degradable than SMC used in the reactive sections, which did not be installed the observation hall, may be helpful. The possible organic matters as substitute for SMC are compost of rice straw and cow manure [20], sawdust [4], oak compost [21,22], oak chip [22], etc. The proper mixing ratio of organic matters for the activity of SRB in the beginning of the operation and for the long-term operation, would have to be obtained. The optimum size of the treatment system adjusted to meet the sulfate concentration of each AMD is also needed. To control of HRT, suitable buffering sections could be considered.

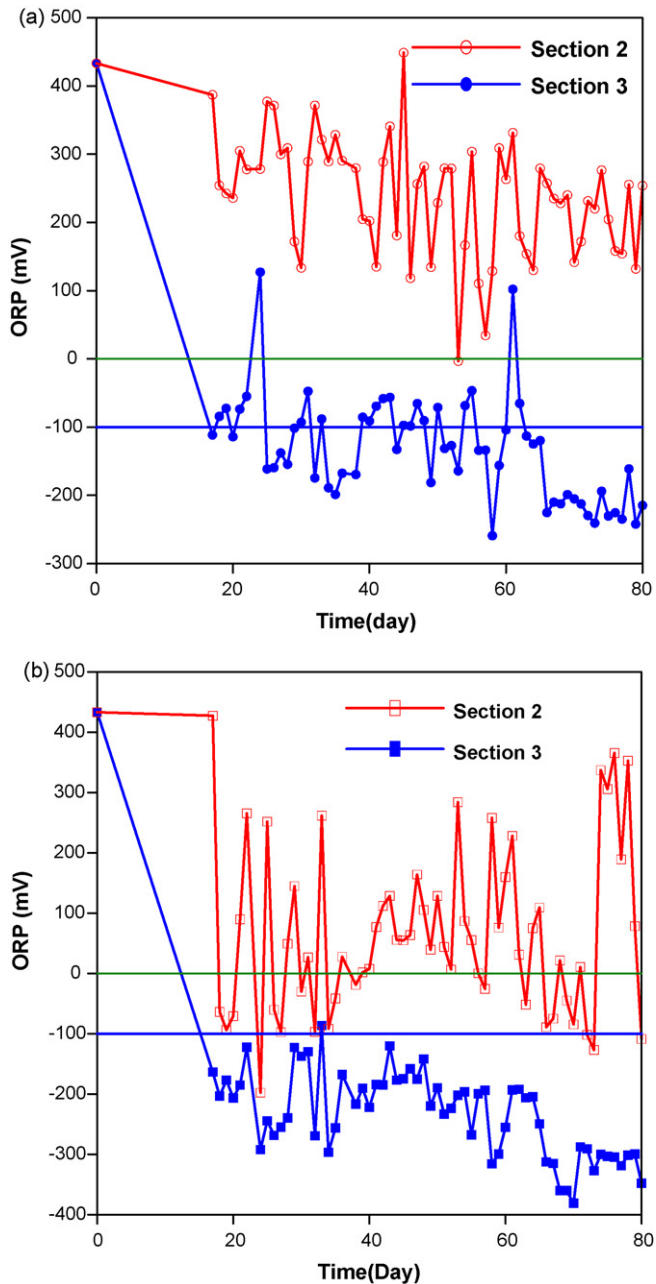


Fig. 9. ORP variations with time at each observation hole of the (a) model 1 and (b) model 2.

4. Conclusions

This study was carried out to examine the possibility of application of IASRS as an alternative method for the improvement of the operating systems.

Experiments with two laboratory scale IASRS models were performed for 80 days. The models 1 and 2 were run at 15 °C and 25 °C, respectively. The model 1 contained about a half of COD in the beginning of the operation than that of model 2. Metal removal ratios were higher than 90% in both systems. Both systems showed the sulfate removal ratios of 23% and 27%, respectively, which were still considerably low, even though higher than those of presently operating systems. However, since the synthetic AMD used was very low in pH (2.8) and

very high in sulfate concentration, if some suggested modifications were applied to the standard design, it is presumed that the sulfate removal ratio would have increased. And the construction of treatment system inside the mine adit has other benefits such as reduction of the site area needed, little leakage or plugging, and makes the system safe from undesirable climatic change.

Acknowledgements

This research was supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science and Technology of Korea.

References

- [1] Coal Industry Promotion Board (CIPB), 2003, <http://www.cipb.or.kr>.
- [2] Y.W. Cheong, et al., A Study on the Evaluation of Environmental Contamination and Restoration in Abandoned Metallic Mining Areas, KIGAM, KR-01-07, 2001, 198 pp.
- [3] S.W. Ji, J.I. Ko, H.B. Kim, H.T. Kang, J.W. Kim, S.J. Kim, The operating status of passive treatment system for abandoned coal mine in Korea, in: Proceedings of the KoSSGE Spring Conference, Seoul, April 18–19, 2003, pp. 352–355.
- [4] N.C. Sung, H.C. Kang, J.M. Im, J.K. Kim, A Study on Increase the Efficiency and Elevate the Ability of the Passive Treatment System for Abandoned Coal Mine, CIPB 97-04, 1997, 289 pp.
- [5] Y.S. Bae, S.P. Lee, J.S. Cho, D.W. Ki, C.H. Nam, Research on Effects of Passive Treatments in Abandoned Mining Area and their Effective Management System, CIPB 2001-11, 2001, 205 pp.
- [6] S.H. Lee, A Study on the Activity of Sulfate Reducing Bacteria in Successive Alkalinity Production System, Thesis for Master's Degree, Hanyang University, Seoul, Korea, 2003, 90 pp.
- [7] M. Canty, R. Hiebert, M.A. Harrington-Baker, D. Bless, Innovative, in situ use of sulfate reducing bacteria to remove heavy metals from acid mine drainage, in: Proceedings of the 2001 International Containment and Remediation Technology Conference and Exhibition, Orlando, FL, June 10–13, 2001.
- [8] R.S. Hedin, R.W. Nairn, R.L.P. Kleinmann, Passive Treatment of Coal Mine Drainage, USDI, Bureau of Mines Information Circular IC 9389, Pittsburgh, PA, 1994.
- [9] J.H. Hwang, A Study on the Environmental and Geochemical Characteristics of the Acid Mine Drainage and its Treatment in the Vicinity of the Dogye Coal Mine, Thesis for Doctor's Degree, Seoul National University, Seoul, Korea, 1998, 103 pp.
- [10] W.J. Drury, Treatment of acid mine drainage with anaerobic solid-substrate reactor, *Water Environ. Res.* 71 (6) (1999) 1244–1250.
- [11] J.R. Postgate, *The Sulphate-reducing Bacteria*, 2nd edition, Cambridge University Press, NY, 1984, 208 pp.
- [12] J. Bolis, T.R. Wildeman, R.R. Cohen, The use of bench scale parameters for preliminary metal removal from acid mine drainage by wetlands, in: Proceedings of the American Society for Surface Mining and Reclamation, Princeton, WV, USA, 1991, pp. 123–136.
- [13] D. Lyew, R. Knowles, J. Sheppard, The biological treatment of acid mine drainage under continuous flow conditions in a reactor, *Trans. IChemE* 72 (Part B) (1994) 42–47.
- [14] J.J. Gusek, Three case histories of passive treatment of metal mine drainage, in: Proceedings of the 19th Annual West Virginia Sulfate Drainage Task Force Symposium, Morgantown, WV, USA, April 7–8, 1998.
- [15] C. Garcia, D.A. Moreno, A. Ballester, M.L. Blazquez, F. Gonzalez, Bioremediation of an industrial acid mine water by metal-tolerant sulphate-reducing bacteria, *Miner. Eng.* 14 (9) (2001) 997–1008.
- [16] L. Barton, *Sulfate Reducing Bacteria*, Plenum Press, New York, 1995, 336 pp.
- [17] P. Eger, J. Wagner, Wetland treatment systems—How long will they really work?, *Sudbury 2003 Mining and the Environment*, Sudbury, Ontario, Canada, 2003, 14 pp.
- [18] J. Skousen, A. Rose, G. Geidel, J. Foreman, R. Evans, W. Hellier, *Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage*, The National Mine Land Reclamation Center, West Virginia University, Morgantown, WV, USA, 1998, 132 pp.
- [19] E.H. Kim, S.H. Chang, A study on biological treatment of abandoned acidic mine drainage using sewage sludge and paper mill sludge as carbon sources, *J. KoSES* 4 (2) (1999) 63–75.
- [20] Y.W. Cheong, J.S. Min, K.S. Kwon, Metal removal efficiencies of substrates for treating acid mine drainage of Dalsung mine, South Korea, *J. Geochem. Exploration* 64 (1998) 147–152.

- [21] S.D. Kim, K.D. Cha, H.J. Seo, In-situ prevention of acid mine drainage by sulfate reducing bacteria, *J. KSEE* 21 (5) (1999) 837–843.
- [22] I.S. Chang, P.K. Shin, B.H. Kim, Biological treatment of acid mine drainage under sulphate-reducing conditions with solid waste materials as substrate, *Water Res.* 34 (4) (2000) 1269–1277.
- [23] P. Elliott, S. Ragusa, D. Catcheside, Growth of sulfate-reducing bacteria under acidic conditions in an upflow anaerobic bioreactor as treatment system for acid mine drainage, *Water Res.* 32 (12) (1998) 3274–3730.
- [24] A. Kolmat, D.B. Johnson, Treatment of acidic waste waters using immobilised, acidophilic sulfate-reducing bacteria, *J. Chem. Technol. Biot.* (78) (2001) 836–843.