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Problems and improvement methods of passive treatment systems for acid mine drainage in Korea

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Abstract: This study has been carried out to evaluate the passive treatment systems for acid mine drainage in Korea and to suggest, if possible, the method for the improvement. 35 passive treatment systems in 27 mines have been constructed since 1996. SAPS, being the main process, was combined with more than one of processes such as anaerobic wetland, aerobic wetland, and oxidation pond for the construction of passive treatment system. Problems observed during the operation include the poor sulfate removal ratio, overflow, leakage, unusabless of the whole system, and inefficiency. The reasons of the poor sulfate removal ratio are believed that the low temperature during the winter prohibits the SRB activity and HRT for bacterial sulfate reduction is insufficient. An alternative method In Adit Sulfate Reducing System which enables to keep the temperature constant at about 15℃ was suggested. IASRS is the methods of placing the SAPS inside the adit, which enables the temperature around the system constant can be maintained. The experiments using the laboratory scaled model systems made up of four sections showed high efficiencies in pH control and metal removal ratios, but showed still low sulfate removal ratio of about 23% also with high COD at the beginning of the operation.

Introduction

Acid mine drainage(AMD), a major environmental hazard that affects aquatic ecosystems around the mines, is resulted from the oxidation of metal sulfides, particularly pyrite(FeS_2). Acid mine drainage causes the degradation of aquatic systems through acidification, high concentrations of iron and sulfate, and elevated levels of soluble toxic metals.

From 1989, most of coal mines in Korea has been closed by the coal industry promotion program and only ten coal mines are operating. Also about nine hundred metal mines were closed or interrupted with presently operating 19 mines(CIPB, 2003). To treat the acid mine drainage from the closed or abandoned mines 35 passive treatment systems in 29 mines have been constructed since 1996. More than one process among SAPS(Successive alkalinity producing systems), anaerobic wetland, aerobic wetland, and oxidation pond were combined and applied for the construction of passive treatment system(Fig. 1.).

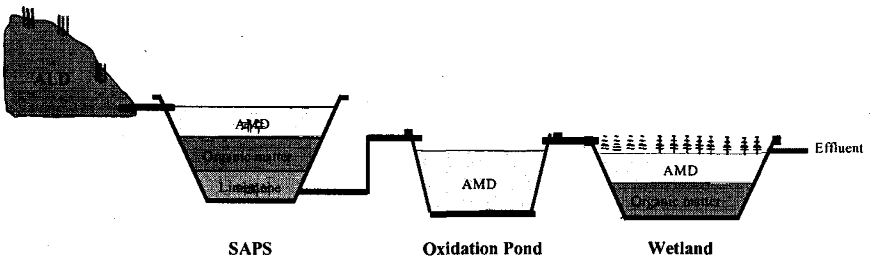


Fig. 1. A generalized schematic diagram of passive treatment system in Korea.

SAPS is the main treatment process for AMD treatment in Korea because it overcomes the alkalinity producing limitations of ALDs(Anoxic Limestone Drains) and needs smaller area than when only wetlands and ALDs are used. However it should be combined with the anaerobic wetlands and/or ALDs. In SAPS the AMD flows downward through the organic layer which has two essential functions. First, dissolved oxygen in AMD is removed by bacteria utilizing biodegradable organic compounds as energy sources. And bacterial sulfate reduction in the anaerobic zone of organic layer generates alkalinity as shown in the Eq.1(Hedin et al., 1994).

$$2CH_2O + SO_4^{2-} \rightarrow S^{2-} + 2HCO_3^- + 2H^+ \qquad (1)$$

Then water flows through the limestone bed. Because dissolved oxygen was removed before contacting the limestone, coating of metal-hydroxide is not made on limestone surface. Therefore alkalinity can be produced succe- ssively.

Sulfate reducing bacteria(SRB) are known to be ubiquitous and to tolerate a wide range of environmental conditions(Postgate, 1984). Their optimal pH range has been reported to be from 5 to 9, but they can control their microenvironment even when the pH of bulk solution is below 5. Some researches reported that sulfate reduction treatment has been successful even when the pH of the drainage was below 3(Bolis et al., 1991; Gusek, 1998).

Reduction of sulfate by SRB can affect the concentrations of dissolved metal ions directly by the precipitation of metal sulfides(Eq.2.).

$$M^{2+} + H_2S + 2HCO_3^- \rightarrow MS + 2H_2O + 2CO_2 \qquad (2)$$

AMD treatment utilizing SRB for the alkalinity production and metal removal also occur in anoxic wetland. Similar type of sulfate reducing bioreactor has been developed(Elliott et al., 1998; Drury, 2000; Garcia et al., 2001; Hard et al., 2003).

Researches and investigations for the passive treatment systems in Korea mostly focused on the removal efficiency of metals(mainly iron) and pH control(Sung et al., 1997, Bae et al., 2001), but do not concerned with the removal of sulfate. However, many systems reveal very low removal ratio or even the increased concentrations of sulfate(Cheong et al., 2001, Ji et al., 2003), which may indicate poor or even no biological sulfate reduction in the system. Therefore this study has been carried out to evaluate problems, if exist, of the passive treatment systems and especially has focused on the status of sulfate removal process. And some preliminary results on the experiment of the In Adit Sulfate Reducing System(IASRS), an alternative method of the present treatment system are discussed.

Field excursions, sampling and analysis

Water samples for twentyseven passive treatment systems at closed coal mines were collected at the mine adits and the effluent spot of each treatment system, both during the dry season (from November to March) and the wet season(from July to September). Water samples for cation determination were filtered through a 0.45 μm cellulose nitrate membrane filter using a hand pump, and were immediately acidified to pH<2.0 by adding HNO_3. Water samples for alkalinity and anion determinations were filtered but not acidified.

The pH, ORP, temperature, DO, conductivity and TDS were measured in situ. Analysis for dissolved cations were performed using an inductively coupled plasma atomic emission spectrophotometer(ICP-AES; Jobin Yvon Co. 138 Ultrace) at the Seoul branch of Korea Basic Science Institute. Anions were determined using ion chromatography(IC; Dionex series 500DX) at the Pusan branch of Korea Basic Science Institute, and alkalinity was determined by the titration method. Acidity were calculated by the following equation (Hedin et al., 1994).

$$Acid_{Calc.} = 50\left(\frac{2Fe^{2+}}{56} + \frac{3Fe^{3+}}{56} + \frac{3Al^{3+}}{27} + \frac{2Mn^{2+}}{55} + 1000\,(10^{-pH})\right) \qquad (3)$$

(50 : the equivalent weight of $CaCO_3$, Unit of metal concentrations : mg/l)

The operating status of treatment systems

Table 1 shows the operating status of 27 passive treatment systems. Normal means that the systems are working properly with no leakage or overflow. Overflow means that overflow occurs at a certain stage of the system of which the reason is that flow rate is exceeding the capacity of the facility or lowered permeability by coating of hydroxides in SAPS prevents water from flowing through the organic substance layer. Leakage means the leaking of AMD at various places of the system. Unusableness means that whole system become useless because of clogged and/or broken pipes at the mouths of the mine adits. Inefficiency means that no apparent leakage or overflow is observed but the efficiency is very low.

Table 1. Operating status of passive treatment systems.

Operation Status	Number of system	Mines
Normal	11	Hambaek-imok, Hambaek-mireuk 1, Hambaek-mireuk 2, Samwang 1, Samwang 2, Sungwon, Pongwon, Hanyang, Dongwon-taeheung 1, Dongwon-taeheung 2, Sukkong-sinsung
Overflow	3	Gapjung, Dongbok, Hotan-taebaek
Leakage	7	Hanchang, Hambaek-bangjae, Donghea, Hwangji, Bongmyung, Danbung, Sungbong
Unusableness	3	Hambaek-jami, Samma-taejung, Honam
Inefficiency	3	Youngdong, Dongwon-kwangjung, Waryong-taewoo

The efficiency of treatment systems

The efficiency of treatment system usually is evaluated by metal(iron) removal ratio. Results of the investigation of 27 systems show the range of metal removal ratio from 51 to 100%(avg. 88%). And acidity removal ratios ranged from 17 to 100%(avg. 68%). However, as shown in Table 2 sulfate removal ratios were very low. Similar results were reported by Sung et al.(1997) and Cheong et al.(2001). It might indicate that sulfate reduction by SRB was very low or even does not occur in SAPS and/or wetland.

Even though systems show fairly good efficiencies in metal removal(mainly iron) ratios and pH control, poor sulfate removal ratio may indicate that the major metal removal process is not the precipitation of metal sulfides, but just adsorption on organic substances. In this case the treatment efficiencies would decrease quickly when the available surface area of organic substances are occupied by adsorbed metals.

Considering the optimal temperature of 30~55℃ for the SRB activity, because of the cold weather in Korea, SRB activity could be very low or even nil during the winter. Also since flow rate decreases in winter, very low flow rate could often result in the exposure of organic layer to the air. From one of the pilot treatment systems in England, it was reported that SRB activity was stressed due to the low water level and air temperature during the winter. Since the stressed SRB were hit with an acidity overload, the metal removal performance of the system suffered(Gusek, 2001). Similar situation was reported at the Burleigh Tunnel in Colorado. Pilot scale treatment system for drainage which have neutral pH and about 50～60 mg/l of dissolved Zn was run. It exposed to a high flow and high concentration drainage (pH 4.1, Zn 109mg/l) in response to the snowmelt. The acidity loading also increased and despite some self-buffering capacity of the substrate, performance of the system suffered(Gusek, 2001).

Iron and aluminium dissolved in AMD will be precipitated as meal-hydroxides when they meet with optimum pH range at the oxidation environment. When AMD is treated with SAPS, at the boundary of AMD and organic substance layer, pH rises by the alkalinity generated from organic substances. It can cause the formation of sludge cake on the surface of organic substance layer, which prohibits AMD from flowing downward through the organic substance layer. Sludge cake may lead to the channelling effect of AMD flow or overflow.

Even though it is not related to technical problem, an important and hard to meet the need is secure the area wide enough for the construction of the system. The construction of passive treatment system needs somewhat large areas. However in Korea, since most coal mines are located in mountain area, it is often difficult to provide enough area for the construction of the system.

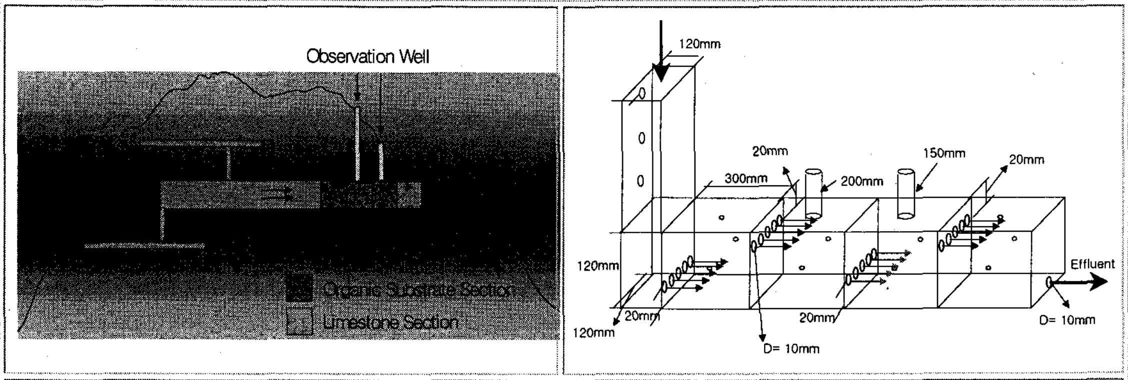
Table 2. The efficiencies of the passive treatment systems.

Treatment System	Inflow				Outflow				Fe TE(%)	Acid. T.E(%)	SO_4^{2-} T.E(%)
	pH	Fe(mg/l)	Acid(mg/l)	SO_4^{2-}(mg/l)	pH	Fe(mg/l)	Acid(mg/l)	SO_4^{2-}(mg/l)			
Waryong-taewoo	-	-	-	-	2.12	158.0	471.9	3,941	-	-	-
Youngdong	2.87	276.0	1,182	3,510	-	-	-	-	-	-	-
Samma-taejung	2.21	134.2	1,076	2,746	-	-	-	-	-	-	-
Hwangji	6.35	73.6	143.0	2,008	7.23	0.0	6.71	1,406	100	95.3	30.0
Pongwon	6.67	10.8	26.2	796.6	6.9	0.0	8.3	762.6	100	68.3	4.3
Hanyang	6.38	18.9	41.7	834	6.66	1.19	7.1	723.8	89.9	82.97	13.2
Donghea	5.8	127.0	241.0	1,413	2.98	20.1	125.5	763.7	84.2	47.93	46.0
Sungwon	7.09	n.d	0.71	574.3	7.54	n.d	0.28	537.3	~	60.6	6.4
Hanchang	6.60	13.3	25.9	247.7	8.3	0.032	0.64	218.7	99.8	97.5	11.7
Hambaek-imok	6.93	n.d	4.59	52.1	7.04	1.14	75.66	52.4	~	~	~
Hambaek-bangjae	6.62	555	1,084	81.3	6.92	65	223.6	137.6	88.3	79.4	~
Hambaek-jami	6.63	18.5	38.1	170.3	-	-	-	-	-	-	-
Samwang 1	6.49	5.58	11.85	68.9	7.41	0.037	0.43	64.3	99.3	96.4	6.7
Samwang 2	6.42	4.48	10.93	138.2	7.35	0.042	0.68	127.4	98.6	93.8	7.8
Dongwon-taeheung 1	6.26	8.82	18.4	92.2	6.3	3.48	8.7	93.1	60.5	52.72	~
Dongwon-taeheung 2	6.11	0.16	0.6	2.47	6.59	0.16	0.5	2.45	~	16.67	~
Hambaek-mireuk 1	6.32	1.16	4.6	69.4	6.19	0.57	2.3	69.1	50.9	50.0	0.4
Hambaek-mireuk 2	6.67	3.75	16.2	82.3	7.01	n.d	10.3	81.4	100	36.6	1.1
Dongwon-kwangjung	-	-	-	-	2.35	91.4	512.7	820.8	-	-	-
Danbung	7.5	n.d	10.49	1,144	7.08	n.d	0.57	975.6	-	94.6	14.7
Sungbong	2.11	0.275	788.2	2,289	3.43	n.d	423.3	2,079	100	46.3	9.2
Gapjung	4.77	n.d	2.43	1,213	7.0	n.d	0.29	1,189	-	88.1	2.0
Bongmyung	2.73	26.2	305.2	1,009	7.77	0.08	14.0	221.8	99.7	95.32	78.0
Dongbok	6.31	0.37	0.7	71.3	6.67	0.0	0.01	68.2	100	98.6	4.3
Honam	5.54	32.7	73.4	541.3	6.65	0.0	13.1	792.2	100	74.0	~
Hotan-taebaek	6.71	0.4	2.6	169.5	7.14	0.02	0.3	272	95	88.5	~
Sukkong-sinsung	6.29	6.77	13.8	88.3	7.23	0.0	0.6	87.2	100	95.65	1.2

TE : Treatment efficiency   n.d : Not detected   - : One of the samples(inflow or outflow) was not sampled.   ~ : TE < 0

In Adit Sulfate Reducing System (IASRS)

To maintain the bacterial activity during winter In Adit Sulfate Reducing System(IASRS) was suggested. This system is simply placing the SAPS inside the adit to maintain the condition of constant temperature of 10~15℃ (Fig.2.(a)). And some modifications include about 3~4 times thicker organic layer than limestone layer and three chambers consisted with organic layer and gravels. Since whole systems are placed inside the adit the anoxic condition would be maintained even if the flow rate decreases. Therefore conditions of sulfate reduction can be maintained. Metals such as Mn which is often difficult to remove and COD which is produced at the beginning of the operation could be removed by the construction of oxidation pond and/or wetland out side the adit.



(a) (b)

Fig. 2. Schematic Diagram of the In-Adit Sulfate Reducing System.

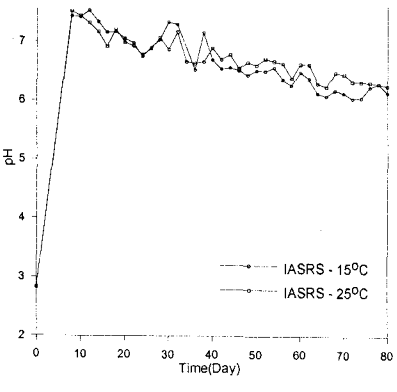
Two IASRS models of laboratory scale were operated(Fig.2.(b)) for 80 days. A model system consisted of four sections and each section is sized by 12cm(H)x12cm(W)x30cm(L). Total volume of system is 17.28*l*, operating HRT(hydraulic retention time) was 10day(flow rate is 1.728*l* /day). The first three sections were filled with gravel and spent mushroom compost and the last section was filled with limestone. Two observation holes were made to measure pH and ORP. In actual system these holes could be used as injection wells to replace organic substances and remove precipitates. Artificial AMD was made by distilled water reacted with tailings from the Samchuk coal mine. The physico-chemical properties of artificial AMD are 1,203ppm of TDS, pH 2.8, 363mg/*l* of Fe, 262.5mg/*l* of Al and 2362mg/*l* of SO_4^{2-}(all are average). The system 1 was run with at about 15℃ and the system 2 was run at about 25℃.

Black precipitates, which indicate the evidence of sulfate reducing reaction occurred after ten days in the system 1 and after five days in the system 2, which showed that the SRB activity in the system 1 is lower than that in the system 2.

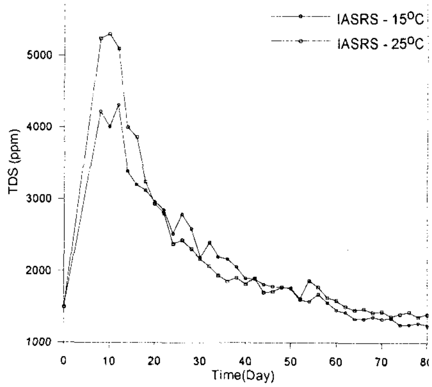
During 80 days of running, they show high efficiencies in pH control and metal removal ratios(Fig.3.(a),(d), (e)). TDS and COD in the effluents of both systems were considerably high during the first twenty days(Fig.3.(b),(c)). However COD of the system 1 was about a half of system 2. It may show that the production of a large amount of organic extraction from the organic substance in the beginning of the operation can be reduced by using the IASRS.

Sulfate concentration in the effluent from the system 1 increased during the first 36 days, which may indicate that sulfate removal ratio during this period was very low and/or a large amount of sulfate was extracted from the organic substances. However sulfate removal ratio converged on about 23% in the system 1 and about 27% in the system 2 after 60 days(Fig.3.(f)), showing not much difference. Even though the ratios are higher than those of the present operating systems, they are still lower than expectations, of which the reasons may be too low pH of artificial AMD and shorter actual HRT than the calculated HRT.

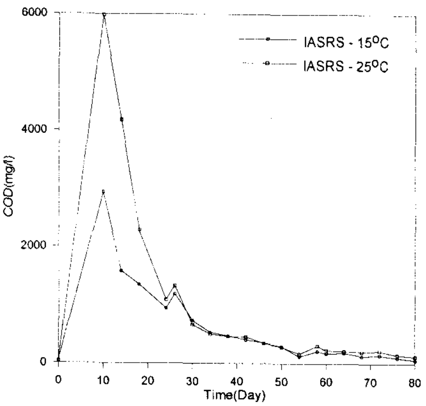
Postgate(1984) suggested that the conditions for the active SRB are the presence of sulfate, the suitable concentrations of organic compounds, pH greater than 4, and the absence of oxidizing agents such as O_2, Fe^{3+}, and Mn^{4+}. Although some researches reported that bacterial sulfate reduction could occur below pH 3(Bolis et al., 1991; Gusek, 1998), many researches favored that the activity of SRB cease below pH 3(Elliott et al., 1998; Kolmert and Johnson, 2001). No black precipitates at the first section and very low pH of about 3.5 at the first observation hole, may indicate that SRB in the first section died due to the too low pH(2.8) condition of artificial AMD at the system. Lee at al.(2003) showed that the appropriate HRT is also the very important factor for the bacterial sulfate reduction. If the first section did not function, the actual HRT would have reduced to about seven days from calculated ten days, which caused insufficient sulfate reducing reaction.



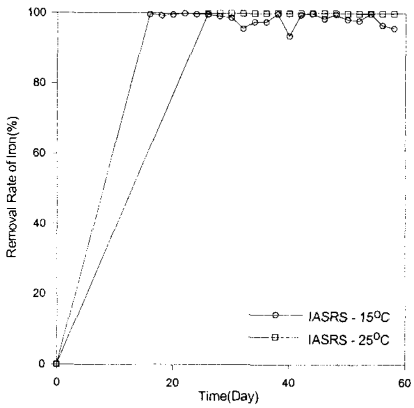
(a) pH



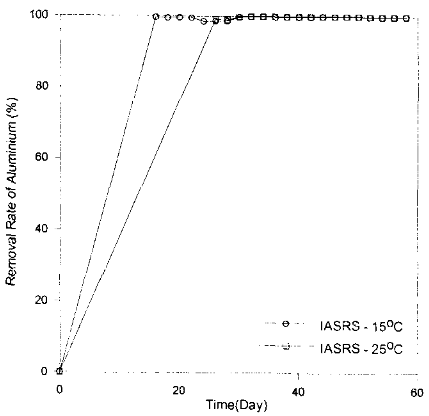
(b) TDS



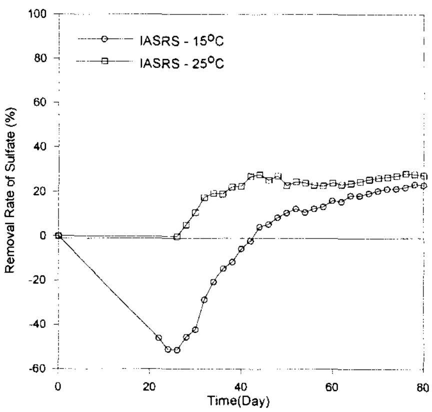
(c) COD



(d) Removal Ratios of Iron



(e) Removal Ratios of Aluminim



(f) Removal Ratios of Sulfate

Fig. 3. Changes of physico-chemical properties in the effluent of IASRS.

Conclusions

Problems observed during the operation include the poor sulfate removal ratio, overflow, leakage, unusabless of the whole system, and inefficiency.

The reasons of the poor sulfate removal ratio are believed that the low temperature during the winter prohibits the SRB activity and HRT for sulfate reduction is insufficient.

An alternative method, In Adit Sulfate Reducing System(IASRS) which enables to keep the temperature constant at about 15℃ was suggested. IASRS is the method of placing the SAPS inside the adit, which enables the temperature around the system constant.

The experiments using the laboratory scaled IASRS model systems made up of four sections showed high efficiencies in pH control and metal removal ratios.

Very high sulfate concentration at the beginning of IASRS operation may be resulted from the low sulfate removal ratio and/or a large amount of extracted sulfate from the organic substances. The sulfate removal ratio converged on about 23% after 60 days.

Even though the sulfate removal ratio is higher than those of the present operating systems, it is still lower than expected ratio, of which the reasons may be too low pH of artificial AMD for bacteria to survive and shorter actual HRT than the calculated HRT.

Acknowledgments

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