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The influences of the amount of organic substrate on the performance of pilot-scale passive bioreactors for acid mine drainage treatment

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Abstract Pilot-scale successive alkalinity producing systems (SAPS) with varying amounts of mushroom compost were installed in a closed coal mine site in Korea to treat acidic mine effluent. The bioreactors were operated for 125 days and monitored for various water quality parameters to evaluate the effect of amount of mushroom compost on the performance of the reactors. The monitored parameters included dissolved oxygen (DO), oxidation– reduction potential (ORP), pH, electrical conductivity, concentrations of sulfate, sulfide and metals, and alkalinity generation. The results demonstrated that acid neutralizing capacity and metal removal efficiency were generally higher for the bioreactors containing greater amounts of mushroom compost. DO and ORP were the most sensitive parameters that readily reflected the effect of the amount of mushroom compost in the bioreactors. The effluents of bioreactors with less amount of mushroom compost consistently gave higher DO and ORP values, although the reactors maintained similar performances in removal of Fe, Al, and sulfate. However, the increase of DO and ORP values is a clear indication of performance deterioration of

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SAPS, especially in extended period of time. Therefore, in a practical sense, DO and ORP could be utilized as diagnostic parameters for implementation of proper corrective measures to SAPS in operation before encountering system failure.

Keywords Successive alkalinity producing system (SAPS) - Acid mine drainage (AMD) - Organic substrate - Mushroom compost - Field column study

Introduction

Successive alkalinity producing system (SAPS) has become one of the most commonly used passive treatment systems for treatment of acid mine drainage (AMD) in recent years. It is a hybrid treatment system incorporating technical merits of anaerobic wetland and anoxic limestone drain. Its primary function is to provide AMD with continuous alkalinity while stabilizing heavy metals via a microbial process (Elliott et al. [1998](#page-9-0)). The microbial process mainly involves sulfate reducing bacteria (SRB), which utilize sulfate as a terminal electron acceptor to transform it into sulfide. Sulfide subsequently reacts with dissolved metals to form metal-sulfide precipitates. SAPS was first suggested as a corrective measure to overcome limited lifetime of limestone drain, mainly incurred by surface coating of limestone by metal hydroxide precipitation. Since this inactivation process is expedited in aerobic conditions, the remedial approach was to pass AMD through anoxic medium before its contact with limestone, thereby inhibiting the formation of metal hydroxides to induce long-lasting dissolution of limestone for AMD neutralization. But not long after its implementation in field application, it was revealed that there existed an additional

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route of metal removal driven by metal-sulfide formation within the medium (Hedin et al. [1989\)](#page-9-0), and it began to be recognized as an important process influencing overall performance of the treatment system (Elliott et al. [1998](#page-9-0); Gusek [2002\)](#page-9-0).

SRB are anaerobic microorganisms and their activity is influenced by several biochemical and operational parameters, including the types of organic substrates, pH, dissolved oxygen (DO), temperature, and hydraulic retention time (HRT). In field operations, SAPS is typically implemented as a vertical flow system where AMD flows downward passing organic substrate layer and subsequently into limestone bed placed beneath the organic layer. Under normal condition, SAPS bioreactors normally develop oxidation–reduction potential (ORP) less than -100 mV and DO less than 1 mg/l during operation (Postgate [1984\)](#page-10-0). In many of the SAPS systems put into operation between 1996 and 2002 in South Korea, the ranges of ORP and DO were reported to be -97 to 310 mV and 0.6–10.1 mg/l (Cheong et al. [2008\)](#page-9-0), respectively, which indicates occasional failure in AMD treatment. Poor performance of SAPS bioreactors could stem from various operational problems such as overflow, leakage, clogging, short-circuiting, and broken pipes, as well as inadequacy or limited availability of organic carbon for sustaining biological activity.

To date, investigations on passive bioreactors for AMD treatment have mainly focused on alkalinity generation and metal stabilization by SAPS (Jage et al. [2001;](#page-9-0) Matthies et al. [2010;](#page-10-0) Ji et al. [2012\)](#page-10-0), and sulfate removal by microbial process (Bhattacharya et al. [2008](#page-9-0); Riefler et al. [2008](#page-10-0)). These studies are mostly based on laboratory experimental work that had limited applicability to field conditions, which exhibit a large variation in geochemical parameters. Some recent studies were advanced into application of various types of organic materials as alternative substrates for the most widely used mushroom compost (Cocos et al. [2002;](#page-9-0) Neculita and Zagury [2008;](#page-10-0) Costa et al. [2009\)](#page-9-0), and investigated potential utilities of those materials for enhancing overall performance of SAPS (Gibert et al. [2004;](#page-9-0) Tsukamoto et al. [2004;](#page-10-0) Neculita et al. [2011\)](#page-10-0). In addition, several investigations have focused on the variation of geochemical parameters such as pH, ORP and temperature, and their potential impacts on the activity of SRB (Kolmert and Johnson [2001;](#page-10-0) Cocos et al. [2002](#page-9-0); Gibert et al. [2004;](#page-9-0) Tsukamoto et al. [2004](#page-10-0); Koschorreck and Tittel [2007;](#page-10-0) Lee et al. [2010](#page-10-0)).

Despite the large venue of SAPS researches, there have been very few studies that reported temporal variation of geochemical parameters in relation to the amount of organic substrates in bioreactors. The amount of organic substrate, along with its type, is a critical factor governing the performance of bioreactors. Limited amount of organic substrates would not sustain satisfactory microbial growth, while excessive amount may lead to clogging and unwanted release of organic and inorganic components from the substrate materials. Therefore, the use of optimum amount of organic substrate is a key factor for successful operation of SAPS. In this context, this study was carried out to investigate the temporal variation of geochemical parameters during field operation of bioreactors containing varying amount of organic substrate (mushroom compost), and thereby to gain some insights into the mechanistic understanding necessary for determining optimum amount of substrate materials.

Materials and methods

Column set up and operation

Pilot-scale field column test was carried out at a closed coal mine site located in Munkyung County, South Korea, over a 125-day period. The daily generation of AMD from the site was $464 \text{ m}^3/\text{day}$ at the time of column installation. A separate drain channel was installed in the main mine effluent channel to feed the AMD into a 200 l storage tank. The storage tank was equipped with overflow bypass in the upper end and valve-controlled outlet in the lower end to constantly maintain AMD level to near its full storage capacity during the column operation. AMD from the tank was gravitationally fed into the bottom of the bioreactor columns with constant flow rate. A total of six columns (0.3 m in diameter and 2 m in height) were built with transparent acrylic polymer with total volume of 141 l. Coarse gravels of 20–30 mm in size were packed at the bottom of the column to 300 mm height, followed by addition of thoroughly mixed mushroom compost. Each column received different amount of mushroom compost— 20, 40, 60, 80, 100 and 120 cm (Fig. [1\)](#page-2-0) (denoted as C1–C6, respectively). Porous acrylic plates (15 mm in height with 7.5 mm diameter holes) covered with a porous nylon disc were placed between mushroom compost and gravels to prevent loss of organic particles and clogging.

The columns were designed to operate upward vertically to prevent clogging by organic particles and gaseous products, as well as for better flow control. Before beginning column operation, the columns were saturated with AMD by fully filling up the columns with AMD while closing effluent valve, followed by vigorous agitation with a rod to remove air pockets within the substrate layer. The reactors were left for one week for bacterial acclimation. This period was necessary to grow enough population of SRB that would produce enough alkalinity to withstand the shock of AMD once the operation started (Waybrant et al. [2002](#page-10-0); Neculita et al. [2008](#page-10-0)). After acclimation period, Fig. 1 Experimental schematics of pilot-scale

compost)

column operation began with upward vertical flow and the flow was valve-controlled to maintain HRT of 2.5 days, a suggested duration required to induce sufficient sulfate reduction in SAPS operation (Neculita et al. [2007](#page-10-0)). The flow of each column was checked on a weekly basis and adjusted accordingly. The top of the columns were loosely sealed with a thick plastic cover to allow venting of gaseous products. Also, the entire bodies of columns were covered with thick non-transparent vinyl cloths to protect them from sunlight and rainfall, and to minimize potential influences of seasonal and daily temperature fluctuation.

Mushroom compost characterization

Mushroom compost was obtained from a regional farmhouse located in Buyeo district, South Korea, and used without pretreatment. This mushroom compost has been widely used as an organic substrate in SAPS in the country, and its physicochemical characteristics are presented in Table 1. The pH of the mushroom compost was measured in deionized water using a solid to liquid ratio of 1:1 (ASTM [1995](#page-9-0)) and a HACH pH-meter (HQ-40D with PHC101-01 probe). Water content of the mushroom compost was measured by subtracting the weight of a sample dried at 105 \degree C for 24 h from that before drying. Total volatile solids (TVS), which are frequently used as an estimate of organic matter content of solid materials (Matthiessen et al. [2005](#page-10-0)), were determined as per Karam [\(1993](#page-10-0)). Carbon–nitrogen–hydrogen content was measured with an elemental analyzer (Flash EA, Thermo Finnigan). Total organic carbon and dissolved organic carbon (DOC)

Table 1 Physicochemical characteristics of mushroom compost

Mushroom compost
7.66 ± 0.02
49.3
55.78 ± 0.16
$3,146 \pm 142$
2.47
25.61
3.28
1.78
10

The mean and standard deviations were calculated with two replicates

were determined using Standard Method 5310 C (APHA [2005](#page-9-0)).

Sampling and analyses

After acclimation period for a week, samples were collected weekly (a total of 15 sampling events) from AMD storage tank and from the exit end of effluent tubing, which drained to oxidation pond. Unfiltered samples were immediately measured for pH (Hach PHC101-01), ORP (Hach MTC101), electrical conductivity (EC, CDC401) and DO (LDOTM). Some portion of samples (about 50 ml) were filtered with 0.45 µm membrane filters (Whatman), and the filtrate was immediately analyzed for sulfide (methylene blue method) and sulfate (sulfaVer 4 method), using a Hach DR 4000

spectrophotometer. The remaining filtrates were acidified using concentrated $HNO₃$ and transported to laboratory for metal analysis. Concentrations of Al, Fe and Mn were measured with an inductively coupled plasma (HORIBA Jobin– Yvon). Unless otherwise stated, all analytical procedures followed Standard Method (APHA [2005\)](#page-9-0).

Results and discussion

The temporal changes of monitored water quality parameters in C1–C6 are presented in Fig. [2.](#page-4-0) The results of temporal changes of each parameter are discussed below.

DO and ORP

DO removal in SAPS mainly occurs in the influent end of substrate layer (oxic zone), driven by aerobic microcosm that utilizes oxygen as a terminal electron acceptor, and the oxic zone progresses down to deeper to the substrate layer with continuous operation of SAPS. This upfront DO removal, accompanied by alkalinity generation by substrate oxidation, produces anaerobic reducing condition in midpH range favorable for SRB growth within the deeper region of the substrate layer.

DO levels in the untreated AMD showed gradual decrease, with the exception of the sample measured on day 14 that registered very low DO of 1.9 mg/l (Fig. [2a](#page-4-0)). The gradual decrease of DO reflects the seasonal temperature effect on DO solubility as the weather became warmer toward the end of the column operation (March– August). DO levels in the effluent from the bioreactors with different mushroom compost depths (C1–C6) indicated the bioreactors effectively removed DO from the beginning of the operation. The extent of DO removal was nearly 100 % in the columns with ≥ 80 cm substrate height (C4–C6) after 14 days, and it lasted until the end of the experiment except the one measurement obtained in C4 reactor at the very last day.

DO levels in the effluent of the bioreactor with \leq 40 cm substrate height (C1 and C2) approached to near 0 mg/l in 27 days and remained constant before starting to elute >1 mg/l DO after 96 and 84 days, respectively. The effluent of C3 (60 cm height) had lower DO levels than C1 and C2 until day 27, but higher DO values on days 34 and 49 despite the amount of more substrate. Considering that the ORP values of C3 at the same time frame did not show any peak values compared to those of C1 and C2 (Fig. [2](#page-4-0)b), and also DO values of C3 became negligible in next two sampling events after day 49, it appears that those high DO values of C3 on days 34 and 49 are due to measurement artifact. For C3, elution of DO similar to C1 and C2 started on day 84 (0.5 mg/l), and the concentration increased to 3.2 mg/l in the end. The breakthrough of DO observed in C1–C3 reactors suggests the aerobic bacteria responsible for oxygen removal became substrate-limited by continuous loading of AMD. Such breakthrough did not occur in the reactors containing more amount of substrate and that >80 cm height of substrate gave almost complete DO removal over 125 days of operation.

ORP is a parameter closely related to DO. ORP values in AMD were maintained relatively constant in the range of 427–532 mV (Fig. [2b](#page-4-0)). The major contributor to ORP is DO and the presence of other redox active species such as SO_4^2 ⁻ and Fe³⁺, despite their high concentration in AMD, would exert very limited contribution to overall ORP increase because they have significantly low oxidation potential compared to oxygen. ORP values within the bioreactors decreased to near 0 mV during acclimation period and showed a gradual decrease during the reaction period, indicating strong reducing condition was developed within the bioreactors. This pattern is consistent with the changes of DO during the operation. ORP values in the bioreactors with substrate height ≤ 60 cm continuously decreased until day 78 as low as -327 mV (C1), but it started to increase thereafter to a value as high as -52 mV on day 104 (C1). On the other hand, the bioreactors containing ≥ 80 cm mushroom compost maintained fairly stable reducing condition, with its value less than -200 mV until the end of the experiment except the one measurement obtained from C4 on day 125. This very low ORP values have rarely been reported for column bioreactors, except for the cases in which the reactors were supplemented with a readily utilizable substrate such as lactate (Waybrant et al. [2002\)](#page-10-0). This result, and also recalling that substrate height greater than 80 cm achieved effective DO removal, indicates the minimal height of substrate layer required for favorable growth conditions for SRB is 80 cm under conditions employed in this study.

pH and EC

The pH values of AMD remained fairly stable until day 104 ranging between 3.6 and 3.7, but there was a notable decrease to 2.9 on day 112, followed by slow recovery to the original value toward the end of the testing period (Fig. [2c](#page-4-0)). This temporary deterioration of AMD could be attributed to reduced dilution of AMD as there was less rainfall toward the end of monsoon season in the late summer in Korea. The bioreactors were very effective in neutralizing pH from the beginning of column operation, giving pH range 7.6–7.9. In general, the bioreactors with more amount of substrate (C4–C6) consistently showed stronger pH neutralization capacity, which is more apparent in the later time of reaction period. The increase of pH

Fig. 2 Temporal changes of a dissolved oxygen (DO), b oxidation–reduction potential (ORP), c pH and d electrical conductivity (EC) in bioreactors with different amounts of mushroom compost

is associated with alkalinity generation by carbonate species formation from the oxidation of substrate by microbial processes, and possibly by dissolution of hydroxyl functional group from substrate materials upon contacting with acidic AMD (Neculita et al. [2011](#page-10-0)). In response to the pH shock in AMD on day 112, the pH values in the bioreactors dropped in a similar fashion, but the drop was more significant in the reactors with ≤ 60 cm substrate height. This is a clear indication that pH neutralization is a substrate-mediated process, and therefore sufficient amount of substrate materials is necessary to withstand intermittent pH shock during SAPS operation.

EC value is generally influenced by ionic species contained in water. For AMD, EC mainly stems from the presence of sulfate since its concentration is overwhelmingly higher than those of other metallic components. The monitoring result indicated EC values of AMD were maintained fairly stable, ranging from 1.15 to 2.73 mS/cm over the operation period (Fig. [2d](#page-4-0)). On the other hand, the effluents of the bioreactors gave higher EC values than AMD from the beginning, and this is probably due to dissolution of additional sulfate from mushroom compost during acclimation period with limited contribution from co-dissolved metals and organic acids. Those initial EC values further increased in next few samplings, followed by slow decrease close to those of AMD. Note that EC data on day 14 were not reported herein due to electrode malfunctioning during onsite measurement. The peak values of EC in the bioreactors were recorded on day 27, with the values generally increasing with the amount of mushroom compost contained in the reactors. Despite some variation, it appears that the temporal changes of EC in the bioreactor are consistent with those of sulfate. This is a direct indication that mushroom compost released a large amount of sulfate, which significantly contributed to EC values. Our previous study indicated EC value in the SAPS effluents is closely correlated with total dissolved solids and salinity, and they had very similar breakthrough pattern (Song et al. [2012\)](#page-10-0), which confirmed the result of another previous fieldscale test by Guo et al. (2001) (2001) .

Sulfate and sulfide

Sulfate concentrations in AMD were in the range 850–1,130 mg/l, except the one occasion on day 14 that recorded extremely high value (Fig. [3](#page-6-0)a). Taking the 14-day data as a transient spike of sulfate, the bioreactors showed distinct patterns of sulfate release. Substantially higher concentrations of sulfate in the bioreactors compared to that in AMD source were observed in early times, indicating a significant amount of sulfate was released from mushroom compost. Mushroom compost used in this study is composed of cow manure as a base material and other inorganic materials such as calcite, gypsum, and ashes (Song et al. [2012](#page-10-0)). Therefore, these materials, especially cow manure and gypsum, might serve as the sources of sulfate under acidic environment, and such a release of sulfate from mushroom compost was also reported in previous studies (Cheong et al. [1998](#page-9-0); Guo et al. [2001](#page-9-0); Cocos et al. [2002;](#page-9-0) Ji and Kim [2008\)](#page-9-0). Accordingly, sulfate concentration after acclimation was higher for the bioreactors containing more amount of mushroom compost. The peak concentrations in the bioreactors with >60 cm mushroom compost ranged from 3,680 (C3) to 4,180 mg/l (C6), while for the reactors with ≤ 40 cm, they were 2,320 (C1) and 2,040 mg/l (C2).

After the peak concentrations, sulfate concentrations in the bioreactors rapidly decreased to the levels below those in AMD on day 49, and then remained similar or less than AMD values until the end of operation, despite the occasional fluctuation observed in C3 and C4 reactors (Fig. [3a](#page-6-0)). The rapid decrease of sulfate until day 49 could be attributed to several processes including flushing out from the reactors, reduced dissolution from substrate material coupled with dilution by continuous AMD flow, and microbial transformation to sulfide. Considering sulfide concentrations have yet reached their maximum values until day 49 (Fig. [3b](#page-6-0)), it appears microbial sulfate reduction accounted for only a fraction of total sulfate removed and that the former two processes were the major routes of sulfate removal in the early period.

Regarding the overall sulfate removal reported in the literature, a survey of 35 passive treatment systems utilizing mushroom compost indicated sulfate treatment efficiency is highly variable in the range of -95 to 63 %, with an average of 12.6 % for systems giving positive efficiency (Ji et al. [2007](#page-9-0)). Another monitoring study indicated a mushroom compost-based SAPS in Korea had sulfate removal efficiency of 7.8–20.3 % (Bhattacharya et al. [2008](#page-9-0)). Furthermore, laboratory scale test with mushroom compost bioreactor gave removal efficiency of 27 % (Ji and Kim [2008\)](#page-9-0).

Sulfide is produced from microbial sulfate reduction and is an indicative parameter used for accessing performance of SAPS. Upon its formation, sulfide reacts with dissolved metals and subsequently precipitates out as metal-sulfide minerals. This formation-and-removal process of sulfide is continuously occurring in entire time frame of SAPS operation, and is also a quite heterogeneous and localized process influenced by various geochemical conditions. Therefore, there is a great variation in temporal changes of sulfide concentration in the effluent of the bioreactors. In our study, sulfide formation was apparent in all bioreactors as black precipitates (i.e. metal sulfides) were formed during acclimation period, along with rotten egg smell from hydrogen sulfide generated during the reaction. The measured concentrations of sulfide on day 14 ranged 20–360 mg/l, with little dependence on the amount of substrate material. Sulfide concentrations were maintained below 350 mg/l until day 34, except for C6, but sharply increased to several thousand mg/l on day 49. This increase suggests microbial process became sufficiently active to Fig. 3 Temporal changes of a sulfate concentration and b sulfide concentration in bioreactors with different amounts of mushroom compost

generate enough sulfides to override the removal via metalsulfide precipitation because other geochemical parameters that potentially influence the fate of sulfide, i.e. pH, ORP, and sulfate, remained stable during corresponding time frame.

Although there is a large fluctuation in the temporal changes in sulfide concentrations in each bioreactor, the sulfide levels were consistently higher in the reactors with >80 cm height of mushroom compost. The peak concentration was observed in C4 reactor, registering 39,800 mg/l on day 91, at which corresponding sulfate concentration was the lowest. On the other hand, sulfide concentrations in the bioreactors with ≤ 60 cm mushroom compost were generally maintained at lower levels and became almost negligible toward the end of reaction period. This microbial inactivation could be linked to the rise of DO and ORP occurred in the same time frame, which presumably resulted from shortage of organic carbon to sustain growth of SRB (Fig. [2\)](#page-4-0). The result confirms the amount of substrate material, or more accurately, the availability of organic carbon, is a key factor governing the long-term performance of SAPS.

Metals

The changes of Fe, Al, and Mn concentrations during SAPS operation in each bioreactor are presented in Fig. [4.](#page-7-0) The total Fe concentration in AMD was less than 70 mg/l until day 34, but suddenly increased to a peak value of 235 mg/l on day 49, followed by gradual decrease to 66 mg/l on day 125. Until day 34, total Fe concentration in the bioreactors were higher than that in AMD with no obvious indication of its removal from the solution (Fig. [4a](#page-7-0)). This suggests additional Fe was leached out from mushroom compost and that there was more supply of Fe to outcompete the Fe removal processes such as adsorption and precipitation. The leaching of metallic components from the same mushroom compost has been observed in our previous study (Song et al. [2012\)](#page-10-0). The decrease of total Fe became apparent after day 34, with approximately 90 % removal efficiency in all bioreactors on day 49, despite Fe concentration in AMD increased to the highest value on the same day. Such an increase of Fe removal coincides with the rise of sulfide concentrations in the bioreactors, suggesting that the formation of metal sulfides was the major pathway of iron removal in the reactors. From day 49 to the end of operation, the bioreactors remained effective in removal of Fe in spite of deterioration of some parameters such as DO, ORP, and sulfide generation, especially in the reactors containing smaller amount of substrate materials.

The bioreactors showed better performances in treating Al in AMD, which ranged from 42 to 172 mg/l (Fig. [4b](#page-7-0)). In most cases, Al treatment efficiencies were higher than 90 % throughout the entire reaction period for all the reactors. The better removal efficiency for Al compared to Fe is attributed to its higher tendency to precipitate as hydroxides at mid pH ranges, which served as an additional sink for Al along with the precipitation as sulfides (Skousen et al. [2000](#page-10-0)). Al has been reported as one of the most readily treatable metals by SAPS reactors (Kepler and McCleary [1997](#page-10-0)), and it appears satisfactory removal of Al can be achieved even in lieu of deterioration of some water quality parameters.

Fig. 4 Temporal changes of concentration of a total iron, b aluminum and c manganese in the bioreactors with different amounts of mushroom compost

Meanwhile, the bioreactors exhibited very poor performances in Mn removal with little differences among the reactors (Fig. 4c). The temporal changes of Mn in the bioreactors showed no consistent trends, making it hard to draw any definitive interpretation about its behavior. Mn has been acknowledged as the most challenging metal to be removed by passive bioreactors (Chang et al. [2000](#page-9-0); Neculita et al. [2007\)](#page-10-0). The poor removal of Mn by SAPS has been attributed to higher solubility of MnS relative to other metal sulfides (Cheong et al. [1998](#page-9-0)), high pH (>6) required for it precipitation as oxides or carbonates (Mariner et al. [2008](#page-10-0)), inhibition of its precipitation as hydroxides by preferential formation of Fe(OH)₃ when Fe/Mn > 4 (Skousen et al. [2000\)](#page-10-0), and reductive dissolution of manganese oxides under high $Fe²⁺$ concentration (Ziemkiewicz et al. [2003\)](#page-10-0).

Acidity removal and alkalinity generation

Acidity values of AMD and column effluents were calculated based on the concentrations of Fe, Al, and Mn in each sampling occasion (Hedin [2004\)](#page-9-0). Acidity of AMD was greatly influenced by Fe and Al due to their high concentrations, which ranged from 660 to 1,660 mg/l as $CaCO₃$. The effluents of the bioreactors had significantly lower acidity values, giving more than 60 % reduction of acidity until day 34 and more than 80 % after day 49 (Fig. [5a](#page-8-0)). There was not much difference in acidity removal among the reactors since acidity reduction is directly related to the removal of metals and the reactors showed comparable metal removal efficiencies.

The alkalinity generation rate was calculated by dividing the daily amount of acidity removed by unit area, or by unit volume of substrate material. The results indicated alkalinity generation rate progressively increased with the height of substrate layer in the bioreactors (Fig. [5](#page-8-0)b). This indicates alkalinity generation is proportional to the amount of substrate material. On the other hand, when alkalinity generation rate is normalized by the volume of substrate material, the bioreactors gave similar performances with respect to alkalinity generation independent of the amount of substrate (Fig. [5](#page-8-0)c), suggesting that acid neutralizing capacity is evenly distributed along the height of the substrate material.

Fig. 5 Temporal changes of a acidity, b alkalinity generation rate per unit area, and c alkalinity generation rate per unit volume in bioreactors with different amounts of mushroom compost

The minimal height of the organic substrate for AMD treatment

Based on the monitoring results of several geochemical parameters during column bioreactors operation, the suggested optimum heights of organic substrate to satisfy the treatment criteria with respect to each parameter are presented in Table 2. The treatment criteria for each parameter were arbitrarily determined based on the suggested values in the literature to ensure sustainable performance of the bioreactors, and were as follows; $DO < 1.0$ mg/l, $pH > 6.5$, ORP < -250 mV, metal removal efficiency $>80 \%$ for iron, and alkalinity generation rate per unit area $>$ 200 g/m²/day as CaCO₃. Note that those suggested values are only valid for the experimental conditions employed in this study, and therefore have limited applicability to other treatment scenarios where operation conditions may widely vary.

Table 2 The suggested height of mushroom compost for satisfactory treatment of AMD

Factor	Criterion	Minimal height (cm)
Removal of oxygen	$DO < 1.0$ mg/l	80
Neutralizing ability	pH > 6.5	80
Reducing condition	$ORP < -250$ mV	80
Metal removal	Iron removal $>80\%$	80
Alkalinity generation	>200 g/m ² /day as CaCO ₃	60

Under the conditions of this study, the suggested minimal height of the organic substrate for satisfactory DO removal was 80 cm, at which DO levels in the bioreactors never exceeded 1.0 mg/l after the bioreactors entered steady phase of operation. But, it might require more amount of substrate during cold weather season in which microbial activity becomes suppressed and

solubility of dissolved oxygen increases. Similarly, 80 cm or greater substrate height was suggested to meet ORP criterion since the reactors with less amount of substrate consistently registered \geq -200 mV ORP values toward the end of the operation. In terms of pH neutralization, >80 cm substrate height was suggested because pH values occasionally dropped below 6.5 in the reactors with ≤ 60 cm substrate height, especially upon the pH shock occurred on day 112.

In terms of metal removal, ≥ 80 cm substrate height was also suggested to maintain $>80 \%$ Fe removal since the Fe removal efficiency of the bioreactor with 60 cm mushroom compost were consistently lower than the criterion after day 76. For alkalinity generation, the bioreactors with ≥ 60 cm mushroom compost successfully met the criterion during steady phase of the operation.

Conclusions

A pilot-scale SAPS column study was performed at a closed coal mine site producing AMD with pH 3–4, and Fe and Al concentration of 50–230 and 40–170 mg/l, respectively. Temporal variations of several water quality parameters in the bioreactors containing different amounts of mushroom compost were monitored to access the influence of the amount of organic substrate on overall performance of the bioreactors. Results indicated that more robust and sustainable acid neutralizing capacity and metal removal were achieved when the amount of mushroom compost increased. The bioreactors containing relatively small amounts of mushroom composts were more vulnerable to pH shock in the AMD influent, and as a result, their pH neutralizing capacity was markedly reduced. Among the monitored parameters, DO and ORP were the most sensitive parameters that readily reflected the effect of the amount of mushroom compost in the bioreactors. Despite the clear signs of deterioration in DO, ORP in the reactors containing smaller amount of mushroom compost, Fe and Al was successfully removed from AMD over 125 days of operation. However, the bioreactors showed very limited efficiencies for Mn removal regardless of the amount of mushroom compost. The water qualities of AMD are very site specific and vary significantly depending on geochemical conditions. Therefore, the optimal amount of organic substrate should be selected accordingly based on the water quality and the treatment target levels. It should be noted that this field study was performed with AMD having very harsh water quality conditions. Therefore, for ordinary AMD with mild acidity, thickness of organic substrate might be designed thinner than the result obtained in this study.

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