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# Successive alkalinity producing system column study for alkalinity generation capacity with respect to influent AMD quality

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Water pollution due to Acid Mine Drainage (AMD) is becomes a matter of serious concern globally, which is a by-product of mining operation. AMD is harmful to aquatic life and corrodes the pumps, pipes and other machinery in mines; hence AMD should be managed economically and in efficient manner. The AMD discharge concentration should be in permissible limit as per requirement of various environmental laws in different countries. There are varieties of methods under active and passive treatment system for AMD treatment. Successive Alkalinity Producing System (SAPS) is widely accepted method, which incorporate the advantage of Anoxic Limestone Drain (ALD) method and wetland system. In this paper experimental studies were conducted using cow compost regarding performance of SAPS with respect to iron, aluminum, manganese removal and alkalinity generation. During this study four different types of synthetic AMD were used as influent and performance of SAPS for different Hydraulic Retention Time (HRT). It has been observed that both iron and aluminum is completely eliminated whereas removal of manganese is limited to 35.33%. In this article the author also make effort to analyze metal removal trends and alkalinity generation response by SAPS cell.

Keywords: Alkalinity, AMD, HRT, SAPS, SRB.

#### Introduction

The ecological disruption due to Acid Mine Drainage (AMD) is one of the most persistent pollution problems in the mining areas<sup>1</sup>. AMD can be defined as the discharge of acidic water from metal or coal mine both in activity or abandoned<sup>2</sup>. The presence of inorganic sulfur in coal mostly in the form of pyrite is the main cause of acidity in mine water<sup>3</sup>. Pyrite is relatively stable under both acidic and alkaline conditions but in the presence of oxidants light O<sub>2</sub> and ferric ion, it is rapidly dissolved in water<sup>4</sup>. The AMD generation can be represented by following equation:

 $\mathrm{FeS_2} + 14\mathrm{Fe^{3+}} + 8\mathrm{H_2O} \rightarrow \mathrm{15Fe^{2+}} + 2\mathrm{SO_4} + 16\mathrm{H^+}$ 

The ore deposits of sulfide minerals are formed in absence of oxygen under reducing conditions and after exposure to oxygen and water the sulfide minerals tend to unstable and oxidation take place<sup>5</sup>. The AMD discharge is most common example of trouble in mines when it pores water in surrounding stream are river<sup>6</sup>. The AMD discharge has detrimental effects on aquatic life, human life, flora and fauna, soil productivity and increases the corrosion of structures<sup>7</sup>. In dealing with AMD, one should focus on minimization of generation of AMD. If generation of AMD cannot be prevented, it must be collected and treated<sup>8</sup>. Therefore the proper management of AMD discharges as per statutory requirements of the respective country is very essential to meet required standards. The concept of SAPS were first reported by Hendricks<sup>9</sup> in 1991 than it was modified by Kepler and Mcleary in 1994. Successive alkalinity producing system (SAPS) is modified form of anaerobic wetlands provided with additional drainage pipe provided at the bottom of limestone layer with a flush valve and stand pipe which helps in maintaining sufficient head of water in SAPS column for downward movement of AMD solution. SAPS have advantages of anaerobic wetlands and efficiency of anoxic limestone drains both<sup>10</sup>. SAPS are also known as reducing and alkalinity producing system (RAPS) or vertical flow reactor. The topography is one of the key constraints for installation of SAPS because sufficient head should be available for causing vertical flow<sup>11</sup>.

#### Materials and methods:

All the unfiltered samples for each SAPS unit are taken for measurement and analysis. The pH, DO, ORP, temperature and electrical conductivity are instantly measured by portable WTW multi 3620 IDS digital meter. Then alkalinity was determined by 0.02 N H<sub>2</sub>SO<sub>4</sub> titration and acidity was also determined by 0.02 N NaOH titration on filtered samples. The collected samples were filtered in 0.45 micrometer. Whatman membrane filter and nitrified with HNO<sub>3</sub> and kept for further analysis in refrigerator at 4°C. The determination of ferrous iron and total iron were carried out using 1,10phenanthroline solution and ammonium acetate buffer solution by spectrophotometer. The ferric iron was calculated as difference of total iron and ferrous iron. Aluminum was determined using Erichrome cyanine R spectrophotometer method. Manganese was determined using ammonium persulphate by spectrophotometer. Sulfate determination was done by using barium chloride method in spectrophotometer. The Lasany UV-Vis spectrophotometer was used in above mentioned tests. Calcium and magnesium were determined by EDTA method. The flow rates were measured by volumetric cylindrical flask and stops watch all the measurement was carried out as per standard methods of APHA, unless specified<sup>12</sup>. The laboratory arrangement for SAPS column study is presented in Fig. 1<sup>13</sup>. In this phase four synthetic AMD namely AMD A<sub>4</sub>, AMD B<sub>4</sub>, AMD C<sub>4</sub> and AMD D<sub>4</sub> of different composition were processed in four SAPS cells (Table 1). In these experiments, all the four SAPS cells (SAPS A, SAPS B, SAPS C and SAPS D) were filled with the cow compost, saw dust and limestone of same composition and same quantity. The experiments were conducted in similar and identical conditions in 24.4°C (min.) to 35.6°C (max.) temperature range. After 15 days acclimation period, the AMD A<sub>4</sub>, AMD B<sub>4</sub>, AMD C<sub>4</sub> and AMD D<sub>4</sub> were allowed to flow in SAPS A, SAPS B, SAPS C and SAPS D respectively. Then all the samples were collected at port P1, port P2, and port P<sub>3</sub> for different HRT's of 1d, 2d, 4d, 7d and 10d respectively.

## **Results and discussion**

# SAPS performance with AMD $A_4^2$

The ORP in SAPS cell A for AMD  $A_4$  at port  $P_3$  showed downward trend from 104.70 mV to -212.30, -210.30, -306.30, -309.80 and -361.40 mV, which indicated that a



Fig. 1. Laboratory arrangement for SAPS column study<sup>13</sup>.

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Table 1. Composition of synthetic AMDs				
	AMD A <sub>4</sub>	AMD $B_4$	AMD C <sub>4</sub>	AMD D <sub>4</sub>
pН	3.60	3.30	2.62	2.44
ORP (mV)	140.70	107.00	106	108.30
DO (mg/L)	6.52	7.12	6.39	6.15
Total Fe (mg/L)	110.70	141.10	174.2	196.80
Fe <sup>2+</sup> (mg/L)	97.10	102.30	89.80	84.40
Fe <sup>3+</sup> (mg/L)	13.60	38.80	87.20	112.40
(Fe <sup>3+</sup> /Fe <sup>2+</sup> ) ratio	0.140	0.379	1.004	1.331
AI (mg/L)	80.00	80.00	80.00	80.00
Mn (mg/L)	15.00	15.00	15.00	15.00
Ca (mg/L)	125.00	125.00	125.00	125.00
Mg (mg/L)	100.00	100.00	100.00	100.00
SO <sub>4</sub> <sup>-</sup> (mg/L)	1440.00	1462.00	1481.00	1498.00
Electrical conductivity (micro S/cm)	2013.00	2049.00	2192.00	2230.00

strong reducing environment was prevailing inside the SAPS cell  $A_4$ . The negative ORP inside the SAPS is an essential condition for efficient operation of SAPS system.

The DO levels in SAPS cell A for AMD  $A_4$  were dropped from 6.52 mg/L to 0.06 mg/L, 0.00 mg/L and 0.00 mg/L for port  $P_1$ , port  $P_2$  and port  $P_3$  respectively for 1d HRT. Similar trends were reported for 2d, 4d, 7d and 10d HRTs. The DO level dropped to 0.00 mg/L at port  $P_3$  for all HRTs, which is in an encouraging indicator of attainment of anaerobic conditions inside the SAPS cell.

Therefore DO and ORP changed status is favorable for anaerobic reducing environment inside all the four SAPS cells. The electrical conductivity and sulfate were also decreasing during SAPS process which confirmed the metal removals and alkalinity generation in SAPS cell. Similar trends we are reported for ORP and DO status for SAPS B, SAPS C, and SAPS D, with AMD B<sub>4</sub>, AMD C<sub>4</sub> and AMD D<sub>4</sub> loading respectively.

pH variations:

In this study maximum pH at port  $P_3$  were raised to 8.72, 8.80, 8.75 and 8.85 for AMD  $A_4$ , AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$  for 10d HRT respectively.

# Iron removal behaviour:

Port P<sub>1</sub>: It is observed that in AMD A<sub>4</sub>, iron removal percentage at P<sub>1</sub> for HRT 1d, 2d, 4d, 7d and 10d were 0.09%, 0.18%, 22.49%, 58.27% and 64.59% respectively and pH was found increased from 3.60 to 5.85, 6.00, 6.28, 6.82 and 6.88 respectively. Further ferric iron are getting converted to ferrous iron in organic substrate layer reducing environment therefore ferric iron concentration has reduced from 13.60 mg/L to 1.20 mg/L for 1d HRT and reached at zero level for all 2d, 4d, 7d and 10d HRTs respectively. Hence same can be justified with increase in ferrous iron concentration from 97.10 mg/L to 109.40 mg/L and 110.50 mg/L for 1d and 2d HRTs respectively up to pH level 6.00. The significant iron removal was observed at port P<sub>2</sub> after 4d HRT and onwards.

Port P<sub>2</sub>: The observed cumulative iron removal percentage for HRT of 1d, 2d, 4d, 7d and 10d were 8.04%, 24.48%, 64.23%, 78.14% and 85.09% respectively and pH increased to 6.15, 6.45, 6.87, 7.13 and 7.28 respectively. The significant iron removal took place at port P<sub>2</sub> from 2d HRT and onwards. The significant reductions in ferric iron concentration were observed at port P<sub>2</sub> equal to zero. Therefore it is obvious that all the ferric iron is reduced to ferrous iron in organic substrate layer.

Port P<sub>3</sub>: The observation at port P<sub>3</sub> showed continue increasing trend in iron removal with increasing HRTs. The observed cumulative removal percentage at port P<sub>3</sub> for 1d, 2d, 4d, 7d and 10d HRTs were 14.45%, 64.23%, 78.14%, 100% and 100% respectively with corresponding pH increase to 6.35, 6.87, 7.13, 8.33 and 8.72 respectivel. Port P<sub>3</sub> is most important terminal because it discharges the treated AMD in oxidation cell and again oxic condition prevails therefore we can assess the performance of SAPS cell by analyzing the discharge from port P<sub>3</sub>. It was observed that iron present at this stage is found in ferrous form. 100% iron removal were observed at port P<sub>3</sub> for 7d and 10d HRTs whereas less removal percentage were reported for 1d, 2d and 4d HRTs therefore iron removal increases with increase in HRTs.

# Iron removal behavior in AMD $B_4$ , AMD $C_4$ , and AMD $D_4$ :

An increasing trend in iron removal like AMD  $A_4$  was observed with AMD  $B_4$ , AMD  $C_4$ , AMD  $D_4$ . The significant iron removal at port  $P_1$  for all AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$  was initiated after 4d HRT and complete removal were achieved at port  $P_3$  after 7d HRT for all the three AMDs as shown in Fig. 2(A).

#### Aluminum removal behavior with AMD $A_4$ :

Port  $P_1$ : In AMD  $A_4$  the initial aluminum concentration was 80.00 mg/L which dropped subsequently during treatment process by SAPS. The AI removal at port  $P_1$  were reported as 98.38%, 100%, 100%, 100% and 100% respec-





Fig. 2. (A) Iron removal in port  $\mathsf{P}_3$  and (B) aluminum removal in port  $\mathsf{P}_3.$ 

tively for 1d, 2d, 4d, 7d and 10d HRTs duration with corresponding level of 5.85, 6.00, 6.28, 6.82 and 6.88 respectively. As initial pH level of influent AMD  $A_4$  was 3.60. The increasing trends in pH level were observed during treatment process with respect to duration of HRTs.

Port  $P_2$ : In port  $P_2$  further increase in aluminum removal were observed the AI removal at port  $P_2$  as 100% for 1d HRT at pH level of 6.15, 6.45, 6.87, 7.13, and 7.28 respectively. These results are also as per AI chemistry expectations.

Port  $P_3$ : All aluminum contamination was removed at port  $P_3$  for each HRT duration as shown in Fig. 2(B). Al is first metal precipitate an SAPS cell. Al precipitation takes place inside the SAPS and deposited in void space available inside the organic substrate. That is why time to time flushing of SAPS cell is required to avoid clogging of pore space of organic substrate and limestone layer.

Aluminum removal behavior with AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$ :

An increasing trend like AMD  $A_4$ , were also observed for all three AMDs i.e. AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$ . The precipitation of AI took place from pH level of 5.10 and onwards for AMD  $D_4$ . The complete removals of AI took place after 7d HRT for all the three AMDs when pH level was around 7.00.

# Manganese removal behavior with AMD A<sub>4</sub>:

Port P<sub>1</sub>: In influent AMD A<sub>4</sub> manganese concentration was 15 mg/L. No significant Mn removal were observed i.e. only 0.2 mg/L reduction was noticed. The reason for above reduction is the adsorption of manganese by organic substrate. Further no significant Mn removals were reported at port P<sub>1</sub> for all 1d, 2d, 4d, 7d and 10d HRTs duration.

Port  $P_2$ : More or less similar observation as port  $P_1$  has been observed at port  $P_2$  for all 1d, 2d, 4d, 7d and 10d HRTs duration.

Port  $P_3$ : No significant manganese removal were observed for 1d, 2d and 4d HRTs but 36.67% and 38.00% Mn removal were observed for 7d and 10d HRTs respectively with corresponding pH level 8.33 and 8.72 respectively as shown in Fig. 3(A).

Manganese removal behavior with AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$ :

The similar trends in Mn removal were observed for all the three AMDs i.e. AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$ . The Mn was started to remove when pH level reached near 8.00 as shown in Fig. 3(A).

Net alkalinity generation (NAG) observations with AMD  $A_4$ :

Port P<sub>1</sub>: The net alkalinity generation at port P<sub>1</sub> were reported as 470 mg/L, 520 mg/L, 650 mg/L, 780 mg/L and 825 mg/L for 1d, 2d, 4d, 7d, and 10d HRT's with corresponding pH level of 5.85, 6.00, 6.28, 6.82 and 6.88 respectively. The



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continuous increases in alkalinity generation in logarithmic manner were observed for 1d HRT to 10d HRT at port  $P_1$ .

Fig. 3. (A) Manganese removal at port P<sub>3</sub> and (B) NAG at port P<sub>3</sub>.

Port  $P_2$ : The alkalinity generation further increases at port  $P_2$ . The observed alkalinity generation at port  $P_2$  were 570 mg/L, 685 mg/L, 860 mg/L, 930 mg/L and 1055 mg/L for 1d, 2d, 4d, 7d, and 10d HRTs with corresponding pH level of 6.15, 6.45, 6.87, 7.13 and 7.28 respectively. Again in this zone alkalinity is generated by microbial activity in organic substrate layer in anaerobic environment inside the SAPS cell.

Port  $P_3$ : The generation of alkalinity increases at port  $P_3$  because of dissolution of limestone in the bottom layer. The alkalinity generation at port  $P_3$  were reported as 700 mg/L, 890 mg/L, 1100 mg/L, 1280 mg/L and 1405 mg/L for 1d, 2d, 4d, 7d, and 10d HRTs with corresponding pH level of 6.35, 6.87, 7.13, 8.33 and 8.72 respectively as shown in Fig. 3(B).

Net alkalinity generation (NAG) observations with AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$ :

The similar increasing trends of alkalinity generation were obtained for AMD  $B_4$ , AMD  $C_4$  and AMD  $D_4$  as shown in Fig. 3(B).

#### Conclusions

The present study demonstrates the utility of Successive Alkalinity Producing System to treat acidity and removal of dissolved metals from AMD. It is clearly evident from this experimental study that the SAPS cell is proven to be very efficient, enabling specifically for both iron and aluminum removal however the manganese removal is partially achieved. Following are the some major finding of this study

- The alkalinity generation increases with increase in hydraulic retention time in logarithmic manner.
- (ii) The maximum partial manganese removal up to 40.67% were reported (AMD D<sub>4</sub>) because a much higher pH level (>8) is required for complete removal of manganese.
- (iii) The alkalinity generation also increases with increase in metal loading in influent AMD from AMD A<sub>4</sub> to AMD D<sub>4</sub>.
- (iv) It was found that all the iron were removed between 5.14 to 8.27 pH level.
- (v) It was evident that before 6 pH level of AMD solution a complete removal of aluminum was achieved.
- (vi) The complete removal of iron and aluminum from AMD is possible by SAPS treatment.
- (viii) It was found that the substantial amount (>50%) of alkalinity generation due to microbial activities up to port P<sub>2</sub>.

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