

# Study of Metal Removal and Alkalinity Generation by Laboratory Successive Alkalinity Producing System (SAPS) during AMD Treatment

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## ABSTRACT

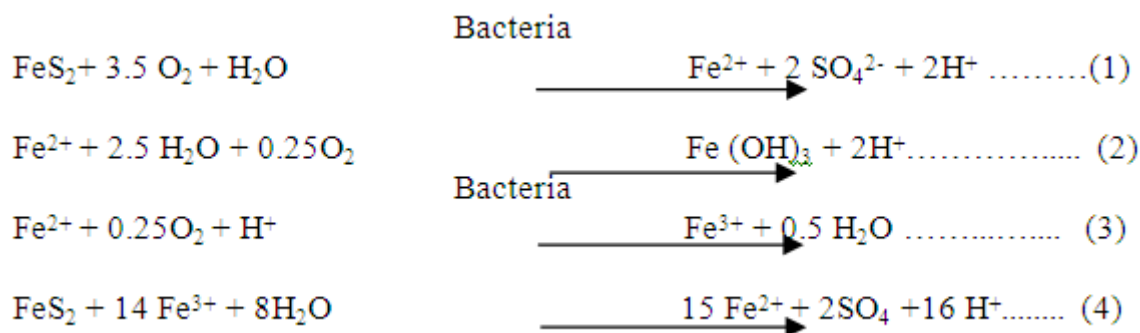
*Successive Alkalinity Producing System (SAPS) is broadly accepted for treatment of acid mine drainage (AMD). The effectiveness of SAPS depends upon many parameters like hydraulic retention time (HRT), influent quality, characteristics of organic substrate and their design aspects. A laboratory SAPS column study, four synthetic AMD solutions were treated for 1 day, 2 days, 4 days, 7 days and 10 days HRTs to determine the performances of SAPS using cow compost as organic substrate, saw dust and lime stone in parallel in identical conditions. In this study, studies were carried out to find the effect of hydraulic retention time on iron, aluminum and manganese removal and alkalinity generation by laboratory SAPS. In this study iron and aluminum removal is almost 100% whereas 44% manganese removal has been found, particularly for 4 days HRTs and more depending upon metal concentration in influent AMD. Higher rate of alkalinity generation was observed in initial reaction period then it got slower down after passage of time. The results of this study will also be useful for design of SAPS for field operations to improve performance of existing SAPS working in mines worldwide.*

**Key Word:** SAPS, HRT, AMD, ORP

## 1. INTRODUCTION

Mining of the coal and metals exposes the pyrite minerals to oxygen and water, which coupled with bacterial activity, leads to formation of AMD that are highly enriched with sulfate, aluminium and heavy metals. (Johnson, 2003, Ackil & Koldas, 2006, Koski et al., 2008). Jamal, Dhar, Siddharth & Tiwari (2003) and Saharan (1995) stated that the ground water seepage from working faces dissolves sulfide minerals and hydrolyses to form AMD. Rawat (as cited in Jamal et al. 1995) suggested that in coal mines the sulfide minerals (pyrite and marcasite) are responsible for generation of AMD.

Barnes & Romberger and Kleinmann et al. (as cited in Watzlaf, 2004) has stated the following chemical reactions, which occurs during formation of AMD.



Stumm & Morgan (1981) has suggested that active and abandoned mine both contribute to AMD generation.

### Factor affecting the AMD generation

Siddharth (2001) stated that the AMD generation is affected by following factors:

- Type of sulfide minerals
- Mode of occurrence of sulfide minerals
- Nature of adjoining rocks
- Hydrogeology of area
- Shape and size of sulfide minerals
- Rainfall in the area
- Temperature variation
- Supply of oxygen and
- Presence of bacteria

Broadly two types of AMD treatment methods are used worldwide i.e.

- Active treatment method and
- Passive treatment method.

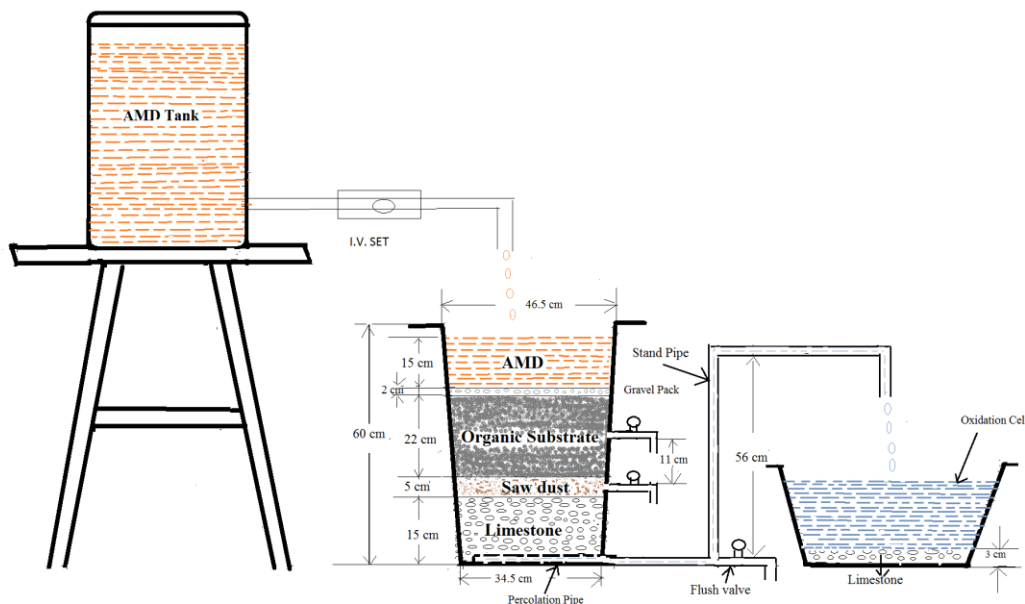
Skousen et al. cited in Jage (2000) described that in active treatment method mainly chemicals like sodium hydroxide, ammonia, hydrated lime, quick lime or soda ash etc. are used to raise the pH of water. In passive treatment system the physical, chemical and biological processes are observed. Passive treatment system is natural process, therefore the rate of neutralization is slower but it is more eco-friendly than active treatment system.

Successive Alkalinity Producing System (SAPS) is a 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 help in maintaining sufficient head of water in SAPS column for downward movement of AMD solution. SAPS has advantages of anaerobic wetlands and efficiency of anoxic limestone drain both (Kepler & Mcclary, 1994)

## 2. METHODS AND MATERIALS

### SAPS Experimental setup and operation

Each SAPS unit consists of 3 components, first the AMD container placed at elevated position, second the SAPS cell in which the various materials such as limestone saw dust and cow compost were filled up as shown in figure 1. Four PVC container of 80 liter capacity were chosen for making SAPS cells. At the bottom of the cell, a 2.5 cm thick gravel bed was filled up. At this portion, a perforated pipe was fitted for the purpose of flushing. The other end of bottom pipe was connected to oxidation cell. Above the layer of gravel, a limestone (>90%  $\text{CaCO}_3$ ) layer of 15 cm thickness was laid. A layer of 5 cm thick made up of saw dust and 22 cm thick cow compost layer were made above the limestone layer. A 2.5 cm thick gravel was packed at the top and finally AMD water was allowed to fill up to 15 cm height above the top gravel pack. The estimation of quantity of limestone and organic substrate were done on the basis of chemical calculations. On this basis, the estimated quantity of limestone was approx. 27 kg and volumes of organic substrate were estimated at approx 29 liters.



**Figure 1: Laboratory Arrangement for SAPS Column Study**

A total of 4 synthetic AMD solutions were prepared with various compositions. All the experiments were performed in identical conditions with the temperature ranges from 19°C to 34°C in parallel four similar SAPS set up simultaneously in the same time period. The cow compost is taken from agricultural farm which is having sufficient population of bacteria. The cow compost in the entire SAPS unit was kept same. A polyethylene net of 16 mesh was placed between different layers of materials to avoid the mixing and for maintaining the easily flow condition inside the SAPS cell and third unit is oxidation cell in which we allow the oxic conditions for water coming from the SAPS cell, where metal gets precipitated and pH increases. In each SAPS system, the oxidation cell of 50 liters volume was attached with 3 cm thick layer of limestone at the bottom.

SAPS column experiments were conducted with four different synthetic AMD with the composition as shown in Table 1, considering major component of coal mine AMD as iron, aluminum and manganese, which are predominantly found. The SAPS filled with cow compost, saw dust, limestone and normal water, then SAPS cells were left for 15 days as acclimation period for sufficient growth of bacteria. High concentration of hydrogen sulfide is produced after 15 days which is indicated by strong smell of rotten egg, confirming the large number of sulfate reducing bacteria (SRB) grown up in the SAPS cell. Growth of SRB is an essential condition for proper functioning of SAPS cell. After 15 days acclimation period all the four synthetic AMD solutions were allowed to pour in the SAPS cell with control flow rate having different HRTs.

### SAPS performance with AMDs

The phase four synthetic AMDs (viz., AMD A<sub>6</sub>, AMD B<sub>6</sub>, AMD C<sub>6</sub>, AMD D<sub>6</sub>) were processed in the four SAPS cells, viz., SAPS A, SAPS B, SAPS C, SAPS D. The composition of the synthetic AMDs is as under (Table 1).

**Table 1: Composition of AMD used in Phase VI experiments**

	AMD A <sub>6</sub>	AMD B <sub>6</sub>	AMD C <sub>6</sub>	AMD D <sub>6</sub>
pH	4.35	3.55	2.72	2.55
ORP (mV)	105.30	109.70	106.30	110.40
DO (mg/L)	6.81	5.79	6.18	5.82
Total Fe (mg/L)	92.50	118.70	172.80	193.00
Fe <sup>2+</sup> (mg/L)	81.30	93.10	78.60	83.90
Fe <sup>3+</sup> (mg/L)	11.20	35.80	94.20	109.10
(Fe <sup>3+</sup> /Fe <sup>2+</sup> ) Ratio	0.137	0.384	1.198	1.300
Al (mg/L)	20.00	20.00	20.00	20.00

Mn (mg/L)	45.00	45.00	45.00	45.00
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>2-</sup> (mg/L)	1155.00	1028.00	1205.00	1232.00
Electrical conductivity $\mu$ S/cm	1958	2011	2167	2192

In this study, all the four SAPS cells (SAPS A, SAPS B, SAPS C and SAPS D) were prepared in similar and identical manner. After acclimation period the AMD A<sub>6</sub>, AMD B<sub>6</sub>, AMD C<sub>6</sub>, and AMD D<sub>6</sub> were allowed to flow in the SAPS cells SAPS A, SAPS B, SAPS C and SAPS D respectively. Each of the SAPS cell performed the treatment process for HRT of 1d, followed by 2d and so on for 4d, 7d and 10d. For each HRT, viz., 1d, 2d, 4d, 7d and 10d, the samples were collected at port P<sub>1</sub>, port P<sub>2</sub>, and port P<sub>3</sub> from each of the SAPS respectively. Based on the experimental observations, computations were performed to determine the iron removal, aluminium removal, manganese removal, sulfate removal, acidity decreased, alkalinity increased, and net alkalinity generation. The salient parameters exhibiting the functioning and performance of SAPS cell like Oxidation Reduction Potential, Dissolved Oxygen, electrical conductivity, sulfate content, pH, Iron removal, aluminum removal, manganese removal and alkalinity generation have been discussed in detail for the AMD A<sub>6</sub>. However, for the AMD B<sub>6</sub>, AMD C<sub>6</sub>, and AMD D<sub>6</sub> only a summary of the observations has been discussed.

### Salient parameters of SAPS operation for AMD A<sub>6</sub>

#### Oxidation Reduction Potential (ORP) and Dissolved Oxygen (DO) Status in SAPS cell for AMD A<sub>6</sub>

It is observed that at Port P<sub>1</sub>, the ORP values are less than -100 mV. The ORP values tend to fall further in the lower stratum of the SAPS cell. For AMD A<sub>6</sub>, at 1d HRT, the ORP in SAPS cell A reduced from 105.30 mV at influent to -111.40 mV at port P<sub>1</sub>, -114.20 mV at port P<sub>2</sub> and -216.50 mV at port P<sub>3</sub> as shown in figure 2. For AMD A<sub>6</sub>, the ORP in SAPS cell A reduced from 105.30 mV at influent to -216.50, -228.30, -311.50, -315.20 and -358.50 mV for 1d, 2d, 4d, 7d and 10d HRTs respectively at port P<sub>3</sub>, which indicated that a strong reducing environment was prevailing inside the SAPS cell A. For AMD A<sub>6</sub>, at 1d HRT, the DO levels in SAPS cell A reduced from 6.81 mg/L at influent to 0.60 mg/L, 0.00 mg/L and 0.00 mg/L for port P<sub>1</sub>, port P<sub>2</sub> and port P<sub>3</sub> respectively as shown in figure 3. Similar trend was observed for HRTs of 2d, 4d, 7d, and 10d. For all the HRTs the DO level reduced to 0.00 mg/L at port P<sub>2</sub> prior to its passage into the limestone layer, which is an encouraging indicator of attainment of anaerobic conditions inside the SAPS cell.

#### Electrical Conductivity in SAPS cell for AMD A<sub>6</sub>

In the SAPS cell, it has been observed that the EC values are highest in the influent AMD, which later decreases in each layer. The lowering of the EC values indicated the reduction in concentration of dissolved metals in AMD which resulted in increase in alkalinity. Considering the two extreme cases of metal reduction in the SAPS Cell, it has been observed that 1d HRT records a minimum activity while 10d HRT exhibits maximum activity. For AMD A<sub>6</sub>, at HRT of 1d, the EC of 1958  $\mu$ S/cm reduces to 1885  $\mu$ S/cm at port P<sub>1</sub>, 1858  $\mu$ S/cm at Port P<sub>2</sub>, and 1702  $\mu$ S/cm at Port P<sub>3</sub>. For AMD A<sub>6</sub>, at HRT of 10d, the EC of 1958  $\mu$ S/cm reduces to 1858  $\mu$ S/cm at port P<sub>1</sub>, 1828  $\mu$ S/cm at Port P<sub>2</sub>, and 1660  $\mu$ S/cm at Port P<sub>3</sub>.

#### Sulfate removal in SAPS cell for AMD A<sub>6</sub>

The cumulative removal of sulfate is observed to increase with higher retention time. For 1d HRT, it has been observed that a minimum cumulative removal of sulfate was 507 mg/L at the discharge of the SAPS cell (Port P<sub>3</sub>). For AMD A<sub>6</sub>, it has been observed that maximum cumulative removal of sulfate, i.e., 675 mg/L occurred in 10d HRT at Port P<sub>3</sub>. At HRT of 10d, for AMD A<sub>6</sub>, the sulfate of 1155 mg/L in the influent reduces to 796 mg/L at port P<sub>1</sub>, 540 mg/L at Port P<sub>2</sub>, and 480 mg/L at Port P<sub>3</sub>. Hence, during the SAPS process the sulfate concentration was observed to be decreasing from influent inlet to its discharge. To understand the contribution of each layer from the SAPS cell, it is observed that for AMD A<sub>6</sub>, at HRT of 10d, the organic compost layer reduces 615 mg/L of sulfate, while limestone layer reduces 60 mg/L of sulfate.

#### pH status in SAPS cell for AMD A<sub>6</sub>

During the treatment process of the SAPS Cell, the pH levels are observed to increase at each stratum of the SAPS cell till it is discharged from the SAPS Cell. As an example, for AMD A<sub>6</sub>, at HRT of 10d, the influent has pH of 4.35 which is raised to pH of 6.80 at Port P<sub>1</sub>, 7.30 at Port P<sub>2</sub>, and 8.50 at Port P<sub>3</sub> (Figure 4). It can be deduced that the contribution of increase of pH by organic compost layer is 2.95 points and that by limestone layer is 1.20 points. To understand the effect of HRT on pH in the SAPS Cell, the observations for 1d, 2d, 4d, 7d, and 10d HRT show that the pH values exhibit an increasing trend. As an example, for AMD A<sub>6</sub>, the pH level at discharge of SAPS Cell after the limestone layer, i.e. at Port

$P_3$ , are 6.35, 6.55, 6.75, 8.30, 8.50 for 1d, 2d, 4d, 7d, and 10d HRT respectively as shown in figure 4. It was observed that pH increases with increase in HRT.

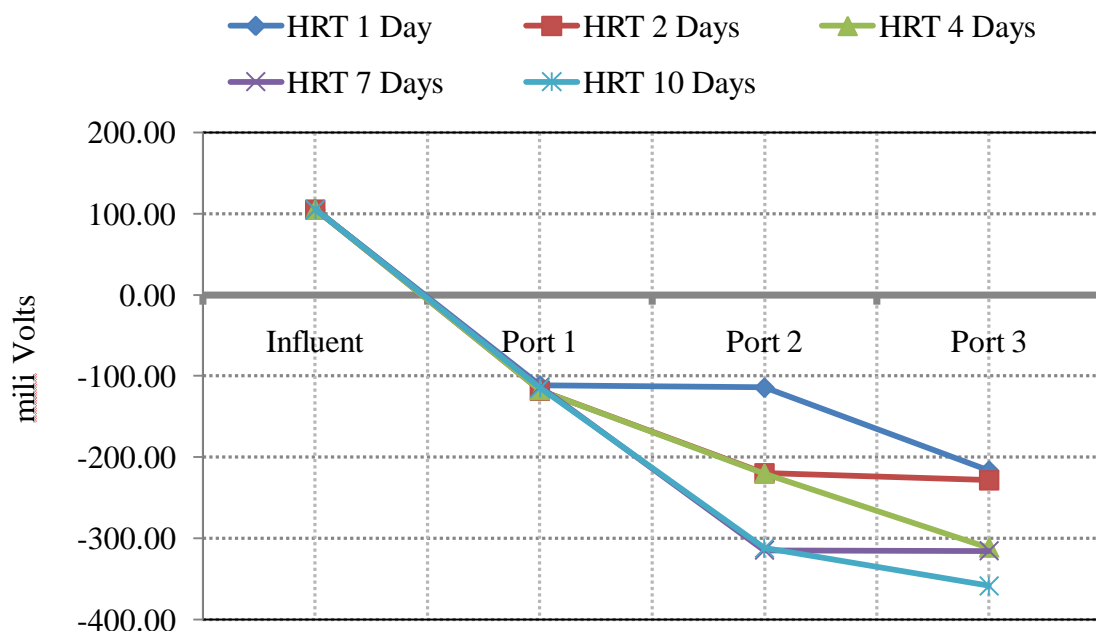


Figure 2: ORP variation in SAPS with AMD A<sub>6</sub>

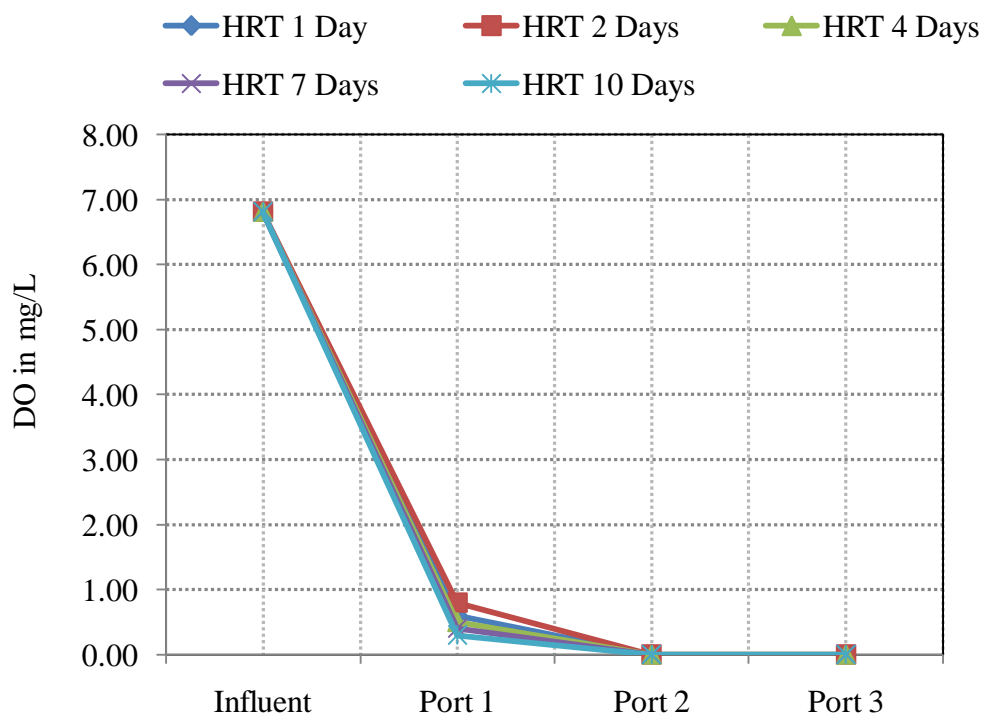


Figure 3: DO variation in SAPS with AMD A<sub>6</sub>

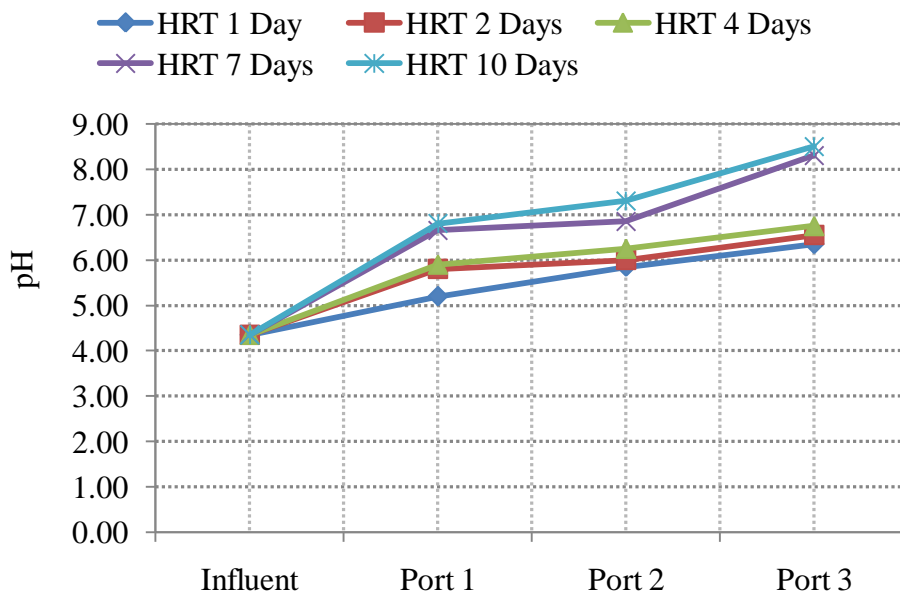


Figure 4: pH variation in SAPS with AMD A<sub>6</sub>

#### Metal Removal Behavior of SAPS for AMD A<sub>6</sub>

During the alkalinity generation process the metal content was removed and the metal removal behaviour of the SAPS has been analysed at each port and presented as under.

#### Iron removal behavior for AMD A<sub>6</sub>

It was observed that in AMD A<sub>6</sub>, cumulative iron removal percentage at port P<sub>1</sub> was 0.00%, 0.11%, 0.11%, 49.30% and 59.40% for HRT 1d, 2d, 4d, 7d and 10d respectively (Figure 5). Correspondingly, the pH was found to increase from an initial pH of 4.35 of the influent to 5.20, 5.80, 5.90, 6.65 and 6.80 for HRT 1d, 2d, 4d, 7d and 10d respectively. Further the ferric iron was getting converted to ferrous iron in organic substrate layer in reducing environment. Therefore, the ferric iron concentration was reduced from an initial value of 11.20 mg/L to 2.20 mg/L, 1.60 mg/L, 1.30 mg/L, 0.00 mg/L and 0.00 mg/L for 1d, 2d, 4d, 7d and 10d HRTs respectively.

Correspondingly, it is observed that ferrous iron concentration increases from 81.30 mg/L in influent to 90.30 mg/L, 90.80 mg/L and 91.10 mg/L for 1d, 2d, and 4d HRTs respectively. However, in case of 7d and 10d HRTs, the ferrous iron concentration has been observed to be 46.90 mg/L and 37.70 mg/L respectively. This reveals that some portion of the ferrous iron has been precipitated in the organic layer and the same is reflected in the cumulative iron removal of 49.30% and 59.24% at port P<sub>1</sub> for 7d and 10d HRTs respectively.

The observations at port P<sub>2</sub> showed that the cumulative iron removal percentage for HRT of 1d, 2d, 4d, 7d and 10d was 0.22%, 0.22%, 15.46%, 62.27% and 86.16% respectively and correspondingly the pH increased to 5.85, 6.00, 6.25, 6.85 and 7.30, and Figure 6. Substantial iron removal took place at port P<sub>2</sub> from 4d HRT and onwards. For 1d and 2d HRTs the ferric iron concentration was observed to be 1.50 mg/L and 1.20 mg/L respectively at port P<sub>2</sub>. At port P<sub>2</sub>, the ferric iron concentration became zero for 4d, 7d and 10d HRTs, thus indicating a complete reduction in ferric iron. Correspondingly, it is observed that ferrous iron concentration changes from 81.30 mg/L in influent to 90.80 mg/L, 91.10 mg/L, 78.20 mg/L, 34.90 mg/L and 12.80 mg/L for 1d, 2d, 4d, 7d and 10d HRTs respectively. Since the ferrous iron has been precipitated in the organic layer, the decrease in the ferrous iron concentration at 4d, 7d and 10d HRTs is observed.

The observations at port P<sub>3</sub> showed a continuous increasing trend in iron removal with increasing HRTs. The observed cumulative iron removal percentage at port P<sub>3</sub> for HRT of 1d, 2d, 4d, 7d and 10d were 8.54%, 24.00%, 57.30%, 100% and 100% respectively with a corresponding increase in pH to 6.35, 6.55, 6.75, 8.30 and 8.50 respectively as shown in figure 7. The limestone layer contributes to the removal of iron even at minimum retention time, i.e. at 1d HRT, the cumulative iron removal percentage of 8.32% was observed. At Port P<sub>3</sub>, It was observed that the iron content was found in ferrous iron form and 100% iron removal was observed for 7d and 10d HRTs.

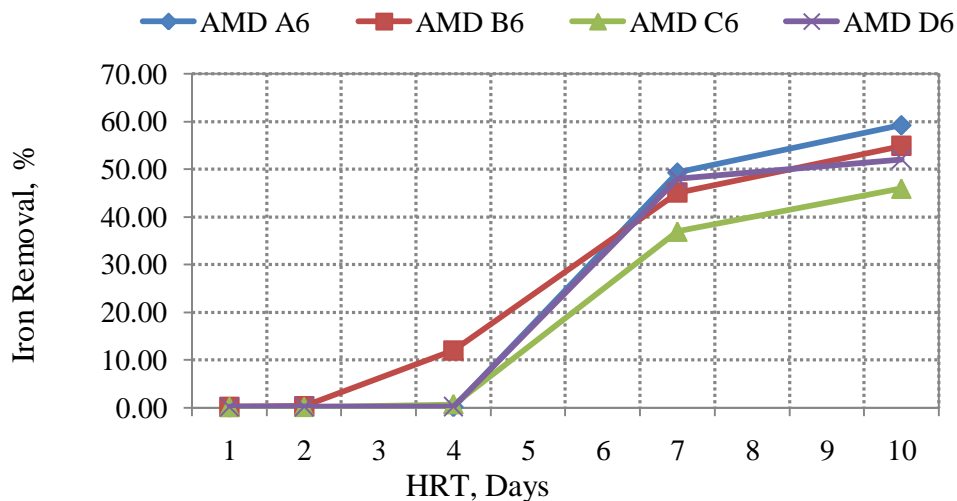


Figure 5: Iron removal percentage in Port P<sub>1</sub>

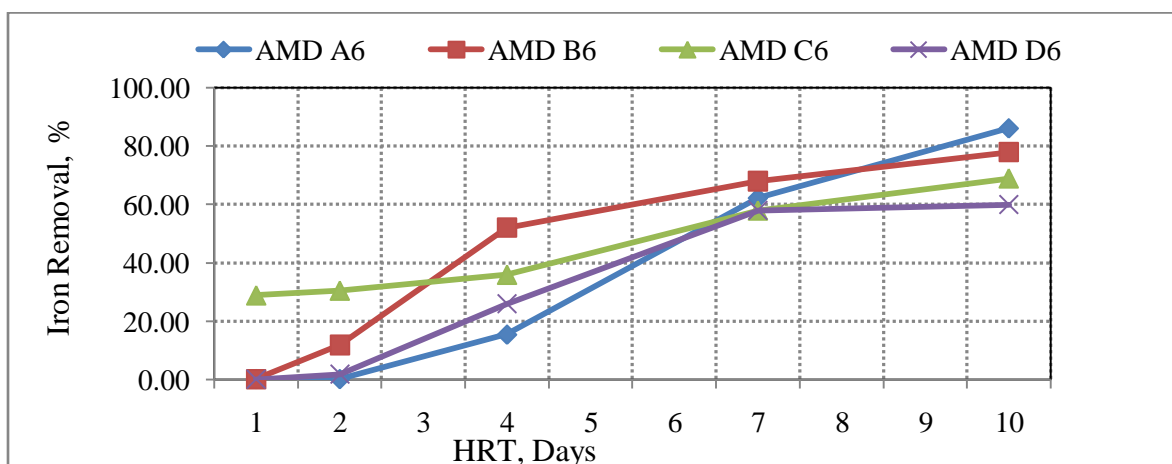


Figure 6: Iron removal percentage in Port P<sub>2</sub>

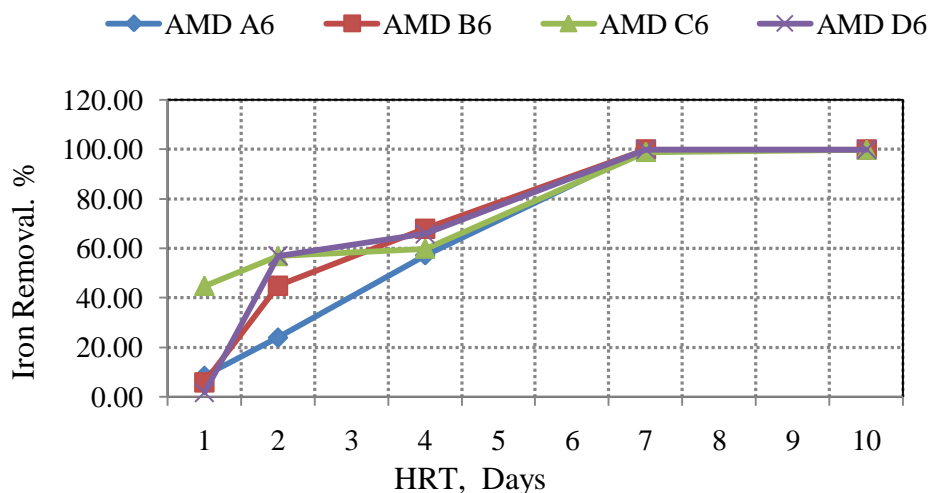


Figure 7: Iron removal percentage in Port P<sub>3</sub>

Similar trends in Iron removals were observed for remaining three AMDs Namely AMD B<sub>6</sub>, AMD C<sub>6</sub> and AMD D<sub>6</sub>.



### Aluminum Removal Behavior in AMD A<sub>6</sub>

At this port P1, the AMD A6 having an initial pH of 4.35 and initial aluminium (Al) concentration of 20.00 mg/L showed substantial removal of Al during the treatment process. The cumulative Al removal at Port P1 was reported as 75%, 85%, 90%, 100% and 100% respectively for 1d, 2d, 4d, 7d and 10d HRTs respectively with the corresponding pH level of 5.20, 5.80, 5.90, 6.65 and 6.80 respectively as shown figure 8. For HRTs of 7d and 10d, 100% Al removal was observed at Port P1. It was observed that a minimum pH of 5.20 occurred at Port P1 and it recorded an early occurrence of precipitation of Al, i.e. 75.00% Al removal at 1d HRT. At Port P2, the cumulative aluminum removal was observed to be 90%, 95%, 100%, 100% and 100% for 1d, 2d, 4d, 7d and 10d HRTs respectively with the corresponding pH level of 5.85, 6.00, 6.25, 6.85, and 7.30 respectively as shown in Figure 9. A 100% cumulative aluminum removal was observed at Port P2 for the 4d, 7d and 10d HRTs. At Port P3, for 1d and 2d HRT the remnant Al in the AMD was removed by the limestone layer of the SAPS (Figure 10).

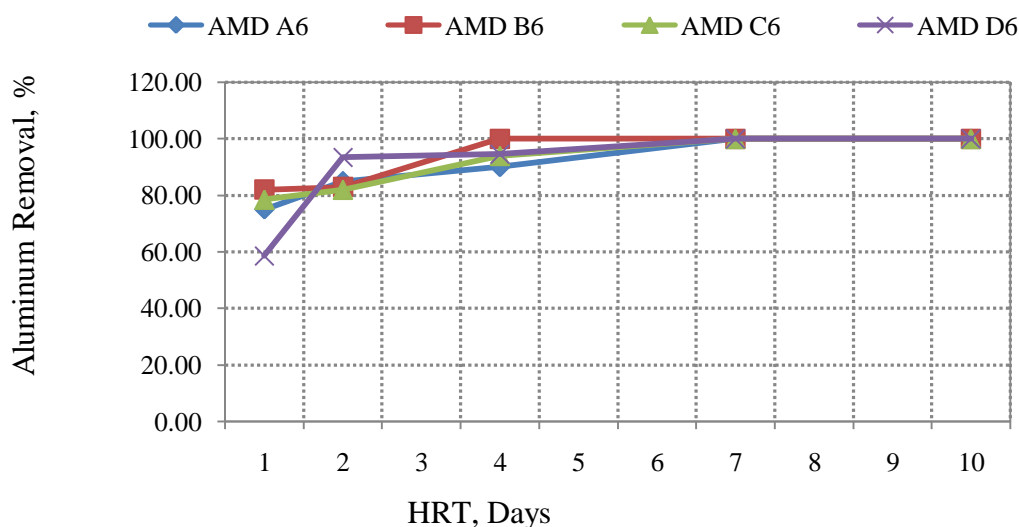


Figure 8: Aluminum removal percentage in Port P<sub>1</sub>

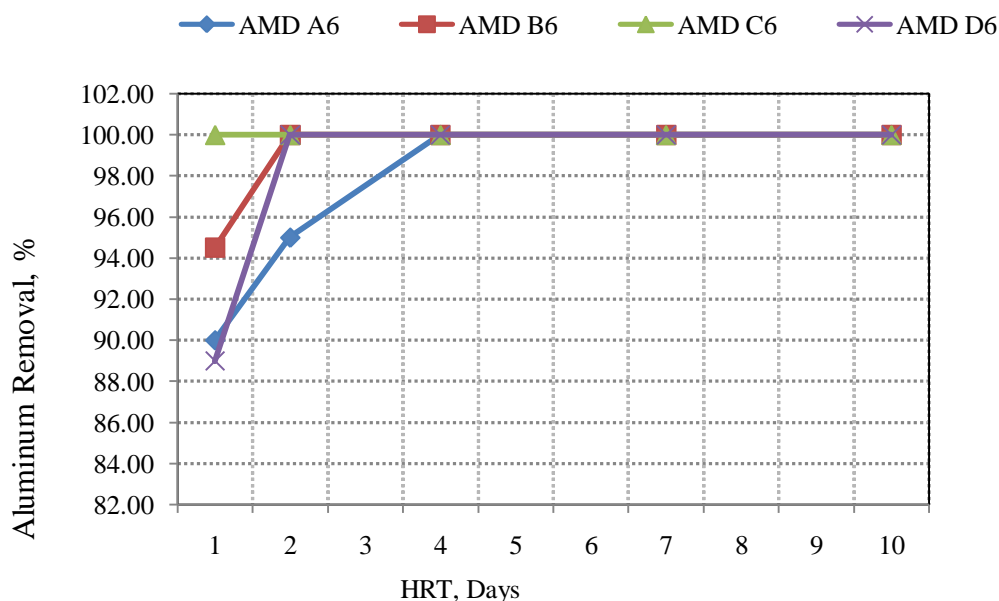
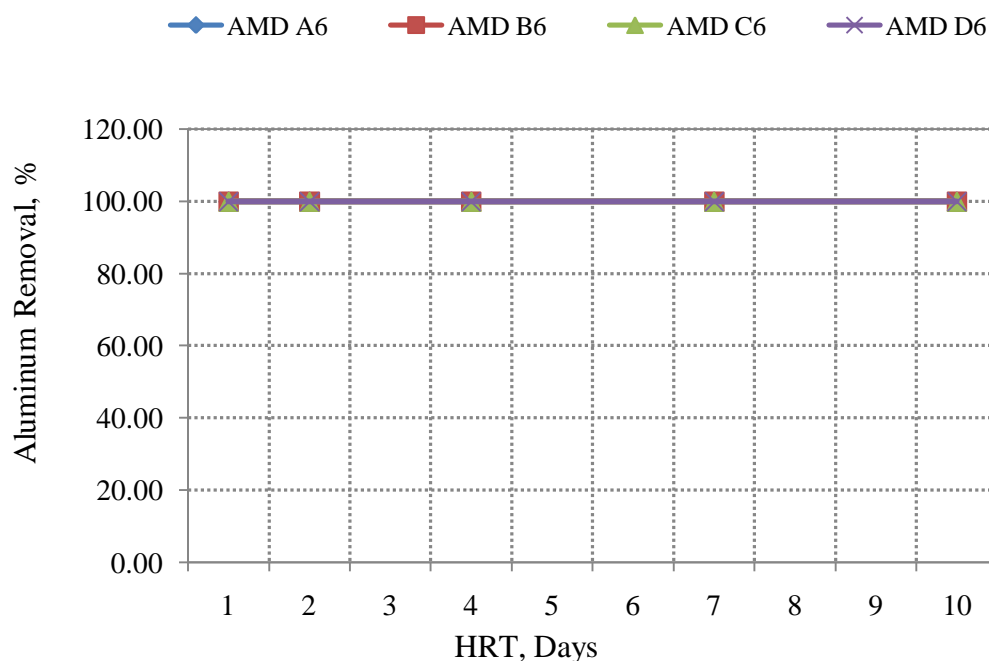


Figure 9: Aluminum removal percentage in Port P<sub>2</sub>



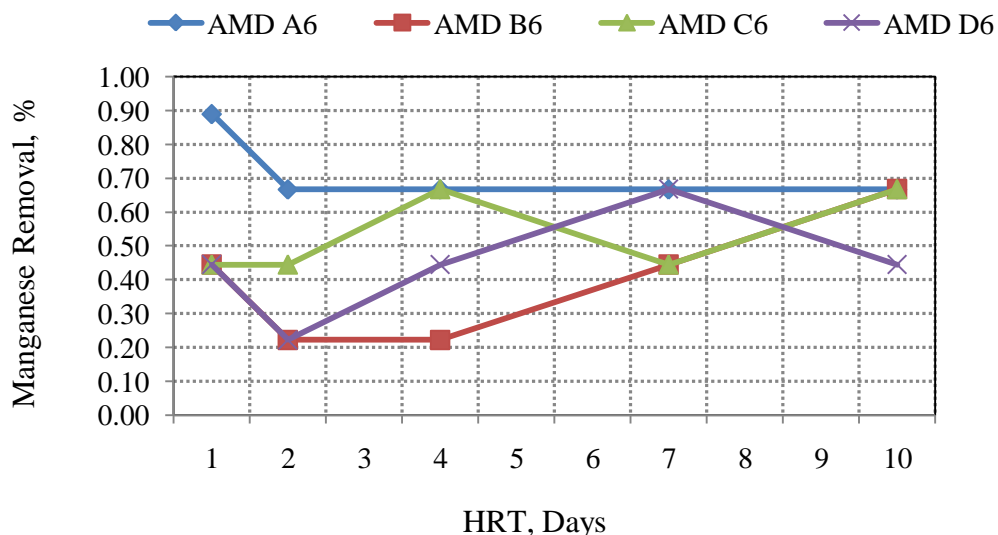


**Figure 10: Aluminum removal percentage in Port P<sub>3</sub>**

Similar trends in Aluminum removals were observed for remaining three AMDs Namely AMD B<sub>6</sub>, AMD C<sub>6</sub> and AMD D<sub>6</sub>.

#### Manganese removal behavior in AMD A<sub>6</sub>

At Port P<sub>1</sub>, the manganese concentration of influent in AMD A<sub>6</sub> was 45 mg/L. The Mn removal at Port P<sub>1</sub> was observed to be a maximum of 0.40 mg/L Mn each for 1d HRT. There has been negligible removal of Mn at port P<sub>1</sub> for all HRTs as shown in figure 11. At Port P<sub>2</sub>, similar to Port P<sub>1</sub>, it was observed that negligible removal of Mn was observed at Port P<sub>2</sub> for all HRTs as shown in Figure 12. At Port P<sub>3</sub>, the Mn removal was observed to be less at HRT of 1d, 2d and 4d, this being 1.11%, 1.11%, 0.89% respectively; the corresponding pH values being 6.35, 6.55 and 6.75 respectively. At HRT of 7d and 10d, Mn removal of 23.56% and 41.33% was observed; the corresponding pH values being 8.30 and 8.50 respectively as shown in figure 13.



**Figure 11: Manganese Removal percentage in Port P<sub>1</sub>**

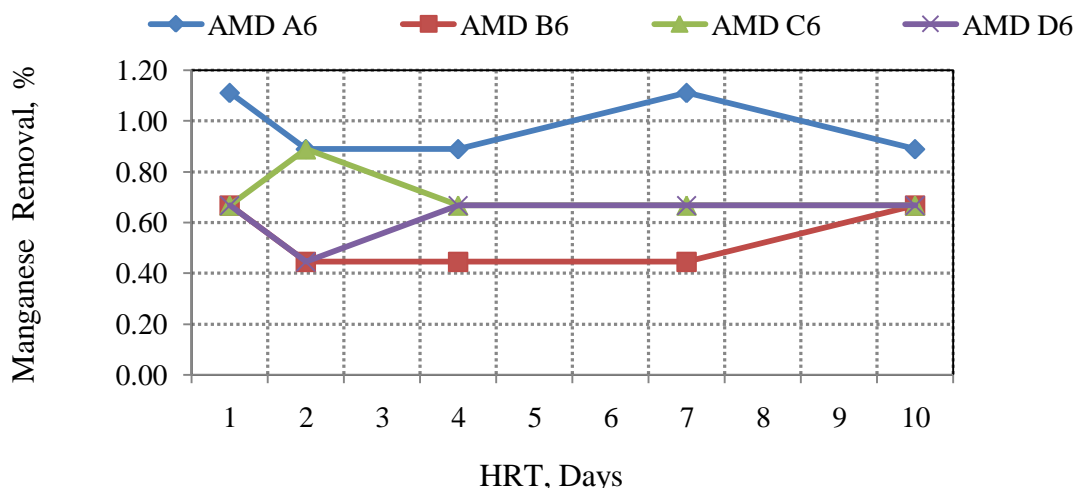


Figure 12: Manganese Removal percentage in Port P<sub>2</sub>

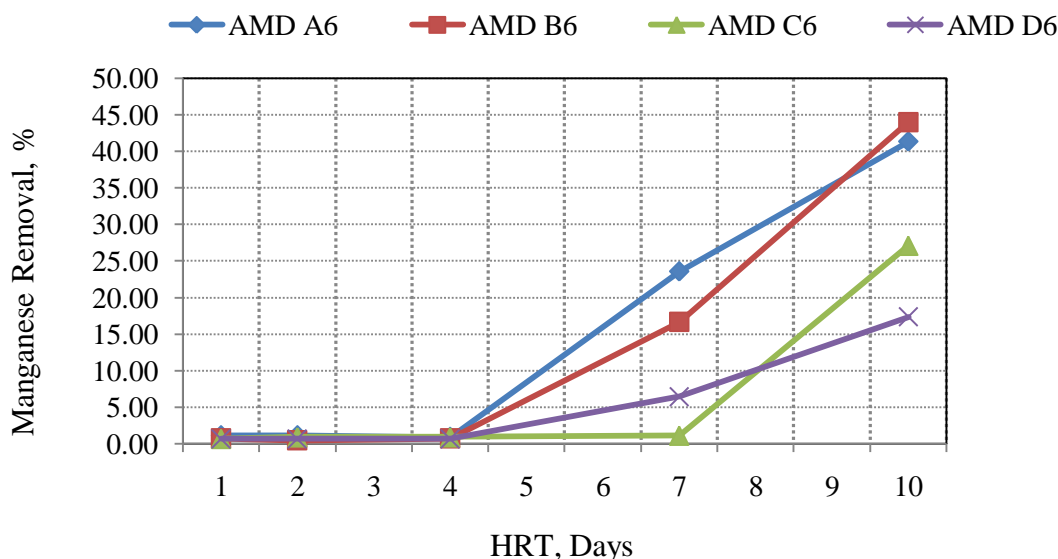


Figure 13: Manganese Removal percentage in Port P<sub>3</sub>

Similar trends in Manganese removals were observed for remaining three AMDs Namely AMD B<sub>6</sub>, AMD C<sub>6</sub> and AMD D<sub>6</sub>.

#### Alkalinity generation in AMD A<sub>6</sub>

At Port P<sub>1</sub>, the net alkalinity generation at port P<sub>1</sub> was observed to be 95 mg/L, 215 mg/L, 245 mg/L, 380 mg/L and 430 mg/L for 1d, 2d, 4d, 7d, and 10d HRTs respectively with the corresponding pH level of 5.20, 5.80, 5.90, 6.65 and 6.80 respectively as shown in figure 14. The net alkalinity generation increased with increased retention time. At Port P<sub>2</sub>, the net alkalinity generation in SAPS cell was further increased at port P<sub>2</sub>. The observed alkalinity generation at port P<sub>2</sub> was 270 mg/L, 340 mg/L, 405 mg/L, 585 mg/L and 665 mg/L for 1d, 2d, 4d, 7d, and 10d HRTs respectively with the corresponding pH level of 5.85, 6.00, 6.25, 6.85 and 7.30 respectively as shown in figure 15. In this zone the alkalinity is generated by microbial activity in organic substrate layer. At Port P<sub>3</sub>, the generation of net alkalinity increases at port P<sub>3</sub> because of dissolution of limestone in the bottom layer. The alkalinity generation at port P<sub>3</sub> was observed to be 440 mg/L, 545 mg/L, 710 mg/L, 935 mg/L and 1075 mg/L for 1d, 2d, 4d, 7d, and 10d HRTs respectively with corresponding pH level of 6.35, 6.55, 6.75, 8.30 and 8.50 respectively as shown in figure 16. The maximum net alkalinity generated is observed to be 1030 mg/L for 10d HRT.

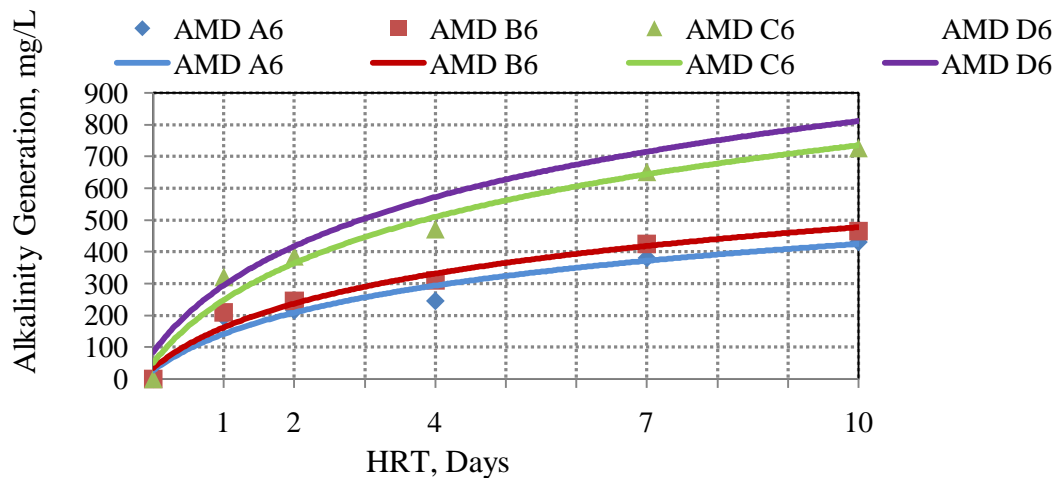


Figure 14: Alkalinity Generation in Different HRT for Port P<sub>1</sub>

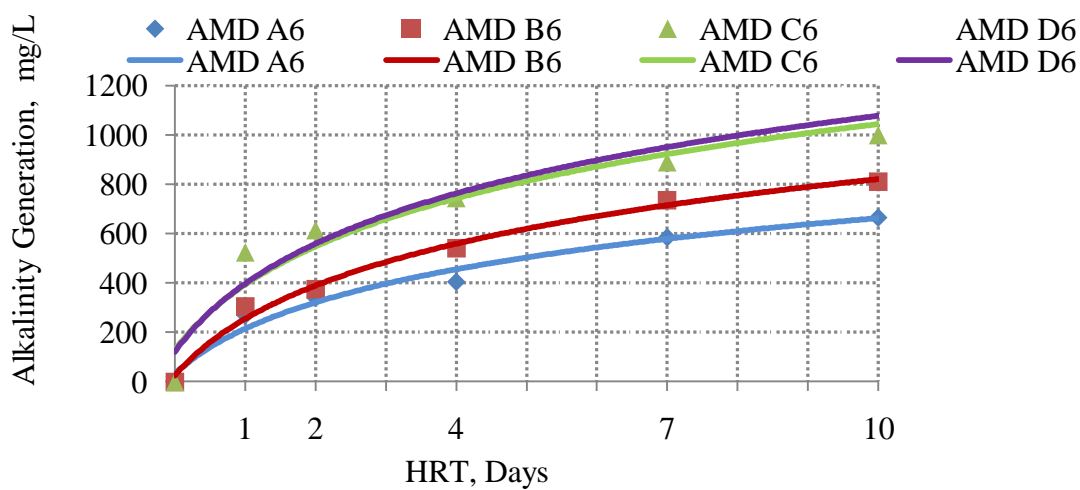


Figure 15: Alkalinity Generation in Different HRT for Port P<sub>2</sub>

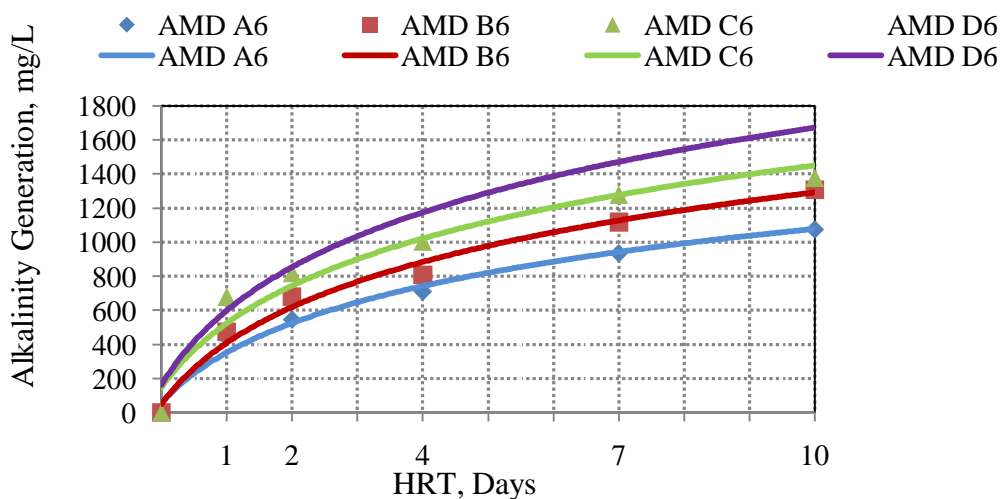


Figure 16: Alkalinity Generation in Different HRT for Port P<sub>3</sub>

Similar trends in Alkalinity generations were observed for remaining three AMDs Namely AMD B<sub>6</sub>, AMD C<sub>6</sub> and AMD D<sub>6</sub>.

### CONCLUSIONS

- SAPS were found effective in removal of iron and aluminium from acid mine drainage.
- The complete removal of iron was found for 7d and 10d HRT for AMD A<sub>6</sub>, AMD B<sub>6</sub> and AMD D<sub>6</sub> where as 99.07% iron removal was found for AMD C<sub>6</sub> for 7d HRT and 100% for 10d HRT.
- The complete removal of manganese is not possible by SAPS however maximum 44% manganese removal was found for AMD B<sub>6</sub>.
- The significant manganese removal were found when pH level reaches near 8.
- The net alkalinity generation increases with increase in HRT.
- The net alkalinity generation increases with increase in metal loading.

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