

## SAPS' INFLUENT AND EFFLUENT GEOCHEMICAL PARAMETERS RELATED TO AMD POLLUTION CONTROL: A CASE STUDY

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### Abstract

This paper presents a time-series study on the geochemical parameters of a Successive Alkalinity Producing System (SAPS) in an abandoned mine of South Korea. Two new performance parameters in terms of ratio are proposed:  $Fe_{\text{influent}} : Fe_{\text{effluent}}$  and  $Sulfate_{\text{influent}} : Sulfate_{\text{effluent}}$ . The ratios directly point to the state of performance of SAPS. After the 6 year study, iron reduction still remains acceptable but sulfate reduction becomes negligible.

### Introduction

The aim of the study was to verify whether the empirical relationships of different wetland geochemical parameters are valid for the Successive Alkalinity Producing System (SAPS) under discussion, as well as to develop measures of long-term performance applicable to all SAPS or treatment wetlands. A SAPS is made up of: a) the entrainment to carry the mine water under a reduced state; b) constructed or naturally embanked wetland containing vertical flow reactor (VFR) and c) one or more aerobic wetlands. The VFR is the main reacting compartment where acidity is neutralized and sulfate ions are decomposed. The reactor contains submerged spent mushroom compost substrate (SMS) on top of a column with limestone particles on bottom. High alkalinity is generated to prevent  $Fe^{2+}$  ions from being converted to  $Fe^{3+}$  ions, with consequent precipitation in the VFR; as well as to decompose  $SO_4^{2-}$  into  $S^{2-}$  and promote the precipitation of sulfides that increase precipitation over and above hydroxides. Since sulfides in water generally have lower solubility than hydroxides over a wider range of pH, when both hydroxides and sulfides occurring together the total metals precipitation increases. Finally, an aerobic wetland allows the settlement of particles and favors further neutralization. Figure 1 gives a complete scheme of SAPS.

### Methods

Over a six year period, influent water to the SAPS and effluent water from the SAPS were studied. Dissolved cations were determined using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES; Jobin Yvon Co. 138 Ultrace). Anions were determined using the ion chromatograph (IC; Dionex series 500DX).

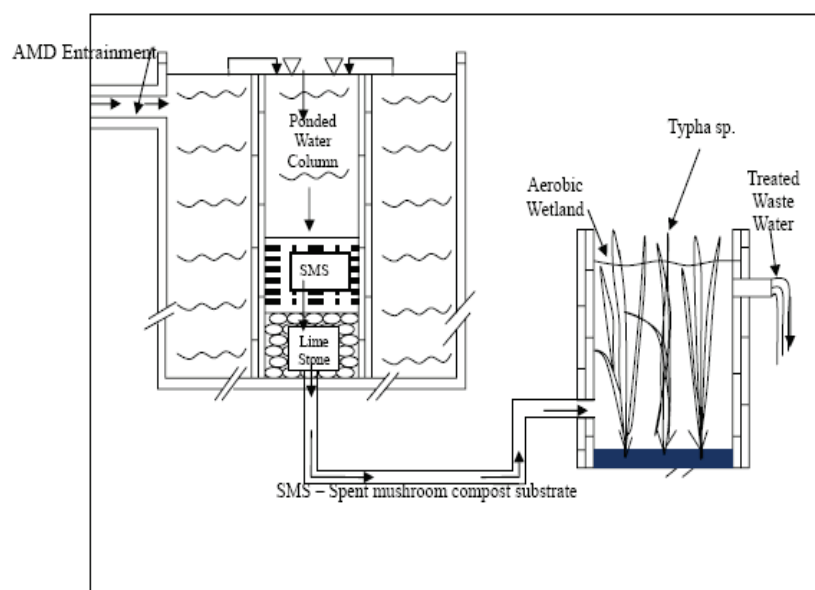


Figure 1. The scheme of a SAPS.

**Table 1. Determined parameters of the influent during the period of study.**

Date	Temp (° C)	EC (mS/cm)	pH	DO (mg/L)	Fe(III) (mg/L)	Fe(II) (mg/L)	Fe(II)/Fe(III)	Al (mg/L)	Mn (mg/L)	Sulfate (mg/L)
Aug-01	16.2	90	5.5	6.9	47.9	0.9	0.02	1.1	5.7	445.9
Nov-01	15.1	130	5.8	5.9	16.6	2.5	0.02	0.9	5	486.4
Mar-02	15	120	5.9	5.3	6	49.9	8.32	0.6	4.4	278.9
May-02	15.5	440	5.8	4.5	43.6	3.2	0.07	0.7	4.1	304.2
Sep-02	15.9	120	5.3	2.9	4.1	35.7	8.71	0.9	4.5	514
Nov-02	15.4	130	5.6	3.9	4.6	58.8	12.8	1.1	5.8	436
Mar-03	14	140	5.7	4.6	0.2	50.8	254	0.8	4.8	478.6
Jun-03	16.2	100	5.8	2.6	16.8	29.1	1.73	0.9	4.9	395.8
Sep-03	16.1	120	4.6	2.4	52.5	17.4	0.33	11.3	6.3	548.6
Dec-03	14.9	90	5.7	3	16.3	50.8	3.11	1.3	11.4	503.6
Mar-04	14.8	110	5.8	3.2	16.3	55.3	3.39	1.1	11	478.4
Jun-04	16.3	378	6	3.7	56.3	1	0.018	1.7	8.1	737.8
Nov-04	14.8	100	5.8	6.2	3	49.2	16.4	4.9	0.5	308
Mar-05	14.6	130	5.8	3.8	2.4	57.6	24	1.8	0.8	443.3
Jul-06	16.9	100	6	3.31	12.3	24.4	1.98	0.01	4.25	436

**Table 2. Determined parameters of the effluent during the period of study.**

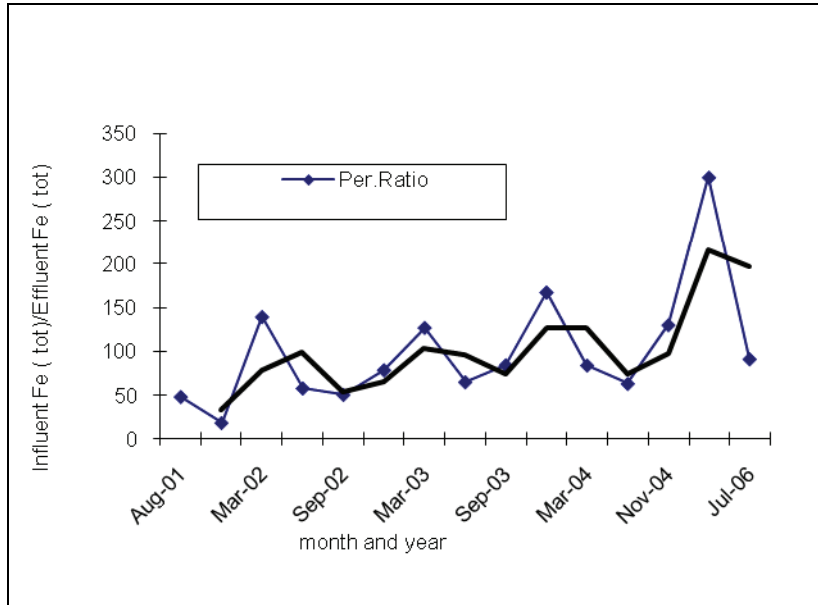
Date	Temp (° C)	EC (mS/cm)	pH	DO (mg/L)	Fe(II) (mg/L)	Fe(III) (mg/L)	Fe(II)/Fe(III)	Al (mg/L)	Mn (mg/L)	Sulfate (mg/L)
Aug-01	24.6	0.09	6.3	3.7	0.4	0.6	0.67	0.4	6.5	181.2
Nov-01	12.3	0.13	6.6	13.1	0.6	0.4	1.5	0.4	5.7	461.1
Mar-02	10.4	0.13	7.1	10.9	0.3	0.1	3	0.3	3.8	389.6
May-02	17.9	3.45	6.6	3.5	0.1	0.7	0.14	0.2	4.2	284.5
Sep-02	22.4	0.14	6.7	5.5	0.1	0.6	0.17	0.9	5.8	554
Nov-02	15.5	0.13	6.7	10.7	0.5	0.3	1.67	0.4	4.4	440
Mar-03	14.1	0.13	6.6	12	0.2	0.2	1	0.6	3.5	487.3
Jun-03	20.5	0.13	6.7	2.6	0.2	0.5	0.4	0.5	4.5	339.8
Sep-03	20.2	0.1	6.5	4	0.1	0.7	0.14	0.5	4.9	467.8
Dec-03	9.3	0.08	6.6	5.6	0.3	0.1	3	0.9	2.2	497.6
Mar-04	8.5	0.11	6.6	4.4	0.5	0.4	1.25	0.9	0.8	499.6
Jun-04	20	0.18	6.9	3.9	0.2	0.7	0.29	0.8	1	283.8
Nov-04	13.6	3.61	6.4	6.3	0.3	0.1	3	1.5	0.2	365.7
Mar-05	8.9	0.01	6.8	4.7	0.1	0.1	1	1	0.8	437.5
Jul-06	23.7	0.17	7.34	3.66	0.3	0.1	3	0.02	2.88	344

Table 1 and Table 2 provide the complete observed data of the influent and effluent connected to the SAPS, respectively. The data sets contain 15 sampling data of parameters such as temperature, electrical conductivity (EC) and pH, and concentrations of dissolved oxygen (DO), Fe(III), Fe(II), Al, Mn and  $\text{SO}_4^{2-}$ .

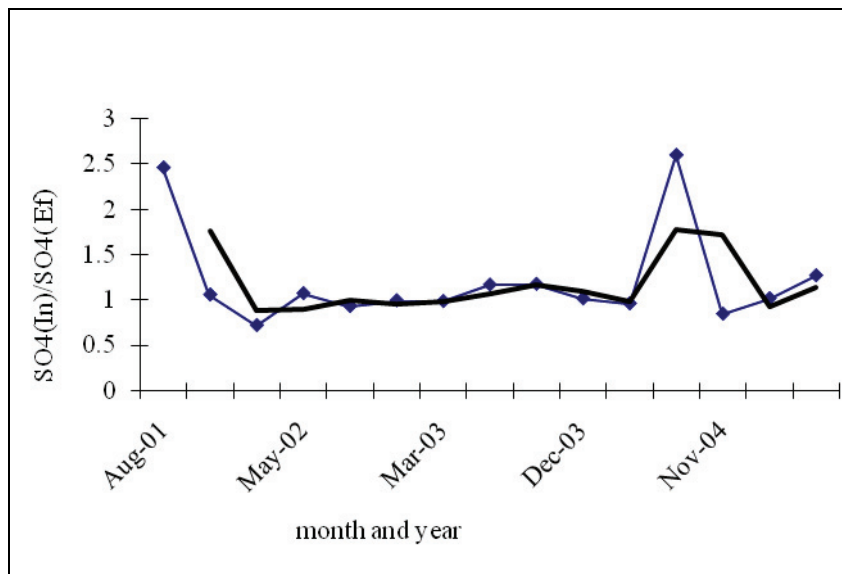
## Results

### 1. Iron loading and treatment efficiency

Ferrous iron in the influent occurs in the 0.9 to 58 mg/L range. The influent  $\text{Fe}^{2+}$  concentration is higher than  $\text{Fe}^{3+}$  in 10 out of 15 cases. Though  $\text{Fe}^{2+}$  concentration is expected to be always higher than  $\text{Fe}^{3+}$ , the variation can be attributed to the lack of equilibrium in the running water. In the effluent,  $\text{Fe}^{2+}$  is higher than  $\text{Fe}^{3+}$  in 7 cases but both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  concentrations are in the range of 0.1-1 mg/L, much lower than in the influent. The total reduction of Fe species is given in a performance ratio of Fe (influent) : Fe (effluent). The SAPS performance can be assessed by the ratio of total  $\text{Fe}_{\text{influent}}$  : total  $\text{Fe}_{\text{effluent}}$  during the period of study: except for the spike observed in June 2004 as shown in Figure 2, the average values remain within a range of 50 to 100. This indicates an efficient iron reduction.



**Figure 2. Performance ratio ( Fe) of the SAPS over the study period.**



**Figure 3. Sulfate reduction Performance ratio during the study period.**

The same cannot be told of sulfate reduction (Fig. 3). In fact, the sulfate reduction performance ratio (influent sulfate to effluent sulfate ratio) shows an average value of about 1, meaning that sulfate is discharged without much reduction. The ratio is high (2.5) in August 2001 but begins to decrease down to about 1 in March 2002 before stabilizing definitely. Neglecting the sulfate contribution from the sediment, this points to organic carbon consumption in the system, a phenomenon that can be called as carbon drought in SAPS.

## 2. Sulfate and Electrical Conductivity

Poor correlation between sulfate and conductivity was observed in both the cases of influent and effluent so that any trend could be recognized. The conductivity values are lower in the influent than in the effluent. Large differences in conductivity ranges was not observed: in influent between 90 and 140 mS/cm, and in effluent 80 to 180  $\mu$ S/cm.

## 3. pH and Aluminum

pH and aluminum values, though not very well correlated, in general show respectively increasing and

decreasing trends in the influent and effluent.

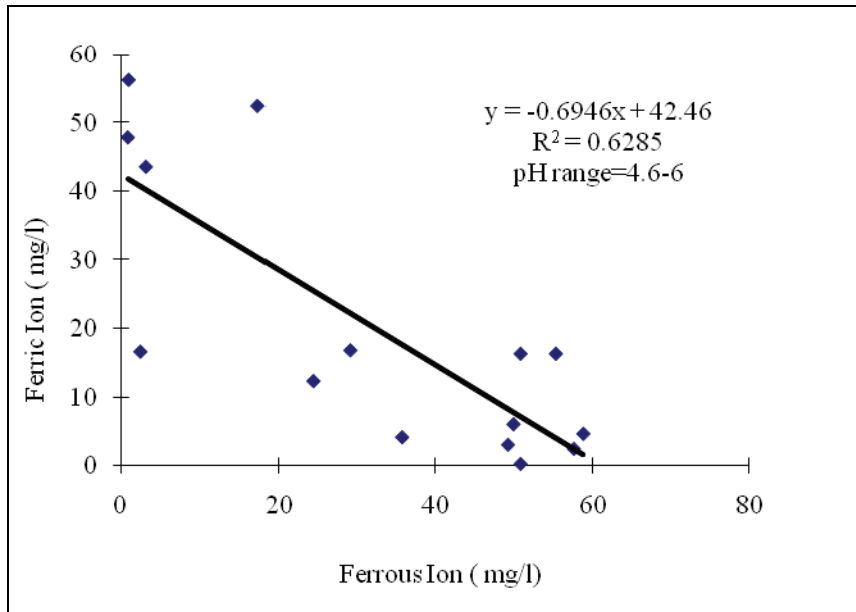


Figure 4. Ferrous Ion and Ferric Ion relationship in the influent.

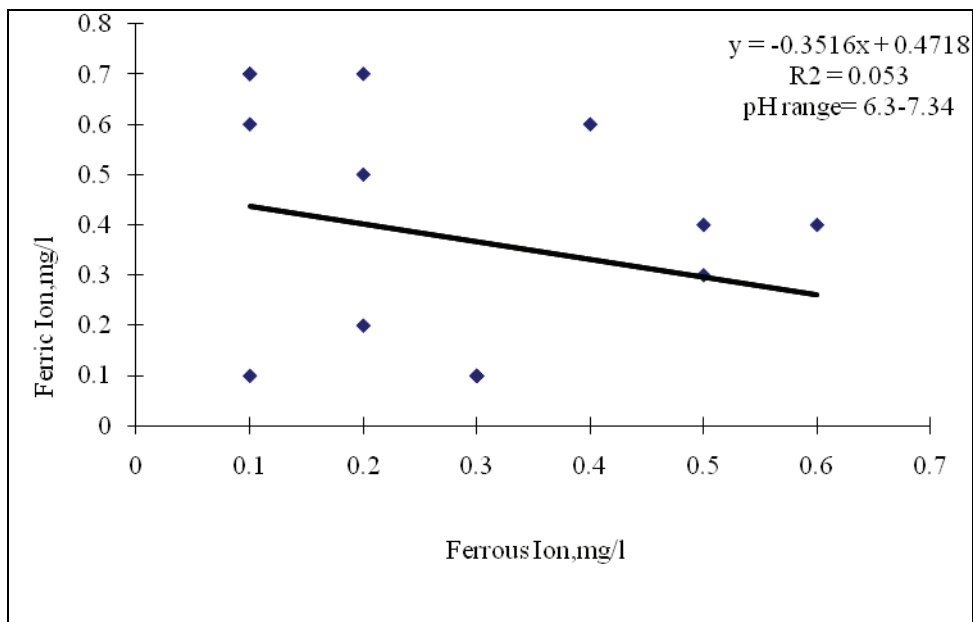


Figure 5. Ferrous Ion and Ferric Ion relationship in the effluent.

#### 4. Ferrous and Ferric Ions

In both the cases of influent and effluent water  $Fe^{2+}$  and  $Fe^{3+}$  exhibit a negative relationship, i.e. one increases at the expense of the other. Figures 4 and 5 show the plots of  $Fe^{2+}$  and  $Fe^{3+}$  in both influent and effluent. This relationship is more definite in the influent water ( $r^2 = 0.6285$ ) than in the effluent water ( $r^2 = 0.053$ ) as concentration decreases. The decrease in  $Fe^{2+}$  and  $Fe^{3+}$  concentrations is supposed to alter the relative concentration of other cations and anions .

### 5. Mn<sup>2+</sup> and Fe<sup>2+</sup> Ions

The Mn<sup>2+</sup> and Fe<sup>2+</sup> ions, in both influent and effluent, are very poorly correlated with each other. Manganese concentration is nearly independent on Fe<sup>2+</sup> concentration in influent as well as in effluent. The average Mn concentration in the influent is about 6 mg/L; Mn concentration in the effluent decreases to about 4 mg/L with the scatter suggesting re-solubilization from the sediment. This signifies that effective co-precipitation in the wetland is only about 33%.

### Discussion

From the results of the study, it can be pointed out that:

1. The proposed performance ratios of iron removal ( $Fe_{\text{influent}} : Fe_{\text{effluent}}$ ) and sulfate removal ( $Sulfate_{\text{influent}} : Sulfate_{\text{effluent}}$ ) can be representative of SAPS performance under steady state operation that possibly sets in after a month.
2. Sulfate reduction to sulfide is stopped within a year possibly because of the decreasing concentration of dissolved organic carbon as the SMS is consummated. Over time, the mineralization of the AMD (the variation in concentration of acid and base) shows a decreasing trend, as indicated by lower values in conductivity.
3. Aluminum concentration, though poorly correlated with pH, decreases as pH values increase, a typical characteristic of AMD.
4. Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations exhibit a negative relationship. This is possibly because of reduction in concentrations of both in the effluent as well as by the increasing influence of other ions.
5. The expected positive linear relationship of Mn<sup>2+</sup> and Fe<sup>2+</sup> failed because of extremely poor correlation.

### Conclusions

The study evaluates the parameters related to performance of SAPS. The salient findings of this work are as follows:

1. Sulfate reduction almost comes to a stop within a year of SAPS operation. As a result, hydroxide precipitation is likely to prevail in the wetland as against the desired combined precipitation of hydroxides and sulfides.
2. In both the cases of influent and effluent water, excluding two high values, the conductivity seems to be independent on the sulfate concentration.
3. pH and aluminum concentration show a poor negative correlation. Not only the value of aluminum decreases as pH increases but also the rate of decrease decreases with increasing pH.
4. In both influent and effluent Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations exhibit a negative relationship, i.e. one increases at the expense of the other.

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