# Passive Remediation of Acid Mine Drainage using Bentonite Clay: A Laboratory Batch Experimental Study

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**Abstract** Acid mine drainage is highly acidic and often contains high concentrations of Fe, Mn, Al and $SO_4^{2-}$ in addition to traces of Cu, Zn, Mg, Ca and Na. This mining effluent has negative impacts on surface and groundwater and requires treatment before release to surface water bodies. Mining houses are in constant search of cheaper treatment technologies. This study evaluates the potential of applying bentonite clay as an initial remediation step in an integrated AMD management concept. A laboratory batch experimental study has been carried out to evaluate the passive treatment of Acid mine drainage with bentonite clay. A simulated AMD was used in these experiments. Powdered bentonite clay was mixed with simulated AMD at specific S/L ratios and agitated in an orbital shaker and its capacity to remove metals assessed over time. XRF analysis shows that the bentonite is a Na-Mg exchangeable type and with a CEC 100 meq $100g^{-1}$.Preliminary results indicate that contact of AMD with bentonite leads to increase in pH, and a reduction in EC and TDS. At constant agitation time of 30 minutes, the pH was observed to increase with dosage of bentonite. Removal of $Mn^{2+}$ and $Fe^{3+}$ was observed to be greatest at 30 minutes of agitation for S/L of 0.2g/100mL of AMD. The results indicate that bentonite can be applied for treatment of moderately polluted mine water.

**Key Words** Acid mine drainage, Passive treatment, bentonite clay, toxic metals, cation exchange capacity

## Introduction

Acid mine drainage (AMD) is produced when sulphide minerals, such as pyrite, found in association with the coal or overburden come into contact with oxygen and water during mining. Sulphide minerals undergo bacterially catalysed oxidation reactions which generate acidity and increases Fe and sulphate concentrations in recipient water bodies. AMD is characterized by high acidity (pH 2—4), high sulphate concentrations (1—20 g/L) and contains high concentration of metals such as Fe, Mn, Al (Gitari *et al.,* 2006). Environmental regulations require that this wastewater be contained and treated before discharge to surface water bodies. The most popular AMD treatment methods include active neutralization by limestone, lime and passive treatment in alkalinity generating artificially constructed wetlands which are costly. Industries and mining companies are in constant search for cheaper AMD remediation technologies. The aim of this research is to determine whether a naturally occurring clay material with high ion exchange capacity can be utilized to effectively remove Fe and Mn in AMD in an initial step to evaluate its application as a liner or a passive reactive barrier in AMD containment ponds or as a first step in the remediation of AMD in containment ponds.

Clays play an important role in the environment by acting as natural scavengers of pollutants by taking up cations and anions either through ion exchange or adsorption or both. The prominent cations and anions found on clay surface are $Ca^{2+}$, $Mg^{2+}$, $H^+$, $K^+$, $NH_4^+$, $Na^+$, and $SO_4^{2-}$, $Cl^-$, $PO_4^{3-}$, $NO_3^-$. These ions can be exchanged with other ions relatively easily without affecting the clay mineral structure. Large specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC) etc., have made the clays excellent adsorbent materials (Bhattacharyya *et al.*, 2008; Tahir and Naseem, 2007; Tahir and Naseem, 2004).

Bentonite has been investigated by various researchers for the adsorption of toxic inorganic metals and other contaminants from different types of wastewater ( Pradas *et al.,* 1993; Olguin *et al.,* 1997; Kozar *et al.,* 1992; Rauf *et al.,* 2001; Rauf *et al.,* 2003). Due to its physical and chemical properties bentonite is considered one of the most promising candidates for use as a buffer material in geological systems. In this study the possibility of utilizing bentonite as a treatment liner or passive reactive barrier in AMD holding ponds will be evaluated. It is anticipated that due to the presence of cationic and anionic exchangeable sites on the surface and voids of the bentonite, both cationic and anionic inorganic contaminants in AMD will be exchanged giving more cleaner water as it percolates through the proposed clay liner or passive barrier. This paper presents preliminary results on the adsorption of Fe and Mn as the AMD interacts with bentonite clay.

## Material and methods

### Preparation of bentonite clay samples

The raw bentonite samples were washed with ultra pure water. It was done by soaking the samples in ultra pure water and draining the water after 10 minutes. The procedure was repeated four times. The washed bentonite was then dried in an oven for 24 hours at a temperature of 105° C. The dried sample was crushed into a fine powder using a mortar and pestle.

### Physicochemical characterization of bentonite samples

*X-ray Fluorescence (XRF) analysis* Major elemental analysis of the powdered bentonite samples was done by first roasting the powder at 1000 °C for 3 hours to oxidize $Fe^{2+}$ and S and to determine the loss of ignition (L.O.I.). Glass disks were prepared by fusing 1.5 g roasted sample and 9 g flux consisting of 35% $LiBO_2$ and 64.71% $LiB_4O_7$ at 1050 °C. The glass disks were analyzed by a PAN analytical Axios X-ray fluorescence spectrometer equipped with a 4 kW Rh tube at Council for Geoscience, South Africa.

*Cation Exchange Capacity* The cation exchange capacity of the bentonite clay samples was done by extracting the exchangeable cations using 1M ammonium acetate buffer at pH 7.4. and 5.4. 0.5g of bentonite clay was extracted using 25ml aliquots of 1.0 M ammonium acetate. The samples mixtures were continuously agitated with the extracting solution for 15 min using a mechanical shaker (Labcon, 1300E). After agitation samples were centrifuged for 15 minutes at 3000 rpm and the supernatant decanted. This procedure was repeated for a total of four times for each sample and the cumulative extract was brought to 100ml. The concentration of the exchangeable cations ($Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$) was determined by AAS (600 PerkinElmer). The results in ppm were then converted to meq per 100g of sample following the method of Radojevic and Bashkin (1999).

*Scanning Electron Microscopy Analysis* The morphology of the raw bentonite and AMD reacted bentonite was examined using a Hitachi X-650 scanning Electron Microanalyser equipped with a CDU- lead detector at 25kV. Samples were mounted on aluminum pegs and coated with a thin film of gold to make them conductive.

### Preparation of simulated Acid Mine Drainage and Working solutions

A stock solution of 2000 ppm $Fe^{3+}$, 200 ppm $Al^{3+}$, and 40 ppm $Mn^{2+}$ was prepared by dissolving 7.16g of $Fe_2(SO_4)_3 \times H_2O$, 2.4698g of $Al_2(SO_4)_3 \times 18H_2O$, 0.0916g of $MnCl_2$ in 0.005 M $H_2SO_4$ solution to prevent immediate precipitation of $Fe^{3+}$. Working solutions were prepared from this stock solution through appropriate dilutions for the batch experiments.

### Batch Adsorption Experiments

*Evaluation of reaction kinetics as a function of agitation time* 8 samples of 100 ml (50 ppm of $Fe^{3+}$, 5 ppm $Al^{3+}$ and 1ppm $Mn^{2+}$) working solution were pipetted into 8, 250 ml Erlenmeyer flask. 0.1g of washed powdered bentonite was added into each flask. The mixture were then agitated for 1, 3, 5, 10, 30, 60, 180 and 360 mins. The agitation was done using a table shaker at 250 rpm (Labcon 3100E). The pH, TDS, Temperature, and EC were measured before and after agitation in order to monitor the change in pH, EC, TDS over time. The pH, EC, TDS and Temperature were measured with a portable HANNA pH/TDS/EC/Temp probe. The reaction mixture was then filtered through a 0.45µm pore nucleopore membrane and two drops of concentrated $HNO_3$ acid added. The samples were then refrigerated at 4ºC until analysis. The analysis of Fe, Mn was done using Atomic Absorption Spectrometer (600 PerkinElmer).

*Evaluation of reaction kinetics as a function of adsorbent dosage* 8 samples of 100 ml (50 ppm $Fe^{3+}$, 5 ppm $Al^{3+}$ and 1ppm $Mn^{2+}$) working solution were pipetted into 8 bottles of 250 ml volume and varying mass of bentonite added. The mass of bentonite used was 0.2g, 0.3g, 0.5g, 0.8g, 1g, 3g, 5g, and 8g. The mixture were agitated for 30 minutes (the optimum agitation time observed in the previous step of reaction kinetics with time) (Labcon 3100E). The pH, TDS, temperature and the EC were measured before and after agitation using a portable HANNA pH/TDS/EC/Temp probe. The reaction mixture was then filtered through a 0.45µm pore nucleopore membrane and two drops of concentrated $HNO_3$ acid added. The samples were then refrigerated at 4ºC until analysis. The analysis of Fe, Mn was done using Atomic Absorption Spectrometer (600 PerkinElmer).

## Results and Discussions

### Physicochemical characterization of bentonite

Table 1 and 2 present the major chemical constituents of raw washed bentonite and cation exchange capacity respectively.

The high concentration of $SiO_2$ and $Al_2O_3$ confirms that bentonite is an alumino-silicate material, the main components in clay materials. The relatively high concentrations of MgO, $Na_2O$, CaO and $K_2O$ is an indication that these are the main exchangeable cations. Analysis of the supernants from ammonium acetate extractions of the bentonite samples indicated presence of $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ confirming that these species contribute to the CEC of the bentonite. Reaction of the bentonite with AMD leads to reduction of CEC indicating the main mechanism of metal removal is ion exchange.

Figure 1 shows the SEM images of washed raw bentonite and the bentonite after interacting with

***Table 1** Chemical composition of the washed bentonite.*

| Species | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO |
|---|---|---|---|---|---|---|---|
| **Conc (% w/w)** | 64.3 | 0.54 | 15.7 | 3.85 | 0.06 | 3.13 | 0.88 |
| **Species** | **$Na_2O$** | **$K_2O$** | **$P_2O_5$** | **$Cr_2O_3$** | **LOI** | **Total** | **$H_2O$** |
| **Conc (% w/w)** | 2.71 | 1.17 | 0.07 | 0.01 | 7.56 | 99.9 | 1.4 |

***Table 2** CEC of the washed bentonite and AMD reacted bentonite.*

| pH | Cation Exchange Capacity(meq/100g) | |
|---|---|---|
| | **Washed Bentonite** | **AMD reacted Bentonite** |
| **7.4** | 115.3 | 59.1 |
| **5.4** | 102.9 | 59.1 |

AMD: Figure 1 shows no difference between the morphology of the raw bentonite and the AMD reacted bentonite. The platy like features characteristic of clay minerals are clearly visible.

### *Evaluation of reaction kinetics as a function of agitation time*

Table 3 presents the variation of pH, EC, TDS, Temperature, $Fe^{3+}$ and $Mn^{2+}$ with agitation time for the AMD and bentonite mixtures.

A decrease in EC was observed at 1st minute of contact decreasing from 65.1 µS/cm to 30.5 µS/cm (Table 3). Thereafter an increase was observed at 3 mins, stabilizing at between 45.9 - 49.7 µs/cm. An increase in TDS was observed at 1st minute of contact to 47.6 mg/L thereafter stabilizing at »29.0. pH increased gradually as agitation progressed stabilizing at »3.0 at 360 mins (Table 3). The EC changes indicates a significant proportion of the attenuation kinetics happens within 10 mins of agitation

A drastic decrease in $Fe^{3+}$ concentration was observed within 1st minute of contact, reducing from 50 mg/L to 1.36 mg/L. A slight increase occurred thereafter at 3—5 mins of contact with the values stabilizing at 0.91—0.38 mg/L (Table 3). The $Mn^{3+}$ removal profile resembles that of $Fe^{3+}$ with 50% of the concentration being removed with 1 min of agitation (Table 3). The value finally stabilizes at »0.4—0.5 mg/L (Table 3). The system seems to stabilize after 30 mins hence this time was chosen as the optimum for subsequent experiments.

### *Evaluation of reaction kinetics as a function of adsorbent dosage*

The effect of the adsorbent dosage on adsorption kinetics was tested at an optimum agitation time of 30 mins by varying the adsorption dosage from 0.2g, 0.3g, 0.5g, 0.8g, 1g, 3g, 5g, and 8g per 100 ml of simulated AMD. Table 4 shows the variation of pH, EC, TDS, Temperature, $Fe^{3+}$ and $Mn^{2+}$ with adsorbent dosage.

The pH was observed to increase gradually with increase in mass of adsorbent upto a dosage of 0.8g, a drastic increase was thereafter observed as the dosage increased to 8g with a pH 8.5 being achieved in the supernatant. The increase in pH indicates a possible release of surface hydroxyl as $Fe^{3+}$ and $Mn^{2+}$ gets adsorbed possibly on the surface of the adsorbent. A gradual decrease in TDS is observed with increase in adsorbent dosage to

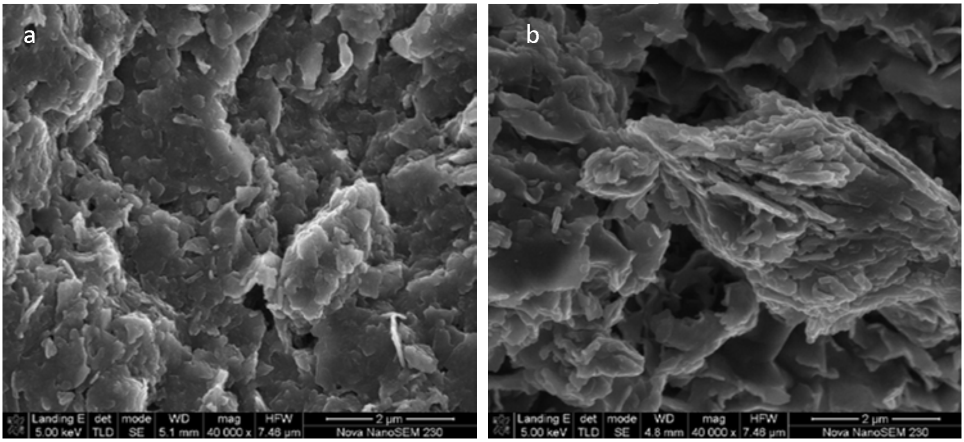

***Figure 1** SEM micrographs of washed raw bentonite (a) and AMD reacted bentonite (b):*

***Table 3*** *Variation of pH, EC, TDS, Temp, $Fe^{3+}$ and $Mn^{2+}$ with agitation time.*

| Agitation time (min) | pH | TDS (mg/L) | EC(µS/cm) | Temp(°C) | $Fe^{3+}$(mg/L) | $Mn^{2+}$(mg/L) |
|---|---|---|---|---|---|---|
| 0 | 2.51 | 41.2 | 62.5 | 21.8 | 50 | 1 |
| 1 | 2.89 | 47.6 | 30.5 | 20.8 | 1.36 | 0.55 |
| 3 | 2.83 | 31.9 | 49.7 | 20.8 | 1.5 | 0.54 |
| 5 | 2.86 | 29.7 | 46.3 | 20.8 | 1.51 | 0.51 |
| 10 | 2.89 | 29.4 | 46.3 | 21.0 | 0.91 | 0.5 |
| 30 | 2.92 | 29.0 | 45.3 | 21.8 | 0.54 | 0.47 |
| 60 | 2.94 | 29.4 | 45.5 | 22.6 | 0.47 | 0.49 |
| 180 | 3.00 | 26.7 | 41.8 | 21.2 | 0.4 | 0.48 |
| 360 | 3.03 | 29.5 | 45.9 | 21.1 | 0.38 | 0.45 |

***Table 4*** *Variation of pH, EC, TDS Temperature, $Fe^{3+}$ and $Mn^{2+}$ with adsorbent dosage.*

| Sample Number | Adsorbent mass | pH | TDS (mg/L) | EC (µs/cm) | $Fe^{3+}$(mg/L) | $Mn^{2+}$(mg/L) |
|---|---|---|---|---|---|---|
| AMD | 0 | 2.76 | 59.2 | 92.3 | 50 | 1 |
| 1 | 0.2 | 2.88 | 58.9 | 92 | 15.04 | 1.63 |
| 2 | 0.3 | 2.99 | 57.1 | 89.1 | 9.35 | 1.52 |
| 3 | 0.5 | 3.37 | 50.1 | 78.3 | 1.43 | 0.98 |
| 4 | 0.8 | 4.39 | 49 | 76.5 | 0.13 | 0.12 |
| 5 | 1.0 | 5.3 | 51.6 | 80.4 | 0.16 | 0.03 |
| 6 | 3 | 8.14 | 73.7 | 116.8 | 0.96 | 0.01 |
| 7 | 5 | 8.17 | 85.4 | 133.3 | 0.36 | BDL |
| 8 | 8 | 8.5 | 104.3 | 165 | 0.1 | 0.01 |

a maximum a 0.8g (Table 4). This dosage also corresponds to the maximum adsorption of $Fe^{3+}$ and $Mn^{2+}$. This was followed by a rapid increase as the adsorbent dosage increased. A similar trend is observed with EC, a minimum being observed at 0.8 g dosage. Higher adsorbent dosages leads to release of species in the supernatant and this will require further investigation.

## Conclusions and recommendations

This preliminary investigation shows that bentonite clay can be used to remediate AMD. Contact of AMD with bentonite leads to increase in pH, and a reduction in EC and TDS. Removal of Mn and Fe was observed to be greatest at 30 mins of agitation for S/L of 0.2g/100mL. At constant agitation time of 30 mins, the pH was observed to increase with dosage of bentonite. TDS and EC decreased to a minimum at dosage of 0.8g/100mL and then increased to a maximum at a dosage of 8g. Higher dosages of bentonite seems to release species in the reaction mixture. $Fe^{3+}$ and $Mn^{2+}$ were observed to decrease with increase of bentonite dosage with a minimum values at 0.8g-1.0g. More investigations are ongoing to test the metal removal capacity at higher concentrations in AMD and to test AMD with more metal contaminants such as $Al^{3+}$, $Cu^{2+}$, $Zn^{2+}$ and $Ni^{2+}$. Upflow column percolation experiments are also planned to test the performance of the bentonite clay in retention of metal contaminants in a dynamic flow regime

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