



# Acid leaching of heavy metals from bentonite clay, used in the cleaning of acid mine drainage

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## Synopsis

Heavy metals and sulphates in acid mine drainage (AMD) can be adsorbed onto bentonite clay, leaving clean water and a heavy metal loaded clay precipitate as products. Due to the toxicity of heavy metals, the clay could not be disposed of safely in the past. A method was thus required to remove the heavy metal content from the clay. Acid leaching was proposed to liberate the heavy metals from the loaded clay. Sulphuric, nitric and hydrochloric acid were considered as lixiviants. Loaded clay samples were leached over a range of pH values from 1 to 3.5 to identify an optimum leaching condition. From the results it was found that metals can be recovered from loaded bentonite clay by means of acid leaching and the optimum pH for heavy metal liberation was found to be 2.5, with uranium as an exception, being optimally leached at a pH of 3. This allows for the possibility of selective leaching. Furthermore, X-ray diffraction analyses indicated that the clay structure did not deteriorate significantly during acid leaching, suggesting that the bentonite could be reused.

The treatment of AMD with bentonite clay, and subsequent acid leaching of the clay, is a sustainable solution, and current outcomes could possibly lead to industrial implementation of the process during water purifying and metal recovery from waste streams.

Keywords: Acid mine drainage, bentonite, heavy metals.

## Introduction

Gold has been mined in the Witwatersrand Basin region of South Africa for over a hundred years. Many of these mines have reached the end of their life spans, leaving large underground cavities where ore was removed. A major environmental concern associated with these mines is the uncontrolled discharge of polluted water from abandoned mine shafts, known as acid mine drainage (AMD). The AMD is acidic and polluted with heavy metals, posing a major ecological threat. The AMD represents a substantial water source and if properly treated, the water, and the valuable heavy metals dissolved in it, can be reclaimed.

A process was developed in previous studies to treat the AMD with bentonite clay (Brink, 2007). Heavy metals and sulphates in the AMD are adsorbed onto the clay, leaving clean water as a product. However, the heavy metal loaded clay is hazardous and cannot be

disposed of. In order for this process to be sustainable, a method was needed to liberate the heavy metals from the clay.

The objective of this study was to develop a method to recover the heavy metals adsorbed onto the clay precipitate obtained during the Clearwater process. A secondary goal was to determine the conditions under which optimal leaching will occur.

## Literature

### Acid mine drainage (AMD)

The rocks of the Witwatersrand Supergroup were deposited at a time when the atmosphere did not contain sufficient oxygen to oxidize the minerals and rocks. As time progressed, a thin crust of the earth's outer rocks was oxidized. Below this crust, the unoxidized metal compounds exist mostly as sulphides. When mining activities occur within these deeper layers, the rock surfaces in tunnels and mined-out cavities are exposed to an oxidizing environment for the first time. The sulphides, particularly pyrite, are oxidized to sulphates by the air. Water from overlying aquifers fills these cavities, reacts with the sulphates, and forms sulphuric acid (Brink *et al.*, 2008:2; Oelofse, 2008:3).

The sulphuric acid dramatically lowers the pH of the water and causes further pollution by serving as a solvent for various contaminants. The residual ions present in AMD have their origin as salts of heavy and other metals that were originally deposited with gold and uranium in the reef conglomerates. Cations are also released into solution by acid extraction of the metals absorbed on mineral surfaces (Burgess and Stuetz, 2002).

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Any ferrous iron present in the AMD will, within a short period of time, be auto-oxidized to ferric oxides and hydroxides, releasing  $H^+$ , effectively forming more acid. In practical terms, this means that if mining companies neutralize the AMD (without precipitating all the iron) and release it into fluvial systems, the water will rapidly become acidic again downstream (Waanders *et al.*, 2008).

### Bentonite clay

Bentonite is an alumina silicate clay made up of sodium and calcium montmorillonites (Agnello, 2005:1; Klein 2002:531). Bentonite consists of aggregates of flat platelets, has a high specific surface area, high plasticity, and can expand several times its original volume when placed in water (Agnello, 2005:1). The clay's ability to swell is a result of the incorporation of water molecules between the *t-o-t* (tetrahedral-octahedral-tetrahedral) sheets in association with the interlayer cations ( $Na^{2+}$  and  $Ca^{2+}$ ), which are driven off when the clay is heated in air. The expulsion of water leads to the layers collapsing, causing the clay to have a somewhat unbalanced structure with an overall slightly negative charge. This is balanced by exchangeable cations that are adsorbed around the edges of the fine clay particles. The basic composition of bentonite is summarized in the Tables I and II (Ramebäck *et al.*, 1999:210).

To enhance the adsorptive properties of bentonite clay, it can be acid activated. This involves all the cations present in the bentonite (typically  $Ca^{2+}$ ,  $Na^{2+}$  and  $Al^{3+}$ ) being replaced by  $H^+$  by the addition of either sulphuric or hydrochloric acid. Acid activation changes the clay's physical and chemical properties, but keeps its layered structure. Initially during

activation the outer cations are replaced by  $H^+$ . As activation continues the individual layers are attacked by the acid and the various ions present, such as aluminium, iron, calcium and magnesium, are released from the lattice. This causes the inner surface of the crystal platelets to increase in size and active acid centres are formed. Physically, the edges of the clay open up, pore diameters increase in size, and the surface area increases. There is, however, a point of maximum activation beyond which the crystal structure disintegrates and silicic acid is formed (Agnello, 2005: 9).

According to Agnello (2005:18) it has been estimated that quality reserves of bentonite in South Africa will be sufficient for up to 67 years at the current production rate of 120 kt/a. The newest bentonite mine and largest deposit ever to be found in South Africa, is the Yellow Star Quarries in the Kroonstad district. According to Waanders (2003:3) it is estimated that this deposit, which contains approximately 750 000 m<sup>3</sup> bentonite, can be mined at 4 000 m<sup>3</sup>/month. The bentonite layer is between 6 and 10 m thick. The mine was commissioned in 2007 and has an expected lifetime of over 10 years during which the clay will be mined and the project will be economically feasible.

### Experimental

The experimental work was conducted in two sections. Initial pilot-plant work to obtain a loaded clay sample was followed by laboratory leach experiments for the recovery of the heavy metals.

### Pilot plant

A 1 000 l sample of AMD was collected from where it is decanting from the Number 8 Shaft of Harmony Gold Mining Company Ltd (currently owned by Rand Uranium). Since the AMD did not contain sufficient amounts of uranium, the AMD was spiked with 1 kg of uranium nitrate. A schematic representation of the pilot plant set-up can be seen in Figure 1 (Table III).

Bentonite was added to the first (continuously) stirred vessel at a solid to liquid ratio of 1:100. The contents of the first vessel were then transferred to a second vessel, which was continuously aerated to ensure that all ions present in solution were oxidized to their highest oxidation state. Slaked lime was also added to increase the pH to above 8 for the precipitation of metal cations. The contents of the second vessel were then sent through two decanting vessels,

Table I

**Typical composition of Bentonite clay (mass %) for constituents with an abundance larger than 1%**

SiO <sub>2</sub>	61–64
Al <sub>2</sub> O <sub>3</sub>	20–21
CaO	1.2–1.4
Fe <sub>2</sub> O <sub>3</sub>	3.8–3.9
MgO	2.4–3.7
Na <sub>2</sub> O	2.1–2.4
LOI <sup>1</sup>	5.2–6.3

<sup>1</sup>Loss on ignition = carbonates, sulphides, sulphates and crystal water

Table II

**Mineral composition of Bentonite clay (mass %)**

Montmorillonite	75
Quartz	15
Mica	<1
Feldspar	5–8
Carbonate	1.4
Coalinites	<1
Pyrite	0.3
Other minerals	2
Organic carbon	0.4

Table III

**Ions of importance found in the AMD during the present experiment**

	Original sample	Spiked sample
pH (on site)	4.85	4.45
pH (in laboratory)	4.51	4.45
Sulphates	3925.77 ppm	3814.60 ppm
Uranium	0.065 ppm	220 ppm
Iron	1100 ppm	1100 ppm
Manganese	130 ppm	110 ppm
Cobalt	6.2 ppm	5.7 ppm
Nickel	14 ppm	13 ppm

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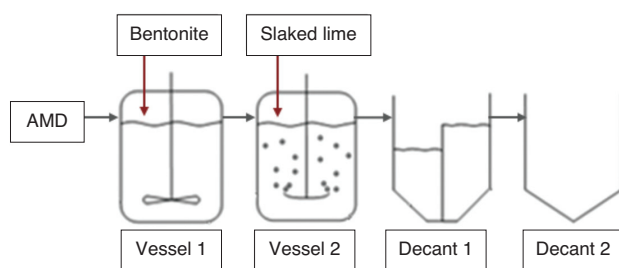


Figure 1—Schematic representation of the pilot plant

allowing the loaded clay to be separated from the water. The loaded clay was collected for the leach tests and both the AMD and subsequent clean water was analysed.

### Laboratory

To determine the optimal leaching conditions, rolling bottle leach tests were carried out on the clay using sulphuric, hydrochloric and nitric acids over a pH range from 1.5 to 3 to determine the optimum operating pH for heavy metal liberation. A clay slurry with a solid to liquid ratio of 1: 10 was leached at the varying pH conditions with a leach time of 20 minutes. Analysis of the clay was conducted with SEM and XRD whereas analysis of the water samples was done by means of ICP-MS (inductively coupled plasma-mass spectrometry) analyses.

## Results and discussion

### Pilot plant

The results of treating the AMD with bentonite clay, in terms of the percentage removal of various ions from the final water product, can be seen in Table IV.

It is clear that most of the cations were removed during treatment. The lower adsorption of the sulphates (mainly gypsum) can be accounted for by the large negatively charged surfaces of the clay particles available for cation exchange.

The loaded clay was analysed using a SEM fitted with EDAX to verify whether or not the ions removed from the AMD had been adsorbed onto the clay surface. Figure 2 is a microphotograph of the loaded clay surface and it can be seen that the clay surface is not homogenous.

Compositional analyses were conducted on the four areas indicated in Figure 2, the results of which can be found in Table V.

From these results it is evident that adsorption of the different constituents in the AMD onto the clay had taken place. The composition of the fresh clay is represented by sample 0, whereas the other four samples are representative of the four areas as identified in Figure 2. It is clear from the tabulated results that area 1 and 3 represents the adsorption of the iron ( $\text{Fe}^{3+}$ ) as an oxide onto the clay. Area 2 represents the gypsum that originated from the addition of slaked lime to the system. Note the characteristic needle shape structure of the gypsum crystals. Area 4 also exhibits iron that has been adsorbed onto the clay surface as iron is one of the

Table IV

### Percentage removal of ions from the treated AMD

	Percentage removal
Sulphates	36.8
Uranium	99.9
Iron	98.2
Manganese	93.4
Cobalt	97.7
Nickel	99.5

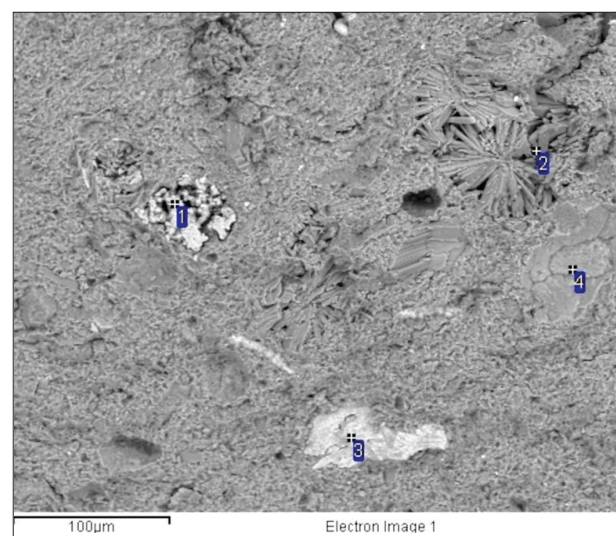


Figure 2—SEM microphotograph of the loaded clay surface

Table V

### Composition of clay given as weight percentages of oxides

	Weight % (oxides)								
	C	Mg	Al	Si	S	K	Ca	Fe	O
0		0.97	8.75	29.79		1.8	0.95	8.95	46.61
1	4.79	-	0.78	2.09	3.98	-	-	51.74	36.62
2	2.28	-	0.42	1.22	20.64	-	24.37	2.03	49.05
3	3.25	-	1.29	3.21	0.97	-	-	59.36	31.92
4	-	1.17	8.85	26.86	0.76	1.37	0.5	15.26	45.23



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most abundant ions found in the AMD and the concentrations vary between a few hundred up to a few thousand ppm.

## Laboratory

The results of the leaching tests indicated that nitric and sulphuric acid could be effectively used as lixiviants to leach the heavy metals from the loaded bentonite clay. Figure 3 illustrates the concentration of leached uranium as a function of the leaching pH. All the graphs for the metals considered in this study followed the same trend.

As can be seen from Figure 3, sulphuric acid has a much clearer and definite point of optimal leaching when it is compared to nitric acid, whereas the leaching with hydrochloric acid did not yield satisfactory results. In Figure 4 the leach curves of various metals, obtained from clay samples treated with sulphuric acid, are superimposed onto

each other in order to compare optimal leach conditions. Error bars are included to show possible experimental errors in the ICP-MS results (5%) and the measuring of pH readings (10%).

The majority of heavy metals are optimally leached at a pH of 2.5. Uranium, however, is an exception being optimally leached at a pH value of 3. This makes the possibility of selective leaching of uranium from the loaded bentonite a reality. The clay structure before and after leaching was analysed by means of XRD techniques and the comparison between the diffraction patterns of the treated and untreated samples is given in Figure 5.

No substantial differences in the clay structure could be identified before and after the acid leaching with sulphuric acid. This indicates that the clay could be reused in the purification of AMD following acid leaching.

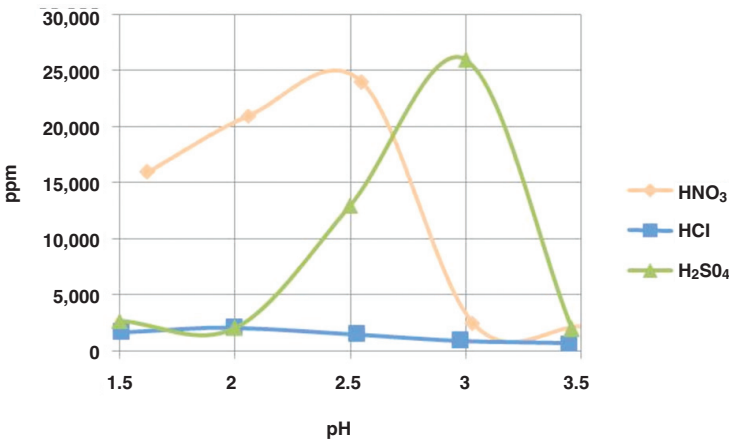


Figure 3—Uranium concentration in leach liquor as a function of leaching pH

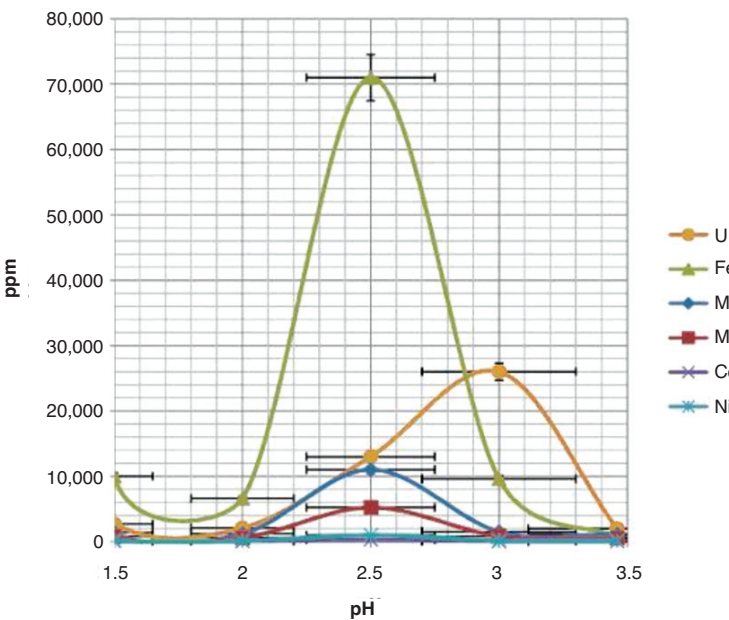


Figure 4—Comparison of heavy metal concentrations peaks in the sulphuric acid treated samples

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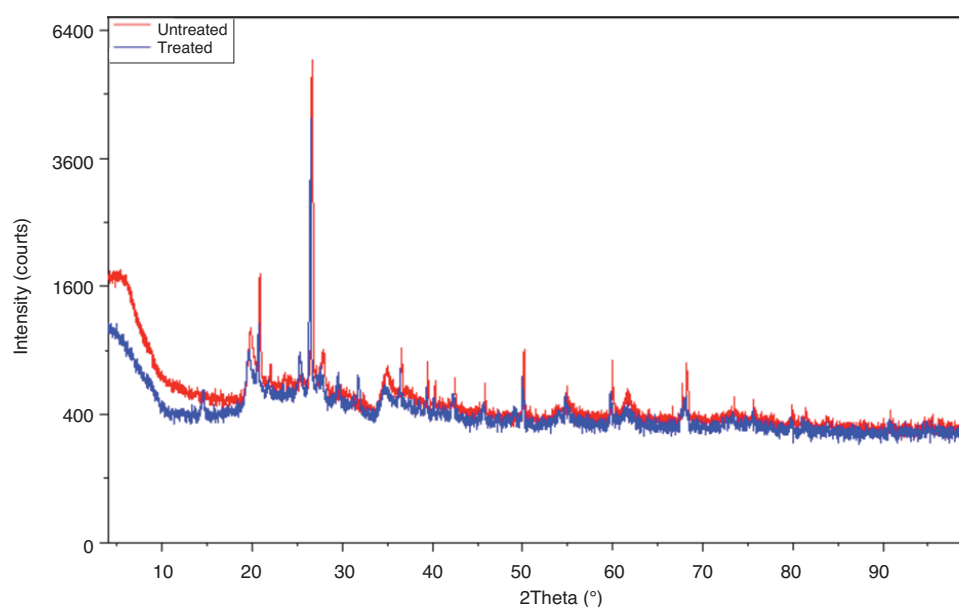


Figure 5—Diffraction patterns of treated and untreated clay

### Conclusions and recommendations

In the treatment of AMD with bentonite clay, heavy metals that have been adsorbed onto the clay can be liberated by means of acid leaching with sulphuric acid, nitric acid, and hydrochloric acid. It has been found that:

- Nitric acid liberates the highest concentrations of heavy metals.
- The lowest liberation of heavy metals occurs when the clay is leached with hydrochloric acid.
- Sulphuric acid liberates lower concentrations of heavy metals than nitric acid, but a clear peak can be determined for sulphuric acid where the optimal liberation of each metal occurs at a certain pH.
- Most of the metals considered in this study are optimally liberated at a pH of 2.5. Uranium is an exception, being optimally liberated at a pH of 3. Uranium can thus be selectively liberated from the loaded clay.

The clay structure does not deteriorate significantly during the acid leaching. The clay can therefore be reused.

From the results and conclusions the following recommendations are made:

- The acid leaching of the clay proved highly effective in the laboratory. Further test work should be conducted to verify the results of this study, especially in terms of acid concentrations required for optimal leaching as well as conditions under which selective leaching is possible.
- Based on the results of further laboratory studies, experiments to acid leach the clay should be conducted at a pilot-plant scale. If these tests are successful, the 'Clearwater process' can be implemented industrially.
- Test work should be done to treat AMD samples with clay that has been acid treated to determine the efficiency of the reused treated clay. Further studies

should also be done to determine under which conditions the clay is no longer reusable and the expected lifetime of the clay.

- Market research should be done to determine the feasibility of recovering the heavy metals extracted from the clay as an extra source of revenue. Recovery of valuable heavy metals could serve as an incentive for mines to utilize the 'Clearwater process' for AMD treatment.

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