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Chapter 3

Removal of Heavy Metals Using Bentonite Clay and Inorganic Coagulants

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Additional information is available at the end of the chapter

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Abstract

Heavy metals have always been defined as elements with a density higher than 5 g/cm^3. They are regarded as serious wastewater contaminants with detrimental effect to human and environment. Their removal from wastewater poses a serious challenge as they require cost-effective reagent and treatment technique. About 200 mL solution of acid mine drainage (AMD) collected from the Western decant in Krugersdorp, South Africa was poured into five 500 mL glass beakers. Three different sets of experiments (employing mixing, shaking and no mixing) were conducted using a jar test and a shaker with 1.5 g bentonite clay, 20–60 mL of 0.043 M $FeCl_3$ and $Al_2(SO_4)_3$ and a flocculent of bentonite clay and $FeCl_3$ dosage, respectively. The experiments were conducted without pH adjustment. The samples settled for 1 hour after which the pH, conductivity and turbidity were measured. The results show that a combination of bentonite clay and $FeCl_3$ exhibits a better turbidity removal efficiency compared to the samples with bentonite clay, $FeCl_3$ and $AlCl_3$ respectively. The variation of the turbidity removal in the samples with mixing shaking and without mixing is insignificant, showing that destabilization-hydrolysis depends upon the strength of the reagent and the physicochemical properties of the solution. The results also show that hydrolysis occurs at low pH, indicating that it plays an insignificant role in destabilization. The SEM micrographs show that turbidity removal is a physical phenomenon.

Keywords: heavy metals, wastewater, pH, turbidity, destabilization

1. Introduction

Heavy metals have always been defined as elements with a density higher than 5 g/cm^3 [1, 2]. On the contrary, most of the heavy metals have density equal or less than 3 g/cm^3, hence the name has been changed to toxic metals. Heavy metals are geologically occurring substances

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which react physicochemically to form economic mineral resources such as coal, gold and copper, among others. They have a semi- or non-degradability property and can accumulate in the food chain, causing danger to human [3, 4]. Apart from their toxicity, they play a pivotal role in domestic and industrial activities. Drinking contaminated water containing heavy metals even in very small quantity may be detrimental to human and aquatic life [4]. A wide range of research projects has been exploited relating to new trends of removing heavy metals from industrial wastewater [5]. Some of the metals are both toxic and radioactive, e.g. uranium, which is normally embedded in mineral deposits of other metals such as gold, radium, selenium and thorium. There are some of the heavy metals, i.e. arsenic, cadmium, chromium, lead and mercury, which are classified as priority metals due to high toxicity to public health [6]. Despite their toxic nature, their use is unavoidable as they are necessary in daily activities of economic value, including metal-containing compounds [7–10]. Apart from normal natural causes, heavy metals are also introduced to the environment through natural phenomena such as weathering and volcanic eruptions [7, 11–14]. They are mostly transition elements where some are metalloids, e.g. arsenic, exhibiting toxicity at low level to soil, vegetation, rivers [6, 10, 11]. Environmental degradation is caused by the emissions from power utilities, mining and chemical industries is a serious global concern. The latter is responsible for the high concentration of lead and chromium in several water bodies, predominantly due to lack or ineffective purification systems [15]. On the other hand, some of the heavy metals, i.e. lead and chromium, are toxic and carcinogenic in their oxidation state, e.g. Pb^{2+} and Cr^{3+}, respectively [16]. Coal and gold mining discharges wastes or wastewater (**Figure 1**) are highly polluted with heavy metals. Alternately, they are the source of pyrite (FeS_2), a geologically, chemically or microbially formed mineral derived from the reaction between iron and sulfur under thermal conditions [17].

Apart from the economic value associated with heavy metals (mineral resources), they play a pivotal role in the formation of clay. On the other hand, clay minerals form a larger fraction of coal and also used as catalysts during coal combustion (oxidation). Extensive alteration of rocks to the formation of clay minerals produces relatively pure clay deposits that serve a variety of economic applications such as manufacturing of cooking pots, bricks, porcelain, drainage pipe, floor and wall tiles, tobacco pipes, oil drilling, cat litter, heat resistant tiles, construction of lime mortars, building materials and equipment, among others [18, 19]. Some are fluxing agent and carry some problematic compounds which are responsible for slagging



Figure 1. Geochemical surface feature along the river concentrated with metals (www.earth.illinois.edu).

and clogging of the boilers of the power utilities. Some are emitted to the atmosphere during industrial operation, thus causing a serious environmental catastrophe. Disposal of the chemicals and barren ore deposits which are polluted with heavy metals is the main attribute to the environmental degradation, which is predominant in the dumping sites.

2. Impact of waste materials on the environment

The purpose of this review does not cover the use of the heavy metals in industrial processes, i.e. cyanide and mercury, among others. The impact of heavy metals is mostly apparent in tailing dumps. Tailings contribute towards environmental degradation, and the impact does not take into account the amounts of toxic materials they contain. They host heavy metals, predominantly gangue minerals such as silicates, oxides, hydroxides, carbonates and sulfides. Some of the heavy metals in the tailings exist as iron-sulfide minerals, e.g. pyrite, pyrrhotite, chalcopyrite, arsenopyrite (FeAsS), sphalerite (ZnS) and galena (PbS), whereas others contain sulfur-containing minerals (Pb, Zn, Cd, Se, As) and compounds that are critically harmful. Apart from that, sulfide-bearing tailings can be oxidized during weathering before the formation of the AMD and release metals/metalloids (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) [9]. The toxic metals are distributed throughout the environment by severely leaching out into the surroundings, causing serious health problem due to non-degradable property [20]. The leaching of the heavy metals into the soil may endanger natural population of bacteria, leading to disintegration of bacterial species responsible for nutrient cycling, thus affecting the ecosystem negatively [21]. Under such conditions, they have to devise means of survival under such adverse conditions, i.e. develop and establish detoxifying mechanisms (biotransformation, biosorption and bioaccumulation) [22].

Uranium, the most radioactive element, has a molecular weight of 238.03 mol/g and detrimental to humans through chemical toxicity, radiation and other uranium by-products. It is highly harmful and can lead to kidney, respiratory and neurological dysfunctionalities [23]. It exists in six radioactive isotopes (232–238) as classified from mother element which causes instability of the highly reactive nuclei. Its radioactivity becomes apparent when the nucleus emits minute particles during elemental transformation (radioactive decay), when α and β particles and γ-rays are emitted. **Figure 2** illustrates the spillage of radioactive uranium. There are countries where millions of tons of tailing cover wide areas, considering South Africa (SA) which produced over 43,500 tons of gold and 73,000 tons of uranium within 1953–1995. The basin covers an area of 1600 km^2 leading to 400 km^2 tailings dams which contained 6 billion tons of pyrite tailings and 430,000 tons (600,000 t) low-grade uranium. That resulted in the contamination of about 6000 km^2 of soils gold mining operations [24].

The most detrimental effects of uranium to human and environment include (1) aquatic physiological defects and fatalities, (2) disruption of water bodies, i.e. aquatic physiological-biochemical process, (3) deterrence of aquatic activities due to the presence of Fe, Zn, Cu, Mn and Pb, (4) disturbance of biodiversity of aquatic life, (5) depression of the dissolved oxygen in the water bodies, (6) modification of the nutrient availability which may cause loss of



Figure 2. Spillages and remaining of dumps of uranium in West Rand (SA) [24].

Fraction	Name	Chemical formula
Gauge	Quartz	SiO_2
Mineral	K-feldspar	$KAlSi_3O_8$
	Na-feldspar	$NaKAlSi_3O_8$
	Ca-feldspar	$CaKAl_2Si_2O_8$
	Serisite	KAl (AlSi)(F,OH)
	Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(OH)_6)$
	Calcite	$CaCO_3$
	Dolomite	$Ca,Mg(CO_3)_2$
Sulfide-oxide	Pyrite/pyrrhotite	FeS_2/FeS
	Arsenopyrite	FeAsS
	Galena	PbS
	Sphalerite	ZnS
	Chalcopyrite	$CuFeS_2$
	Magnetite	Fe_3O_4

Table 1. Mineralogy of a tailing dump in South Africa [29].

vegetation, (7) change of the direction of the roots growth and (8) cause of ailments due building up in aerian organs of plants and human.

Lead (Pb) and chromium (Cr) are toxic metals especially to plants and animals and cannot be easily treated due to non-biodegradability and subjection to bioaccumulation in living cells [25, 26]. They can form multiple-oxidation states, where Cr forms Cr^{2+}, Cr^{3+} and Cr^{6+}, the highly toxic and reactive and highly soluble in solutions of varying pH values [27]; however, their toxicity is less compared to Cr^{6+}. Pb is a bluish-white, soft metal, which is highly flexible and ductile and resistant to corrosion [28]. The types of mineral matter (**Table 1**) are complex compounds, which are main constituents of both clay and coal.

Oxidation of the pyrite acidifies the water percolating through the dumps, which then enters the groundwater regime beneath the dumps [30]. This acidic water is believed to be entering



Figure 3. Gold mine tailing dumps in Johannesburg, South Africa (UGS stock photo by George Steinmetz).

streams along the Witwatersrand in SA [30, 31]. Apart from direct metals contamination, tailings are also sources of environmental degradation. Gauteng Province (SA) is highly concentrated with tailings, which contaminate the environment through metals leachate during heavy rainfall [30]. **Figure 3** illustrates tailing dump.

A general characteristic of tailings is the pyrite content of up to 6% pyrite, highly saline, low nutritional value and low organic matter content [32–34]. High sulfide content causes high acidity and high metal concentrations in groundwater around the proximity of the tailings [32]. Rafiei et al. [35] reported a pH value of 7.35 in gold mine tailings in Iran, whereas Mitileni et al. [36] reported pH values of 3.25–6.28 in South Africa. Harish et al. [37] reported pH value of 3.48–8.12 in India. pH is essential to aquatic life as different species behave differently, whereby high soil acidity from mine pollution may destroy microbes responsible for breaking down organic matter into nutrients. In addition, acidity can dissolve aluminum to form free organic materials, which is toxic to plant roots, and also reduce the concentrations of essential nutrient. The characteristic features of gold mine tailings are the elevated concentrations of toxic heavy metals, i.e. As, Cd, Ni, P, Cu, Zn, Co and Hg [38].

3. The effect of chemical treatment to the ecosystem

Industrial and population expansions are the main attributes to increasing concentration of heavy metals, and inevitably, their escalating quantity is uncontrollable as their genesis is natural and anthropogenic [39]. Gold mining has been identified as an operation which results in the accumulation of thousands of voluminous tailings dumps scattered all over the countries, potentially degrading the ecosystem [40]. Nuclear power generation is another source of toxic waste generation as it uses uranium as fuel. The problem with nuclear is its difficulty in handling waste materials. This review study suggests that one of the solutions around the management of toxic minerals is proper mineral processing using mineral liberation-classification, but mineral slipping is inevitable. Although mineral liberation-classification does not produce all the minerals in their pure form, some are in complex compounds which require further separation. There is an enormous amount of waste generated during various processes, especially in gold mining where approximately 99% of the waste disposal consists mainly of ore [41]. The use of bacteria is another technique but the main problem is the rate of

production and the timing for their growth as they rely mainly on pH and temperature. The pH-dependent bacteria, e.g. acidophilic, chemolithotrophic iron- and sulfur-oxidizing bacteria, assist in solubilizing the sulfides contained in the gold ore deposits by liberating gold from the deposit [42]. Although biomining poses less danger to the environment than many physico-chemical extraction processes [42], it is perceived to be unsustainable. Bacteria such as *Acidithiobacillus* obtain energy by oxidizing Fe^{2+} to Fe^{3+} ions or elemental sulfur (S^0). Eqs. (1)–(3) illustrate oxidation-reduction of iron and sulfur from pyrite, a mineral exposed during both gold and coal mining. The bacteria (*acidithiobacvillus*) obtain energy by oxidizing ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) or reduction of elemental sulphur (S^0) to form sulphuric acid [45, 46], thus resulting in the production of AMD.

$$2\,S^0 + 3\,O_2 + 2\,H_2O \rightarrow 4\,H^+ + 2\,{SO_4}^{2-} \tag{1}$$

$$FeS_2\,(Au) + 2\,Fe^{3+} \rightarrow 3\,Fe^{2+} + 2\,S^0 + (Au) \tag{2}$$

$$FeS_2\,(Au) + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,{SO_4}^{2-} + 16\,H^+ + Au \tag{3}$$

Another distinct characteristic of the bacteria in gold purification includes their ability to excrete ligands that stabilize gold by forming gold-rich complexes and/or colloids [43–45]. This review invokes the functions and integrity of the use of bacteria in gold purification, but residual heavy metals remain a challenge, moreover that they form part of waste which is a danger to the ecosystem.

Mercury, one of the toxic metals used in gold purification, is accomplished by mixing it with mineral ore deposits extracted from the ground or stream beds to form an amalgam. The burning of the latter vaporizes elemental mercury into a toxic plume, resulting the separation of the gold from the ore deposit. The technique is globally regarded as the second largest source of atmospheric mercury pollution after coal combustion [46]. Apart from mercury, cyanide is another toxic metal which is employed in gold purification process (Eq. (4)), a two-stage process which includes extraction and recovery. Eq. (4) shows dissolution of gold:

$$4\,Au(s) + 8\,NaCN(aq) + O_2(g) + 2\,H_2O(l) \rightarrow 4\,NaAu(CN)_2(aq) + 4\,NaOH(aq) \tag{4}$$

Cyanide, one of the toxic metals, is employed in the extraction process of gold. The process also uses another toxic metal, i.e. zinc to cement cyanide solution [46]. Environmental degradation occurs during the spillages of cyanide solution, whereas activated carbon can also be used when the gold content is high. The ground and crushed ore deposits are enclosed in large tanks with agitators to dissolve gold which then adhere to particles of activated carbon. The activated carbon and the gold are separated from the solution, which is discarded together with the leached ore [46]. The residual trace heavy metals from the process act as potential hazards to the ecosystem. It has been noted that sludge from gold and cold operations contains mercury amalgam, cyanide, uranium and mineral matter, among others. Since gold recovery from ore deposit is not 100%, small quantities remained in the tailings, where they will subsequently decompose to form other complexes or react with other toxic substances to form new toxic compounds.

Lime has been used in previous studies to regulate the pH of the AMD solution [47]. The challenge with such a technique is excess sludge generated, which requires further treatment of heavy metals polluted sludge. Instead, the sludge is pumped to large dumps (slimes dumps).

4. The effect of metal salts during the removal of turbid materials

Mine wastewater and AMD are the main carriers of the heavy metals produced from mining operations. According to a trend of various studies to investigate a cost-effective mine wastewater treatment, the use of inorganic coagulants seems to be regarded as a primitive technique. The study conducted in this review study focuses on conventional treatment process using inorganic coagulants. Their advantage is based on their hydrolysis potential to form flocs which are adsorbents. In case of Fe, there are at least four species that co-exist in aqueous solution in the pH range of 1–5, namely Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2{}^{+}$ and a very small fraction of dimer $Fe_2(OH)_2{}^{4+}$ [48]. On the other hand, Al species prefer a slightly higher pH than Fe in a range of 3–8. Apart from positive contributions, naturally formed iron is a source of AMD formation. It reacts with sulfur through a geological phenomenon to form FeS_2, which has negative environmental impact. Pyrite is not toxic as a mineral until it is oxidized by oxygen in an aquatic medium to form sulfuric acid, an environmental degradation agent, Eq. (5).

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4{}^{2-} + 4\,H^{+} \tag{5}$$

Fe^{2+} ions may be oxidized to form Fe^{3+} ions (Eq. (5)), which oxidize excess pyrite:

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4{}^{2-} + 16\,H^{+} \tag{6}$$

Eq. (6) yields unstable Fe^{2+} ions species which are further oxidized by excess Fe^{3+} ions that are subjected to hydrolysis when added to wastewater.

The catastrophe associated with the AMD (**Figure 4**) is not only about the surface or ground water pollution and degradation of the quality of the soil, but endanger it poses to aquatic sediments and fauna, allowing heavy metals to seep into the environment.



Figure 4. Diagram of AMD pumped from the underground workings [48].

Long-term exposure to drinking water polluted with AMD may lead to increased rates of ailment such as cancer, decreased cognitive function and appearance of skin lesions. Heavy metals in drinking water may impair the development of the neurons of the fetus, resulting in mental retardation. In addition, AMD is attributed to loss of stream bed, drying of the rivers, limited water supply for growing industrialization and population and limiting the quantity of water for irrigation. Acidified water (AMD) seepage from the mine tailing dumps concentrated with heavy metals causes serious environmental degradation especially stream flow around the vicinity [49, 50]. The condition reduces the pH and adds high metal loads to the water resulting in extreme iron hydroxide precipitation in the stream which endangers aquatic life. Possible evaporation of groundwater from the capillary zone above the water table may contaminate the surface soil layer with heavy metals. Dissolution of the metals on the Earth's crust and surface soil may add to the metals load in the stream. The oxidation of iron introduced into the stream by seepage may behave as redox buffer, controlling the pH of the stream water. Increasing the pH of AMD above 3, either through contact with fresh water or neutralizing minerals, precipitates Fe^{3+} ions to form iron hydroxide species. Other types of iron precipitates are possible, including iron oxides and oxyhydroxides [48]. All such species cause discoloring of the water and smother aquatic plant and animal life, disrupting stream ecosystems.

Literature [47] states that optimal removal of turbid materials occurs in an alkaline medium; however, the findings of this review portray a different view. Despite the findings of this review, the results of the studies on the AMD samples using inorganic coagulants, metal hydroxide and bentonite clay [51, 52] revealed that the removal of turbid materials/heavy metals is dependent upon the physicochemical properties of both the colloidal suspension and the reagents and that which also includes structural morphology of the flocs (SEM micrographs).The hypothesis relating to pH adjustment is not only depend upon the metal hydroxide but also the OH^- ions released from the cleavage of bipolar water molecules. This is based on the high ionic strength of the AMD and the charges in the solution to enhance dehydroxylation of hydrated metal ions, releasing the OH^- ions which react with metal ions to form metal hydroxide precipitates.

5. Factors that affect the removal of heavy metals

A lot of studies have been conducted on the investigation of ideal techniques employable in the removal of heavy metals, but most are costly and complicated in operation. Factors, such as dosage, destabilization-hydrolysis, time, concentration of the heavy metals, type of colloidal suspension, the reagent(s), temperature, retention time, sorption capacity and structural morphology of a substrate, among others, are most influential during treatment. Although pH is considered as a determinant of the removal of turbid materials as alluded later, studies conducted by Ntwampe et al. [53, 54] on paint wastewater and AMD using traditional inorganic coagulants, metal hydroxide or bentonite clay revealed that pH of the colloidal suspension plays an insignificant role in the removal of turbid material/heavy metals. The studies revealed that the optimal removal of turbid materials is a physicochemical phenomenon,

which is determined by the rate of destabilization-hydrolysis. Although the reaction consists of two reactions, this review considers them as a single stage because of their co-existence, i.e. destabilization occurs on the colloidal suspension whereas hydrolysis on the metal ions [55].

5.1. Destabilization-hydrolysis reaction

In this reaction, the reagent disturbs the equilibrium state of a colloid due to equal counter forces of van der Waals attractive and electrostatic repulsive force [56, 57]. The reaction which is a physico-chemical phenomenon, determines the effectiveness of the succeeding reactions. The colloid is separated into two ionic regions, namely diffuse and Stern layers to form electrical double layer (EDL) [58]. The efficiency of a reagent during treatment is determined by the ability to compress EDL, resulting in the reduction of the radius which enhances particle-particle collision to form agglomerates, flocs.

5.2. Type of a colloid

Colloids are classified according to hydrophilicity (water-loving) or hydrophobicity (water-hating), where treatment with the former is difficult as turbid materials dissolve completely in the solvent, making flocculation difficult. On the other hand, hydrophobic colloid consists of suspended solids, some of which settle spontaneously due to gravitational force [58].

5.3. Type of a reagent

An effective coagulant is characterized by destabilizing potential attributed to high valence and electronegativity. This is apparent after addition to a colloidal suspension when the metal ions of a salt disperse throughout the colloidal particle to destabilize the system, resulting in flocs formation. Nucleation occurs and small flocs form larger flocs, which remove turbid materials [58].

5.4. Structural morphology

The crystal morphology shown by the scanning electron microscopy (SEM) micrographs is illustrative of the ability of a reagent to adsorb the absorbate. Most of the SEM micrographs which correspond to optimal adsorption consist of dense flocs joined together with limited or without voids [51]. Such a SEM micrograph is indicative of no slipping through of the turbid materials (heavy metals); on the contrary, the SEM micrograph with flocs and voids has less adsorption potential [51].

5.5. pH of the solution

Some studies [59–61] state that the rate of adsorption of turbid materials/heavy metals is more favorable in an acidic colloidal suspension, i.e. low pH. This observation is in agreement with aforementioned studies revealing that the treatment of the AMD using inorganic coagulant(s) without pH adjustment yields optimal adsorption. An acidic solution is highly concentrated with hydronium ions (H^+), which are prone to strengthen the electrostatic forces of attraction

between negatively charged heavy metal oxyanions and protonated sorbent, and the reaction occurs according to Eq. (7).

$$Fe^0 + 2\,H^+ + Fe^{2+} + H_2 \tag{7}$$

Fe^{2+} can be further oxidized to form Fe^{3+}.

$$2\,Fe^{2+}{}_{(aq)} + 2\,H^+{}_{(aq)} + 0.5\,O_{2(aq)} \rightarrow 2\,Fe^{3+}{}_{(aq)} + O \tag{8}$$

6. Treatment of the AMD to remove heavy metals

The removal of heavy metals from industrial effluent discharge has been a serious challenge for decades due to the complex compounds formed during chemical reactions. The wastewater consists of metals as pure and trace elements, where the latter always disperse throughout the solution and sorbed onto other compounds or form other compounds during nucleation. The problem associated with trace elements or compounds consisting of trace elements is a plausibility to slip through the adsorbents. The residual heavy metals are caused by the existence of the trace elements in the system [62], a problem caused by low adsorption potential of an adsorbent in a medium with low concentration of absorbate. Technologies such as membrane separation, electrochemical, precipitation, ion exchange and adsorption were investigated to treat wastewater/AMD [63]. The results showed that they are expensive and incur high waste disposal costs, apart from high costs, some studies [64] revealed that some of the new technologies have a tendency of regenerating pollutants back to the environment by producing toxic chemicals such as sodium borohydride ($NaBH_4$). Chemical reaction between iron salt and sodium borohydride to release flammable hydrogen gas [65] is shown in Eq. (9).

$$4Fe^{3+} + 3BH_4^+ + 9H_2O \rightarrow 4F^0\downarrow + 3H_2BO_3^- + 12H^+ + H_2\uparrow \tag{9}$$

Some studies were conducted [51, 54] to reduce turbid materials from AMD using a combination of bentonite clay and inorganic coagulants. Among their studies, a combination of bentonite clay and Na_2CO_3 [53] was employed to remove the heavy metals from the AMD sample. Inorganic coagulants, mainly the metal ions (M^{n+}), have exhibited a significant influence in wastewater and AMD treatment [51–53], including the pivotal role played by the bentonite clay. There are more studies which have been conducted in the treatment of AMD sample using a variety of metal salts without or with a combination of bentonite clay [51–53]. The results show that the turbid materials removal efficiency of inorganic coagulants is optimal when dosed alone or in combination. The observations show that they are all subjected to hydrolysis to form species which are adsorption substrates. On the other hand, bentonite clay also exhibits ionic exchange, sorption and intercalation as the main reactions leading to the removal of turbid materials/heavy metals [52, 53]. The mineralogy of the AMD (**Table 2**), i.e. pH and conductivity of the AMD sample, treated with a combination of bentonite clay and Na_2CO_3 with mixing is shown in **Figure 5**.

Element	Conc. (ppm)
Al	1.171
Ca	182.1
Co	39.7
Cu	0.14
Fe	28.3
K	4.5
Mg	67.3
Mn	35.3
Na	44.5
Ni	27.6
Pb	35.2
As	45.2
Se	0.71
Zn	31.7

Table 2. ICP-OES analyses of untreated AMD sample with clay (5× dilution).

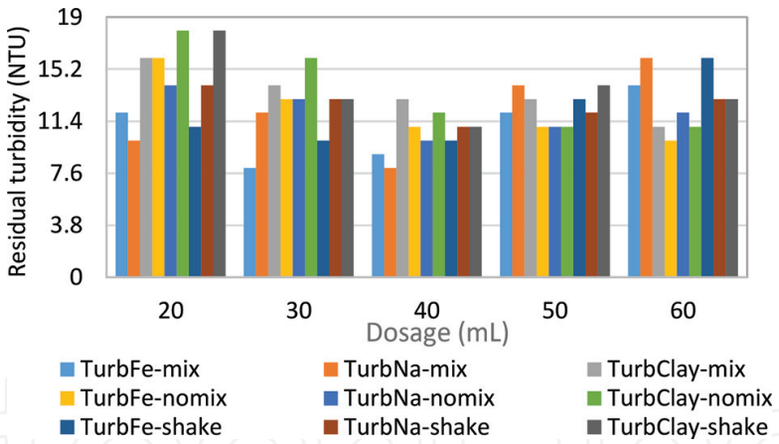


Figure 5. Residual turbidity of AMD with $FeCl_3$, Na_2CO_3 and a combination of bentonite clay and Na_2CO_3 with and without mixing and shaking.

According to **Table 1**, the concentration of the metals, i.e. Ca, Mg and Na, in the AMD is high, 182, 67 and 46 ppm, respectively, and that of non-toxic heavy metals, Fe and Mn, is 28 and 35 ppm, respectively. The concentration toxic metal content, Co, Ni, Pb, As and Zn is also high, the main toxic metals to the ecosystem.

The turbid materials of the AMD (**Figure 5**) are identified as turbidity, which includes the suspended and soluble solids, inorganic material, heavy metals and any trace substances.

The treatment with shaking and without mixing does not form part of this review study and therefore will not be elucidated extensively. Owing to a high turbidity of the AMD sample, residual turbidity below 10 NTU is highly acceptable, 10–15 NTU acceptable, above 15–20 NTU moderately acceptable and above 20 NTU is poor. However, the experimental results of the samples with $FeCl_3$ and Na_2CO_3 mixing are in the range of 8.4–14.0 and 8.2–16.5 NTU, respectively. Notwithstanding the fact that they are both efficient, dosage in a pure form is unaffordable compared to the dosage recommended in the study by Ntwampe et al. [51], which includes the investigation of the efficiency of bentonite clay in AMD treatment. **Table 3** shows the weight percentage of the mineral matter of the bentonite clay.

The weight % mineral content (**Table 3**), where CO_2 and FeO representing siderite ($FeCO_3$) form a larger weight % (33.2 and 45.3 wt. %) of the total complex compounds contained in both coal/gold mineral composition, and the rest are trace elemental compounds. The particle size of the bentonite clay is 180 μm mesh size with intensive mineral liberation (**Table 3**). The mineralogy of the tailing dump (**Table 1**) shows complex compounds of which some are original and others reacted to form new complex compounds; however, the chemical compounds are also representative of the clay minerals. Pulverizing the mineral compound (**Table 1**) results in minerals liberation to form simple compounds (**Table 3**). The elements/metals with high weight percentage include Fe, K and O, an indication of oxidation-reduction of ferric and ferrous ions during chemical reactions. A simple chemical composition of simple compounds (**Table 3**) indicates a high rate of chemical reactions by the colloid or the reagent(s).

The residual turbidity in the samples with bentonite clay mixing is in a range of 9.8–12.0 NTU, without mixing in a range of 10.5–19.2 NTU and shaking in a range of 10.4–13.3 NTU. As indicated, the method of chemical dispersion, i.e. mechanical agitation, is insignificant in this review, and the focus is on the efficiency of the combination of bentonite clay and Na_2CO_3 during AMD treatment. The mineral matter composition and structural configuration of the

Element	Wt.%	Wt.%	Atomic%	Compd%	Formula	No. of ions
C K	9.07	0.46	16.55	33.22	CO_2	2.15
Mg K	0.91	0.08	0.82	1.50	MgO	0.11
Al K	1.56	0.08	1.26	2.94	Al_2O_3	0.16
Si K	5.06	0.13	3.95	10.82	SiO_2	0.51
S K	1.48	0.10	1.01	3.69	SO_3	0.13
Ca K	1.14	0.08	0.62	1.60	CaO	0.08
Ti K	0.53	0.09	0.24	0.89	TiO_2	0.03
Fe K	35.25	0.49	13.84	45.34	FeO	1.79
O	45.02	0.58	61.70			8.00
Total	**100.00**					

Where Wt is weight and Compd is compound.

Table 3. Weight % of the mineral content in the bentonite clay.

bentonite clay play a pivotal role during treatment process. The former identifies the metals and content present in the colloidal suspension, the information which are indicative of inevitable electrochemical reactions. On the other hand, the latter is distinguished by the planar layers, which include octahedral and tetrahedral formation to form T-O-T. According to mineralogy of the bentonite clay (**Table 1**), dehydroxylation and processes are plausible. On the other hand, the structural configuration (T-O-T) is effective in sorption by intercalation of the turbid materials (heavy metals) onto the sheets and porous surface of the bentonite clay. In addition, the mineralogy (**Table 1**) is indicative of a series of physicochemical reactions in the system, especially on the serisite and chlorites, and oxidation of Fe on the iron-bearing compounds (chlorite, pyrite, pyrrhotite, arsenopyrite, chalcopyrite and magnetite). The formation of CO_2 from the decomposition of dolomite is inevitable, including oxidation of metals and other physico-chemical reactions. These form the main chemical reactions occurring in the bentonite clay in the system to form new simple compounds suitable for further reactions or sorption. Na_2CO_3 component in the flocculent also plays a pivotal role which includes increasing of the pH when it solubilizes to $NaCO_3^-$ and CO_3^{2-}. A slight pH rise decreased the solubility of the metals in the colloidal suspension, thus ameliorating the rate of agglomeration. **Table 4** illustrates the ICP-OES results of treated AMD samples.

The results of the treated AMD with a bentonite clay mixing (**Table 4**) show a considerable heavy metals removal of As, Co, Ni, Pb and Zn from 45.5, 39.7, 27.6, 35.2 and 31.7 to 4.1, 3.2, 6.6, 5.4 and 4.8 ppm, respectively. **Figure 6** shows SEM micrograph of the sludge of the AMD samples with $FeCl_3$ (**Figure 6A**) and bentonite clay (**Figure 6B**) mixing, respectively.

Element	Conc. (ppm)
Al	1.023
Ca	142.1
Co	3.2
Cu	0.14
Fe	19.2
K	4.14
Mg	55.7
Mn	23.1
Na	27.4
Ni	6.6
Pb	5.5
As	4.1
Se	0.71
Zn	4.8

Table 4. ICP-OES analyses of treated AMD sample with clay (5× dilution).

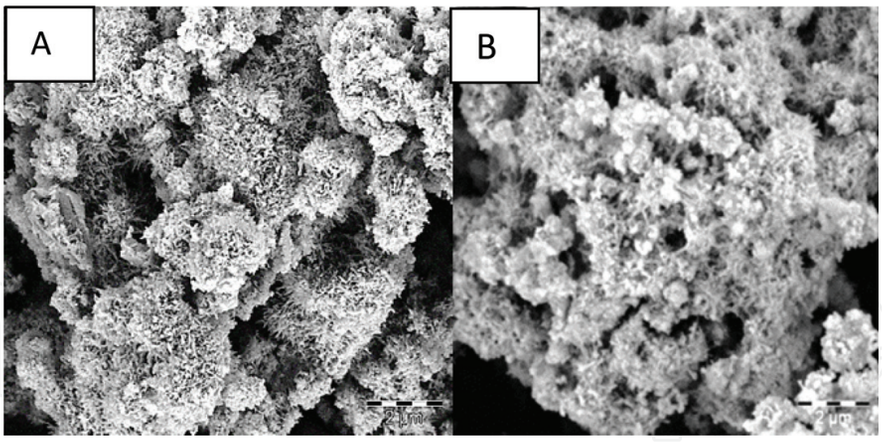


Figure 6. SEM of samples the sludge of AMD sample with $FeCl_3$ and bentonite clay respectively (25,000×) [53].

The SEM micrographs show the dry sludge of the AMD (**Figure 6**) with $FeCl_3$ (**Figure 6A**) and bentonite clay (**Figure 6B**) dosage. The former shows flocs which are bound together to form clusters of separate dense and small non-spherical porous structures with some voids in-between surface. The structural morphology is indicative of subjection of shear stress during treatment. On the other hand, the micrograph (**Figure 6B**) exhibits more condensed clusters of flocs with uniform crystal morphology, showing fewer voids compared to those obtained in **Figure 6A**.

7. Conclusion

Heavy metals have exhibited both economic and detrimental implications, a condition which uplifts the economy and degrades the environment, respectively. The removal of heavy metals from the medium (solvent) is not cost-effective as they sometimes appear as trace elements which are not easily removable. On the other hand, the trace elements found in tailings accumulate with time and form new complex and toxic compounds to the environment. Treatment of tailings is a very expensive exercise, which has never been deliberated, thus causing degradation especially after rainfall where the toxic compounds dissolve and disperse throughout the environment. A majority of modern technologies which have been explored are not cost-effective and sustainable, a conclusion emanating from employing sophisticated and foreign equipment. In addition, developing and underdeveloped countries cannot cope with such expenditures.

The only solution to the existing challenge relating to environmental degradation by the mine's wastewater is around a choice of a cost-effective treatment technique, which includes a simple operation and uses the most abundant reagent(s) that are affordable in any way. Natural inorganic coagulants have been used to treat industrial wastewater, but the problem is the damage to plant and equipment when dosed in pure form, i.e. corrosion, scaling or addition to sludge. The present review investigates the efficiencies of a combination of bentonite clay and inorganic coagulants (flocculent) in the treatment of the AMD sample in reduced mass fraction. Bentonite clay was chosen due to chemical composition and crystal morphology, which are indicative of effective physicochemical adsorption. On the other hand, inorganic

coagulants also employ a physicochemical reaction to remove turbid materials as exhibited by SEM micrographs, but the bentonite clay is prone to perform better as it applies ion exchange, adsorption and intercalation. The advantage of the mixture of bentonite clay with inorganic coagulants in reduced molarity by half, i.e. 50% molarity ($^{m}/_{m}$%), serves both to reduce their detrimental effect and alleviate over or underdosage, which may cause restabilization and deflocculation, respectively. A flocculent, prepared by a combination of bentonite clay and Na_2CO_3, employed in the present review exhibited an optimal heavy metals removal potential.

Although some of the inorganic coagulants exhibited optimal turbid materials removal, varying atmospheric conditions affect the operating conditions during treatment, thus requiring continuous adjustments. Although it is also plausible that such a phenomenon can still occur with the flocculent used in this study, bentonite clay always behaves as a principal substrate due to multiple adsorption characteristics. The other advantage with this technique is that it does not require pH adjustment as the reagents exhibited a high destabilization-hydrolysis potential, a reaction which is shown by the removal of the turbid materials. The removal of the turbid materials from the AMD indicates that bentonite clay and Na_2CO_3 (flocculent) are complementary.

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