Heavy Metals and Radioactivity Reduction from Acid Mine Drainage Lime Neutralized Sludge

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Abstract. The worldwide known treatment processes of acid mine drainage result into the formation of hydrous ferric oxides that is amorphous, poorly crystalline and into the generation of hazardous voluminous sludge posing threat to the environment. Applicable treatment technologies to treat hazardous solid material and produce useful products are limited and in most cases nonexistence. A chemical treatment process utilizing different reagents was developed to treat hazardous acid mine drainage (AMD) sludge with the objectives to conduct radioactivity assessment of the sludge generated from lime treatment process and determine the reagent that provides the best results. Leaching with 0.5 M citric acid, 0.4 M oxalic acid, 0.5 M sodium carbonate and 0.5 M sodium bicarbonate was investigated. The leaching time applied was 24 hours at 25 °C. The characterization of the raw AMD revealed that the AMD sludge from lime treatment process is radioactive. The sludge was laden with radioactive elements namely, 238U, 214Pb, 226Ra, 232Th, 40K and 214Bi. 0.5 M citric acid provided the best results and the hazardous contaminants were significantly reduced. The constituents in the sludge after treatment revealed that there is a great potential for the sludge to be used for other applications such as building and construction.

1. Introduction
Acidic mine effluent such as AMD is commonly treated through lime neutralization. This process remains the most widely applied technology due to the high efficiency in removing dissolved metals and the fact that lime costs are low as compared to other alternatives chemicals. The technology is effective in raising the pH of the water and precipitating the metals to below regulatory limits. However, one of the major challenges with simple lime neutralization treatment process is the production of a voluminous, hard to settle, radioactive and hazardous sludge, laden with metals. The two major drawbacks regarding the AMD sludge are the volume of the sludge generated from the treatment processes, the long-term chemical stability and the negative potential impact the sludge poses to the environment, ground water and human beings.

Various industries produces significant quantities of acid mine drainage sludge, lignite and fly ash, however the beneficial reuse technologies for these materials are limited [1]. The growing global urbanization of society coupled with increasingly stringent sludge reuse/disposal regulations and increasing public pressure, is forcing both public and private sludge generators to re-evaluate their sludge management strategies [2]. Conventionally, the waste sludge is disposed by means of incineration, landfiling or ocean disposal as well as reused as soil conditioner in agriculture. Legislation requires that sludge from neutralization plants be discharged into lined ponds to prevent metal leachate from polluting ground water [2]. The volume of sludge to be disposed also influences the cost and processes that produce sludge. An estimated amount of 20 t/d of sludge is produced from
1 Ml/d of discard leachate when neutralized with lime or limestone [3]. The principle of lime neutralization lies in the insolubility of heavy metals in alkaline conditions. Metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated when pH is adjusted to a set point of about 9.5 [4]. When dry lime is added to the waste stream, the hydrated lime reacts or dissociates to increase pH. Hydrolysis reactions occur causing the metals present to precipitate as hydroxides [4]. The following two equations illustrate these reactions:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (2)$$

A common by-product of lime neutralisation process is gypsum (calcium sulphate bi-hydrate). Gypsum precipitation occurs as acidic drainage is often rich in sulphate and calcium added from the lime will bring the solubility product well above saturation. Gypsum is a major sludge component and contributes significantly to the volume of sludge generated [3].

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \quad (3)$$

Another common by-product of lime neutralization is calcium carbonate. The inorganic carbon for this reaction can either come from the AMD itself or as a result of carbon dioxide from air, which is dissolved during aeration. This carbon dioxide converts to carbon bicarbonate and then partially to carbonate due to the high pH. The carbonate fraction will precipitate with high calcium content of the slurry to form calcite (calcium carbonate). This calcite can play an important role in the stability of the final sludge product as it provides neutralizing potential to the sludge, as it is stored [5].

Radioactive materials which occur naturally and where human activities increase the exposure of people to ionizing radiation are known by the acronym 'NORM'. NORM results from activities such as burning coal, making and using fertilizers, oil and gas production [6]. NORM levels are typically expressed in one of two ways: Becquerel per kilogram (or gram) indicates level of radioactivity generally or due to a particular isotope, while parts per million (ppm) indicates the concentration of a specific radioisotope in the material [6]. The materials may be original (such as uranium and thorium) or decay products thereof, forming part of characteristic decay chain series, or potassium–40. The two most important chains providing nuclides of significance in NORM are the thorium series and the uranium series [6]:

In the acid mine drainage treatment process, using lime to reduce acidity in the effluent and precipitate some heavy metals from the water, a radioactive sludge is produced and may emit radioactive gas. Several hundred of mine dumps and tailing dams, each containing millions of tonnes of waste are located along a long line of Witwatersrand. They are exposed to the elements with winds blowing the finer particles away and heavy summer rains wash larger quantities of acidic and radioactive particles into surrounding watercourses. The material utilized for building contains small amounts of radioactive substances. These are radionuclides in uranium (238U), thorium (232Th) decay series and radioactive potassium isotope (40K), which mostly originate naturally from rock and soil. In addition to the natural occurring radionuclides, some industrial by-products also contain the radioactive substance such as cesium (137Cs). Incorporating the by-product into building and construction material, the final produced product may contain these radionuclides [7]. To assess whether an action level is exceeded, the activity index must be calculated from activity concentration measurements of the material. For the activity indexes, radionuclides such as radium (226Ra), thorium (232Th), potassium (40K) and cesium (137Cs) are considered. Other radionuclides may need to be taken into consideration in special cases [8]. It is critical to assess the radiological hazard associated with the exposure to the radiation from 40K, 226Ra, and 232Th, to account for the collective effect of the activity concentrations of these radionuclides in a material.

This study was undertaken to evaluate the radioactivity of AMD sludge generated from a lime neutralization treatment process in a gold mine and determine the best reagent to remove or reduce the radioactivity in the material and investigate the possibility of utilizing the raw or treated product for other applications.
2. Experimental

This section present the experimental procedure and methodology followed.

2.1. Method

AMD sludge sample was obtained from a gold mine in Randfontein. Salts were used to prepare different concentrations of leaching reagents, namely 0.4 M citric acid, 0.5 M oxalic acid, 0.5 M sodium bicarbonate and 0.5M sodium carbonate. AMD sludge samples were first prepared prior conducting the experimental work. The raw sample was dried in an oven for 24 hours at 50 °C. The dried sample was then milled in a rod mill for 2 hours. Sieves were utilized to remove all the solid particles that could not be milled, i.e. rocks in the AMD sludge. A representative sample was obtained using Eriez Magnetic Rotary riffler for characterization. The specific gravity of the material was determined using a gas pycnometer. A pH meter was used to measure pH. The prepared reagents of citric acid, oxalic acid, sodium carbonate and sodium bicarbonate were added to AMD sludge at 15% solid loading.

A thermostatic shaker was utilized to conduct the leaching experiments. 4 flat bottom beakers containing the material were placed in a thermostatic shaker at 35 °C, and agitated at 170 rpm for 24 hours. After 24 hours, the thermostatic shaker was switched off, the samples were filtered, the solution stored for further characterization and the solids were dried in an oven at 50 °C. After drying the solid products were analyzed using XRF and XRD to check the effect of the different reagents on the leaching of AMD sludge. Relative density was determined using a gas pycnometer by weighing 5 g of AMD sludge into a pycnometer cup. The cup was then inserted into the measuring equipment. After the relative density was measured, the reading displayed in g/cm3 was recorded. To determine the pH of AMD sludge, AMD sludge/water mixture was prepared by adding 50 g of sludge into 100 ml of deionized water under continuous stirring and measuring the pH after 30 minutes.

AMD sludge composites were prepared to determine the unconfined compressive strength (UCS) of the raw and citric acid treated sludge. The composites were casted and cured at the temperatures of 40°C. The strength was allowed to develop over 14 days. After the curing period, the UCS was determined. The treated AMD sludge was stabilised with fly ash and lime at the ratio of 50:30:20 to enhance the pozzolanic reaction and cured at 40 °C for 14 days.

2.2. Analysis

X-ray Floroscence (XRF, Rigaku ZSX Primus II) was used to determine the semi quantitative chemical composition of AMD samples. Mineral species were determined by X-ray diffraction (XRD, Rigaku Ultima IV)). Radionuclides activity concentrations in the sample were determined using Gamma Ray Spectroscopy (GRS). Using GRS, the samples were packed, hermetically sealed and stored for about six weeks prior to counting so as to ensure radioactive equilibrium between 226Ra and its short-lived progeny.

3. Results and discussions

The measured specific activities in the raw samples collected for AMD sludge are presented in table 1. The activity of radionuclides in the samples is given in Bqkg⁻¹ dry weight. The world average activity concentrations of 226Ra, 232Th and 40K are 35, 30 and 400 Bqkg⁻¹, respectively [8]. The activity in AMD sludge ranges from 32 Bqkg⁻¹ to 153 Bqkg⁻¹. The highest concentration was observed in 238U, followed by 226Ra, and the lowest concentration was that of 232Th. All the major natural occurring radionuclides were detected in AMD sludge, 238U, 226Ra, 232Th and 40K. The largest contribution of the radioactivity in the sample is due to 238U. 226Ra is drastically above the world’s average activity of 35 Bqkg⁻¹. 40K is within the standards of 400 Bqkg⁻¹ and 232Th slightly exceeding the stipulated concentration of 30 Bqkg⁻¹.
Table 1. Radioactivity of AMD sludge.

| Detected nuclides | Radioactivity concentration (Bq/kg) |
|-------------------|-----------------------------------|
| $^{214}$Pb        | 91                                |
| $^{214}$Bi        | 98                                |
| $^{226}$Ra        | 150                               |
| $^{40}$K          | 43                                |
| $^{238}$U         | 153                               |
| $^{232}$Th        | 32                                |

The AMD sludge showed to have a pH of 10.24, relative density of 2.66 g/cm$^3$, liquid limit of 49.71 and plastic limit of 14.53. The coefficient of gradation ($C_c$) and uniformity coefficient of the material was found to be 4.327 and 1.716, respectively. Numerous studies conducted previously reveals that pH values for the sludge from various lime neutralization treatment processes ranges from 8.2-10.8 [9]. Mostly the aged sludge showed a lower pH as compared to their counterparts. The measured pH for AMD sludge is 10.24, an alkaline material due to the basic neutralization reagent used (lime), this value agrees with results obtained by other researchers for the sludge from neutralization processes [9].

Most of sludge have a specific gravity of 1.0, i.e. they are almost equal to the weight of the water [6]. The specific gravity of AMD sludge was found to be 2.6568. For sand, if Cu is greater than 6 and Cc is between 1 and 3, it is considered well graded. However, for a gravel to be well-graded, Cu should be greater than 4 and Cc must be between 1 and 3 [7]. The Cu and Cc for AMD sludge is 4.327 and 1.716, respectively. Therefore, it is not well graded, but gravel. The liquid limit for AMD sludge is 49.71 and plastic limit is 14.53, respectively.

3.1. Chemical treatment of AMD sludge with different reagents

Comparing the final product with the raw material the sulfur relative proportion in citric acid medium was reduced by 33%, Figure 1(a). Calcium and iron relative proportion was increased by 8% and 5%, respectively. Sulphur reduction shows that it was leached out during the treatment process. Other elements leached are Mg, Al, Si and K, Figure 2(e). Citric acid drastically decreases the sulfur relative proportion contained in AMD sludge and calcium and iron proportion slightly went up.

Using oxalic acid as a leaching reagent Figure 2(b), sulfur relative proportion was reduced from 5.45 wt% to 3.17 wt%. Calcium and iron relative proportion was increased from 28.57 wt% to 31.05 wt% and 24.83 wt% to 26.685 wt%, respectively. Oxalic acid dissolved the sulfur initially available in the material and its relative proportion decreased by 42%, while calcium and iron relation slightly increased by 8% and 7.5%, respectively.

The results obtained when sodium carbonate was employed as a leaching agent, Figure 2(c), indicates that sulfur relative proportion was drastically reduced by 82.1%. Calcium relative proportion increased by 7.73% and iron increased by 5.52%. Leaching with sodium bicarbonate, Figure 2(d), resulted in the sulfur reduction of 82.72% in the final product, hence the increase in calcium relative proportion by 6.26% and 5.5% for iron. For both sodium carbonate and sodium bicarbonate, optimal leaching of sulfur is evident, more than 80% reduction in sulfur relative proportion is observed.

Other elements detected in AMD sludge by XRF are sodium, magnesium, aluminum, silicon, potassium and manganese as shown in Figure 1(e). Magnesium, aluminum, silicon and potassium were leached out in citric acid medium and manganese relative proportion slightly increased by only 2%. Using oxalic acid, only magnesium was leached out and the relative proportion for other elements slightly increased. The elements contained in AMD sludge behaved the same when sodium carbonate and sodium bicarbonate were used. In mediums, sodium, magnesium, aluminum, silicon and manganese relative proportion increased and the only reduction in relation was observes in potassium.
There was a drastic increase in relative proportion of sodium when sodium carbonate and sodium bicarbonate were utilized. Sulfur was leached out from AMD sludge with all the leached agents employed, and the highest reduction was obtained with sodium carbonate and sodium bicarbonate. Calcium and iron relative proportion slightly increased with all the leaching reagents.

3.2. Elemental analysis of AMD sludge treated with different agents

The chemical components of cement include SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, SO$_3$ and MgO. Therefore, the chemical constitution of the AMD sludge is typical of construction materials. The SO$_3$ is very high due to the precipitation of sulphate normally available in high concentration in the acid mine effluent and the SiO$_2$ very low in the AMD as expected. Depending on the application of the material produced, a treatment process that introduces more or increase SiO$_2$, Al$_2$O$_3$ and suppress SO$_3$ contents is desirable. Using the different reagents sodium carbonate and sodium bicarbonate managed to drastically reduce the sulphate composition by 80% and 81%, respectively. The best reagent that increased the aluminium composition to the highest is sodium carbonate. All the reagents used increased SiO$_2$ content; however, both sodium carbonate and sodium bicarbonate showed best results. Al$_2$O$_3$ composition was enhanced best in sodium carbonate medium.

3.3. Mineralogical study of AMD sludge treated with different reagents

Figure 2 indicates the XRD results for the AMD sludge treated with citric acid, oxalic acid, sodium carbonate and sodium bicarbonate.

**Figure 1.** Effect of different reagents on the leaching of AMD sludge at 35°C mixing for 4 hours (a) citric acid, (b) oxalic acid, (c) sodium carbonate, (d) sodium bicarbonate.
Figure 2. XRD results for AMD sludge after treatment at 35°C mixing for 4 hours (a) citric acid, (b) oxalic acid, (c) sodium carbonate, (d) sodium bicarbonate.

The XRD results in figure 2 (a) indicates that the predominant mineralogical phase in the final AMD sludge treated with citric acid was Augite aluminia (Ca (MgAlFe)Si₂O₆) with a content of 34.26%, followed by 29.78% marcasite (FeS₂), 14.58% silicon oxide (SiO₂), 14.34% (di-calcium di-iron oxide (Ca₂Fe₂O₅)) with a content, 3.86% gypsum (Ca(SO₄) (H₂O)₂) and 3.16% bustamite calcian (Ca₁.18Mn₀.19SiO₃). All the detected phases after the leaching process contain compounds that were initial present in the raw AMD sludge. Citric acid reacted with AMD sludge to form a predominant compound bonded with calcium-magnesium-aluminum-iron and silicate. The final product also contained a calcium sulphate compound with a different compound from the anhydride initially detected in the raw material.

The predominant phase when oxalic acid was used as a leaching agent is quartz (SiO₂) as determined by XRD, Figure 2 (b). The final product contains a total of 87.91% content of SiO₂ in different forms (51.03% quartz, 19.54% hypothetical silica and 17.31% silicon dioxide). The material initially contained 8.29% SiO₂ and 16.6% MgSi₂ and oxalic acid increased the total quartz content to 87.91%. This increase is also evident in the XRF results obtained, the Si relative proportion increased from 1.07 to 1.145 wt%. Calcium sulphate reacted with oxalic acid and produced a compound containing Ca-Mg-Si-O with a content of 6.76%, the compound contains elements initially available in the raw AMD sludge. Manganese oxide and iron oxide initially contained in the AMD sludge both reacted with the leached sulfur to form sulfide compounds, MnS² and Fe₂SiS₄ respectively.

The XRD results using for sodium carbonate, figure 2 (c) shows that the predominant phase is 78.81% SiO₂. The final product contained 71% more coesite as compared to the initial content. Sodium carbonate as a leaching agent promoted the formation of SiO₂. Iron oxide reacted with silicon and formed iron silicate, FeSi₂. Magnesium relative proportion was drastically increased from 1.67 wt% to 2.725 wt%, raw AMD sludge contained 16.6% Mg₃Si and during leaching, magnesium reacted with iron to form 3.99% MgFe. Sulphur contained in the raw AMD sludge was associated with calcium (Anhydrite, CaSO₄) with a content of 15.87%. After the leaching process, a calcium sulphate compound with hydrate was formed with 0.14% content. In the presence of sodium carbonate, calcium sulphate reacted with phosphorus to produce 15.46% brushite (CaHPO₄ (H₂O)₂), the leaching agent exposed phosphorus contained in the raw material as detected by XRF. The final product produced when sodium carbonate was employed as a leaching medium is predominated by SiO₂ with a content of 78.81%.

Calcite magnesium (MgCaCO₃) is the predominant compound in the final product with a content of 51.198%, followed by 41.05% coesite (SiO₂), in a sodium bicarbonate medium figure 2 (d). This
shows an increase of 32.76% SiO$_2$ in content from raw material to the final product. It is evident that sodium bicarbonate increased the formation of coesite. Magnesium reacted to form three different compounds containing magnesium in the final product, namely, magnesioferrite (MgFe), magnesium oxide (MgO) and calcite magnesium (MgCaCO$_3$). MgO was initially available in raw AMD sludge as detected by XRF and its relative proportion increased drastically by 57%. The manganese oxide reacted with the sulphur leached out to produce 0.45% MnS.

3.4. Radioactivity analysis of AMD sludge and unconfined compressive strength

The treated AMD sludge was measured for radioactivity and the results are presented in figure 3.

![Figure 3. Radioactivity of AMD sludge treated with citric acid.](image)

![Figure 4. Unconfined compressive strength of AMD sludge.](image)

The radioactivity results of the citric acid treated AMD sludge show a significant decrease in the radionuclides. Uranium the dominant contributor to overall radioactivity was reduced by 28%. All the other contaminants were also reduced; this resulted to a lower radioactivity as compared to the raw AMD sludge. It is crucial and it is highly recommended to assess the radiological hazards associated with exposure to the radiation from $^{40}$K, $^{226}$Ra, and $^{232}$Th. This is conducted to account for the collective effect of the activity concentrations of the radionuclides in a material.

Figure 4 depicts the UCS for the raw, treated AMD sludge and fly ash lime stabilized AMD over 14 days curing. The results show that the strength for both the raw and citric acid treated AMD sludge improved over 14 days. The effect of curing time on UCS was investigated by measuring the compressive strength of specimens. The highest strength obtained is 2.79 MPa for the treated AMD sludge and 1.83 MPa for the raw AMD sludge. There was a significant strength gain after 14 days curing. The chemical composition of both the raw and treated AMD sludge showed that there was insufficient pozzolans in the materials to trigger the pozzolanic reaction for strength development. To further improve the UCS of the treated AMD, the sludge was stabilised with fly ash and lime and the UCS of 4.9 MPa was obtained. The strength obtained for the treated sludge is close to the minimal applicable strength for masonry brick, therefore there is a great potential for this material to be utilized in building and construction and it can be applied for load bearing. A minimum of 3.5 MPa is required on burnt masonry clay [10-12]. The results showed that the treated sludge can attain load bearing strengths without using a binder such as cement or lime.

The composite developed from the treated AMD sludge is presented in figure 5. The identified constituents in the treated AMD composite are Gypsum (G), CaSO$_4$·2H$_2$O (32.35%), calcium aluminium sulphate, Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_2$·26H$_2$O (33.18), wollastonite (W), CaSiO$_3$ (17.93%), hedenbergite (H), CaFeSi$_2$O$_6$ (1.48%) and keatite (K), SiO$_2$ (15.01%). The constituents in the mineralogy are associated with of silicate, iron and calcium. The new hydration products formed are, calcium aluminium sulphate, wollastonite and hedenbergite. Due to the addition of fly ash, high content of silicate oxide is observed, a compound which has silicate as the predominant compound. The results also reveal that lime addition activated the alumina and silica phases and the final material contained keatite with higher proportion than the raw material.
As presented in figure 6, the raw AMD sludge showed more flakes like particles that are irregular shaped. Fairly stronger and intact particles were observed in the treated AMD sludge, this might have led to the voids between the larger particles to be filled by the smaller grains particles in the treated AMD sludge and contribute to higher strengths development.

4. Conclusion
The activity concentrations showed that the highest contributor to radioactivity is $^{238}$U. The measured activity concentration levels for radium, thorium and potassium revealed that radium was above the average world activity, thorium and potassium slightly exceeds the required standards. No radionuclides were detected in the raw AMD sludge by XRF and XRD; however there was evidence of the radionuclides when GRS was used to characterize the raw material. There was a drastic increase in sodium relative proportion when sodium carbonate and sodium bicarbonate was utilized; this is due to the sodium available in NaCO$_3$ and NaHCO$_3$ salt, as the XRD results did not reveal any Na contained in the raw AMD sludge. Using citric acid as a leaching reagent extracted most metals from the AMD sludge as the relative proportion of most metals was reduced as compared to oxalic acid, sodium carbonate and sodium bicarbonate. Citric acid proved to be the best organic extracting agent for hazardous metals contained in the AMD sludge. It is the most preferred because it is environmental friendly as it a naturally occurring organic complex, showed consistent removal efficiency and it is cost effective as compared to oxalic acid, sodium bicarbonate and sodium carbonate. In respect to unconfined compressive strength, the final treated AMD sludge proved to have a potential to be used for load bearing. Other application for the sludge may be in the treatment of acid mine drainage/wastewater that is acidic and contaminated with high concentration of heavy metals [13].

5. References
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