Acid Solvent Extraction of Aluminium from Portable Water Sludge at Low Temperatures

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Abstract : In this article aluminium was extracted from portable water sludge using acid solvent extraction technique at low temperatures and at a pressure of 1atm.The portable water sludge samples were obtained fromCriterion Water Works Bulawayo, Zimbabwe .The composition of sludge was determined using X-Ray Fluorescence (XRF) spectroscopy analysis. Theconstituents found in abundance in the sludge were Al_2O_3,SiO_2 and Fe_2O_3 in quantities of 62.00%, 36.00%, and 0.81% by sludge weightrespectively.The sulphuric acid was used as the solvent and the aluminium extracted from sludge was determinedcalorimetrically. The extraction of aluminium was optimised by varying temperature, contact time andacid concentration from ranges of $30\text{-}60^oC$ at 30^oC interval,30-240 minutes at 30 minutes interval and 1-5.5M at 0.5M interval respectively .The solid –to -liquor ratio was optimised by varying it at 1:2,1:3,1:4,1:5,1:6,1:7,1:8,1:9, 1:10ratios . The optimum temperature, contact time, acid concentration and solid to liquid ratio for the optimum extraction of aluminium were found to be 40^oC, 90minutes, 5.5M and 1:2 respectively. The optimum efficiency obtained was 37.5% implying that for 100% extraction the process was to be carried out in 3 batch stages in series.

Key words; portable water sludge,solvent extraction, aluminium extraction, waste management, low temperatures.

1.0 Introduction

In the processing of portable water at the Criterion Water Works in Bulawayo Zimbabwe,aluminium sulphate is used as a coagulant which resultsin the formation of sludge[1]. This sludge is produced in the coagulation, flocculation, and filtration stages as in any conventional portable water treatment plant during the treatment process[1, 2, 3, 4]. The sludge from the process is normally disposed in lagoons and drying beds[4, 5]. In the research carried out the quantities of aluminium in the sludgeswere found to range from 10% to 18%, by sludge weight[2, 6, 7, 8]. The danger of aluminium being contained in the sludge is thatduring the rainy season the aluminium in these deposit sites can be washed away into the surface waters or leached into underground waters, resulting in contamination of these water bodies[6, 9]. The aluminium contaminated waters when consumed can cause adverse effects on health such as damage to the central nervous system, dementia, memory loss, littleness, and severe trembling[10].The aluminium canalso affect the environment in
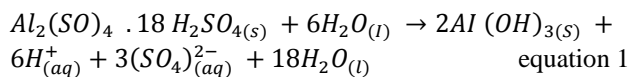
that its ions can react with phosphates, resulting in depletion of phosphates in the land and water,hence affecting plants and aquatic life[5, 9, 11]. The other environmental concern of aluminium is that when it is present in high concentrations in the soils, can result in the damage of roots of trees leading to their death [5, 9, 11]. The Environmental Management Agency (EMA) in Zimbabwe is placing strict restrictions on the quality of portable water sludge to be disposed into the environment which enforces the pre-treatment of portable water sludge before discharge to the environment[12].According to the Environmental Management Agency Act, the quantity of aluminium in the portable water sludge should be less than 0.1 ppm[13],therefore the portable water sludge produced at Bulawayo Criterion water works has aluminium content well above the Environmental Management Agency specifications, implying that the sludge should be treated prior to disposal.This problem is not only encountered in Zimbabwe,it is also prevailing in other countries where aluminium sulphate is used as a coagulant in the treatment of portable water[2, 4, 8, 14].The extraction of the   aluminium from the portable water sludge will be an added advantage to any portable water treatment works using aluminium sulphate, as the extractant (aluminium) can be reused in the process or recovered to aluminium metal for use in other industries such as in the manufacturing of alloy parts for aeroplanes[15],cars [15] industrial equipment or tools ,kitchen utensils and tins for beverage industries[8, 16]. Regarding the fore mentioned waste management's concern on the disposal of portable water sludge containing aluminium and the industrial market demand ofaluminium,a lot of research is being carried out on extraction of aluminium from various aluminium secondary sources [1, 2, 7, 8].The research being carried out on extraction of aluminium from secondary sources is mainly focused on the removal of aluminium using alkaline and acid solvent extraction methods at high temperatures,above 60^oC up to 100^oC[1, 4, 14].The heating of alkali or acidsolutions to temperatures as high as 100 ^oC result in the production of fumes which pollute the environment,corrode equipment and materials in the vicinity[1].Regarding the issue of using high temperatures in extraction implies that the energy needed for extraction is high

hence the technology is energy intensemeaning high cost of extraction[8].The forementioned facts implythat themethods of extracting aluminium using alkali or acid solvent extraction methods at high temperature are environmentally unsustainable and not economic[4, 14]. In this article the researchers have carried out a detailed study of identifying and optimising factors that significantly influence the

aluminium extraction from portable water treatment sludge at low temperatures using acid solvent extraction technique. Therefore the objective of this research is to extract aluminium from portable water sludge using acid solvent extraction method at low temperatures. To the best knowledge of the researchers and literature survey carried out, no work has been done to extract aluminium by the method studied in this article at low temperatures.This study provides a solution to a waste management problem due to the aluminium in portable water sludge and a lead to an alternative secondary source of aluminium for an increasing industrial aluminium demand.

2.0 Theoretical background

In the treatment of portable water,aluminium sulphate is added as a coagulant and the reaction proceeds as follows[1, 2, 5, 8].

$$Al_2(SO)_4 . 18 H_2SO_{4(s)} + 6H_2O_{(I)} \rightarrow 2Al(OH)_{3(S)} + 6H^+_{(aq)} + 3(SO_4)^{2-}_{(aq)} + 18H_2O_{(l)} \qquad \text{equation 1}$$

The effect of a coagulant is based on the ability to aggregate particles into a removable form by chemical precipitation[3, 8]. The chemical precipitation process is mainly based on coagulation, which can be divided into two main mechanismswhich are: charge neutralization and sweep coagulation[3]. These two mentioned mechanisms occur simultaneously i.e. when the charge neutralization is occurring the negative surface charge of contaminant particles is reduced by adding aluminium sulphate into wateras a result the repulsion between contaminants is reduced and the formation of dense flocs is enabled[2, 3]. Whilst at the sametime the sweep coagulation occurs (i.e. there will be formation of sludge based on the formation of an amorphous metal hydroxide precipitate). In this mechanism impurities are trapped inside aluminium hydroxide floc or swept down by thesinking floc[3]. When the size and mass of the aluminium hydroxide floc increases enough for gravitation to exceed the buoyancy of the water, the floc starts to sink[3, 8].The precipitated metal-hydroxides collect in subsequent sedimentation and filtration treatment processes, resulting in the production of bulky gelatinous sludge suspensions[1, 3]. This sludge formed contains aluminium in substantial quantities in the ranges of 10-18%[4, 6, 8].The alkali or acid solvent extraction methods are effectively used for the extraction of aluminium mainly from secondary sources such as from portable water sludge[1, 4, 17]. These extraction methods are mainly dependent upon the sourceof aluminium and the constituents of the source[18].

Properties of aluminium

Aluminium (Al) is a silver-white amphoteric metal with a face-centred cubic crystalline structure[19]. The most stable oxidation state of aluminium is its trivalent state[19].Aluminium exhibits this trivalent state both in compounds and in solution[19, 20]. This trivalent cation (Al^{3t}) has an ionic radius of 0.5 and a hydration number of 6[19]. The melting point and boiling point of aluminium is 660.4 °C, 2467 °C respectively[16]. Effective aluminium dissolution can be achieved in both acidic and alkaline conditions to form monomeric cations and aluminate ions respectively[2].

Alkaline leaching of aluminium

Alkaline leaching is traditionally used in the extraction of aluminium[4],such as in the industrial processing of bauxite to produce alumina(Bayer process)[1, 15, 21]and in the extraction of aluminium from coal fly ash[18].The fore mentioned processes involve the use of elevated temperatures[21]. In the fore mentioned sources (bauxite ore, coal fly ash),the aluminium is not the only metallic specie but there are many other metallic species such as iron present in these sources [18].In the alkali leaching of aluminium in the presence of iron, only the aluminium metallic ions will dissolve in favour of the iron metallic species[18]. Therefore in alkaline leaching of aluminium there is selective dissolution[20]. The extraction of aluminium at high temperatures, in alkaline media results in the formation of sodium aluminate silicate which isan insoluble gel in which the aluminium is inseparable and hence it is difficult to isolate the aluminium [18, 22, 23].This has been found in research carried out in extraction of aluminium fromsources such as bauxite, coal fly ash which have high content of silica[24, 25, 26].

Acid leaching of aluminium

The extraction of aluminium from portable water sludge using acid leaching is achieved by displacement of aluminium cation by the hydronium ion (This process is normally referred to as proton attack [18]), andthereaction is represented as follows[2, 4, 8]:

$$Al(OH)_{3\,(s)} + 3H^+_{(aq)} \leftrightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$$
equation 2
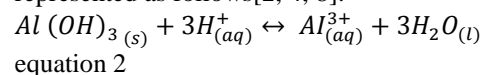
The acid solutions can dissolve a wide range of metals including aluminium[27].The acid extraction processes in the case of aluminium extraction from non bauxitic sources is preferred because these sources have high content of silica which is insoluble in acid[28].This means that the rest of the metals in these sources will dissolve except silica[26, 29].Therefore in this article,acid solvent extraction methodis used in favour of the alkaline route in that the aluminium source used (portable water sludge) has high content of silica.

3.0 METHOD
3.1 Equipmentand Materials

- Niton XL2 X-ray fluorescence (XRF) spectrophotometer analyser Thermo Scientific (Model: XL2500 ,Serial Number 92533 ,Date 09/23/14)

- Electronic top-loading Sartorius AG Gottingen Electric mass balance, Model: CP323S, 1997
- UV-Visible Spectrophotometer, Model: UV-1800, Manufacturer: Shimadzu Corporation Analytical & Measuring Instruments Division, 2008.
- Electric muffle heater coupled with stirrer
- What man filter Glass fibre filter paper GF/C diameter 17mm
- 75μm Sieves
- 50ml Beakers
- 100ml Graduated Measuring cylinders
- Spatulas
- 250 ml Round bottomed flask
- Glass Mercury Thermometer (0°C-110°C)
- Glass fibre What man 3 piecefilter funnel

- 250 ml Buchner flask

3.2 Reagents
- Sulphuric acid (H_2SO_4) ,AR 98% supplied by Merck
- Portable water sludge
- Distilled water

3.3 Portable water sludge sampling
The portable water sludge samples used in this study were collected directly from the Criterion Water works (Bulawayo, Zimbabwe). 20kgs of dry portable water sludge were sampled randomly from 3 different drying beds of $2500m^2$.A composite sample from the three 20 kg beds was made from which 10 kg of sample was obtained using the cone and quarter method of sampling. The 10 kg portable water sludge sample was then put into a 10kg plastic bag which was then sealed and devoid of air to avoid external contamination. The sealed plastic bag was stored in a dark, cool cupboard away from any heat source, direct sunlight or fluctuating temperatures.

3.3.1Preparation of Portable Water Sludge Sample
The portable water sludge collected in section3.4 was pulverised and sieved using a 75 microns sieve. The underflow portable water sludge sample was heaped and mixed thoroughly. A cone and quarter method of sampling was applied to collect 5 x 32g samples of a homogenous portable water sludge mixture which were taken for X-Ray fluorescenceAnalysis.

4.0 Experimental procedure
i. 100ml of 1M sulphuric acid were poured into a 250 ml round bottom flask
ii. The flask from (i) was inserted into an electric muffle heater and heated to a temperature of 30^oC
iii. A magnetic stirrer was put into the flask from (ii) and 10g of sludge from section3.4.1 were added into the flask
iv. The mixture in (iii) was agitated at 100 rpm for 30 minutes
v. After 30 minutes the flask was removed from the electric muffle heater and the mixture was filtered using a glass fibre What man 3 piece filter funnel The filtrate was poured into a 50ml beaker and left to cool in a desiccator
vi. The filtrate from (v) was analysed for aluminium calorimetrically.
vii. The experiments were carried out following the same procedure from stage i-vi changing the acid concentration from 1M -5.5M at 0.5M intervals,temperature from 30 -60^oC at 5^oC intervals and time from 30minutes -240 minutes at 30 minute interval.

4.1Colorimetric determination of Aluminium
The Aluminium concentration in the filtrate was determined as described in the Standard Methods[30].

5.0ANALYSIS OF RESULTS
5.1 Characterisation of portable water sludge
The results obtained from experiments carried out in section 3.4.1 on the characterisation of portable water sludge using XRF analysis are shown in Table 1.

Table 1:XRF analysis results of portable water sludge

Compound	Average Composition (% wt.)
Al_2O_3	62.000
SiO_2	36.000
Fe_2O_3	0.810
MgO	0.420
CaO	0.214
CO_2	0.210
Cr_2O_3	0.071
Na_2O	0.069
P_2O_5	0.054
ZrO_2	0.034
K_2O	0.030
V_2O_5	0.016
ThO_2	0.015
La_2O_3	0.013
CeO_2	0.012
SO_3	0.008
Mn_2O_3	0.006
MoO_3	0.005
Ga_2O_3	0.005
NiO	0.005
Y_2O_3	0.002
PbO	0.001
As_2O_3	0.001
TiO_2	0.001

The results in Table 1 show the average composition of the various constituents of the portable water sludge from Criterion water works determined using the XRF Spectroscopy Analysis. The most abundant compounds in the portable water sludge analysed were found to be aluminium (Al_2O_3),silica (SiO_2) and iron (Fe_2O_3)in quantities of 62,36 and 0.81 % by weight

respectively. The large value of aluminium content in the portable water sludge is mainly due to the fact that during the water treatment process in this plant excess aluminium sulphate is added into the raw water (approximately 2000kg of 17% aluminium sulphate is added to treat 120 mega litres of raw water) .The portable water from this plant ready for consumption has a concentration of aluminium of contains approximately 0.1 mg/L which is very compliant with the world health organisation specifications.[13].The portable water sludge from Criterion Water Works is a potential source of aluminium due to its high aluminium content as compared to the primary sources of aluminium which have quantities of aluminium in the ranges of 30-60% by weight[18].

Determination of Optimumleaching conditions

5.2 Determination of leaching time
The results obtained from the experiments carried out in section 4.0 for the determination of optimum leaching time are shown in Fig 1.
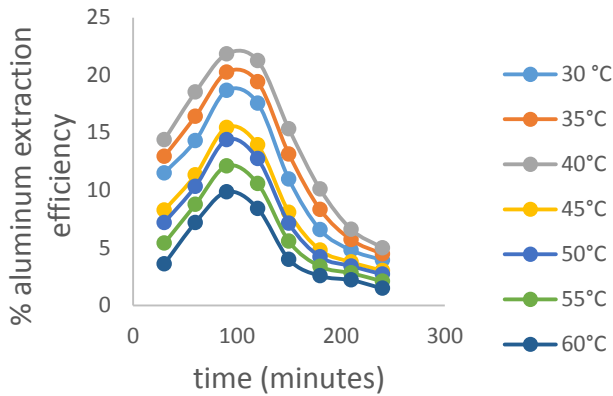
Fig.1 Graph of percentagealuminiumextraction efficiency against leaching time for varying temperatures

The graphs in Fig 1 shows a trend of percentage extraction efficiency against leaching time for varying temperatures at a constant pressure of 1 atm, acid concentration of 3M and solid liquor ratio of 1:4.The graph depicts that the percentage extraction efficiency gradually ascends to a maximum which is denoted by a peak and then descends gradually as the leaching time increases for varying temperatures.The peaks or maxima for the varying temperature of the graphs in Fig 1 coincide at the leaching time of 90 minutes.The fact that the peaks denote the maximum percentage extraction efficiency therefore the optimum leaching time is 90 minutes.

5.3 Determination of Optimum temperature

The graph of maximum percentage extraction efficiency against temperature is obtained from Fig 1.The percentage maximum extraction efficiencies at varying temperatures are shown in Fig 2.
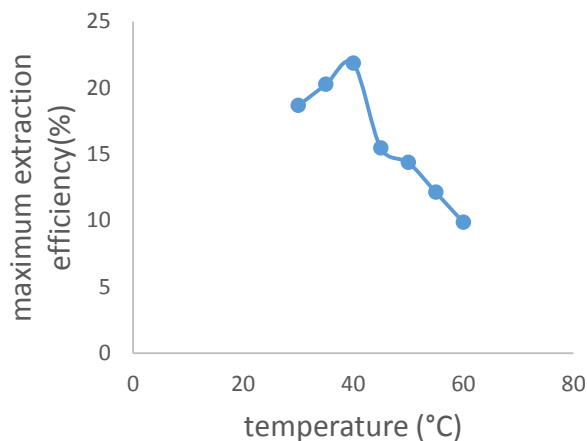

Fig. 2 Graph of percentage maximum aluminium extraction efficiency against temperature at an optimum time of 90mins.

The graph in Fig 2 illustrate that the maximum extraction efficiency ascends gradually to a maxima or peak at $40^{o}C$ and then descends gradually as temperature increases. At temperatures above $40^{o}C$, compounds such as silica, iron oxide and organic compounds dissolve in solution and interfere with aluminium ions in solution[23],resulting in decrease of aluminium ions in solution, hence lowering the percentage extraction efficiency as the temperature increases. Therefore the optimum extraction temperature is $40^{o}C$.

5.4 Determination of optimum solid liquor ratio

The results obtained from the experiments carried out in section 4.0 for the determination of optimum solid liquor ratio are shown in Fig 3.
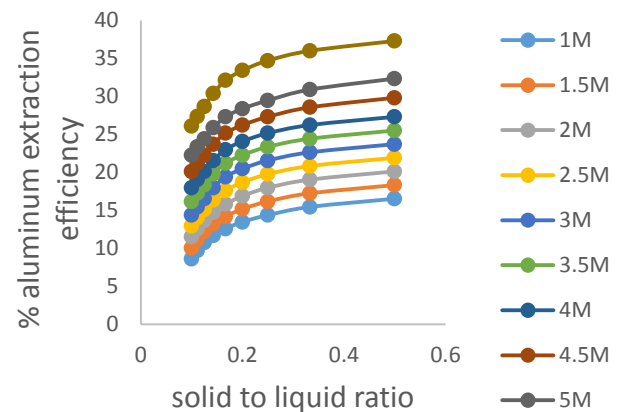

Fig. 3 Graph of percentage extraction efficiency for varying solid liquor ratio and varying acid concentration at a constant optimum leaching time of 90minutes and optimum temperature of $40^{o}C$.

The graphs in Fig 3depict that the percentage extraction efficiency gradually ascends to a constant value for the varying acid concentrations.The highest extraction efficiency coincides to a solid liquor ratio of 1:2 (0.5).Therefore the optimum solid liquid ratio is 1:2(0.5).

5.3 Effect sulphuric acid concentration

The effect of varying the concentration of sulphuric acid and solid liquor ratio at a constant optimum time of 90minutes and temperature of $40^{o}C$ and at a constant pressure of 1atmis shown in Fig 4.
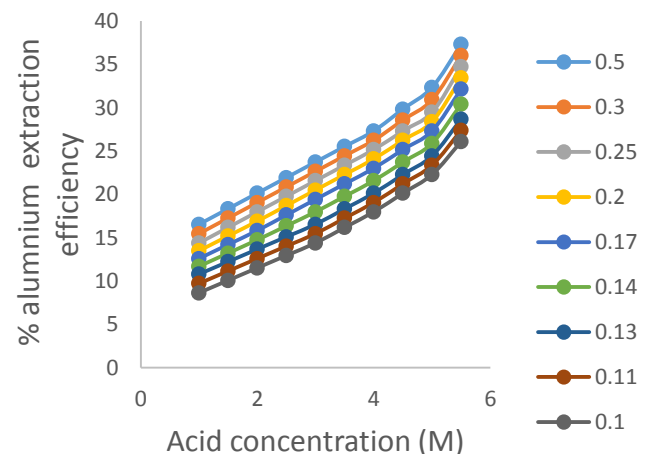

Fig. 4Graph of percentage aluminium extraction efficiency against varying acid concentration for varying solid liquor ratios.

The graphs in Fig 4illustrate that the percentage extraction efficiency increases gradually up to a concentration of 5.5M.For the concentrations above 5.5M, during the experiment there was a formation of a gel which was inseparable from the solids posing difficulties in separation the liquid phase for aluminium determination. This formation of the gel could be due to the dissolution and complexing of the other constituents of the sludge. Therefore the highest extraction efficiency was obtained at an acid concentration of 5.5M which correspond to a pH of

1.35.During the experiment it was observed that at acid concentrations above 5.5M,a gel starts to form, which is inseparable from the solids. In similar studies done on extraction of aluminium from water treatment sludge the optimum acid concentration was found to be in the pH range of 1-2[2, 7].In Fig 4 the graphs depict that as the concentration of the acid increases the percentage extraction efficiencies increase as the solid ratios increase respectively from the smallest to the highest ratio. The maximum percentage extraction efficiencies for all the ratios are attained at an acid concentration of 5.5.M. The highest solid liquor ratio of 1:2 at an optimum acid concentration of 5.5M has a percentage extraction efficiency of 37.5% .Therefore the optimum percentage extraction at an optimum leaching time of 90 minutes,optimum solid liquor ratio of 1:2,optimum temperature of 40^oC, and acid concentration of 5.5M is 37.5%. If the extraction is carried out in 3 stages in series then 100% aluminium extraction efficiency from portable water sludge will be achieved under these optimum studied conditions.

Conclusions

In this project aluminium was extracted at low temperatures from portable water sludge obtained from Criterion Water Works Bulawayo, Zimbabwe using acid solvent extraction method. The optimum conditions for extraction were found to be at an optimum leaching time of 90 minutes, solid liquor ratio of 1:2,optimum temperature of 40^oC, and acid concentration of 5.5M.The extractionefficiency was found to be is 37.5%.The optimum temperature of 40^oC is a low temperature thus the process is less energy intensive and the fumes produced are very low as compared to other works that have been carried out at high temperatures, rendering the process environmentally friendly.

Acknowledgements

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