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Optimum Parameters for the Recovery of Caesium Alum from Pollucite Ore by Sulphuric Acid Leaching

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Abstract

This work investigated the optimum parameters for the recovery of caesium alum (aluminium caesium sulphate dodecahydrate) from pollucite (caesium alumino silicate ore) obtained from Bikita in Zimbabwe by sulphuric acid leaching. The pollucite ore was characterized by AAS before leaching and after leaching. The mineralogical composition of the polucite ore before leaching was found to contain of the following phases: 17.17% aluminium oxide, 25.68% caesium oxide, 49.73% silica and less than 2% impurities of rubidium, potassium, sodium, lithium and iron. Batch optimisation studies were carried out to investigate the effects of process parameters namely leaching time and acid concentration at a constant temperature. -200 mesh size pollucite ore particles were digested in sulphuric acid at 100°C with a 30%-55% solution of sulphuric acid within a time frame of 1 – 6hs. Acid digestion was followed by hot water wash and vacuum filtration. Caesium alum was crystallized from the leach filtrate by stage cooling to room temperature. Optimum conditions to achieve 90% mass recovery of caesium alum with caesium content of 23% analysed by AAS after leaching were, leach time of 4h at 100°C and acid concentration of 40%. It is possible to economically recover caesium alum from Bikita pollucite ore by sulphuric acid leaching.

Keywords
Pollucite, Caesium alum, Optimum, Caesium, Leaching

1. Introduction

Caesium is an important rare metal element that has great application prospects in medical and biotechnology applications, atomic clock, oil drilling, as a getter in internet technology and space robotics and other contexts (Koch 2002, Li and Xu 2015, Liu et al.2019). At present, the most important commercial source of caesium is the mineral pollucite, a caesium aluminium silicate, $Cs_2O.Al_2O_3.4SiO_2$ (Lee et al.2022). Pollucite which is the ore of caesium, is found in a few zoned pegmatites around the world and is often associated with the more commercially important lithium ore, lepidolite. The deposits are sought and mined primarily for their lithium content. Almost all the world's supply of caesium is from zoned pegmatites. Pegmatites in the Bikita district of Zimbabwe and at Bernic Lake, Canada, contain the world's two largest deposits of lepidolite and pollucite (Lu et al. 2022).

Sulphuric acid leaching is the commercially preferred process because the method yields a sparingly soluble double salt without the need for another compound. The sulphuric acid leaching process of caesium recovery from pollucite ore efficiency is influenced by several parameters that include acid concentration and leaching temperature. The process takes place at temperatures between 100^0C and 180 ^{0}C with a 35% – 60% solution of acid followed by a water wash and vacuum filtration. Caesium alum is crystallized from the leach filtrate by stage cooling to 50^0C then 20^0C. The caesium alum is roasted in 4% carbon, the aluminium sulphate in the alum is converted to insoluble aluminium oxide. The resulting product (residue) is then leached with water to yield caesium sulphate which is then converted to caesium chloride. Reacting the aqueous caesium sulphate with barium azide gives caesium azide (CsN_3). The caesium azide is decomposed at 390^0C to caesium metal and nitrogen (Xie et al.2023). Optimizing these parameters is crucial for maximising caesium extraction, minimizing energy consumption, acid consumption and reducing environmental impact. Currently the country exports pollucite as raw ore at very low prices without processing. There is need to develop local processes to add value to the pollucite ore in order to increase the profit margins of beneficiation.

1.1 Objectives

The study focuses on investigating the effect of sulphuric acid concentration and leaching time at a constant minimum extraction temperature of 100^0C for the extraction of caesium from pollucite ore from Bikita Zimbabwe.

2. Literature review

Caesium has been extracted from pollucite ore mainly by direct reduction, alkaline decomposition and acid digestion (Burt 1993). Direct reduction involves heating the mineral ore with calcium, potassium, or sodium metal in a vacuum or an inert atmosphere, which yields an impure caesium metal. This method is not commercially viable, because of low yield, impurity of the product, and engineering difficulties (Zhang et al.2021, Xie et al.2023, Butterman 2004). Alkaline decomposition involves roasting the pollucite with either a $CaCO_3$ -$CaCl_2$ mixture or a Na_2CO_3 -NaCl mixture, leaching the calcine with water or dilute ammonia to extract a dilute CsCl solution, and then converting the chloride to caesium alum [$C_2 SO_4$: $Al_2 (SO_4)_3$:$24H_2 O$] or $Cs_2 CO_3$. Acid digestion is the principal commercial method used for pollucite ore and hydrobromic, hydrochloric, hydrofluoric, or sulfuric acids may be used. The hydrobromic and hydrofluoric acids are not used commercially owing to processing difficulties. Digestion of pollucite in hydrochloric acid at elevated temperature yields an impure CsCl solution that is converted to double chloride salts, such as caesium antimony chloride [4CsCl:$SbCl_3$], caesium iodine chloride [Cs_2 ICl], or caesium hexachlorocerate [Cs2 ($CeCl_6$)], which are purified and then decomposed by hydrolysis to yield purified CsCl. While the above processes are capable of producing caesium allum in relatively high purity, these processes have proven to be difficult and expensive for commercial application. Hence the need to develop local viable commercial processes for the extraction of caesium from pollucite ore at Bikita minerals Zimbabwe.

3. Methods

3.1 Sample collection

-200 mesh size pollucite ore mined from Bikita minerals was used in this research. Random sampling was used for sample collection using a metal scoop and a metal container. Four samples were collected into 5kg metal containers. A composite sample was then prepared by uniformly mixing the four samples using a shovel. Cone and quartering method was used to obtain smaller fractions of the composite sample. For subsequent use in the research the samples were thoroughly mixed and collected into labelled plastic bags (Bai et al.2010).

3.2 Characterisation of Pollucite Ore

-200 mesh size pollucite was first digested in hydrofluoric acid and the mineralogical composition of the ore was analysed by AAS before and after leaching according to previously reported procedure (Kaviyarasu et al.2022).

3.3 Acid Leaching

A 2000ml glass beaker reaction vessel fitted with a stirrer with 400 rpm constant stirring speed was used in this study. Heating was achieved using a hot plate to control and maintain the desired temperature of 100°C. A 5mm thick asbestos sheet was used as an insulator to help maintain a steady supply of heat to the reaction vessel. 98% industrial sulphuric acid was used as the lixiviant. An additional 100 mls of boiling demineralised water was added during the leaching to keep the mixture stirrable. Dilution was achieved using distilled water. After the pollucite had been leached for a specific time, it was filtered via vacuum filtration. The slurry was poured through a filter paper in a ceramic Buchner funnel. The solid silica was trapped by the filter and the solution was drawn through the funnel into the Buchner flask by a vacuum. The solution obtained was left to crystallize on cooling at room temperature for about an hour. The wet crystals were washed, weighed and dried at 150°C for 2hs and their chemical composition was analysed by AAS (Kaviyarasu et al.2022).

3.4 Effect of Leaching Time

To determine the optimum leach time, a mixture of 150grams, -200 mesh pollucite, 100 ml of demineralised water and 124,5grams of 98% sulphuric acid was boiled at 100°C at atmospheric pressure for varying times from 1 to 6hs (Burt 1993). After digestion 100 ml of boiling demineralised water was added under stirring and left to leach for an hour. The slurry was poured through a filter paper in a ceramic Buchner funnel. The solid silica was trapped by the filter and the solution was drawn through the funnel into the Buchner flask by a vacuum. The solution obtained was left to crystallize on cooling at room temperature for about an hour. The wet crystals were (Kaviyarasu et al.2022). washed, weighed and dried at 150ºC for 2hs and chemical composition was analysed by AAS. The recovery was calculated from the crystals formed using the formula,

$$\text{Recovery} = ((\text{Weight of Product} \times Cs_2O)/ (\text{Weight of Feed} \times Cs_2O)) \times 100$$

3.5 Effect of Lixiviant Concentration

A mixture of 150 grams - 200 mesh pollucite, 100 ml of demineralised water and 124.5 grams of 98% sulphuric acid which gives an acid dilution of 55% at atmospheric pressure was used. The leaching time for all experiments was four hours obtained from the optimum leach time. The acid concentration was then varied from 30% to 55% and all other parameters were kept constant (Pholosi 2012). The slurry was poured throughout a filter paper in a ceramic Buchner funnel. The solid silica was trapped by the filter and the solution was drawn through the funnel into the Buchner flask by a vacuum. The solution obtained was left to crystallize on cooling at room temperature for about an hour. The wet crystals were washed, weighed and dried at 150ºC for 2hs and the chemical composition was analysed by AAS (Kaviyarasu et al.2022). The recovery was calculated from the crystals formed using the formula,

$$\text{Recovery} = ((\text{Weight of Product} \times Cs_2O)/ (\text{Weight of Feed} \times Cs_2O)) \times 100$$

4. Data collection

To investigate the effects of leaching time and sulphuric acid concentration a series of experiments were conducted using sulphuric acid leaching. Three replicate experiments were performed for each variable and the mean value was used for data analysis.

5. Results and Discussion

5.1 Chemical composition of Bikita Pollucite Ore

The chemical composition of Bikita pollucite ore before leaching by AAS analysis is as shown Table 1.

Table 1. Chemical composition of Bikita Pollucite ore from AAS analysis

Mineral		% Oxide
Caesium	Cs_2O	25.68
Aluminium	Al_2O_3	17.17
Silica	SiO_2	49.73
Rubidium	Rb_2O	1.90
Potassium	K_2O	1.74
Sodium	Na_2O	2.83
Lithium	Li_2O	0.92
Iron	Fe_2O_3	0.03

The chemical composition of the pollucite ore before leaching from AAS assay results was found to contain the following phases: 17.17% aluminium oxide, 25.68% caesium oxide: and 49.73% silica and less than 2% impurities of rubidium, potassium, sodium, lithium and iron.

Effect of Leaching Time

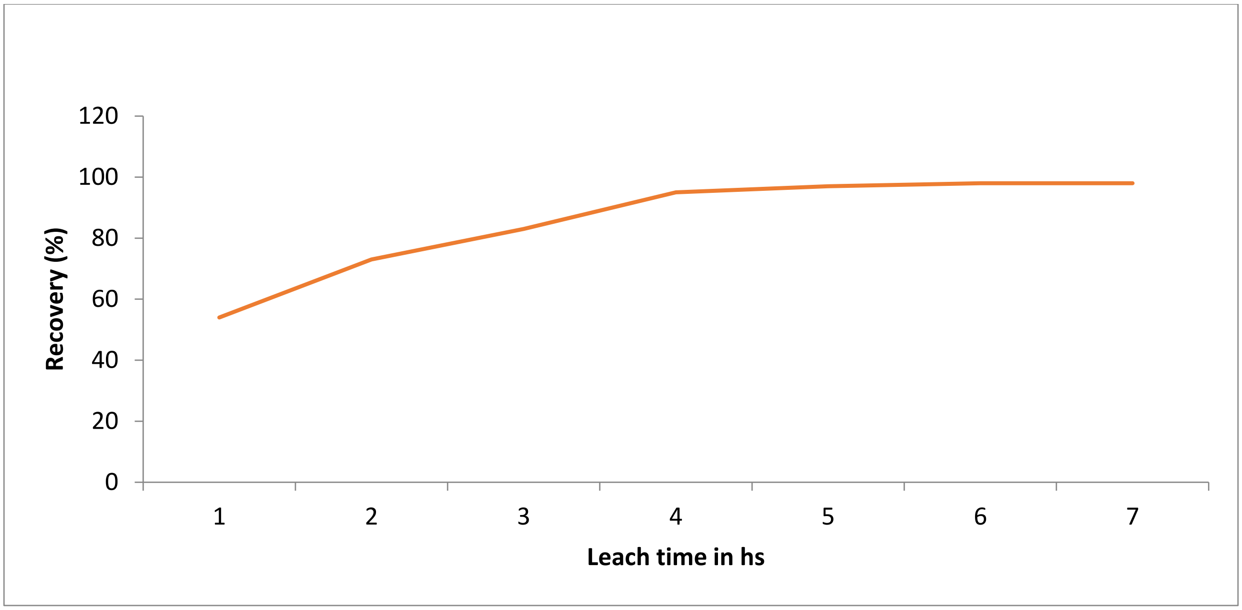

Figure 1. Effect of leach time on recovery.

Figure 1 shows the effect of leach time on recovery. The recovery increases as the leach time increases. The optimum leach time with a mass recovery of not less than 90% and caesium content of not less than 23% in the caesium alum is 4hs after which there was no significant increase in recovery. The results are in agreement with Burt (1993) who concluded that sulphuric acid digestion of pollucite ore is carried out at 100^0C using 35 – 40 % acid concentration for 3 to 8 hours.

5.2 Effect of Acid Concentration

Figure 2 shows the effect of lixivant concentration on recovery at constant leach time of four hours. The optimum acid concentration that produces a mass recovery of not less than 90% with caesium content of not less than 23% in the caesium alum is 40%. An acid concentration of 40% to 55% percent also produces a mass recovery that meets the recovery requirements. It can be argued that the 55% acid concentration was to ensure that all the caesium reacted with the acid. The quantity of acid used is critical and this was also proved by experiments by Berthold and Kane (1963) who found out that an excess of acid decreases yield rather than increasing it. They noted that a 10 – 15% increase over the stoichiometric quantity of acid required is what should be used. A 50% increase lowers the caesium recovery by as much as 13% and a 100% lowers recovery by 45%.

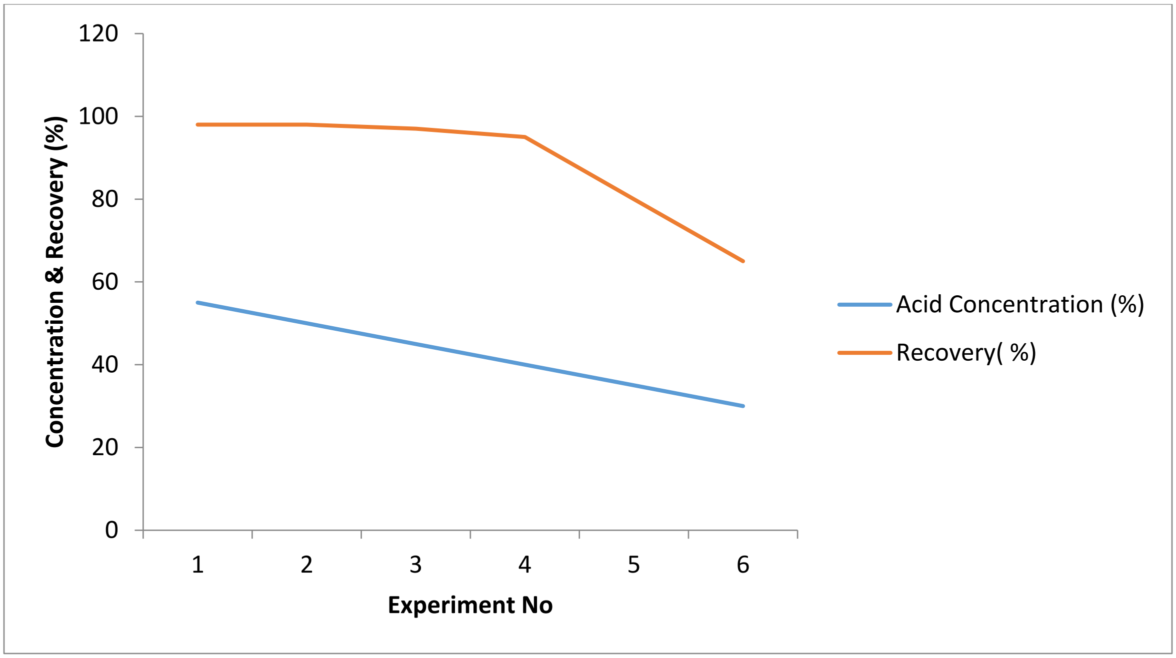

Figure 2. Effect of lixiviant concentration on recovery at constant leach time of four hours.

6. Conclusion

The research conducted demonstrates that it is possible to economically recover 90% caesium from Bikita pollucite ore using sulphuric acid as a lixivant under optimum parameters; of raw material particle size -200 mesh, leach time of 4hs, temperature of 100^0C and lixiviant concentration of 40%. Reduction in acid dosage to 40% will reduce the chemical reagent usage in the recovery thereby reducing the cost of recovery and increasing the profit margins. It will also reduce the amount of free acid present in the effluent water, and this will reduce the amount of lime required to treat the water before disposing it to the environment. This will result in better compliance with the safety and environmental regulations.

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Biographies

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