This invention relates to the recovery of cesium values as cesium salts from cesium aluminosilicate ore, pollucite. This ore can be represented by various formulas from $\text{Cs}_4\text{Al}_2\text{Si}_5\text{O}_{18}\cdot\text{xH}_2\text{O}$ to $\text{Cs}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{yH}_2\text{O}$ where $x$ is a number from 0 to 15 and $y$ is usually 1 or less than 1. When $x$ is 16 the mineral is termed anilite. Heretofore, it has been necessary to subject this ore to long and severe chemical treatment to decompose it and provide the cesium value in a recoverable form. For example, processes described in Inorganic Synthesis, vol. IV, pp. 6-9, McGraw-Hill (1953), utilize approximately four times the stoichiometric amount of sulfuric hydrochloric acid theoretically required by the alkali metals and aluminum in the ore. The ore-acid solution is heated to boiling and refluxed for periods of up to 30 hours to enable a 90% recovery of the cesium contained in the ore as cesium alum or cesium aluminum chloride. Multiple leaches are also employed to increase the cesium recovery. After digesting the ore-acid mixture for the required period, one is faced with the problem of conveying, pumping, and filtering a hot, very corrosive, abrasive slurry. The demands upon materials of construction by such a combination are very severe, with the result that operating costs and maintenance requirements are both very high.

I have discovered a new and novel method of treating pollucite ore which obviates these heretofore severe treatment methods and affords a simple, economical, and relatively rapid means of recovering cesium salts from the ore. In addition, it eliminates the need for handling a hot, very acid and very corrosive, abrasive slurry with its attendant problem.

I have found that, if a mixture of finely ground pollucite ore and the stoichiometric quantity of sulfuric acid required for reaction with the alkali metals and aluminum present in the ore is heated to a temperature of about 150°F for a period of about four hours, and a weight of water equal to at least one-fourth the weight of the pollucite ore used is added to the ore-acid mixture during this period, substantially complete extraction of cesium values as cesium alum from the ore results. More than this quantity of water may be added if necessary to keep the ore-acid paste in a storable condition, since, as the reaction progresses, the originally thin paste thickens to a very stiff, hard-to-stir paste unless water is added to restore it to a fluid consistency. Using less than the above mentioned quantity of one-fourth the ore weight of water results in a decreased recovery of cesium values from the ore. The water may be added with the acid to the powdered ore if desired or part of the water can be so added and the remainder during the acid treatment period. To ensure maximum acid-ore contact the ore is finely ground, usually to minus 200-mesh.

In arriving at the quantity of acid one can take into account the alkali metals and the aluminum present as oxides:

$$\text{M}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{M}_2\text{SO}_4 + \text{H}_2\text{O}$$
$$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2\text{(SO}_4)_3 + 3\text{H}_2\text{O}$$

where $M$ is any one of the alkali metals. The alkali metals and aluminum metal may not be present as oxides in the ore and this method of dealing with them is for simplicity; it has proven to be reliable. One must deal with ore composition for it is the ore which must be decomposed. Pollucite, the mineral, occurs in association with other minerals. For example, a petrographic examination of Bikita pollucite ore showed the presence of albite, lepidolite and quartz in addition to pollucite.

It has been found convenient to operate the ore-acid reaction within a temperature range of about 100°F to about 180°F. Temperatures lower than 100°F require longer reaction times while at temperatures above about 180°F too much water is lost from the reaction mixture, thereby necessitating frequent addition of water or operation under reflux and so increasing the cost of the reactor vessel.

The quantity of acid used to form cesium alum has been found to be critical. In contrast to classical methods heretofore described, we have found an excess of acid decreases the yield rather than increasing it as would be expected. We have found that about 10% increase over the stoichiometric quantity of acid required is all that can or should be used. A 50% increase over the stoichiometric acid requirement lowers the cesium recovery by as much as 13%, all other reaction conditions being the same. If a 100% excess of acid is used, the cesium recovery is decreased by 45%, maintaining other reaction conditions the same.

The cesium alum then is crystallized a number of times and further processed to form the desired cesium salt. The purified cesium alum is then added to a hot slurry of calcium hydroxide in distilled or demineralized water to yield a solution of cesium sulfate and a solid residue of calcium sulfate hydrate and aluminum hydroxide.

In general, the calcium hydroxide is added in amount sufficient to stoichiometrically convert substantially all of the cesium alum to cesium sulfate and aluminum hydroxide.

The solution of cesium sulfate is separated from the solid material by filtration, centrifugation, sedimentation or any combination of these.

Pure cesium sulfate can be recovered by evaporating the solution to dryness and calcining the salt so obtained at about 500°F to remove the last traces of water.

Conversion of cesium sulfate into other cesium salts can be accomplished by adding an aqueous barium hydroxide mixture to the cesium sulfate liquor obtained as above. The resulting mixture of cesium hydroxide and barium sulfate is separated by filtration, centrifugation, sedimentation, or a combination of these to yield a solution of cesium hydroxide. Cesium hydroxide can then be converted into the desired cesium salt by acidification with the desired acid.

Another way of obtaining cesium salts other than the sulfate or hydroxide is to treat the cesium sulfate solution with a barium salt of the desired acid such as barium chloride or barium nitrate. The barium sulfate precipitate is again removed as before and the solution of the desired cesium salt is concentrated and evaporated to dryness.

The practice of the invention is further illustrated by the following examples.

Example 1

One hundred pounds of minus 200-mesh Bikita pollucite ore was charged to a 15 gal. cast iron kettle equipped with a motor driven agitator and a steam jacket. Both high pressure (150 p.s.i.g.) and low pressure (35 p.s.i.g.) steam were piped into the heating jacket with appropriate valving so that either heat source could be used.

The Bikita pollucite ore used contained 25.5% Cs₂O. A total of 65.4 pounds of 102% H₂SO₄ was slowly mixed
in with the ore and sufficient water added to yield a thin slurry. The steam was slowly turned on in the jacket and the paste mixed for a period of 5 hours. During the reaction period, the temperature of the pot contents ranged from 250° F. (121° C.) to 300° F. (149° C.). Several times during the reaction period, the reaction became violent and the charge foamed badly so that the steam pressure was reduced or shut off entirely to allow the reaction mixture to cool down. After the 5-hour reaction period was completed, the charge was dumped into 100 gallons of hot (200° F.) water in an agitated stainless steel tank. The slurry was leached for one hour and then filtered in two vertical, plastic-lined, pressure filters. The filter cakes were washed with two 10-gallon portions of hot (200° F.) water to remove as much of the soluble cesium values as possible. A total of 97.5 pounds of cesium alum containing 23.5% Cs₂O was obtained for an 89.8% cesium recovery.

A batch of 115 pounds of cesium alum prepared as described above was slurried in 50 gallons of hot (200° F.) distilled water and a slurry of 24 pounds of calcium hydroxide in 10 gallons of distilled water was slowly added. After digesting for 30 minutes the slurry was filtered on vertical pressure filters, and the cake was washed with 40 gallons of hot distilled water. A total of 140 pounds of wet calcium sulfate-aluminum hydroxide hydrate cake containing 0.19% residual cesium oxide was recovered from the filters. A cesium recovery of 99% was obtained in this operation.

The cesium sulfate solution obtained as just described was combined with additional cesium sulfate solution to yield a total of 158 gallons of liquor containing 46.7 pounds of cesium oxide. This solution was treated with 70.0 pounds of barium hydroxide octahydrate dissolved in about 15 gallons of distilled water to convert the cesium sulfate to cesium hydroxide and form a precipitate of barium sulfate. Following this step, the slurry was filtered on a Sweetland filter and the cake washed with 35 gallons of hot distilled water. A total of 74 pounds of wet barium sulfate cake was obtained containing 0.75% cesium oxide. By difference, there was 46.2 pounds of cesium oxide remaining in the filtrate for a recovery of 98.8% in this operation. This dilute cesium hydroxide solution was then concentrated and carbonated to convert it to cesium carbonate liquor and also to precipitate any excess barium hydroxide as barium carbonate. An over-all recovery of 87.8% of the cesium values in the ore was obtained as a 98.5% pure cesium carbonate.

Example 2

A reaction vessel loaded with 1750 pounds of palladite ore and 1750 pounds of 102% sulfuric acid was run in. Sufficient water was run in to maintain a workable slurry while ore decomposition was in progress.

Thereafter, the contents of the reaction vessel were dumped into 2000 gallons of hot (200° F.) water, leached under agitation for 30 minutes, and filtered. The filter cake was thoroughly washed with 800 gallons of hot (200° F.) water. Analysis of the washed residue indicated a cesium extraction of 95.0%. The filtrate and wash water were cooled to 90° F. to crystalize out about 2000 pounds of cesium alum. This cesium alum was then recrystallized four times, using about 1000 gallons of water for each recrystallization to yield a 99.9% pure product.

The purified alum then was dewatered and the cesium alum was dumped into 800 gallons of hot (180° F.) deionized water containing 375 pounds of calcium hydroxide. After about 3 hours digestion at 180° F., the slurry temperature was lowered to 150° F. and the slurry was filtered. The calcium sulfate-aluminum hydroxide hydrate filter cake was washed with deionized water to remove entrainment. The residual cesium oxide content of the filter cake was 0.67%. At this point, the over-all recovery of cesium values from the ore was 84.8%.

The resulting cesium sulfate solution was concentrated to reduce the volume to about 800 gallons, and to it was added a hot solution of 530 pounds of barium hydroxide octahydrate in 250 gallons of deionized water. This slurry of barium sulfate in cesium hydroxide solution was then filtered and the barium sulfate cake was washed with 500 gallons of hot deionized water. The residual (absorbed) cesium oxide of this filter cake was 1.47%. Following this filtration, the cesium hydroxide solution was carbonated and concentrated to yield a cesium carbonate liquor which was then polish-filtered to remove barium carbonate and dried. A total yield of 424 pounds of 99.9% cesium carbonate was obtained, corresponding to an over-all yield of 77%.

I claim:

1. The process for preparing cesium sulfate which comprises treating cesium alum with calcium hydroxide in an aqueous medium, the calcium hydroxide being employed in an amount sufficient to stoichiometrically convert the cesium alum to a mixture containing a solution of cesium sulfate and insoluble aluminum hydroxide and insoluble calcium sulfate, and separating a soluble cesium sulfate solution consisting essentially of water and cesium sulfate.

2. The process of claim 1 in which the separated soluble cesium sulfate solution is evaporated to dryness to recover anhydrous cesium sulfate.

3. The process for preparing cesium compounds which comprises treating cesium alum with calcium hydroxide in an aqueous medium, the calcium hydroxide being employed in an amount sufficient to stoichiometrically convert substantially all of the cesium alum to a mixture containing a solution of cesium sulfate, insoluble aluminum hydroxide and insoluble calcium sulfate, said solution consisting essentially of water and cesium sulfate, treating said cesium sulfate solution with barium hydroxide to form an aqueous mixture containing soluble cesium hydroxide and insoluble barium sulfate, and separating an aqueous solution of soluble cesium hydroxide consisting essentially of water and cesium hydroxide.

4. The process for preparing cesium compounds which comprises treating cesium alum with calcium hydroxide in an aqueous medium, the calcium hydroxide being employed in an amount sufficient to stoichiometrically convert substantially all of the cesium alum to a mixture containing a solution of cesium sulfate, insoluble aluminum hydroxide and insoluble calcium sulfate, said solution consisting essentially of water and cesium sulfate, treating said cesium sulfate solution with barium hydroxide to form an aqueous mixture containing soluble cesium hydroxide and insoluble barium sulfate, said cesium hydroxide being dissolved in a solution consisting essentially of water and cesium hydroxide, and carbonating the aqueous solution of soluble cesium hydroxide to form a solution consisting essentially of water and soluble cesium carbonate.

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