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(54) **OXIDATION OF AMERICIUM IN ACIDIC SOLUTION**

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(57) **ABSTRACT**

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A process is for oxidizing americium(III) to americium(VI) includes providing a aqueous acidic composition comprising americium(III) and a mineral acid and exposing the composition to ozone and silver ion under conditions suitable for oxidation of the americium(III) to americium(VI). Nitric acid is a suitable mineral acid for the process. Extraction of the americium from the silver is possible using organic phosphonate extractant.

OXIDATION OF AMERICIUM IN ACIDIC SOLUTION

PRIORITY CLAIM TO A RELATED APPLICATION

[0001] This application claims the benefit of copending U.S. Provisional Patent Application No. 62/000,868 entitled "Oxidation of Americium in Acidic Solution," filed May 20, 2014, which is incorporated by reference herein.

STATEMENT REGARDING FEDERAL RIGHTS

[0002] This invention was made with government support under Contract No. DE-AC52-06NA25396 awarded by the U.S. Department of Energy. The government has certain rights to in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates generally to actinide separation and more particularly to oxidation of americium in acidic solution to facilitate a separation of americium from other elements including but not limited to fission products and other actinides.

BACKGROUND OF THE INVENTION

[0004] The presence of long-lived radioisotopes of americium ("Am") and radio-decay of particular isotopes of Am (such as Am-241 to the long-lived Np-237 and Am-243 to Pu-239) contribute to the thermal loading in a repository and to the radiotoxicity of used nuclear fuel. A simple method to separate Am from fission product lanthanides could reduce the cost of separation options for partitioning minor actinides from used nuclear fuel.

[0005] One approach for separating the americium present in used nuclear fuel involves oxidization of Am(III) to Am(IV), Am(V), or Am(VI). These higher oxidation states are accessible for Am but not for the lanthanides or for the curium present in used nuclear fuel. Am(VI) in the form of AmO_2^{2+} , for example, can be separated selectively from trivalent lanthanides (Ln(III)) using a range of techniques based on oxidation state discrimination. A challenge with this approach involves identifying oxidants that are suitable for forming and stabilizing the Am(IV), Am(V), and/or Am(VI) long enough to perform the separation. Sodium bismuthate (NaBiO_3), for example, has been reported to oxidize Am(III) selectively to Am(VI) in nitric acid solutions. The Am(VI), which is in the form of AmO_2^{2+} , is extracted selectively from nitric acid using an organic extractant such as tributylphosphate (TBP) or diamylamylphosphonate (DAAP). Drawbacks to using sodium bismuthate as an oxidant are its low solubility (it must be used as a slurry), and slow oxidation kinetics. The solid bismuthate salts must be filtered from the process solution before proceeding with other processing steps.

[0006] If ozone (O_3) could be used instead of sodium bismuthate to oxidize Am(III) selectively to Am(VI), the bismuthate filtration step would be eliminated. Ozone is a gaseous oxidant, and it decomposes to form oxygen (which is also gas). Therefore, the use of ozone would not result in additional by-products that would have to be treated along the processing stream. Ozone is relatively inexpensive to prepare and is already used routinely for other oxidation processes on a large scale (e.g. for treating wastewater on an industrial scale). Although the oxidation of americium(III) to ameri-

um(VI) using ozone is thermodynamically favorable, in practice, it has been demonstrated that ozone is not a suitable oxidant for oxidizing Am(III) to Am(VI) in acidic solution.

SUMMARY OF THE INVENTION

[0007] To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, a process is provided for oxidizing americium(III) to americium(VI). The process includes providing a aqueous acidic composition comprising americium(III) and a mineral acid and exposing the composition to a combination of ozone and silver ions under conditions suitable for oxidation of the americium(III) to americium(VI). Combinations of ozone with cobalt ion, or ozone with cerium ion are also expected to be suitable for the oxidation of americium(III) to americium(VI).

[0008] A process for separating americium from a lanthanide is also provided. This process includes providing an aqueous acidic composition comprising americium(III) and at least one lanthanide and/or curium, exposing the aqueous acidic composition to silver ions and ozone under conditions suitable for oxidizing the americium(III) to americium(VI), and thereafter separating the americium(VI) from at least one lanthanide, curium, and/or silver.

[0009] A composition is also provided that comprises a homogeneous mixture of silver ions, ozone, nitric acid, and water.

DETAILED DESCRIPTION

[0010] An embodiment process is provided for oxidizing Am(III) to Am(IV) in nitric acid that uses ozone in combination with silver ions. The ozone together with the silver ions provide a suitable combination for oxidizing americium(III) to americium (VI) in acidic solution.

[0011] An embodiment process is also provided for separating americium from a composition that includes americium along with other components such as, but not limited to, other actinides (curium, for example), and lanthanides. This embodiment process includes using silver ions and ozone to oxidize the americium(III) to americium(VI) in the composition followed by separating the americium(VI) from the other components.

[0012] The oxidation reactions described herein may be performed using aqueous mineral acid. Mineral acids include nitric acid, hydrochloric acid, perchloric acid, phosphoric acid, sulfuric acid, and mixtures of these acids. In an embodiment, the oxidation of Am(III) to Am(IV) was demonstrated using nitric acid. The americium is present typically in these aqueous mineral acids as a plurality of radioisotopes of americium, including but not limited to radioisotope Am-243, which has a half life ($t_{1/2}$) of 7380 years. The concentration of the nitric acid in these solutions was in a range of from 0.001 molar to 6 molar.

[0013] The oxidation state of the americium was determined spectrophotometrically using a CARY 6000i or a CARY 5-UV-vis-NIR spectrophotometer. Americium concentrations were standardized in 2 M K_2CO_3 using a characteristic absorbance band for Am(III) at 508 nm with a molar absorptivity (ϵ) of $330 \text{ M}^{-1} \text{ cm}^{-1}$. The absorbance bands in nitric acid are shifted slightly relative to the bands in carbonate solutions, and molar absorptivities for Am(III) ($\epsilon(503$

nm)=386.7), Am(V) ($\epsilon(513 \text{ nm})=72.5$), and Am(VI) ($\epsilon(666 \text{ nm})=24.6$) in nitric acid solutions were adopted from the literature.

[0014] Ozone was produced using ozone generator model HC-30 (OZONE SOLUTIONS). This ozone generator uses pure O_2 as the feed source and can produce from 5 weight percent ozone to 12 weight percent ozone at a flow rate of 1-10 liters per minute. The maximum concentration of ozone for long-term operations was approximately 10%; higher concentrations of ozone could be produced for short-term operation. The ozone concentration was quantified using in-line ozone monitor model UV-106H (OZONE SOLUTIONS). The ozone monitor determined the concentration of ozone via UV absorbance. A slip-stream of ozone was sparged through 1-2 ml of an americium solution in a 4 ml borosilicate vial using a $\frac{1}{8}$ inch TEFLON needle. Aliquots were removed periodically for analysis by UV spectrometry and were replaced after the analysis.

[0015] An initial set of tests were performed to verify the unsuitability of ozone alone as an oxidant for oxidizing Am(III) to Am(VI) in nitric acid solutions. Nitric acid having a concentration in a range of from 0.001 M to 1 M nitric acid was used. After four hours of testing, no evidence of oxidation of Am(III) oxidation to Am(VI) in 0.001 M nitric acid to 1 M nitric acid with ozone concentrations up to 10 weight percent was observed via UV-vis spectroscopy. These test results are consistent with what others have found, namely that ozone alone is not a suitable oxidant for oxidizing Am(III) to Am(VI) in acidic solution.

[0016] Having confirmed the reported lack of suitability of ozone alone for oxidation of Am(III) to Am(VI) in acidic solution, we thought that it might be possible to find some combination of ozone with one or more materials that together would be suitable for oxidizing Am(III) to Am(VI) in acidic solutions. We found that a combination of ozone with silver ions was suitable for oxidizing Am(III) to Am(VI) in acidic solutions. Reaction of Am(III) with this combination of ozone with silver ions resulted in quantitative oxidation of the Am(III) to Am(VI) in nitric acid solutions in a range of 0.01 M nitric acid to 3 M nitric acid solution. We also found that at least partial oxidation was achieved in 6 M nitric acid solutions. We expect that other metal ions besides silver ions, in combination with ozone, will also be suitable for oxidizing americium(III) to americium(VI). One such combination expected to be suitable is a combination of ozone with cobalt ions (e.g. cobalt(II) and/or cobalt(III)). Another such combination is a combination of ozone with cerium ions (e.g. cerium(III) and/or cerium(IV)).

[0017] The rate of oxidation of Am(III) to Am(VI) with ozone in the presence of silver ions is dependent on the concentration of the nitric acid. The rate of oxidation of Am(III) to Am(VI) in nitric acid solution appears to be slower at higher concentrations of nitric acid. For example, 96% of the Am(III) was oxidized to Am(VI) after 3 hours in 0.01 M HNO_3 . By contrast, 86% of the Am(III) was oxidized to Am(VI) after 24 hours in 1M HNO_3 . Only 25% of the Am(III) was oxidized to Am(VI) after 24 hours in 3M HNO_3 .

[0018] When the flow of ozone to the solution was stopped, the Am(VI) underwent a reduction to Am(III). The reduction was stepwise; the Am(VI) species present in solution first undergoes reduction to Am(V). The Am(V) undergoes a slower reduction to Am(III).

[0019] The rate of reduction of Am(VI) appears to follow pseudo-first order kinetics. The rate of reduction varies with

the concentration of the nitric acid. In dilute nitric acid solutions, the Am(VI) begins to reduce immediately after stopping the flow of ozone to the reaction mixture. Approximately 40% of the Am(VI) reduces to Am(V) during the first 15 hours. The reduction rates in 0.01 M HNO_3 are comparable to the reduction rates that we measured in 1M HClO_4 . At higher (3 molar, for example) acid concentrations, there was an induction period of approximately 5 hours before the Am(VI) begins to reduce, and only 15% of the Am(VI) reduces to Am(V) in the first 15 hours and only 25% over the first 24 hours.

[0020] Once the Am(VI) undergoes reduction, the reduced species of Am(III) can be re-oxidized to Am(VI) if the flow of ozone to the solution, which also contains silver ions, is restarted.

[0021] Various extraction and/or ion exchange techniques may be used for separating americium. After performing an oxidation of Am(III) to Am(VI) in a nitric acid solution using ozone and silver ions, we performed a partial extraction of the Am(VI) from the solution using a dilute solution of the extractant diamylamylphosphonate (“DAAP”) in dodecane. Alternatively, Am(VI) may be separated from trivalent lanthanides and/or curium using a column of an ion exchange resin—the Am(VI) would be preferentially adsorbed to the resin while the trivalent lanthanides and/or curium would preferentially elute and remain in solution as cationic species in solution.

[0022] Extraction of hexavalent actinides (i.e. An(VI)) from acidic solutions using dilute solutions of organic phosphonates in organic solvents (kerosene, dodecane, for example) has been reported. Tributyl phosphate (“TBP”), dibutylbutylphosphonate (“DBBP”) and DAAP have been tested for extraction of Am(VI) from nitric acid (after oxidation of Am(III) to Am(VI) using a slurry of sodium bismuthate). After performing an oxidation of Am(III) to Am(VI) using ozone and silver ions in aqueous nitric acid, the Am(VI) was extracted (i.e. separated) using DAAP. The separation of the Am(VI) was performed as follows: ozone was bubbled through a 3 molar aqueous nitric acid solution that contained americium(III). This resulted in oxidation of the americium(III) to americium(VI). A solution of 1 molar DAAP in dodecane was pre-equilibrated with a 3 M aqueous nitric acid solution containing silver ions. Following the oxidation, an equal volume of the 1 molar solution of DAAP in dodecane was added and the resulting solution was mixed for about 15 seconds using a vortex mixer. The phases were allowed to separate and then were placed into separate vials. An analysis by UV-Vis spectroscopy indicated that approximately 30% of the americium(VI) had been extracted.

[0023] We also tried to extract silver ions from nitric acid solutions using DAAP. A 1M solution of DAAP in dodecane was pre-equilibrated with a solution of nitric acid and silver ions. After the pre-equilibration, solutions of nitric acid and silver ions were contacted with an equal volume of the pre-equilibrated 1M solution of DAAP in dodecane. A series of extractions were performed using various concentrations of HNO_3 , up to a maximum of about 8M HNO_3 . Sometimes extraction procedures included mixing for 15 seconds using a vortex mixer. Other times, extraction procedures included stirring on a laboratory stir plate for 24 hours. The concentration of silver ions was quantified using ICP-AES (“Inductively Coupled Plasma-Atomic Emission Spectroscopy”). For this series of analyses, the silver containing samples were diluted to the appropriate concentration with 2% HNO_3 and

analyzed on a Thermo Electron iCAP 6500 DUO ICP connected to a Cetac ASX520 autosampler. We found that DAAP extracted less than 0.1% of the silver, which indicates that DAAP does not significantly extract silver(I). Further support was found when we prepared a solution containing silver ions and nitric acid, exposed the solution to ozone (to oxidize the silver(I) to a higher oxidation state (silver(II) and/or silver(III)), and then added some of the 1M DAAP/dodecane solution and mixed everything for 15 seconds using a vortex mixer. After the phases were allowed to separate, they were partitioned into separate vials and examined spectroscopically. No silver(II) was detected in either the phase with DAAP/dodecane or the nitric acid phase. Prior experiments show that silver(I) is not extracted with DAAP/dodecane while americium was extracted into the DAAP/dodecane phase. These results indicate the ability to separate Am(VI) from silver ions using DAAP.

[0024] Although the present invention has been described with reference to specific details, it is not intended that such details should be regarded as limitations upon the scope of the invention, except as and to the extent that they are included in the accompanying claims.

What is claimed is:

1. A process for oxidizing americium(III) to americium(IV), comprising
 - providing an aqueous acidic mixture comprising americium(III) and a mineral acid, and
 - exposing the mixture to a combination of ozone and metal ions selected from silver ions, cobalt ions, cerium ions, or a combination of the metal ions, under conditions suitable for oxidation of americium(III) into americium(VI).

2. The process of claim 1, wherein the mineral acid is selected from nitric acid, hydrochloric acid, perchloric acid, phosphoric acid, sulfuric, or a combination thereof.

3. The process of claim 1, wherein the aqueous acidic mixture comprises a trivalent lanthanide.

4. An aqueous composition comprising a homogeneous mixture of americium, ozone, nitric acid and one of either silver ions or cobalt ions.

5. The composition of claim 4, wherein the silver ions comprises silver(I).

6. The composition of claim 4, wherein the silver ions comprises silver(II).

7. The composition of claim 4, wherein the silver ions comprise silver(III).

8. The composition of claim 4, wherein the cobalt ions comprise cobalt(II).

10. The composition of claim 4, wherein the cobalt ions comprise cobalt(III).

11. A process for separating americium from a composition including at least one lanthanide, comprising:

- providing an aqueous acidic composition comprising americium(III) and at least one lanthanide,

- exposing the aqueous acidic mixture to ozone and metal ions selected from silver ions, cobalt ions, and cerium ions, under conditions suitable for oxidizing the americium(III) to americium(VI), and

- separating the americium(VI) from the at least one lanthanide and from said metal ions.

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