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A TEST FOR OXIDATION OF ACTINIDES IN CONCENTRATED CsF SOLUTIONS*

H. P. Holcomb
Savannah River Laboratory, E. I. du Pont de Nemours & Company,
Aiken, South Carolina 29801

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Abstract—A chemical test was devised to differentiate between tracer concentrations of the actinide (III) state and higher oxidation states in 12–15 M CsF. Attempts to oxidize Cm(III) and Cf(III) with sodium perxenate in this matrix were unsuccessful although Am(III) was readily oxidized.

INTRODUCTION

Transplutonium elements normally exhibit only an oxidation state of (III) in aqueous solutions; Bk(IV), Am(V) and Am(VI) are exceptions. Although direct preparation of Cm(IV) in solution has not been reported, this oxidation state has been prepared by the oxidation of CmF_3 with F_2, and then dissolution and stabilization of the Cm(IV) in highly concentrated solutions of alkali fluorides.(1) Am(IV) has been stabilized in highly concentrated solutions of ammonium and alkali fluorides.(2) Am(VI) and U(V) have been stabilized with fluoride.(3,4) Californium has not been reported in oxidation states higher than Cf(III). If, however, a higher oxidation state of californium can be prepared, it should have properties similar to those of Am(IV) and Cm(IV).

To explore the possibility of formation of higher oxidation states of curium and californium in solution, three conditions were desired: (1) a matrix with a high concentration of a ligand, such as fluoride, that would help stabilize tetravalent actinides; (2) an oxidant with a high oxidation potential that is relatively stable and easy to use; and (3) a test for successful oxidation that should be applicable on a tracer scale to conserve limited amounts of transcurium actinides and to avoid complicating radiation effects caused by the high specific activity of the available curium and californium isotopes (^{244}Cm and ^{252}Cf). The first two conditions appeared to be met by using 12–15 M CsF solutions as the matrix and sodium perxenate (Na_4XeO_6)(5,6) as the oxidant. To meet the third condition, a tracer-scale test applicable in the concentrated CsF matrix was developed. This test is based on the ability of CaF_2 to carry trivalent actinides while leaving in solution tetra-, penta- and hexavalent actinides.(7,8)

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Americium tracer in concentrated solutions of CsF was used to determine the conditions necessary for oxidation, for stabilization of the oxidized state, and for testing a method at tracer scale for the identification of the higher oxidation state, (V) or (VI). Tracer concentrations of Pu(IV) and Np(V) in concentrated CsF solutions were used similarly to test the behaviour of the (IV) and (V) states, respectively. Although macro quantities of trivalent actinides are relatively insoluble in fluoride solutions, tracer quantities are soluble in CsF.

EXPERIMENTAL AND RESULTS

Reagents and solutions

Sodium perxenate, Na_4XeO_6: Peninsular ChemResearch, Gainesville, Florida.

Caesium fluoride, CsF: A 15 M CsF solution was prepared by dissolving an appropriate quantity of the salt (99+ per cent pure) in water. This solution was filtered; then ozone (approximately 1 per cent by volume O_3 in O_2) was bubbled through the solution for 6–7 hr to oxidize impurities that could cause reduction.

Actinide tracer solutions: Caesium fluoride solutions containing actinide tracers were prepared by pipetting small aliquots of the tracer solution into the CsF. After thorough mixing, the solution was centrifuged and a diluted aliquot was counted for alpha activity (disintegrations/min).

Calcium fluoride, CaF_2: J. T. Baker Chemical Co., Phillipsburg, New Jersey. CaF_2 was treated to remove oxidizable impurities.(8)

Sorption of americium by CaF_2

About 20 mg of solid CaF_2 was added to 1 ml of 15 M CsF containing $2{\cdot}20 \times 10^7$ d/m of Am(III) tracer. This mixture was shaken mechanically for 30 min and then centrifuged for 30 min; the supernate was analysed for americium by alpha counting. This cycle was repeated three times.

A similar test was made with Am(VI) tracer prepared by a silver-catalysed persulphate oxidation of Am(III).(3) Any Am(III) remaining in the Am(VI) tracer solution was coprecipitated with LaF_3. The 15 M CsF solution contained $2{\cdot}30 \times 10^7$ d/m of Am(VI). As seen in Table 1, Am(III) was effectively removed from the concentrated CsF by CaF_2, while most of the Am(VI) remained in solution.

TABLE 1.—SORPTION OF TRACER AMERICIUM BY CaF_2 IN CsF SOLUTION

Mix-centrifugation cycle	Americium activity not sorbed (%) Am(III) tracer	Am(VI) tracer
First	13	74
Second	10	66
Third	9	64
Fourth	4	46

Oxidation of Am(III) *with sodium perxenate*

In another test, perxenate was shown to be an effective oxidant for the Am(III) to Am(V) or Am(VI) transition in 12 M CsF. Ten milligrams of solid Na_4XeO_6 was added to 1 ml of a CsF solution containing 100 μl. of concentrated HF and $2{\cdot}28 \times 10^7$ d/m of Am(III) tracer. The final solution (~12 M CsF) was mixed for 30 sec to allow the perxenate to react, 20 mg CaF_2 was added, and the mixture subjected to the mix-centrifugation cycle. The results of this test and a blank control test are summarized in Table 2.

TABLE 2.—OXIDATION OF Am(III) TRACER WITH PERXENATE IN CsF

Mix-centrifugation cycle	Americium activity not sorbed (%) Am(III) tracer	 Am(III) tracer $+Na_4XeO_6$
First	15	85
Second	4	75
Third (after 10 days)	—	53

A similar test with Na_4XeO_6 added to Am(III) tracer in 15 M CsF with no added HF showed that 61 per cent of the Am(III) was oxidized even in the absence of acid. (In a control experiment without perxenate, only 25 per cent of the initial activity was not sorbed.) These results verify that sodium perxenate is a powerful oxidant in this highly salted system. Am(V) or Am(VI) formed directly in CsF was stable.

Reduction of Am(V) and Am(VI)

To determine whether the oxidized americium could be reduced readily in the CsF solution, the final solution of Am(V) or Am(VI) from the perxenate test with no added HF was reacted with five successive 50-μl. portions of 3% H_2O_2. After the addition of each portion of H_2O_2, which was followed by the CaF_2 mix-centrifuge cycle, the CsF solution contained respectively 92, 94, 88, 70 and 2 per cent of the americium as Am(V) or Am(VI).

The amount of oxidized americium increased after the addition of the first portion of reductant, apparently because of the additional contact of Am(III) with excess perxenate. However, after addition of sufficient H_2O_2, the residual perxenate was reduced and then the oxidized americium was reduced readily.

A similar solution of americium containing 10 μl. of concentrated HF had only 5% Am(V) or Am(VI) after the addition of 50 μl. of 3% H_2O_2 and subsequent CaF_2 treatment. In this test, the acid apparently reacted with excess perxenate.

Sorption of plutonium and neptunium by CaF_2

Approximately 20 mg of CaF_2 was slurried for 30 min in 1 ml of 15 M CsF containing $1{\cdot}67 \times 10^7$ d/m of Pu(IV) tracer. After centrifuging for 30 min, the supernate contained 98 per cent of the plutonium. Hydroxylamine hydrochloride catalysed with Fe(III) was added to reduce Pu(IV) to Pu(III), which would be sorbed by CaF_2. However, reduction was quite slow, and after a mix-centrifugation cycle, the supernate still contained 85 per cent of the plutonium. After a second treatment with reductant, mixing, and centrifuging, the supernatant solution still contained 66 per cent of the plutonium. The reduction of Pu(IV) to Pu(III) was apparently inhibited by the strong fluoride complexing.

When Np(V) tracer was mixed with a slurry of CaF_2 in a 15 M solution of CsF and centrifuged as in the Pu(IV) tests, none of the neptunium was sorbed.

In summary, Pu(IV) and Np(V), like Am(V) or Am(VI), were not sorbed by CaF_2 in concentrated CsF solutions. In contrast, Pu(III), Am(III) and Cm(III) were sorbed. This sorption behaviour was used as the analytical test for differentiating between the trivalent and any higher oxidation state in the attempted oxidation of curium and californium.

Attempted oxidation of Cm(III) *and* Cf(III) *with sodium perxenate*

Attempts to oxidize Cm(III) in 15 M CsF with Na_4XeO_6 to a stable Cm(IV) were not successful. No indication of a higher oxidation state was obtained when HF was added to decrease the basicity of the CsF solution and increase the oxidation potential of the perxenate. A similar experiment at 100°C gave no evidence of Cm(IV).

An attempt to oxidize Cf(III) (5×10^5 d/m in 1 ml of 15 M CsF) by Na_4XeO_6 at 100°C was not successful. Following the CaF_2 mix-centrifugation cycle, the supernate was counted for spontaneous fission neutrons in a neutron counter,(9) so the test could be made with much less californium than would be required for alpha counting.

Further work is planned to examine the possible oxidation of curium and californium in other systems in which Na_4XeO_6 or alternative oxidants would have a higher oxidation potential.

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