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ELECTROCHEMICAL REDUCTION OF ACTINIDE IONS IN AQUEOUS SOLUTION

APPLICATIONS TO SEPARATIONS AND SOME INTERMETALLIC COMPOUND SYNTHESIS

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Electrochemical reduction of heavy elements from aqueous solution to amalgams was studied by radiopolarography and radiocoulometry. Mechanism of actinide reduction on a mercury pool is discussed through simulation techniques. Special emphasis is placed on redox reactions and potentials, kinetics of the process and effect of acetate and citrate ions as complexing agents. Three groups of actinides have been found. The first group represents actinium and from uranium to berkelium. Reduction occurs in the experimental conditions via an irreversible 3-0 process. The second group consists of the elements from fermium to nobelium, which are reduced in non-complexing solutions, or with acetate ions, similarly as barium and radium, via a reversible 2-0 reaction. Finally, californium and einsteinium behave as intermediate elements. It is noticeable that such groups are also observed in the actinide series by studying the structure of the trivalent aqua ions. On the basis of the above mentioned investigations of actinides and lanthanides several examples of electrochemical application are presented. Californium has been separated from preceding transuranium and lanthanide elements (except europium) by electrochemical reduction to amalgams in acetic solution. Separation factors from 25–90 are achieved with appropriate cathodic potentials. Similarly, this element could be separated from several heavier actinides with citric media. The electrochemical preparation of mixed uranium–nickel and uranium–tin amalgams from aqueous acetate solutions is investigated. The dependence of redox potentials of mixed amalgams on different atomic ratio U : Ni and U : Sn in amalgams is measured. The large shift of redox potentials of mixed amalgams to the positive direction is detected when the atomic ratio U : Ni or U : Sn in amalgams reaches 1 : 5. The thermal distillation of mercury from mixed amalgams with different U : Ni and U : Sn atomic ratios was carried out and the products were identified by chemical analysis and X-ray diffraction. The intermetallics UNi_5 and USn_3 were prepared from mixed amalgams with the atomic ratios U : Ni = 1 : 5 and U : Sn = 1 : 3. The uranium and neptunium amalgams are prepared by electrolysis of aqueous acetate solutions and are processed into metals or nitrides U_2N_3, NpN by thermal distillation of mercury in vacuum or in nitrogen atmosphere.

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Introduction

Radioelectrochemical reactions of actinides have been studied by comparison with lanthanides. First reviews on electrochemical properties,[1] radiopolarography[2,3] and radiocoulometry[3,4] have been published, but more recent data were obtained on heavy elements: Md[5,6] and No.[7,8] Moreover, the structure of the aqua ion, especially trivalent ions, has been studied[9-15] and accurate redox potential are available[16] up to californium. Therefore, it is now possible to draw a more complete and exhaustive picture of electrochemical properties of heavy elements and to discuss and understand more precisely the reduction mechanism and kinetic differences.

Finally, best conditions for applications are more easily deduced.

After a bried review of the radiopolarographic and radiocoulometric data, we will discuss the reduction mechanism and present new results about electrochemical separation procedures, preparation of amalgams and synthesis of some actinide intermetallics.

Radiopolarography

Nine actinides have been studied by radiopolarography: Ac,[17,18] U,[19] Am,[2,20] Cm,[2,20] Bk,[2] Cf,[2,20] Es,[2] Fm[2] and Md.[6] Half-wave potential data are reported in Table 1 with corresponding media, pH and proposed mechanism. We also have added data corresponding to lanthanides and alkaline earth ions as comparison.

From the analysis of these data and effect of complexing agents like citrate ions, it is concluded that Ac, U, Am, Cm and Bk are reduced to the amalgam via a 3 → 0 irreversible process.[2] The observed uranium wave at −1.65 V* has been interpreted by the authors[18] as a 3 → 2 reduction reaction. However, in light of our present knowledge of thermodynamic properties of uranium 3/2 redox potential is expected to be −4.7 V,[21] we should retain a 3 → 0 reaction.

Consistently with the proposed reduction mechanism, the observed waves are shifted to high negative potentials when citrate ions are present in the electrolyte.[3]

On the other hand, in the case of Fm[2,5,22] Md[5,6] and No,[8] data are clearly consistent with a 2 → 0 mechanism.

First of all, we have a logarithmic transformed wave with about 30 mV slope.[2,5,8] But, of course, this is not sufficient to conclude on a 2 → 0 mechanism since with such a slope an irreversible 3 → 0 reaction could be stated. More convincing is the fact that measured shift with citrate ions (60 to 100 mV) coincides with those obtained with divalent ions such as Eu^{2+},[3] Mn^{2+},[2] Ca^{2+},[3,23] or Ba^{2+}.[24] It is in agreement with

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***All potentials are with reference to the standard hydrogen electrode.**

Table 1
Radiopolarographic data of some actinide, lanthanide, and alkalino-earth ions in non-complexing media

Element	Medium	pH	$E_{1/2}$ /S.H.E.	Mechanism	Reference
Ac	0.1M $LiClO_4$	2.5/3.2	−1.96 ± 0.02	3 → 0 irr	18
U	0.005M $(CH_3)_4$ Cl_4	1.5/3	−1.65 ± 0.05	3 → 0 irr	19
Am	0.1M LiCl	1.8/2.25	−1.60 ± 0.01	3 → 0 irr	2, 20
Cm	0.1M LiCl	1.8/2.25	−1.61 ± 0.01	3 → 0 irr	2, 20
Bk	0.1M LiCl	1.8/2.25	−1.63 ± 0.01	3 → 0 irr	2
Cf	0.1M LiCl	1.8/2.25	−1.51 ± 0.01	3 → 0 r	2, 20
Es	0.1M LiCl	1.8/2.25	−1.46 ± 0.01	3 → 0 r	2
Fm	0.1M LiCl	2.4	−1.49 ± 0.01	2 → 0 r	2
Md	0.1M LiCl	2.4	−1.51 ± 0.01	2 → 0 r	6
Ce	0.1M $LiClO_4$	2.2/2.6	−1.84 ± 0.01	3 → 0 irr	42
Sm	0.1M $LiClO_4$	2.95/3.65	−1.72 ± 0.01	2 → 0 irr	42
Eu	0.1M $LiClO_4$	3.0/5.8	−1.711 ± 0.006	2 → 0 r	20
Gd	0.1M $LiClO_4$	4.0/5.5	−1.784 ± 0.006	3 → 0 irr	20
Tb	0.1M $LiClO_4$	3.3/3.4	−1.74 ± 0.01	3 → 0 irr	42
Ho	0.1M $LiClO_4$		−1.78 ± 0.01	3 → 0 irr	42
Yb	0.1M $LiClO_4$	2/3.5	−1.813 ± 0.006	2 → 0 irr	20
Lu	0.1M $LiClO_4$	3.5	~−1.69	3 → 0.irr	42
Ca	0.1M LiCl	3	−1.98	2 → 0	23
Ba	0.1M LiCl	1.8/5.3	−1.690 ± 0.005	2 → 0 r	24
Ra	0.1M LiCl	4	−1.625 ± 0.005	2 → 0 r	24

the calculated shift corresponding to the formation constant of the M^{II} cit-complex ($\log \beta \sim 3$).[25]

The expected shift for trivalent lanthanides and actinides is 200 mV, taking into account $Mcit_2^{3-}$ complex with $\log \beta \approx 12$[26] and a reversible reaction. Irreversible process would correspond to larger shift.

Moreover, half-wave potentials of europium or ytterbium are independent of the pH in the indicated pH ranges (Table 1). This experimental fact proves that the behaviour of divalent lanthanide and actinide ions in the neighbourhood of the cathode is not affected by hydrolysis. The absence of competing chemical reactions such as hydrolysis is also attested by the variation of the plateau height of the wave versus the square root of the mercury column above the mercury drop.[2]

Finally, all experimental observations are in agreement with a diffusion controlled 2 → 0 mechanism. They are consistent with the accepted 3/2 redox potentials.[16]

Between these two actinide groups, californium and einsteinium look like intermediate elements. From radiopolarographic experiments obtained with non-complexing media and tracer scale concentrations, the logarithmic transformed wave gives a 20 mV slope.[2] It is consistent with a reversible 3 → 0 reduction mechanism. As expected, the presence of citrate ions shifted the wave to more than 200 mV.[4]

On the other hand, polarographic data obtained with higher concentration and in presence with sulfate ions would indicate a 3 → 2 and 2 → 0 reduction mechanism.[27] This apparently contradictory result could be interpreted since the 3/2 redox potentials (−1.60 and −1.55 V respectively)[28] as well as 3/0 and 2/0 amalgamation potentials are close to each other according to actinide and lanthanide data (Table 1). Therefore, depending on the complexing agents and pH, we could first have less negative potential for the 3 → 0 reaction (with non-complexing conditions) or the 3 → 2 followed by the 2 → 0 reaction (when M^{3+} ions are complexed).

Beside the apparent reversibility of the 3 → 2 reduction reaction, a second feature has to be emphasized. The californium and einsteinium half-wave potentials are significantly less negative than the corresponding americium, curium and berkelium half-wave potentials. Part of these data could be interpreted by the increase of the standard 3/0 redox potential.[16] This corresponds to an increased reducibility of trivalent ions to divalent state as was previously remarked.[29,30] However, we could also observe that for the trivalent Cf and Es aqua ions, the number N of water molecules in the inner hydration sphere decreases from nine to eight.[13,29] Thus, according to the interaction energy with water molecules which increases with N,[31] we can understand that the reducibility to the metallic state, which needs the removal of N water molecules, is easier for Cf and Es in comparison with Am, Cm and Bk (where N ~ 9).[13,29]

Similarly, the reducibility of heavy actinides to divalent aqua ions is also ocrrelated with the change of structure of these ions: for divalent ions, the aqua structure should correspond to M = 6 water molecules[29] and for that reason the reaction:

$$An(H_2O)_N^{3+} + e^- \rightarrow An(H_2O)_M^{2+}$$

is easier for transcalifornium elements since N = 8.[13,29]

Radiocoulometry

In order to apply coulometry theory[32] to the case of elements like actinides which could (or have to) be studied at tracer scale, the general expression[3] was derived, which relates the time of half reaction τ (or the slope of the tangent at the origin to the curve c = f(t), c being the concentration of the element studied at time t of the reduction process) to different parameters characterizing the process: formal amalgamation potential E_a^0 and corresponding formal rate constant k_e^0, cathodic potential E, mercury cathode area S, diffusion coefficient D, thickness of diffusion layer δ, the number 1 and 2 in Eq. [1] refer to the aqueous and mercury phase, respectively:

$$\tau = 0.693\frac{V_1\delta_1}{SD_1}\left(1 + \frac{D_1\delta_2}{D_2\delta_1}\exp\frac{nF}{RT}(E-E_a^0) + \frac{D_1}{\delta_1 k_e^0}\exp\frac{\alpha nF}{RT}(E-E_a^0)\right) \qquad (1)$$

With such an expression, it was possible to interprete and simulate the data obtained with Am, Cm, Bk, Cf, Es and Fm with citrate media and determine kinetic parameters.[3,4] The same authors also have remarked that radiocoulometric data could be analyzed by observing the variations τ/τ_l vs. E, τ_l being the limiting value of τ when $E-E_a^0$ is sufficiently negative.

When elements are studied at the atom per atom scale, such as nobelium, it is also possible to determine the variations A(Hg)/A(init) vs. E,[8] where A(Hg) denote the amalgamated atoms and A(init) the atoms initially present in aqueous solution.

In both cases the observed variations are similar to polarographic waves. Therefore, half-wave potentials and logarithmic transformed waves are deduced.

Data obtained by radiocoulometry are summarized with references in Table 2.

Table 2
Radiocoulometric data of some actinides, Eu, Ca and Ba in acetate and citrate solutions

	$-E_{1/2}$, V/S.H.E.			
Element	Acetate, 0.10M	Reference	Citrate, 0.10M	Reference
Am	1.66	22	2.16	4
Cm	1.68	22	2.18	4
Bk			2.07	4
Cf	1.51	22, 8	1.90	3, 4
Es	1.46	8	1.76	4
Fm	1.49	5, 22	1.54	4, 5
Md	1.49	5	1.60	5
No	1.47	8	1.53	8
Eu			1.80	3
Ca			2.07	3
Ba			1.75	3

According to weak complexation with acetate ions, half-wave potential determinations with such ions are in agreement with radiopolarographic measurements in non-complexing media (Table 1). Moreover, the very small amount of atoms needed by such a method allow half-wave determination for fermium,[22,5] mendelevium[5] and nobelium[7,8] at a 10^{-16}M concentration scale.

Finally, normalyzed polarographic waves of some actinides in non-complexing media, and radiocoulometric waves, with citric complexing agent are reported in Figs 1 and 2.

Electrochemical separations of actinides

The possibility of electrochemical separation of actinides was demonstrated in several papers, especially in References 33 and 34. But electrochemical parameters for the optimal separation were not determined. Radiopolarographic and radiocoulometric

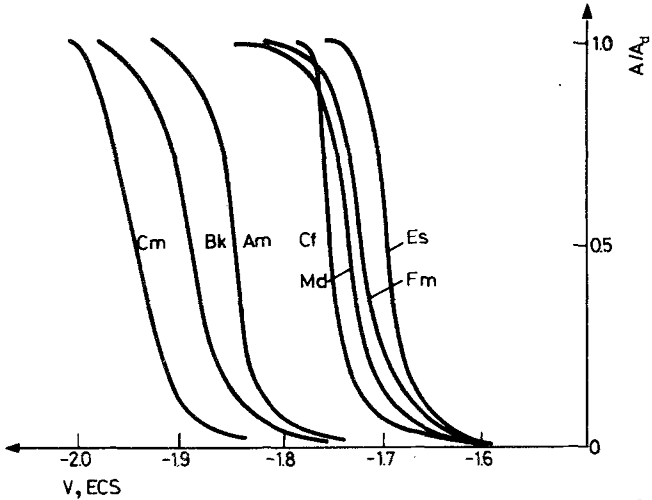

Fig. 1. Radiopolarograms of some actinides in 0.1M LiCl (pH 2.2, 25 °C)

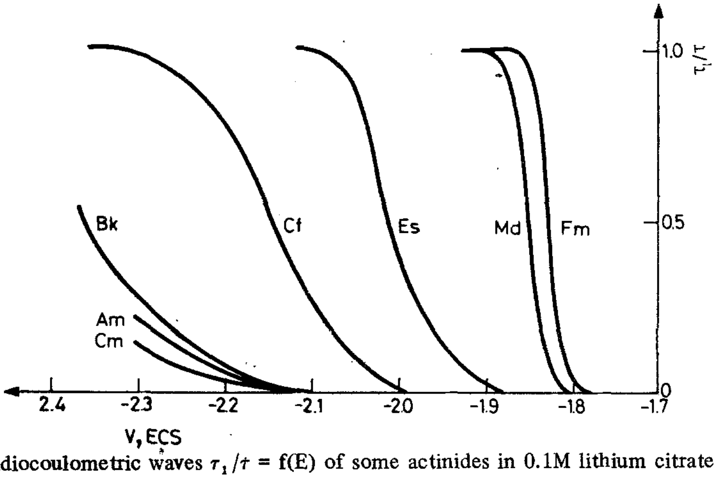

Fig. 2. Radiocoulometric waves τ_1/τ = f(E) of some actinides in 0.1M lithium citrate (pH 6)

studies allow to define experimental conditions to separate some actinides from a lanthanide and actinide mixture. Recently, electrochemical properties were successfully applied to separate californium from other f elements.[30] However, it is clear that data of Tables 1 and 2 could be used to achieve other separations.

For these purpose, two main factors have to be taken into account: cathodic potential and nature of the complexing agent. They control the kinetics of the amalgamation process (τ value) for the element considered, essentially through the difference ($E-E_a^0$) and the kinetic parameters α and k_e^0 of expression.[1]

For instance, at −1.80 V, and with acetic buffer, separation coefficients of californium versus plutonium, americium, curium, berkelium, europium and thulium are: 22, 28, 39, 54, 20 and 64, respectively, when 100 minute electrolysis are used.[30]

With 0.10M lithium citrate, excellent separations are achieved between californium from divalent or trivalent actinides (group 1 and 3 of Table 1), or divalent actinides (transeinsteinium elements with the exception of lawrencium) from trivalent actinides and the whole lanthanide series.

We would also notice that concentration of the complexing agent is modifying the $E-E_a^0$ difference, but also kinetic parameters as was previously observed.[35]

Another possibility has also been checked. It concerns the electrolysis with different supporting electrolytes. Different cations, such as alkalis, are giving amalgams with different highly negative E_a potentials. Thus, their amalgamation is controlling the cathodic potential and, consequently, the separation of actinides or lanthanides. Such a procedure has been applied for instance for the production of carrier free europium 155 at the curie level[36] and the production of weighable quantities of actinium (70 μg) after neutron irradiation of 120 mg of radium-226 and its electrochemical separation with cesium citrate as electrolyte.[37] Owing to this production and separation, weighable amounts of actinium were used to confirm the decay by ^{14}C radiation.[38]

Electrochemical synthesis of some intermetallic compounds of uranium and neptunium via amalgamation

The actinide amalgams are suitable materials for the preparation of metals, nitrides, carbides, intermetallics and other useful compounds of actinides. The preparation of uranium and plutonium metals from their aqueous solutions via amalgamation was reported.[39,40] The preparation of neptunium metal and intermetallic compounds of uranium and neptunium with nickel and tin is reported in this paper.

The electrolysis of aqueous solutions was carried out in glass cell with mercury cathode and platinum anode separated by a cation exchange membrane (soviet type MKL-1). This membrane keeps pH of catholyte at a constant value and prevents the diffusion of uranium(III) to the anode. Stock solution of 50 g/l Np(V) in 0.5M HCl was placed in cathodic compartment of the cell and Np(V) was reduced to Np(III) at a –0.2 V/NHE cathodic potential. Then, acetic buffer solution (1M HAc + 1.5M NaAc) was added to the cathodic compartment of the cell to pH 3. The concentrations of nitrate ions and hydrazine have to be less than 0.1M.[41] The current was increased to 100 mA/cm^2 and 99% of neptunium was transferred to amalgam during 1.5 hours of electrolysis. The amalgam with a maximum of 250 mg Np per ml of mercury was washed several times with 0.1M HCl and with water to the reextraction of small impurities of sodium, also reduced at the cathode during electrolysis. The drying and thermal decomposition of the neptunium amalgams was carried out in a quartz cell and in a crucible covered by aluminum oxide with argon atmosphere and vacuum. The main quantity of mercury was distilled at 350 °C. Then, the temperature was increased to 800 °C and kept constant for 2 hours. Thus, complete evaporation of mercury, followed by decomposition of neptunium mercury compounds and formation of small neptunium metal pieces (2–5 g) were achieved. No impurities of mercury and sodium except small quantities of neptunium dioxide less than 1% weight of oxygen in the metal were detected in neptunium metal by chemical spectral analysis (atomic absorption spectrophotometry, laser induced spectroscopy).

Mixed uranium or neptunium amalgams with nickel and tin were prepared by a two step electrolysis from acetic solution with a –1.8 V cathodic potential in accordance with previous discussion. Then, the catholyte was changed by a nickel or tin chloride solution and electrolysis continues with –1.0–1.1 V cathodic potential. The mixed amalgams were heterogeneous systems containing solid intermetallic particles in liquid mercury. Yields of amalgamation of actinides, nickel and tin from the solutions are close to 99%. A scheme of the intermetallic compound preparation is given in Fig. 3.

After electrolysis, the redox potential of mixed amalgam with acetic solution was measured against Ag/AgCl reference electrode. A constant value of the potential (with accuracy ±5 mV) was observed for 5–10 minutes after electrolysis. We have called this value stationary potential. Figure 4 shows the variations of the stationary potential versus atomic ratio An/Ni and An/Sn in the amalgams. That ratio was determined by diminution of metal concentration in catholyte and by the element analysis of the thermal decomposition of amalgams made by atomic absorption spectrophotometry. Phase composition of the products of thermal decomposition of amalgams was determined by X-ray diffraction analysis. Redox potentials and decomposition products were investigated also for mechanical mixtures of individual amalgams of uranium (C_U = 250 n U per ml Hg) and nickel (C_{Ni} = 300 mg Ni per ml Hg). It has been shown that mechanical stirring of individual amalgam of uranium and nickel in the solution 0.1M KCl in dimethyl sulfoxide for 6 hours gives no change of potential in these mixtures of amalgams. The potential remains equal to those of individual amalgam of uranium

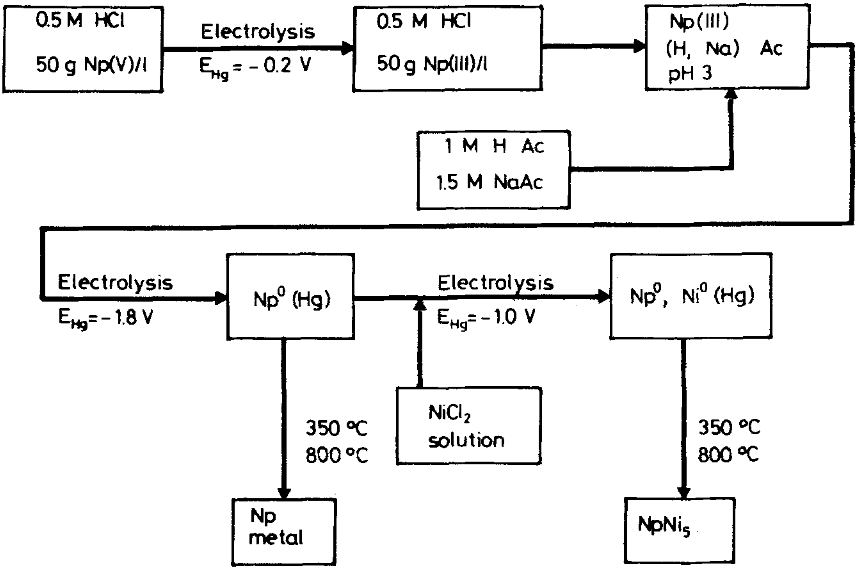

Fig. 3. The scheme of the preparation of neptunium metal and $NpNi_5$ via amalgamation

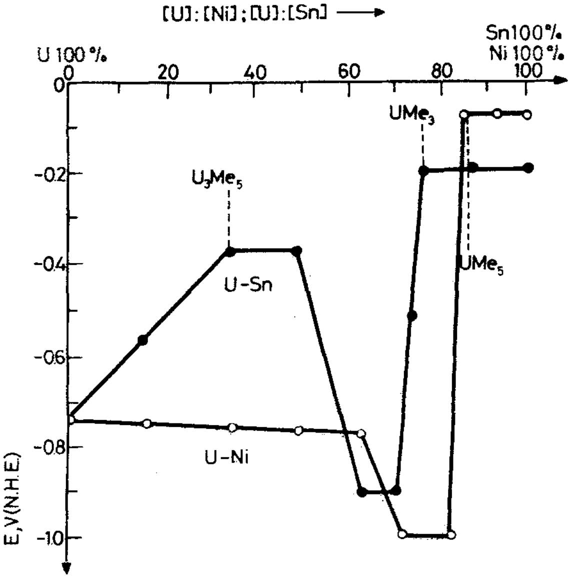

Fig. 4. Variation of redox potential of mixed amalgam on atomic ratio U:Ni and U:Sn

in the DMSO solution (−1.2 V). The properties of electrochemically prepared mixed amalgams U–Ni and U–Sn were shown to be different from those of mechanically stirred mixtures of individual uranium and nickel amalgams. It has been shown that the potential values of electrochemically prepared mixed amalgams (U, Ni) Hg and (U, Sn) Hg depend strongly on the ratio U/Ni and U/Sn in amalgams (Fig. 4). The variations of amalgam redox potentials are correlated with the disappearance of some compounds and appearance of another one in the thermal decomposition products. Especially large shifts of redox potentials are observed at the atomic ratio U:Ni = 1:5 and U:Sn = 1:3 at 800 °C, with a product containing only UNi_5 or USn_3. The same procedure applied with mechanically stirred mixture of individual amalgams of uranium and nickel (or uranium and tin) has given a mixture of metallic U and Ni powder, containing less than 1% of intermetallic U–Ni compounds.

The above mentioned difference in the behaviour of electrochemically prepared amalgams (U, Ni)Hg (U, Sn)Hg and those of the mechanically stirred mixture of individual amalgams can be explained in the following way. The formation of intermetallic compounds uranium-nickel and uranium-tin takes place during electrolysis into mercury cathode at room temperature as follows:

$$U(Hg) + nNi(Hg) \rightarrow UNi_n + nHg$$

$$U(Hg) + nSn(Hg) \rightarrow USn_n + nHg$$

Probably, the nickel or tin atoms generated by electrochemical reduction from their ions on the mercury cathode are more chemically active than nickel or tin in the form of solid particle distributed in the bulk of the individual amalgams. The absence of chemical reaction between uranium and nickel individual amalgams during their mixing and heating to 800 °C can be understood because the melting points of these metals were not achieved. Thus, electrochemical reduction of the actinide ions in aqueous solutions to amalgams and their following thermic decomposition permits to carry out the synthesis of intermetallic compounds of actinides at a temperature lower than the melting points of the metals.

Intermetallic compounds $NpNi_5$ and $NpSn_3$ were prepared by us in the same way as analogous compounds of uranium.

Conclusion

The investigations of electrochemical reduction of actinide ions to metallic state on a mercury cathode and determination of electrochemical parameters permitted to elaborate effective procedures of electrochemical separation and synthesis of intermetallic compounds of actinides. Californium could be separated from lighter or heavier actinides as well as lanthanides through electrochemical amalgamation. The above described procedure for synthesis of UNi_5, USn_3, $NpNi_5$, $NpSn_3$ could be used for the synthesis of other actinide intermetallic compounds at temperatures lower than melting points of their metals.

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