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*Short Communication*

# Separation of Plutonium from Intermediate Level Liquid Waste by Precipitation with Alkyl-Pyridinium Nitrates

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**Summary.** Plutonium as hexanitrato complex can be separated from intermediate level liquid waste by precipitation with various alkylpyridinium nitrates. The residual concentrations of Pu are below $10^{-6}$ mol/l.

**Keywords.** Separation of plutonium; Cationic surfactants.

**Abtrennung von Plutonium aus mittelaktivem flüssigen Abfall durch Fällung mit Alkylpyridiniumnitraten**

**Zusammenfassung.** Plutonium wird als Hexanitratokomplex aus einem mittelaktiven Abfall durch Fällung mit verschiedenen Alkylpyridiniumnitraten abgetrennt. Die Restkonzentrationen von Pu betragen weniger als $10^{-6}$ mol/l.

In the liquid wastes arising from reprocessing of spent power reactor fuel plutonium is present at minor concentrations only. However, on account of the very long half-lives of some isotopes, it characterizes crucially the long-time hazard potential of the wastes. Plutonium separation from the liquid wastes can be performed in the alkaline range by precipitating it as hydroxide [1], but in this process other hydroxides are coprecipitated. This is of no importance in cases where plutonium will be solidified in a stable matrix for repository storage. However, if the goal consists in returning plutonium into the nuclear fuel cycle, the separation must be selective in order to avoid impurities to be present. This is suitably done in the acid range using specific reagents.

Plutonium as $[Pu(NO_3)_6]^{2-}$ was precipitated with alkylpyridinium nitrates from nitrate bearing acid solutions [2, 3]. To test this reagents with real waste solutions, experiments were carried out with an intermediate level liquid waste concentrate. It originates from the reprocessing of spent fuels (Obrigheim nuclear power plant, FRG, cooling time 3 years) in the Karlsruhe reprocessing plant (WAK). The composition of the waste is given in Table 1. The waste contained also residua of organic compounds from the radiolyses of kerosene and tributyl phosphate.

**Table 1.** Composition of the intermediate level liquid waste concentrates

| $HNO_3 = 1.7$ mol/l | | Density = 1.2 g/ml | $Pu = 3.36 \cdot 10^{-6}$ mol/l |
|---|---|---|---|
| a) Inactive compounds | | b) Active compounds | |
| Na | 44.0 g/l | Am-241 | $2.2 \cdot 10^8$ Bq/l |
| Fe | 0.25 g/l | Ce-144 | $1.8 \cdot 10^8$ Bq/l |
| Cr | 0.06 g/l | Co-60 | $7.7 \cdot 10^7$ Bq/l |
| | | Cs-137 | $2.0 \cdot 10^8$ Bq/l |
| F | 0.4 g/l | Cs-134 | $6.5 \cdot 10^8$ Bq/l |
| Cl | 1.0 g/l | Ru-106 | $1.6 \cdot 10^9$ Bq/l |
| $SO_4$ | 2.0 g/l | Sb-125 | $2.6 \cdot 10^8$ Bq/l |
| $NO_3$ | 235.0 g/l | | |
| $C_2O_4$ | 0.05 g/l | | |

The plutonium was precipitated in 50 ml waste solution with 200 mg surfactant, which corresponds to the 20 fold molar surplus. In all experiments the solution was heated up to 35 °C, then the surfactant was added as solid and the solution was stirred 15 min at this temperature. After cooling to 22 °C and precipitation the suspensions were stirred 1 h and then filtered.

In the first set of experiments the initial Pu concentration was increased to about $1.35 \cdot 10^{-4}$ mol/l and/or the plutonium was stabilized in the fourth oxidation state. For the stabilization the plutonium was reduced to Pu(III) with Fe(II) ions and then with $NO_2^-$ ions reoxidized to Pu(IV). The results of the experiments are presented in Table 2.

In further experiments the Pu concentration was not increased and the plutonium was precipitated with alkylpyridinium nitrates with various chain lengths. The amount of surfactant was also, with one exception, 200 mg, which corresponds to the 3 000 fold molar surplus. This surplus of surfactant is necessary to prevent the precipitates from setting sticky. The organic residues must be probably solubilized. The results are summarized in Table 3.

It is evident from the results in the Table 2 that the stabilization of Pu(IV) is important at high Pu concentrations. But there is practically no influence of stabilization (Table 3) at very low initial concentrations of plutonium. Because only

**Table 2.** Precipitation with $C_{16}PyNO_3$

| Pu (initial): | $1.35 \cdot 10^{-4}$ mol/l | |
|---|---|---|
| Precipitation conditions | Pu-concentration in the filtrate [mol/l] $(\cdot 10^{-5})$ | % Pu separated |
| Pu(IV) stabilized | 0.64–1.60 | 88–95 |
| Pu(IV) not stabilized | 4.0 –6.2 | 54–70 |

**Table 3.** Precipitation with $C_xPyNO_3$

| Pu (initial): | $3.43 \cdot 10^{-6}$ mol/l | |
|---|---|---|
| Surfactant | Pu concentration in the filtrate [mol/l] $(\cdot 10^{-7})$ | % Pu separated |
| $C_{14}PyNO_3$ | 7.13–8.31 | 75–79 |
| $C_{15}PyNO_3$ | 4.48–4.57 | 86–87 |
| $C_{16}PyNO_3$ | 7.52–9.54 | 72–78 |
| $C_{16}PyNO_3$ No Pu(IV) stabilization | 6.44–8.31 | 75–81 |
| $C_{16}PyNO_3$ (500 mg/50 ml) | 2.56–2.75 | 92 |
| $C_{17}PyNO_3$ | 1.87–3.93 | 88–94 |

Pu(IV) forms negatively charged hexanitrato complexes which can be precipitated with cationic surfactants, we suppose, therefore, that the plutonium at very low concentration is present only as Pu(IV) or adsorbed on the surfactant, irrespective of the valence state. The low residual concentration of Pu with very high surplus of surfactant implies the adsorption of complex ions of Pu on the solid surfactant. This is supported by the fact that a further increase in the amount of surfactant giving a surplus of 7 500 leads to a further decrease in the Pu concentration.

There is a relatively small difference in the precipitation efficiencies between the chain lengths $C_{14}$, $C_{15}$, and $C_{16}$. But the lower residual concentrations in the case of $C_{17}PyNO_3$ and $C_{15}PyNO_3$ reflect the interesting different physical-chemical behavior of surfactants with odd carbon chains. The solubility of precipitates with "odd" surfactants seems to be lower.

Irrespective of the mechanism, the precipitation of Pu(IV) from acid nitrate solutions with cationic surfactants can compete with other separation methods.

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