# The Application of Acetohydroxamic Acid to the TBP Extraction of Uranium and Neptunium from a Simulated Solution

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## 1. Introduction

Irradiated spent nuclear fuel is usually reprocessed by a chemical process to recover the U and Pu from the radioactive fission products. However, a spent nuclear fuel usually contains minor actinides other than the useful U and Pu. A solvent extraction process is currently being developed to separate uranium, which will meet the criteria for a nuclear waste disposal as a class C low-level waste.[1] In this case, Np and Pu are generally regarded as unwanted components and particularly the U products have restrictive specifications. Therefore, their effective control during a chemical process is important for an efficient production of a purified U product. Such a process must also minimize the waste volume by converting all the chemicals to gases during a subsequent processing. To meet this requirement, the current process was designed to use reagents in the scrub stream. Recently, new salt-free reagents to separate Pu and Np from U, suitable for use in a single cycle flowsheet, have been developed.

Acetohydroxamic acid (AHA) has received considerable interest as a reductant/complexant of choice for the process to reject Np along with Am, Cm, and fission products because it can reduce Np(VI) to Np(V) quickly and it can create a Np(IV) complex.[2] These characteristics will allow U(VI) to be extracted free of transactinides. Since AHA is composed of only C, H, O and N atoms they can be readily decomposed to gases so that their incorporation in to industrial processes will not lead to increases in a waste volume.

In this study, distribution ratios of Np(IV), Np(VI) and U between 30 vol% TBP/n-dodecane and 1M nitric acid were measured with varying concentrations of AHA.

## 2. Experimental

Distribution experiments were undertaken by contacting a 1:1 volume ratio of 30% TBP/n-dodecane with aqueous nitric acid solution. Distribution ratios for Np were calculated as $[Np]_{org}/[Np]_{aq}$. Np(IV) and Np(VI) extraction distribution ratios were also measured from an simulated solution. The simulated solution was prepared on the basis of a component of a PWR spent fuel, and it contained the following 10 elements including Np, Ce, Nd, Mo, Zr, Fe, Sr, Ni, Pd, Ru and U. The composition of the simulated solution is shown in Table 1.

Table 1. The composition of a simulated solution.

| Elements | Sol'n name, conc. (M) | |
|---|---|---|
| | Me | U+Me |
| U (g/l) | 0 | 4.86 |
| Np | 0.001 | 0.001 |
| Ce | 0.033 | 0.033 |
| Nd | 0.0434 | 0.0434 |
| Mo | 0.0118 | 0.0118 |
| Zr | 0.069 | 0.069 |
| Fe | 0.038 | 0.038 |
| Sr | 0.0165 | 0.0165 |
| Ni | 0.006 | 0.006 |
| Pd | 0.018 | 0.018 |
| Ru | 0.034 | 0.034 |

## 3. Results

Neptunium exhibits three stable oxidation states in a nitric acid solution, each with a different chemical behaviour, Np(IV), Np(V) and Np(VI) ($Np^{4+}$, $NpO_2^+$, $NpO_2^{2+}$ ions). Np(V) is almost inextractable, while Np(IV) and Np(VI) can be readily extracted from a nitric acid solution into TBP/n-dodecane solutions.
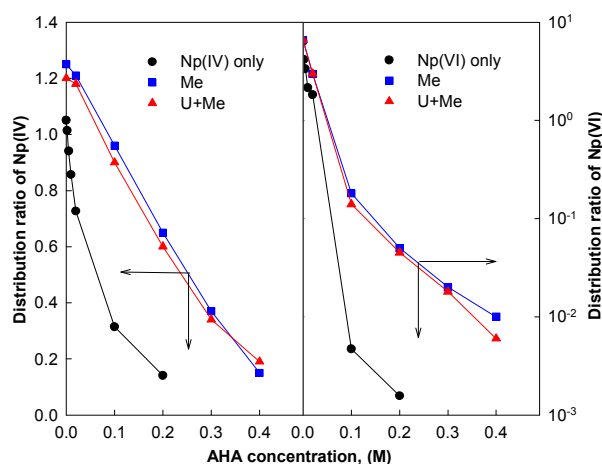


Figure 1. Distribution ratios of Np(IV) and Np(VI) with a change of the AHA concentration at $[HNO_3]$=1.0M.

Distribution data of a Np(IV) and a Np(VI) between $HNO_3$ and TBP/n-alkane solutions has been reported by several workers.[3] For a TBP/n-dodecane solution, as the $HNO_3$ concentration increases, the extraction of

Np(IV) and Np(VI) also increases. However, at a high $HNO_3$ concentration, the increasing extraction rate of $HNO_3$ by TBP reduces the amount of free TBP available for the extraction of neptunium, causing a decrease in the distribution ratio.

Np(IV) distribution experiments were undertaken between 30 vol% TBP/n-dodecane and an aqueous phase containing various concentrations of AHA at 1.0 M $HNO_3$ and 0.001M Np(IV). Also, Np(IV) extractions were carried out from a simulated solution with the AHA concentration at 1.0 M $HNO_3$. The results obtained with the variable concentrations for AHA are shown in Figure 1. Distribution ratio of Np(IV) in a 1.0 M nitric acid concentration is about $D_{Np(IV)}$=1.0. But, it can clearly be seen that Np(IV) is stripped into in the aqueous phase by a AHA (stability constant, $\beta_1$=12.83) and that stripping is increased with the AHA concentration. Therefore, Np(IV) stripping is directly related to complexation with AHA. The values of the Np(IV) distribution ratio as a function of the AHA concentration in the simulated solution are higher than the data from the Np(IV) single component extraction system. The various elements existing in the solution should cause a decline in the Np(IV)-AHA complexation, so, the distribution ration of Np(IV) in the simulated solution increases.

Also, Figure 1 shows the experimental results for the Np(VI) distribution between 30% TBP/n-dodecane and 1.0 M $HNO_3$ solution as a function of the AHA concentration at [Np]=0.001M. Distribution ratio of Np(VI) in a 1.0 M nitric acid concentration is about $D_{Np(IV)}$=6.36. But, it can clearly be seen that the Np(VI) distribution ratio rapidly decreases with the AHA concentration. These results are caused by a reduction of Np(VI) to Np(V), which is highly inextractable and has very low distribution ratios. AHA acts to rapidly reduce Np(VI) to Np(V) with the rate constant, k=191.2 $M^{-1}s^{-1}$ at 25°C and a 1.0 M nitric acid concentration,[4] but a reduction of Np(V) to Np(IV), as indicated by the onset potentials, is not expected since the hydrolysis of AHA by nitric acid is likely to be much faster than the reduction of Np(V) to Np(IV) which requires a breaking of the covalent Np-O bonds in the $NpO_2^+$.[5] Similar to Np(IV), the Np(VI) distribution ratio as a function of the AHA concentration in the simulated solution is higher than the data from the Np(VI) only extraction system.

Distribution ratios of Np(IV) and Np(VI) in a 1.0 M nitric acid concentration brought about a remarkable reduction with the AHA concentration, but there were no significant differences in the uranium distribution ratios with the AHA concentration (Figure 2).

## 4. Conclusion

Distribution ratios of Np(IV) and Np(VI) from $HNO_3$ solutions into 30% TBP/n-dodecane were decreased by a complexation with AHA and a reduction of Np(VI) to Np(V) by AHA, thus making it feasible to reject Np to

the waste during a solvent extraction process for a recovery of U. AHA has useful physical and chemical properties that allows it to be effectively used in an solvent extraction process to control both Np(IV) and Np(VI).
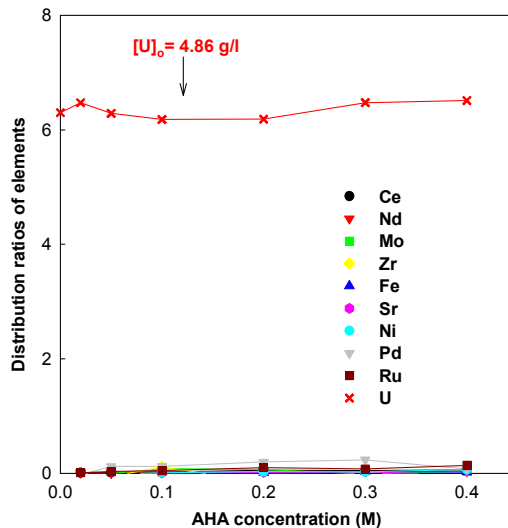


Figure 2. Distribution ratio of U(VI) and other elements with a change of the AHA concentration at $[HNO_3]$=1.0M.

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