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# Calculated Critical Concentrations of Uranium and Plutonium in Advanced Solvents

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## INTRODUCTION

Since the birth of the nuclear industry, solvent extraction in various forms has been the preferred large-scale method for processing of irradiated materials.

At a basic level, this method requires dissolving the irradiated material in an acidic or caustic solution, performing some mechanical and/or chemical clarification, then contacting the clarified solution with an extractant. Oxidants and reductants are added as needed to control the valence state of the desired or undesired components. This process allows the components to be partitioned and either discarded or recovered.

Solvent extraction remains popular because of its flexibility and efficiency, despite the waste generation issue. Nearly every actinide from thorium through americium can be quantitatively isolated with relative ease. Most processes can be operated with less than 1% product loss even for metric ton size operations. The process does lose some flexibility for higher actinides (i.e. atomic numbers greater than 95), because all prefer to be in the trivalent state and it is difficult to adjust one element without affecting the others. Solvent extraction also works well on rare earth and some transition metals, making it favorable for select fission product recovery and for certain nuclear related non-radioactive applications (e.g. separation of hafnium and zirconium). Still, its most well-known use in the nuclear industry revolves around separation and purification of uranium and plutonium.

Critical data and limits for operations with U-235 and Pu-239 are readily available. There are several caveats, however, that must be considered. If one uses the ANS 8.1 minimum critical mass parameter as a control (Ref. 1), it is unlikely one will achieve large scale operation with just a few hundred grams of U or Pu in the system. Large equipment is preferred for throughput but requires a different set of parameters for criticality control. One may be tempted to use ANS 8.7 (Ref. 2) for convenience and simply space the separations stages out according to their volume. It is unlikely that the cost, facility size, or process chemistry will allow for the spacing necessary to apply this standard. The facility is then left with the choice of applying a complex set of chemistry controls, a very conservative total system mass, or onerous concentration controls.

If these caveats alone were not restrictive, one will note that the concentration limits ANS 8.1 are also based on an idealized, most reactive, chemistry. That is, they are safely subcritical for optimal moderation of the pure U-235 or Pu-239 metal in water.

In searching the literature, it is quite easy to find voluminous references for U-235 or Pu-239 critical concentrations in water. While much rarer, there is some publicly available information on the concentrations with excess nitrates present (nitric acid) or with the chemical forms of uranyl nitrate or plutonium nitrate accounted for. This is mainly to demonstrate nitrogen's effect as a neutron poison. Ever rarer are published data of safe or critical concentrations in the most widely used extractant, tri-butyl phosphate.

There are many more extractants than just tri-butyl phosphate. The authors could find no summary publication of critical data (calculation or experiment) for U-235 and Pu-239 in various solvents and extractants that also accounted for the chemical form of the actinide.

This work makes minimum critical calculations for U-235 and Pu-239 concentrations in a variety of solvent extraction solutions used in advanced extraction processes. These are compared to the U-235 and Pu-239 in water limits as a baseline for consistency with ANS 8.1. All calculations are performed in SCALE 6.1 using the ENDF-VII 238 group cross section library (Ref. 3) and using publicly available nominal chemical parameters.

## METHODOLOGY

### Traditional and Advanced Solutions

Nine extraction solutions were selected for evaluation in this study based on a summary survey of the literature (Ref. 4). The traditional solution, upon which PUREX and its derivatives are based, is tri-butyl phosphate in a hydrocarbon diluent. The other traditional diluent found in these solutions is water with nitric acid. These are the solutions most processing engineers will be familiar with. The other eight solutions come from advanced processing schemes which will be discussed later. The solutions evaluated are:

- Tributyl phosphate (TBP)
  - Chemical Form:  $C_{12}H_{27}O_4P$
  - Density:  $0.973 \text{ g/cm}^3$
  - Diluent: Dodecane ( $C_{12}H_{26}$ ,  $0.75 \text{ g/cm}^3$ )
  - Concentration Range: 2.5 to 35 volume %
- Acetohydroxamic acid (AHA)
  - Chemical Form:  $C_2H_5NO_2$
  - Density:  $0.973 \text{ g/cm}^3$
  - Diluent: Water including 0.5 M nitric acid
  - Concentration Range: 0.05 to 1 M
- Carbamoylmethyl phosphine oxide (CMPO)
  - Chemical Form:  $C_{24}H_{42}NO_2P$
  - Density:  $1.00 \text{ g/cm}^3$

- Diluent: Dodecane including 1.4 M TBP
- Concentration Range: 0.01 to 0.25 M
- Chlorinated cobalt dicarbollide (CCD) + Polyethylene glycol (PEG)
  - Chemical Form:  $(C_2B_9H_8Cl_3)_2Co + C_2H_6O_2$
  - Density: 1.2 g/cm<sup>3</sup> (CCD), 1.125 g/cm<sup>3</sup> (PEG)
  - Diluent: phenyltrifluorosulfone ( $C_7H_5F_3O_2S$ , 1.249 g/cm<sup>3</sup>)
  - Concentration Range: 0.01 to 0.2 M CCD, 0.02 to 0.4 M PEG maintaining 1:2 molar ratio
- Cyanex-301
  - Chemical Form:  $C_{32}H_{70}P_2S_4$
  - Density: 0.95 g/cm<sup>3</sup>
  - Diluent: Dodecane including 0.15 M TBP
  - Concentration Range: 0.025 to 0.75 M
- Diethylene triamine penta-acetate (DTPA)
  - Chemical Form:  $C_{14}H_{23}N_2O_{10}$
  - Density: 1.5 g/cm<sup>3</sup>
  - Diluent: Water including 0.5 M glycolic acid ( $C_2H_4O_3$ , 1.27 g/cm<sup>3</sup>)
  - Concentration Range: 0.01 to 0.50 M
- Bis(d2-ethylhexyl) phosphoric acid (HDEHP)
  - Chemical Form:  $C_{16}H_{35}O_4P$
  - Density: 1.00 g/cm<sup>3</sup>
  - Diluent: Water including 0.5 M glycolic acid
  - Concentration Range: 0.05 to 0.75 M
- Ethylene diamine tetra-acetate (EDTA)
  - Chemical Form:  $C_{10}H_{16}N_2O_{10}$
  - Density: 1.6 g/cm<sup>3</sup>
  - Diluent: Water including 0.5 M glycolic acid
  - Concentration Range: 0.01 to 0.50 M
- Aliquot 336
  - Chemical Form:  $C_{25}H_{54}ClN$
  - Density: 0.88 g/cm<sup>3</sup>
  - Diluent: Dodecane
  - Concentration Range: 0.25 to 0.75 M

Results from these solutions were compared to calculated metal-water mixture values which are consistent with the data from ANS 8.1.

No cases involving simple solutions of fissile material in nitric acid are examined. The neutron poisoning effect of nitrogen is recognized, marginal, and commonly retained as defense in depth for criticality safety analyses by assuming an aqueous mixture with no excess nitrates.

The TBP mixture was chosen because of its obvious widespread use.

AHA is used in UREX type processes. It is the reducing agent in the scrub acid that rejects Np and Pu to waste together, where in PUREX type processes one or the other would be carried forward.

CMPO is used in UREX and TRUEX type processes because it has an affinity for the trivalent actinides. Am<sup>+3</sup> and Cm<sup>+3</sup> are recovered, however it will also pick up trivalent lanthanides. This is good for waste partitioning or for productive recovery of Am/Cm.

CCD-PEG is also used in UREX processes and simple waste treatment processes. The combined concoction selectively removes Cs and Sr which again makes it good for either waste partitioning or recovery of Cs and Sr. CCD-PEG will also pick up Eu and, for the criticality concern, Am, if there is sufficient reagent left after the Cs and Sr recovery.

Cyanex-301 is used in less known processes. It also partitions trivalent species, namely Am and Eu. If the Cyanex-301 is not pure, it will tend to pick up any trivalent actinide or lanthanide. The appeal of Cyanex-301 is that it can be a solution added to the solvent extraction process but it can also be made into a silicon-based resin for ion exchange systems.

HDEHP and DTPA are both components of the TALSPEAK process which can be run stand alone or may be appended to a UREX process. TALSPEAK partitions the trivalent lanthanides and actinides from the waste and further separates the lanthanides and actinides so that there is a pure Am/Cm stream for recovery. The draw back is that it will also pick up volatile Ru, toxic Tc, and any Pu that may have been reduced to the Pu<sup>+3</sup> state.

EDTA and Aliquot 336 are perhaps the least well-known solutions, or specialty extractants. Both work somewhat like a liquid anion exchange system and require a salting agent like aluminum nitrate to be present. EDTA traditionally has been used to scavenge (through chelation) thorium. EDTA could therefore make appearance in polishing of U-233, or the recovery of Ac-225 from decayed Th/U-233. Aliquot 336 is a trivalent actinide scavenger. Its appeal is that it has rapid metal ion exchange kinetics, meaning it will function efficiently in high radiation environments where chemical separations must be done in a few minutes before the solvent degrades or overheats. This makes Aliquot 336 appealing for recovering Cm, Es, Fm, and Cf.

### Fissile Material and Modeling

Uranium is assumed to be 100 wt.% U-235. When in an aqueous diluent, since there is excess water, the chemical form is assumed to be uranyl nitrate  $UO_2(NO_3)_2$  at a nominal 3.5 g/cm<sup>3</sup>. When the uranium is in a non-aqueous diluent the chemical form is assumed to be uranyl nitrate hexahydrate,  $UO_2(NO_3)_2 \cdot 6H_2O$  at a nominal density of 2.81 g/cm<sup>3</sup>.

Plutonium is assumed to be 100 wt.% Pu-239. The solution chemical form is assumed to be plutonium nitrate,  $Pu(NO_3)_4$  at a nominal density of 2.9 g/cm<sup>3</sup>.

All solutions are input to SCALE as atom densities. Other than the U and Pu isotopic choices above, all elements are assumed to have their naturally occurring atomic masses and were input to SCALE as the elemental number density. Solutions are developed based on the mass fraction of each component and its nominal density, translated from a volume fraction where necessary.

All calculations were an infinite homogenous solution modeled as a sphere of 300 cm radius and mirror boundary

conditions. Concentration of the fissile compound was adjusted until the calculated k-effective was between 0.995 and 1.005. Sufficient histories were run so that every case yielded a Monte Carlo uncertainty less than 0.0005  $\Delta k$ .

## RESULTS

Pu-239 metal in water and U-235 metal in water mixtures had calculated critical concentrations of 7.26 g Pu/L and 12.13 g U/L which is consistent with expectations based on the subcritical values from ANS 8.1.

Fig. 1 presents the data for uranium and Fig. 2 presents the data for plutonium. Both figures present the results as a function of the hydrogen density of the solution where the metal-water baseline is represented by the large red triangle.

Presentation of the data by hydrogen density is chosen because of the moderation condition. It is often argued that the metal-water mixture is conservative because of the hydrogen density of water. Another way to view this is a comparison of the moderating ability of water versus other solutions.

Fig. 1 and Fig. 2 present all of the results except CCD-PEG mixture. Fig. 3 presents the results for CCD-PEG. The reason for this presentation is obvious – the CCD-PEG critical concentration calculations are 0.5 to 1.5 orders of magnitude larger than all of the others. CCD contains a significant amount of boron, chlorine, and cobalt.

## CONCLUSIONS

In all cases, the metal-water mixture is the most limiting critical concentration. As such, it can conservatively be used.

For uranium, most of the advanced solvents fall between 15 and 21 g U-235/L for a critical concentration. This may allow some improvement in operation over the 12.13 g/L value of metal-water, but the value added to the process would have to be assessed versus the cost of the calculations (and their validation). However, AHA and Aliquot 336 are more than twice the metal-water mixture concentration and warrant further investigation for use of a higher concentration limit.

For plutonium, AHA, Aliquot 336, and even TBP warrant further investigation as these have calculated critical

concentrations two to three times higher than the metal-water mixture. At the very least, this implies that plutonium rich PUREX and UREX solutions are even less reactive than assumed if the metal-water limit has been applied. The rest of the advanced solvents fall between 8.7 and 14.6 g Pu/L and would have a similar economic argument as for uranium.

CCD-PEG is essentially a self-poisoning solvent because of the boron, and to a lesser extent the chlorine and cobalt. All of these elements act as neutron absorbers integral to the solution. The CCD-PEG critical concentrations can challenge the precipitation limits of the uranium and plutonium nitrates. This would be excellent for criticality control, unfortunately CCD-PEG is mostly used for fission product partitioning and only trace actinides appear in those solutions.

## ACKNOWLEDGEMENTS

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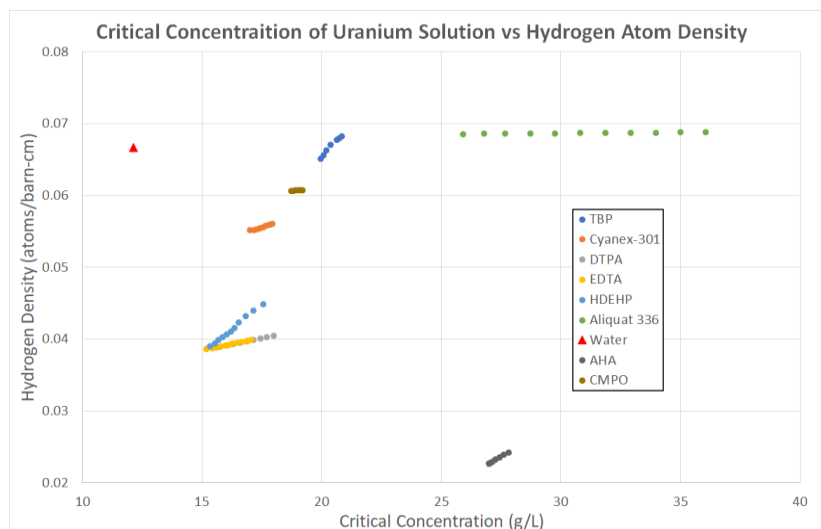


Fig. 1. Calculated critical concentrations of U-235 in various solutions.

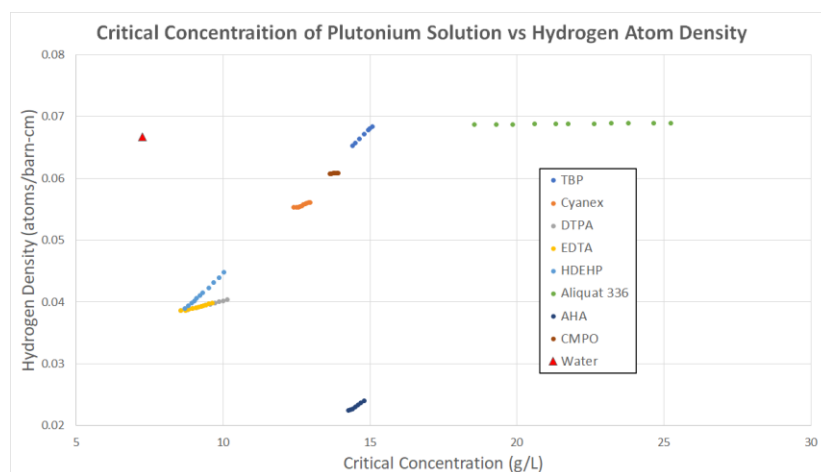


Fig. 2. Calculated critical concentrations of Pu-239 in various solutions.

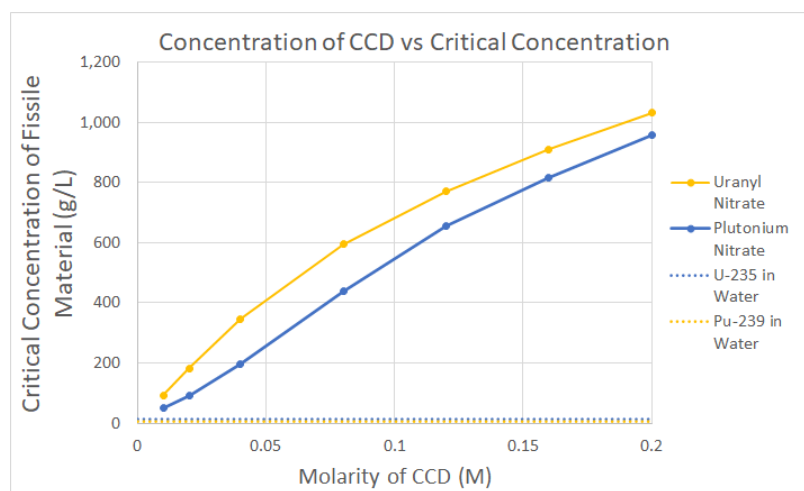


Fig. 3. Calculated critical concentrations of U-235 and Pu-239 in CCD-PEG solutions.