Removal of Acetic Acid from a UREX+ Raffinate Stream

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Abstract

In the UREX+ process, acetohydroxamic acid is added to the UREX step to suppress plutonium extraction. Hydrolysis of acetohydroxamic acid (AHA) produces acetic acid and hydroxyl ammonium nitrate (HAN). The capability to remove acetic acid from aqueous process solutions is desirable as UREX+ flowsheets continue to evolve. Reasons for acetic acid removal include enabling recycle of the nitric acid solution and prevention of problems in downstream process steps.

After a literature review, solvent extraction was determined to be the most promising approach for removal of acetic acid at the low concentrations involved. The goal was to identify a solvent that is both insoluble in the aqueous phase and will selectively remove acetic acid. Solutions of tributylphosphate (TBP) have been shown to selectively extract acetic acid over nitric acid with sufficiently high distribution coefficients. Extractant solutions tested in this study include TBP in dodecane and TBP in phenyltrifluoromethyl sulfone (FS-13). The two solvents are both compatible with the UREX+ process flowsheets, so selection of the solvent will be based on the placement of the removal step. The location of the removal step within the process is dependent on many factors including avoiding raffinate stream solutions containing quantities of actinides that TBP would extract, interference of acetic acid with the process steps, and the ratio of nitric to acetic acids in each step so the distribution coefficient can be maximized.

Introduction

The purpose of the UREX+ process is to recover uranium from used fuel while avoiding recovery of purified plutonium.. Nitric acid recycled from the process is used to dissolve the spent nuclear fuel as part of continuous operations. In the first step of this process (the UREX step), acetohydroxamic acid (AHA) is added to the aqueous feed stream to suppress plutonium extraction. This acid then hydrolyzes into acetic acid (HAc) and hydroxyl ammonium nitrate (HAN). The acetic acid interferes with the recycle of nitric acid, and it may interfere with some downstream separations steps. Therefore, the acetic acid must be removed somewhere in the process before the recycle of nitric acid can occur.

This removal step is examined in three parts. The first is to determine a suitable way or ways to remove acetic acid effectively. To accomplish this, common separation technologies are examined through literature review to make observations on the effectiveness of removing acetic acid from a tenfold stronger nitric acid stream. Next, the top separation technology or technologies is/are examined by gathering experimental data to determine the specifics of the removal process in a 10:1 nitric to acetic acid aqueous environment. Finally, once this removal step is created, it must be determined where in the UREX+ process it can be placed so that interference with current process steps is avoided.

The UREX+ process flow sheet used during this entire study is shown in Figure 1. It uses UREX to extract uranium and technetium, CCD-PEG or the option of using a newer FPEX method to remove cesium and strontium, NPEX to remove plutonium and neptunium, TRUEX to remove fission products, and TALSPEAK to separate lanthanides from actinides—mainly americium and curium. [1-3]

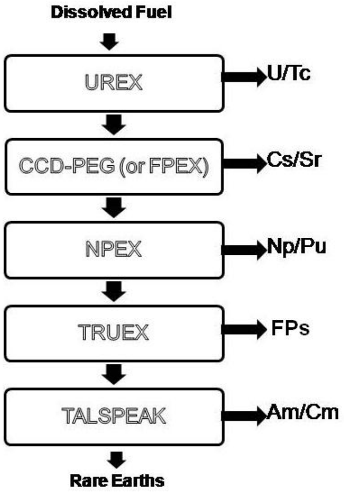


Figure 1. The UREX+ Process.

Technology Selection

Many technologies have been studied to remove acetic acid from water, as shown in Table 1. Most of the literature reports the separation properties for the simple binary acetic acid and water systems. Our model system contains nitric acid, acetic acid, and water which complicates the system. Through literature review of these technologies, ion exchange and membrane separation were ruled out almost immediately for their lack of a membrane or adsorbent selective to acetic acid. Destruction is not viable unless conditions are at high temperatures and pressures, both unfavorable options for a nuclear process. Crystallization would require a preceding process to concentrate the acetic acid. Distillation was deemed a viable option, but due to the ternary system, the process would be much more complex and would fit at the end of the process or where nitric acid needs to be concentrated for recycle. Solvent extraction was determined to be the most viable option for removal of acetic acid from the raffinate stream. This technology was chosen because of its ability to fit most places in the process flow sheet, extractants already present in the process can be used, and sufficiently high distribution coefficients are found in literature for the acetic acid-water system. Solvent extraction is used regularly in other industries to remove acetic acid from dilute solutions such as those expected in UREX+. Distillation is more likely to be used to remove acetic acid from more concentrated solutions.[4,5]

Table 1. Technology Comparison.[5]

Technology	Pros	Cons
Crystallization	**• Used with distillation** **• Feasible** **• Favors acetic acid over nitric acid**	**• Requires concentration** **• Some mechanical operation needed**
Distillation	**• Feasible** **• Used with Crystallization** **• Used with concentration of nitric acid**	**• Removes water first which concentrates nitric acid** **• May require multiple towers required to remove acetic acid and nitric acid in appropriate streams**
Adsorption/Ion Exchange	**• Uncertain Feasibility**	**• No suitable adsorbent found**
Solvent Extraction	**• Similar to other UREX+ operations** **• Could use extractant and diluent already in process** **• Data exist on similar systems**	**• Restricted to solvents already used in UREX+** **• Strip step required** **• Possibly wash and/or solvent scrub step required** **• More likely to be selected for removal from dilute concentrations of acetic acid**
Destruction	**• Could possibly eliminate acetic acid** **• Creation of hydroxyl radicals will completely breakdown acetic acid**	**• Mainly need high temperature and pressure** **• High pH needed for corona discharge** **• Could also destroy nitric acid**

Solvent System Selection

Once solvent extraction was selected, the next step was to find a suitable solvent system that would selectively remove acetic acid over nitric acid. The diluent-only option was first explored; the results showed the distribution coefficients were insufficient for an efficient separation. Tributyl phosphate (TBP) was added as an extractant to the organic diluents to increase the extraction coefficients.[6] These results are shown in Table 2.

The 1.5M TBP-Dodecane solvent system was chosen as the solvent system that would be best to selectively remove acetic acid from nitric acid with a sufficiently high distribution coefficient to allow reasonable solvent flow ratios. This system was selected in the flow sheet of the acetic acid removal step (Figure 3). Since no data exists on the removal of acetic acid from nitric acid systems in UREX+, a literature review and analysis were needed to determine the placement of acetic acid removal in the UREX+ process flow sheet.

Table 2. Distribution Coefficients and Separation Factors of the system of TBP-Dodecane.

AQUEOUS SYSTEM	ORGANIC SYSTEM	K_D Nitric Acid	K_D Acetic Acid	Separation Factor
0.25M Nitric Acid 0.025M Acetic Acid Water	Dodecane	0.022	-0.021	N/A
	1M TBP-dodecane	0.049	0.183	3.735
	1.5M TBP-dodecane	0.098	0.878	8.959
	2.5M TBP-dodecane	0.308	1.481	4.808
	TBP	0.620	2.573	4.150
0.5M Nitric Acid 0.05M Acetic Acid Water	Dodecane	-0.003	-0.043	N/A
	1M TBP-dodecane	0.078	0.342	4.385
	1.5M TBP-dodecane	0.150	0.525	3.500
	2.5M TBP-dodecane	0.299	1.038	3.472
	TBP	0.660	1.751	2.653

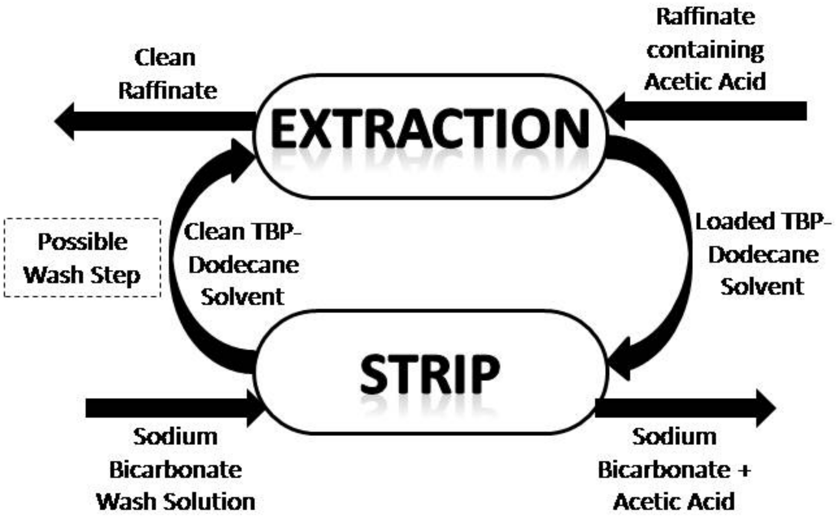
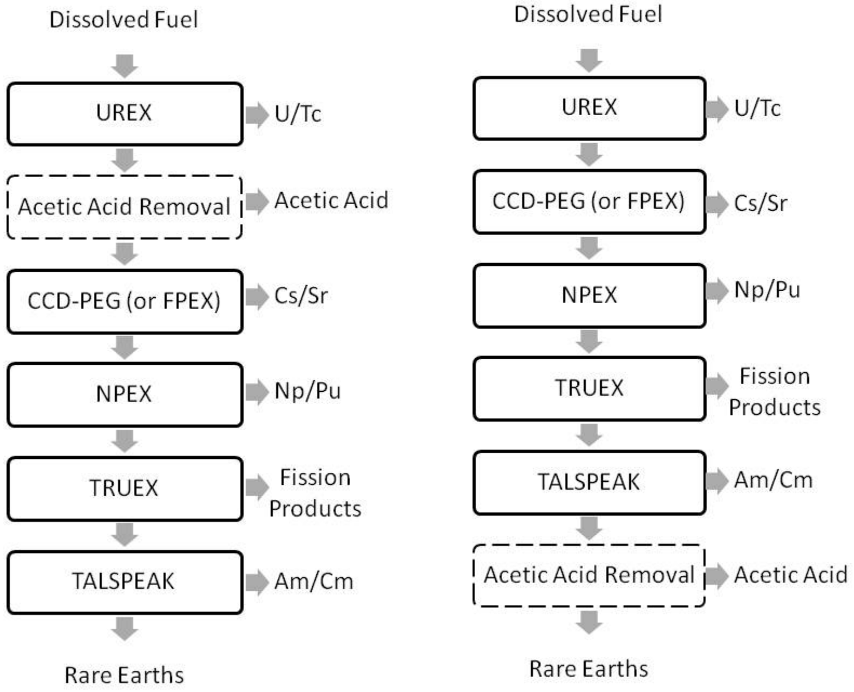


Figure 3. Acetic Acid Removal Step

Placement of Acetic Acid Removal Step

Each step of the UREX+ process was examined to determine whether acetic acid would be expected to interfere with that process step. For the first step (UREX), acetohydroxamic acid (AHA) suppresses plutonium from being extracted, so not all the AHA will hydrolyze in this step. Therefore, the amount of acetic acid present in this step that could potentially interfere with uranium extraction is determined not to be a problem. The following step is cesium and strontium removal. This step is carried out either by CCD-PEG or by FPEX. In the CCD-PEG step, degradation products of acetohydroxamic acid can interfere with the cesium and strontium extraction, however, which degradation product which interferes is unclear. [7] If FPEX is used instead of CCD-PEG to extract Cs and Sr, the hydroxyl ammonium nitrate would interfere with cesium and strontium removal; so all acetohydroxamic acid would have to be completely hydrolyzed prior to this step to remove the HAN. Acetic acid would also be in its most concentrated form just prior to FPEX which could be a viable option for the removal step as shown in Figure 4a. The next step is NPEX which removes neptunium and plutonium. Based on distribution coefficients and organic to aqueous ratios found in literature for the radioactive metals [8,9], their extraction can be compared to acetic acid extraction in a similar organic solvent system. In NPEX, these conditions are 1.1M TBP-dodecane with a 1M nitric acid. Using the equation for extraction factors ($E=K_D(O/A)$) all in molar units, the extraction factors can be compared. For both neptunium and plutonium extraction factors, acetic acid's extraction factor is much lower and does not seem to cause a problem for this step. The next step TRUEX uses an organic solvent of 0.2M CMPO-1.4M TBP-dodecane. This solvent was tested with the aqueous concentration of 0.25M nitric acid and 0.025M acetic acid. Distribution coefficients resulted in 0.952 for acetic acid and 0.328 for nitric acid. Using a similar system for americium extraction, [10] the extraction factors again were compared with no expected interference of acetic acid in this step. The final step of TALSPEAK uses 0.8M HDEHP (di(2-ethylhexy) phosphoric acid) dissolved in diisopropylbenzene (DIPB). [11] The amount of acetic acid extracted by the TALSPEAK solvent was tested in an organic system of 0.8M HDEHP-DIPB and 0.2M HDEHP-0.3M TBP-Dodecane. There is no extraction of acetic acid in either system. Acetic acid does not show any noticeable interference in any step of the process, therefore another possible flow sheet is shown in Figure 4b with the extraction of acetic acid at the end of the process along with nitric acid recycle.



a. b.

Figure 4. Flow Sheet Proposals.

Conclusion

Out of the available technologies shown to effectively remove acetic acid, the most promising—and the one further explored in this study—was solvent extraction. A suitable solvent system of 1.5M TBP-dodecane was chosen due to its sufficiently high distribution coefficients and selective separation factor in a system wherein the nitric acid concentration is about ten times that of the acetic acid concentration. It was determined acetic acid may be removed anywhere in the UREX+ process, but is recommended that the separation be placed either after the UREX step where it is likely most of AHA hydrolysis will have been completed or at the end of the process where nitric acid recycle occurs. If it is placed at the end of the process, a closer look at distillation may be needed to determine if the re-concentration of nitric acid for recycle and removal of acetic acid can be a combined process.

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