Purex co-processing of spent LWR fuels: flow sheet

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Abstract

Purex co-processing of spent LWR fuel is investigated. In purex co-processing, uranium and plutonium in spent fuel are processed and recovered together as a single stream, while in standard purex reprocessing uranium and plutonium are obtained as separate streams. A two-step (co-decontamination and co-stripping) flow sheet for purex co-processing is devised; concentrations, recoveries and decontamination factors are calculated; and methods to co-convert uranium–plutonium nitrate to mixed oxide are reviewed. A closed nuclear fuel cycle in which at no point uranium and plutonium are separated from each other is reached. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. Recycling

All nuclear fuels contain fissile and fertile isotopes. In a nuclear reactor, while fissile isotopes undergo fission to produce energy, fertile isotopes are converted by neutron capture to fissile ones, which also contribute to energy production. Spent fuel
(SF) discharged from a nuclear reactor contains fissile isotopes, fertile isotopes, fission products (FPs) and other actinides.

In a typical light-water reactor (LWR) of 1000 MWe, fresh fuel is composed of UO₂, which is about 3.3 weight percent (wt%) enriched in U-235, and after producing 33,000 MWd per ton U during 3 years of exposure, SF is discharged from the reactor. This SF contains nearly 95.5 wt% UO₂ (0.85 wt% fissile), 0.9 wt% Pu (70 wt% fissile), 3.5 wt% FPs and 0.1 wt% other actinides.

Would it ever be reasonable to classify a material about 96.4% of which is more valuable than natural resources as “waste” and try to bury it deep underground so that it cannot be reached or retrieved? Efforts should be focused on how to recover the valuables from this mixture, and then to dispose of the remnants, “real waste”.

By reprocessing SF, fissile and fertile isotopes contained in SF can be recovered and barren materials (FPs and several actinides) can be put into a proper form to be disposed of as high-level waste (HLW). By reintroducing the recovered materials into a nuclear reactor, “recycling”, further energy production can be achieved, in a so-called “closed” nuclear fuel cycle.

1.2. Purex reprocessing

In reprocessing SF, a solvent extraction method, Plutonium Uranium Recovery by EXtraction (PUREX), which serves to recover U and Pu separately in highly pure forms, is conventionally used. The recovered U can be re-enriched, re-fabricated and re-fed into a nuclear reactor. The recovered Pu is diluted with a fertile material to produce mixed-oxide (MOX) fuel with an appropriate fissile content.

Purex method employs tri-butyl phosphate (TBP) in a hydrocarbon diluent as the solvent and consists of three main steps: (1) co-decontamination, where U and Pu are separated from most of the FPs and other actinides, (2) partitioning, where Pu is partitioned from U, and (3) stripping, where U is washed back into the aqueous solution. If U and Pu products obtained are not sufficiently decontaminated from FPs, additional decontamination steps are required.

The extent of decontamination required determines the amount of FP activity to be allowed to remain in the product, and thus depends on subsequent use of the recovered products. If U product of reprocessing is to be re-enriched, then its activity should not considerably exceed that of natural U in equilibrium with its short-lived daughters since operations in enrichment are by direct contact. In that case, decontamination of U from FPs should be nearly complete, requiring a large decontamination factor, defined as activity in the feed divided by that in the product.

If Pu product of reprocessing is to be re-fed into a nuclear reactor as MOX, then it is not necessary to decontaminate the Pu product from FPs to a large extent since the inherent activity of Pu itself is high enough. Thus much smaller decontamination factors are tolerable. Besides, since the Pu product of reprocessing is to be mixed with a fertile material (such as natural, depleted or recovered U), then it should not be necessary to separate Pu from U completely in the first place. Why separate a material from another if it is going to be mixed with that later on? This consideration leads to the “co-processing” concept.
Is it not a contradiction to design purex reprocessing plants in order to obtain pure U and Pu in SF as separate streams if that Pu is to be blended with U before being introduced into a nuclear reactor anyway, and at the same time to criticize the safeguardability of reprocessing plants because they produce pure Pu? Efforts should be focused on recovering all the valuable materials in SF in the most proper form by the most economical methods. This study is a modest effort in that direction.

The idea of co-processing, investigated around 1980s (Gray et al., 1978; Lambert and Wilson, 1978; Zabunoglu and Spinrad, 1991), is revisited; a simple co-processing flow sheet, devised and calculated, is presented in this paper, and cost aspects are discussed in a following paper (Zabunoglu and Ozdemir, 2004).

2. Purex co-processing

2.1. Flow sheet

In purex co-processing, it is aimed to reprocess SF in such a manner that, at no point in the process, U and Pu are separated from each other. So, it is “reprocessing with no partitioning”, and can appropriately be named “complete co-processing” to distinguish it from partial co-processing schemes (Zabunoglu and Spinrad, 1991).

The only product of purex co-processing is an aqueous solution of U + Pu, with a fissile content of approximately that of the SF solution (about 1.47 wt% for SF from a typical LWR). In order to produce MOX fuel for typical LWRs from this mixture, it is necessary to add a fissile material (fissile makeup) to it. Enriched U, or 70 wt% fissile Pu (probably from a conventional reprocessing plant), or weapons-grade U or Pu can be used as fissile makeup.

A flow sheet for purex co-processing is shown in Fig. 1. As can be seen, with omission of the partitioning, the purex method of conventional reprocessing turns into a simple, two-step process in complete co-processing. Concentrations and flows of the streams in Fig. 1, together with recoveries and decontamination factors for the process, are to be calculated.

2.2. Calculational method

Assumptions and approximations made to facilitate the calculations are:

1. The solubilities of H$_2$O and TBP in each other are ignored.
2. The TBP degradation is not taken into account.
3. In the aqueous phase, all U is in the U(VI) valence state and all Pu in the Pu(IV), and in the organic phase, U exists as UO$_2$(NO$_3$)$_2$·2TBP and Pu as Pu(NO$_3$)$_4$·2TBP.
4. Fission products are grouped according to their extraction behavior. Zirconium (Zr) group contains Zr, Nb and Ce; ruthenium (Ru) group represents Ru and Rh; and rare earth (RE) group consists of all others. For each group, the extraction properties of the named species (zirconium, ruthenium, rare earth) are taken for all the elements of the group.
Actinides other than U and Pu are not taken into account. The column contactors are treated as cascades of theoretical stages; within each stage, complete equilibrium is assumed.

The equilibrium relations (expressions for distribution coefficients) for solutes were obtained from the literature. For HNO$_3$ and U(VI), the correlation of Goldberg et al. (1972) was applied. For Pu(IV), the relation from SEPHIS code (Watson and Rainey, 1975) as reported in Benedict et al. (1981) was used. For FPs, the data from Benedict et al. (1981) were fitted to analytical formulas for numerical work. Formulas for computing density changes and relative flow rates as materials transfer across phases were also needed, and developed as described in (Zabunoglu, 1988).

For a single stage, identifying streams at one end of the stage, calculations of concentrations and flows were carried out by an iterative procedure. Iteration is necessary because not all relations in the equilibration of a stage are linear. For a simple cascade (e.g., the extracting portion or the scrubbing portion of the co-decontamination step), single-stage calculations were repeated until streams at the other end of the cascade were obtained.

For a compound cascade, consisting of two simple cascades, it is necessary to balance the flows and inputs to the simple cascades that comprise it so that streams passing from one simple cascade to the other are the same. This also required a series of iterations. However, whereas the iterations for single stages and/or simple cascades could be converged rapidly by machine algorithms, human judgment was necessary for combining cascades. Thus, iteration proceeded by adjustment of
concentrations and flows entering or leaving the simple cascades until the compound system was entirely consistent (Ozdemir, 2003).

An extracting-scrubbing compound cascade, which is the model for the co-decontamination process, can be viewed as two simple cascades connected at the “fit point”, where the organic phase leaving the extracting section enters the scrubbing section as it is. A block diagram describing an extracting-scrubbing cascade calculation is presented in Fig. 2 and the fit point is shown in Fig. 3 together with the results of the co-decontamination process.

2.3. Co-decontamination

In the co-decontamination step, U and Pu are separated from FPs to a sufficient extent. The aqueous feed solution containing 4.2 M HNO₃, 2.0 M U, 0.019 M Pu, and 1.35 M FPs (Zr, Ru and RE groups) is fed near midpoint of an extracting-scrubbing cascade. Mole ratios of U to Pu and U to FP are 106.5 and 15.1, respectively; which are the mole ratios in SF from a typical PWR, calculated using the
ORIGEN-S code (Hermann and Westfall, 1998). Thirty volume percent TBP in \( n \)-dodecane is used as solvent and a 2.5 M HNO\(_3\) solution is used as scrub solution. Compositions and flow rates of the phases entering and leaving the cascade are exhibited in Fig. 3.

Change of recoveries and decontamination factors with molarity of scrub solution is shown in Figs. 4 and 5. Decontamination factors slightly decrease as the molarity increases. Recoveries increase until around 2.5 M, but then, they start decreasing as molarity of scrub solution increases.

Change of recoveries and decontamination factors as a function of solvent-to-scrub flow ratio is presented in Figs. 6 and 7. As solvent-to-scrub flow ratio increases, recoveries increase, but decontamination factors decrease (see Fig. 7).

flow: relative volumetric flow rate
M: molarity

Fig. 3. Results for the co-decontamination.
2.4. Required decontamination

Required decontamination of the mixed U + Pu product is determined by the following criterion: FPs remaining in the U + Pu product should not add significantly to the inherent activity of the product. In other words, FPs remaining in the U + Pu product should not interfere with subsequent processing, which is MOX fabrication.
where main operations are anyway by remote means, thus not requiring a very clean feed. As a result, since the inherent activity of the U + Pu product, resulting mainly from Pu isotopes, is already high enough, it is not necessary to completely decontaminate the U + Pu product of purex co-processing from FPs; so, a relatively small decontamination is readily tolerable.

Upon noting the activity values in Table 1, it can be stated that the FP activity remaining in the U + Pu product does not exceed 10% of the total activity of the
product for 150-day cooled fuel and a much smaller fraction for longer-cooled fuels. Consequently, a two-stage extracting and two-stage scrubbing cascade is sufficient to obtain required decontamination and desirably high recoveries. No additional decontamination is needed. What is left to do is to wash U + Pu back into the aqueous phase by co-stripping.

### 2.5. Co-stripping

The only purpose of co-stripping is to wash U + Pu in the organic phase into the aqueous phase with a recovery as high as possible. Since both U and Pu exhibit very low distribution coefficients (affinities for organic phase) at very low HNO₃ concentrations, co-stripping can easily be achieved by contacting the organic phase containing U + Pu with a very dilute (0.01 M) HNO₃ solution, “strip solution”.

Results of the co-stripping calculations are shown in Fig. 8. Recoveries are depicted as a function of molarity of the strip solution in Fig. 9. As can be observed, when a 0.01 M strip solution is employed in three stripping stages, there is practically no loss of valuable materials (U + Pu) during co-stripping.

### 2.6. Co-conversion

Conversion of a mixed nitrate solution of U + Pu to mixed U + Pu oxides can be achieved by calcining a co-precipitated U + Pu compound (Benedict et al., 1981). Peroxide or oxalate precipitation can be applied to co-precipitate U + Pu from a
Fig. 8. Results for the co-stripping.

Fig. 9. Recovery versus concentration of HNO₃ in strip solution.
nitrate solution. After co-precipitating U + Pu peroxide by hydrogen peroxide or U + Pu oxalate by oxalic acid, calcining the co-precipitated compound and reducing UO$_3$ and/or U$_3$O$_8$ to UO$_2$ by hydrogen, mixed U + Pu oxides can be obtained. An example flow sheet, based on the peroxide method and adaptable to co-conversion of U + Pu, can be found in Bonini and Cabrejas (1998).

Note that fabrication into MOX fuel assemblies can be done either by a standard powder–pellet process or a sol–gel method (Spinrad and Azar, 1984; Vaidya, 2002). While input to the powder–pellet process is in oxide form and concentration adjustment is done during milling, the sol–gel process can directly accept a nitrate solution and blending (concentration adjustment) is done in the solution phase. Then, in case of a sol–gel method, co-conversion to mixed oxide prior to fabrication is not required unless shipping considerations make it necessary.

3. Conclusion

Purex co-processing is a two-step process recovering almost all of the U + Pu in SF as a single stream, which has a total fissile content of 1.47 wt% for SF from a typical LWR. The flow sheet proposed for purex co-processing proves to be very simple compared to purex reprocessing. The partitioning step of purex reprocessing separating U and Pu almost completely from each other is eliminated in co-processing. The partitioning of U and Pu is the most difficult part of operations in conventional reprocessing since it involves the reduction of Pu to the inextractable trivalent state. Besides, because inherent activity of the U + Pu product is high enough, a modest decontamination from FPs is sufficient for subsequent processing of the U + Pu product, thus not requiring any further decontamination steps.

Noting that purex co-processing itself consists of about two thirds of the main operations in purex reprocessing and also taking into account the elimination of the most difficult operation and the omission of any additional decontamination steps, it is expected that overall simplification over the conventional purex reprocessing is at least by a factor of two. That is, purex co-processing is predicted to be smaller and easier than the conventional purex reprocessing by a factor of two or more.

A comparative fuel cycle cost analysis of the purex co-processing cycle is to be the subject of a following paper (Zabunoglu and Ozdemir, 2004).

References


