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CHEMICAL PROCESSING OF HTR FUELS APPLYING EITHER THOREX OR PUREX FLOW SHEETS

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Introduction

Two fuel cycles are considered for utilization in high temperature gas-cooled reactors (HTR's): the high-enriched thorium-uranium (HEU ≙ 93 % U-235) and the low-enriched uranium (LEU ≙ 8-12 % U-235) fuel concept [1].

For both fuel compositions suitable reprocessing procedures are required which are capable to separate the actinides thorium, uranium and plutonium from fission products and from each other. In any case, the processes under consideration utilize Tri-n-butylphosphate (TBP) together with a straight-chain paraffinic diluent (C_8-C_{14}, to day usually dodecane) as extractant in an aqueous nitrate system; most commonly, the related processes are known by the acronyms PUREX and THOREX.

The PUREX process has become the reprocessing procedure quite generally used for all fuel types containing natural, slightly or highly enriched uranium together with lower or higher contents of plutonium. The THOREX process on the other hand has been developed to separate thorium, uranium and fission products from thorium based irradiated fuel.

Generally, the utilization of the thorium fuel cycle is most attractive for High Temperature Reactors. On the other hand, the strong recommendation of INFCE to abandon the use of high-enriched uranium for nuclear energy applications virtually rules out the thorium fuel cycle, since economic utilization of thorium as a fertile material requires the use of high-enriched U-235. Thus, it was decided in the Federal Republic of Germany to switch over, at least for the foreseeable future, to the low enrichment uranium-plutonium fuel cycle, well aware of its economic shortcomings [2].

In this paper various THOREX flowsheets as well as a PUREX variant suitable for LEU fuel reprocessing are described. Both processes have in common that the main stream is always presented by the fertile material, that means thorium and U-238, respectively.

Head-End Procedures for HTR Fuel

Graphite containing fuel elements of HTR's require a more laborious head-end procedure than does metal clad fuel. Details are described elsewhere [3,4] and are not dealt with in this paper. In general, the head-end procedure does not influence the aqueous chemical process because after dissolution, the history of the fuel has disappeared almost completely. However, if too much carbon is left in the fuel after burning off the graphite (viz. more than 0.1 % carbon in the ash) problems might encounter in the solvent extraction. By reaction of the graphite with HNO_3 oxalic acid can be produced. Oxalic acid formes complexes with plutonium, thus a satisfactory plutonium recovery in the extraction step may be upset. This fact must be taken into account if low enriched fuel is to be processed in a PUREX plant after having burned the graphit fuel elements in a special head-end extension.

It is a very important drawback of the thorium fuel cycle that ThO_2 and $(Th,U)O_2$ do not dissolve in pure HNO_3, on the contrary to UO_2. The common reagent for the dissolution of thorium bearing fuel is the so-called THOREX reagent [5]. It consists of

$$13\ \underline{M}\ HNO_3;\ 0.05\ \underline{M}\ F^-;\ 0.1\ \underline{M}\ Al^{3+}$$

The fluoride ions do not catalyze only the thorium dissolution but cause also corrosion of the dissvoler system. No influence of the fluoride on the extraction has been reported so far. The aluminium contained in the THOREX solution serves as complexing agent for F^-, thus reducing the corrosion, particularly in the initial phase. The Al has a minor effect as a salting-out reagent in the extraction step, on the other hand it increases the waste volume because it accompanies the fission products.

History of thorium/uranium solvent extraction

The first technical-scale separation of irradiated thorium-uranium fuel was achieved in 1952 with the so-called THOREX process No. 2 [6].

Examples of the successful application of variations of THOREX flowsheets are the reprocessing of more than 850 tons of irradiated thorium in existing USAEC plants at Savannah River and Hanford yielding 1.4 tons of purified U-233 [7,8]. Since the burnup of the fuel was rather low, the concentration of uranium in the irradiated thorium did scarcely exceed 0.2 %.

Preferentially, the flowsheets first developed at the Knolls Atomic Power Laboratory [9] and at Oak Ridge National Laboratory [6] have been applied.

Because these flowsheets made use of high concentrations of $Al(NO_3)_3$ as salting-out reagent ORNL developed in the late 1950's the so-called Acid THOREX process, in which nitric acid is substituted for most of the aluminium nitrate [10]. The need for reprocessing of fuel with a larger uranium content arised for the first time from the primary fuel loading of Consolidated Edison Company's Indian Point-1 nuclear power plant. The fresh fuel was composed of 94 % Th and 6 % U. Although the preliminary tests with the Acid THOREX process flowsheet have proved its suitability, the fuel from this reactor was later processed by Nuclear Fuel Services plant at West Valley applying an Interim-23 flowsheet, capable only for recovery of uranium.

In the Federal Republic of Germany the necessity for reprocessing of thorium fuel came up in the sixties with the advent of HTR commercialisation. Farbwerke Hoechst in cooperation with KFA has optimized the dual cycle THOREX process flowsheet, originally proposed by BRUCE et al. [11].

The JUPITER experimental facility at KFA-Jülich was designed to reprocess 2 kg/day of heavy metal of spent (Th,U)O_2 AVR fuel [12]. This development work was greatly impaired by the decision to abandon the use of high enriched uranium, as already mentioned.

THOREX FLOWSHEETS

Like the PUREX process, the different variants of the THOREX process use a 30 % solution of TBP in an organic solvent such as kerosine. The extraction behaviour of thorium, however, requires the use of a salting agent. In the first THOREX process $Al(NO_3)_3$ was used, this salt being present in the feed solution anyway after the dissolution of aluminium-bearing fuel elements. In contrast, thorium-containing fuel elements from power reactors do not contain aluminum, and the addition of $Al(NO_3)_3$ to feed solutions would lead to an undesirable increase in the waste volume during reprocessing. Thus, processes using this salting agent will not be discussed further.

Thorium may also be salted out by HNO_3, which is relatively easy to recycle and destroy, and virtually all of the processes taken into consideration today use this acid as a salting agent.

In designing a THOREX flow sheet, it must be recognised that a second organic phase (third phase) is precipitated if too high a loading of the organic phase occurs. This phase consists of TBP and thorium and perturbs the function of the extraction apparatus due to its physical properties. THOREX flowsheets must therefore be designed such that the formation of this third phase can be avoided with certainty. Maximum loadings of thorium in the organic phase should be limited to about 30 % of the theoretical capacity.

Fig. 1 shows a generalized flowsheet of the extraction step of the THOREX processes. Due to the poor extraction of thorium, a comparatively high flow ratio of the organic to the aqueous phases is required. At a working temperature of 20°C the feed concentration must be limited to about 1 mol/l of thorium if the third phase formations is to be avoided. However, since the formation of the third phase is also influenced by the acid concentration, it is also necessary to limit the overall supply of HNO_3 via the feed solution and scrub. Formulated more generally: the feed solution either contains 1 mol/l HNO_3 and the scrub 0.01 to 0.1 mol/l HNO_3, or the feed solution does not contain any HNO_3 and the scrub contains 1 mol/l HNO_3.

However, the relatively low supply of acid via the feed solution and scrub will lead to high thorium losses via the waste flow due to the poor extractability of thorium. For this reason, concentrated HNO_3 is added to the aqueous stream shortly before it leaves the extraction apparatus. With the resulting acid concentration, the thorium losses are reduced to an acceptable level. Here, the formation of the third phase is not possible due to the low concentrations of thorium.

The first THOREX process, which uses only HNO_3 as a salting agent, was developed by ORNL [13]. An $Al(NO_3)_3$ content of less than 0.1 M in the feed solution results from the use of THOREX solution for dissolving the fuel. The process uses a feed solution of 1.1 M $Th(NO_3)_4$, a special feature being the acid deficiency of about -0.15. The scrub solution is 1 M HNO_3. The acid deficiency is adjusted by steam stripping of the feed solution. Fission product decontamination (particularly with respect to zirconium) is improved due to the low acid concentration. On the other hand, undesirable precipitates can be encountered during feed adjustment of high burnup fuels from power reactors. For this reason, a dual cycle THOREX process was developed by Farbwerke Hoechst as part of the German project of reprocessing thorium-bearing fuel from HTR's [14].

The dual cycle process (Tab. 1) uses a 1 M HNO_3 feed solution in the first cycle and a 0.1 M HNO_3 scrub, thus avoiding hydrolytic precipitates during feed adjustment. After having separated the main volume of fission products in the first cycle, an acid deficient feed solution is used in the second cycle to reach the desired decontamination factors. In this cycle the scrub is 1 M HNO_3.

COMPARISON OF THE ACID WITH THE ACID DEFICIENT THOREX PROCESS

As already mentioned above, the acid THOREX process and the acid deficient THOREX process differ very much in their HNO_3 supply via feed solution and scrub. The low HNO_3 concentration of the incoming scrub solution in the acid THOREX process suggests that there is a substantially lower HNO_3 concentration in the scrub section. The question arises whether both flow sheets can be stable in such different process configurations.

An analysis of the HNO_3 profile by means of mixer-settlers and pulsed columns provided the following results (Fig. 2):

Although the acid concentration in the vicinity of the scrub inlet is lower in the acid THOREX process, it is still considerably higher than expected and will then quickly rise to higher values than in the acid deficient process. HNO_3 is obviously transported into the scrub section via the organic phase.

As can be demonstrated by McCabe-Thiele diagrams, the acid and acid deficient THOREX processes differ only slightly in the extraction part, the thorium concentration being slightly higher in the vicinity of the feed point in the acid deficient THOREX process. However, the influence on the scrub part is minor. The extraction isotherms in the scrub section are almost equal for both processes. The concentration of the organic product flows differ due to the different volume flows.

CONSIDERATION FOR THOREX PROCESS SELECTION

The dual cycle THOREX process was developed for reprocessing high-burn-up fuel for reasons mentioned above. Decontamination factors of 10^4 for thorium and 10^5 for uranium can be achieved only with this process.

However, when looking at the entire thorium fuel cycle, the question arises whether such high decontamination factors are required at all. It is known that bred U-233 always contains a few 100 ppm U-232, which has some very radioactive daughters. During refabrication, production amounts of U-233 can only be handled in hot cells, so that a solvent extraction decontamination factor above 10^2 to 10^3 is not necessary.

The same applies to reprocessed thorium which contains considerably more Th-228 than its equilibrium value. Thorium, if recycled immediately, must be processed in Hot Cells in the same way as U-233. On the other hand, reprocessed thorium can also first be stored for 10 half-lives of Th-228, i.e. for about 20 years, so as to reach the radioactivity of unirradiated thorium again. However, high decontamination factors are probably not worthwile for this concept either. The most disturbing radionuclide, Zr-95, with a half-life of 64 days, will have decayed completely. It is also doubtfull that a very good purification of thorium by solvent extraction will provide advantages with respect to other radionuclides.

These considerations lead to the proposal to use a single-cycle THOREX process for reprocessing thorium-bearing fuel from power reactors. An optimized process with acid feed solution (1 $\underline{M}$ HNO_3) should be capable of providing the required decontamination factors of up to about 10^3 for both uranium and thorium. As previously discussed,an acid deficient feed solution cannot be used in a single-cycle operation due to the formation of precipitates during feed adjustment.

Re-extraction can be accomplished both by a co-stripping and by a partitioning process. In a single-cycle THOREX process, joint re-extraction of thorium and uranium is only promising if the aqueous solution produced is to be used either directly for refabrication or after adding U-235. However, the fuel cycle can be designed much more flexibly if uranium and thorium leave the reprocessing plant separately; in other words, if the extraction process is followed by partitioning.

A further argument against applying a co-stripping process is the occurence of process-perturbing crud formations observed in both mixer-settlers and pulse columns. Initially the crud is formed in the vicinity of the inlet of the aqueous phase by interaction with the unloaded organic phase, i.e. in those places where the acid concentration is lowest.

In-depth investigations have shown that the presence of thorium and decomposition products of TBP, especially DBP, will cause emulsification. The disturbances due to emulsion propagates from the place of origin along the entire extraction apparatus.

In cold experiments, the DBP concentration formed by hydrolysis during the extraction process was sufficient for the formation of a Th-DBP crud in the co-stripping stop. The disturbances due to the crud could be avoided in mixer-settlers by substantially reducing the flows (while maintaining the flow ratios). This leads to sufficiently long residence times in the settler chambers for the emulsion to separate again. Hot tests will have to show whether this measure will suffice for high-burn-up fuel when much higher DBP concentrations are to be expected.

Our experiments have demonstrated that no crud formation takes place if the acidity of the aqueous phase is higher than 0.4 M HNO_3. Since partitioning is possible at this acidity, but co-stripping only with serious process implications, partitioning is the preferable procedure.

Recommended Flow Sheet

As a result of the above investigations and considerations, a modified flowsheet is recommended for reprocessing high burnup thorium-containing nuclear fuel, comprising each an extraction-, partitioning- and an U-stripping cascade. It is based upon the following principles:

- An extra co-extraction/decontamination cycle proved to offer no decisive advantages. On the contrary, crud formation problems arising in co-stripping of thorium and uranium are difficult to overcome.

- Re-extraction should be carried out instead as Th/U partitioning at high acidity in order to prevent Th-DBP crud formation.

- For extraction, an acid feed solution should be used because precipitates might be formed during adjustment of acid deficiency. The decontamination factors achieved should be sufficient, and difficulties during feed adjustment are not expected.

- Lower acidity in the scrub section yields higher decontamination factors for Zr/Nb, but lower ones for Ru. If an effective Zr decontamination is required, the formation of low extractable hydrolyzed Zr species is advantageous. Therefore, it might be worthwile to strive for a procedure which generates the hydrolyzed Zr species in an aqueous feed solution without producing precipitates.

The recommended flowsheet characteristics are schematically depicted in table 2.

SELECTION OF THE EXTRACTION APPARATUS

Pulse columns as used for reprocessing LMFBR fuel should also be used preferentially for reprocessing shortly cooled thorium-bearing nuclear fuel. In pulse columns the significantly shortened contact times of the organic phase with fission products lead to a reduced decomposition of TBP, especially to DBP, as compared to mixer-settlers. Process disturbances associated with the presence of DBP can thus be greatly reduced when using pulse columns. Moreover, precipitates such as the so-called "crud", formed from zirconium and DBP, present less disturbance in pulse column operation due to the higher flow velocity as compared to mixer-settlers where the crud formation is likely to cause clogging, which will interrupt the whole extraction process.

An argument in favor of using pulse columns is also their behaviour with regard to the third phase. First of all, the third phase occurs more seldom in pulse columns than in mixer-settlers. This may be attributed to a more rapid mixing of the phases. The feed solution, for example, is distributed in the pulse column in such a short time that formation of the third phase due to locally elevated concentrations is avoided. For this reason, pulse columns can, in principle, also be operated, with a higher a/o ratio than mixer-settlers.

The following guidelines have been established for selecting the continuous phase for the THOREX process in pulse columns: At a flow ratio of a/o ≈ 0.3, a column with a continuous organic phase has a much higher throughput. At a flow ratio of a/o ≈ 1, a column with continuous aqueous phase exhibits the higher throughput. Thus, a continuous organic phase column should be selected for extraction and a continuous aqueous phase column for re-extraction [15].

An important result obtained during the examination of partitioning in pulse columns is the fact that the uranium concentrations observed in the upper part of the column (thorium strip section) are one order of magnitude higher than in the feed solution. This fact must be taken into account for a critically safe design of the column [16].

Low-Enriched Uranium Reprocessing

More recently, the utilization of low-enriched uranium fuel has been selected for HTR's instead of the hitherto favored HEU-thorium fuel cycle. Besides non-proliferation considerations as the main objective for this change, a second reason is the possibility to avoid the development and installation of special reprocessing facilities. Only a specially designed head-end treatment extension is required. Afterwards usual existing PUREX plants might be used for chemical separation.

However, to aid in acceptance of this philosophy it is crucial to assure power plant owners that these fuels also will be processed at a reasonable cost. The primary difference between common LWR- and LEU-HTR fuel is its initial U-235 enrichment. Therefore, reliable criticality prevention measures are of prime importance.

Also expected burnups are twice as high thus giving rise to a considerable higher overall fission product content in spent fuel. Once the fuel is in solution and clarified, the prior history of the fuel has relatively minor influence on the solvent extraction operations. Nevertheless, the higher U-235 enrichment makes the application of a specially designed diluted flowsheet necessary. Also equipment alterations may prove necessary.

Valuable information about the process behaviour may be deduced from previous experience gained at the U.S. Savannah River reprocessing plant. In the frame of their so-called Reduced Enrichment for Research and Test Reactor Program with the goal of reducing the enrichment in research reactors below 20 % U-235, several reprocessing campains have been successfully carried out with low-enriched U/Pu fuel in the existing PUREX plant. The flowsheet adapted is illustrated in figure 3 [17].

Although the applicability of the plant flowsheet has proved successful several particular problems remain to be resolved. They relate to salting-out problems, excessive reflux of uranium in the IB partitioning bank, unsatisfactory mixer-settler stage efficiency and as yet unexplainable difficulties in solvent clean-up. Also proper Ru and Zr decontamination calls for process improvements.

Prevention of criticality in reprocessing LEU-HTR fuel in an existing PUREX plant

A nuclear fission chain reaction in a reprocessing plant is an accident that must be carefully guarded against. Existing PUREX plants are normally designed for safe handling of U/Pu fuel with an initial enrichment of up to 4 % U-235 at the maximum. Safety precaution measures allow no credit due to neutron poisoning by fission products. It is not as yet decided if this rather conservative attitude will be maintained even at very high burnups like in the case of LEU-HTR fuel. Still lacking today is the availability of an absolute reliable reactivity montoring system which guarantees a precise measurement of an approved upper limit value for $K_{\infty}^{het.}$ of the various individual technical configurations.

Processing of LEU fuel with an initial enrichment of 8 to 12 % U-235 requires at all times enforced technical and administrative provision for criticality prevention. Due to the fact that one has to deal with an existing facility design of fixed apparatus geometry, the remaining choiceable criticality controlling parameters are restricted to fissile material concentrations and their absolute mass. As a consequence, the application of a dilute flowsheet and additionally sophisticated neutron measuring equipment is the only acceptable solution. Although technical feasible, there are two inevitable disadvantages connected to it: Cost penalties on the one side as well as the necessity for strict observation of administrative regulations on the other. In any case, a prerequisite is the fulfillment of the double contingency principle.

A homogeneous poisoning of the process solution has from time to time been suggested as a suitable measure for criticality prevention [18]. However, there are several strong arguments against it, the drawbacks linked to its usage are too serious. The assumption for existence of homogeneous systems at all times in all parts of process equipment is not granted because accumulations of deposites, precipitates and residues in the process vessels and piping can not be excluded for sure. Finally, the amount of waste would be increased considerably by this concept.

References

[1] K.J. Notz: Report ORNL-TM-4747 [1975]

[2] P. Engelmann, et al.: Report JÜL-1612, ISSN 0336-0885 [1979]

[3] N.G. Hoogen, E.R. Merz: Nuclear Technology 61 [1983] 380-387

[4] G. Kaiser, et al.: Head-end processing of HTR fuel. This conference

[5] W.D. Bond: Report ORNL 2519 [1958]

[6] A.T. Gresky: Progress in Nuclear Energy, Series III, Process Chemistry Vol. 1 [1956] 212

[7] R.R. Jackson, R.L. Walser: Report ARH-2127 [1977]

[8] D.A. Orth: Nuclear Technology 43 [1979] 63-74

[9] W.O. Haas, D.J. Smith: Report KAPL-1306 [1956]

[10] H.C. Rath von,et al.: USAEC-CONF-660524 [1966] 765-824

[11] F.R. Bruce, et al.: Proc. 2nd U.N. Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva 17 [1958] 49

[12] G. Kaiser, et al.: Kerntechnik 20 [1978]

[13] R.H. Rainey, J.G. Moore: Report ORNL-3155 [1962]

[14] L. Küchler, et al.: Kerntechnik 13 [1971] 319-322

[15] H. Fumoto, et al.: Nucl. Technol., 58 [1982] 447-464

[16] H. Fumoto, E. Zimmer, R. Kiyose, E. Merz: Atomkernenergie-Kerntechnik 41 [1982] 273-278

[17] D.A. Orth, et al.: Int. Solvent Extraction Conference, ISEC'83, Denver, Colorado/USA, 26.8.-2.9.1983; Paper DP-MS-83-1, 16 p.

[18] American Nuclear Society: Report ANSI N 16.1-1975 [1975] La Grange Park, III

FIRST CYCLE		SECOND CYCLE	
EXTRACTION		EXTRACTION	
Feed:	1.15 M TH 1.0 M HNO_2	Feed:	1.15 M TH -0.15 M HNO_3
Scrub:	0.1 M HNO_3	Scrub:	1.0 M HNO_3
Salting Acid:	13 M HNO_3	Salting Acid:	13 M HNO_3
CO-STRIPPING of TH + U		PARTITIONING of TH from U	
Strip:	0.01 M HNO_3	Strip:	0.01 M HNO_3
		Scrub:	30 % TBP

Tab. 1: Simplified Flowsheet of the Two-Cycle Thorex Process of Farbwerke Hoechst AG

Extraction		Relative Flowrates
Feed:	1.0 M Th; 0.5-1.0 m HNO_3	1.0
Scrub:	0.1 M HNO_3	1.0
Salting Acid:	13.0 M HNO_3	0.2
Solvent:	30 % TBP/Dodecane	9.0
Partitioning		
Feed:	0.15 M Th; 0.2 M HNO_3	6.0
Strip:	0.5 M HNO_3	5.0
Scrub:	30 % TBP/Dodecane	1.0
U-Stripping		
Strip:	0.3 M HNO_3	5

Tab. 2: Recommended THOREX flowsheet for high burnup fuel (approximate values for concentrations and flowrates)

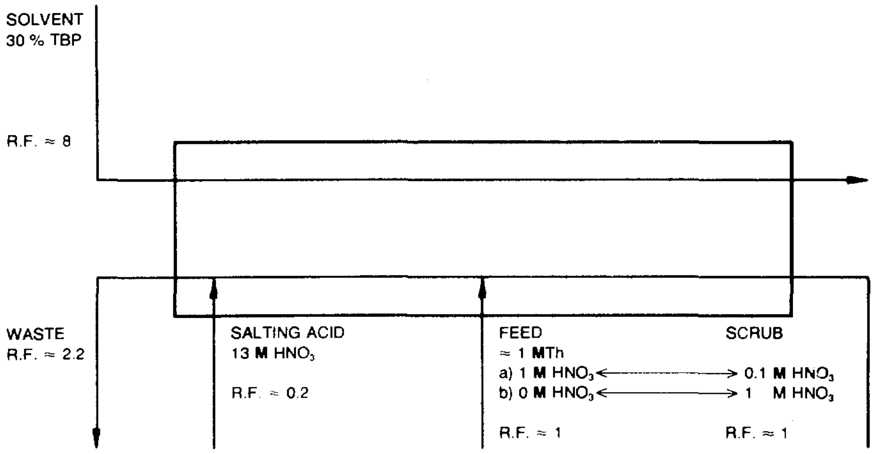


Fig. 1: Generalized Flowsheet of THOREX Processes (Extracting-Scrubbing Cascade)

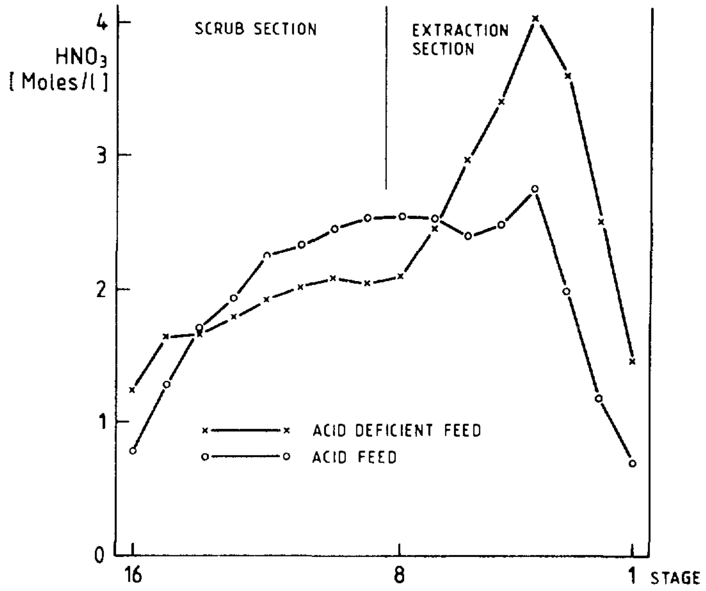
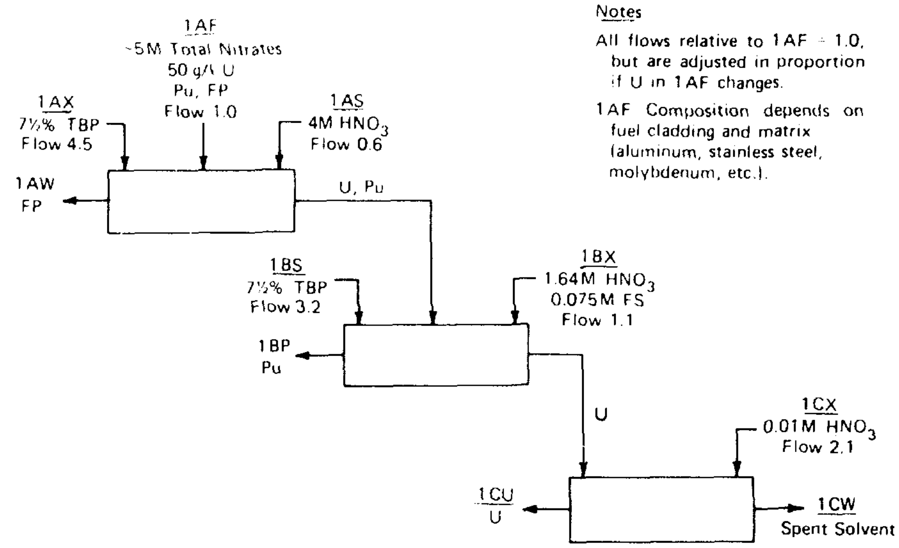


Fig. 2: HNO_3 Profile in Mixer Settler



Notes

All flows relative to 1AF = 1.0, but are adjusted in proportion if U in 1AF changes.

1AF Composition depends on fuel cladding and matrix (aluminum, stainless steel, molybdenum, etc.).

Fig. 3: Nominal Low-Enriched Uranium Flowsheet (D.A. Orth et al., DP-MS-83-1)