

Extended abstract of the lecture to be delivered at the International School of Solvent Extraction, Barcelona, Spain, October 1-6, 1984

CONF-8410131--2-Abst.

DE84 016321

SOLVENT EXTRACTION IN THE NUCLEAR INDUSTRY*

Pier R. Danesi

Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

* Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

CONF-8410131--2-Abst.
CONF-8410131--2-Abst.
It has been determined that the best available copy is hereby being furnished in possible event.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

See

The industrial use of solvent extraction has been pioneered by the nuclear industry since the early forties. Solvent extraction, one of the most powerful purification technologies, is particularly suitable for nuclear applications, where very high recoveries and separation factors are required, for the following reasons: (a) it is a multistage operation (b) it can be easily engineered for remote control (c) it generates small volumes of wastes (d) the radiolytic degradation of the solvent can be easily and continuously compensated.

Since 1950 the leading solvent extraction process of the nuclear industry has become the PUREX process, which is the most important and challenging extraction process ever used in the technological world. The name PUREX stands for Plutonium Uranium Recovery by Extraction. The PUREX process has been used successfully for more than 30 years by several countries to recover and purify plutonium and uranium from dissolved irradiated nuclear fuels both in civilian and military reprocessing plants. The PUREX process utilizes the property of the tri-n-butyl phosphate, TBP, to extract uranium(VI) and plutonium(IV) from nitric acid solutions, while leaving in the aqueous phase the fission products. The selectivity of TBP for U(VI) and Pu(IV) over fission products is shown in Table 1, where the distribution coefficients of selected metal species are reported. Since Pu(III) is very little extracted by TBP and the distribution coefficient of U(VI) dramatically decreases by lowering the aqueous HNO₃ concentration a good separation of U and Pu from the various actinides and fission products is obtained by using different acidities in the extraction and stripping steps and by using selective reductants for reducing Pu(IV) to Pu(III). The extremely high purity Pu and U products are obtained by repeating the separation scheme more than one time. The flow-sheet of the PUREX process is shown in Figure 1. The most difficult fission products to be

removed from U and Pu are ruthenium and zirconium because of their complicated aqueous chemistry in nitric acid solutions. Nevertheless, the PUREX process produces U and Pu which have been decontaminated from fission products of factors as high as 10^6 to 10^8 . Moreover, more than 99% of the uranium and plutonium are recovered.

The solvent extraction of U and Pu by TBP and their separation from the fission products is just one of the many steps which are contained in the entire fuel cycle, which is schematically represented in Figure 2. The fuel cycle involves the handling of the nuclear materials which are necessary for the production of the nuclear energy as well as of the radioactive products generated during the operation of the nuclear reactor.

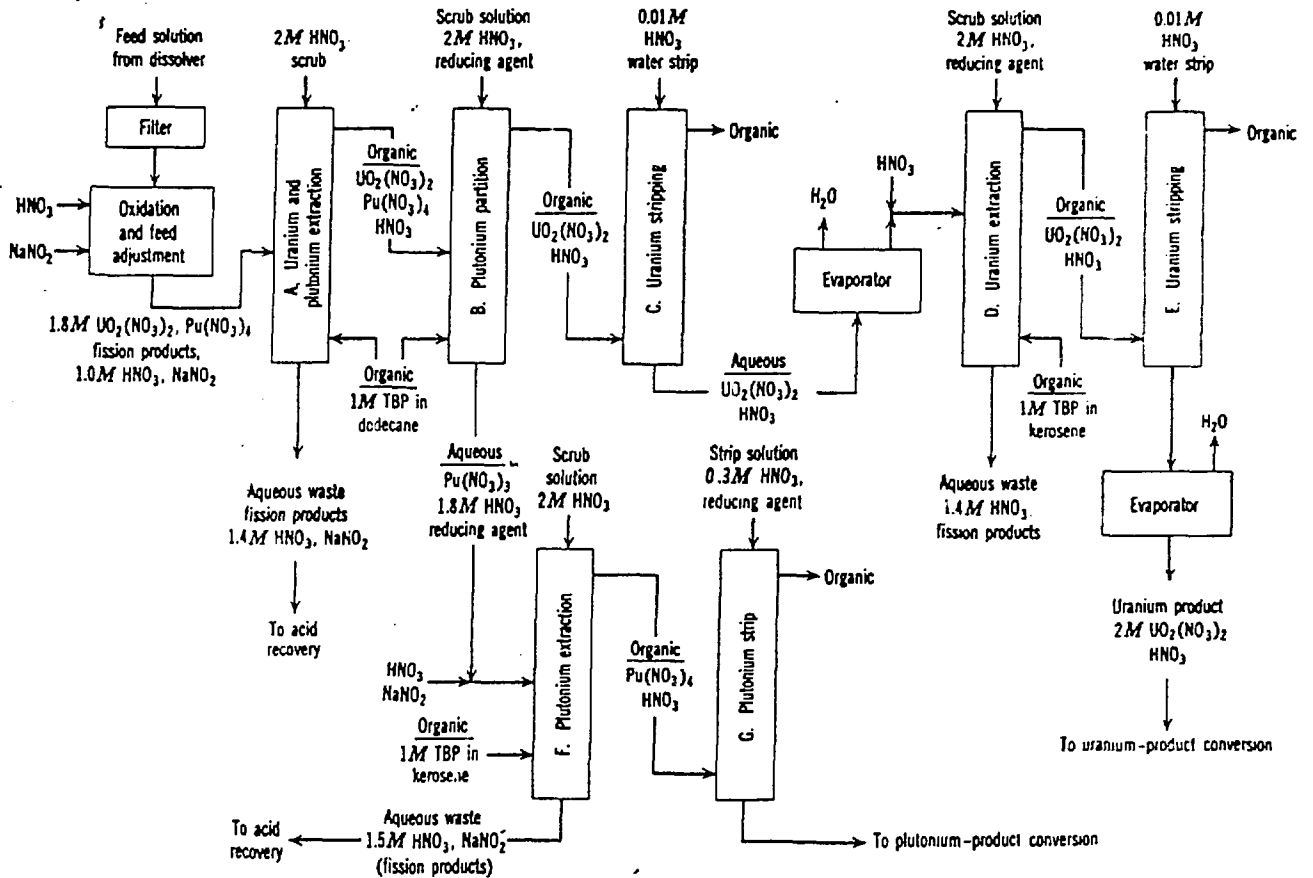
Solvent extraction is used in the fuel cycle also for the extraction and concentration of uranium from its ores. Basic extractants, such as long chain tertiary amines, or mixtures of neutral and acidic extractants, such as TBP and alkylphosphoric acids, are used in these extraction processes. Two of these processes are: the AMEX (amine extraction) and the DAPEX (di-alkylphosphoric acid extraction) processes.

Finally, solvent extraction can also be used for decontaminating the acid streams (containing small amounts of actinides, fission products and corrosion products) which are generated during the reprocessing of the irradiated nuclear fuel. Recently a new class of bifunctional extractants of the carbamoylmethylphosphoryl type have been intensively studied as potential solvent extraction reagents suitable for this aim. These reagents are particularly interesting since they have the ability to extract actinides and rare earths fission products from other fission and corrosion products using concentrated nitric acid solutions.

TABLE 1. Distribution Coefficients of U, Pu and Selected Fission Products Between 1 M HNO₃ and 30% TBP in Kerosene at 25°C.

Species	D
UO ₂ ²⁺	8.1
Pu ⁴⁺	1.55
PuO ₂ ²⁺	0.62
HNO ₃	0.07
Zr	0.02
Ce ³⁺	0.01
Ru	0.01
Pu ³⁺	0.008
Nb	0.005
Rare Earths	0.002
Combined Beta Emitters	<0.0001

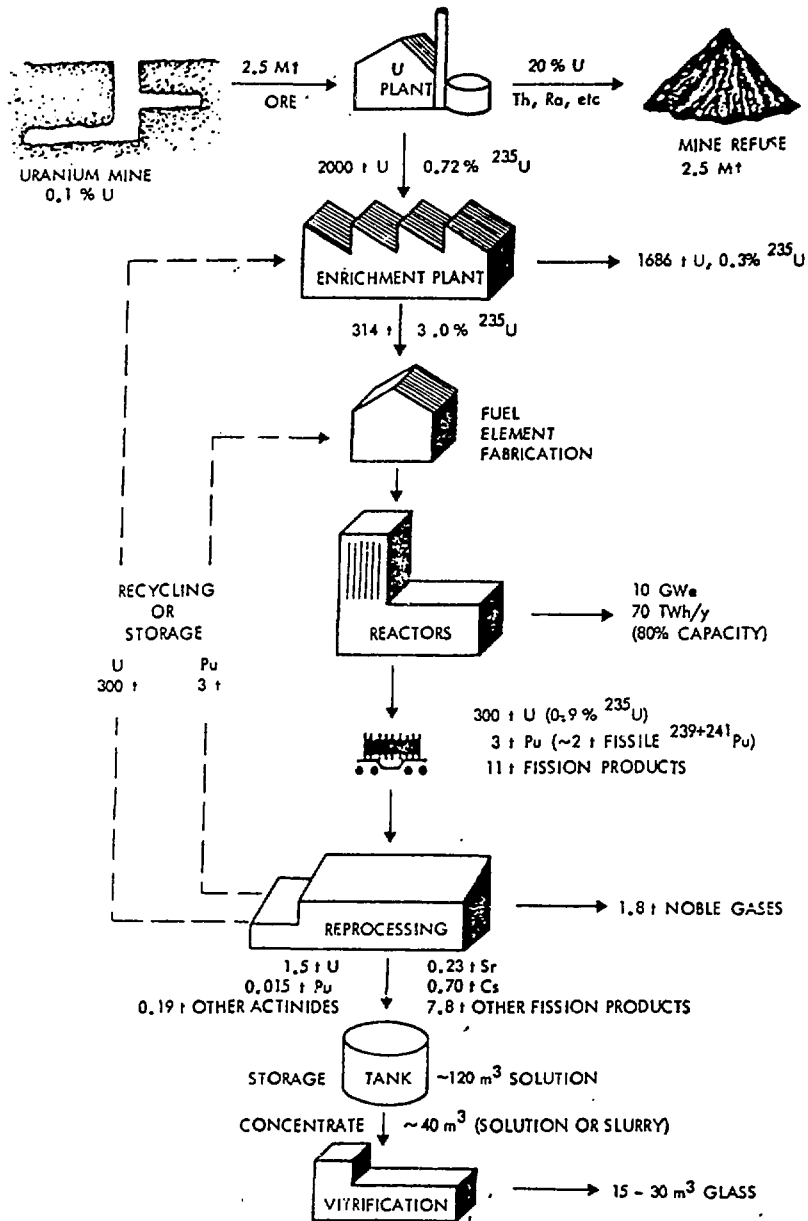
Fig. 1



Flow sheet of Purex process for separation of uranium, plutonium, and fission products by solvent extraction with tributyl phosphate.

Approximate concentrations of major constituents in some of the process streams are shown.

Fig. 2



Annual flow of materials in a 10 GWe LWR fuel cycle program.