PROPOSED AQUEOUS PROCESSES FOR RECOVERING
POWER REACTOR FUELS

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ABSTRACT

Aqueous fuel reprocessing methods that have been proposed for the principal power reactor fuels are described. The volume and composition of decladding waste, of solvent extraction feed, and of high level waste are summarized for each fuel reprocessing method. The status of the process development work for each fuel reprocessing method is summarized.

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INTRODUCTION

In this paper, development of processing methods for a variety of power reactor fuels is summarized. Fuel processing is only one of the steps in the fuel cycle, but must be considered in the overall economic evaluation of each reactor type. Development of processing methods, of course, lags behind evolution of new reactor types and often requires simultaneous evaluation of several potential methods for chemically processing one type of reactor fuel. Ultimate choice of the processing method, as with selection of optimum reactor designs, must await full-scale engineering tests. To illustrate the applicability of the relatively versatile aqueous processes which have been developed, or which are being developed, reactors were classified into several groups and typical examples were chosen. For each example, the aqueous processes which apply are briefly summarized with respect to mechanical pre-treatment, dissolution reagents for cladding and core, solvent extraction method, and volumes of radioactive waste which would be generated in the processing plant. The state of development for each method is indicated. A bibliography is given.

Table I gives the approximate flowsheet conditions for one fuel element of each of the selected representative reactor types. The processes for (1) cladding dissolution or removal, (2) core dissolution, and (3) solvent extraction are described generally in the numbered notes. Table II lists other reactor fuels similar to the representative reactors in Table I.

The processes in the following tabulation (Table I) are based on flowsheets that have been developed in the laboratory to the point where they can be used with a reasonable assurance of success in existing plants, taking into account such factors as fuel dissolution equipment, corrosion, criticality control, solvent extraction, and waste storage practices that are used at various sites at present. Where reasonably firm flowsheets were not available, (and this is the case for most of the proposed processes in the accompanying tabulation), approximately standard Purex or Thorex solvent extraction flowsheets were assumed to follow fuel dissolution without restricting the fissionable material concentration to achieve criticality control by dilution as is proposed for existing plants. Instead,
soluble nuclear poisons (Reference 37) were assumed to be present in process solutions for criticality control, thus permitting high concentrations of fissionable material in geometrically unsafe vessels.

There are many properties of fuel elements that significantly complicate reprocessing. Table II presents a short summary of a few of these. If fuel elements incorporate features in this table, additional development will be required and revisions to flowsheets will have to be made.

**PROPOSED DECLADDING PROCESSES**

1. **Sulfex Process** (References 1-5)

   Stainless steel cladding is dissolved in three times the stoichiometric amount of boiling $4\ M\ H_2SO_4$, yielding a solution containing about 67 g of stainless steel per liter. Off-gas is hydrogen, 1.1 moles for each 55 g of stainless steel dissolved. After decladding, $UO_2$ and ThO$_2$-$UO_2$ cores are washed with a volume of water equal to 25% of decladding solution. Decladding solution is centrifuged to remove fuel particles and neutralized, evaporated, and stored as a sludge containing >50 g of stainless steel per liter. Swaged $UO_2$ fuels may present major handling problems due to release of gross amounts of powdered $UO_2$ in the dissolver when cladding is removed. Low carbon Monel or HW-BMI-20 dissolver.

2. **Chopping** (References 6-9, 43)

   Stainless steel- and zirconium-clad oxide, carbide, or uranium alloy fuels are chopped into short 1/2-1 in. sections using a shear. Sodium or NaK bonding agents possibly can be hydrolyzed with steam prior to core dissolution in acid (not yet tried). The off-gas would be hydrogen. Steaming of chopped Hallam 2 fuel would hydrolyze the sodium bond and the UC core and produce water, hydrogen, and methane as off-gas (proposed; not yet tried). Volume of cladding scrap may be decreased 50% or more by crushing the rings. Stainless steel dissolver.

3. **Zirflex** (References 10-13)

   Zirconium or Zircaloy cladding is dissolved in boiling $5.5\ M\ NH_4F$-$0.5\ M\ NH_4NO_3$ ($F/Zr$ mole ratio of 7). The off-gas contains ~5 moles of ammonia and 0.1 mole of $H_2$ per mole of zirconium dissolved. Ammonia is removed from
the off-gas by water scrubbing. Hot decladding solution is diluted with 0.3 volume of water (used to wash the oxide core) to prevent precipitation of ammonium fluorozirconates on cooling, and is centrifuged to recover UF₄ and UO₂ fines. At F/Zr mole ratio of 7, maximum attainable stable zirconium concentration in waste solution is 0.6 molar. Decladding waste may be neutralized with 0.07 liter of 50% NaOH per liter of waste and stored in carbon steel-lined tanks. Stainless steel, HW-BMI-20, or low-carbon Niemodel dissolver.

4. Combustion (Reference 14)

Burning graphite-matrix fuels in oxygen at 750-900°C produces residues of U₂O₃ or ThO₂–U₂O₃ which are dissolved by conventional methods in a stainless steel or low-carbon Niemodel dissolver. Nickel or stainless steel furnace. (Proposed only)

5. Grinding (References 14-15)

Graphite-matrix fuels containing 100- to 400-micron fuel particles coated with pyrolytic carbon or sintered Al₂O₃ must be ground fine enough (about 200 mesh) to ensure rupture of fuel particles. Uranium and thorium are recovered from the resulting powder by leaching with HNO₃ or HNO₃–HF, respectively. An appreciable fraction of the fission product activity may remain in the graphite sludge. Substantial engineering problems are anticipated with all graphite fuels. Stainless steel or low-carbon Niemodel dissolver. (Proposed only)

6. Darex (References 1, 4, 16, 23, 25)

Stainless steel cladding is dissolved in dilute aqua regia. ThO₂–UO₂ cores are largely insoluble but losses prohibit clad solution discard; UO₂ is soluble (see below). Chloride is removed from the decladding solution by distillation-stripping, and recycled. Uranium and thorium contained in the declad solution are recovered by simultaneous extraction with the core solution (see below). A chloride-bearing waste may be generated if 90% HNO₃(90-95% HNO₃ recommended) is used to batch strip the chloride from decladding or fuel plus clad solutions, or if chloride is scrubbed from process off-gases prior to disposal. Direct disposal of chloride-bearing off-gases, after filtration, to the plant stack may be feasible if excessive radiiodine escape is prevented by long decay of
the fuel. Titanium dissolver and chloride stripping system.

7. Electrolytic Disintegration (References 17, 27)

Zirconium and Zircaloy claddings are anodically disintegrated to zirconium oxide sludges in nitric acid. Uranium oxide cores are simultaneously dissolved. \( \text{ZrO}_2 \) sludge handling may be a problem in the head end system. With washing, \( \sim 0.1\% \) uranium is lost to the sludge. Niobium cathode and platinum clad niobium anode (liquid contact electrode system) in a stainless steel dissolver vessel.

8. Carbonaceous Film Removal (Reference 34)

OMRE fuel is coated with a carbon film that is removed by alkaline permanganate ("Turco") to permit dissolution of the fuel.

PROPOSED CORE DISSOLUTION PROCESSES

1. Nitric Acid (References 1-13, 18-21)

Uranium oxide cores dissolve in boiling nitric acid solutions with evolution of nitrogen oxides and require 3-5 moles of \( \text{HNO}_3 \) per mole of uranium, depending on nitric acid recovery in the condenser and off-gas equipment. The nitric acid concentration used depends on the fuel concentration and acidity desired in the solvent extraction step. Solutions from leaching chopped fuel elements may be dilute due to washing of the cladding but may be evaporated to desired feed concentration. Hydrous uranium (IV) oxide, from hydrolysis of uranium monocarbide, dissolves in nitric acid. Concentrated (11-13 M) \( \text{HNO}_3 \) is used for dissolution of U-10\% Mo alloys if virtually complete precipitation of \( \text{MoO}_3 \) is desired. Terminal acidity must be 8 molar for maximum precipitation of \( \text{MoO}_3 \). \( \text{MoO}_3 \) is collected by centrifugation and then dissolved in hot 5 M NaOH leaving occluded uranium and plutonium as a \( \text{HNO}_3 \)-soluble precipitate. Dissolution of U-3\% Mo in boiling 6 M \( \text{HNO}_3 \) produces stable solutions containing 0.6 M U and \( \sim 3 \text{ M } \text{HNO}_3 \). Maximum molybdenum solubility at \( \sim 3 \text{ M } \text{HNO}_3 \). Aluminum nitrate may be required in the acid for dissolving Zirflex-declad \( \text{UO}_2 \) cores to minimize corrosion from traces of fluoride carried over from decladding step. Stainless steel dissolver.
2. **Darex** (References 1, 22-24)

Stainless steel-clad UO₂ and stainless steel-UCO₂ cermet fuels dissolve completely in boiling 5 M HNO₃--2 M HCl; concentrations up to 100 g/liter of both uranium and stainless steel are attainable. The off-gas is a mixture of nitrogen oxides, NOCl, and chlorine. Prior to solvent extraction, chloride is removed by distillation-stripping from concentrated nitric acid solutions. Chloride is recycled to dissolution equipment. (See Darex decladding above.) Titanium dissolver and chloride stripping system.

3. **HNO₃-cat. HF** (References 1, 25, 26, 35)

Sintered ThO₂-UO₂ dissolves in boiling 13 M HNO₃ containing 0.04 M HF as catalyst to produce concentrations of 1 M Th and 8 M HNO₃ when using 3 times the stoichiometric amount of acid. Without the fluoride catalyst, both uranium and thorium recoveries are low from ground graphite-matrix-fuels. Little off-gas is produced from thorium. Low-carbon Nickel or stainless steel dissolver (Darex requires titanium).

4. **Electrolytic** (References 17, 27-30, 36)

Stainless steel-clad UO₂, stainless steel-UCO₂ cermet, and Zr-clad U-Mo alloy plus stainless steel structural parts are dissolved electrolytically using nitric acid as the electrolyte. If Zr is present, a ZrO₂ sludge will result. Generally, the fuel rests in a niobium basket anode submerged in the acid. However, in a series dissolver, the fuel does not contact the electrolyte but becomes an induced electrolytic cell in the solution between the electrodes. Niobium dissolver and electrodes or niobium cathode and platinum clad niobium anode in a stainless steel dissolver.

5. **HNO₃-Fe(NO₃)₃** (References 19-21)

Uranium-molybdenum alloys dissolve in nitric acid--ferric nitrate solutions. Iron solubilizes molybdenum by complexing as a heteropolyacid. A 1 M uranium solution can be produced by dissolution of U--10% Mo in 4 M HNO₃--1 M Fe(NO₃)₃ and U--3% Mo in boiling 8 M HNO₃--0.5 M Fe(NO₃)₃. HW-EMI-20 or low-carbon Nickel dissolver.

6. **HF-HNO₃** (Reference 31)

Zircaloy-2--clad U-Zr alloy containing less than 2% uranium dissolves in 4.0 M HF without exceeding the solubility limit of UF₆.
Two moles of hydrogen are produced per mole of zirconium dissolved. After dissolution, nitric acid and chromic acid are added to oxidize U(IV) to U(VI) and dissolve tin. Aluminum nitrate is added to complex fluoride and reduce corrosion and to increase salting strength for solvent extraction. Monel dissolver.

7. **Modified Zirflex** (References 32, 33)

Zircaloy-2--clad U-Zr alloys containing up to 10% uranium dissolve in boiling 6 M NH₄F--1 M NH₄NO₃ to which hydrogen peroxide is added continuously. The off-gas is mainly ammonia, 5 moles NH₃ per mole of zirconium dissolved and also contains about 1% H₂ and 0.3% O₂. After dissolution, nitric acid and aluminum nitrate are added to produce an extraction feed solution similar to that for the HF-HNO₃ process. Stainless steel or low-carbon Monel dissolver.

8. **Dilute Niflex** (Reference 17)

The zirconium-clad U-Mo and Zircaloy-2--clad U-Zr alloy fuels are dissolved in 1 M HNO₃ to which HF is added continuously. Alternatively, zirconium cladding on U--10% Mo alloy is dissolved in 0.075 M HF and then 3 M HNO₃--0.075 M Al(NO₃)₃ is added to dissolve the core. At 12 g U/liter or less, molybdenum does not precipitate and criticality control is adequate. Stainless steel dissolver.

9. **HNO₃--H₂SO₄** (Reference 34)

In processing CANDU fuel, stainless steel--UC₂ cermets are dissolved in the presence of steel wool as an activator in 6.5 M H₂SO₄. An equal volume of 6 M HNO₃ is added to dissolve the UC₂. Carpenter 20 dissolver.

**PROPOSED SOLVENT EXTRACTION PROCESSES**

1. **Purex Process** (Reference 38)

Uranium and plutonium are extracted from nitric acid solutions using 30 vol % tributyl phosphate in a hydrocarbon diluent (dodecane). Scrub solution is 2 M HNO₃. Typical flow ratios are, feed: scrub: extractant: 1: 0.7: 3.5. Flowsheet is applicable where the bulk of the cladding and/or alloying constituents are separated from the uranium in the head end process. Some hot laboratory tests were performed at 100 g
U/liter rather than 320 g/l (Ref. 13). Subject to high-level waste storage cooling limitations, the extraction waste may be concentrated by a factor of \( \leq 80 \) prior to storage.

2. **Modified Purex Process** (References 38, 17)

When the feed contains stainless steel, iron, aluminum, zirconium, or molybdenum salts, and possibly fission products in such concentrations that stable solutions are not obtained at normal Purex feed uranium concentrations, the feed concentration is reduced until a stable solution is achieved. Feed and scrub acidities and flow ratios are adjusted as required for extraction. The solvent may be \(<30\%\) TBP in dodecane. Feed solutions are also diluted for criticality control purposes. Evaporation of high-level extraction waste is usually limited by salt solubility rather than fission product heat generation. Storage of wastes after neutralization may be complicated by precipitation of metallic salts.

3. **Zirconium Alloy Fuel Process** (References 31, 39, 40)

The flowsheet was developed for zirconium-uranium alloy fuels containing \(~1\%\) U and has been modified for the higher uranium content in the PWR-1 seed. Extractant is 12.5 vol \% TBP in Amsco 125-90W (or dodecane) hydrocarbon diluent. Flow ratios are, feed : extractant; 1 : 0.625. The scrub column is separate from extraction column to avoid dilution of the high-level waste. An alternate flowsheet uses a compound extraction-scrub column with 1 M HNO\(_3\) as scrub and 5\% TBP in dodecane as solvent. Flow ratios are, feed : scrub : extractant; 1 : 0.2 : 1 (Reference 41).

4. **Fermi Core Flowsheet** (References 17, 42)

Developed for use in existing equipment using dilution for criticality control. Scrub is 3 M HNO\(_3\) and the extractant is 10\% TBP in dodecane. Flow ratios are, feed : scrub : extractant; 1 : 0.5 : 4.

5. **OMRE** (References 34, 44)

Extractant is 10\% TBP in Amsco 125-90W (or dodecane). Flow ratios are, feed : extractant; 1 : 0.55. The scrub column is separate from extraction column to avoid dilution of high level waste. The high-level waste could be, but is not, evaporated prior to storage as acidic waste.
6. Acid Thorex (References 45, 46)

Flowsheet developed to give the maximum decontamination factor when recovery of both uranium and thorium is desired. Nitric acid is substituted for the aluminum nitrate previously used in the Thorex process to achieve a lower waste volume. Scrub #1 is 0.5 M HNO₃, Scrub #2 is 0.01 M Na₃PO₄, 0.01 M Fe(NH₂SO₄)₂, the salting agent (introduced several stages below the feed plate) is 13 M HNO₃, the extractant is 30% TBP in dodecane.

Flow ratios are, feed : Scrub #1 : Scrub #2 : salting agent : extractant; 1 : 0.2 : 0.8 : 0.3 : 7.

For Darex-Thorex, the 13 M HNO₃ salting agent stream is replaced by the chloride-free stainless steel decladding solution to simultaneously recover U and Th contained in the Darex declad solution.

7. Interim-23 Type Thorium Flowsheet (Reference 46)

This flowsheet is used when thorium is not recovered. The scrub is 5 M HNO₃, and the extractant is 5% TBP. Flow ratios are, feed : scrub : extractant; 1 : 0.4 : 2.
REFERENCES

8. V. P. Kelly, HW-62842 (1960).
17. E. S. Occhipinti, et al., DP-393 (1959); DP-439 (1959); DP-491 (1960); DP-519 (1960); DP-546 (1961); DP-588 (1961); DP-706 (1962).
42. H. L. Hull in TID-7583, p. 199.
Table II. Features Which Can Complicate Aqueous Processing

1. Very long fuel elements.
2. Very large cross-section elements.
3. Bundle sheaths not removed at reactor.
4. Use of stainless steel and Zircaloy in same element.
5. Presence of spring materials of different metal than clad.
6. Central solid stainless steel rods, and/or boron impregnated metal or ceramic poison rods inside fuel tubes.
7. Presence of refractory insulators, thermocouples, or burnable poisons that are insoluble.
8. Components with appreciable silicon, niobium, or ceramic content resulting in solids in process solutions.
9. Sodium or sodium-potassium liquid metal bonds.
10. Clad or core dissolutions procedures that evolve potentially hazardous gases (i.e., H₂, CH₄, etc.)
11. Coated fuel particles.
12. Use of U²³⁵O₂-ThO₂ and slightly enriched UO₂ in the same element.
13. Fuels requiring combustion as a precursor to aqueous processing.
14. Fuels with core alloying components that require addition of complexing agents to insure solubility (i.e., Fe(NO₃)₃ in dissolvent for U-Mo cores).
15. Swaged or vibratory compacted oxide powder fuels that may disintegrate into powder during a chemical decladding step.
16. Low theoretical density ceramic fuels or irradiation induced solubility effects that may require recovery of fuel values from decladding waste solutions.
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