

TESTING AND ECONOMICAL EVALUATION OF U(IV) IN PUREX^a

Thomas C. Hsu and James E. Hoisington
E. I. du Pont de Nemours & Co., Inc.
Savannah River Laboratory
Aiken, South Carolina 29808

ABSTRACT

The use of uranous nitrate, U(IV), as a plutonium reductant in the Purex solvent extraction process could significantly reduce the waste generation at the Savannah River Plant. The current reductant is a ferrous sulfamate (FS)/hydroxylamine nitrate (HAN) mixture. The iron and sulfate in the FS are major contributors to waste generation. The U(IV) reductant oxidizes to U(VI) producing no waste. The Savannah River Laboratory has developed an efficient electrochemical cell for U(IV) production and has demonstrated the effectiveness of U(IV) as a plutonium reductant. Plant tests and economic analyses are currently being conducted to determine the cost effectiveness of U(IV) implementation. The results of recent studies are presented.

INTRODUCTION

The Savannah River Plant (SRP) has utilized the Purex solvent extraction process to recover uranium and plutonium from reactor fuel since the plant was started in the early 1950's. In the SRP Purex process, plutonium and uranium are extracted from an oxidizing nitric acid solution into an organic tributyl phosphate phase as Pu(IV) and U(VI) nitrates. Partitioning of the plutonium and uranium is achieved by back-extracting the plutonium into a reductive nitric acid solution as Pu(III). Historically, ferrous sulfamate (FS) has been utilized as the plutonium reductant in the SRP Purex process. The ferrous ion functions as the reductant to reduce Pu(IV) to Pu(III), and the sulfamate stabilizes the Pu(III) and Fe(II) ions in the normally oxidizing nitric acid media. A 40-fold excess was required to obtain acceptable separation efficiencies. Upon neutralization of the waste with 50% caustic the iron forms an insoluble hydroxide and the sulfamate ion forms sulfate salts.

A one-third reduction in solids formation was obtained with the addition of hydroxylamine nitrate (HAN). HAN is currently added to reduce Pu(IV) to Pu(III) and helps stabilize the oxidizing nitric acid solution. Upon oxidation HAN is converted to gaseous nitrogen oxides and water. The current use of HAN has reduced the amount of FS required by one-third. Plant tests of an improved FS/HAN flowsheet are in progress that could lead to a two-thirds reduction in FS use.

A further reduction in solids can be obtained by replacing the FS/HAN reductant with U(IV). The U(IV) is oxidized to U(VI) producing no solids. A small amount of iron (one-fourth of the reference flowsheet amount) is required to assist the U(IV) in reducing Pu(IV). In addition to reducing the plutonium directly, the U(IV) reduces the Fe(III) to Fe(II). This regeneration effect of U(IV) is the reason for the lower iron requirements relative to the FS/HAN reductant. To eliminate the formation of sulfate salts, the iron is added as ferric nitrate. The acid solution is stabilized with hydrazine (N₂H₄), which is converted to gaseous nitrogen oxides and water.

U(IV) CELL DEVELOPMENT

U(IV) was proposed as a plutonium reductant by Rydberg in 1957.¹ In the late 1970's, Orebaugh and Propst² of the Savannah River Laboratory (SRL) successfully produced U(IV) with essentially a 100% current efficiency using a new flow-through laboratory-scale electrochemical cell. The flow-through cell features four major improvements over earlier cell designs. These are:

- a Nafion® (Du Pont) membrane that effectively separates the catholyte from the anolyte preventing reoxidation of U(IV) at the anode.
- in-situ mercury plating of the platinum cathode to provide the required hydrogen overvoltage to suppress hydrogen generation.
- a porous cathode with a high surface area to volume ratio to provide intimate cathode contact with the cell feed solution.
- the in-cell use of hydrazine stabilizer.

In the normal operational mode at a given flow rate, U(VI) concentration, nitric acid concentration, and mercury plating condition, the cell operating voltage is selected to be the mid-point of the the overvoltage plateau. Figure 1 shows the overvoltage plateau for the laboratory cell is typically 150 to 200 mV. This "wide" plateau provides stable cell operation and results in high currents with current efficiencies approaching 100%.

The cell reaction rate is dependent on the mercury coating, the cell flow rate, the U(VI) concentration and the nitric acid concentration. The mercury plating has the most dominant effect on the reaction rate. The quantity and quality of the mercury plating essentially determine the amount of current that can be passed through the cell.

U(IV) PILOT PLANT

The pilot scale U(IV) generation facility utilizes a single full-scale cell with a capacity 60 times that of the laboratory cell. The single cell provides one-sixteenth of the capacity required to support routine SRP solvent extraction operations. The cell typically draws 375 amps at 3 VDC during steady-state operation.

a. The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

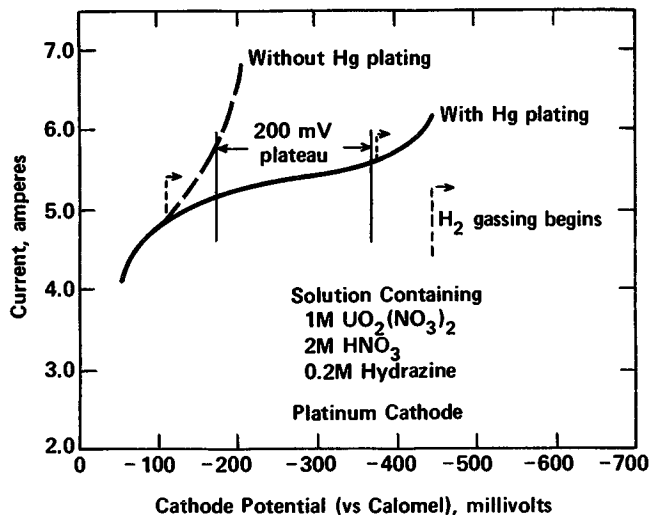


Fig. 1. Typical Performance Curve for Laboratory-Scale Electrochemical Cell.

Full scale production can be obtained with the addition of fifteen cells and upgrading the power supply to 6000 amps.

Figure 2 shows the U(IV) pilot plant flow diagram. The electrochemical cell along with the associated process pumps, tanks and piping are located inside an enclosed operating space similar to a large laboratory hood. The enclosed operating space is kept slightly below atmospheric pressure to contain any hydrazine or nitric acid vapors. Thirty-four hundred liter U(VI) and U(IV) storage tanks are located outside surrounded by a dike to contain any spills. The hydrazine mononitrate and the nitric acid drums are also located outside in a controlled access area.

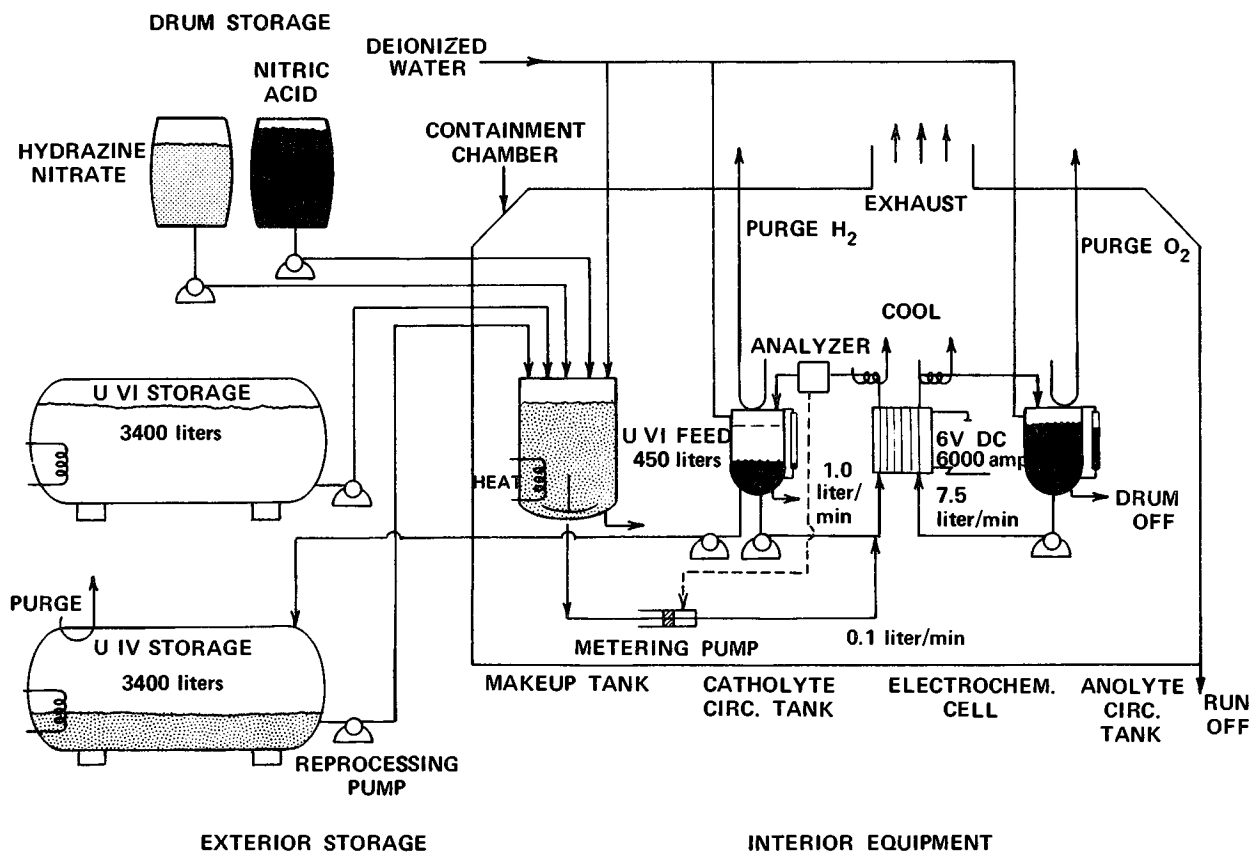


Fig. 2. Uranium (IV) Pilot Plant.

In July, 1982, the pilot plant was operated continuously for 504 hrs. The goal was to produce enough U(IV) for a test in the second uranium cycle of the Purex plant. Almost 2300 liters of U(IV) at 0.8 M concentration were produced. The pilot plant performed as designed with no major operational problems.

SECOND URANIUM CYCLE PLANT TEST

The second uranium cycle was chosen for the initial test because a U(IV)/hydrazine flowsheet can be introduced into the process with minimal impact on Purex operations. The only part of the normal second cycle operation that required modification was the feed adjustment step. The test objective was to gain operating experience in full scale operations and to develop basic data for the eventual U(IV) plant test in the Purex first cycle. The plant test was conducted with the 2300 liters of U(IV) solution produced by the U(IV) pilot plant facility. The test continued for approximately 125 hours of operation, extending over two weeks.

Operation of the second uranium cycle was successful using the SRL developed U(IV) flowsheet. Plutonium decontamination of the uranium product was comparable to that achieved with the normal flowsheet. Figure 3 shows the amount of plutonium in the uranium was within the normal operating range throughout the test. High reducing conditions were maintained in the feed solution throughout the test, although it was found that the U(IV) was oxidized much more rapidly than anticipated at the 50°C feed temperature. However, before it decomposed, the U(IV) performed its reductant function by reducing all available cations in the feed solution, particularly Fe(III) carried over from the first cycle. Once reduced, this Fe(II) and the hydrazine stabilizer maintained a sufficiently high reducing normality to ensure successful second cycle operation.

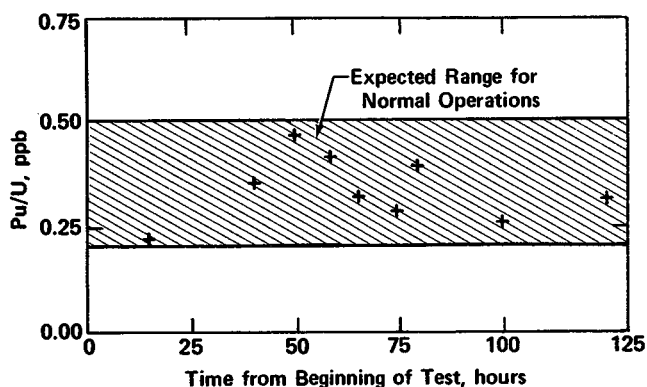


Fig. 3. Uranium (IV) Flowsheet Performance.

ECONOMIC ANALYSIS

A preliminary economic analysis shows implementation of the U(IV) flowsheet in the first solvent extraction cycle would save about \$9.0 million (present value) over a ten year period. This estimate is based on a discounted cash flow analysis with a 10% discount rate. The cost savings are the difference between the incremental reductant chemical costs and the incremental waste disposal costs.

In the SRP Purex process, reductant is added in the second mixer-settler bank of the first solvent extraction cycle and in the second uranium cycle. This analysis only considers the effect of the reductant change in the first cycle. The second uranium cycle is not considered. Implementation of the U(IV) flowsheet in the second uranium cycle would increase the savings by 2%.

The analysis is based on ten years of U(IV) operation beginning in 1985. The \$2.5 million capital cost for a U(IV) production facility is recovered during the study period. The annual Purex throughput is predicted to average 1950 MTU throughout the period. The reductant requirements for the existing FS/HAN flowsheet are 40 kgs/MTU of FS and 12 kgs/MTU of HAN. The U(IV) flowsheet has several reductant and chemical requirements. The U(IV) solution is added to the solvent extraction system at a rate of 62.5 l/MTU. The aqueous solution consists of 0.8 M U(IV), 0.2M U(VI), 1.4M HNO₃ and 0.2M N₂H₄. Forty-two liters per MTU of 50% HNO₃ and 16 kgs/MTU of ferric nitrate are also added.

The amount of low activity waste (LAW) generated by each flowsheet is shown in Table I. The LAW

Table I. Purex Low Level Waste

Component	Kgs/MTU	
	0.08M FS/0.06M HAN ^a	0.025M U(IV) ^a
Na ₂ SO ₄	63	18
NaNO ₃	567	532
NaOH	45	45
Fe(OH) ₃	17	4
NaAlO ₂	125	125
NaNO ₂	29	29
H ₂ O	2389	2393
Total	3235	3076
Specific Gravity	1.23	1.23
Volume (liters)	2630	2500

a. Reductant concentration in the mixer-settler feed stream.

Table II. Purex High Level Waste

Component	Kgs/MTU
Na ₂ SO ₄	11
NaNO ₃	71
NaOH	8
Fe(OH) ₃	5
NaAlO ₂	10
NaNO ₂	-
H ₂ O	280
Total	385
Specific Gravity	1.25
Volume (liters)	308

Table III. Composite Purex Waste

Component	Kgs/MTU	
	0.08 M FS/0.06 M HAN ^a	0.025M U(IV) ^a
Na ₂ SO ₄	74	29
NaNO ₃	638	603
NaOH	53	53
Fe(OH) ₃	22	9
NaAlO ₂	135	135
NaNO ₂	29	29
H ₂ O	2669	2603
Total	3620	3461
Specific Gravity	1.23	1.23
Volume (liters)	2938	2808

composition for the FS/HAN flowsheet is based on current SRP operation. The U(IV) flowsheet LAW composition is calculated based on the solids reduction described previously. The volume of the U(IV) LAW is based on the assumption that the U(IV) LAW will be evaporated to the same specific gravity (1.23) as the current LAW. Reductant changes do not affect the high activity waste (HAW) composition, the HAW composition shown in Table II is used for each flowsheet. Table III shows the composite Purex waste (LAW plus HAW) for each flowsheet. The quantities shown in Table III are used as the basis for the cost savings.

The results of the economic analysis are shown in Table IV. The results are expressed in both discounted and undiscounted dollars. The U(IV) flowsheet has a net present value of \$9.0 million corresponding to a unit cost of \$1128/MTU compared to \$1568/MTU for the FS/HAN flowsheet. The undiscounted savings are considerably higher. Over the ten year period, the undiscounted U(IV) savings are \$69 million with a unit cost of \$7746/MTU. This compares the FS/HAN unit cost of \$11292/MTU.

Table IV. Discount Analysis

Discount Rate	0%			10%		
	Unit Cost (\$/MTU)	Annual Cost ^a (\$10 ⁶)	Annual Savings (\$10 ⁶)	Unit Cost (\$/MTU)	Annual Cost ^a (\$10 ⁶)	Annual Savings (\$10 ⁶)
Flowsheet						
0.08M FS/0.06M HAN	11292	22.0	-	1568	3.1	-
0.025M U(IV) ^b	7746	15.1	6.9	1128	2.2	0.9

a. Based on average processing rate of 1950 MTU/yr.

b. The U(IV) generation facility capital costs recovered over 10-year production campaign.

FUTURE PROGRAM

The analysis is conducted in constant 1982 dollars at 0 and 10% discount rates. The 0% rate reflects constant undiscounted 1982 dollars. The 10% rate is the rate at which alternatives are evaluated per the Office of Management and Budget. The reductant chemical costs are assumed to be incurred immediately at the time of processing. The interim waste management costs (waste tank storage) are spread evenly over the 15 year period between Purex processing and vitrification in the proposed Defense Waste Processing Facility (DWPF). All vitrification and emplacement costs are assumed to be incurred 15 years after the initial processing. The \$2.5 million capital cost for the U(IV) production facility is assumed to be incurred in 1984, one year before flowsheet implementation.

The reductant chemical costs used are based on the material costs shown in Table V. The FS/HAN flowsheet reductant cost is \$159/MTU. The U(IV) flowsheet reductant cost is \$134/MTU. The U(IV) solution cost is \$0.65/l which only includes the operating costs of the U(IV) production facility. No U(IV) capital costs are included.

The incremental waste disposal costs used in the analysis are also shown in Table V. Included are the amounts of glass and saltcrete produced by each flowsheet.³ Inspection of Table V shows the incremental glass production and disposal cost is significantly higher than either the saltcrete costs or the interim waste management costs. Since iron is a major component of the glass, the potential for significant waste disposal cost savings through the implementation of the U(IV) flowsheet becomes apparent.

The viability of U(IV) and the amount of waste reduction achievable with U(IV) as a plutonium reduction still need to be verified with a first cycle test in the Purex plant. In order to supply enough U(IV) solution for a first cycle test, the production capacity of the pilot plant must be expanded or the single cell facility operated for an extended period. In the interim, the pilot plant facility will be operated to provide the engineering data required to optimize future cell designs.

Additional solvent extraction plant tests and economic analyses are being conducted with U(IV) and with improved FS/HAN flowsheets. A decision on the preferred reductant flowsheet will be made in late 1983.

References

1. Rydberg, J. "The Reduction of Plutonium by Tetravalent Uranium," J. Inorg. & Nucl. Chem. 5, 1, 79 (1957).
2. Orebaugh, E. G. and R. C. Propst, "Electrolytic Production of Uranous Nitrate," DP-1549, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC, (April 1980).
3. Final Environmental Impact Statement, Defense Waste Processing Facility, DOE-EIS-0082, E. I. du Pont de Nemours and Co., Savannah River Plant, Aiken, SC, (February, 1982).

Table V. Unit Processing Costs

Component (Price)	Unit Cost (\$/MTU)	
	0.08M FS/0.04M HAN ^{a,b}	0.025M U(IV) ^{a,c}
FS (\$0.17/kg of 50% FS)	66	-
HAN (\$0.23/kg of 16% HAN)	81	-
U(IV) solution (\$0.75/l) ^d	-	41
50% HNO ₃ (\$0.005/kg)	-	2
30% N ₂ H ₄ (\$0.29/kg)	-	84
Fe(NO ₃) ₃ ·9H ₂ O (\$0.017/kg)	-	1
NaOH and NaNO ₂ ^e	12	6
Subtotal	159	134
Interim Waste Management (\$0.57/l)	1,682	1,608
DWPF Glass Production (\$82.54/kg) ^f	6,108	3,017
DWPF Saltcrete Production (\$0.55/kg) ^g	3,343	2,859
Subtotal	11,133	7,484
Total	11,292	7,618

- a. Reductant concentration in the mixer-settler feed stream.
- b. The 0.08M FS/0.06M HAN flowsheet generates 2938 liters of waste/MTU producing 74 kg of glass and 6079 kg of saltcrete.
- c. The 0.025M U(IV) flowsheet generates 2808 liters of waste/MTU producing 37 kg of glass and 5197 kg of saltcrete.
- d. U(IV) solution cost shown does not include \$2.5 million capital cost.
- e. NaOH and NaNO₂ used for waste neutralization. Costs available only as dollars/MTU.
- f. Includes glass production and repository emplacement costs.
- g. Includes saltcrete production and onsite Savannah River disposal costs.