10/30/79

DK. 204

[redacted]

Work Performed Under Contract DE-AC09-78ET-35900

ALLIED-GENERAL NUCLEAR SERVICES
P.O. BOX 847
BARNWELL, SC 29812

MASTER

[redacted]

[redacted]

[redacted]

[redacted]

AGNS-35900-3.2-10

Distribution
Category UC-83

STUDIES AND RESEARCH CONCERNING BNFP

FLOWSHEETS FOR RECOVERY OF NEPTUNIUM FROM LWR FUELS

FINAL REPORT

E. Wesley Murbach

September 1979

[redacted]

ALLIED-GENERAL NUCLEAR SERVICES
POST OFFICE BOX 847
BARNWELL, SOUTH CAROLINA 29812

PREPARED FOR THE
DEPARTMENT OF ENERGY
FUEL CYCLE PROJECT OFFICE
UNDER CONTRACT DE-AC09-78ET-35900

[redacted]

ACKNOWLEDGMENT

Discussions with the following were of assistance in the evolution of the flowsheets: A. L. Ayers, A. F. Cermak, J. H. Ellis, J. H. Gray, J. C. Hall, and W. B. Sumner of AGNS and G. E. Benedict of General Atomic Company.

ABSTRACT

Flowsheets for the separation and purification of neptunium from spent LWR fuels have been developed. The neptunium nitrate product would be suitable for transfer to an oxide conversion/refabrication facility.

TABLE OF CONTENTS

PAGE

ACKNOWLEDGMENT

ABSTRACT

APPENDIX A - THE NEPTUNIUM-NITROUS ACID SYSTEM

APPENDIX B - CALCULATION OF ACTIVITY IN NEPTUNIUM PRODUCT

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

Neptunium is the first of the transuranium elements, and appropriately was the first such to be discovered. The isotope Np-239 was identified as one of the products from irradiation of uranium with slow neutrons. Subsequently, it was learned that the long-lived isotope Np-237 is produced from uranium by the following nuclear reactions:

$$^{238}U(n,2n)^{237}U \xrightarrow{\beta^-} {}^{237}Np$$

and

$$^{235}U(n,\gamma)^{236}U(n,\gamma)^{237}U \xrightarrow{\beta^-} {}^{237}Np$$

In the 1950's Np-237 became of interest as a source material for the production of Pu-238 by the nuclear reaction

$$^{237}Np(n,\gamma)^{238}Np \xrightarrow{\beta^-} {}^{238}Pu$$

Pu-238 is a useful isotopic heat source as its output is slightly over 0.5 watt per gram. Based on this interest, programs were initiated for Np-237 recovery at both Hanford and Savannah River as outlined in the excellent monograph by Shulz and Benedict.(1)

Recently the recovery and recycle of Np-237 in LWR fuel has been proposed as a method to increase the proliferation resistance of power reactor fuels.(2) By recycling Np-237 with fresh fuel, the plutonium produced by irradiation will contain sufficient Pu-238 so that it would be even less attractive as a weapons material than first discharge power reactor material. Reprocessing could then proceed with a diminished threat of proliferation.

The early recovery programs utilized relatively low burnup military production fuels as a source of neptunium. LWR fuels which may be irradiated to over 30,000 MWd/T will contain considerably more neptunium than production fuel. Thus, adaptation of technology developed earlier for neptunium recovery should be adequate for LWR fuel.

The solvent extraction chemistry of neptunium is more complex than either uranium or plutonium which complicates its separation from irradiated fuel. In acid solution, neptunium can exist as Np^{+4}, NpO_2^{+}, and NpO_2^{++}. Np^{+4} and NpO_2^{++} are extractable into TBP while NpO_2^+ is inextractable. The distribution coefficients for neptunium as a function of nitric acid concentration are shown in Figure 1.1. Also shown is the extraction coefficient for NpO_2^{++} in the presence of 0.3 M uranium and single points for uranium and plutonium in the presence of 0.3 M uranium.(1,3) As can be seen, the presence of uranium decreases the extraction coefficients for all species. However, NpO_2^{++} is more extractable than plutonium, so if neptunium can be maintained in the plus 6 valence state, it can be extracted.

Neptunium valence can be controlled by nitric and/or nitrous acid. High concentrations of nitric acid stabilize NpO_2^{++} and in the presence of nitric acid small concentrations of nitrous acid, approximately 1×10^{-3} M, catalyze the oxidation of NpO_2^{+} to NpO_2^{++}. On the other hand, nitrous acid at about 10^{-2} M stabilizes NpO_2^{+}. Other strong oxidizing agents will oxidize neptunium to NpO_2^{++}. For example, Tajik(4) recommends vanadyl ion to produce NpO_2^{++} in the first extraction cycle; however, this has not been demonstrated on the plant scale.

The standard dissolvent for spent nuclear fuel is nitric acid. Operational experience has demonstrated that most of the neptunium is NpO_2^{++} during dissolution in nitric acid.(5) However, the valence state of neptunium in the dissolver solution will vary as a function of cooling time and time between dissolution and extraction. Nitrite ion is produced in dissolver solution by radiolysis of nitric acid, the extent being a function of radiation dose, which in turn is a function of cooling time. With relatively short cooled fuels sufficient nitrite could be produced to stabilize NpO_2^{+}. Also, neptunium ions can disproportionate while waiting reprocessing. The net result of all these variables is that it is difficult to predict the valence state of neptunium entering the first extraction cycle.

The neptunium recovery processes at both Hanford and Savannah River are based on valence control by application of nitrite ion.(1) In the Hanford process, an aqueous stream containing sodium nitrite is introduced near the bottom of the first extraction column (above the organic inlet). Nitrous acid is formed in the aqueous stream some of which is extracted by the organic stream. Oxidation of NpO_2^{+} to NpO_2^{++} takes place in the upper sections of the column. The equilibrium data for nitrous acid between 30% TBP and nitric acid have been studied by Burger and Money.(6) At 2 M nitric acid the distribution coefficient, E_a°, is in the range 5 to 8.

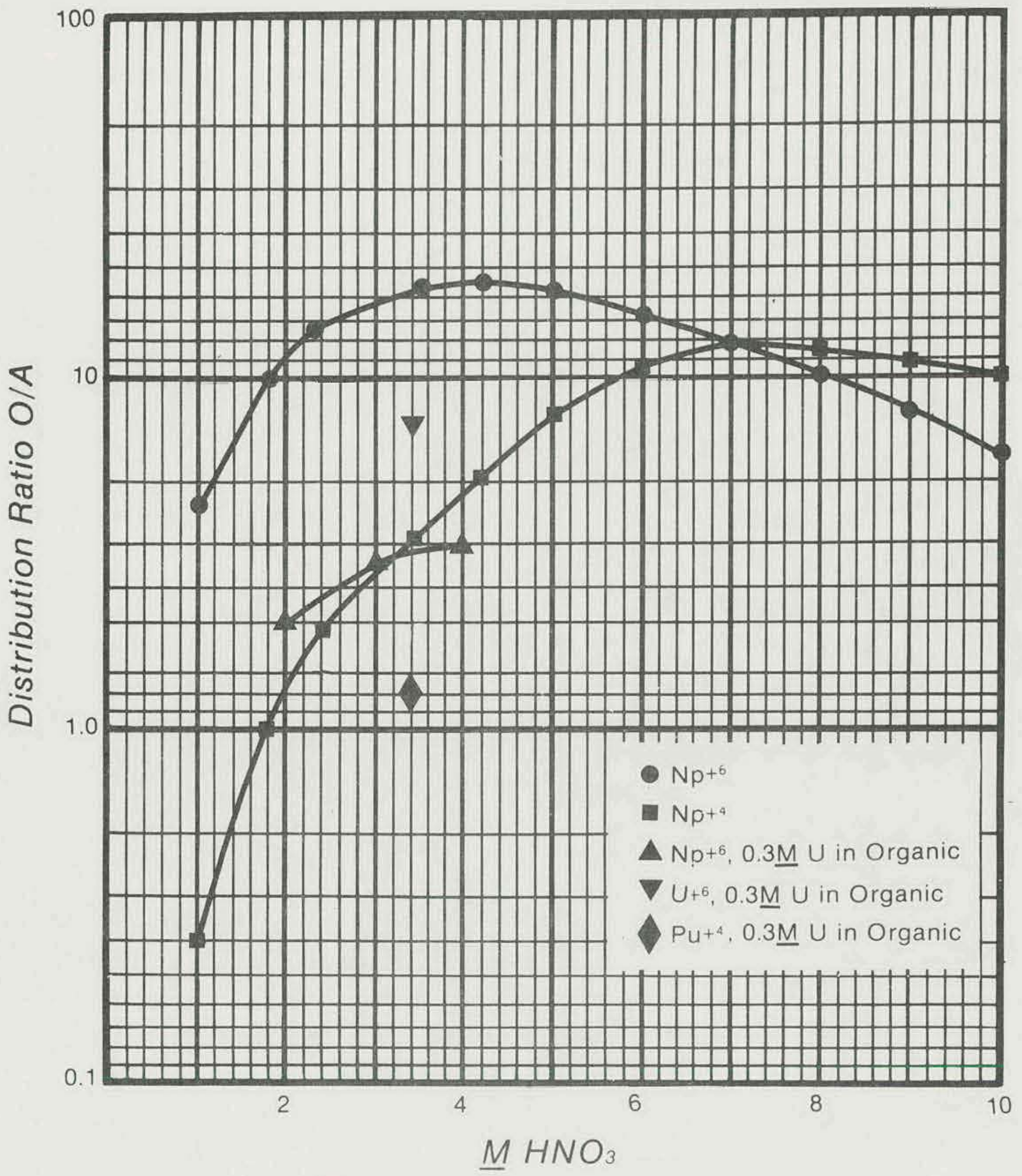
In contrast to the Hanford process, at Savannah River sufficient nitrite is added to the first contactor to stabilize NpO_2^{+}. Nitrite is added to the next to the last stage of the 1A mixer-settler equivalent to 7×10^{-3} M in the solvent phase.(7) The neptunium exits the mixer-settler with the first cycle waste from which it subsequently is recovered by ion exchange.

After review of these two processes, it appeared that recovery of neptunium from first cycle LWR wastes would be complicated by the higher level of fission products and actinides. Using an ion exchange process, the higher radiation levels would lead to more rapid deterioration of the resin, probably to the detriment of neptunium recovery. The spent resin might also be a significant waste volume.

Based on this rather negative evaluation of the Savannah River process, it was decided to adapt the Hanford approach to the recovery of neptunium from LWR fuels. The separated neptunium requires further decontamination from uranium, plutonium, and fission products. The coextraction, separation, and purification steps are discussed in the body of this report.

As a part of the 1978 DOE-funded study conducted by AGNS, a coprocessing (uranium-25% plutonium product), high-DF flowsheet was developed.(8) In this study neptunium recovery is integrated into the coprocessing high-DF flowsheet.

One tonne of LWR fuel irradiated to 33,000 MWd will contain approximately 500 grams of neptunium. Thus, a model plant such as the BNFP could recover as much as 2.5 kilograms per day of neptunium. Discharged fuel from the first "spike" reload would contain approximately 1200 grams of neptunium per tonne.(9) However, the differential between 2.5 and 6 kilograms per day will have no impact on the conversion facilities which have been conceptualized.(11)



NEPTUNIUM EXTRACTION COEFFICIENTS BETWEEN NITRIC ACID AND 30% TBP

FIGURE 1-1

2.0 SUMMARY

Flowsheets have been developed for the recovery of neptunium from LWR fuels using the BNFP as a model plant. In the first extraction cycle the oxidation of neptunium to NpO_2^{++} is catalyzed by small amounts of nitrous acid so that it coextracts with uranium and plutonium. Neptunium is subsequently rejected to the 1S system by valence changes in the uranium and plutonium columns. Neptunium is separated from the bulk of the residual uranium and plutonium in the 1S column. The neptunium is then purified in two additional extraction-strip cycles. The neptunium nitrate product is concentrated to 30 grams/liter for transfer to oxide conversion.

3.0 NEPTUNIUM EXTRACTION

In standard Purex processing, the bulk of the neptunium follows the fission products to the high activity waste. The objective in neptunium extraction is to coextract neptunium, uranium, and plutonium in the first cycle and to subsequently remove neptunium into a separate stream for final purification. In this section, flowsheets for recovery of a neptunium bearing stream are discussed.

In order to adapt the Hanford process for neptunium recovery to the AGNS plant, some changes in flows and stream routings are required. In the Hanford process, the first solvent extraction cycle is operated at a uranium saturation of 0.3 M as compared to 0.34 M in the AGNS flowsheet. The higher uranium saturation tends to force neptunium to remain in the aqueous phase while the lower saturation allows Np^{+6} to extract. Thus, at a given uranium throughput, the solvent to the first cycle must be increased.

The basic AGNS flowsheet is shown in Figure 3-1. The first cycle extractor is a centrifugal contactor. On the assumption that the feed to the contactor contains some NpO_2^+, the residence time in the contactor is probably too short for all of the NpO_2^+ to be oxidized to NpO_2^{++} and be extracted. However, the HS column which is a pulse column can be operated in the dual extraction-scrub mode which should provide time for the oxidation and thus, efficient extraction. If relatively long-cooled fuel (> one year) is processed, increased residence time in the column should not result in excessive radiation damage to the solvent which is one of the reasons for using a centrifugal contactor for first cycle extraction.

The neptunium extraction flowsheet is shown in Figure 3-2 in which neptunium in the HAF is extracted with uranium and plutonium into the HSP. A nitrite addition stream, the HSN, is shown on the flowsheet. This stream will be dependent on the amount of nitrous acid in the HAP. (The possible nitrous acid material balance is discussed in Appendix A.) A scrub ratio of 0.15 is recommended for the Hanford process, also the acidity is decreased for better fission product decontamination.

As can be seen, the solvent to the HS Column is comprised of two streams, the HAP and the HSX. The rationale for this is as follows: In the basic AGNS flowsheet, the organic raffinates from the second and third plutonium cycles are combined into the POR (Plutonium Organic Raffinate) and returned to the 1B Electrocell. The organic product from the 1S Column is normally returned to the HA Contactor. In the coprocessing flowsheet,(8) the POR is a rather substantial amount, 550 liters per hour, in part because of an organic recycle stream from an assumed MOX conversion facility. To limit the volume of solvent through the extraction-partition cycle, the POR is used as a part of the extractant in the 1S Column. Otherwise, combining the HSP and the POR in the 1B system would decrease heavy metal saturation with a decrease in throughput.

The organic raffinates from the neptunium purification cycles (see Section 4.0) are also returned to the 1S Column. The primary purpose of the 1S Column is to recover uranium and plutonium from the second uranium cycle waste and the second and third plutonium cycle wastes. However, in the neptunium recovery process, the 1S Column also serves to separate neptunium from recycle uranium and plutonium and to recover neptunium from additional waste streams. The 2DW contains hydrazine so N_2O_4 is added to the 1S Feed Tank to destroy the hydrazine and to reoxidize any Pu^{+3} to Pu^{+4}. Some of the nitrous acid formed from the N_2O_4 will extract into the organic in the 1S Column. Thus, it is believed that better control of nitrous acid would be possible if the 1SP was processed through the HA Contactor before entering the first extraction cycle. If too much nitrous acid reaches the HS Column, neptunium losses to waste would be excessive. By processing the 1SP through the HA Contactor along with the HSR, additional uranium and plutonium may be recovered from the waste stream and hydrazine could be added to the HSR to destroy excess nitrous acid. Using the HA Contactor in the process increases possible flowsheet options for process improvements.

Some fresh solvent, the HAX, is also added to the HA Contactor. The combined HAX-1SP then becomes the HAP. The HAW follows its normal routing to concentration and storage.

Separation of neptunium from uranium and plutonium is discussed in Section 4.0.

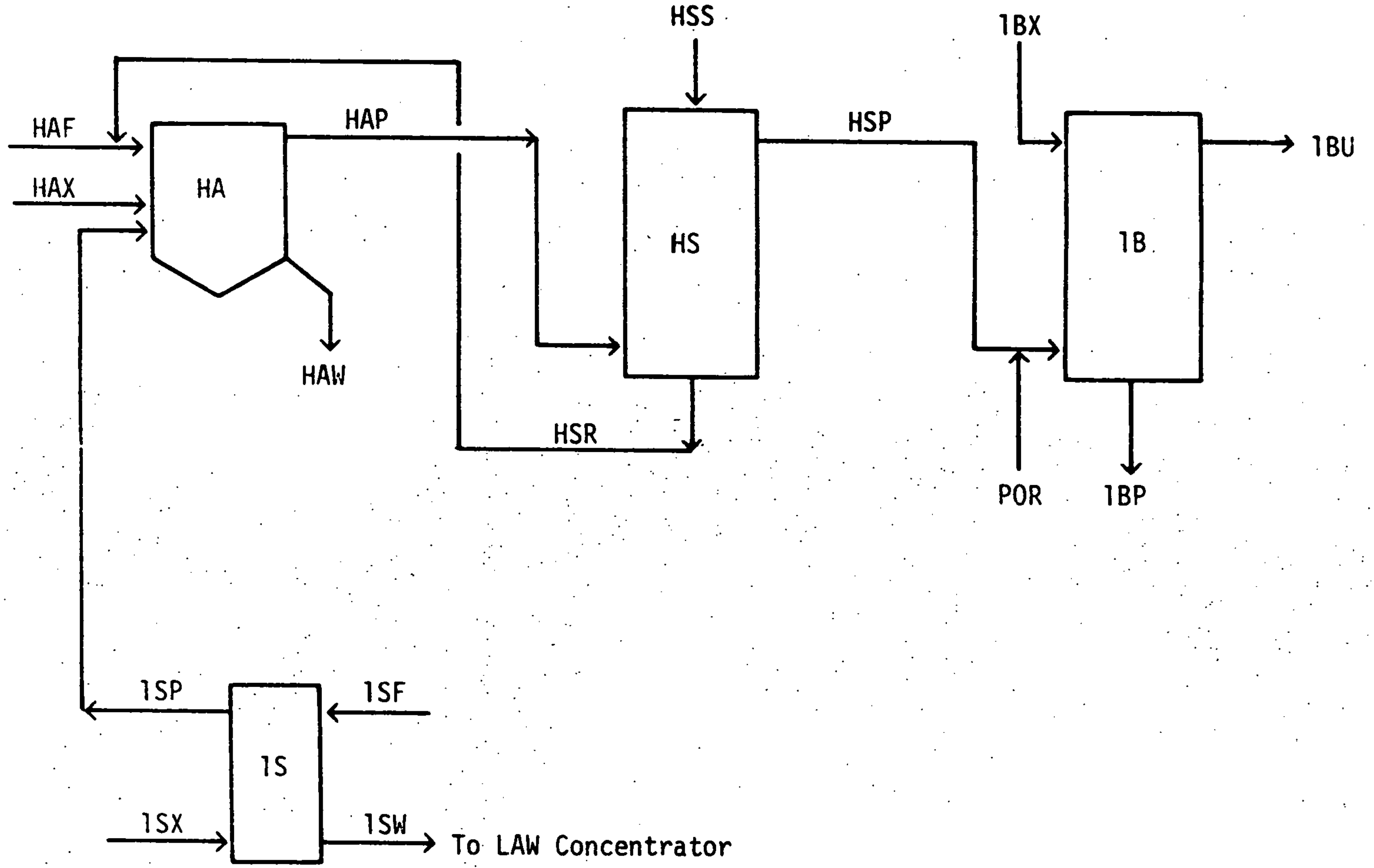
The material balance for this portion of the flowsheet is given in Table 3-1.

It should be realized that this is a "state-of-the-art" flowsheet. In practice in an operating plant, process parameters such as flow rates, acidity, additions, etc., would be "fine-tuned" to optimize neptunium recovery.

TABLE 3-1

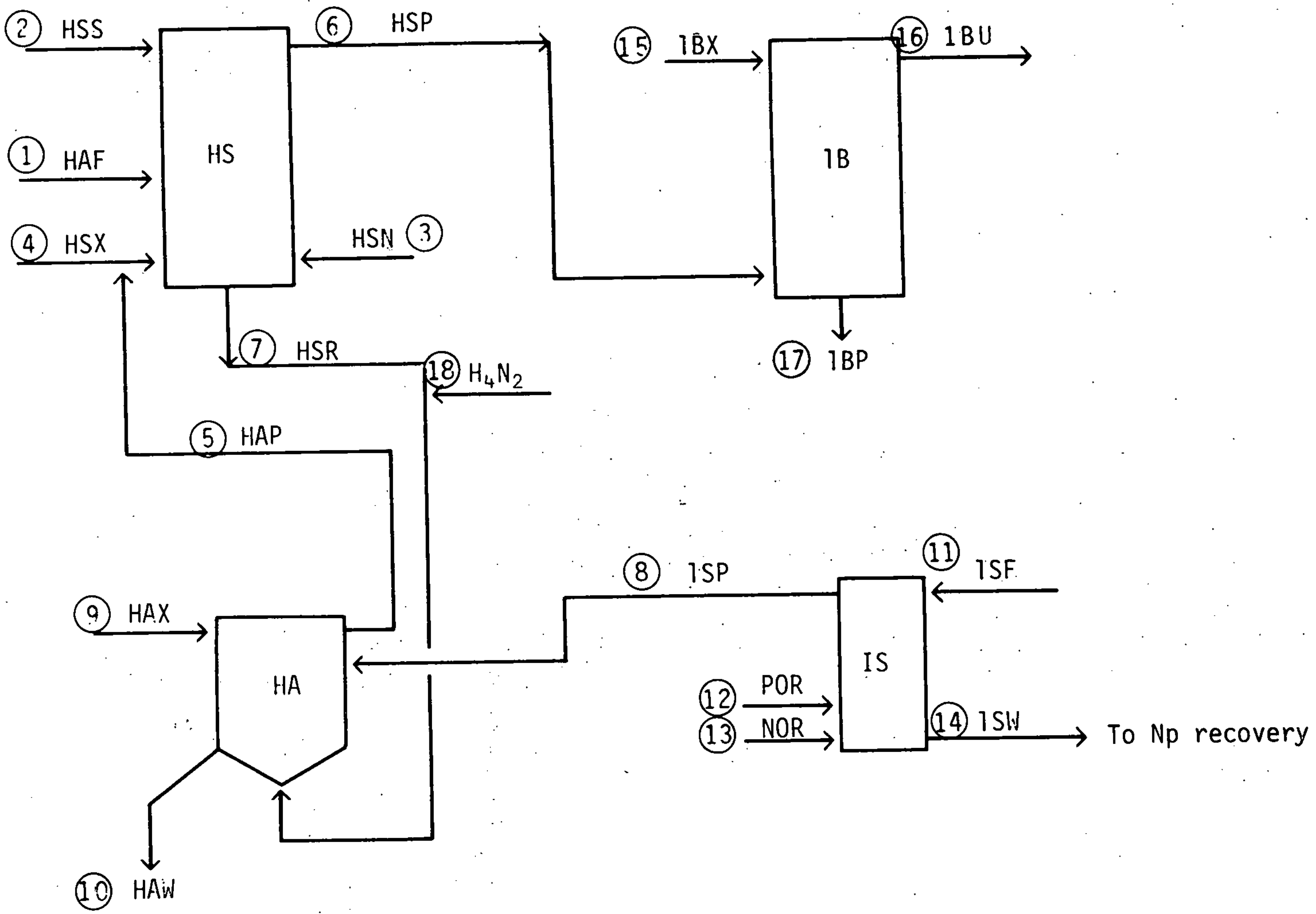
MATERIAL BALANCE - NEPTUNIUM RECOVERY

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	HAF	HSS	HSN	HSX	HAP	HSP	HSR	1SP	HAX	HAW	1SF	POR	NOR	1SW	1BX	1BU	1BP	HSR Butt
Type	A	A	A	O	O	O	A	O	O	A	A	O	O	A	A	O	A	A
Temp °C	49	35	30	45	40	45	45	31	31	45	38	35	30	37	30	31	31	25
Sp. G.	1.47	1.06	1.01	.795	.83	.91	1.07	.83	.81	1.07	1.06	.83	.81	1.06	1.04	.91	1.05	1.0
Flow 1/hr	723	450	1.13	2043	1035	3140	1078	635	400	1090	3001	550	76	2991	568	3135	573	12.5
COMP.																		
HNO_3, M	2.46	2.0			.16	.16	2.08	.14		2.08	2.1	.03	.01	2.1	1.3	.13	1.3	
U, M	1.22				.062	0.3		.10			.015	.0443		tr		.284	.089	
Pu, g/1	2.86				.008	.663		.013				.015		tr			3.69	
Other	FP, Gd		0.77 NO_2^-				FP Gd			FP Gd				Np	0.19 M H_4N_2		0.19 M H_4N_2	2 M H_4N_2



STANDARD AGNS HEADEND FLOWSHEET

FIGURE 3-1



NEPTUNIUM EXTRACTION FLOWSHEET

FIGURE 3-2

4.0 NEPTUNIUM SEPARATION AND PURIFICATION

In the basic coprocessing flowsheet, partial partitioning of uranium and plutonium is accomplished in the 1B Electrocell.(8) The acidity and flow ratios in the 1B Electrocell are adjusted so that some uranium is stripped into the 1BP in order that the final product from the plutonium cycles will be uranium-25% plutonium. The bulk of the uranium remains in the organic phase and exits the electrocell in the 1BU stream. The plutonium entering the electrocell is reduced to Pu^{+3} so that it strips into the aqueous phase. It is expected that the neptunium in the feed to the electrocell will be reduced to Np^{+4}. The distribution coefficient for Np^{+4} between TBP and nitric acid is much lower than NpO_2^{++} (see Figure 1-1) so the neptunium will split between the 1BP and 1BU streams in roughly equal amounts.

The neptunium in the 1BU will co-strip with uranium in the 1C Column. The 1CU is concentrated and butted with nitric acid to prepare feed to the 2D Column. The 2D Column is operated at high uranium saturation in the organic to enhance fission product decontamination. Under these conditions, the neptunium will be rejected to the 2DW which is transferred to the 1SF Tank for uranium recovery.

The 1BP stream containing uranium, Pu^{+3} and Np^{+4} is transferred to the 1BP surge tank. N_2O_4 is line blended to the 1BP as a source of NO_2^- ion to oxidize Pu^{+3} to Pu^{+4} and to destroy hydrazine in the 1BP. The NO_2^- should oxidize and stabilize neptunium as NpO_2^+. In the 2A Column, uranium and plutonium will extract into the organic but the neptunium will remain in the aqueous stream and exit the column in the 2AW. The 2AW is routed to the 1SF Tank for uranium and plutonium recovery.

These routings are shown in the neptunium purification flowsheet, Figure 4-1. Thus, the bulk of the neptunium which enters the process will be collected in the 1SF Tank. From this point on, the process will deviate from the Hanford flowsheet. In the Hanford process, the back cycle waste was concentrated, part returned to the headend, and part to neptunium recovery so there was considerable neptunium recycle.

In the standard AGNS process, these accumulated waste streams are extracted with TBP in the 1S Column to recover uranium and plutonium. N_2O_4 is line blended to the feed to the 1SF Tank to reoxidize any plutonium to Pu^{+4} and to destroy hydrazine introduced with the 2DW. As in the 1BP Surge Tank, this should oxidize and stabilize neptunium as NpO_2^+. Thus, in the 1S Column, uranium and plutonium will extract, but as shown in Figure 4-1, neptunium remains in the aqueous phase and exits the column in the 1SW. Besides neptunium, the 1SW will contain small amounts of uranium, plutonium, and fission products. Therefore, the neptunium must be subjected to additional purification steps to yield a "clean" product.

In the basic AGNS flowsheet, the 1SW is routed to the LAW Concentrator. However, for neptunium recovery the 1SW will be routed to a new concentrator to provide feed to the neptunium purification system. An alternative being considered is to route the 1SW to the LAW Concentrator, but divert the other streams such as the HAW concentrator condensate to a new concentrator. The reason for this is that this second concentrator could be considerably smaller than that required for a new 1SW Concentrator. The 1SW will be concentrated to produce a bottoms stream of 100 liters per hour. The nitric acid concentration in the bottoms should increase to about 7 M which will oxidize neptunium to NpO_2^{++}. The bottoms will be cooled and routed to a surge tank. The overheads from the 1SW concentrator will be routed to the fractionator for nitric acid recovery.

The neptunium will be purified in two sets of extraction-strip columns. In the 2NA Column, NpO_2^{++} as well as any residual plutonium and uranium in the 1SW will be extracted into 30% TBP. Under the high acid conditions fission product zirconium will partially extract so a low acid scrub is added to improve zirconium decontamination. Ruthenium decontamination in this column should be excellent. The aqueous raffinate will be routed to the LAW Concentrator.

The extract from the 2NA Column, the 2NAP, will be transferred to the 2NB column where the neptunium, uranium, and plutonium are stripped with dilute acid. The strip stream is butted with nitric acid to prepare the feed to the 3NA Column where the actinides are again extracted with TBP. A scrub stream can be added to the 3NA Column if needed. The 3NAW Stream is returned to the 1SF Tank to recover any neptunium not extracted due to loss of valence control.

The 3NB Column will utilize a reductive strip to separate neptunium from uranium and plutonium. The strip stream will be 2 M nitric acid. Sufficient N_2O_4 or $NaNO_2$ will be added to the column to reduce NpO_2^{++} to NpO_2^{+} so that neptunium will transfer to the aqueous phase. This process step has been discussed by Koch.(10) It is probable that some of the nitrite would be added near the bottom of the column to produce NpO_2^{+} and reject it to the aqueous. This step is similar to the Savannah River Plant's first extraction cycle. Uranium and plutonium will remain in the organic for recycle to the 1S Column. Any neptunium not stripped would also be returned to the 1S Column so the reduction process does not have to be 100% efficient.

The 3NAP Stream will be washed with diluent in the diluent wash column to remove any entrained solvent. The product will then be concentrated to approximately 30 grams per liter and transferred to the neptunium conversion facility.

The overheads from the product concentrator will be routed to one of the waste concentrators (LAW or GPC) for disposal.

The material balance for neptunium purification is presented in Table 4-1.

TABLE 4-1

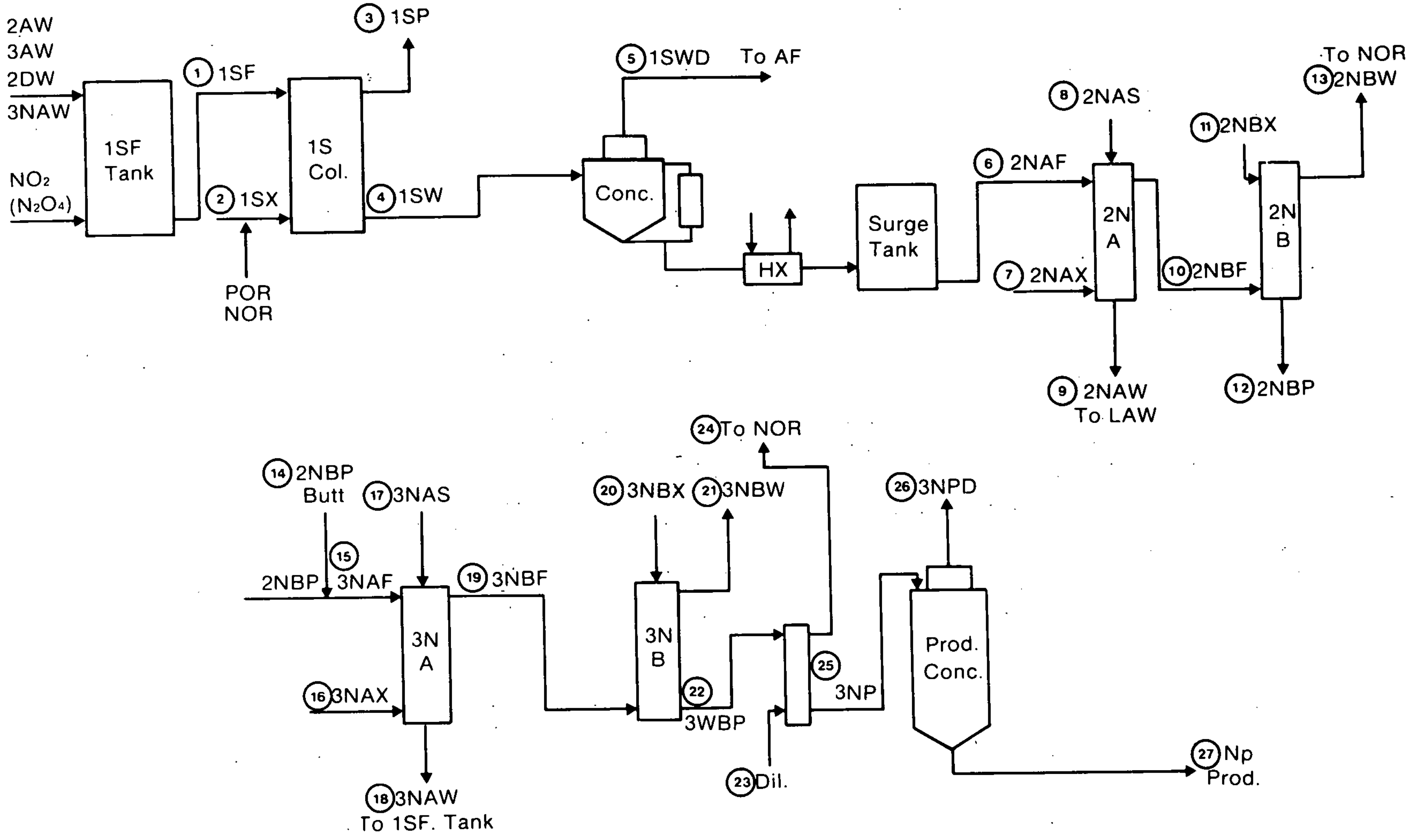
MATERIAL BALANCE - NEPTUNIUM PURIFICATION

STREAM	1 1SF	2 1SX	3 1SP	4 1SW	5 1SWD	6 2NAF	7 2NAX	8 2NAS	9 2NAW	10 2NBF	11 2NBX	12 2NBP	13 2NBW
Phase	A	O	O	A	A	A	O	A	A	O	A	A	O
Flow, l/hr	3001	626	635	2991	2891	100	50	10	110	50	25	25	50
Np, g/l*	.033 (.079)	---	tr	.033 (.079)	---	1 (2.4)	---	---	tr	2 (4.8)	---	4 (9.6)	---
HNO_3, M	2.1	---	0.1	2.1	2.0	7	---	1	6.4	.2	.01	.01	.01

STREAM	14 2NBP Butt	15 3NAF	16 3NAX	17** 3NAS	18 3NAW	19 3NBF	20 3NBX	21 3NBW	22 3NBP	23 DILUENT	24 3NPW	25 3NP	26 3NPD	27 Np PROD
Phase	A	A	O	A	A	O	A	O	A	O	O	A	A	A
Flow, l/hr.	6.5	31.5	2.5	10	31.5	25	25	25	25	1	1	25	520 l/d (408 l/d)	80 l/d (192 l/d)
Np, g/l*	---	3.2 (7.7)	---	---	tr	4 (9.6)	---	---	4 (9.6)	---	---	4 (9.6)	---	30
HNO_3, M	12	2.5	---	1	2.5	.16	2.0 0.02 M $NaNO_2$	.01	2.0	---	---	2.0	1.3	3.4

*( ) corresponds to discharge fuel spiked with Np.

**Optional Stream - if used, streams 18, 1, 4, and 5 would increase by 10 l/hr.



NEPTUNIUM PURIFICATION FLOWSHEET

FIGURE 4-1

5.0 DISCUSSION

The modifications in flows and routings in the headend of the process should result in good recovery of neptunium from the feed solution. In actual operation some "fine tuning" of the operating parameters would be expected. The amount of NO_2^- ion in the HS Column is critical, with either too much or too little, neptunium will be lost to the waste. In this flowsheet, the HS Column will be the limiting equipment item as to plant capacity. With the given flows the HS Column would be operating at a volumetric throughput of about 1400 gallons/hour-square foot. However, the HA Contactor will be operating at a low solvent saturation so it might be possible to operate the HS Column at slightly higher solvent saturation, thus reducing flow rates. Neptunium not extracted in the HS Column could then be extracted in the HA Contactor.

One potential problem with the neptunium purification flowsheet is poor zirconium decontamination. The 2D Column is operated at high uranium loading in order to squeeze residual fission products into the waste. Thus, the zirconium follows neptunium to the purification cycles. In the 2NA Column the distribution coefficient for zirconium at 7 M nitric acid is >0.1.(3) The decontamination factor for zirconium will be higher in the second neptunium cycle, however, with short-cooled fuel appreciable activity could accompany the neptunium product. If short-cooled fuel was ever processed for neptunium recovery, the 1SW might be concentrated even farther and then diluted with water to prepare a lower acid feed to the 2NA Column.

Ruthenium decontamination should be excellent, the distribution coefficient is <.01 at 7 M nitric acid.

Plutonium and uranium separation will be accomplished by the reductive strip in the 3NB Column.

Possible activity levels in recovered neptunium are given in Table 5-1. Calculations on which this table is based appear in Appendix B. Protactinium grows into recovered neptunium with a half-life of 27 days. For purposes of comparison, the activity level of pure Np-237 is 0.7 mCi/gram.

In aged neptunium product, the gamma activity from protactinium is the major contributor to shielding requirements. Approximately 46% of the protactinium decay yields gamma rays above 0.3 MeV.

The previous comments apply to the neptunium recovered from present generation LWR fuel. The first recycle fuel recovered from "heat spike" material would contain about 1200 grams of neptunium per tonne of fuel. The plutonium impurity in the recovered neptunium would be approximately 5% Pu-238; however, this would have essentially no impact on the radiation level of the product. If the same decontamination factors were obtained in the neptunium cycles, the impurities on a per gram neptunium basis would be less by a factor of about two, except of course for protactinium.

Using the BNFP as a model plant, addition of the neptunium purification cycles would be the major modification. In referring to the neptunium extraction flowsheet in Figure 3-2, most of the pipe routings are available. The piping to use the HS Column as the first cycle extraction unit is installed. However, there are a few piping changes required as detailed below.

The routing to return the HSR to the HA Contactor is via the 1AF metering head pot which would in this mode recycle the HSR to the HS Column. (This head pot routes the 1AF to the HS Column.) Therefore, line 21P43 would be cut in the head tank gallery and a new head pot installed. The new head pot would be tied into line 21P44 below the block valve on 21P44. The HSR would then flow to the HA Contactor.

A new air lift on line 33P59 would be required to route the POR to a new head pot in order to transfer the POR to the 1S Column. The NOR is a new stream which would be air lifted to the new POR head pot.

The 1SW must be routed to a new concentrator (Figure 4-1). Line 42P115 would be cut below the 1SW Decanter and connected to a new line feeding the new concentrator. All the piping and equipment beyond the 1S Column on Figure 4-1 is new.

TABLE 5-1

ACTIVITY IN NEPTUNIUM PRODUCT

ISOTOPE	COOLING TIME, YEAR			STORAGE TIME, DAYS		
	.44	1	2	27	54	81
Zr-95	2.05	0.23	0.0047			
Ru-106	0.0588	0.0403	0.0201			
Pu-241	0.60	0.583	0.555			
Pa-233				0.35	0.53	0.61

NOTE: All values in millicuries per gram Np.

6.0 CONCLUSIONS

The BNFP can readily be adapted to continuous neptunium recovery from LWR fuels. Additional equipment would include two sets of extraction-strip columns for neptunium purification.

Neptunium would be coextracted with uranium and plutonium in the first extraction cycle, separated from the bulk of the uranium and plutonium by shifts in the valence state, and finally purified by two additional extraction-strip cycles.

Some new equipment would be required, such as the pulse columns for neptunium purification, a waste concentrator, and a product concentrator.

The flowsheets presented in this report would be subject to modification during plant operation to optimize neptunium recovery.

7.0 REFERENCES

1. Shulz, W. W. and Benedict, G. E., "Neptunium-237 Production and Recovery," TID-25955, October 1972.

2. Godfrey, W. L., Gray, J. H., Waltz, W. R., and Williams, A. K., "A Fuel Cycle Concept Utilizing Pu-238 as a Heat Spike to Enhance Proliferation Resistance," Appendix A to AGNS-1040-3.1-32, October 1978.

3. Stoller, S. M. and Richards, R. B., Editors, "Reactor Handbook, Volume II, Fuel Reprocessing," Interscience Publishers, Inc., New York, 1961.

4. Tajik, S., "Recovery of Neptunium in the Modified Purex Process," Thesis, Massachusetts Institute of Technology, January 1979.

5. Bathellier, A., "Transuranium Elements in the Reprocessing of Nuclear Fuels," Bulletin D'Information Scientifique et Techniques, No. 212, pp 7-16, September 1976.

6. Burger, L. L. and Money, M. D., "Nitrous Acid Behavior in Purex Systems," HW-60278, May 1959.

7. Poe, W. L., Joyce, A. W., and Martens, R. I., "Np-237 and Pu-238 Separation at the Savannah River Plant," I&EC Proc. Des. and Dev., Volume 3, Number 4, October 1964.

8. Hall, J. C., "Engineering Evaluation of Alternatives for Processing Uranium Base Fuels," Appendix F, AGNS-1040-3.1-32, October 1978.

9. Waltz, W. L., Private Communication, AGNS, April 1979.

10. Koch, G., "Some Aspects of Uranium, Plutonium, and Neptunium Characteristics in Nuclear Fuel Reprocessing Technology," Lecture at University of Liege, Belgium, May 1977.

11. Tepp, H. G., "Conversion of Neptunium Nitrate to Neptunium Oxide," AGNS-35900-3.4-9, September 1979.

FLOWSHEETS FOR RECOVERY OF NEPTUNIUM FROM LWR FUELS

APPENDIX A

THE NEPTUNIUM-NITROUS ACID SYSTEM

ALLIED-GENERAL NUCLEAR SERVICES
POST OFFICE BOX 847
BARNWELL, SOUTH CAROLINA 29812

APPENDIX A

THE NEPTUNIUM-NITROUS ACID SYSTEM

Chemistry

Neptunium can be oxidized to NpO_2^{++} by nitric acid catalyzed by small amounts of nitrous acid. The chemical reaction is:

$$2NpO_2^{+} + 3H^{+} + 5NO_3^{-} \rightarrow 2NpO_2^{++} + 4NO_3^{-} + HNO_2 + H_2O \qquad (1)$$

As can be seen, nitrous acid is a product of the reaction so that excess nitrous acid can drive the reaction to the left. Simplifying Equation (1) gives:

$$NpO_2^{+} + 3/2H^{+} + 1/2NO_3^{-} \rightleftharpoons NpO_2^{++} + 1/2HNO_2 + 1/2H_2O \qquad (2)$$

The equilibrium expression for Equation (2) is:

$$K = \left[\frac{NpO_2^{++}}{NpO_2^{+}}\right] \frac{(HNO_2)^{1/2}\ (H_2O)^{1/2}}{(a_{H^+})^{3/2}\ (a_{NO_3^-})^{1/2}}$$

The neptunium ions are at sufficient dilution that their activities can be assumed equal to concentration. The same is true for the un-ionized nitrous acid. The activity of water is unit and thus drops out of the expression. The activities of hydrogen ion and nitrate ion are not equal to concentration in the range of interest. Further, on the assumption that the major nitrate ion is due to nitric acid, the concentrations of H^+ and NO_3^- are equal. Thus, the equilibrium expression reduces to:

$$K = \left[\frac{NpO_2^{++}}{NpO_2^{+}}\right] \frac{(HNO_2)^{1/2}}{(a_{HNO_3})^{2}}$$

Swanson,(1) among others, has studied reaction (2). He reported that the equilibrium constant can be expressed as the third power of the nitric acid concentration, or as the second power of the nitric acid activity. To quote Swanson "...the latter is more aesthetically gratifying since it is the dependence expected." On this basis, we have utilized Swanson's data for process calculations.

Swanson studied reaction (2) at both 24°C and 46°C. The equation which correlates his results is:

$$\ln K = -(1747/T) - 1.381$$

where T is in ° Kelvin and ln K is the natural logarithm of the equilibrium constant. This expression allows calculation of K at other temperatures, for example in the 1S Column which operates at 38°C, $K = 9.12 \times 10^{-4}$.

Swanson also studied the kinetics of reaction (2). As expected the rate increases with temperature. The rate also increases with nitrous acid concentration but the equilibrium amount of NpO_2^{++} is smaller. One of the interesting results of Swanson's study was that rate accelerating materials (RAM) can be formed, such as products from the dissolution of carbides in metal fuel or from solvent degradation products. This could be very important in the first extraction cycle; if neptunium recovery was poor, a deliberate addition of RAM could be made.

Calculations

In order to illustrate the careful control of nitrite required, a nitrous acid balance was calculated throughout the process. A distribution coefficient for nitrous acid between the organic and aqueous streams of five was assumed.

The 1BP containing Pu^{+3} also contains residual hydrazine introduced in the 1BX. N_2O_4 is line blended in the feed to the 1BP Surge Tank to destroy the hydrazine and reoxidize plutonium to Pu^{+4}. In this step it is also assumed that neptunium is oxidized to NpO_2^+. The N_2O_4 addition is controlled so that a slight excess of nitrite is present in the 1BP Surge Tank. If this excess is equivalent to 0.01 M, the 2AX is 246 liters/hour and the 2AF is 657 liters/hour, then the 2AP will be 0.015 M and the 2AW will be 3×10^{-3} M in nitrous acid. In the 2B column some nitrous acid will strip into the 2BP so that the 2BW will be 0.0125 M. The 2BW and the 3BW comprise the POR as part of the extractant in the 1S Column. The 2AW is routed to the 1SF Tank where it combines with other waste streams to form the 1SF.

The 2DW containing 10 moles per hour of hydrazine is part of the 1SF. This requires an N_2O_4 sparge to destroy hydrazine. Original material balance calculations were based on a 10% excess of N_2O_4. However, it should be possible to control the nitrous acid to a slight excess by the continuous nitrite monitor. For purposes of illustration, assume one mole excess nitrous acid per hour added to the 1SF Tank from the 2AW and the N_2O_4 sparge.

The NOR will also contain nitrite as a result of the reductive strip in the 3NB Column. Based on nitrous acid addition in the 3NBX of 0.024 M the 3NBW could contain nitrous acid at 0.013 M so that the NOR would carry 0.33 mole per hour to the 1S Column.

All these streams would introduce a total of 4.41 moles per hour of nitrous acid to the 1S Column, 1 from 1SF, 3.08 from the 2BW(POR), and 0.33 from the 3NBW(NOR). The 1SP would then contain 3.6×10^{-3} M nitrous acid.

In the HA Contactor, the HSR would introduce about 0.22 mole per hour of nitrous acid which combined with the 1SP yield 1.9×10^{-3} M nitrous acid in the HAP. Thus, the addition of nitrous acid through the 1SP-HAP route is about twice that indicated in the material balance flowsheet.

The desired amount of nitrite in the HSX stream is 2.6 x 10^{-4} $\underline{M}$ (see Table 3-1). In order to reduce nitrous acid in the HAP to this level, the hydrazine addition would be adjusted to 10 liters per hour of 0.075 $\underline{M}$ hydrazine. This would react with 1.5 moles of nitrous acid so that nitrous acid in the HAP would be 8.4 x 10^{-4} $\underline{M}$. No nitrite addition to the HS Column would then be required.

The major source of nitrous acid to the 1S Column is the 2BW. It may be possible to control the N_2O_4 addition to the 1BP surge tank so that ultimately the correct amount of nitrous acid would be transferred to the HS Column via the 1SP-HAP route.

In the 1SF Tank neptunium may exist in both the +4 and +5 states from the 2DW and 2AW, respectively. The N_2O_4 addition should oxidize the +4 and +5. If the residence time is sufficient, some neptunium could be converted to Np^{+6}. As mentioned above, the equilibrium constant for the 1S Column is 9.12 x 10^{-4}. The column operates at 2.1 $\underline{M}$ nitric acid. The activity of nitric acid at this concentration was estimated to be 1.82 from data given by Swanson(1) and Glasstone.(3) Therefore, the ratio of Np^{+6} to Np^{+5} was calculated by:

$$\frac{Np^{+6}}{Np^{+5}} = \frac{9.12 \times 10^{-4}(1.82)^2}{(\underline{M}_{HNO_2})^{0.5}}$$

The results are given in Table A-1 below:

TABLE A-1

EQUILIBRIUM Np(VI) IN 1S SYSTEM

HNO_2 - $\underline{M}$	PERCENT Np(VI)
0.001	8.7
0.01	2.9
0.05	1.4
0.1	1.0

If a small amount of Np^{+6} is formed in the 1S Feed Tank or Column, it will be extracted and recycled.

These calculations illustrate the potential problems with nitrite control. The incorrect amount of nitrite in the neptunium recovery system would cause a process upset with losses.

References

(1) Swanson, J. L., "Oxidation of Neptunium (V) in Nitric Acid Solution - Laboratory Study of Rate Accelerating Materials (RAM)", BNWL-1017, April 1969.

(2) Burger, L. L. and Money, M. D., "Nitrous Acid Behavior in Purex Systems," HW-60271, May 1959.

(3) Glasstone, S., Thermodynamics for Chemists, D. Van Nostrand Company, Inc., New York, 1947.

FLOWSHEETS FOR RECOVERY OF NEPTUNIUM FROM LWR FUELS

APPENDIX B

CALCULATION OF ACTIVITY IN NEPTUNIUM PRODUCT

ALLIED-GENERAL NUCLEAR SERVICES
POST OFFICE BOX 847
BARNWELL, SOUTH CAROLINA 29812

APPENDIX B

CALCULATION OF ACTIVITY IN NEPTUNIUM PRODUCT

Zirconium

- For short-cooled (160-day) fuel Zr-95 activity in 1SW = 1.025 x 10^3 Ci/hr.
- Distribution coefficient in 7 M HNO_3 ~ 0.1.
- Therefore DF = 10, Zr extracted = 1.025 x 10^2 Ci/hr.
- Assume all Zr strips in 2NP column.
- In 3NA Column, assume DF = 500.
- Therefore Zr to 3NB Column = 0.205 Ci/hr.
- If no DF in 3NB Column, Zr in Np = $\frac{0.205 \text{ Ci}}{100 \text{ g}}$ = 2.05 mCi/gm.
- If fuel one-year cooled, $\frac{2.05}{8.85*}$ = 0.232 mCi/gm.
- If fuel two-year cooled, $\frac{0.232}{49**}$ = 0.0047 mCi/gm.

Ruthenium

- For 160-day cooled fuel, Ru-106 activity in 1SW = 1.47 x 10^3 Ci/hr.
- At 7 M HNO_3, DF for Ru ~ 5 x 10^3.
- Therefore Ru to 2NB Column = 2.94 x 10^{-1} Ci/hr.
- Assume all Ru strips in 2NB Column.
- In 3NA Column, assume DF = 10.
- Therefore Ru to 3NB Column = 2.94 x 10^{-2} Ci/hr.
- In 3NB Column, assume DF = 5.
- Therefore Ru in product = 5.88 x 10^{-3} Ci/hr = 0.0588 mCi/gm Np.
- If fuel one-year cooled, $\frac{.0588}{1.46}$ = .0403 mCi/gm.
- If fuel two-year cooled, $\frac{.0403}{2}$ = .0201 mCi/gm.

---

*3.15 additional half-lives.
**5.6 additional half-lives.

Plutonium

- Assume 99.5% of Pu in HSP transfers to 1BP, then .5% or 10 g/hr transfers to 1BU and to 2DW.
- Assume 1% loss to 2AW and 1% loss to 3AW, 20 g/hr to each.
- Total Pu to 1S system = 50 g/hr.
- Assume 99% extracts in 1S Column.
- Therefore, 1% transfers to 1SW.
- Assume Pu follows Np in 2NA, 2NB and 3NA Columns.
- Assume DF of 100 in 3NB Column.
- Pu to Np = 5×10^{-3} g/hr or 50 ppm.
- Plutonium = 11.9% Pu-241.
- Therefore Pu-241 activity = 0.6 mCi/gm Np.

Protactinium

- Half-life Pa-233 = 27 days.
- Therefore in 27 days after neptunium recovery Pa-233 activity = 50% of Np activity, 75% after 54 days, etc.

DISTRIBUTION FOR TOPICAL AND FINAL REPORTS

AGNS/DOE CONTRACT NO. DE-AC09-78ET-35900
UC-83

Report No.: AGNS-35900-3.2-10

Date Issued: September 7, 1979

Standard AGNS Internal Distribution:

K. J. Bambas (1)
J. A. Buckham (1)
R. J. Cholister (1)
P. F. Highberger (1)
G. K. Hovey (1)
W. Knox (1)
R. I. Newman (1)
R. C. Ravasz (1)
G. T. Stribling (1)
W. B. Sumner (1)
A. K. Williams (1)
Library (1)
Records Management (12)

Additional AGNS Internal Distribution:

J. H. Ellis
J. H. Gray
E. W. Murbach
R. G. Spaunburgh

DOE Distribution:

Mr. R. E. Erickson (2)
Fuel Cycle Project Office
U. S. Department of Energy
Savannah River Operations Office
Post Office Box A
Aiken, South Carolina 29801

Dr. J. Spencer (3)
Savannah River Laboratory
E. I. du Pont de Nemours & Company
Document Transfer Station, 703-A
Aiken, South Carolina 29801

William Burch (3)
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee 37830

W. W. Ballard (3)
Acting Chief
Nuclear Fuel Cycle Program Branch
Nuclear Power Development Division
U. S. Department of Energy Headquarters
Washington, D. C. 20555

TIC Distribution:

*US DOE Technical Information Center (100)
Post Office Box 62
Oak Ridge, Tennessee 37830

*Per attached list.

TIC STANDARD DISTRIBUTION (Total 100)

UC-83 Distribution List Converter Fuel Processing

DOE Operations Office

1	Albuquerque
1	Chicago
1	Savannah River, Manager
1	Savannah River, Contracting Officer
1	Idaho
1	Oak Ridge
1	Richland
1	San Francisco
1	Nevada
9	Savannah River, FCPO
1	Savannah River, Classification Officer

DOE Prime Contractors

1	Mound Lab, DAO
1	Rockwell International, RFP
1	Argonne National Lab, CH
1	Battelle Pacific Northwest Lab, RL
2	Savannah River Lab, SR
1	Hanford Engineering Development Lab, RL
2	Los Alamos Scientific Lab, AL
2	Oak Ridge National Lab, OR
1	Sandia Lab, AL
1	Lawrence Livermore Lab, SAN
1	Rockwell Hanford Operations, RL
1	Oak Ridge Gaseous Diffusion Plant, OR
1	EG&G Idaho Inc., ID
1	Brookhaven National Lab, Upton, NY
1	Allied Chemical Corporation, ID

Government, Other

3	DOE Nuclear Power Development, Fuel Cycle, Assistant Director HQ
1	DOE Division of Spent Fuel Storage and Transfer, Director, HQ
1	Library of Congress
1	DOE Nuclear Power Development Division, Director, HQ
1	DOE Rocky Flats Area Office, Golden, CO
25	DOE TIC
25	National Technical Information Service (COMM)
1	DOE Office of Safeguards and Security, HQ
2	DOE Waste Management Division, HQ
1	Air Research Lab, NOAA, MD
1	DOE Grand Junction Office, Grand Junction, CO
1	DOE Division of Uranium Resources and Enrichment, HQ

EXTERNAL DISTRIBUTION FOR TASK 3 DOE REPORTS

Frank Arsenault, Director
Division of Safeguards, Fuel Cycle, and Environmental Research
Office of Nuclear Regulatory Research
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dr. R. E. Brooksbank
Building 3019
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee 37830

William H. Chambers
Associate Division Leader
Nuclear Safeguards Operations
Mail Stop 550
Q-Division
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

Dr. L. D. Chapman, Supervisor
Systems Analysis Division I
Sandia Laboratories
Albuquerque, New Mexico 87115

R. J. Jones, Chief
Materials Protection Standards Branch
Division of Siting, Health, and Safeguards Standards
Office of Standards Development
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dr. G. Robert Keepin
Associate Division Leader
Nuclear Safeguards Program Director
Mail Stop 550
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

George Weisz, Director
Office of Safeguards and Security
U. S. Department of Energy
Washington, D. C. 20545

Dr. Harry Lawroski
Allied Chemical Company
Idaho Chemical Processing Plant
550 Second Street
Idaho Falls, Idaho 83401

R. G. Page, Special Assistant to the Director for Licensing
Division of Safeguards
Office of Nuclear Material Safety and Safeguards
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dr. P. J. Persiani
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

T. A. Sellers, Supervisor
Advanced Facilities Protection Division
Division 1761
Sandia Laboratories
Albuquerque, New Mexico 87115

Sylvester Suda
Technical Support Organization
Building 197
Brookhaven National Laboratory
Upton, Long Island, New York 11973

Don Crandall
Bechtel, Inc.
Post Office Box 3965
San Francisco, California 94105

R. W. Peterson
Battelle Project Management Division
Office of Nuclear Waste Isolation
505 King Avenue
Columbus, Ohio 43201

F. A. O'Hara
Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

J. V. Cupo
Westinghouse Electric Corporation
Power Systems
Nuclear Center
Post Office Box 355
Pittsburgh, Pennsylvania 15230

H. T. Kerr, Safeguards Task Leader
Consolidated Fuel Reprocessing Programs
Engineering Technology Division
Oak Ridge National Laboratory-Nuclear Division
P. O. Box Y
Oak Ridge, Tennessee 37830