THE HANFORD PUREX PLANT EXPERIENCE
WITH REDUCTANTS

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Rough Guide

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ABSTRACTTHE HANFORD PUREX PLANT EXPERIENCE
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This paper describes experience with ferrous sulfamate-sulfamic acid (standard), ferrous sulfamate-hydrazine, ferrous nitrate-hydrazine, uranium (IV)-hydrazine, and hydroxylamine nitrate-hydrazine reductant systems in the Hanford Purex Plant. Alternate reductant systems are being considered for routine use to reduce the iron and sulfate content of the high level waste.

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THE HANFORD PUREX PLANT EXPERIENCE
WITH REDUCTANTS

I. Introduction

In the Purex process used at Hanford, aluminum cladding is removed from irradiated nuclear fuel elements with sodium hydroxide-sodium nitrate solutions and Zircaloy cladding is removed with ammonium fluoride-ammonium nitrate solutions (Zirflex process). The irradiated fuel is then dissolved with nitric acid and the solution is adjusted to solvent extraction feed concentrations.

Solvent extraction operations at the Hanford Purex Plant are conducted in pulse columns of 7 to 34 inch-diameter with cartridges of 18 to 32 feet in height. Pulse amplitudes are fixed between 0.6 to 1.86 inches and pulse frequencies vary from 40 to 110 cycles per minute. (Columns for the Third Plutonium Solvent Extraction Cycle, which are now under construction, will be 3.5 inch-diameter and the pulse amplitude will vary with pulse frequency since the columns will be pulsed with air.) The solvent used throughout the plant is 30 volume percent tributyl phosphate (TBP) with normal paraffin (n-decane to n-tetradecane) hydrocarbon (NPH) diluent.

The major fission product decontamination and partitioning of the plutonium from uranium and neptunium are accomplished

in the First Decontamination and Partition Cycle. Additional fission product decontamination is attained in the Second Plutonium and Second Uranium Cycles. Neptunium and residual plutonium are also separated from the uranium in the Second Uranium Cycle. At the present time, an anion exchange system is used for final fission product and uranium decontamination of the plutonium product, but this will be replaced in early 1971 with a Third Plutonium Solvent Extraction Cycle. Aqueous waste streams from the Second Plutonium Cycle, Second Uranium Cycle, Second Neptunium Cycle, and the plutonium anion exchange system are recycled to the Decontamination and Partition Cycle and to the Second Neptunium Cycle via the Backcycle Waste System. Neptunium is continuously accumulated and decontaminated from plutonium in the Second Neptunium Cycle until a sufficient quantity is contained in the system to warrant a processing campaign through a batch ion exchange system for final purification and concentration. (1,2,3)

The current flowsheet requires the use of plutonium reductants in the Partition Cycle, the Second Uranium Cycle, and the Second Neptunium Cycle. The present plan is to also use a plutonium reductant in the Second Plutonium Cycle to obtain uranium decontamination following installation of the Third Plutonium Solvent Extraction Cycle. This paper describes the experience with reductant systems that have been used or tested

in the Hanford Purex Plant including ferrous sulfamate-sulfamic acid (standard in Partition Cycle), ferrous sulfamate (standard in Second Uranium Cycle), ferrous sulfamate-hydrazine (standard in Second Neptunium Cycle), ferrous nitrate-hydrazine, uranium-IV-hydrazine, and hydroxylamine nitrate-hydrazine. Alternate reductants are being considered for routine use to reduce the iron and sulfate content of the high level waste. These constituents increase the volume of radioactive wastes to be stored, increase the cost of subsequent waste processing, and decrease the recovery of strontium from the waste. Iron must be complexed and sulfate ion is a major cause of solids which interfere with strontium recovery.

II. Ferrous Sulfamate-Sulfamic Acid (Partition Cycle - 1BX Column)
(Fig. 1)

Ferrous sulfamate has been used as the plutonium reductant in the 1BX stream since startup of the Hanford Purex Plant in 1956. The ferrous sulfamate concentration of 0.03M used in the present flowsheet has not been changed since startup, but the 1BX flow has since been reduced by one-third. An additional 0.04M sulfamic acid was added in 1958 when regular addition of nitrite to the HA Column (First Decontamination Cycle extraction column) was started to permit recovery of neptunium. Although not capable of reducing plutonium, sulfamic acid protects ferrous ion from oxidation by reacting with nitrite ion. Thus the ferrous ion is available for reducing plutonium.

Partition Cycle performance with ferrous sulfamate has been excellent. Only three partition failures are known to have occurred (1956, 1961, 1964) while using ferrous sulfamate in the 1BX stream. The first was attributed to excessive nitrite recycle from the Second Plutonium Cycle and the latter two occurred when sulfamic acid was omitted from the makeup. Plutonium concentrations in the first cycle uranium product are routinely less than one part per million parts uranium. Essentially all of the neptunium follows the uranium through this cycle and the uranium concentration in the plutonium product is routinely less than 100 parts per million parts plutonium.

III. Ferrous Sulfamate (Second Uranium Cycle - 2D Column) (Fig. 2)

The Second Uranium Cycle extraction (2D Column) flowsheet utilizes low-acid and high saturation to obtain maximum removal of zirconium-niobium and neptunium from the uranium product. The high saturation also maximizes removal of ruthenium. Ferrous sulfamate has been used since plant startup to reduce the residual plutonium to nearly inextractable Pu III and neptunium to Np IV which is also relatively inextractable in low acid. The separation is further enhanced by deliberately operating with a controlled "loss" of about five percent of the input uranium to the recycled aqueous waste (2DW). The 2DW which contains more than 85 percent of the neptunium, less than 0.5 percent of the plutonium, and about five percent of the uranium (all on a plant input basis)

is routed to the Backcycle Waste System for recycle to the HA Column and the Second Neptunium Cycle (less than five percent of the Np leaves in the uranium product stream).

Ferrous sulfamate has performed very well as a reductant in this system. The uranium product typically contains less than 0.5 parts plutonium per billion parts uranium. Although always added as a 2.0M solution, the flow has been reduced by sixty percent from that used in the original flowsheet and the process entry point was changed in 1968 from the feed tank to the intermediate scrub distributor located about seven feet above the feed distributor on the 2D Column. The latter change was made to obtain improved neptunium and fission product decontamination.

IV. Ferrous Sulfamate-Hydrazine

A. Second Neptunium Cycle - 2N Column (Fig. 3)

Neptunium has been routinely accumulated and recovered in the Hanford Purex Plant since the initial test studies in June, 1958. Until the Second Neptunium Cycle solvent extraction system was installed in late 1962, the neptunium was accumulated in the Backcycle Waste System during normal operation and recovered in Second Plutonium Cycle equipment during plant shutdowns. Neptunium is now continuously accumulated separate from the main plant streams by routing about one-third of the backcycle waste (3WB)* to the Second

**The remainder of the 3WB is routed to the HA Column where the uranium, plutonium, and neptunium are extracted. Most of the neptunium follows the uranium to the Second Uranium Cycle and re-enters the backcycle waste in the 2DW stream.*

Neptunium Cycle until a sufficient quantity is available for batch purification. The 3WB containing plutonium IV, neptunium VI, and uranium VI is mixed with recycled neptunium IV from the Second Neptunium Cycle strip column (2P) as feed to the 2N extraction column. The extraction column scrub stream (2NS) contains a reductant to reduce plutonium to the nearly inextractable plus three valence. The neptunium is extracted into the organic solvent as Np IV and is then stripped into the aqueous phase for recycle to the feed. When the accumulation phase is completed, the 3WB flow to the Second Neptunium Cycle is turned off, nitric acid is added to the recycled neptunium, and the operation is continued until the uranium, plutonium, and fission product concentration is low enough to permit transfer to the anion exchange system for final purification and concentration.

Ferrous sulfamate-hydrazine has been used as the 2NS reductant in this flowsheet since startup with excellent results. The concentrations of hydrazine and ferrous sulfamate used have been reduced from the initial 0.15M to 0.05M and 0.10M, respectively, without adversely affecting performance. Recent samples indicate that only one to two percent of the added hydrazine is extracted into the organic as hydrazoic acid in this application.

B. Partition Cycle - 1BX Column

A process test, to determine the effects of substituting hydrazine for sulfamic acid in the 1BX Column, was conducted during a two-month period from September to November, 1969. This substitution results in a 20 percent reduction of sulfate in the high level waste. Changes made in the 1BX flowsheet for the process test are summarized as follows:

1BX Flowsheet Changes for Hydrazine Test

	<u>Normal 1BX</u>	<u>Test 1BX</u>
Flows	20	20
Ferrous Sulfamate, <u>M</u>	0.03	0.03
Sulfamic Acid, <u>M</u>	0.04	-----
Hydrazine, <u>M</u>	-----	0.03
Nitric Acid, <u>M</u>	0.30	0.33

The use of hydrazine as the holding reductant in the 1BX column produced no undesirable effects upon plutonium partitioning. The concentration of plutonium in the uranium, the gamma levels in the first cycle plutonium and uranium products, and the second plutonium solvent extraction losses were no greater than those experienced while using sulfamic acid at comparable processing rates.

Information obtained during the test indicated that hydrazine was reducing some ferric ion to ferrous ion during the six to eight hour holdup in the process. The criticality

prevention specifications for the Hanford LBX Column are based on an always-safe ferrous ion concentration which could not be guaranteed under test conditions. This fact, plus the increased Purex operating cost and the desire to test other reductants, have precluded further testing of ferrous sulfamate-hydrazine in the LBX stream.

V. Ferrous Nitrate-Hydrazine

A. Partition Cycle - LBX Column

Hydrazine-stabilized ferrous nitrate ($0.03M \text{ Fe}(\text{NO}_3)_2 - 0.075M \text{ N}_2\text{H}_4$) was plant tested as the reductant in the LBX Column during February and March, 1968. The first test was started on February 1 with the first of three transition batches which contained gradually increasing amounts of ferrous nitrate-hydrazine and decreasing amounts of ferrous sulfamate-sulfamic acid. The test continued successfully for a period of six days with no change in plutonium partitioning. However, a partition failure, as indicated by increased readings on the LBX Column neutron monitor and decreasing readings on the LBXP neutron monitor, was recognized at midnight of the seventh day. Hydrazine was added to the LBX feed tank and partitioning was re-established with ferrous nitrate-hydrazine still on stream. The use of ferrous sulfamate-sulfamic acid was then resumed.

This partition failure resulted in carryover of plutonium into the partition cycle uranium product (1BU) and required the rework of several tons of uranium. The apparent cause of the failure was the recycle of excessive nitrite to the 1BX Column feed tank via the organic waste stream (2BW) from the Second Plutonium Cycle strip column. (Sodium nitrite is added to the Second Plutonium Cycle feed tank to reoxidize the plutonium to Pu IV. The excess nitrite ion is extracted essentially quantitatively by the organic which is then recycled.) At the time of partition failure, the nitrite addition was about ten percent above flowsheet as the rotameter was indicating less than the actual flow.

Testing of hydrazine stabilized ferrous nitrate was resumed in March with an abrupt change from a normal 1BX makeup to a test makeup. Operation was normal for about a day, then the 2AW plutonium losses exceeded 75 percent of the column input on two occasions. On the first occasion, the 2AW losses were reduced by increasing the nitrite addition to the 2AF feed tank by about ten percent. On the second occasion, batch addition of nitrite and an additional ten percent increase in the nitrite addition rate reduced the losses. The first nitrite rate adjustment brought the nitrite addition rate to the posted flowsheet value; however, due to a malfunctioning flow recorder-controller system, the nitrite addition rate sometimes exceeded flowsheet by as much as 40 percent. After about two days of test operation a partition

failure occurred in the LBX Column. Following a prompt shutdown of the first cycle, extra hydrazine was added to the LBX stream and operations resumed. Partitioning was regained, but flow control problems continued with the nitrite addition to the 2AF. Testing was suspended following another loss of partitioning on the fourth day of testing. Data obtained during more recent tests indicate the test would probably have been successful if the LBX hydrazine concentration had been increased to 0.1M.

B. Second Uranium Cycle - 2D Column

Hydrazine-stabilized ferrous nitrate was successfully substituted for the ferrous sulfamate normally used as the plutonium reductant in the 2D Column (Second Uranium Cycle extraction column) during a ten-day test period in 1968. The hydrazine stabilized ferrous nitrate was added via the intermediate scrub distributor located seven feet above the feed distributor on the 2D Column whereas ferrous sulfamate had previously been added to the 2D Column feed tank.

Second Uranium Cycle and overall plant operations during the test period were normal. The iron and plutonium concentrations in the Second Uranium Cycle product (2EU) during the test remained at the respective pretest levels of less than 5 parts per million parts uranium and 0.5 parts per billion parts uranium. It was also noted that the zirconium-niobium-95 activity and the neptunium concentration in the 2EU decreased

by about a factor of two during the test. As a result of these findings, the ferrous sulfamate addition was changed to the 2DIS distributor.

C. Second Neptunium Cycle - 2N Column

Hydrazine stabilized ferrous nitrate was substituted for the ferrous sulfamate normally used as the reductant for plutonium decontamination in the 2N Column (Second Neptunium Cycle extraction column). The 2N scrub stream (2NS) was made up to the normal iron-II concentration with the test reductant and added at the same rate. No change in waste losses or plutonium decontamination performance was noted during the 32-hour test period which completed the initial plant testing of this material in 1968.

VI. Uranium-IV - Hydrazine (Partition Cycle - 1BX Column)

A plant test of hydrazine stabilized uranium IV as the reductant in the 1BX Column of the Partition Cycle was performed during April, 1970. Uranium IV was produced for the test by the aluminum powder reduction of uranyl nitrate. Initial operation appeared normal with the light blue color characteristic of dilute Pu III solutions detected in the Partition Cycle plutonium product stream (1BP) for several hours. Subsequently, although laboratory tests indicated the presence of 0.01 to 0.03M hydrazine, the plutonium in the 1BP was Pu IV as indicated by loss of color and laboratory analysis. Correlation of the 1BP alpha monitor readings with the 1BXP (1BX column plutonium product)

flow and the LBXP-HNO_3^* flow indicated the split of plutonium between the LBSU (recycle stream to the LBX feed tank) and the LBP was influenced by the nitric acid concentration. Incremental reductions in the LBP acidity from 4.2M to 3.3M were followed by corresponding increases in the LBP alpha monitor reading. Operation continued for about seven hours when the spontaneous oxidation of U IV in the makeup tank forced a plant shutdown. The process was restarted with a new makeup batch but the test was discontinued for about two weeks when high 2A Column plutonium waste losses were experienced.

When testing of hydrazine-stabilized uranium-IV as the reductant in the LBX Column was resumed following the two-week interim, the transition was made while processing hot feed. In addition, the flowsheet was modified previously to add the acid required for the 2AF downstream of the LBS Column. Problems encountered initially with excessive recycle of plutonium from the LBS Column to the LBX Column via the LBSU were largely corrected by increasing the hydrazine concentration in the LBX from 0.075 to 0.1M although occasional additions of hydrazine directly to the LBX feed tank were required to reduce the quantity of nitrite ion entering the LBX Column.

**Nitric acid is normally added here for adjusting the feed to the Second Plutonium Cycle to the desired acidity so that Purex recovered acid contaminated with uranium may be used.*

About midway through the four and one-half day test period, the U-IV entry point was lowered from eight feet to four feet above the bottom of the cartridge. As anticipated, this lowered the plutonium profile in the LBX Column and increased the uranium concentration in the first cycle plutonium product (1BP). A significant reduction in the LBSU plutonium recycle and a modest increase in the plutonium concentration in the first cycle uranium product (1CU) were also noted.

Major findings from the test are:

1. Uranium-IV is an effective reductant for use in the LBX Column as the plutonium level in the 1CU remained at acceptable levels throughout the test.
2. Hydrazoic acid, present only as an intermediate product in the reaction of hydrazine with nitrite in an aqueous solution, is extracted into the organic in a pulse column containing both organic and aqueous phases. The hydrazoic acid does not react with nitrite in the organic phase, but is removed by the carbonate wash in solvent treatment as sodium azide. Sodium azide is not hazardous at the concentrations expected in the Purex Plant or during subsequent processing of the waste. However, since analytical results indicate that as much as sixty percent of the hydrazine was converted to hydrazoic acid during this test, the efficiency of hydrazine as a nitrite suppressor is lower than expected.
3. The neptunium concentration in the plutonium product did not increase during the test.

VII. Hydroxylamine Nitrate - HydrazineA. Second Plutonium Cycle Uranium Decontamination Flowsheet - 2B Column (Fig. 4)

Installation of the Third Plutonium Solvent Extraction Cycle will eliminate the uranium decontamination currently attained in the plutonium anion exchange purification cycle. A hydroxylamine nitrate-hydrazine ($\text{HN-N}_2\text{H}_4$) reducing flowsheet (shown below) was developed to obtain the required uranium decontamination in the Second Plutonium Cycle. A successful plant demonstration of the process was made during two one-week periods in late 1969.

SECOND PLUTONIUM CYCLE URANIUM
DECONTAMINATION FLOWSHEET

<u>Stream</u>	<u>2AP</u>	<u>2BX</u>	<u>2BS</u> ^(a)	<u>2BW</u>	<u>2BP</u>
Flow	6.0	2.3	2.0	8.0	2.3
Temp., °C	~45	Amb.	45	Amb.	Amb.
SpG@25°C	0.82	1.015	0.81	0.811	1.04
HNO_3 , M	0.2	0.3	0.01	0.06	0.6
HN	---	0.1	---	---	---
N_2H_4	---	0.05	---	---	---
Pu, %	100	---	---	<.01	~100
U, ppm	30-2300	---	---	---	2-5
U DF ^(b)	---	---	---	---	15-950

(a) 30 Volume Percent TBP - 70 Vol. NPH

(b) Decontamination Factor

The 2BX stream contained 0.1M HN as the reductant with 0.05M N_2H_4 as the holding reductant to reduce plutonium IV to inextractable plutonium III which left the 2B column in the aqueous 2BP stream. The 2AP entry point was raised about 8½ feet and a new organic stream (2BS) was added to the bottom of the column to strip uranium from the aqueous plutonium stream. Sodium nitrite was then added to the 2BP stream to reoxidize the plutonium prior to anion exchange processing. The range of the hydrazine concentration in the 2BX was limited due to problems encountered with the use of existing equipment for adding sodium nitrite in the anion exchange system. On several occasions, the nitrite flow was lost completely for up to twenty minutes with no increase in anion exchange waste losses. This would indicate that the plutonium was reoxidized by nitric acid addition alone (the anion exchange feed is 7.1M HNO_3). Based on prior laboratory observations, this should not have occurred if the anticipated hydrazine concentration was present.

Operational control of the process was generally excellent using the test flowsheet. However, an apparent reflux and a subsequent dumping of plutonium from the 2B Column did occur near the end of the second test period. The reflux was apparently due to a buildup of nitrite within the system which reoxidized some of the plutonium III to plutonium IV near the bottom of the 2B column. The Plutonium IV was then

extracted and carried up the column by the organic 2BS. However, at the top of the column, the hydroxylamine nitrate reduced the plutonium to plutonium III and prevented it from exiting via the organic 2BW stream. During one sixteen-hour period the 2BP plutonium concentration varied by +30 percent, showing the effect of the nitrite-caused reflux within the column. The return to normal 2BX containing sulfuric and sulfamic acids immediately resulted in a significantly increased 2BW-plutonium loss for about four hours and later caused a factor of two increase in the 2BP plutonium concentration for about three hours.

During the early part of the test, the uranium concentration of the first cycle plutonium product stream (1BP) ranged from 30 to 50 parts uranium per million parts plutonium (pUpmpPu). Since this low concentration made it impossible to get a good test performance evaluation, the 1BS column pulse frequency and organic flow were gradually reduced to deliberately increase the 1BP uranium concentration to a high of 2300 pUpmpPu. Uranium concentrations in the 2BP stream ranged from the analytical detection limit of two to five pUpmpPu throughout the test. Thus the reported uranium decontamination factors ranged from 15 to 950.

The test data indicate that use of the test flowsheet will provide the uranium decontamination required after installation

of the Third Plutonium Cycle and that operating problems can be minimized if control of the nitrite concentration is maintained. A nitrite monitor scheduled for installation on the 2AF stream should provide the information needed for the required nitrite control in the system.

B. Second Uranium Cycle - 2D Column

The use of hydroxylamine nitrate-hydrazine as the reductant to obtain plutonium and neptunium decontamination in the Second Uranium Cycle was successfully demonstrated during a two-and-a-half week test period starting in late May, 1970. The amounts of hydroxylamine nitrate and hydrazine added were approximately equivalent to the ferrous and sulfamate concentrations used in the normal flowsheet. The hydroxylamine nitrate was added to the 2D Column intermediate scrub stream (2DIS) and the hydrazine was initially added to the first cycle uranium strip solution (1CX), but was later added to the 2D Column feed tank.

It was hoped that hydrazine in the 1CX would react with nitrite and reduce some of the tetravalent plutonium to the desired trivalent state during the several hour holdup in the 1C Column, First Uranium Cycle product concentrator, and the 2D Column feed tank. If successful, this would have minimized the amount of the more expensive hydroxylamine nitrate required to reduce the remaining plutonium IV.

However, 2D Column feed analyses obtained during the early part of the test indicated very little hydrazine remained after concentration. This fact, plus a plutonium concentration near the specification limit of ten parts plutonium per billion parts uranium (pPupbpU) in the product* resulted in a four-day interruption of the test. During this period, the hydrazine was rerouted to the feed tank and steady state operation was attained using ferrous sulfamate as the reductant in the 2DIS.

No further problems were encountered after resuming the test which continued until just prior to shutdown or approximately ten days. Except for two cases, the reported plutonium concentration did not exceed 0.5 pPupbpU and there was no increase in the gamma activity of the uranium product. In contrast to the test of hydrazine stabilized uranium-IV where about sixty percent of the added hydrazine was converted to hydrazoic acid, only about five percent of the hydrazine was converted to HN_3 in this test. Although the planned hydroxylamine nitrate flow reductions were not attempted, some reduction may be feasible.

Routine use of hydroxylamine nitrate-hydrazine in the Second Uranium Cycle during uranium-plutonium processing has been recommended. This change will reduce the process additions of both iron and sulfate by about 30 percent.

*The plutonium contamination was later determined to be associated with the 2D Column operation during startup.

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Plutonium Monitor

FIGURE 2
SECOND URANIUM CYCLE

FIGURE 4
SECOND PLUTONIUM CYCLE