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Purex Technology Operation
Research and Engineering Operation
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PUREX PLANT BIRCH ISOLATION RUN
APRIL 1961

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I. INTRODUCTION

Interest in neptunium recovery became active in early 1958. At this time neptunium chemistry was sketchy, the path of neptunium through the Purex Plant was not clearly defined nor were the effects of operating variables on the path. An intensive research and development program carried out in Hanford Laboratories Operation, Research and Engineering Operation (CPD), and Purex Operation led to the first recovery attempt in June 1958. Continuing efforts on flowsheet improvement resulted in the following neptunium recovery from Purex.

<u>CY</u>	<u>Kg.</u> <u>Neptunium</u>
1958	0.5
1959	5.6
1960	6.7
1961 (to date)	1.7

In April 1961 a routine neptunium isolation run was undertaken. During the course of this run approximately 75 per cent of the accumulated neptunium was lost to the high level waste storage tanks. It is the purpose of this report to document the facts surrounding this occurrence.

II. SUMMARY

Following the shutdown of normal uranium processing operations, a neptunium isolation run was started on April 16 with approximately 1.3 kgs. of neptunium available for recovery in the waste backcycle stream. The usual flowsheet and operational procedures were used for the run except for minor deviations described below. Initially the recovery pattern for the run appeared to be normal. During the latter stages of the run some discrepancies were noted in the product levels of the process streams which were not resolved before the run was terminated. On April 22 the run was completed with the recovery of only 0.2 kgs. of neptunium, compared to an expected recovery of 1 kg. or more. Investigations conducted after the run led to the conclusion that the poor recovery was caused by an unusual continuous loss of the product-containing organic stream from the first solvent-extraction column (2A Column), via the column vent and a waste receiver tank to underground waste storage. Full confirmation of this conclusion by sampling and analysis was not possible. The flow of this process stream to the vent system was caused by a restriction in the normal process route between the two solvent-extraction columns. The loss was estimated to be 0.8 to 0.9 kgs. of neptunium. No evidence of flowsheet inadequacies or operational error were found.

III. DESCRIPTION OF PUREX NEPTUNIUM RECOVERY

Neptunium recovery in the Purex Plant is presently carried out by refluxing the neptunium through the Co-decontamination Cycle, Final Uranium Cycle and Waste Backcycle equipment during normal operation and then separating and decontaminating the neptunium from the backcycle waste using the Final Plutonium Cycle equipment during a plant shutdown period.

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A. Recovery During Normal Processing

The recovery of neptunium during normal processing is shown schematically in Figure I. Recovery is accomplished by adjusting the neptunium valence to the extractable (VI) state in the bottom of the Co-decontamination Column (HA). The neptunium extracted into the organic phase leaves the HA Column with the plutonium and uranium and follows the uranium through the Partition Column to the Final Uranium Cycle. High organic phase uranium saturation forces the neptunium out of the Final Uranium Cycle with the aqueous waste stream. The aqueous waste is combined with other waste streams, concentrated and becomes the backcycle waste (3WB) which is returned to the HA Column. The neptunium is continually refluxed through the plant in this manner, and the accumulation continues to increase as long as irradiated uranium is being processed.

There are two possible routes for neptunium loss during normal processing. These are: (1) to the high level waste via the waste stream leaving the HA Column and (2) to the uranium product. Currently, these losses can be controlled as follows:

<u>Loss To</u>	<u>% of Np in Virgin Feed</u>
High Level Waste	5 to 20
Uranium Product	1 to 5

B. Neptunium Isolation and Decontamination

During a shutdown, the neptunium accumulated in the backcycle waste (3WB) is separated from the associated uranium and plutonium, decontaminated from fission products and thermally concentrated as shown schematically in Figure 2. The backcycle waste is adjusted in composition and used as feed for the Final Plutonium Cycle columns. In the Extraction Column (2A) the neptunium is extracted into the organic phase along with the uranium and the plutonium leaves with the aqueous waste. In the Stripping Column (2B) conditions are maintained which permit the uranium to remain with the organic phase while the neptunium is transferred to the aqueous phase. Since the neptunium has not yet been decontaminated from fission products, the aqueous stream leaving the 2B Column is returned to the 2A Column as a portion of its feed.

After all the backcycle waste has been processed (Phase I), the flow-sheet is changed, and the neptunium is recycled through the 2A-2B Columns to decontaminate it from fission products (Phase II). After adequate decontamination is achieved, the aqueous stream leaving the 2B Column is routed to a concentrator (Phase III). The concentrate is the neptunium product.

Experience has shown that 95 per cent of the neptunium accumulated in the building can be segregated in the backcycle waste system. During the isolation run, there are two sources of neptunium loss: (1) with the aqueous stream leaving the 2A Column and (2) with the organic stream leaving the 2B Column. Each of these can be controlled to 5 per cent of the neptunium being processed. Thus, 85 per cent of the neptunium accumulated in the plant at shutdown is loaded out as product. It is

important to note, however, that the remainder is not lost, but is in the plant and accumulates in the backcycle stream during the next operating period.

Process control methods for neptunium isolation campaigns closely parallel methods used during normal uranium and plutonium processing, being divided into the general areas of operational control of process equipment and analytical control of process stream compositions.

1. Operational control of equipment is maintained by the following methods:
 - (a) Detailed operating procedures are prepared for use by the process operators. These procedures are reviewed prior to each neptunium recovery campaign and minor revisions are made as necessary to coordinate the recovery run with other scheduled plant shutdown operations.
 - (b) Equipment control values --- flow rate values, pulse generator frequencies, vessel liquid levels, etc. --- are specified in writing and are used directly by the process operators during operating of the equipment. The process operators also read and record the various control instrument values every two hours.
2. Control of process stream composition is maintained as follows:
 - (a) The chemical flowsheet is published and is made available during each isolation run.
 - (b) Based on the chemical flowsheet, Purex Technology Operation has published a sample schedule specifying the streams to be sampled, the frequency of sampling required, and the chemical analyses required. Frequency of analysis varies from every two hours to daily, depending on the particular variable and on the particular operation.
 - (c) Analytical results are recorded as they are received from the laboratory. In addition, analyses of the most significant variables are plotted versus time as they are received, in order to give a better picture of the progress of the operation. All of this data is available for inspection continuously by all concerned personnel.

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IV. DESCRIPTION OF APRIL ISOLATION RUN

A. Flowsheet

The flowsheet for the April campaign was identical to those used previously except as follows:

1. During Phase I and Phase II 0.01 M sulfuric acid and 0.01 M sulfamic acid were added to the aqueous extractant (2BX) in the second (2B) solvent-extraction column. This change was made on the basis of laboratory data developed during the previous campaign which

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showed that a substantial reduction in losses in this column could be effected by one or both of these additions. April experience showed an approximately 10-fold reduction in losses during the Phase II portion of the campaign due to the presence of sulfate. There were no other process effects.

2. During the last 8 hours of Phase III the 2A Column scrub rate (2AS) was lowered and the 2B Column extractant flow (2BX) was increased to alleviate a suspected reflux of neptunium in the solvent extraction system. These changes could only improve product recovery, possibly at the expense of a slightly higher level of gamma activity.

B. Analysis of Principal Data

Neptunium levels for the 2BP aqueous product stream and for the "waste" streams are shown plotted versus time in Figures 3 and 4. The total time is divided to indicate the three normal phases of the campaign.

The actual pattern of product stream neptunium levels experienced is shown by the solid line in Figure 3; and a pattern which might be considered typical for a normal campaign involving the same amount of feed material is shown by the broken line. Analysis of the so-called "typical" line shows

1. The gradual accumulation of neptunium in the system during Phase I waste backcycle processing;
2. A constant neptunium level during the Phase II decontamination and purification; and
3. A rapid depletion of neptunium from the system during the Phase III stripping operation in which the neptunium is concentrated by evaporation.

For the April campaign the product stream levels advanced normally during the first two days. On the third day (April 19) the change to an abnormal pattern was noted; however, waste losses were not excessive and the failure of the 2BP level to increase further was thought to be due to internal reflux in a solvent-extraction column. Such behavior has been previously experienced. On April 20 during Phase II, the sharp decline in the reported product level was also noted. Again, analytical data was rechecked and still no loss could be found. At the same time, process equipment instrumentation gave no indication of any abnormal process flow patterns or other variations. A possible loss via the solvent-extraction column vent system had not yet been suspected. Subsequently, the continuation of the unusual results led to supplementary shutdown operations, following Phase III, which were aimed at removal of a possible neptunium reflux from the 2A Column. Results of this effort were negative.

Waste losses for the April campaign are shown plotted in Figure 4. Both for the aqueous-phase losses from the 2A Column (2AW stream) and for the organic-phase losses from the 2B Column (2BW stream), the patterns and levels are generally normal. The notable exception is the sharp

decline in the 2BW losses during Phase II which is credited to the addition of sulfate to the 2BX. The integrated values for the 2AW and 2BW neptunium losses are 20 grams and 65 grams respectively. These values were confirmed within the limits of measurement accuracy by analyses of samples from the waste accumulator vessels.

C. Investigation of the Neptunium Loss

Following the isolation campaign, initial efforts to locate the missing neptunium included the following:

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1. The contents of the waste stream (2AW and 2BW) vessels were again sampled and analyzed.
2. The contents of the 2A and 2B Columns were sampled and analyzed after transfer to vessels which could be sampled.
3. The contents of the cell sump was sampled and analyzed.
4. The neptunium product was resampled for analysis by thieving a sample from a shipping container (PR Can).

The negative results of the efforts listed above led to the initial suspicion of possible loss of the neptunium product via a column vent to a waste tank. Referring to the product stream accumulation shown in Figure 3, the discrepancy between the actual performance and the expected normal performance could be explained by an approximate loss of 10 per cent by volume of the organic product stream (2AP) from the 2A Column. The 2A Column was suspected because a loss is hydraulically more likely, due to the unusual height of that column. Subsequently, on April 26 tests were conducted in the 2A Column to determine the possibility of loss of 2AP via the vent system. The testing was observed from the canyon crane and showed that a substantial carryover of liquid to the vent system was undoubtedly occurring at the normal operating conditions required for the isolation campaign. This unusual behavior prompted investigation of a possible flow restriction, and the line was partially backflushed from the 2B Column. When further flow testing indicated marked improvement in 2AP flow characteristics, additional backflushing was scheduled. Finally, the flow pattern was judged to be normal, and altogether satisfactory for operation during normal uranium processing. At one point during the flushing operation, some dark-colored foreign material was observed coming from the bottom of the 2B Column. With the large volumes of water being used, sampling of this material was not feasible. Its appearance was that of normal column interface "cruds" --- flocculent, particulate matter containing principally iron and silica. Analysis of the flushes following their transfer to a sampling tank showed no unusual product content.

Purex canyon vessels, including the solvent-extraction columns, are vented via a header, the low point of which drains to the TK-F18 waste tank. The normal use for this 5000-gallon tank is the receipt of wastes from fission-product recovery processing and from all canyon sumps. From TK-F18 the wastes are transferred to underground storage after neutralization with caustic. Between the time when the 2AP loss apparently began (on April 18) and the time when the 2AP loss was initially suspected

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(following the isolation campaign, on April 25), thirteen batches of waste, varying between 1300 and 4500 gallons each, were processed via TK-F18 to underground storage. Seven of these were transferred out after the time of completion of the neptunium isolation campaign. Thus, it was concluded that the neptunium had been irretrievably lost to underground storage. After-the-fact sampling of TK-F18 showed that perhaps 100 grams remained in the vessel on April 28. The attempted recovery of this amount was not advisable from the standpoint of the risks associated with rework of waste.

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The problem of the 2AP flow restriction was aggravated by a change in 2A Column design and the actual replacement of the 2A Column which was made during February of 1961. Compared to the original column, the new column requires a considerably higher pulse frequency (approximately 75 cycles/min. versus the former 20 cycles/min.) for efficient performance. While pulse frequencies in the range of 75 cycles/min. are commonplace for solvent-extraction columns, in this particular case, observations during the 2AP flow test described above showed the higher frequency to be a factor in the carryover of liquid to the vent system. This new 2A Column was originally used for neptunium isolation in the March 1961 isolation campaign. In retrospect, it now appears that a poor material balance during the March run may actually have been a loss of roughly 200 grams of neptunium via the vent at that time.

The design and construction of a secondary knockout pot to be located between the column and the vent header are underway. Such a device will insure against future entrainment losses.

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FIGURE I
PUREX NEPTUNIUM RECOVERY
DURING NORMAL OPERATION

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FIGURE II
PUREX NEPTUNIUM ISOLATION
AND DECONTAMINATION

FIGURE III

NEPTUNIUM ACCUMULATION ©
APRIL ISOLATION RUN

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NEPTUNUM LOSSES
APRIL ISOLATION RUN

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