CONDENSATE RECYCLE - A METHOD OF
REDUCING RADIOACTIVE DISCHARGES
TO THE GROUND FROM THE HANFORD
PUREX PLANT

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FROM THE HANFORD PUREX PLANT

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Abstract

This paper describes the Hanford Purex Plant experience with the in-canyon recycle of process condensate streams. The resulting reductions in radioactivity discharged to the environs and the effects of recycle programs upon the Purex process are discussed. Alternatives for further process condensate recycle applications are also presented.

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Introduction

The Hanford Purex Plant processes irradiated nuclear reactor fuels to separate and recover uranium, plutonium, and neptunium as products. Feed solution for solvent extraction processing is prepared by selective dissolution of the aluminum or Zircaloy fuel element cladding material and subsequent dissolution of the irradiated uranium metal core in nitric acid. Separation of plutonium, uranium, and neptunium from fission product wastes and partitioning of plutonium from uranium and neptunium are accomplished in the First Decontamination and Partition Cycle. The aqueous waste stream from this solvent extraction cycle, containing over 99 percent of the fission product activity entering the process, is evaporated in the high-level waste concentrator for volume reduction and partial recovery of its nitric acid content. The high-level waste stream is further denitrated by reaction with sugar prior to further processing in separate facilities. Separation of neptunium and residual plutonium from the uranium product and additional decontamination from fission products is performed in the Final Uranium Cycle. The plutonium product stream undergoes further decontamination from fission products and uranium in the Second Plutonium Cycle. An anion exchange system presently in use for final plutonium purification will be replaced in early 1971 by the Third Plutonium Solvent Extraction Cycle. Aqueous waste streams from the Second Plutonium Cycle, Final Uranium Cycle, Second Neptunium Cycle,

and the plutonium anion exchange system are routed to the Backcycle Waste System for concentration and reprocessing in the Second Neptunium Cycle and the First Decontamination and Partition Cycle. Neptunium is accumulated in the Second Neptunium Cycle and processed batchwise through an ion exchange system for final purification and concentration.

The chemical reprocessing of irradiated nuclear reactor fuels results in the generation of a wide variety of radioactive liquid waste streams which, excluding the high-level waste stream, represent less than one percent of the fission product activity entering the process. Some of the more radioactive wastes result from such plant operations as fuel element decladding, solvent washing, and equipment flushing. Other less radioactive wastes include process condensates, steam condensates, ammonia scrubber effluents, cooling waters, and miscellaneous non-radioactive liquid effluents. The concentration of radioactive contaminants present in a given liquid waste has been the major criterion for determining the appropriate waste management method applicable to the waste stream.

Process condensates are slightly radioactive liquid waste streams which result from evaporation and overheads condensation steps in the following portions of the Purex process:

1. Evaporation of high-level waste and recovery of nitric acid prior to further high-level waste processing in separate facilities.
2. Evaporation of backcycle waste preceding further processing through the Second Neptunium Cycle and the First Decontamination and

Partition Cycle.

3. Evaporation of the uranium product stream from the First Decontamination and Partition Cycle.
4. Evaporation of the Final Uranium Cycle product stream.

Internal recycle of other process condensates was initially designed into the Hanford Purex Plant. For example, the vessel and condenser vent system condensate, the final plutonium product concentrator overheads condensate, and the final neptunium product concentrator overheads condensate are routed into the Backcycle Waste System to reclaim potentially high fission product discharges, plutonium losses, and neptunium losses, respectively.

The radionuclide concentrations in the Purex Plant combined process condensate effluent exceed applicable limits for release to the environment; therefore the condensate stream must be further treated and/or released under controlled conditions. The discharge of process condensate into a sub-surface ground disposal site, commonly called a "crib," has proved to be an effective and safe method of radionuclide containment. A crib facility is a backfilled excavation containing a below-grade vented liquid distributor system. An adjacent network of ground water monitoring wells allows early detection if extensive radionuclide travel were to occur. Only a small percentage of the large soil depth between land surface and the ground water at Hanford (over 200 feet) is required for effective service as a mechanical filter of particulate contaminants and an ion exchange medium for selected soluble radionuclides. Nevertheless, pollution abatement incentives and the slight potential for ground water

radioactive contamination warrant application of technology aimed toward reducing the amount of radioactivity discharged to ground with liquid effluents.

The Purex Plant process condensate stream formerly represented about 45 percent of the volume and about 20 percent of the total beta curie emitters routinely discharged to sub-surface disposal sites. Re-use of process condensates to replace previous demineralized water inputs to the process was selected as the first major step toward minimizing radioactivity discharges via this stream.

This paper describes the Hanford Purex Plant experience with the in-canyon recycle of process condensate streams. The resulting reductions in radioactivity discharged to the environs and the effects of condensate recycle programs upon the Purex process are discussed. Alternatives for further process condensate recycle applications are also presented.

Recycle of Nitric Acid Absorber Overheads Condensate

In the Hanford Purex Plant the high-level aqueous waste stream from the solvent extraction First Decontamination and Partition Cycle undergoes evaporation in the high-level waste concentrator for volume reduction and partial recovery of its nitric acid content. The concentrator feed solution is diluted with water to increase the nitric acid recovery efficiency. The concentrated high-level liquid waste is denitrated by batch-wise reaction with sugar solution at elevated temperatures. The oxides of nitrogen evolved by the sugar denitration reaction discharge into the

de-entrainment section of the concentrator and, along with the overheads from this concentrator, discharge into a nitric acid absorber for partial recovery of nitric acid vapors and absorption of oxides of nitrogen. The vapors leaving the nitric acid absorber are condensed prior to discharge of the non-condensable gaseous stream into the condenser vent system. The recovered nitric acid stream is joined by dilute nitric acid from the Purex Backup Facility, which is an absorber system installed to minimize releases of radioactive iodine-131 and oxides of nitrogen to the atmosphere from dissolver off-gases. The combined stream is further rectified in the nitric acid fractionator prior to reuse in uranium dissolution and solvent extraction operations.

Prior to implementation of the process condensate recycle program, the total condensate stream (AAD) from the nitric acid absorber overheads condenser was discharged with other process condensates to a crib. It was estimated that approximately 95 percent of the radioactivity and about 25 percent of the liquid volume discharged to the process condensate crib originated with the AAD stream. Thus, achievement of a significant reduction in radioactivity discharged to the environs was possible by recycling AAD to points in the process where this slightly acidic stream could be used. However, the potential operating problems that could result from such recycle include the following:

1. Organic solvent entrainment from the first solvent extraction column (HA Column) could appear in the recycled condensate stream, resulting in poor performance of solvent extraction cycles receiving recycled AAD.

2. Recycle of AAD could result in a general increase in radionuclide concentration in AAD and other process condensate streams.
3. Introduction of AAD into the physical and chemical environments of other processing equipment could alter the volatility characteristics of specific radionuclides present, especially radioactive ruthenium isotopes.

A process test AAD recycle system was installed to determine whether severe processing problems would result from such recycle. The following process application points were selected for the AAD recycle test:

1. Reflux water to the nitric acid absorber to be used in place of an existing demineralized water input stream.
2. Dilution water to the high-level waste concentrator feed solution to be used in place of an existing demineralized water input stream.
3. Additional input to the Backcycle Waste Concentrator feed solution for additional evaporative decontamination.

Since the proposed AAD recycle application points lacked sufficient capacity to process the total AAD stream, the test equipment design included provision for partial AAD overflow into the existing process condensate header leading to the crib. A flow diagram of the AAD recycle test system is shown in Figure 1.

In November, 1967, the test work was begun by recycling about 25 percent of the AAD stream as reflux water (AAR) to the nitric acid absorber. During the relatively short test period, a significant

increase in fission product content of the AAD and recovered acid streams was experienced. However, this increase was primarily due to increased quantities of radioactive ruthenium isotopes, which are known to volatilize readily under the influence of other process variables, such as low nitrite ion concentration in the high-level waste stream. More extensive testing during a subsequent processing campaign showed a decreased fission product activity in the AAD stream when 25 percent of the AAD was recycled as acid absorber reflux water (AAR). A similar decreased AAD radioactivity was observed when 25 percent of the AAD was recycled as AAR and 40 percent as dilution water to the high-level waste concentrator feed solution. Recovered nitric acid fission product activity increased somewhat but remained at acceptably low levels. An additional 15 percent of the AAD flow was then recycled to the Backcycle Waste Concentrator feed solution for additional evaporative decontamination. Throughout the test period, no detectable adverse effects on either solvent extraction performance (i.e., fission product decontamination and column operating performance) or Backcycle Waste Concentrator overheads condensate radioactivity levels were observed. For nearly three years the AAD recycle system operation has been successfully continued. Approximately 80 percent of the AAD recycle stream is being recycled to the process accompanied by a corresponding reduction in radionuclide discharge via this stream of at least 80 percent. As an additional environmental benefit, the nitric acid discharge to the process condensate crib via this stream was also reduced by about 80 percent.

Recycle of First Cycle Uranium Concentrator Overheads Condensate

In the First Decontamination and Partition Cycle of the Purex process, the bulk of the fission products are separated from the uranium and plutonium products. Plutonium is partitioned from the uranium and routed to the Second Plutonium Cycle for further purification. The uranium product is stripped from the organic solvent phase in the 1C Column by a dilute aqueous nitric acid stream (1CX). The resulting aqueous uranium product solution is concentrated in the 1CU Concentrator prior to further purification in the Final Uranium Cycle. The overheads condensate (1UD) from this concentrator, prior to recycle, was discharged into the process condensate disposal system. The success of the AAD recycle process test gave some indication that recycle of process condensates to aqueous solvent extraction streams was feasible. However, laboratory-scale solvent extraction studies and analytical data indicated that impurities may be present in 1UD which could adversely affect column performance. For example, the presence of dibutylphosphate and monobutylphosphate (degradation products of the Purex Plant solvent, tributylphosphate) could conceivably result in column instability and/or increased product losses to the solvent treatment portion of the process if 1UD were recycled. Therefore a process test system was installed to investigate the feasibility of recycling the 1UD stream to the 1C Column as 1CX water. The incentives for this test included the following:

1. Successful test operation would further indicate the feasibility of recycling other process condensates as aqueous solvent extraction

streams, thereby achieving a significant reduction in the amount of radioactivity discharged to the environs via the process condensate stream.

2. The amount of silica introduced into the process via demineralized water additions would be reduced. Silica is believed to form troublesome scale in the Backcycle Waste System and to limit high-level waste processing efficiency.

The LUD recycle test equipment consisted of a LUD collection vessel, a recycle pump, and associated piping and instrumentation. Since insufficient LUD was available to satisfy totally the LCX water requirements, about 10 percent of this water was continuously supplied to the LUD collection vessel by the existing LCX water addition system. Moreover, the required LCX nitric acid concentration was attained almost totally by input of fresh acid from the existing system. The capability to revert entirely to the old LCX supply system was retained. A flow diagram of the LUD recycle test system is shown in Figure 2.

The LUD recycle test system has been in routine use since October, 1969. The LCW (LC Column organic waste) uranium losses have been controlled to normal low levels, indicating satisfactory LC Column stripping performance. No differences in LC Column operability characteristics or in plant organic quality have resulted from recycle operation. Thus, the feasibility of using the LUD stream as LCX water has been successfully demonstrated.

Alternatives for Further Process Condensate Recycle Applications

Various points remain in the Purex process which could accept recycled process condensates either as direct replacement of existing demineralized water input streams or as additional aqueous feed to evaporators. The existing demineralized water inputs which could perhaps be replaced by recycled process condensate include: (1) aqueous solvent extraction stripping streams, (2) absorber water in nitric acid recovery equipment, and (3) dissolver makeup and rinse water in solvent extraction feed preparation. Excess evaporative capacity exists in the Acid Recovery and Backcycle Waste systems to allow recycle of a small amount of process condensates to these portions of the process. It is unlikely that total recycle of all process condensates would be feasible or economically justifiable. However, by selectively recycling those process condensates highest in radioactivity and nitric acid content, the radioactivity and nitric acid discharged to ground via the process condensate stream may be reduced to about one percent of that discharged prior to process condensate recycle.

The major benefits attainable through future process condensate recycle applications at the Hanford Purex Plant may be summarized as follows:

1. Reduced radioactivity and nitric acid discharges by virtue of evaporative decontamination and reduced potential for accidental release.
2. Reduced demineralized water usage resulting in operating cost savings and a decreased silicon impurity input.

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ARH-SA-68
Page 11.

3. Reduced volume of process condensate discharges, thus rendering the remaining condensate stream more amenable to further decontamination treatment if required in the future.

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Figure 1 – RECYCLE OF NITRIC ACID ABSORBER OVERHEADS CONDENSATE

Figure 2 – RECYCLE OF FIRST CYCLE URANIUM CONCENTRATOR OVERHEADS CONDENSATE