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WESTINGHOUSE SAVANNAH RIVER COMPANY
INTEROFFICE MEMORANDUM

July 19, 2004

TO: Distribution

FROM: W. G. Dyer

RE: **Characterization of H–Canyon Wastes When Processing Unirradiated Materials**
WSRC–TR–2004–00328, Rev 1

The subject Technical Report has been revised to correct the discussion concerning Low Level Waste and Mixed Low Level Waste. Specifically, the waste can not be classified as LLW in lieu of MLLW. Since the Tank Farm and Saltstone facilities are permitted as Industrial Waste Water Treatment Units under the Clean Water Act, they are both authorized to process MLLW. This key clarification was incorporated into the report. In addition, other minor changes were made to provide additional clarity.

A copy of the revised Technical Report is attached.

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Characterization of H–Canyon Wastes When Processing Unirradiated Materials

W. G. Dyer

WSRC–TR–2004–00328, Rev 1

July 2004

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RO: W G Dyer
W. G. Dyer, Senior Technical Advisor
Date: 7/16/04

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Characterization of H–Canyon Wastes When Processing Unirradiated Materials

Reviews and Approvals

7/16/04

W. G. Dyer, CBU Process Development and Integration — Date

7-19-04

M. R. Price, H–Canyon Outside Facilities Engineering — Date

7/16/04

M. C. Chandler, Environmental Support Services, Project Support Manager — Date

7/16/04

W. T. Goldston, Chairman, DOE Order 435.1 Subcommittee — Date

Table of Contents

Acronym List

CFR	Code of Federal Regulations
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EIS	Environmental Impact Statement
ETP	Effluent Treatment Project
EUS	Enriched Uranium Storage
GPE	General Purpose Evaporator
HAW	High Activity Waste
HEU	High Enriched Uranium
HLW	High Level Waste
INEEL	Idaho National Engineering and Environmental Laboratory
LAW	Low Activity Waste
LLW	Low Level Waste
MLLW	Mixed Low Level Waste
Np	Neptunium
PuCS	Plutonium Contaminated Scrap
PUREX	Plutonium Uranium Extraction
RCRA	Resource Conservation and Recovery Act
SNM	Special Nuclear Material
SRS	Savannah River Site
TF	Tank Farm
TR	Technical Report
TRU	Transuranic
TVA	Tennessee Valley Authority
UMTRCA	Uranium Mill Tailings Radiation Control Act
WSMS	Washington Safety Management Solutions
WSRC	Westinghouse Savannah River Company

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Characterization of H–Canyon Wastes When Processing Unirradiated Materials

W. G. Dyer

1.0 Introduction

Since the introduction of spent (irradiated) enriched uranium fuel into H–Canyon in 1959, the facility has processed irradiated uranium fuel from both on–site and off–site reactors. When the on–site reactors were shut down in the early 1990s, a significant number of unirradiated enriched uranium fuel tubes remained on site. In January 2004, H–Canyon began processing these unirradiated Mk–22 fuel tubes. These tubes are similar in composition to the spent fuel (without the associated fission or activation products) that has been processed throughout the history of H–Canyon.

Since the unirradiated fuel tubes have not been irradiated in a reactor, the raffinate stream from processing this material, when discarded, can be characterized as low level waste (LLW). This paper provides the basis for that characterization. In addition to the unirradiated fuel tubes, other unirradiated materials are being processed through H–Canyon. The raffinate from processing these materials can also be characterized as LLW and are included in this report. Specifically, this includes uranium oxide material from Idaho National Engineering and Environmental Laboratory (INEEL) and plutonium–contaminated uranium scrap. In addition to the raffinate being generated during canyon operations, other wastes are generated that are not a direct result of processing, specifically the General Purpose Evaporator bottoms. In this report, all of these wastes are collectively referred to as wastes from unirradiated materials.

Since the waste being generated by H–Canyon can be classified as LLW, sending these wastes directly to a low level waste treatment and disposal facility will result in considerable savings when compared to managing the liquid volume as high level waste in the Tank Farm as is currently being done. In addition, this will reduce the number of Defense Waste Processing Facility (DWPF) canisters generated. Finally, utilizing the Saltstone low level waste treatment and disposal facility is cost effective when compared to offsite vendor treatment and disposal. (Reference 1)

2.0 Background

The purpose of processing enriched uranium materials in H–Canyon is primarily to recover enriched uranium, blend the recovered solution with natural uranium, and produce a product that can be converted into fuel for use in a commercial nuclear reactor. This program is called the High Enriched Uranium (HEU) blenddown program.

2.1 Irradiated Fuel Processing

Historically, H–Canyon has received irradiated fuel and charged the material to the dissolver. After dissolution in the dissolver, the material is processed through the Head

End evaporator and centrifuge where the solution is concentrated and silica impurities removed. The clarified solution is chemically adjusted and fed to the First Cycle mixer–settlers. The effluents from the First Cycle process are a uranium product stream and two raffinate streams. One raffinate stream predominantly contains fission products and aluminum and one contains neptunium (Np). The raffinate stream containing fission products is processed through the high activity waste (HAW) evaporators, neutralized and transferred to the H–Area Tank Farm. [The use of the term "waste" in H–Canyon processing is not a regulatory definition but a historical term.] The Np raffinate stream is concentrated by evaporation and stored for future processing.

The uranium product stream from First Cycle is chemically adjusted, concentrated and fed to the Second Uranium Cycle mixer–settlers. The effluents from the Second Uranium Cycle process are the uranium product stream and a raffinate stream containing additional fission products. The raffinate stream containing fissions products is processed through the low activity waste [again a historical term] (LAW) evaporators, neutralized and transferred to the H–Area Tank Farm.

2.2 Unirradiated Fuel Processing

Since January, 2004, H–Canyon has been processing unirradiated enriched uranium fuel. The unirradiated fuel was fabricated in the M–Area fuel fabrication facilities for processing in the Savannah River Site (SRS) reactors. When the reactors were shut down in the early 1990s, the fuel tubes were stored pending disposition. The unirradiated fuel is being processed utilizing essentially the same flowsheet and transfer routes as the irradiated fuel process. The fuel is dissolved, concentrated, clarified, chemically adjusted and fed to First Cycle. As is the case with processing irradiated fuel, there are three effluent streams from First Cycle; the unirradiated uranium product stream and two raffinate streams. The first raffinate stream predominantly contains aluminum with fuel contaminates and is processed through the HAW evaporators, neutralized and transferred to the H–Area Tank Farm. However, since unirradiated fuel does not contain Np and only very low levels of contaminates, the second raffinate stream is processed through the LAW evaporators, neutralized and transferred to the H–Area Tank Farm.

Similar to irradiated fuel processing, the unirradiated uranium product stream from First Cycle is chemically adjusted, concentrated and fed to the Second Uranium Cycle mixer–settlers. The effluents from the Second Uranium Cycle process are the unirradiated uranium product stream and the raffinate stream containing additional contaminates. The Second Uranium Cycle raffinate stream is processed through the LAW evaporators, neutralized and transferred to the H–Area Tank Farm.

One additional stream is also being recycled as feed to Second Uranium Cycle. During prior processing of irradiated fuel, HEU solution was stored in the Enriched Uranium Storage (EUS) tank. Due to the LEU specifications for shipment to TVA, this material is being reprocessed through Second Uranium Cycle. Again, after concentration and chemical adjustment, the recycled material is processed in the same manner as the uranium solution from First Cycle.

2.3 Miscellaneous Unirradiated Material

In addition to the unirradiated fuel tubes being processed, other material is or will be processed through H–Canyon. Currently, uranium oxide material from INEEL is being dissolved in the HB–Line facility. This material was identified by DOE in an Unallocated Off–Spec HEU Study as material to be dispositioned through H–Area (Reference 2). The solution is being transferred to an H–Canyon vessel and blended with the fuel from H–Canyon dissolvers.

In addition to the INEEL material, plutonium contaminated uranium scrap (PuCS) currently stored in WSRC storage facilities will be processed in H–Canyon (Reference 3). The PuCS material will be dissolved in a second H–Canyon dissolver. After dissolution, the solution will be transferred to a storage tank, blended with other unirradiated fuel and processed through the normal H–Canyon process.

2.4 General Purpose Evaporator Process

The General Purpose Evaporator (GPE) is located in H–Canyon Outside Facilities. The GPE processes rainwater collected in Outside Facility basins and aqueous solutions from plutonium uranium extraction (PUREX) solvent washing. The PUREX solvent stream from the H–Canyon mixer–settlers is a closed loop stream that is continuously washed with low concentrations of nitric acid and sodium carbonate solutions. These solutions are replaced on a periodic basis and the discarded wash solutions processed through the GPE. Both the rainwater and wash solutions are neutralized, concentrated in the evaporator and transferred to the H–Area Tank Farm.

3.0 Waste Definition and General Guidance

To adequately characterize waste, a proper understanding of waste is required. A review of the DOE orders and Code of Federal Regulations (CFR) shows that H–Canyon is a generator of waste and is not used to treat or store waste.

The DOE Order definition of waste defaults to that found in 40 CFR 261.2. Based on this definition of waste, the H–Canyon facilities generate waste from production processes when the product material is no longer capable of being extracted from the material and any Special Nuclear Material (SNM) associated with the effluent stream is authorized to be discarded. The liquid effluent stream then becomes a waste when it is discharged from the canyon and enters the waste header. This definition of when waste is generated is consistent between the Radioactive Waste Management Basis (Reference 4) documented for the H–Canyon facility and the current Tank Farm and Effluent Treatment Process (ETP) Waste Water Treatment permits.

The only condition under which H–Canyon would contain waste would be when material in the facility is abandoned. This is discussed in the DOE Guide 435.1, Chapter II (Reference 5). If a reprocessing operation shuts down, material streams are left in the facility and time as elapses, the “as left” materials must be categorized by waste type for proper management and disposal when being reviewed for final disposition. This situation does not apply to the current H–Canyon operation since operations have not ceased. Therefore, there is no waste internal to the H–Canyon facility.

The following flowchart from DOE M 435.1, Chapter 1 provides a logic diagram to assist in determining the proper waste type and appropriate program for managing wastes.

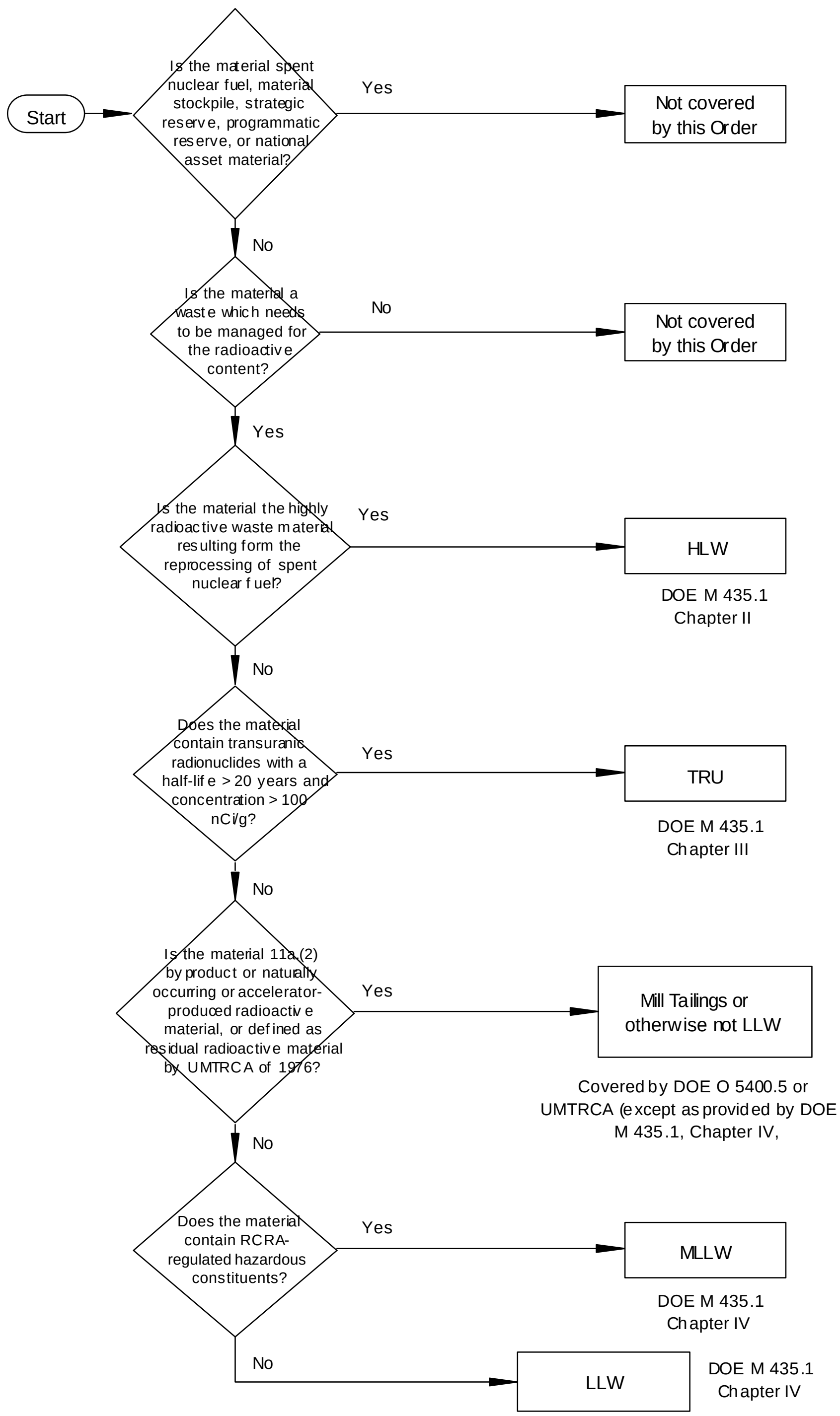

Figure 1

4.0 H–Canyon Waste Characterization

There are four primary waste streams generated by H–Canyon processing; HAW, LAW, GPE and evaporator overheads. The evaporator overheads stream is currently characterized as LLW and is being discarded to ETP. The other three streams are currently being processed as HLW. This report will only address a change in characterization of the HAW and GPE effluent streams to LLW. Although the LAW effluent stream could also be characterized as non–HLW, the presence of actinides currently makes it unacceptable for Saltstone receipts.

The logic diagram in Figure 1 will be utilized to determine the characterization of the HAW and GPE waste streams.

4.1 HAW Waste Stream

Q1. Is the material spent nuclear fuel, material stockpile, strategic reserve, programmatic reserve, or national asset material?

The HAW material being characterized is a discharge effluent from H–Canyon reprocessing of unirradiated fuel. Since it is a discharge effluent, the answer to Q1 is NO. Therefore Q2 is applicable.

Q2. Is the material a waste which needs to be managed for the radioactive content?

The discharge effluent from H–Canyon reprocessing contains the raffinate stream from unirradiated fuel processing and therefore contains radioactive contaminants. Since the effluent contains radioactive contaminants, the answer to Q2 is YES. Therefore Q3 is applicable.

Q3. Is the material the highly radioactive waste material resulting from the reprocessing of spent nuclear fuel?

The enriched uranium material currently being processed in H–Canyon is either unirradiated fuel tubes that have not been charged to a reactor since it has been fabricated into fuel or unirradiated uranium oxide and metal scrap being recovered. Since the material being processed is not spent nuclear fuel or highly radioactive, the effluent stream can not be highly radioactive material and the answer to Q3 is NO. Therefore Q4 is applicable.

Q4. Does the material contain transuranic radionuclides with a half–life > 20 years and concentration > 100 nCi/g?

The H–Canyon raffinate stream from the First Cycle mixer–settlers will not contain transuranics meeting this criteria since the feed material is unirradiated fuel. While the PuCS material contains contamination levels of plutonium that would not challenge the criteria above, the H–Canyon process is operating to partition any plutonium to the LAW process stream. Any plutonium present will be processed with the raffinate material from the Second Uranium Cycle mixer–settlers. [Since the raffinate material from the Second

Uranium Cycle mixer–settlers has the potential to contain transuranics and is processed through the LAW evaporators, the LAW effluent will continue to be disposed to HLW.] Since the HAW effluent stream does not contain transuranic radionuclides, the answer to Q4 is NO. Therefore Q5 is applicable.

Q5. Is the material 11a.(2) byproduct or naturally occurring or accelerator–produced radioactive material, or defined as residual radioactive material by UMTRCA of 1976?

The H–Canyon effluent stream is generated from unirradiated fuel reprocessing and can not be identified as any of the descriptions above. Since the answer to Q5 is NO, Q6 is applicable.

Q6. Does the material contain RCRA–regulated hazardous constituents?

The H–Canyon process requires the use of mercury as a catalyst for enriched uranium fuel dissolution. The mercury is carried through the process and is in the feed to the First Cycle mixer–settlers. The mercury is partitioned from the uranium and is a constituent in the raffinate stream. This stream is processed through the HAW system and is present in the effluent being considered. Since mercury and other Resource Conservation and Recovery Act (RCRA) regulated hazardous constituents may be present, the waste stream generated from HAW contains a RCRA regulated hazardous constituent. Since the answer to Q6 is YES, then the discharged HAW effluent stream can be characterized as mixed low level waste (MLLW). It should be noted that the Tank Farm and Saltstone facilities do not fall under RCRA regulations but under an Industrial Waste Water Treatment Unit permitted under the Clean Water Act (Reference 6) and are both authorized to process this waste.

4.2 GPE Waste Stream

Q1. Is the material spent nuclear fuel, material stockpile, strategic reserve, programmatic reserve, or national asset material?

The GPE material being characterized is a discharge effluent from H–Canyon Outside Facilities processing of rainwater collected in basins and aqueous solvent wash solutions. Since it is a discharge effluent, the answer to Q1 is NO. Therefore Q2 is applicable.

Q2. Is the material a waste which needs to be managed for the radioactive content?

The discharge effluent from the GPE contains radioactive contaminates from solvent wash solutions. Since the effluent contains radioactive contaminates, the answer to Q2 is YES. Therefore Q3 is applicable.

Q3. Is the material the highly radioactive waste material resulting from the reprocessing of spent nuclear fuel?

The enriched uranium material currently being processed in H–Canyon is either unirradiated fuel tubes that have not been charged to a reactor since it has been fabricated into fuel or unirradiated uranium oxide and metal scrap being recovered. Since the material being processed is not spent nuclear fuel or highly radioactive, the radioactive contaminants being removed by the aqueous washing of the solvent stream can not be highly radioactive material and the answer to Q3 is NO. Therefore Q4 is applicable.

Q4. Does the material contain transuranic radionuclides with a half–life > 20 years and concentration > 100 nCi/g?

The GPE effluent will not contain transuranics meeting this criteria since the only source of the material is the aqueous washing of PUREX solvent in contact with unirradiated fuel or rainwater collected in Outside Facilities basins. The PUREX solvent is an in–process solution that is relatively low in radionuclide content. Even when PUREX solvent used in spent fuel processing is designated to be discarded as waste, it has been characterized as LLW (Reference 7). Since the PUREX solvent contains low radionuclide content and would not by classified as HLW upon being discarded, any wash solution generated will not contain transuranic radionuclides meeting the above criteria. In addition, the rainwater collected in the Outside Facilities basins may contain contaminations levels of radionuclides, but will not contain transuranic radionuclides meeting the criteria above. Since the GPE effluent stream does not contain transuranic radionuclides, the answer to Q4 is NO. Therefore Q5 is applicable.

Q5. Is the material 11a.(2) byproduct or naturally occurring or accelerator–produced radioactive material, or defined as residual radioactive material by UMTRCA of 1976?

The GPE effluent stream is generated from rainwater collection and aqueous washing of solvent in contact with unirradiated fuel and cannot be identified as any of the descriptions above. Since the answer to Q5 is NO, Q6 is applicable.

Q6. Does the material contain RCRA–regulated hazardous constituents?

The H–Canyon process requires the use of mercury as a catalyst for enriched uranium fuel dissolution. The mercury is carried through the process and is in the feed to the First Cycle mixer–settlers. Most of the mercury is partitioned from the uranium and is a constituent in the HAW raffinate stream. However, some may be absorbed in the solvent and removed in the solvent washing operations. Since mercury and other RCRA regulated hazardous constituents may be present, the waste stream generated from the GPE may contain a RCRA regulated hazardous constituent. Since the answer to Q6 is YES, then the GPE effluent stream can be characterized as MLLW. It should be noted that the Tank Farm and Saltstone facilities do not fall under RCRA regulations but under an Industrial Waste Water Treatment Unit permitted under the Clean Water Act (Reference 6) and are both authorized to process this waste.

5.0 Additional Considerations

Using the logic diagram in Figure 1, it is evident that the HAW and GPE effluent streams can be classified as mixed low level waste. However, prior to January 2004, H–Canyon was processing spent nuclear fuel. The transitioning to processing of unirradiated fuel does not completely assure that generated waste streams are LLW. DOE Order 435.1

defines HLW as the raffinate streams from the separations/decontamination process in reprocessing facilities processing spent nuclear fuel. The potential source of HLW remains until the raffinate material from spent fuel processing is purged from the process.

The purging of HLW material is discussed in the DOE G 435.1–1, Chapter II (Reference 5). The guide states that after ceasing the processing of spent nuclear fuel, "significant quantities of additional high level waste will not be generated in the future from these [fuel reprocessing] operations." The guide also points out that facility cleanout activities, decontamination solutions and other operations may, or may not be, high level waste. Once the raffinate material from spent fuel processing has been purged as HLW, the various streams are no longer HLW. This discussion emphasizes that at some point the source of HLW material can be purged from the process once spent fuel is not being received in the facility.

As stated previously, H–Canyon has been processing unirradiated fuel since January 2004. The process flowsheet is essentially unchanged from that prior to January. All raffinate streams have been and are continuing to be disposed to HLW. In essence, the facility has been purging the source of HLW from spent fuel processing out of the facility. The following discusses the purging of the canyon processes.

5.1 Purging H–Canyon Vessels

The process of transferring solutions in H–Canyon from one vessel to another is accomplished by steam transfer jet. Typically, transfers from one tank to another are completed when the transferring tank is empty or at transfer jet heel. In those cases where the transferring tank is not empty, solution is usually not added to the tank until it has been emptied to jet heel.

The quantity of solution remaining in the vessel that has been emptied to jet heel is usually less than 500 pounds. This is almost always at least an order of magnitude less than the original quantity. For example, the H–Canyon dissolver will contain less than 200 pounds of solution after transfer to the downstream tank. For the subsequent charge, a total of 30,000 pounds of chemicals will be added to the dissolver. Therefore, any solution in the dissolver prior to the chemical addition was diluted over two orders of magnitude. While this is not typical of all canyon vessels, there is almost always an order of magnitude dilution of vessel's heels. Each time the solution in a vessel heel is diluted, the quantity of residual HLW potentially present from prior processing of spend fuel decreases.

Since H–Canyon commenced processing unirradiated fuel in January 2004, a total of 22 charges have been processed through the H–Canyon dissolver. Each charge involves adding dissolution chemicals to an empty dissolver, charging the unirradiated fuel, dissolving the fuel, and transferring the dissolved solution to an accountability tank. At the completion of the transfer, the dissolver is empty. Based on the argument above, there has been over 20 orders of magnitude dilution of any dissolver heel remaining from spent fuel processing. With the exception of the center section of the First Cycle decanter, the same argument can be applied to the vessels downstream of the dissolver.

5.2 Purging First Cycle Decanter

The raffinate stream from First Cycle is received into a decanter. The decanter has a settling section, an organic section and an aqueous section. The settling section is an unagitated region in the center of the decanter that allows any organic entrained in the raffinate to separate and rise to the top of the aqueous. Any entrained organic or organic from a process upset will overflow into the organic section. The aqueous solution underflows a weir and accumulates in the aqueous section.

5.2.1 Decanter Aqueous Section

The same purging argument as that discussed in Section 5.1 can be applied to the aqueous section. The aqueous section has a heel of 150 pounds solution. The section is emptied when the quantity of solution increases above a nominal 6000 pounds. Similar to other vessels, each transfer out and refilling with aqueous solution ensures there is greater than an order of magnitude dilution of the heel. In the case of the aqueous decanter, there have been approximately 40 transfers out of the aqueous section since First Cycle commenced processing unirradiated material and any residual raffinate from processing spent fuel has been purged from the aqueous section.

5.2.2 Decanter Organic Section

Any entrained organic or organic from a process upset is collected in the organic section. Since H–Canyon restart in 1997, there has been no accumulation of organic in the decanter. Any accumulated solvent would be transferred back to the process. This stream is not applicable to this discussion.

5.2.3 Decanter Center or Settling Section

The center section of the 12.4 decanter remains full during normal operations. At the completion of each First Cycle run, the level in the center section is lowered by two-thirds from about 2,200 pounds to 700 pounds. While this does not provide the same level of heel dilution as other vessels, there is still a minimum five orders of magnitude dilution and purging of the decanter contents. In addition, the dilution of any raffinate that might remain from spent fuel processing occurs from the normal flow of unirradiated raffinate through the section.

Since First Cycle started processing unirradiated fuel, there have been 12 cycle runs. Each cycle run lasts approximately 60 hours with a raffinate flow of 18.2 pounds per minute. Based on this information and the cycle flushing occurring at the initiation and completion of each run, approximately 325,000 pounds of solution has passed through the center section. Since the center section has a capacity of about 2,200 pounds, there has also been a factor of 150 decrease in any residual raffinate from processing spent fuel that might be present in the settling section. Based on the reduction from partially emptying the center section and the volume of unirradiated material processed through the decanter, the decanter center section has been sufficiently purged of residual raffinate from spent fuel processing.

6.0 Conclusions

A review of the DOE Orders related to the characterization of waste clearly indicates the HAW and GPE effluent streams can be classified as low level waste since the facility is processing unirradiated fuel. However, that alone is insufficient justification since H–Canyon processed spent nuclear fuel prior to January 2004.

A review of H–Canyon operations since January 2004 indicate residual HLW from spent fuel processing that may remain in H–Canyon equipment has been sufficiently purged such that there is not a co–mingling issue with the current HAW and GPE streams. Therefore, the HAW and GPE effluent streams from H–Canyon operations can be characterized as low level waste and be discarded to a low level waste treatment facility such as Saltstone.

7.0 References

1 P. D. d'Entremont, et. al., "Alternative Paths for Tank Farm Influents", WSRC–TR–2003–00383. Rev 1, October 15, 2003.

2 J. R. Fadeley, "**Shipper – Receiver Agreement (SRA)** between the **Savannah River Site** and the **Idaho National Engineering and Environmental Laboratory** for the transfer of **Uranium Oxide Material Group C** to HB–Line for material disposition or to 235–F or K–Area for lag storage", WSRC–RP–2003–1023, Rev 2, January 26, 2004.

3 M. K. Hackney, "Pu Contaminated Scrap Project Scope of Work", M–SOW–H–00139, December 9, 2003.

4 S. J. Livingston, "Closure Business Unit Implementation of DOE Order 435.1 Container Staging, Inspection, and Monitoring Requirements", CBU–ENG–2003–00052, Rev 1, June 2004.

5 U.S. Department of Energy, "Implementation Guide for use with DOE M 435.1–1," Chapter II, "High–Level Waste Requirements," July 9, 1999.

6 A. R. Gough, Legal Basis for the Permitting of the F/H Tank Farms", GCO–LGL–940128, April 15, 1994.

7 W. T. Goldston, "Managing Low–Level Waste PUREX Solvent Solutions Discarded from the Canyons," OBU–SWE–2003–00037, March 14, 2003.