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CRITICALITY ASSESSMENT OF THE DEFENSE WASTE PROCESSING FACILITY

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ABSTRACT

Assessment of nuclear criticality potential of Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) is required to ensure the safe processing of radioactive waste for final disposal. The high level waste (HLW) is vitrified in the S-Area Defense Waste Processing Facility (DWPF) for long term storage and disposal. Assessment of the DWPF operation using the 16-group Hansen Roach cross section in the WSRC Joshua 70 criticality system showed the risk of nuclear criticality to be minimal. Criticality poses only a negligible risk in the DWPF process because of the characteristics of the radioactive wastes and the DWPF process. The wastes contain low concentrations of fissile material and many elements which act as neutron poisons. Also, the DWPF process chemistry does not effect separation and accumulation of fissile materials.

During the analyses, there were several concerns that nuclear criticality might be possible under certain abnormal and process upset conditions. Experiments were performed to resolve these concerns. These experiments provided a better understanding of the process chemistry and more realistic assumptions for nuclear criticality and safety modeling and calculations. The results confirmed that the DWPF can process all of the high level radioactive wastes currently stored at the Savannah River Site with negligible risk of nuclear criticality under normal and abnormal/process upset operation.

I. INTRODUCTION

At the Savannah River Site, high level radioactive wastes are stored as caustic slurries. During storage, the nuclear wastes separate into a supernate layer, normally referred to as salt solution, and a sludge layer. The radionuclides from the sludge and supernate feeds are immobilized into borosilicate glass by the Defense Waste Processing Facility for long term storage and eventual disposal. The fissionable material in the radioactive waste has been the result of process losses in separation processes. The fissionable material is currently stored in the tank farm at very low concentrations. Due to the large volume of waste to be processed in one DWPF sludge batch cycle, about 6,500 gallons of sludge and 7,000 gallons of precipitate feed, low concentrations of fissionable material may represent significant quantities. It has been shown that the DWPF sludge-only operation can process high level radioactive wastes with a minimal risk of nuclear criticality under normal and abnormal/process upset conditions.[1] This paper demonstrates further that nuclear criticality poses only a negligible risk in the DWPF process during the couple operation because of the characteristics of the waste and the DWPF process chemistry.

A. Overview of the DWPF process

The DWPF is receiving two HLW feed streams from the tank farm: the precipitate slurry resulted from the In-Tank Precipitation (ITP) processing of the salt solution and the sludge slurry.

High level waste salt solution is processed in the ITP process to remove cesium-137 and to adsorb strontium on monosodium titanate (MST). Soluble uranium and plutonium are also adsorbed on monosodium titanate. The tetraphenylborate slurry containing potassium and cesium tetraphenylborate precipitates and MST with adsorbed strontium, uranium, and plutonium is then washed in the DWPF Late Wash Facility (LWF) before it is sent to the DWPF Salt Processing Cell (SPC).

In the Salt Processing Cell, the precipitate slurry is first stored in the Precipitate Reactor Feed Tank (PRFT) and then processed in the Precipitate Reactor (PR). In the PR, tetraphenylborate is destroyed by acid hydrolysis reactions to produce benzene and an aqueous phase containing radionuclides.

The sludge feed is slurried, washed, and filtered several times in Tanks 40, 42, and 51 and become homogenized during ESP operation. Alkaline sludge feed is then transferred from the tank farm to the Sludge Receipt and Adjustment Tank (SRAT) in the DWPF Chemical Processing Cell (CPC). The sludge slurry is treated with nitric acid in the SRAT to control the rheological properties of the sludge slurry and to react with several components on the slurry, primarily nitrites, carbonates, and soluble hydroxides.

The Precipitate Hydrolysis Aqueous product (PHA) is combined with the sludge slurry and the borosilicate glass frit in the DWPF Chemical Process Cell (CPC) to produce melter feed. The high level radioactive waste is finally immobilized in a glass matrix contained in sealed stainless steel canisters.

To summarize the overall DWPF process operation, there are two HLW feed streams from the tank farm delivered to the DWPF. The precipitate feed slurry is processed in the Salt Processing Cell to produce the PHA for subsequent SRAT and Melter operations. The sludge slurry is processed in the SRAT, and combined with the PHA. The amount of PHA, or more correctly the amount of soluble and insoluble solids in the PHA, is half of the sludge solids. All of the HLW slurry feeds are combined in the SME with the glass forming frit. The Melter immobilizes all of the HLW feeds in a waste borosilicate glass form.

B. Fissionable Material

Of the fissionable isotopes available in the DWPF process, only those which are fissile (i.e. those which can undergo thermal fission such as U-235, U-233, Pu-239, Pu-241) are of concern. The process involves aqueous solution and solid slurries maintaining sufficient hydrogen to allow the non-fissile but fissionable isotopes to be ignored. This eliminates the need to evaluate the criticality safety impact of many of the fissionable but non-fissile isotopes.

II. BASIS FOR THE DWPF CRITICALITY ASSESSMENT

A. Sludge Feed

Two abundant and relatively effective neutron absorbers contained in the waste sludge are iron and manganese. The minimum for iron and manganese have been established in a criticality assessment with the 16-group Hansen Roach cross section in the WSRC Joshua 70 criticality system. The safe weight ratios specify mixtures in an infinite system that cannot achieve criticality.

Minimum Safe Weight Ratio for Fe and Pu-239:[1,2]

Fe:Pu-239: 160:1

Minimum Safe Weight Ratio for Mn and Pu-239:[1,2]

Mn:Pu-239: 64:1

Minimum Safe Weight Ratio for a mixture of Fe, Mn, and Pu-239:[1,2]

Fe:Mn:Pu-239: 26.5:53:1
60:40:1
80:32:1
94.5:27:1
110:22:1

The weight ratios of Fe, Mn, or a combination of Fe and Mn in excess of the minimum safe ratios exist for all planned major DWPF sludge batches. In particular, all of the DWPF sludge batches are safe based solely on the ratios of Fe to fissile material. Two batches, Batch 3 and 4, are safe solely based on the ratios of Mn to fissile material. All of the sludge batches are safe based on the combined ratio of Fe and Mn to fissile material.

A significant contributor to the criticality safe operation of the DWPF is the low uranium enrichment in the sludge feed slurries. At 0.95% U-235 enrichment, the subcritical mass limit for homogeneous oxide is essentially infinite. All of the planned sludge batches have a uranium enrichment of 0.76% or less.

B. Precipitate Feed

The radioactive tetraphenylborate precipitates resulted from pretreatment of the waste supernate are processed in the Late Wash Facility and the Salt Processing Cell. Fissile materials in the precipitate feed come from (1) fissile nuclides in the entrained insoluble sludge solids of the salt, and (2) fissile nuclides adsorbed on the monosodium titanate (MST). The potential of a nuclear criticality associated with a sludge solid containing fissile material has been shown to be negligible.

The MST-adsorbed fissile material processed in the Late Wash Facility and the Salt Processing Cell also remains safe from a nuclear criticality because of the following reasons:[2]

(1) The adsorbed fissile material on MST is safe due to the abundance of the neutron absorbing titanium in MST. It has been established that if the fissile material is adsorbed on MST and there is an accumulation of solids in the salt process areas, the risk of nuclear criticality is negligible because of the ratio of titanium in MST to fissile material well above the safe ratio. This safe ratio was established in a criticality assessment with the 16-group Hansen Roach cross sections in the WSRC Joshua 70 system. In particular, assuming a bounding enrichment of 86% U-235 and an infinite system, at least thirty six (36) overbatching of MST mass additions in the tank farm's In-Tank Precipitation process are required before sufficient mass for criticality can accumulate. This means that all of the fissile material in the salt solution currently stored in the tank farm can accumulate in the DWPF salt process area and still there is no nuclear criticality.

(2) For fissile material desorbed from MST during the Precipitate Reactor process cycle, it is safe because they become soluble in the Precipitate Hydrolysis Aqueous (PHA) product. The maximum fissile material, which are adsorbed on MST, to be present in one nominal salt processing batch cycle of 11,355 liters, is about 590 grams of uranium and 78 grams of plutonium. The high hydrogen-to-soluble-fissile ratio in the solution prevents a nuclear criticality.

(3) Furthermore, the fissile material content in one precipitate batch is low enough that a critical mass does not accumulate in tanks in the Late Wash Facility and Salt Processing Cell.

Other neutron absorbers such as boron, which is the main chemical reagent in the precipitate process stream, also mitigates against a nuclear criticality.

III. CRITICALITY ASSESSMENT

During the analyses, there were several concerns that nuclear criticality might be possible under certain abnormal and process upset conditions. The following experiments were performed either in the Savannah River Technology Center (SRTC) shielded cells or in a radioactive laboratory hood to resolve these concerns. These experiments also provided a better understanding of the process chemistry and more realistic assumptions for nuclear criticality and safety modeling and calculations.

A. Ratios of Iron and Manganese to Uranium and Plutonium in the S-Area DWPF Process.

There is no chemical reaction separating or isolating fissionable material in the sludge process streams throughout the S-Area DWPF process. All of the fissile materials remain in the sludge solid phase through the entire DWPF processing scheme. Iron and manganese are the two chemical species of interest in the sludge solids, due to their role as neutron absorbers, which will be discussed fully later. There is only one chemical reaction involving manganese in the SRAT, which effectively removes about half of the manganese from the sludge solids into the aqueous solution. There are redox reactions involving iron and manganese in the Melter, but it does not affect the criticality safety characteristics since they still remain with the fissile materials within the glass matrix.

Tank 51 radioactive sludge was processed in a demonstration of the DWPF process in the Savannah River Technology Center's Shielded Cells.[3] The ratios of iron and manganese to uranium and plutonium in the dried sludge solids, which include both the soluble and insoluble solids, and glass, show that they remain rather constant throughout this DWPF process demonstration, as follows.

	Fe/U	Fe/Pu	Mn/U	Mn/Pu
Sludge Feed	9.4	3069	1.0	332
SRAT product	11.1	---	1.1	---
Melter product	9.5	3545	1.0	377

It is important to note that although the manganese to uranium and plutonium ratios remain essentially the same throughout the DWPF process, only 50% of Mn can be counted as neutron absorbers.

During the nitric acid addition of the SRAT cycle, up to 50% Mn becomes soluble and is no longer in the sludge solids with fissionable material. Under abnormal or upsets conditions, the presence of soluble Mn or ratio of soluble Mn to the fissile material (or sludge solids) cannot be guaranteed. Therefore, only the insoluble Mn, which amounts to more than 50% of the manganese in the sludge feed and is always present throughout the DWPF process, can be counted as a neutron absorber.

B. The Uranium and Plutonium Content of the Precipitate Process Streams.

There are two different streams of fissionable material entering the S-Area DWPF process in the precipitate feeds: (1) fissile material adsorbed on the monosodium titanate (MST), and (2) fissionable material in the entrained insoluble sludge solids of the salt solution. There is no chemical reaction involving either fissionable material in the entrained sludge or fissile material, primarily U and Pu, adsorbed on MST in the Late Wash Facility and the Salt Processing Cell. However, during the benzene distillation and subsequent total reflux in the Precipitate Reactor's process cycle, fissile material may be partially desorbed from MST.

Following is a discussion of effects of formic acid boiling on adsorbed uranium and plutonium on MST. A small amount of monosodium titanate containing 2.2 wt% depleted uranium was boiled in a formic acid solution to simulate the PR reaction cycle.[4] The MST to 90% formic acid ratio in the experiments[4] was about 15 mg/ml, compared to 65 mg/ml in a typical PR reaction cycle. It was found that about 34% of the depleted uranium was desorbed from MST after 5 hours of boiling the MST in a formic acid solution. Increasing the boiling time of the experiment to 12 hours did not effect additional desorption of depleted uranium, since only 35% depleted uranium was desorbed. Three important conclusions were derived from the experimental work.

(1) The depleted uranium desorbed from MST is soluble uranium. It was not a surprise, since uranium adsorbed on MST during the ITP process cycle comes from soluble uranium in the salt solution.

(2) The concentration of uranium in the formic acid solution after experiments was about 5 ppm. It was much lower than 25 grams

U per liter of saturated solution as estimated from the solubility data of UO_2 in formic acid solution.[5] It is an indication that the remaining U is still strongly adsorbed on MST.

(3) Scanning Electron Microscopy analysis confirmed that there is depleted uranium still adsorbed on MST.

Reference 4 also reviewed experimental data from the small scale Precipitate Hydrolysis Process demonstration with radioactive precipitate feed from Tank 48. No soluble plutonium was found in PHA, as none was detected by the Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS) analysis. There was also evidence that no measurable amount of soluble uranium was desorbed from MST.

C. Plutonium Solubility in Mercury

There was a concern that plutonium oxide may be dissolved in the mercury in the mercury trap in the SRAT. It was postulated that plutonium could accumulate over time in the mercury trap, and cause a nuclear safety concern. The distribution of plutonium was experimentally determined between the aqueous sludge slurry phase and the mercury phase using simulated sludge doped with a known amount of plutonium and Tank 42 sludge. It was found that the plutonium dissolved in the mercury in the mercury trap during the SRAT reaction cycle was less than 6×10^{-6} grams of plutonium per gram of mercury, which amounts to about 2 grams of Pu-239. This concentration is too low to accumulate enough plutonium in the mercury trap to cause a concern.

D. Process Cleaning Procedure

The abnormal process upset which blinds the coils with sludge solids is a scenario that could cause changes in the Fe and Mn to fissile material safe weight ratios. There is a concern relating to fouling of the SRAT vessel after the process upset and subsequent clean-up procedure. However, there is no reference cleaning procedure and, therefore, a nuclear criticality safety evaluation of the clean-up operation of the SRAT has not been performed. If the SRAT internals are fouled by the sludge solids and a clean-up procedure has to be performed to restore the SRAT to operational status, the clean-up procedure is viewed as an abnormal operation which is not covered under this assessment. Once this process is defined, its safety (in terms of criticality) will then be evaluated.

In general, if a cleaning procedure does separate the uranium from other solids, nuclear criticality safety would not be compromised if uranium enrichment remains below 15% (K_{eff} = 0.929 for Batch 1 sludge composition).[1]

E. Melter Accumulation

There has been a concern about plutonium accumulation in the melter which could be a potential source of a nuclear criticality incident during the melter's 2-year life. Experimental data indicates that the plutonium oxide is soluble in borosilicate glass at the ratio of 6×10^{-3} g PuO_2 per gram of frit.[6] Using optical and Mossbauer spectra, Karraker[6] inferred that from the valence state, Pu is a part of the borosilicate network. The plutonium oxide to frit ratio during Batch 1 operation in S-area will be about 2×10^{-5} g PuO_2 per gram of frit. Thus, the amount of plutonium in the melter will be low compared to the amount of plutonium which, based on experiments, can be easily accommodated in solid solution in the borosilicate glass matrix. Under normal melter operation, no plutonium separation and, hence, no accumulation in the melter is possible. There is also no known abnormal process upset which might separate the plutonium from the borosilicate glass matrix.

IV. CONCLUSIONS

Following are characteristics of the DWPF process which ensures operation with a negligible risk of nuclear criticality during normal operation and abnormal operation or process upset conditions.

1. The DWPF sludge feeds from the current tank farm inventory contain an abundance of neutron absorbers, primarily iron and manganese, which prevent nuclear criticality.

2. The DWPF process chemistry does not cause separation of fissile material from the sludge solids, which contain neutron absorbers.

3. As a special case which only applies in the Late Wash Facility and the Salt Processing Cell, adsorbed fissile material on monosodium

titanate in the precipitate process streams are critically safe because:

a. Monosodium titanate (MST) is also an effective neutron absorber.

b. In case of fissile material desorbed from MST during the acid hydrolysis reaction, the high hydrogen to fissile ratio prevents the soluble fissile material from undergoing criticality.

c. Furthermore, the fissile material content in one precipitate batch is low enough that a critical mass does not accumulate in tanks in the Late Wash Facility and Salt Processing Cell.

These conclusions were reached without consideration of other neutron diluents or absorbers which are prevalent throughout the entire DWPF process. In the special case of the Late Wash Facility and the Salt Processing Cell, boron, which is a very effective neutron absorber, is one of the main reagents in the salt processing chemistry and is present in all precipitate process streams. In the sludge process streams, there are Al, Ni, Hg, U-238, Mg, and Cr, which are also neutron diluents or absorbers in sludge solids with the fissile material. Of special interest is the abundance of U-238 as the uranium enrichments of the six planned major sludge batches are all less than 1%.

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REFERENCES

1. B. C. Ha and T. G. Williamson, "Criticality Assessment of Initial Operations in the Defense Waste Processing Facility", Proceedings of the HLW, LLW, Mixed Wastes and Environmental Restoration Waste Management Symposium '94, February 27- March 4, 1994, pg. 585-588.

2. T. G. Williamson, "Nuclear Criticality Safety Evaluation DWPF Late Wash Facility, Salt Processing Cell, and Chemical Processing Cell," EPD-CTG-940037, October 1994.

3. M. K. Andrews and N. E. Bibler, "Radioactive Demonstration of DWPF Product Control Strategy," ACS Ceramic Transactions: Environmental and Waste Management Issues in the Ceramic Industry, Vol. 39, pg. 205-211, 1994.

4. B. C. Ha, D. M. Ferrara and N. E. Bibler, "Criticality Issues in the DWPF Precipitate Hydrolysis Process," A presentation for the "ACS Spring '96 National Meeting," The American Chemical Society National Meeting, Division of Industrial and Engineering Chemistry, Tank-Waste Chemistry, March 24 - 28, 1996, New Orleans, Louisiana.

5. W. F. Linke, <u>Solubilities Inorganic and Metal-Organic Compounds K-Z,</u> Volume II, Fourth Edition, Van Nostrand, New York, 1965, page 1598-1599.

6. D. G. Karraker, "Actinide Valences in Borosilicate Glass," J. of Am. Ceramic Soc, Vol. 65, No. 1, pg. 53-55, January 1993.