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THE EVALUATION OF URANIUM-235 ISOTOPIC DILUTION WITH THE ADDITION OF DEPLETED URANIUM TO SUPERNATANT LIQUID WASTE.

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ABSTRACT

This paper describes laboratory-scale results on experiments performed to examine the feasibility of isotopic dilution of uranium-235 in supernatant liquid storage tanks at the Savannah River Site. The isotopic dilution tests were accomplished by adding an alkaline depleted uranium solution to small portions of simulated and actual storage tank waste solutions with enriched U-235 compositions. Based on the laboratory observations, recommendations were made, which involved the addition of significant quantities of uranyl carbonate solution to over four million liters of U-235 enriched waste stored in Tank 43H at SRS to reduce the risk for criticality.

A post-uranyl carbonate addition analysis on the tank supernate confirmed the effectiveness of depleted uranium in isotopic dilution of U-235. The U-235 enrichment in the Tank 43H was isotopicaly diluted from an original high of over 4 wt % down to less than 0.5 wt % as predicted from the laboratory investigations.

Keywords: Isotopic dilution, Uranium enrichment, Fissile material, Evaporator.

I. INTRODUCTION

The high-activity alkaline waste from the Savannah River Site (SRS) is normally stored as a two-layered mixture in storage tanks. The two basic layers can be described simply as the supernatant layer and the sludge or solid layer. The sludge layer contains the hydrolyzed cations, including most of the actinides while the supernatant, which forms the bulk of the solution waste, is a strong base salt solution containing mostly soluble radioactive cesium. During waste processing, the supernatant layer is normally evaporated to increase storage space. Although actinide concentrations, in particular uranium, are low in the supernatant liqueur, evaporation raises the possibility of its accumulation in the evaporators. Thus, reducing the U-235 enrichment below that of natural uranium abundance in the storage tanks ensures that the evaporators can be operated safely without risk of criticality.

The Tank 43H, which holds more than four millions liters of supernatant waste, serves as the feed tank to the 2H evaporator at SRS. Analyses[1] of Tank 43H supernatant samples indicates that the supernate has an average total uranium concentration of 15.0 ± 2.9 mg/L and an average uranium-235 enrichment of 3.12 ± 0.63 wt %. Because of this high uranium-235 enrichment in Tank 43H, plans are to add depleted uranium (DU) as a uranyl carbonate solution to Tank 43H to reduce the U-235 enrichment in the supernatant liquid[2] The target uranium-235 enrichment for the Tank 43H supernate is less than 0.70 wt %.

To ensure adequate mixing of the uranyl carbonate solution with the tank supernate, the solution was introduced at a Flygt mixer, which was positioned at about 3.3 meters from the sludge and pointed up at an angle.[3, 4, 5]

This paper presents experimental results conducted at the Savannah River Technology Center (SRTC) to examine the feasibility, extent and rate of isotopic dilution of uranium-235 with the addition of alkaline depleted uranium solution to Tank 43H supernate simulant and to the real waste supernatant liquid currently stored in Tank 43H. The results of a post-uranyl carbonate addition analysis for U-235 enrichment in representative Tank 43H samples, collected at different regions in the tank, are also reported.

II. EXPERIMENTAL

Before the addition of a significant amounts of alkaline depleted uranium solution to the large U-235 enriched waste reservoir (Tank 43H) and eventual post depleted uranium addition analysis for extent of isotopic dilution of Tank 43H, several laboratory tests were performed. Some of these tests included bench top evaluations of isotopic dilution involving the use of simulants based on chemistry of the contents of the Tank 43H. The non-bench top isotopic dilution experiments, involving the utilization of actual radioactive samples from Tank 43H waste reservoir, were performed inside a shielded radioactive cell facility. In both the bench top and shielded radioactive cell studies, alkaline DU solution was used in the isotopic dilution of U-235 in the enriched Tank 43H simulant and the supernatant samples from Tank 43H waste reservoir. In these tests, 4 mL DU solution (10 g uranium per liter), a calculated amount needed to reduce the U-235 enrichment well below 0.70 wt % was added to 100-mL portions of the simulant or real waste under various delivery and mixing conditions. An inductively coupled plasma-mass spectroscopic technique was used to quantitatively measure the uranium content and isotopic distribution in the resulting mixtures of DU and simulant or real waste. The efficiency of the supernate isotopic dilution process was based on the differences, if any, in the magnitude of experimental isotopic distribution data obtained versus the expected theoretical values. How good the isotopic dilution process worked experimentally was also judged on changes in the equilibrium uranium-235/total uranium ratio with mixing time and observations related to the behavior of uranium precipitates formed.

Test conditions were defined to monitor for the effects of DU delivery rate, mixing rate, and quantity of DU solution added on the isotopic dilution efficiency on the U-235 enriched Tank 43H simulate and supernatant liqueur. In these tests we made the following approximation [a]

U-235/U-238 ≈ U-235/U-total.

The composition of the Tank 43H simulant used in this study featured the most recently reported values from dip samples taken from this water reservoir[6]. Simulants were prepared in liter–size storage Teflon® containers from which 100-mL portions were used for the laboratory tests. The simulant compositions are shown in Table I. During the preparation of the simulant solution the simulant components were added in the mixture in such a manner as to minimize the generation of oxides of nitrogen or other gases. The simulant stock solution was spiked with the right amount of 50 wt % U-235 enriched stock solution to produce 4.37 wt % U-235 enriched test solutions. To prepare a one-liter simulant solution with U-235 enrichment of 4.37 wt %, 213 micro-liters of the 50 wt % U-235 stock solution was used.

This target U-235 enrichment for the simulant of 4.37 wt % is based on the average U-235 enrichment from several Tank 43H sample measurements plus two times the standard deviation of this data set. Similarly, the target total uranium concentration is based on the average total uranium concentration of 18.95 mg/l plus approximately one times the standard deviation. The density of the Tank 43H simulant was 1.21 g/mL compared to a value of 1.20 g/mL for the Tank 43H supernatant waste.

The depleted uranium solution used in these tests was prepared by dissolving 21.1 grams of uranyl nitrate ($UO_2 (NO_3)_2.6H_2O$) in approximately 5 mL of 1.5 M nitric acid. The resulting solution was added to a one-liter volumetric flask containing 500 mL of a 0.37 M sodium carbonate ($Na_2CO_3.H_2O$) solution. The flask was then filled to the mark with additional distilled and deionized water. Analysis of this alkaline DU solution for total uranium concentration gave a value of 10.00 ± 0.01 mg/mL and a U-235/U-total ratio of 0.30 ± 0.02 wt %. The density of this DU solution was 1.04 g/mL. The mixing of depleted uranium with Tank 43H simulant or real waste was carried out in capped transparent 250-mL Teflon bottles with receiving holes on each cap. These holes were connected to a syringe pump via Teflon tubing. In a typical test run, 4 mL of DU solution was added to a 100-mL portion of 4.37 wt % U-235 enriched simulant solution or to the Tank 43H supernatant liqueur.

II. A. Simulant Test Design

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[a] Other uranium isotopes are present in low concentrations and subsequently fall below detection levels.

The measured uranium-238 for Tank 43H simulant was 18.95 mg/l with a U-235 concentration of 0.766 mg/L. Based on these uranium concentrations, the addition of 4 mL of the DU solution to 100-mL of the simulant solution provides a theoretical U-235/U-total ratio of 0.0047 (0.1966/41.9716). A comparison of the experimental value for U-235/U-total ratio in the filtrate obtained from laboratory and shielded cell blending of DU with enriched Tank 43H simulant and real waste with this theoretical value of 0.0047 wt %, was used as a measure of the extent of isotopic dilution.

The test plan for the simulant work consisted of three principal test categories, which included addition rate, mixing rate and utility test. The addition rate test (instantaneous addition versus slow addition at two flow rates into a 250-mL Teflon® bottle: 0.267 and 0.013 mL/min.) was designed to evaluate the effects of depleted uranium addition rate under well and poorly mixed conditions. The utility test was designed to evaluate changes in U-235/U-total ratio with increase in the amount of DU solution added. Here, we maintained the volume of the simulant constant at 100 mL for nine different runs and increased the volume of DU solution (0.5, 1, 2, 3, 4, 10, 15, 20 and 25 mL). The goal was to determine if the desired U-235/U-total theoretical ratio of 0.30 wt % could be eventually attained in the resulting mixtures with increase in DU solution volume. This expectation would only be met if the dissolution of uranium in the alkaline solution supersedes the precipitation of uranium. This test was performed under well-mixed conditions and with instantaneous addition of the DU solution. The mixing test was used to characterize the effects of mixing on the isotopic dilution experiments and it was evaluated by running experiments with and without effective mixing using either a magnetic stirrer or an orbital shaker, or a combination of both mixing devices.

In most of the tests, samples were collected at the following time intervals: 3, 9, 24, 48, 72, 96 and 120 hours after adding depleted uranium to the simulant or real waste supernate. In a typical run, approximately 1 mL of the resulting test mixture was withdrawn using a 10-mL plastic syringe filter and filtered after connecting a syringe filter disc (0.2-micron membrane) to it. In some cases, unfiltered samples were submitted for uranium isotope analysis as well. The filtrate (0.5 mL) was delivered into a sampling vial containing 1.0 mL of dilute nitric acid and submitted for uranium analysis.

III. RESULTS

III.A. Addition Rate Tests: Instantaneous addition of depleted uranium

In a typical test, 100 mL of the simulant was measured and delivered into a Teflon® bottle containing a magnetic stirring bar. The magnetic stirrer was operated in a manner to avoid the introduction of excess air into the solution. While the simulant solution was stirring, 4 mL of the DU solution was measured and delivered into the mixing simulant within 3 seconds. Three hours after the introduction of the DU into the solution the 3-hour samples (filtered and unfiltered) were collected. Six hours later the 9-hour samples were collected. Thereafter, samples were collected at 24-hour intervals after the initiation of the test. Figure 1 shows a typical isotopic dilution profile for the instantaneous addition of DU solution into the Tank 43H simulant. The average U-235/U-total ratio from the seven post-DU addition samples obtained as part of this test was 0.458 ± 0.024 wt %. The U-235/U-total ratio for the filtered samples collected after 3 and 120 hours, respectively, were 0.472 and 0.487 wt %. These results compare favorably with the expected U-235/U-total ratio of 0.470 wt %.

III.B. Addition Rate Test: DU Delivered at 0.267 mL/minute

We ran this test in duplicate in a manner similar to the instantaneous addition test described above with the exception that the 4 mL DU solution was delivered into the reaction bottle at 0.267 mL/minute using a syringe pump. The complete delivery of 4 mL DU into the simulant solution took about 15 minutes at this delivery rate. The average U-235/U-total ratio for the first test was 0.478 ± 0.025 wt %. The U-235/U-total ratio for the filtered sample collected after 3 and 120 hours of running the test, respectively were 0.440 and 0.480 wt %. The corresponding U-235/U-total ratios for the duplicate test were 0.454 ± 0.026 wt %, 0.410 wt % for the 3-hour sampling and 0.460 wt % for the 120-hour sampling. The U-235/U-total ratios for the unfiltered samples collected at the same times (containing uranium precipitates) were 0.440 and 0.470 wt %, respectively. These experimental U-235/U-total ratios for the two runs agree favorably with the expected value of 0.470 wt %. Similarly, the average U-235/U-total ratio for the unfiltered samples, 0.454 wt %, is within the one sigma uncertainty value of the expected value. These results indicate that isotopic dilution equilibrium has been reached between the supernatant liquid and precipitated uranium solids.

III.C. Addition Rate Test: DU Delivered at 0.013 mL/minute

In this test, the 4 mL DU solution was delivered into the 100 mL enriched Tank 43H simulant solution using a syringe pump calibrated to deliver 0.013 mL of the DU per minute. Therefore, it took approximately 300 minutes to deliver the entire 4 mL of the DU solution into the test bottle. The test mixture was magnetically stirred during the

120- hours test period. Because of the approximately 5 hours required to deliver the DU solution into the test bottle the first sampling was performed at the ninth hour of mixing. The average U-235/U-total ratio obtained was 0.488 ± 0.096 wt %. The U-235/U-total ratio for the filtrate sample collected after 9 and 120 hours of running the test were, respectively, 0.380 and 0.483 wt %. Again, these values are not statistically different from the theoretical value of 0.470 wt %.

III.D. Utility Test

This set of tests was designed to evaluate the efficiency of the isotopic dilution process by varying the amount of added DU solution and comparing the resulting U-235/U-total ratio with the corresponding calculated theoretical value. With significant increase in the amount DU solution added to the 4.37 wt %U-235 enriched simulant, the U-235/U-total ratio is expected to approach the DU enrichment value of 0.3 wt %. These nine test mixtures were continuously stirred throughout the test duration of 120 hours. Due to time constraints and analytical costs we only sampled at the end of each test. Table II provides a summary of the results for the entire efficiency test. The experimental values reported in Table II come from filtrate samples only. In Table II, the theoretical equilibrium value for each test is provided in column 3 and the corresponding experimental value in column 2. Column 4 shows the average depleted U-235/U-total ratio of 0.3 wt %**.** Figure 2 shows a plot of the variation in amount of DU added with changes in enrichment of the simulant solution. This figure also shows an overlay plot of the enrichment in the depleted uranium as a reference. In general, there is good agreement between the theoretical and measured values for the isotopic ratios as a function of amount of added DU solution. We attribute the small differences between the two values to experimental errors associated with sampling and analysis.

III.E. Mixing Test: Instantaneous Addition with Stirring

A new batch of Tank 43H simulant, with a U-235 enrichment of 4.69 wt % was used in this mixing test. In this test, 4 ml of the DU solution was injected within 3 seconds into the reaction vessel containing 100 mL of the Tank 43H simulant under well-mixed conditions. The mixture was vigorously stirred without excessive vortex for five minutes and then transferred to an orbital shaker maintained at 44 rpm for the test duration. The average U-235/U-total ratio obtained was 0.557 ± 0.051 wt %. The U-235/U-total ratio for the filtrate sample collected after 3 and 120 hours were 0.550 and 0.550 wt %, respectively.

III.F. Mixing Test: Instantaneous Addition without Stirring

The mixing test above was repeated. This time the mixture was not magnetically stirred during the introduction of DU. After the addition of DU the mixture was transferred onto an orbital shaker that was set to operate at 44 rpm for the test duration of 120 hours.

The average U-235/U-total ratio obtained was 0.477 ± 0.027 wt %. The U-235/U-total ratio for the filtrate sample collected after 3 and 120 hours of running the test, respectively were 0.495 and 0.461 wt %. The experimental U-235/U-total values obtained by mixing DU and U-235 enriched simulant with moderate or vigorous stirring of the mixture (instantaneous addition) were, respectively, 0.477 ± 0.042 and 0.557 ±

0.051 wt %. These results are not statistically different from the expected U-235/U-total ratio of 0.470 wt %.

III.G. Mixing Test: DU Delivered at 0.013 mL/minute with Stirring.

In this test, the 4 mL DU solution was delivered into the 100 mL enriched Tank 43H simulant solution using a syringe pump calibrated to deliver 0.013 mL of the DU solution per minute. Hence, it took approximately 300 minutes to deliver the entire 4 mL DU into the simulant solution. The solution was magnetically stirred just before the first drops of DU were delivered until the end of the 120 hours test period. Because of the approximately 5 hours required to deliver DU into the enriched simulant the first sampling was done only at the ninth hour of mixing. The average U-235/U-total ratio obtained was 0.442 ± 0.046 weight percent. The U-235/U- total ratio for the filtrate sample collected after 9 and 120 hours of running the test were 0.400 and 0.410 wt %, respectively.

III.H. Mixing Test: DU Delivered at 0.013 mL/minute Without Stirring

Here, the DU delivery was similar to the description in tests above (0.013 mL/minute), however, the solution was not magnetically stirred during the entire 300 minutes of the DU delivery. As the DU was delivered at this rate without mixing, droplets of the DU solution fell to the bottom of the reaction vessel producing two distinct liquid layers or phases. At the end of the DU solution delivery, solid particles were observed in the bottom of the test bottle. The mixture was put in the orbital shaker at 44 rpm. Figure 3 shows the isotopic dilution profile for this test. Equilibrium U-235/U-total ratio was not attained within the 120 hours of running the experiment as observed in other well-mixed tests. The average U-235/U-total ratio obtained was 0.945 ± 0.377 weight percent. The U-235/U-total ratio for the filtrate sample collected after 9 and 120 hours of running the test were, respectively, 0.470 and 0.470 wt %. This significant variation, which was not observed in other experiments, may be attributed to either sampling location or real time effects.

The U-235/U- total ratio obtained by slowly adding DU solution (0.013 mL/minute) into the Tank 43H simulant, with vigorous stirring is comparable in magnitude (0.442 ± 0.046 wt %) to the ratios obtained with instantaneous addition of DU under similar mixing conditions. However, the delivery of DU into the enriched simulant with no immediate stirring to ensure effective mixing produced isotopic dilution ratios significantly higher than the theoretical values of 0.470 wt %.

III.I. TANK 43H SUPERNATE: U-235 ENRICHED LIQUEUR

Archived Tank 43H supernate samples were used for this part of the uranium isotopic dilutions study. The initial uranium isotope concentration in the archived sample was analyzed in triplicate to give an average U-235/U- total ratio of 2.67 wt %. The uranium-238 concentration was 18.957 mg/L and 0.507 mg/L for the U-235. As in Tank 43H simulant tests discussed previously, we planned to add 4 mL of the DU solution to 100 mL of the archived samples from Tank 43H supernate (4 mL DU contains 40 mg total uranium with 0.12 mg U-235). Therefore, total uranium-238 in 100 mL of “real waste” plus added DU is 41.8957 mg (40 + 1.8957 mg) and the total U-235 in the mixture is 0.1707 mg (0.12 mg from 4 mL DU solution and 0.0507 mg from “real waste”). The expected U-235/U-total ratio is 0.407 wt %. Based on the results from the

Tank 43H simulant tests, three types of tests with real waste were planned. These included:

- Slow delivery of the DU solution into "real waste" solution under well-mixed conditions using a magnetic stirrer and a syringe pump to deliver DU solution at 0.267 mL per minute (active mixing of DU solution and real waste),
- Slow delivery of DU solution into real waste under well-mixed conditions using a magnetic stirrer and a syringe pump to deliver DU solution at 0.267 mL DU per minute. At the end of DU solution delivery, we planned to mounted the mixture onto an orbital shaker set at slow shaking rate of 44 rpm (Active mixing of DU and real waste followed by gentle rocking of mixture) and
- Delivery of DU solution into the real waste at 0.267mL DU per minute using a syringe pumps. This time the mixture is not magnetically stirred (slow delivery of DU with poor mixing).

Because of high radiation background in the shielded cell, the digital syringe pump after functioning well during pre-test evaluations, malfunctioned after a couple of days in the cell. Consequently, we modified this test plan to add DU solution in small increments of 500 μL every five minutes while magnetically stirring. This modification is supported by simulant test results above, which show that the rate of DU solution addition was less important than mixing in obtaining effective isotopic dilution.

III.J. TANK 43H SUPERNATE:DU Addition with Continuous Stirring

The DU solution and real waste mixture was actively stirred with a magnetic stirrer through out the duration of the test. The average U-235/U-total ratio obtained with the real waste using this approach was 0.397 ± 0.015 wt %. The U-235/U-total ratio for the filtrate samples collected after 3 and 120 hours were 0.420 and 0.370 wt %, respectively. The U-235/U-total ratio for the unfiltered samples during this same period (containing all of the uranium precipitates) was 0.390 and 0.400 weight percent, respectively.

III.K. TANK 43H SUPERNATE: DU Addition without Continuous Stirring

Here, the real waste and DU solution mixture (100 mL real waste supernate and 4 mL DU solution) was vigorously mixed with a magnetic stirrer during DU delivery followed by gentle rocking of the mixture in an orbital shaker set at 44 rpm for the duration of the test. The average U-235/U-total ratio obtained with the real waste was 0.426 ± 0.021 wt %. The U-235/U- total ratio for the filtrate samples collected after 3 and 120 hours were 0.410 and 0.430 wt %, respectively. The U-235/U- total ratio for the unfiltered samples during this same period (containing uranium precipitates) were 0.410 and 0.420 wt %, respectively.

III.L. TANK 43H SUPERNATE: DU Addition without Stirring

The mixture here was not magnetically stirred while delivering the DU solution into the real waste solution. After delivery of the DU solution the test bottle was put on an orbital shaker at 44 rpm. The average U-235/U- total ratio obtained with the real waste was 0.407 ± 0.014 wt %. The U-235/U- total ratio for the unfiltered samples collected after 3 and 120 hours were 0.391 and 0.421 wt %, respectively. The U-235/U-total ratio for the unfiltered samples during this same period (containing all of the uranium precipitates) were 0.391 and 0.403 wt %, respectively. The isotopic dilution of these archived Tank 43H supernate samples with DU solution was quite successful. The U-235 enrichment in Tank 43H supernates dropped from a high of 2.67 wt % to less than 0.4 wt % with the addition of DU solution.

III.M. POST-URANYL CARBONATE ADDITION CHARACTERIZATIONS

Based on the above laboratory observations with the successful isotopic dilution of both U-235 enriched simulant and Tank 43H supernatant liqueur, recommendations were made to the plant tank 43H operators. This recommendation called for the addition of significant quantities of uranyl carbonate solution to over four million liters of enriched U-235 waste stored in Tank 43H at SRS. About 80,000 liters of a depleted uranyl carbonate solution were added to Tank 43H and agitated with two Flygt mixers. The depleted uranium addition served to decrease the U-235 enrichment in the Tank 43H supernate so that the supernate could be evaporated with no risk of accumulating enriched uranium.

After all the uranyl carbonate had been added, the Flygt mixers were turned off, and the solids in the tank were allowed to settle. A total of nine samples were taken at different locations in the tank and analyzed to demonstrate that the U-235 enrichment in the supernate liquid was below the acceptance criteria of 0.7 wt %. The samples were taken from different depths, 0.61 meters below liquid surface, middle of the tank, (5.1 meters) and 0.61 meters above sludge level in the tank. Six of these samples were sent to an independent laboratory and we analyzed the remaining three samples. Of the three variable depth samples received only the last sample contained any visible solids. This sample collected from 0.61 meters above the sludge level in the tank 43H contained about 50% solids by volume. Prior to characterization, all three variable depth samples were centrifuged for several minutes and the liquid fraction from each sample was analyzed. No solids were observed in the bottom of the centrifuge tubes for the 0.61 meters below liquid surface and middle depth samples. The densities of the three as-received variable depth samples were determined at shielded cell temperature of 26 °C prior to centrifugation of each sample. The values obtained were, respectively, 1.236 ± 0.002, 1.242 ± 0.002 and 1.330 ± 0.010 g/mL for the 0.61-meters below liquid surface sample, middle sample and 0.61-meters above sludge surface sample. The third variable depth sample containing solids was agitated to ensure a uniform matrix prior to sampling for density measurements. Without further processing, aliquots of Tank 43H as-received liquid fractions resulting from centrifugation were diluted with distilled water and analyzed for uranium.

Three portions of the solid fraction isolated from the third variable depth sample (0.61 meters above sludge) were dried overnight to constant weight at 110 °C. The solid fraction was not washed to remove interstitial liquids and soluble solids prior to the drying treatment. The dried samples were digested in two ways (aqua regia and peroxide fusion dissolution[b] in triplicate) and analyzed as previously described for the supernate fractions. Analytical results are summarized in Tables III and IV. In general, there was a good agreement between the two dissolution methods, although slightly higher analytical values were reported for the aqua regia dissolution method compared to those from the peroxide fusion. The last column in Table IV refers to the average values based on the

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[b] Aqua regia: 3:1 by volume mixture of HCL and HNO_3, respectively. . Peroxide fusion is a salt mixture of 1.5 g Na_2O_2 and 1 g NaOH.

two digestions. For the uranium isotopic measurements, there was no statistical difference in the analytical results for the two dissolution methods above.

IV. DISCUSSION

Table V shows a summary of the isotopic dilution results for both the simulant and real waste investigations. From left to right, this table shows the experimental designs, initial U-235 enrichment in the simulant and real wastes, mixing conditions, expected or theoretical U-235/U-total ratios and observed U-235/U-total ratios. The addition rate tests were performed to evaluate the affect of depleted uranium addition rate on isotopic dilution under well-mixed conditions. The measured isotopic dilution ratios for the three DU solution addition rate tests were not statistically different and agreed with the expected value of 0.470 wt %. In all of these tests, the isotopic dilution ratios of the mixtures dropped from 4.32 or 4.69 wt % to below 0.5 wt % for all mixing conditions involving continuous stirring and mixing. Thus, we conclude that the rate of DU addition did not significantly affect isotopic dilution provided the system was well mixed. The isotopic dilution ratios obtained after 3 hours were almost identical in magnitude to the ratios obtained at end of the test. This indicates that equilibrium U-235/U-total ratio is rapidly established within the first few minutes of adding the depleted uranium with the Tank 43H simulant and that the dilution of the U-235 is faster than depleted uranium precipitation under well mixed conditions. The measured utility curve, variation of U-235/U-total ratio with increase in amount of depleted uranium solution added, is in good agreement with the predicted curve (Figure 2). Thus, under well mixed conditions, isotopic dilution in the supernatant proceeds smoothly upon addition of the DU solution with little of the DU precipitating before mixing and diluting the U-235 in the supernate.

In the mixing tests, the plan was to determine the effects of various mixing conditions (vigorous magnetic stirring versus orbital shaker-based rocking of the bulk mixture) on the attainment of isotopic dilution. The syringe pump approach to delivering of depleted uranium solution into a magnetically stirred U-235 enriched simulant provided the best isotopic dilution results, when compared to the expected theoretical value of 0.470 wt %. On the other hand, an equivalent delivery method of depleted uranium solution into an unstirred enriched solution gave the worst isotopic dilution results. In this unstirred blend, the mixing was limited to rocking the mixture in an orbital shaker. The observed U-235/U- total ratio was 0.945 ± 0.377 wt % with a range of 0.47 to 1.32 wt % (Figure 3). This deviation from the expected U-235/U-total ratio 0f 0.470 wt % is quite significant.

One other interesting observation in this particular test, rests in the fact that a similar test with depleted uranium added all at once (instantaneous addition) and with minimal mixing, too, gave a significantly different result. This time the U-235/U- total ratio obtained, 0.477 ± 0.027 wt %, is in agreement with the expected value of 0.470 wt %. This was also an isotopic dilution from 4.69 wt % down to 0.477 ± 0.027 wt % and the values were independent of the sampling location in the mixing vessel. The only difference between this test and the previous one was in the manner the depleted uranium solution was added to the Tank 43H simulant; instantaneous addition versus slow addition rate (0.013 mL/minute). Both tests were not stirred, but gently rocked at 44 rpm using an orbital shaker. In the slow addition case, the bulk of the DU solution did not disperse into the Tank 43H simulant resulting in two separate liquid phases. A small amount of solids formed and settled to the bottom of the vessel. Using an orbital shaker to rock the bulk of the liquid from side to side, did not result in depleted uranium diffusion into the bulk of the Tank 43H simulated solution. This test exhibited a poorer isotopic dilution response. This result suggests that bulk addition of depleted uranium solution, which led to acceptable mixing, may be more effective in ensuring appreciable isotopic dilution than slow depleted uranium addition in the absence of effective mixing.

All the real waste tests were essentially performed by instantaneous addition of the depleted uranium to the real waste. However, the method of mixing varied among the three tests. In the first test, the depleted uranium and waste solution mixture was stirred continuously using a magnetic stirrer. In second test the mixture was magnetically stirred while the 4 mL of depleted uranium was added into the real waste solution at 0.5 mL every five minutes. After the addition of depleted uranium solution, the mixture was placed into an orbital shaker and rocked at 44 rpm. In the third test the depleted uranium was added to the real waste at 0.5 mL every 5 minutes without any stirring and then transferred to the orbital shaker and rocked at 44 rpm for the duration of the experiment. In all three tests, the value of U-235/U-total ratio obtained was in excellent agreement with the expected or theoretical value of 0.407 wt %. This again confirmed the findings from simulant testing, which showed that the desired isotopic dilution can be attained provided the DU solution was added in a manner that enhanced its dispersion through out the waste solution.

One important aspect of this investigation, which did not receive sufficient attention, was the monitoring and characterization of solids formed upon the addition of the depleted uranium to the simulated or real waste solution. After the mixing of the depleted uranium with the Tank 43H simulant for 120 hours, the stirring mechanism was turned off and the solution allowed to settle at ambient laboratory conditions. Within a few minutes, we observed fine solids slowly settling to the bottom of the bottle with a clarified solution layer at the top. These changes in clarity and settling of the particles were more pronounced after leaving the solution overnight. As a general observation, the solids were easily re-suspended in solution using a magnetic stirrer at low speeds. With the solution left overnight again, most of the solids settled to a fine "powder" on the bottom of the Teflon® vessel.

A post-uranyl carbonate addition analysis of supernate from Tank 43H, Table II, shows that the average U-235 enrichment (U-235/U-total) in all three variable-depth samples were less than 0.5 wt %. The 0.61-meters above sludge sample had the highest U-235 enrichment of 0.483 ± 0.037 wt % (liquid fraction) and 0.464 ± 0.042 wt % (dry and digested solid). The U-235 enrichments in the other variable depth samples was 0.363 ± 0.008 wt % for the 0.61-meters above liquid surface sample and 0.361 ± 0.007 wt % for the middle depth sample. These results indicate that the U-235 enrichment in the supernatant liquid in Tank 43H was successfully diluted below the targeted value of 0.7 wt % by addition of depleted uranium in the form of a uranyl carbonate solution. . This U-235 enrichment in Tank 43H is well within the acceptance criteria established in the Nuclear Criticality Safety Evaluation for restart of the 2H-Evaporator[7].

Results from the three samples described in this report agreed well with the six samples that were analyzed at an independent laboratory[8]. The U-235 enrichment for the three samples measured at SRTC averaged 0.402 ± 0.070 wt % compared to 0.390 ±

0.001 wt % for the six samples analyzed at an independent laboratory. This agreement was significant since sample preparation and analysis techniques were different at the two laboratories. The data from both of these sets of samples showed that the reduction in enrichment required for restart of the 2H Evaporator had been achieved by a wide margin, which was an essential milestone for the successful restart of the evaporator.

V. CONCLUSIONS

We have used laboratory testing to evaluate the effectiveness of diluting U-235 enrichment of simulated and real waste solutions upon addition of an alkaline solution of depleted uranium. These experiments have provided insight into regions of Tank 43H near the Flygt mixer with maximum mixing conditions, regions farthest away from the Flygt mixer where there is bulk solution movement and intermediate regions of the tank where well mixed liquid phases are in transition to areas with limited mixing.

On a laboratory-scale, we used moderate magnetic stirring without excessive vortex to simulate the mixing conditions near the Flygt mixer and an orbital shaker to simulate areas with limited mixing conditions in the tank. A transfer of a well-mixed liquid from a magnetic stirrer to an orbital shaker was used to simulate regions with bulk solution movement and limited mixing.

The following conclusions are based on the observations and results obtained in this laboratory-scale investigations.

- We observed rapid dilution of the U-235 enrichment in the supernatant liquid to less than 0.5 wt % upon addition of an alkaline solution containing depleted uranium.
- The depleted uranium delivery mode and addition rate were not important parameters affecting isotopic dilution in the supernatant liquid.

- Mixing is the most important parameter affecting isotopic dilution in the supernatant liquid.
- Under appropriate mixing conditions, isotopic dilution of uranium-235 is faster than precipitation of depleted uranium.
- With effective mixing, isotopic dilution to an acceptable level occurred in minutes.
- Where there is limited or no effective means of mixing the depleted uranium solution with the supernatant liquid containing enriched uranium, instantaneous bulk addition of the depleted uranium appears more effective in ensuring appreciable isotopic dilution than a slow measured delivery of depleted uranium.
- Slower addition of the depleted uranium solution is beneficial for isotopic dilution only when it is accompanied by effective mixing.
- Precipitated solids formed upon addition of depleted uranium solution are micron size particles, which are easily suspended in solution with minimal stirring.

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Table I.

Tank 43H Simulant Composition.

Added Component	**Concentration**	**Units**
Free NaOH	1.25E+00	M
Total $NaNO_3$	6.15E-01	M
$NaAl(OH)_4$	1.00E-01	M
$NaNO_2$	4.05E-01	M
Na_2SO_4	9.00E-03	M
Na_2CO_3	2.50E-02	M
$Na_2C_2O_4$	3.45E-03	M
Na_3PO_4	3.20E-03	M
U-235	0.766	mg/L
Total uranium	18.95	mg/L
Total sodium concentration	2.45	M

Table II.

Utility Test Data: Instantaneous Addition of 4 mL DU to 100 mL of Tank 43H Simulant.

DU Solution, ml	**U-235/U-total observed, %**	**U-235/U-total expected, %**	**DU, U-235/U-total, %**
0	4.320	4.370	0.3
0.5	1.347	1.328	0.3
1	0.926	0.896	0.3
2	0.773	0.624	0.3
3	0.627	0.522	0.3
4	0.458	0.469	0.3
10	0.406	0.370	0.3
15	0.358	0.347	0.3
20	0.359	0.335	0.3
25	0.393	0.328	0.3

Table III.

Post-uranyl carbonate addition results for uranium analysis

	0.61 meters Below Liquid Surface		**Middle (5.1 meters)**		**0.61 meters Above Sludge** (Liquid fraction)
	Average	Std. Dev.	Average	Std. Dev.	Average
U-Total	5.28E+0, mg/L	2.39E+00	5.43E+0, mg/L	2.79E+00	2.09E+01, mg/L
U-235/U-238	3.63E-03	8.00E-05	3.61E-03	5.51E-05	4.83E-03
U-235/U-Total	3.61E-03	7.51E-05	3.59E-03	5.51E-05	4.80E-03

Table IV.

Post-uranyl carbonate addition data for dried solid fraction (0.61 meters above sludge sample).

	Aqua Regia Digestion		**Peroxide Fusion Digestion**		**Combined digestion**
	Average	Std. Dev.	Average	Std. Dev.	Average
U-Total	5.43E+00, mg/L	8.47E-01	4.55E+00, mg/L	8.57E-01	4.99E+00, mg/L
U-235/U-238	4.55E-03	3.41E-04	4.73E-03	2.50E-04	4.64E-03
U-235/U-Total	4.52E-03	3.39E-04	4.69E-03	2.42E-04	4.60E-03

Table V

Experimental Conditions and Results for Simulant and Real Waste Tests.

Test Design	**Initial Enrichment Wt %**	**Mixing Conditions.**			**Expected U-235/Utotal ratio, wt %**	**Observed U-235/U-total ratio, wt %**
		Stirring while mixing	Continuous stirring :120 h.	Shaker at 44 rpm		
ADDITION TEST	-	-	-	-	-	-
Instantaneous DU addition.	4.32	Yes	Yes	NO	0.468	0.458 ± 0.024
DU delivered at 0.267 ml/minute.	4.32	Yes	Yes	NO	0.468	0.478 ± 0.025
DU delivered at 0.267 ml/minute.	4.32	Yes	Yes	NO	0.468	0.454 ± 0.026
DU delivered at 0.013 ml/minute	4.32	Yes	Yes	NO	0.468	0.488 ± 0.096
UTILITY TEST	-	-	-	-	-	-
0.5 ml DU added	4.32	Yes	Yes	NO	1.314	1.347
1.0 ml DU added	4.32	Yes	Yes	NO	0.888	0.850
2.0 ml DU added	4.32	Yes	Yes	NO	0.620	0.712
3.0 ml DU added	4.32	Yes	Yes	NO	0.520	0.578
4.0 ml DU added	4.32	Yes	Yes	NO	0.471	0.458
10.0 ml DU added	4.32	Yes	Yes	NO	0.369	0.435
15.0 ml DU added	4.32	Yes	Yes	NO	0.347	0.406
20.0 ml DU added	4.32	Yes	Yes	NO	0.335	0.359
25.0 ml DU added	4.32	Yes	Yes	NO	0.328	0.393
MIXING TEST	-	-	-	-	-	-
Instantaneous DU addition with stirring.	4.69	Yes	NO	Yes	0.468	0.557 ± 0.051
Instantaneous DU Addition; No stirring.	4.69	NO	NO	Yes	0.468	0.477 ± 0.027
DU delivered at 0.013 ml/min. with stirring.	4.69	Yes	Yes	NO	0.468	0.442 ± 0.046
DU delivered at 0.013 ml/min. NO stirring.	4.69	NO	NO	Yes	0.468	0.945 ± 0.377 Range: 0.47-1.32
REAL WASTE TEST	-	-	-	-	-	-
Instantaneous DU addition, 0.5 ml every 5 minutes.	2.67	Yes	Yes	NO	0.407	0.397 ± 0.015
Instantaneous DU addition, 0.5 ml every 5 minutes.	2.67	Yes	NO	Yes	0.407	0.426 ± 0.021
Instantaneous DU addition, 0.5 ml every 5 minutes.	2.67	NO	NO	Yes	0.407	0.407 ± 0.014

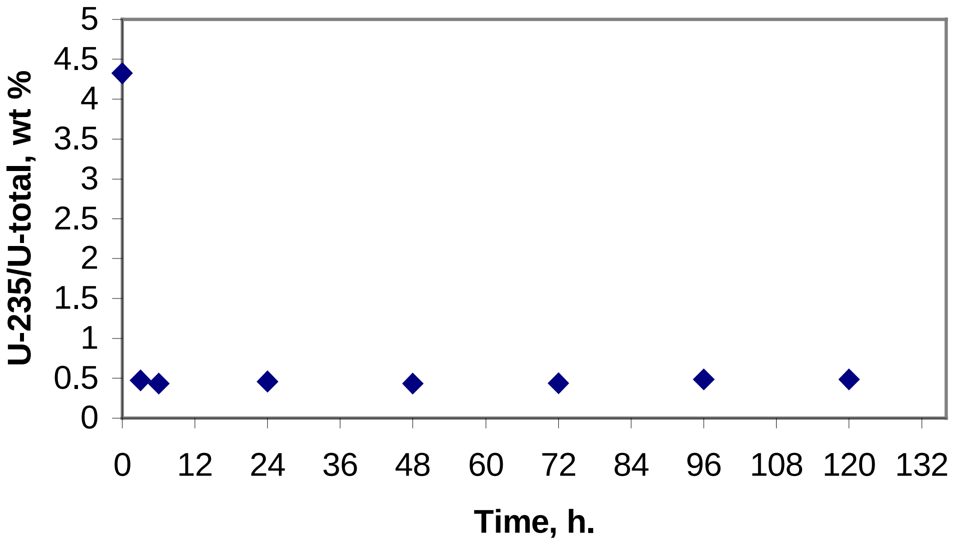

Figure 1. A typical isotopic dilution profile for instantaneous addition of DU to a 4.37 wt % U-235 enriched simulant. Average U-235/U-total ratio of 0.458 ± 0.024 wt %.

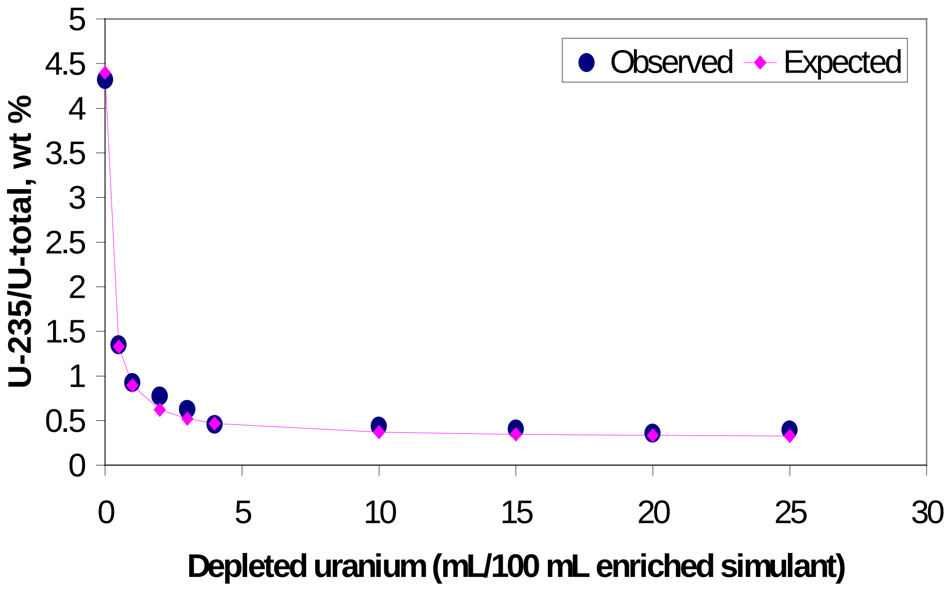

Figure 2. Utility test: Variation of f DU solution added with U-235/U-total ratio.

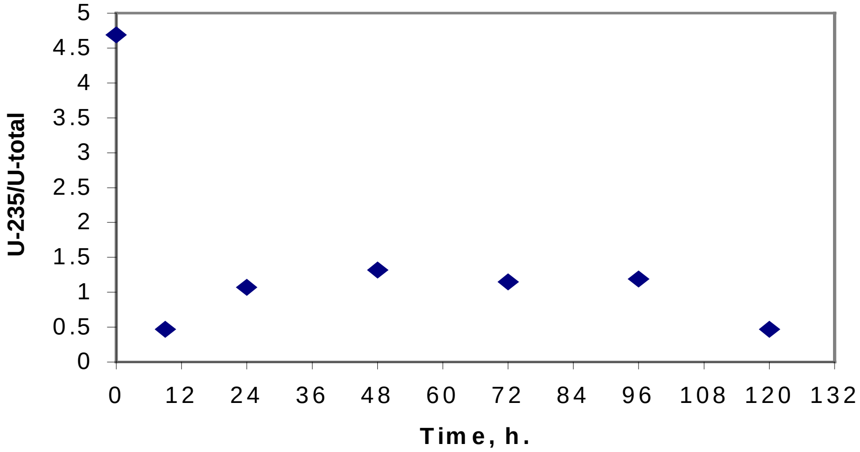

Figure 3. Dilution profile for unstirred and poorly mixed solution of DU solution and simulant. Average U-235/U-total ratio of 0.945 ± 0.377 wt %.

Figure captions

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