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MARTIN MARIETTA

**Independent Verification
of Reprocessing Input
and Process Volumes**

Progress Report

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MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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**INDEPENDENT VERIFICATION OF REPROCESSING
INPUT AND PROCESS VOLUMES**

PROGRESS REPORT

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1.0 INTRODUCTION

One of the most difficult challenges in the nuclear fuel cycle is to establish a material balance for tanks containing spent fuel solutions. These tanks present an extremely hostile environment to the analyst, making determination of the amount of fissile material in them difficult. Historic methods used to determine the volumes of solutions in these tanks are usually based on use of tank geometry in conjunction with depth and density measurements, both of which vary with temperature and are normally controlled by the operator of the facility. Changes in the interior geometry of tanks due to addition of various types of equipment, minor structural modifications, and accumulation of insoluble materials at the bottom and on the interior surfaces of the tanks affect the available volume and make difficult its accurate measurement. For safeguards purposes, it is thus desirable to have a repeatable method of volume determination independent of the operator and other factors.

To determine the quantity of uranium and plutonium in a given tank, aliquots are withdrawn and subjected to analysis; both isotopic abundances and the amount of each element present are determined. Isotope dilution mass spectrometry is the method of choice for quantitative measurements in this application and yields values more precise and accurate than other methods. In the research that is the focus of this project, the application of isotope dilution mass spectrometry has been extended, through use of a double lutetium spike, to the determination of the volume (or weight) of the solution in tanks of any size and shape, regardless of the nature of the solutions within them.

Previous reports have documented progress made on this project. These include descriptions of proof-of-principle testing,¹ our interaction with the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC),² and the chemical procedure developed for isolation of lutetium from gadolinium, which was required by PNC.³

In brief, the technique consists of adding a known amount of natural lutetium to the tank in question (the first spike). The spike and tank solution are thoroughly mixed to equilibrate the two. Aliquots are withdrawn; these can be the same aliquots used for assay of uranium and plutonium. A known amount of spike enriched in ¹⁷⁶Lu is added to each aliquot (the second spike). Once isotopic equilibrium is attained, quantitative recovery of lutetium is not necessary. Lutetium is chemically separated from the sample solutions, and the ratio of its two isotopes measured by thermal ionization mass spectrometry. Performing isotope dilution calculations yields the concentration of lutetium in the tank; because the total amount of lutetium is known (the amount of lutetium added to the tank), calculation of the total amount of solution is simple. Precision will vary with instrumentation and with the nature of the solution in the tank; we have consistently achieved about $\pm 0.2\%$.^{1,3,4}

This method has received widespread attention. After a description of it appeared in a widely read journal,⁴ it was favorably evaluated in Great Britain by Reed et al.⁵ Trincerini et al. compared the use of erbium to lutetium.⁶ The principle is, of course, the same for both elements;

their motivation was primarily economic: erbium is cheaper than lutetium, but the choice of element is not that straightforward. Erbium has six isotopes to lutetium's two, and thus requires about three times as much of the element to yield comparable ion signals for the isotopes of interest; the situation is even more complex than this, of course (ionization potentials need to be considered). Either element is suitable, and there are almost certainly others worthy of consideration. The criteria to be met are: (1) that the element not be a fission product and thus be present as background in the tank; (2) that it be readily amenable to thermal ionization, the only analytical method sensitive enough for this work; and (3) the element be readily soluble in the solutions of interest and create no difficulties for chemical processing.

The goal of the work described in this report was to develop a hot-cell compatible chemical separation procedure for lutetium and to try to devise a better method for quantitatively introducing natural lutetium to the tank.

2.0 EXPERIMENTAL

2.1 CHEMICAL PROCEDURE

The chemical separation procedure originally developed used solvent extraction procedures to isolate lutetium from the rest of the contents of the tank. Solvent extraction, because of the nature of the apparatus used, is not readily adapted to hot cell use because the necessary operations are very cumbersome to perform using remote manipulators. We thus decided to develop a column-based separation scheme using new resins that have recently become available.⁷ The procedure was developed in the laboratory and tested in a mock-up hot cell before being used with solutions taken from the same tank used in previous experiments.^{1,2} An outline of the procedure is given in Appendix 1.

Resins designed specifically to separate elements of interest have recently become available from Eichrom Corporation.⁷ Columns can either be packed by the user or purchased already packed from Eichrom. For our purposes, two different columns were required: one to remove organic materials so they would not contribute interference peaks to the mass spectrum and another to effect separation of lutetium. These columns were mounted in tandem, with that for removing organic matter on top of the other. Eichrom's UTEVA Spec fine particle resin columns were used for lutetium separation. The columns were rinsed with 5 ml of 4 M nitric acid before introducing the sample. The sample, in a solution of 4 M nitric acid, was introduced to the head of the organic-removing column; it is important not to have a sample volume so large that lutetium begins to elute. Both lutetium and uranium were retained on the UTEVA Spec column. When the sample solution had passed fully through the column, lutetium was eluted by rinsing with 5 ml of 4 M ultrex nitric acid solution (6 ml maximum); uranium was retained on the column under these conditions. The waste generated for each sample thus consisted of the 5 ml of 4 M nitric acid used for initial rinse of column and solid low level material (uranium contaminated UTEVA Spec resin).

The high concentration of uranium (> 600 g/l) in the tank solution necessitated modifications of the procedure outlined above as it presented a load too heavy to be accommodated by a column of reasonable length; to perform the separation of such solutions using columns is not only time-consuming but expensive. As a rule of thumb, if the initial uranium concentration in the tank is ≥ 200 g/l, tributyl phosphate extraction must be used to remove uranium.

The eluted lutetium sample is taken to dryness and dissolved concentrated nitric acid (ultrex grade) to destroy any organic material. The sample is dried again and dissolved in 0.05 M ultrex nitric acid. It is then loaded on a rhenium filament for mass spectrometric analysis.

We found that using chromatographic columns was preferable to solvent extraction. Separation was achieved faster and just as completely, and the amount of waste generated was substantially less, an important consideration where waste disposal is time-consuming and costly.

2.2 DELIVERY SYSTEM

The tank used in this project is shown schematically in Fig. 1. This tank has a capacity of about 3000 L and was originally the feed adjustment tank for a fuel reprocessing pilot plant. It is equipped with an internal air lift recirculator and can be heated using a hot water supply system. Like many tanks used for similar purposes, remote delivery involves traversing a complex network of piping, complete with bends and dead ends that make quantitatively passing solutions problematic. Numerous experiments have shown that rinsing the delivery line with dilute acid to wash any lutetium caught in the line is mandatory for quantitative work. Repeatedly, rinsing with acid to sweep all the solution of interest into the tank is undesirable in many situations because alterations to the tank contents must be kept to a minimum. It was thus decided to try a radically new approach. The concept involves using a container to hold the natural lutetium oxide used as the initial spike; the container would be delivered intact to the tank, where the acid medium would dissolve both the container and the lutetium oxide.

The container evaluated was a small steel ball with a hole drilled through the center. One end of the hole was sealed with a copper plug and the lutetium oxide added on top of it. The other end of the hole was then capped with a second copper plug to provide a tightly contained unit. These balls can be introduced to the tank via chemical addition or air purge lines. The balls are introduced into the tank, where they along with their contents, dissolve.

Figure 2 is a photograph of the balls. The balls were designed to dissolve in the dilute nitric acid solutions (2 to 3 M) that typify tank contents. Material of construction of the balls can be modified as demanded by tank solutions. The copper plugs are dimensioned so that a hammer is necessary to set them in place in the ball and thus provide a secure seal for containment of the lutetium oxide. The balls are 1.27 cm in diam., and the hole is 0.07 cm in diam. The plugs are stamped out of 0.07 cm thick annealed copper plate. The weight of a ball is about 5.3 g without the plugs and 6.6 g with them in place.

Experiments were run to determine the conditions appropriate for dissolving the balls. These are summarized in Table 1.

Fig. 1. Schematic drawing of Tank 11F03.

Fig. 2. Carrier balls.

Table 1. Dissolution Test Results

Test	Initial HNO ₃ conc. (M)	Heated to 50°C or not	Air sparged or not	Final HNO ₃ conc.	Time to dissolve
1	0.85	no	yes	<0.01	> 8 h
2	0.85	yes	yes	<0.01	>8 h
3	3.0	no	no	N/A	N/A
4	3.0	no	yes	2.0	≤24 h
5	3.0	yes	yes	2.0	1 h 10 min

In Tests 1 and 2, the experiment was halted after 8 h because depletion of the available acid had halted dissolution. Test 3 was halted after the copper plugs had dissolved sufficiently to expose the lutetium oxide within; this required 1 h 50 min under the experimental conditions listed. In Test 4, the ball was allowed to stand in the solution overnight; it dissolved during that time, so an exact time of dissolution is not available. The effect of modest heating is shown in Test 5, where the ball completely dissolved in a little over 2 h.

A sample from the Integrated Process Demonstration facility tank (Feed Tank 11F03) to be used in the experiment was analyzed and found to be 3.3 M HNO₃ and to have 343 g/L uranium. Two 200-ml aliquots of this material were drawn and used to determine the time required for dissolution of a ball. At ambient temperature, it required about 21.5 h and at 75°C less than 1 h.

To insure that the balls would be successfully transported, a piping system that simulated typical conditions was fabricated and installed on existing equipment. Figure 3 shows this installation along with various test equipment. The test piping system was made of 1.27 cm diam. pipe and included a combination of 90 and 45 degree angles. Compressed air was used to propel the balls along the pipe and into the receiver tank. It required ≥28 psi to move the ball about 1.67 m vertically; maximum available pressure was 90 psi. The total length of the test pipe was about 4 m and included a 2.3 m vertical drop into the tank.

One of the concerns with the chosen design was that the plugs might come out during transfer of the ball through the pipe. The balls were retrieved from the receiver tank after traversing the pipe and inspected for damage. Fifteen tests were run according to the following procedure.

1. The isolation valves on either side of the addition port were closed and the air pressure set to the desired value.

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Fig. 3. Tank with piping system.

2. A ball was introduced via a tee downstream of the air pressure regulator and isolation valve.
3. The isolation valve upstream of the tee was opened to pressurize the tee holding the ball.
4. The isolation valve upstream of the addition port was rapidly opened to propel the ball through the piping system into the tank.

Observations from these tests showed that the copper plugs remained in the balls and that protruding welds inside the piping necessitated choosing ball diameters small enough to pass them.

For the experiments described in this report, a new line was installed that simulated a typical chemical addition line. Figure 4 is a photograph of the tank showing the new line coming in from the top. It was constructed in one piece and included 45 and 90 degree bends in its route to the tank. The total length was 5.4 m and included a vertical rise of 2.7 m and a vertical drop of 0.5 m. The pipe was terminated at a funnel on top of the feed tank to provide a positive means of observing the delivery of the balls to the tank.

Fig. 4. Tank with new line.

3.0 RESULTS AND DISCUSSION

For these experiments the tank contained about 1075 L of uranyl nitrate solution (3.3 M HNO_3 and 343 g/L U). The laboratory experiments summarized in Table 1 showed that it was desirable to heat the tank contents to accelerate dissolution of the balls. The solution in the tank was accordingly heated to 55°C. Two balls containing a total of 0.4914 g of Lu_2O_3 (0.4321 g Lu) were introduced into the tank. The contents of the tank were mixed using the internal air lift recirculator. An aliquot was withdrawn before introduction of the balls to serve as a blank; thereafter aliquots were withdrawn at 0.5, 1.0 (2 aliquots), 1.5, 2.5, 4.0, and 24 h after introduction of lutetium.

Table 2 lists isotopic abundances for the two spikes (natural and enriched in ^{176}Lu).

Table 2. Isotopic Composition of Lu Spikes

	175	176
Natural	97.40	2.60
Spike	1.48	98.52

Unexpected problems were encountered in chemical processing of the samples. The uranium concentration was about three times higher than previously met (343 g/L vs. 120 g/L) and required significantly more effort to separate from the solution than anticipated. A second problem was the presence of ^{88}Zr , which had been added to the tank for another experiment. Zirconium concentration was several times higher than that of lutetium. This much zirconium caused considerable inconvenience by occupying exchange sites on the resin, thus increasing the time required to achieve separation of lutetium. Significant amounts of zirconium eluted from the column with lutetium, causing grief for the mass spectrometric analysis. Strenuous efforts reduced zirconium concentrations to the point where adequate ion currents of lutetium were obtained, but it still adversely affected the precision of the isotope ratio measurements. As discussed below, this had no effect on data interpretation, and it was decided it was not a cost-effective investment in time to clean the samples further. It is very unlikely that such high concentrations of zirconium would be encountered in a reprocessing facility.

The isotopic results obtained from the samples are summarized in Table 3.

Table 3. Isotopic Results

Sample time, h	$^{175}\text{Lu}/^{176}\text{Lu}$	conc, $\mu\text{g/ml}$
0.0 (Blank)	0.0165	0.0046
0.5	0.0361	0.0804
1.0	0.0643	0.2103
1.0	0.0799	0.2750
1.5	0.0918	0.3198
2.5	0.0984	0.3249
4.0	0.1167	0.4545
24	0.1431	0.5411

The concentration of lutetium already in the tank (0.0046 $\mu\text{g/ml}$) was subtracted from all other concentrations calculated. Uncertainties for the values in the above table were on the order of $\pm 1\%$.

It is clear from the data in Table 3 that equilibration between the spike and tank contents was not achieved. Even after 24 h, where the measured concentration of lutetium in the tank was highest, the amount of solution calculated to be in the tank does not agree well with that determined via other methods (805 L vs 1075 L). Experimental tests performed in the laboratory showed that the balls should have dissolved within about 2 h (see Table 1, Test 5). Acid strength was about the same (3.3 M in the tank vs. 3.0 M for the experiment), so the steel ball would have reacted with the acid and should certainly have dissolved within the 24 h of the tank experiment. That it did not indicates that there were conditions in the tank which were different than those in the laboratory experiment. The most likely explanation is that solid material collected at the bottom of the tank and in the drain line connected there. The ball or balls could have become buried, either completely or partially, and would thus not be completely exposed to the acid in the tank. The fact that two balls were used complicates the issue slightly, for only one of them would have to be buried to explain our observations. It is clear from the results in Table 3 that the balls were dissolving, but so slowly that it would require an unacceptably long time for complete dissolution.

4.0 CONCLUSIONS AND RECOMMENDATIONS

A procedure suitable for use in a hot cell was developed and tested. Separation using Eichrom resin on anion exchange columns was found to be just as effective in separating lutetium from the original solution as solvent extraction and had in addition several benefits such as reduced waste generation. This was the key fact that allowed development of a hot cell method. This procedure is ready for implementation in routine applications.

The new method of delivery of natural lutetium oxide to the tank offers several advantages when compared to introduction as a solution used in previous experiments. The ball is transported as a discrete unit containing the lutetium; thus, when it enters the tank, all the lutetium is known to be with it. This contrasts to the concerns of losing solution at tees, dead ends, and other irregularities encountered in most delivery systems. In this particular experiment, we encountered unanticipated problems when the steel balls used as delivery capsules for Lu_2O_3 failed to dissolve in the 24 h allotted for the experiment. As discussed above, the most probable explanation is that the balls (or ball) became buried in solid material (precipitates from solution, etc.) that collected at the bottom of the tank. This is a condition not expected to be encountered in tanks in active fuel reprocessing operations, and dissolution should be readily achieved in situations where the ball is fully exposed to acid. In our opinion, this matter warrants further investigation.

It seems highly desirable to take this work to its logical conclusion. More work is needed to perfect a delivery system to the tank. Carrier materials other than steel (e.g., aluminum) should be investigated to identify a material that will readily dissolve under almost any conditions expected in holding tanks. Modifications to the shapes of the carriers, such as making the walls as thin as practicable, should hasten dissolution. This experiment would require that enough time be devoted to the experiment to allow complete dissolution of the carriers, and to verify it. Tank contents should be kept as simple as possible (e.g., no zirconium) so chemical processing is as straightforward as possible and thus allow timely reports on the progress of the dissolution.

At the 2nd TAME Meeting held in Ispra, Italy, on October 6-8, 1993, the strong consensus of attendees was that the double spike technique was the most promising of all methods for tank calibration.⁸ The most urgent need was to have it demonstrated on a real dissolver solution tank. Unfortunately, tanks at the Joint Research Centre at Ispra have such severe constraints put on their use as to preclude using them; the one on display not only could have no actinides put into it, but also no acid--not very useful. Inquiries among other attendees led nowhere. Thus, to bring the technique to fruition, help is needed in identifying a tank to use for this last experiment.

APPENDIX 1**Sample Prep Sequence for Lu Isolation****I. Equipment and reagents**

UTEVA.Spec (Eichrom) column resin
4 M ultrex nitric acid
 ^{176}Lu spike
0.45 μm Millex HV filters
Clean plastic columns
Analytical balance
500 μL Eppendorf pipet and tips
Column racks (6 in. and 9 in.)
Eichrom preppacked pre-columns
Gloves, safety glasses, and lab coat
Ultra pure water

II. UTEVA.Spec Column Resin Isolation of Lu

1. Filter sample with a 0.45 μm Millex HV filter to remove solids (if needed).
2. Spike sample with a known amount of ^{176}Lu (mix thoroughly).
3. Pack UTEVA.Spec columns (≈ 0.35 g per column). The higher the uranium concentration the more UTEVA is required for separation of uranium. Pre-packed columns can be purchased and used.
4. Place UTEVA.Spec column in 6 in. column rack and rinse with 4 M ultrex HNO_3 .
5. Place pre-columns in 9 in. column rack above UTEVA.Spec columns, (pre-column removes organics). Rinse pre-column with 4 M ultrex HNO_3 prior to use.
6. Add sample to head of pre-column and allow it to elute through both pre-columns and UTEVA column.
7. After sample elutes, rinse column with 4 M HNO_3 . Uranium is retained on UTEVA and Lu passes through.
8. Evaporate Lu samples to near dryness.
9. Add 2 mL concentrated HNO_3 to dried sample and then dry again to eliminate organic material.
10. Dry samples down and bring up in desired HNO_3 concentration. Samples are now ready for MS analyses.

REFERENCES

1. J. A. Carter, D. H. Smith, and R. L. Walker, "An Independent Technique for Fissile Inventory of Holding Tanks in the Nuclear Fuel Cycle: Status Report," ORNL/TM-10814, May 1988.
2. D. H. Smith, D. A. Bostick, E. H. McBay, J. A. Carter, and M. H. Ehinger, "The Joint PNC-ORNL Tank Calibration Experiment of 1991," ORNL/TM-12001, November 1991.
3. D. T. Bostick, D. O. Vick, M. P. May, and R. L. Walker, "The Isolation of Lutetium from Gadolinium Contained in Purex Process Solutions," ORNL/TM-12000, September 1992.
4. D. H. Smith, R. L. Walker, and J. A. Carter, *Anal. Chem.* **55**, 578-580 (1983).
5. W. J. Reed, C. N. Ramsden, M. R. James, and G. E. Taylor, "Use of Lutetium as a Chemical Tracer in Calibration of Tank Volumes," IAEA-SM-293, pp. 179-187.
6. P. R. Trincherini, V. Altamura, and S. Miglietta, "Comparison between Lutetium and Erbium Used as Tracers in Determination of the Mass of U Present in a Tank at the ITREC Reprocessing Plant," ESARDA Bulletin No. 10, June 1989.
7. E. P. Horwitz, R. Chiarizia, H. Diamond, and M. L. Dietz, "Novel Extraction Chromatographic Schemes for the Separation of the Actinides," cited in TEVA-Spec. Bulletin *Extraction Chromatographic Material for Rapid Separation of Tetravalent Actinides*, unnumbered and undated but ca. 1991.
8. D. H. Smith, "Report of Foreign Travel," ORNL/FTR-4818, October 1993.

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