

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

### **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900, email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov) online ordering: <http://www.ntis.gov/ordering.htm>

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865) 576-8401, fax: (865) 576-5728, email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)



# INTER-OFFICE MEMORANDUM

SAVANNAH RIVER PLANT

DPSPU-85-272-26

February 27, 1985

TO: D. F. CHOSTNER, 221-F

FROM: H. P. HOLCOMB, 772-F *HPH*

## ANALYSIS OF RFSA CAMPAIGN #2 DISSOLVER SOLUTION FOR Hg(I) & Hg(II)

### INTRODUCTION AND SUMMARY

The Separations Technology Laboratory has analyzed for mercury before and after chloride removal in dissolver solution from the second Rocky Flats scrub alloy (RFSA) campaign in F-Canyon. Tank 10.2 contained the dissolver solution following dissolution in 6.4D but prior to any head end treatment. Its mercury content was from the Hg(II) added to facilitate dissolution of the RFSA aluminum components. Tank 11.2 contained the solution following head end which included removal of chloride by the addition of Hg(I) to precipitate Hg<sub>2</sub>Cl<sub>2</sub>. Tank 11.2 contained not only the Hg(II) from dissolution but also excess Hg(I) added in the chloride removal step.

A composite sample for each tank was prepared by combining individual samples known to be representative of each tank's contents. Mercury(II) in tank 10.2 composite was determined to be 0.0068M, very close to the desired 0.006M that the processing TA specifies. For tank 11.2 composite, an initial oxidation of the Hg(I) content was made by heating an aliquot in strong nitric acid to produce Hg(II). Then total Hg(II) was analyzed to be 0.027M in tank 11.2. If the tank 10.2 Hg(II) content is normalized (because of dilution) to the tank 11.2 content, then the Hg(II) content of the tank 11.2 aliquot prior to oxidation of Hg(I) was 0.0054M. Therefore by difference, the Hg(I) content of tank 11.2 was 0.022M.

This concentration is an excellent compromise between the excess of Hg(I) necessary to promote chloride removal and the minimization of mercury in processing solutions to lessen its environmental impact (such as that from evaporator overheads that go to seepage basins). Excess Hg(I) in future RFSA campaigns may be lowered following planned studies to examine the impact that the covalent character of mercuric chloride has on the removal of chloride

D. F. CHOSTNER

Page 2

February 27, 1985

from RFSA solutions by mercurous ion. Part of this study will be to ascertain optimum excess Hg(I) for chloride removal.

## EXPERIMENTAL

### Analysis Scheme - Removal Of Actinides

Mercury(II) in the samples was analyzed by H. M. Forrest of Laboratories using DCAP spectrometry. However, it was first necessary to reduce the alpha activity, primarily Am<sup>241</sup> and Pu<sup>239</sup>, to a maximum activity of  $1 \times 10^5$  d/m/mL. This was accomplished via an ion exchange technique<sup>1</sup> suggested by S. L. Maxwell of Laboratories. The technique employs Dowex 50X8 cation exchange resin and a weak HCl-ethanol liquid matrix.

The small sample aliquot was placed in a relatively large volume of the matrix and passed through a pretreated column of cation resin. Mercury(II), being a neutral covalent compound or possibly even a chloride anionic complex, was not retained by the resin. The tri- and tetravalent actinides were. The column was washed with several column volumes of the matrix. Both the feed effluent and the wash, containing the Hg(II), were collected in a volumetric flask. The alpha content of these solutions was much less than the DCAP requirement with DFs of  $10^5$  typical. A portion of the flask contents was submitted for DCAP analysis along with a matrix blank.

### Oxidizing Hg(I)

During development work for chloride removal from RFSA, the Sep Tech Lab observed<sup>2</sup> that certain spectrometric techniques for mercury analysis produced differing responses (and results) for Hg(II) versus Hg(I). For reliable analysis, mercury should be totally in the divalent state.

Tank 11.2 contained a mixture of Hg(I) and Hg(II). However, since all the Hg(II) therein came from the Hg(II) added for initial dissolution, then the total mercury content of 11.2 less the normalized 10.2 Hg(II) equivalent would result in the Hg(I) content of 11.2.

Fairly strong oxidizing conditions<sup>3</sup> are necessary to convert Hg(I) to Hg(II). For our analysis, the same size aliquot used for 10.2 was injected into twice its volume of concentrated (15.7M) nitric acid and heated at 90-95°C for 2 hours in a controlled-temperature heating block. Previous experiments<sup>4</sup> in the Sep Tech Lab verified that Hg(I) is converted to Hg(II) on heating at the boiling point for 5 minutes in the presence of a minimum of 5M HNO<sub>3</sub>. This treated solution was placed in the HCl-ethanol matrix. The resulting

D. F. CHOSTNER

Page 3

February 27, 1985

solution underwent cation exchange treatment to remove the actinides using a freshly prepared and treated resin column. Like tank 10.2, feed effluent and washes from the tank 11.2 sample were diluted to volume in a volumetric flask, alpha counted, and then submitted for DCAP analysis.

### CALCULATIONS AND RESULTS

#### Normalization of Tank 10.2 Contents to Tank 11.2

The composite solution from each tank underwent parametric analysis which was coordinated by H. E. Henry of Laboratories. These solutions are destined for use in our study of the effect of the covalent character of mercuric chloride in RFSA processing. Mercurous chloride chemistry has been previously documented.<sup>5</sup> Results of these analyses, to be used in normalizing tank 10.2 Hg(II) content to that in tank 11.2, were:

<u>Parameter</u>	<u>10.2</u>	<u>11.2</u>	<u>11.2/10.2</u>
Gross alpha, d/m/mL	$3.01 \times 10^9$	$2.46 \times 10^9$	0.82
Total Pu, d/m/mL	$7.80 \times 10^8$	$6.21 \times 10^8$	0.80
Acidity, M	0.86	0.655	0.76
		Avg.	= 0.79

Agreement of the analysis ratios was excellent, especially since these parameters were determined by Laboratories' shift technicians without any discrimination as to their origin. Therefore, the Hg(II) content of tank 11.2, originally in tank 10.2, will be 0.79 times the 10.2 Hg(II) value, due to dilution during processing.

#### Hg(II) Results From DCAP Analysis

The Hg(II) content of the two composites via preliminary oxidation for the 11.2 sample, ion exchange treatment, and DCAP analysis was:

<u>Tank</u>	<u>Hg(II), M</u>
10.2	0.0068
11.2	0.027

#### Hg(I) Content of Tank 11.2

Therefore, the tank 10.2 Hg(II) content normalized ( $\times 0.79$ ) to tank 11.2 was 0.0054M. Thus, the Hg(I) content of 11.2 was 0.022M, obtained from the difference, (0.027 - 0.0054).

D. F. CHOSTNER

Page 4

February 27, 1985

### CONCLUSIONS AND RECOMMENDATIONS

TA 2-1083, under which RFSA processing is conducted, calls for a nominal mercuric ion concentration in the dissolver solution of 0.006M with a maximum of 0.01M. The second RFSA campaign operated according to these guidelines with the initial Hg(II) concentration being 0.0068M.

The TA does not specify a Hg(I) content because the excess Hg(I) following chloride removal in head end will be dependent upon the chloride content prior to and after precipitation as Hg<sub>2</sub>Cl<sub>2</sub>. The first RFSA campaign saw this value to be approximately 800 ppm<sup>6</sup>; the second, 1600-1800 ppm<sup>7</sup>. These values in the RFSA dissolver solution were subsequently reduced to less than 100 ppm following precipitation and centrifugation of Hg<sub>2</sub>Cl<sub>2</sub>.

From the foregoing analyses, an excess of 0.022M Hg(I) was present in tank 11.2 and subsequently went to first cycle solvent extraction. Based on the quantity of chloride removed, which is dependent upon the excess of precipitant due to common ion effect, I recommend that future RFSA campaigns contain a Hg(I) excess in the range of 0.020-0.025M. Such will allow maintaining a lowered chloride value to <100 ppm in material destined for solvex feed. This concentration will also follow current operating philosophy to reduce mercury content of waste streams to as low as reasonably achievable to minimize any subsequent environmental impact.

We shall, in future RFSA campaigns, likely reduce the Hg(I) excess. However, I desire first to investigate the RFSA chemistry prior to solvex to better define the mercury and chloride species present and the impact of the mercuric chloride covalency on the chloride removal by Hg(I). I believe we need to know more about these before lowering the Hg(I) excess to a level that might result in solutions with >100 ppm chloride and thereby increase the potential for corrosion.

### REFERENCES

1. Strelow, F. W. E. et al., Anal. Chem. Acta, 45, p. 81 (1969).
2. Memorandum, Problem With DCAP Analysis of Hg(I) Solutions, H. P. Holcomb to W. R. Jacobsen, C. E. Coffey, et al., November 11, 1984.
3. Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd Ed., p. 179, Prentice-Hall, Englewood Cliffs, NJ (1952).

DPSPU-85-272-26

D. F. CHOSTNER

Page 5

February 27, 1985

4. DPSPU-83-272-185, Chloride Removal From Actual Rocky Flats Scrub Alloy Dissolver Solution, H. P. Holcomb to D. F. Chostner, p. 5, November 30, 1983.
5. DPSPU-84-272-12, Processisng Rocky Flats Scrub Alloy in F-Canyon-Fate of Mercurous Chloride in Waste System, H. P. Holcomb to J. T. Buckner, Jr., February 18, 1984.
6. DPSPU-84-60-5, Separations Technology Monthly Report Draft, Canyons, B-Line And Associated Facilities, p. 3, May 1984.
7. DPSPU-85-272-16, Chloride Analysis of RFSA Second Campaign Dissolver Solution, H. P. Holcomb to J. T. Buckner, Jr., p. 5, February 11, 1985.

HPH/h