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INTER-OFFICE MEMORANDUM

SAVANNAH RIVER PLANT

DPSPU-85-272-16

February 11, 1985

TO: J. T. BUCKNER, JR., 703-F

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

CHLORIDE ANALYSIS OF RFSA SECOND CAMPAIGN DISSOLVER SOLUTION

SUMMARY

Extensive experimentation and testing in the Separations Technology Laboratory has measured chloride levels in solutions of Rocky Flats scrub alloy (RFSA) dissolved in F-Canyon during the end of December and the first of January. These solutions were from the second RFSA campaign. The first was conducted last May. Processing RFSA material in F-Canyon is part of the program to recover weapons-grade plutonium from scrap and to reuse it in DOE's production complex.

Chloride values were determined by the recently-developed turbidimetric technique.¹ Tank 10.2 contents following dissolution, but prior to head end treatment, were approximately 1600 ppm Cl^- . Following removal of the chloride by precipitation as mercurous chloride² and its centrifugation in head end, the chloride content was reduced to some 75 ppm. Chloride removal to less than 100 ppm is necessary to prevent excessive corrosion to the canyon waste handling system.³ During the first campaign, very similar, lowered chloride levels were obtained for solution to be processed through the first Purex solvent extraction cycle. However, the initial campaign only had approximately one-half as much chloride per unit volume following dissolution due to differences in quantities of alloy processed then versus that for the latest campaign.

INTRODUCTION

RFSA buttons are processed in F-Canyon to recover weapons-grade plutonium. The buttons are dissolved in 6.4D using nitric acid catalyzed with mercury [Hg(II)] to facilitate dissolution of the aluminum containers as well as the Pu-Al alloy button matrix. Fluoride is added to assist dissolution of any plutonium oxide

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to prevent possible sludge formation. The buttons are produced from chloride salt mixtures at Rocky Flats. The buttons therefore contain chloride impurities of 2-10 wt% as surface contamination or as inclusions. On dissolution, the resulting chloride content in solution can range between 400 and 2000 ppm, approximately, primarily depending upon the number of buttons dissolved per dissolver solution charge.

The solution resulting after head end treatment is processed through first Purex cycle to remove the primary radionuclidic contaminant, Am²⁴¹. Chloride appears in the LAW which is further processed in waste handling. Chloride levels in first cycle feed should be less than 100 ppm in order to minimize corrosion to waste handling equipment. Reduction to this level is accomplished by precipitation of the chloride as Hg₂Cl₂ which is removed via centrifugation in head end treatment.

The chloride levels in solution before and after the chloride removal step must be monitored. Several techniques are available for determining the larger quantity. However, a turbidimetric analysis application was developed for the lower quantities of chloride since no on-site method was applicable for the RFSA dissolver solution's high alpha, complex matrix. Solutions from this second RFSA campaign were the first production samples analyzed using this new technique. Previously, only a semi-quantitative method, involving comparison of turbidities, was available for the solutions with lowered chloride values.

EXPERIMENTAL

The turbidimetric method as published¹ was used to determine chloride values for both tank 10.2 and tank 11.2 samples. These respectively represent the chloride content in the RFSA dissolver solution before and after the head end treatment step with Hg(I). Initial values reported to F-Canyon Separations Technology personnel, approximately 400 and 20 ppm respectively, were found to be too low by a factor of about four. First indication of this discrepancy appeared when tank 10.2 values were compared with those (1600-1800 ppm) obtained by S. L. Maxwell of Laboratories who used a combination of ion exchange and ion chromatography.

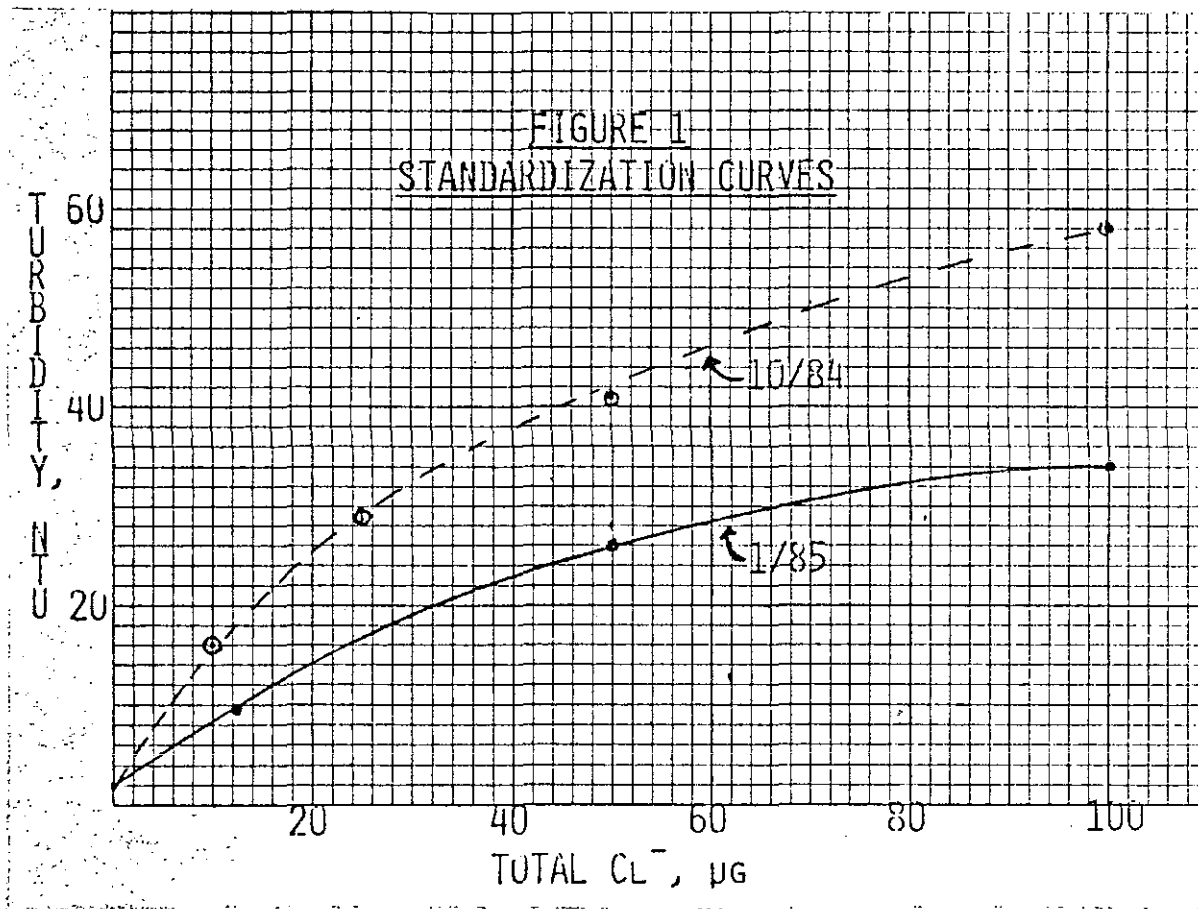
A comprehensive investigation then followed to determine the cause of the discrepancy. A newly-received Hach Turbidimeter was placed in operation in a radioactively-cold mode to facilitate the experimental inquiry and to verify the operation of the "hot" instrument. Both instruments agreed to within ± 1 NTU (nephelometric turbidity unit) for newly-prepared chloride standards.

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However, when a new standardization curve was prepared, the turbidity readings per unit chloride in the individual standard samples were much lower than those reported for the standardization curve obtained during the latter stages of method development. The reason for the difference is currently unexplained. Figure 1 graphically shows the divergence in the two curves.



The use of twice the quantity of Na₂EDTA used previously also improved sensitivity. This complexing agent is used to free chloride from the tight covalent bond the latter has with Hg(II). Therefore, it is possible that the as now unanalyzed Hg(II) content of the solutions is higher than expected. There could be other unknown interferences in these solutions from the second RFSA campaign. As time permits, such possibilities will be investigated.

Standard solutions, prepared in the simulated RFSA dissolver solution matrix, were analyzed along with the samples described below. Their results fell within the $\pm 17\%$ accuracy for the method¹, thereby lending assurance that the analysis technique was performing satisfactorily.

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RESULTS

Analysis of Tank 10.2 Samples For Chloride By Turbidimetry

Duplicate 50 μ L aliquots from each of two tank 10.2 samples were analyzed for chloride. The small aliquot was necessary because of the high chloride value of the tank 10.2 solution. This aliquot was injected into 1.0 mL of simulated RFSA dissolver solution, containing no chloride, to maintain as constant a matrix as possible for the sample pretreatment and turbidity formation. The results were:

10.2 Sample #40976

Aliquot 1 = 1800 ppm Cl^- , original sample basis (OSB)

Aliquot 2 = 1300 ppm Cl^- , OSB

10.2 Sample #40978

Aliquot 1 = 1600 ppm Cl^- , OSB

Aliquot 2 = 1800 ppm Cl^- , OSB

The average of these four determinations is 1625 ppm chloride and is the recommended value for the RFSA dissolver solution prior to chloride removal in head end.

Analysis of Tank 11.2 Samples For Chloride By Turbidimetry

For the determination of the lowered values of chloride, 1.00-mL duplicate aliquots from two separate tank 11.2 samples were analyzed without any simulated matrix material present. The results (OSB) of these analyses were:

11.2 Sample #41209

Aliquot 1 = 58 ppm Cl^-

Aliquot 2 = 58 ppm Cl^-

11.2 Sample #41214

Aliquot 1 = 96 ppm Cl^-

Aliquot 2 = 88 ppm Cl^-

The average of these 4 determinations is 75 ppm chloride and is the recommended value for the second campaign RFSA dissolver solution following head end and prior to solvent extraction.

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Indirect Determination of Chloride in Tank 10.2 Sample #40978

As part of the investigation to ascertain the reason for the initially low chloride values, tank 10.2 sample #40978 was analyzed for chloride by indirect gravimetric means. This technique, originally used to monitor chloride values in raw RFSA dissolver solution from the first campaign⁴, precipitates AgCl from a sample aliquot. The precipitate is washed and then dissolved in ammonium hydroxide. Silver in this solution is analyzed by spectrometry (DCAP). The corresponding chloride value is then determined by stoichiometry.

Silver sulfate, although not considered a gravimetrically insoluble compound as such, does have limited solubility, about 8 g/L in water.⁵ Ferrous sulfamate was added to the RFSA dissolver solution to adjust the oxidation state of plutonium. Under processing conditions of heat and acidity, the sulfamate should have been hydrolyzed to sulfate. Therefore, to verify that sulfate was not an interference in the indirect determination of chloride, one duplicate set of aliquots was first treated with barium nitrate to remove the sulfate as precipitated barium sulfate. The resulting supernate was then used as the sample for AgCl precipitation. Another set of aliquots underwent AgCl precipitation without any pretreatment. The results of the indirect determinations, given below, indicate very little interference, although the addition of barium did produce a noticeable quantity of barium sulfate precipitate.

Indirect Cl⁻ Analysis of 10.2 Sample #40978, SO₄⁻² RemovedAliquot 1 = 4747 ppm Ag⁺ = 1562 ppm Cl⁻, OSBAliquot 2 = 4760 ppm Ag⁺ = 1566 ppm Cl⁻, OSBIndirect Cl⁻ Analysis of 10.2 Sample #40978, UnpretreatedAliquot 1 = 4910 ppm Ag⁺ = 1615 ppm Cl⁻, OSBAliquot 2 = 4810 ppm Ag⁺ = 1583 ppm Cl⁻, OSB

These analyses support the approximately 1600 ppm chloride values obtained independently by the turbidimetric method and by S. L. Maxwell of Laboratories who employed ion exchange and ion chromatography.

CONCLUSIONS

The dissolver solution from the second RFSA campaign was analyzed for chloride using the recently-developed turbidimetric method.

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Prior to chloride removal in head end, the solution contained 1625 ppm chloride. After chloride removal with Hg(I) and prior to feeding to solvent extraction, the solution contained only 75 ppm chloride. This reduced value meets the <100 ppm criterion to maintain corrosion of process equipment at a minimum.

Initial difficulties with low chloride results from using the new turbidimetric method were overcome by preparing a new standardization curve and by increasing the quantity of Na₂EDTA employed for mercury (II) complexing. Reasons for the discrepancy are not known. Further studies of the behavior of the covalent mercuric chloride in processing RFSA are planned. These may provide insight. It is recommended that new standardization curves be prepared for each series of chloride determinations. Inclusion of standard solutions in the appropriate matrix alongside actual samples being analyzed aids in monitoring the performance of the method.

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