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AUTHORIZATION FOR CHANGE IN OPERATING STANDARDS
221 AND 224 BUILDING

Pertaining to Process Changes During the Period 3-1-51 to 12-1-52

INTRODUCTION

Since the issuance of HW-17398, Separations Section, Operating Standards Part I relating to the Bismuth Phosphate Process on March 1, 1951, several changes in the process have been found desirable and have been reduced to practice. This document presents these changes and by signature constitutes Technical Section written approval.

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I. METAL DISSOLVING

Procedure in Standards

The procedure written in the Operating Standards, HW-17398, as 221-22 specifies that the uranium metal be dissolved with 2.27 pounds of 60 per cent nitric acid per pound of metal or 5000 pounds of acid per 2200 pounds of uranium. The solution is reacted at the boiling point until a specific gravity of 1.82 is reached. The metal solution is diluted to 50 per cent UNH and cooled to 40°C. The metal solution is transferred to a storage tank and the dissolver is flushed with sufficient water to reduce the UNH concentration to 40 per cent.

Revised Procedure

In the revised procedure mercuric nitrate is added to a concentration of 5×10^{-4} molar after a specific gravity of 1.82 is reached and before the metal solution is diluted to 50 per cent UNH. Limits for mercuric nitrate concentration as described in the paragraph below are set at a minimum of 5×10^{-4} molar and a maximum of 10^{-3} molar.

Basis for Approval of Change

The complexing with mercury of the iodine in metal solution as a means of controlling the amount of radioiodine in the canyon exhaust ventilation air was evaluated under Production Test 221-T-15, HW-21426. The final report of test results, HW-25151, recommended a mercuric nitrate concentration of 5×10^{-4} molar to adequately suppress radioiodine evolution. Test data indicate that at least this concentration of mercuric nitrate should be added, but show also that there is no practical benefit in adding more than this. There is no harmful effect on the process, however, if the concentration is as high as 10^{-3} molar. The presence of mercury in the concentration specified had no effect on waste losses or decontamination.

II. EXTRACTION

Procedure in Standards

The procedure written in the Operating Standards, HW-17398, as 221-31 specifies that bismuth nitrate solution be added to give a final Bi/Pu ratio of 95, with limits of 40 to 110, in the extraction step.

Revised Procedure

In the revised procedure bismuth nitrate solution is added in the extraction step to give a final Bi/Pu ratio of 37. This ratio is set as a minimum to avoid excessive loss of plutonium to metal waste solution. The upper limit of 110 for this ratio, as given in the Standard 221-31, is retained.

Basis for Approval of Change

Production Test 221-B-10, HW-19528, evaluated the bismuth concentration in extraction. The final report of test results, HW-24878, recommended a bismuth concentration in extraction of 2.5 grams per liter which corresponds to a Bi/Pu ratio of 37 for 600 MWD per ton pile metal. A net saving of approximately \$500 per run was realized through diminished chemical consumption and waste storage requirements.

III. FIRST OXIDE DECONTAMINATION

Procedure in Standards

The procedure as written in the Operating Standards, HW-17398, as 221-41 includes the following steps.

1. Bismuth phosphate with ceric and zirconium scavengers is precipitated and separated by centrifugation once.
2. The bismuth phosphate by-product cake is removed from the centrifuge with a mixture of nitric acid and hydrogen peroxide. The procedure specifies a mixture of 48 per cent nitric acid (limits 40 to 60 per cent) and 27.5 per cent hydrogen peroxide (limits 20 to 30 per cent) equivalent to 20 pounds (limits 10 to 20 pounds) of 60 per cent nitric acid per pound of bismuth phosphate and 0.5 pounds (limits 0.25 to 2.0 pounds) of 27.5 per cent hydrogen peroxide per pound of bismuth phosphate.

Revised Procedure

1. To the effluent from the first centrifugation is added sufficient NaBiO_3 slurry to make effluent 0.002 molar in NaBiO_3 with limits of 0 to 0.01 molar. Sufficient Ce-Zr scavenger solution is added to give a final concentration of 50 mg. each of Ce and Zr per liter with limits of 10 to 100 mg per liter. The slurry is centrifuged at 430 G with a bowl retention time of 3 to 10 minutes.
2. The bismuth phosphate cake is removed from the centrifuge with a mixture of 48 per cent nitric acid (limits 40 to 60 per cent) and 50 per cent hydrogen peroxide (limits 20 to 50 per cent) equivalent to 23 pounds (limits 10 to 30 pounds) of 60 per cent nitric acid per pound of bismuth phosphate and 0.3 pounds (limits 0.25 to 2.0 pounds) of 50 per cent hydrogen peroxide per pound of bismuth phosphate.

Basis for Approval of Change

1. Pile metal with a minimum 40 day cooling period was found to require additional steps to achieve the necessary decontamination. The reprecipitation of bismuth phosphate with ceric and zirconium scavengers and a second centrifugation was demonstrated to have a beneficial effect on decontamination and no effect on plutonium losses. This procedure was included in Operating Standard 221-61.1, a part of Hanford Engineer Works Operating Standards, 7-1184, dated December 13, 1944. The procedure was not used when processing metal with a nominal 30 day cooling period, therefore it was omitted from the present operating standards, HW-17398. With shorter cooled metal the procedure may at times be necessary addition to the standard procedure in order to secure adequate decontamination.

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2. The 27.5 per cent hydrogen peroxide has been replaced by the 50 per cent hydrogen peroxide as an essential material. The amount of bismuth phosphate was reduced by volume reduction under Production Test 221-B-10, HW-19528. The amount of nitric acid remained constant due to minimum volume and agitation considerations using existing equipment.

IV. SECOND OXIDIZED DECONTAMINATION

Procedure in Standards

The procedure written in the Operating Standards, HW-17398, as 221-61 specifies that bismuth phosphate by-product cake is removed from the centrifuge with the quantity of 40 per cent nitric acid (limits 40 to 60 per cent) equivalent to 15 pounds (limits 10 to 20 pounds) of 60 per cent nitric acid per pound of bismuth phosphate.

Revised Procedure

In the revised procedure the bismuth phosphate is removed from the centrifuge with the quantity of 48 per cent nitric acid (limits 40 to 60 per cent) equivalent to 23 pounds (limits 10 to 30 pounds) of 60 per cent nitric acid per pound of bismuth phosphate.

Basis for Approval of Change

The amount of bismuth phosphate was reduced by volume reduction under Production Test 221-B-10, HW-19258. The amount of nitric acid remained constant due to minimum volume and agitation considerations using existing equipment.

V. BISMUTH OXIDIZED CROSSOVER

Procedure in Standards

The procedure as written in the Operating Standards, HW-17398, as 224-21 specifies a bismuth phosphate precipitation from an oxidized solution. Centrifugation removes the bismuth phosphate carrier which allows a change to a lanthanum fluoride carrier in the succeeding step. The procedure has been used when processing metal which has received a nominal 90 day cooling period.

Revised Procedure

- In the revised procedure, a barium sulfate scavenger is employed to effect the required decontamination on pile metal which has received a minimum of 40 day cooling. The scavenger precipitate is formed by the addition of a sodium sulfate - barium sulfate mixture to make the solution 0.05 molar in sulfate and 0.5 gram barium sulfate per liter. Not more than 0.5 gram barium sulfate per liter is added to avoid possibility of carryover to Isolation. However, it is desirable to use as much as this in order to effect the desired decontamination of material cooled only a short time. Digestion for one hour at 75°C follows. This step precedes the bismuth phosphate precipitation by addition of phosphoric acid.

Basis for Approval of Change

When processing pile metal with a minimum 40 day cooling period it has been necessary to take additional steps to effectively decontaminate plutonium with respect to Ba^{140} and its daughter La^{140} . CN-2021, Recommendations for Process Conditions at Hanford Engineer Works, recommends a barium sulfate scavenger be used for pile metal cooled shorter than 60 days. Production Test 224-B-6, HW-22302, evaluated the barium sulfate scavenger for use in the bismuth oxidized crossover step. The required decontamination was demonstrated with no effect on plutonium waste losses. Plant runs have been processed with a barium sulfate scavenger since November, 1951.

VI. LANTHANUM OXIDIZED CROSSOVER

Procedure in Standards

The procedure as written in the Operating Standards, HW-17398, as 224-31 includes the following steps.

1. Oxidation of the run and the rework with potassium permanganate is accomplished during a digestion period specified at 30 minutes with limits of 20 to 60 minutes.
2. Lanthanum fluoride is precipitated with hydrofluoric acid added at a uniform rate over a 15 minute period with limits of 15 to 60 minutes.
3. Lanthanum fluoride is precipitated and separated by centrifugation once.

Revised Procedure

1. The digestion period for oxidation of the run and the rework is 15 minutes with limits of 15 to 60 minutes.
2. Hydrofluoric acid is added at a uniform rate.
3. To the effluent from the first centrifugation is added 1.5 pounds of La as fresh $\text{La}(\text{NO}_3)_3$ solution. The solution is digested for 30 minutes (limits 20 to 60 minutes) at 35°C . (limits 20 to 50°C .). The slurry is centrifuged at 1720 G with a bowl retention time of 2 to 5 minutes.

Basis for Approval of Change

1. Process changes to effect a time cycle reduction for the lanthanum oxidized crossover step were evaluated under Production Test 224-B-5, HW-17512. Complete oxidation was demonstrated within the time specified.
2. Volume reduction, evaluated under Production Test 221-B-10, HW-19528, has reduced the amount of hydrofluoric acid to so small a volume that a specification on the time for addition is impractical using the existing equipment.

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3. Pile metal with a minimum 40 day cooling period was found to require additional steps to achieve the necessary decontamination. The reprecipitation of lanthanum fluoride and a second centrifugation was demonstrated to have a beneficial effect on decontamination and no effect on plutonium losses. Supporting data have been published in the Separations Technology Unit Progress Reports for October, November, and December, 1951, HW-22701, HW-23015, and HW-23224. This procedure was included in Operating Standards 224-31, a part of Hanford Engineer Works Operating Standards, 7-1184, dated December 13, 1944. The procedure was omitted from the present Operating Standard, HW-17398, as it had not been used when processing metal with a nominal 90 day cooling period. With shorter cooled metal the procedure may at times be a necessary addition to the standard procedure in order to secure adequate decontamination.

VII. LANTHANUM REDUCED CROSSOVER

Procedure in Standards

The procedure as written in the Operating Standards, HW-17398, as 224-41 includes the following steps.

1. Lanthanum fluoride is precipitated by the addition of $\text{La}(\text{NO}_3)_3$ solution to give a concentration of 110, 105, and 50 mg. La per liter with limits of 40 to 150 mg. La per liter for the first, second, and third precipitations in the lanthanum reduced crossover step.
2. The $\text{La}(\text{NO}_3)_3$ solution is added uniformly over a 40 minute period with limits of 15 to 60 minutes for each of the three precipitations.

Revised Procedure

1. The $\text{La}(\text{NO}_3)_3$ solution is added to give a concentration of 180, 170 and 80 mg. La per liter with limits of 40 to 180 mg. La per liter for the first, second, and third precipitations.
2. The $\text{La}(\text{NO}_3)_3$ solution is added uniformly over an 80 minute period for the first and second precipitations and a 40 minute period for the third precipitation with limits of 15 to 120 minutes.

Basis for Approval of Change

1. The volume was reduced in the lanthanum reduced crossover step through process changes evaluated under Production Test 221-B-10 HW-19528. The lanthanum nitrate was the only chemical not reduced in proportion to the volume reduction. This effectively increased the lanthanum concentration beyond the presently specified limits for the first and second precipitations. The effect of concentration of La on Pu loss is not known quantitatively but is believed to be slight and such that there would be little economic change with a La variation within these limits.
2. It has been demonstrated that under present conditions increasing the time for the addition of $\text{La}(\text{NO}_3)_3$ solution by a factor of two decreases the plutonium loss by approximately a factor of two. Diminishing returns only would result from further lengthening of the time of addition. Supporting data have been published in the Separations Technology Unit Progress Report for February 1952, HW-23817.

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