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MEMORANDUM REPORT - SE-PC-#60

# REMOVAL OF ZIRCONIUM-COLUMBIUM ACTIVITIES FROM EXTRACTION STEP $BiPO_4$ PRECIPITATES BY VARIOUS WASHING PROCEDURES

## Introduction

During the development of the present separation-decontamination process, some consideration was given at various times to the possibility of using a decontaminating wash for the removal of by-product activities from $BiPO_4$ product precipitates and some exploratory experiments were carried out, but in general, the results obtained were not particularly promising. Some preliminary work at Site X (CN-2029), however, indicated that washing of $BiPO_4$ extraction precipitates with $NH_4HF_2$ solutions was sufficiently effective to justify further investigation of precipitate washing as a means of improving decontamination. If a sufficiently effective decontaminating wash of the extraction step $BiPO_4$ precipitate were developed, it might make possible the elimination of the second decontamination cycle or of operating without scavengers in a two-cycle process. Removal of a larger portion of the activity early in the process would also be advantageous in that less activity would be carried down the canyon, and waste activity levels would be lower except for the extraction step.

## Summary and Conclusions

1) Very effective removal of zirconium-columbium activities from $BiPO_4$ extraction step precipitates was obtained by washing with $NH_4HF_2$ solutions by a multiple wash procedure at volume ratios which could be handled in the plant centrifuge bowl. A 10% solution was found to be the most effective but there was little difference between 10% and 20%.

2) A single corrosion test on 25-12 stainless steel at Site X had indicated that a concentrated solution of $NH_4HF_2$ (5M or about 27%) was not particularly corrosive but more extensive tests here showed that $NH_4HF_2$ solutions (5%-20%) were sufficiently corrosive to make their use in stainless steel equipment questionable. Some recent experiments on corrosion inhibitors have indicated that corrosion by $NH_4HF_2$ solution is significantly decreased by the addition of $Na_2CrO_4$. Data obtained from one experiment indicated that the effectiveness of the wash was decreased by the presence of $Na_2CrO_4$ but this has not been fully established and further experimental work may be justified.

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3) In washing of $BiPO_4$ with $NH_4HF_2$ solutions conversion of $BiPO_4$ to $BiF_3$ takes place to a large extent. Such a precipitate, however, is readily converted to $Bi(OH)_3$ and fluoride effectively removed by a wash with a 15% KOH solution.

4) Some removal of zirconium-columbium activity from extraction step $BiPO_4$ precipitates was obtained by washing with $H_3PO_4$ solutions (6M) but the procedure did not appear attractive because rather extensive washing with large volumes of wash solution was required. Furthermore, such extensive washing resulted in significant product losses.

5) A number of organic acid solutions were also evaluated in a preliminary way, but of those tested, including oxalic, acetic, tartaric, citric and benzoic (alcoholic solution) only oxalic acid was at all effective. In washing with oxalic acid $BiPO_4$ is partially converted to the oxalate. The bulk of the oxalate, however, can be removed by washing with a 15% KOH solution.

## III Experimental Details

In this study most of the experimental work on the decontamination of $BiPO_4$ product precipitates by washing dealt with the use of fluoride solutions and of $H_3PO_4$ solutions as the washing reagents. Some limited exploratory experiments were also carried out on the evaluation of a number of organic acids. In all cases the $BiPO_4$ extraction precipitates on which the washing experiments were carried out were precipitated from 20% UNH solutions under the conditions specified in the October 5, 1944 flowsheet. Unless otherwise indicated, inactive isotopes of fission elements (equivalent to 250g Pu/ton of metal) were added along with Zr-Cb tracer activity. Washings were made by slurrying the extraction precipitate in the wash solution, the volume of which is expressed as a percentage of the volume of the extraction solution. For washes simulating the washing of a precipitate in the centrifuge bowl, the most attractive procedure from the standpoint of plant operation, a wash volume equivalent to 2% of the extraction volume was used.

In the presentation of the experimental details only the most significant results are given along with with notebook references plus a summary of the findings from experiments which served only to expand and substantiate primary findings.

### A Washing of Extraction Step $BiPO_4$ Precipitates with Fluoride Solutions

Composition of Wash Solution. Most of the washing experiments with fluoride solutions were with $NH_4HF_2$ solutions which were shown to be more effective in removing Zr-Cb activities than HF solutions or than solutions in which the mole ratio of $NH_3$ to HF was greater than 1:2. Data given below show the effect on gamma decontamination of variations in the composition of the wash solutions. In these experiments the extraction precipitates were washed three times with separate portions of the wash solution, each wash being equivalent to 20% of the volume of the extraction solution. The washings were made by slurrying the precipitate in the wash solution for one minute followed by centrifuging, pouring off the supernatant and repeating the procedure with a fresh portion of the wash solution.

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| Experiment | Wash Solution | Percent of total product in washes | Gamma decontamination Factors. Extraction plus three 1-minute washes, each at 20% of extraction volume. |
|---|---|---|---|
| A | $H_2O$ (control) | 0.3 | 5.8 |
| B | HF 0.5M | 3.4 | 7.4 |
| C | $NH_3$:HF=1:4* | 0.0 | 23.3 |
| D | $NH_3$:HF=1:2* | 0.1 | 13.7 |
| E | $NH_3$:HF=3:4* | 1.9 | 7.3 |
| F | $NH_3$:HF=1:1* | 4.1 | 6.6 |

* Mole ratio. $F^-$ concentration in all cases 0.5M.

Experiments (C) and (D) were repeated but the washings were made by stirring for three 20-minute instead of the 1-minute periods. More effective washing was obtained with the longer contact time and the data given below show that the bulk of the activity was removed in the first wash.

Distribution of Activity* - % of total in the starting UNH solution

| Wash Solution $NH_3$:HF mol ratio | Extraction Waste | | Water Wash | | First $F^-$ Wash | | Second $F^-$ Wash | | Third $F^-$ Wash | | Washed Precipitate | | Total in Washes | | Overall γ decontamination factor, extraction plus washes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | G | A | G | A | G | A | G | A | G | A | G | A | G | A | |
| 1:4 | 38.9 | 0.6 | 0.7 | 0.2 | 50.5 | 1.1 | 2.6 | 0.1 | 0.3 | 0.1 | 2.1 | 110.3 | 54.1 | 0.8 | 48 |
| 1:2 | 37.3 | 0.6 | 0.6 | 0.2 | 44.2 | 0.2 | 6.8 | 0.2 | 0.4 | 0.2 | 1.1 | 102.8 | 52.0 | 0.8 | 91 |

* G = gamma activity
A = alpha activity

Some comparative experiments were also carried out in which a master extraction was made, the extraction $BiPO_4$ precipitate dried, an aliquot of the precipitate washed with 5% solutions of the reagents tested. Data given below are for one 20-minute wash with a volume of wash solution equivalent to 10% of the extraction volume.

| Wash Solution (Concentration-5%) | % of Gamma Activity Removed (one 20-min. wash) |
|---|---|
| HF | 8.6% |
| $NH_4HF_2$ | 36.0% |
| NaF | 5.2% |

**Effect of Concentration of $NH_4HF_2$.** Data presented in Table I show that a 10% solution was the most effective although the difference between 10% and 20% was not great and may not be significant. In these tests wash volumes equivalent to 2% of the extraction solution volume were used to simulate washing in a plant centrifuge bowl.

Other experiments indicated that at a specific concentration a higher percentage of activity was removed in a wash if the wash volume were larger but from the standpoint of plant application washing in the centrifuge bowl is much more attractive operationally than washing in a tank. Further supporting data are recorded in notebook 142-T.

Table I

Effect of Concentration of $NH_4HF_2$ Wash on Removal of Zr-Cb Activity From a $BiPO_4$ Ext4action Precipitate

| Concentration (%) | 2 | 5 | 10 | 20 |
|---|---|---|---|---|
| Number of Washes | 3 | 3 | 3 | 3 |
| Wash Contact Time in Minutes | 20-10-10 | 20-10-10 | 20-10-10 | 20-10-10 |
| Cumulative gamma decontamination factors | | | | |
| (1) Extraction | 7.7 | 6.6 | 6.6 | 9.1 |
| (2) After one wash | 8.4 | 9.7 | 17.2 | 24.0 |
| (3) After two washes | 8.8 | 13.6 | 66 | 28.2 |
| (4) After three washes | 9.2 | 17.5 | 125 | 31.4 |
| (5) After three $NH_4HF_2$ washes plus a water wash | 9.2 | 19.8 | 146 | 142 |
| Improvement in decontamination (factor) due to washes. | 1.2 | 3 | 22 | 15.6 |

Effect of zirconium phosphate precipitation prior to extraction on decontamination of the $BiPO_4$ extraction precipitate by $NH_4HF_2$ washes. A series experiments was carried out to determine the decontamination of a $BiPO_4$ extraction precipitate by washing as related to the concentration of zirconium in the extraction solution. It was felt that the effectiveness of the wash might be increased by precipitation of small amounts of zirconium phosphate prior to the precipitation of the $BiPO_4$ carrier. Such a precipitate might not be as firmly held or picked up by the $BiPO_4$ precipitate in the same manner as activity carried by the $BiPO_4$ precipitate from a solution containing zirconium at concentrations low enough that precipitation of zirconium phosphate would not occur.

The data given in Table II show that the addition of zirconium in amounts greater than normally present, and the precipitation of zirconium phosphate prior to $BiPO_4$ was of questionable significance. The results, however, are somewhat erratic but illustrate the effectiveness of the $NH_4HF_2$ wash in the removal of Zr-Cb activity from the $BiPO_4$ extraction precipitate.

The above experiments, with the exception of the two in which Clinton metal solution was used, were carried out with product concentrations equivalent to 250 grams per ton of metal. The data on product losses show that relatively little product was lost in the washes and except for one experiment were consistently low. Details of these experiments are recorded in notebook 86-T.

Conversion of $BiPO_4$ to $BiF_3$ by washing with fluoride solutions. In washing $BiPO_4$ precipitates with $NH_4HF_2$ and also with HF solutions, the $BiPO_4$ is converted to a greater or lesser extent to $BiF_3$, the degree of conversion depending upon the extent of washing (volume used, time of contact, number of washes, and concentration of the wash solution). It appears quite probable that the degree of decontamination achieved is related to the extent of conversion although no specific data to substantiate this point are available. This means then that if a washed precipitate were dissolved in $HNO_3$ followed by a standard decontamination cycle sufficient fluoride would be present to interfere with removal of residual zirconium and columbium activity in the by-product precipitation step. Furthermore, the fluoride concentration during the oxidation step might be high enough to increase corrosion during oxidation. No specific corrosion tests to check this point have been made. However, the fluoride is readily removed by a KOH wash of

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## Table II

## Effect of Zirconium Concentration in the Extraction Solution Prior to Extration on Decontamination of the Extraction Precipitate by Washing with $NH_4HF_2$ Solutions

(In the cases where the extraction precipitate was given two washes, the total volume of the washes was 30% of the volume of the extraction solution and the length of time of the first and second washes was 20 minutes and 10 minutes, respectively. In the cases where three washes were employed, the volumes were 20%, 10%, and 10%, of the volume of the extraction solution, respectively; and the length of time of the washes were 20 minutes, 10 minutes, and 10 minutes, respectively. In all cases the washing was done at room temperature, the concentration of ammonium bifluoride was 0.5M, and the precipitates were stirred during washing with a mechanical stirrer).

| Expt. No. | 1(2) | 2(2) | 3(2) | 4(2) | 5(3) | 6(4) | 7(3) | 8(3) | 9(3) | 10(5) | 11(5) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. of Zr(1) (mg/l) | 103 | 103 | 3 | 3 | 3 | 53 | 3 | 0.3 | 0.0 | 0.0 | 25 |
| Fraction | | | | | Amount of Product (%) | | | | | | |
| Ext'n. waste | 7.3 | 1.4 | 1.2 | 2.3 | 4.1 | 3.6 | 3.8 | 7.3 | -- | -- | -- |
| First wash | 10.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | -- | -- | -- |
| Second wash | 1.0 | 0.2 | 0.2 | 0.1 | 0.1 | 0.03 | 0.1 | 0.1 | -- | -- | -- |
| Third wash | -- | -- | -- | 0.02 | 0.02 | 0.05 | 0.04 | 0.05 | -- | -- | -- |
| Final Ext'n.Ppt. | 81.4 | 98.2 | 98.5 | 94 | 95 | 96 | 96 | 93 | -- | -- | -- |
| | | | | | Amount of Zr-Cb Activity (%) | | | | | | |
| Ext'n. waste | 25 | 29 | 37 | 50 | 90 | 33 | 90 | 67 | 70 | 83 | 51 |
| First wash | 72 | 66 | 59 | 45 | 9 | 60 | 8 | 22 | 20 | 14 | 45 |
| Second wash | 2.8 | 2.9 | 2.0 | 4 | 1.4 | 3.9 | 1.2 | 10 | 8.8 | 1.5 | 2.7 |
| Third wash | -- | -- | -- | 0.2 | 0.1 | 0.2 | 0.1 | 0.5 | 0.66 | 0.3 | 0.2 |
| Final Ext'n.Ppt. | 0.33 | 2.1 | 1.5 | 0.95 | 0.37 | 2.2 | 0.26 | 0.6 | 0.97 | 0.86 | 1.65 |
| Overall D.F. | 300 | 48 | 66 | 106 | 270 | 45 | 384 | 167 | 103 | 108 | 61 |

(1) The estimated concentration of Zr at "W" product levels (20mg Pu/l) is 3mg/l. In the experiments where the concentration of Zr was greater than 3mg/l, additional Zr was added. In experiments 8 and 9 less Zr was added in order to study the effect of Zr concentration. In experiments 10 and 11 Clinton plant material was employed.

(2) Solutions were pre-digested 1 hour at 75°C, after addition of Zr and Bi, with an $H_3PO_4$ concentration of 0.1M in order to precipitate zirconium phosphate before $BiPO_4$. The concentration of $H_3PO_4$ was then increased to 0.6M and given an additional digestion of 2 hours at 75°C.

(3) Regular flowsheet procedure; that is, no pre-digestion prior to precipitation of $BiPO_4$ by making the solution 0.6M in $H_3PO_4$.

(4) As (2) except the concentration of $H_3PO_4$ was 0.05M during the pre-digestion.

(5) Washing procedure tested with Clinton plant metal solution which had cooled about 90 days. The regular flowsheet procedure of digestion was employed. In this case, the activity was that of the fission product elements present in the Clinton metal solution. The gamma decontamination therefore is for the total gamma activity present and not for that of Zr-Cb activity only as in the other experiments.

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the precipitate. Details on the KOH washing or metathesis of extraction precipitates following washing with $NH_4HF_2$ solutions are given in memorandum report SE-PC #25, file number 32529. Data given in this report indicate that product losses in the KOH wastes were slightly higher from an $NH_4HF_2$ washed precipitate than from an untreated precipitate but were not excessive.

Corrosion of Stainless Steel by $NH_4HF_2$ Solutions. Although washing of $BiPO_4$ precipitates with $NH_4HF_2$ solutions is a very effective method for removing zirconium and columbium activities, the use of such solutions in plant equipment appears very questionable in view of the corrosive nature of such solutions. This is particularly true at a point early in the decontamination process where it is very important to keep maintenance at a minimum due to the high levels of activity.

Data on the corrosion of 25-12 stainless steel by $NH_4HF_2$ solutions are given in Table III. In these tests a sample of Merck's $NH_4HF_2$ was used. The salt contains some copper as an impurity which deposited on the steel test strips forming a protective layer which tended to decrease the attach of the metal. No advantage can be taken of the protective effect of such a deposit because it would be removed when the precipitate is subsequently dissolved in nitric acid. Tests made involving such a cycle showed that the corrosion rate was higher when the test strips were cleaned with $HNO_3$ and re-exposed to a fresh solution than during the original exposure. In all cases, the penetration rates were calculated by weighing the samples after the copper deposit on the test strip had been removed by treatment with nitric acid.

Table III

Corrosion of 25-12 Stainless Steel by $NH_4HF_2$ Solutions

| Concentration of $NH_4HF_2$ Solution | Temperature °C | Added Reagents | Hours of Exposure | Penetration in inches per month. | |
|---|---|---|---|---|---|
| | | | | Initial Exposure | Re-Exposure |
| 5% | 40 | None | 72 | 0.0006 | 0.0022 |
| | 75 | None | 72 | 0.0035 | 0.0096 |
| 10% | 40 | None | 72 | 0.0009 | 0.003 |
| | 75 | None | 72 | 0.0073 | 0.0149 |
| | 40 | 1% $Ca(NO_3)_2 3H_2O$ | 72 | 0.0004 | |
| | 40 | 10% $NH_4NO_3$ | 72 | 0.003-0.0061 | |
| | *45° | 5% $Na_2CrO_4$ | 72 | 0.0002 | |
| 20% | 40 | None | 72 | 0.0006 | 0.0013 |
| | 75 | None | 72 | 0.0046 | 0.0014 |

* See discussion in text.

Some tests on the use of various corrosion inhibitors were carried out and it was found that the addition of $Na_2CrO_4$ to HF solutions was quite effective in decreasing the corrosion rate. In similar tests made with $NH_4HF_2$ solutions, a very strongly adhering coating was deposited on the surface of the steel and the test specimens increased in weight. This deposit was not removed by heating in concentrated $HNO_3$ and appeared to be quite effective in protecting the steel from attack. The $NH_4HF_2$ used in these tests contained some copper as an impurity.

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Corrosion tests were repeated using a sample of $NH_4HF_2$ free of copper and the result given in Table III (marked with an asterisk) was obtained. The apparent effectiveness of $Na_2CrO_4$ as an inhibitor suggested that further washing experiments be carried out using $NH_4HF_2$ solutions containing $Na_2CrO_4$. Only one such test has been made and the results were not encouraging in that less activity was removed by this wash than obtained in a control wash with $NH_4HF_2$ solution containing no added $Na_2CrO_4$. Further tests are necessary, however, to determine with certainty that the presence of $Na_2CrO_4$ has an adverse effect since this one test was made using a comparatively dilute $NH_4HF_2$ solution (0.25M) and it has been shown that more concentrated solutions are more effective.

## B Washing of Extraction $BiPO_4$ Precipitates with Phosphoric Acid Solutions

For the experiments on washing of $BiPO_4$ extraction precipitates with $H_3PO_4$ solutions, the extractions were made under conditions described previously. In addition, two series of experiments were made in which varying amounts of either $Cb_2O_5$ or zirconium phosphate were precipitated prior to the precipitation of $BiPO_4$. In all experiments in which columbium was used, a solution of potassium columbate was added slowly with good agitation followed by digestion for 1 hour at 75°C prior to precipitation of $BiPO_4$. When zirconium was added prior to extraction, the metal solution was made 0.1M in $H_3PO_4$ to precipitate zirconium phosphate prior to the addition of Bi(III) and the precipitation of $BiPO_4$ under standard flowsheet conditions. It was felt that the precipitation of a small amount of carrier (columbium or a zirconium compound) which would be expected to pick up the active isotopes of these elements and the portion of the precipitate carried down with the $BiPO_4$ might be more easily removed by a wash. Both $Cb_2O_5$ and zirconium phosphates are somewhat soluble in phosphoric acid and it was on this basis that it was selected for evaluation as a washing reagent.

Appreciable decontamination of $BiPO_4$ precipitates was obtained by washing with $H_3PO_4$ solutions (6M) but several washes of fairly large volume were required. The results obtained indicated that with wash volumes that could be handled in a centrifuge bowl relatively minor improvement was obtained. Furthermore, although data were somewhat erratic, the extensive washing required to obtain significant decontamination resulted in appreciable product loss in the wash solutions. No significant improvement in the decontamination obtained with a $H_3PO_4$ wash was observed in runs in which $Cb_2O_5$ was precipitated in the metal solution prior to precipitation of $BiPO_4$. Some evidence was obtained that precipitation of $ZrPO_4$ prior to extraction was advantageous but this may be open to some question in view of the finding that there appeared to be no significant change in decontamination as the amount of $ZrPO_4$ precipitated was increased.

## C Washing of $BiPO_4$ Precipitates with Organic Acids

Of the various wash solutions tried, which included 10% solutions of acetic, tartaric, citric and oxalic acids and alcoholic solutions of tartaric and benzoic acids, only oxalic acid was found to be at all effective. In washing a $BiPO_4$ precipitate with oxalic acid considerable conversion to bismuth oxalate occurs, but the bulk of the oxalate can be removed by a wash with KOH solution (15%).

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D Notebook References

| Subject | Notebook Number | Experimental Work By |
|---|---|---|
| 1. Washing of $BiPO_4$ Extraction Precipitates with $NH_4HF_2$ Solutions | 142-T<br>86-T | B.F.Faris<br>J.L.Dreher |
| 2. Washing of $BiPO_4$ Extraction Precipitates with $H_3PO_4$ Solutions | 134-T<br>135-T | R.P.S.Black<br>B.H.Perkins |
| 3. Corrosion Studies | 146-T,378-T | E.H.Turk |

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