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Subject SE-PC# 86 The Use of Fluomolybdic Acid for Improving Decontamination in the Product Precipitation Step

To D.A. Miller-T.N. Stapleton-M.H.Smi

From B.F. Faris

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SE-PC-#86

## THE USE OF FLUOMOLYBDIC ACID FOR IMPROVING DECONTAMINATION IN THE PRODUCT PRECIPITATION STEP

### Introduction

In SE-PC-#28, File No. 3-2371, the preliminary evaluations of fluomolybdic acid (along with other complex fluo derivatives) as an agent for improving decontamination in the $BiPO_4$ product precipitation steps are recorded. The present report describes additional work with the objective of developing the fluomolybdate-no scavenger process to the point where a plant test would be justified.

J E Savely 11-20-98

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For The Atomic Energy Commission
H. R. Carroll
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Summary and Conclusions

Laboratory data indicate that fluomolybdic acid is several times as efficient as fluosilicic acid in effecting decontamination in the $BiPO_4$ product precipitation step. Laboratory data and Head-End Semi-Works data show that the use of fluosilicic acid in a no-scavenger process gives a cumulative decontamination for the extraction and first cycle of approximately 300. The comparable use of fluomolybdic acid, however, results in a decontamination factor of 1500-2700 for the same steps. As can be seen from the data in Table I, the fluomolybdate-no scavenger shows at least a 5 to 6 fold improvement over the fluosilicate process in the first cycle, and is one-half as effective as the present scavenger process. At the end of two cycles, however, all three processes show better than $10^5$ decontamination. The fluosilicate-no scavenger process evaluation runs at Clinton showed that decontamination of $10^7$ through the cross-over could not be expected, although laboratory tests at H.E.W. indicated the converse. It is believed that the increased decontamination resulting from the use of fluomolybdic acid will guarantee at least $10^7$ decontamination prior to isolation.

A 1.5% product loss in the plant occurs in the first cycle scavenger by-product precipitate, whereas Head-End Semi-Works data indicate that a loss of no more than 0.5% would result if scavengers were omitted. Therefore, a no-scavenger process would effect a saving of 1.0%. This saving would justify an increased cost of processing chemicals.

Fluomolybdic acid has a complexing action on bismuth phosphate, but a minor adjustment of process conditions assures the expected yield in the $BiPO_4$ product precipitation steps. This alteration of conditions comprises the adjustment of the phosphoric acid concentration to 0.3M prior to the bismuth strike.

There are four fluomolbydic acid derivatives of formulas $H_2MoO_3F_2$, $HMoO_2F_3$, $H_2MoO_2F_4$, and $HMoOF_5$ described in the literature. The last three of these derivatives appear identical with respect to ability to effect decontamination. Corrosion data in Table III show that all three are satisfactory. The ammonium and sodium salts of these acids are quite soluble; this permits flexibility, such as volume reduction by partial neutralization, to be introduced into the process.

The $H_2MoO_2F_4$ is recommended for plant evaluation.

Experimental Details and Discussion

A - Gross Fission Decontamination

Gross fission decontamination was determined on UNH fortified with dissolver solution and inactive isotopes of "…" fission elements. The data in Table I show that fluomolybdate is appreciably more effective than fluosilicate in the first cycle decontamination.

Two-cycle comparative decontamination experiments starting with UNH fortified with dissolver solutions were carried out to determine the relative efficiency of (1) the standard process, (2) the fluomolybdate-no scavenger process, and (3) the fluosilicate-no scavenger process. There was not enough activity present at the end of two cycles to carry the runs through the cross-over. The fluomolybdate process showed a 5 to 6 fold improvement over the fluosilicate process in one cycle and was one-half as effective as the scavenger process. At the end of two cycles, however, all three processes showed better than $10^5$ decontamination. Since extraction, decontamination is no longer measured in the plant, a value of 10 is assumed for the data reported below, although an extraction decontamination factor of 12 would bring the results of the standard process run in line with plant data.

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## Table I

### Gross Fission Decontamination in Extraction Plus First Cycle

| Added Agent | Decontamination Factor For Product Precipitation Step | Decontamination Factor For Cycle | Decontamination Factor for Cycle Plus Extraction |
|---|---|---|---|
| Control | 4.0 | 19.2 | 129 |
| 0.05M Fluosilicate | 8.4 | 40.6 | 272 |
| 0.05M Fluomolybdate | 84.4 | 407 | 2725 |
| Control | 4.2 | 29.4 | 218 |
| 0.05M Fluosilicate | 7 | 49 | 363 |
| 0.05M Fluomolbydate | 54 | 378 | 2787 |
| Control | 6 | 25.4 | 138 |
| 0.05M Fluosilicate | 18 | 70.2 | 420 |
| 0.05M Fluomolybdate | 51 | 199 | 1198 |

## Table IA

### Two Cycle Gross Fission Decontamination

| | Standard Process | Fluosilicate Process | Fluomolybdate Process |
|---|---|---|---|
| Extraction + 1 cycle | 3800 | 323 | 1890 |
| Extraction + 2 cycles | $>2x10^5$ | $>2x10^5$ | $>2x10^5$ |

### B - Specific Decontamination

#### 1 - Lanthanum Removal

It is known that ammonium fluosilicate adversely affects lanthanum removed in the $BiPO_4$ product precipitation steps. One test was run to determine what effect fluomolybdic acid has on lanthanum removal, using orphan tracer La. As can be seen from the following data, fluomolybdic acid has essentially the same effect as does fluosilicate.

| Agent present in Product Precipitation Step | Lanthanum Separation Factor |
|---|---|
| None (control) | 60 |
| 0.05M Fluosilicate | 30-40 |
| 0.05M Fluomolybdate | 29 |

#### 2. Ruthenium Removal

In one set of runs employing tracer ruthenium, its separation was determined in one cycle in runs involving (1) control run - no added agent, (2) ammonium fluosilicate added, and (3) fluomolybdic acid process. It was found that the ruthenium removal was higher in the fluomolybdate run than in the other two. This was unexpected. The results are as follows.

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| Added Agent | Decontamination Factor for One Cycle |
|---|---|
| Control -No added Agent | 105 |
| 0.05M $H_2SiF_6$ | 86 |
| 0.05M $H_2MoOF_4$ | 158 |

## B - Zirconium-Columbium Decontamination

The following test shows that fluomolybdic acid is nine times as effective as fluosilicic acid in effecting Zr-Cb removal. Dead UNH was spiked with Zr-Cb tracer and with inactive isotopes of "N" fission elements. The decontamination results are as follows:

| Added Agent | Decontamination Factor For Product Precipitation Step | Decontamination Factor for Cycle | Decontamination Factor for Cycle And Extraction |
|---|---|---|---|
| Control | 2.7 | 19 | 61.3 |
| 0.05M Fluosilicic Acid | 7.1 | 52.5 | 168.1 |
| 0.05M Fluomolybdic Acid | 46.4 | 469.5 | 1502 |

## C - Conditions for $BiPO_4$ Product Precipitation in The Fluomolybdate Process

Fluomolybdic acid complexes bismuth to a somewhat greater extent than does fluosilicic acid. The data are recorded in Table II.

Table II

Complexing of Bismuth in Process Solutions-.03M $Fe^{+3}$ and 0.6M $H_3PO_4$

| Added Agent | mg. Bi/liter in Effluent from $BiPO_4$ Product Precipitation |
|---|---|
| None (control) | 100 |
| 0.05M Ammonium fluosilicate | 160 |
| 0.05M $HMoO_2F_3$ | 550 |
| 0.05M $H_2MoO_2F_4$ | 500 |
| 0.05M $HMoOF_5$ | 495 |

When $BiPO_4$ product precipitations in the presence of 0.05M fluomolybdic acid were made under normal flowsheet conditions, product losses of 1-2% were encountered. By a slight change in conditions, however, losses can be reduced to values identical with those of control runs. The change is exceedingly simple and would not complicate plant procedure. The proposed conditions comprise making the process solution 0.3M in phosphoric acid prior to the bismuth strike in the $BiPO_4$ product precipitation steps, then eventually increasing the $H_3PO_4$ concentration to 0.6M as is ordinarily done in plant practice. In spite of the fact that some of the bismuth remains in solution, carrying is essentially quantitative. The apparent reason that the higher phosphoric acid is required during the strike is that bismuth phosphate does not begin to precipitate in the presence of fluomolybdic acid until a concentration of 0.3M $H_3PO_4$ is reached.

## D - Corrosion Data

A product process solution 0.03M in Fe, 1.25M in $HNO_3$, 0.1M in $H_3PO_4$ and 0.05M in fluomolybdate has the same corrosion rate on stainless steel as a comparable solution that is 0.05M in fluosilicate.

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Corrosion data on 25-12 Cb steel at room temperature was determined using 1M $HMoO_2F_3$, 1M $H_2MoO_2F_4$, and $HMoOF_5$. The values, as recorded in Table III, show that corrosion is not a serious problem. Undoubtedly, the sodium or ammonium molybdates would be even less corrosive.

Table III

Corrosion Rate of 25-12 Cb Steel at 25oC

| | Inches Penetration/month |
|---|---|
| 1M $HMoO_2F_3$ | 0.000041 |
| 1M $H_2MoO_2F_4$ | 0.00021 |
| 1M $HMoOF_5$ | 0.00056 |

## E - Advantages of a Fluomolybdate Process

There would be certain advantages inherent in the use of a fluomolybdate-no scavenger process. They are as follows:

1 - The average product loss in the first by-product precipitate is 1.5%. Based on the Head-End Semi-Works data, the loss would be approximately 0.5% if scavengers were omitted. This would decrease the over-all product loss by approximately 1.0%.

2 - In case any high product losses should be encountered in any of the first cycle by-product precipitates, the process of reworking would be appreciably simpler.

3 - One and one-half hours would be cut from the time cycle in Section 13 operations.

4 - A saving of 500g. each of $Ce^{+4}$ and $Zr^{+4}$, and of 12.5kg. of Bi would be realized in each run.

5 - Solutions of fluomolybdate appear somewhat more stable than solutions of fluosilicate.

6 - A smaller number of chemicals would be required for plant operations, and a smaller number of solution tanks would have to be maintained.

## F - Disadvantages of a Fluomolybdate Process

There are also certain disadvantages that would be associated with a fluomolybdate-no scavenger process. The more obvious ones are as follows:

1 - Equipment in Sections 14 and 16 in the plant would become more contaminated, (probably by a factor of 2) which might contribute to maintenance difficulties.

2 - A suitable source of a fluomolybdate would have to be located. In the absence of that, a suitable source of molybdic acid, sodium - or ammonium molybdate would be required.

3 - If the fluomolybdate cannot be purchased as such, it will have to be synthesized at HEW from a suitable molybdate and HF.

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4 - No improvement in lanthanum removal prior to the cross-over would be effected in switching from the use of fluosilicate to fluomolybdate in the $BiPO_4$ product precipitation steps.

## G - Solubility Considerations

Ammonium fluomolybdate is every bit as soluble as ammonium fluosilicate. Also, the sodium and potassium salts of fluomolybdic acid are as soluble as the ammonium salt, and this would permit fluomolybdic acid to be used if volume concentration by partial neutralization were employed.

## H - Cost Considerations

The differences in costs in the two processes are illustrated in Table IV.

Table IV

Differences in Cost in the Scavenger-Fluosilicate Process and the No Scavenger-Fluomolybdate Process

| Costs of Chemicals Used in Only One Process | Scavenger Fluosilicate Process | No-Scavenger Fluomolybdate Process |
|---|---|---|
| **1st Cycle** | | |
| $Ce^{+4}$ Scavenger | 4.20 | |
| $Zr^{+4}$ Scavenger | 4.33 | |
| 1.25g. Bi/liter | 37.63 | |
| Ammonium fluosilicate (0.12¢/lb.) | 26.46 | |
| Ammonium fluomolybdate: | | |
| Ammonium molybdate (81.5% $MoO_3$ at $0.90 /lb.) | | 195.00 |
| HF (at 22¢/lb.) for $(NH_4)_2MoO_2F_4$ | | 22.00 |
| Total for each process | 72.62 | 217.00 |
| Increase in Cost for Cycle | | 144.38 |
| **2nd Cycle** | | |
| Ammonium fluosilicate | 19.50 | |
| Ammonium fluomolybdate | | 160.00 |
| Increase in cost for cycle | | 140.50 |
| Total increased cost | | 284.88 |

An increased operational cost of $284.88 is incurred, but three grams of plutonium is saved. The cost of this product would have to be balanced against the increased operational cost to determine the net saving of the new process.

Also, a process based on fluomolybdate and no scavengers in the first cycle, and fluosilicate in the second cycle may prove to be adequate for the desired decontamination.

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J - Solid Fluomolybdates

Crystalline fluomolybdic acid and ammonium fluomolybdate were prepared in the laboratory by evaporation of the corresponding solutions under reduced pressures at temperatures not exceeding 80°C.

K - Feasibility of a Plant Trial

Since ammonium fluomolybdate is not obtainable commercially, at present, it would have to be synthesized in one of the make-up tanks in 271. An HF line that passes through the building would have to be tapped and a lead introduced into the mixing tank.

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