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By I. J. J. J. J.

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MAY 10, 1946

MEMORANDUM REPORT SE-PC-#28

Use of Ammonium Fluosilicate Analogs
for Improving Decontamination in the Product
Precipitation Steps

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Introduction

Ammonium fluosilicate is now added to the process solutions in both bismuth phosphate decontamination cycles just prior to the reduction. The advantage of using fluosilicate is that it increases the decontamination of zirconium and columbium by the bismuth phosphate product precipitation step. This is presumably accomplished in part at least by dissolving the "fines" of radioactive columbic oxide and zirconium phosphate that are not separated completely by the by-product centrifugation and tend to carry partially with the product precipitate.

If an agent even more effective than fluosilicate in improving decontamination in the product precipitation step were found, its use would aid in more rapid decontamination and perhaps contribute to a shortening of the separations process. This report describes the search for new agents for this purpose and compares their effectiveness with that of fluosilicic acid.

Summary and Conclusions

1. A large number of inorganic and organic compounds were evaluated as solubilizing agents for colloidal fission, and their effectiveness was compared with that of fluosilicic acid. Of those tested, only the metal fluo-complexes showed promise. A comparison of these compounds is recorded in Table I, and a discussion as to their applicability follows:
 - a) The best agent uncovered from the standpoint of effectiveness and availability is fluoboric acid (HBF_4). As can be seen from the data in Table I, its use improves decontamination to a somewhat greater extent than does fluosilicic acid. Fluoboric acid is equivalent to fluosilicic acid in reducing product losses in the product precipitation step and the two are identical in their corrosion rates of 25-12 Cb steel. Furthermore HBF_4 does not form an insoluble sodium or potassium salt as does fluosilicic acid. This allows a little more flexibility in process changes. Evaluation in the Hot Semi-Works may be warranted.
 - b) Ammonium fluorotitanate was investigated in some detail because of its potential availability. This compound, though effective in improving decontamination, had the unfortunate and unpredictable property of complexing bismuth, completely preventing the precipitation of the phosphate under some conditions and inhibiting the precipitation under all conditions.
 - c) The use of fluomolybdic acid resulted in very good decontamination, but probably would not be practical for plant use because of its relative unavailability.
 - d) Fluovanadic acid offered some improvement over fluosilicic acid, but the difficulty of procuring large amounts of vanadium compounds makes its use prohibitive.
 - e) Fluouranic acid offered some improvement in decontamination, while the use of fluozirconic acid resulted in decontamination inferior to the control.
2. The use of free HF in conjunction with fluosilicic acid resulted in decontamination better than that obtained by the employment of fluosilicate alone. (Table I).

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3. The properties of certain metal fluocomplexes made their evaluation impossible. These are recorded in Table II.
4. A list of a number of agents evaluated that had little or no effect on decontamination improvement is recorded in Table III.
5. Several agents were evaluated for the improvement of decontamination at the extraction step by adding the compound to the UNH solution. Only oxalic acid (Table IV) has a beneficial effect. The use of oxalic acid as a pre-reduction agent in the plant might be warranted.

Experimental Details

Extractions were made from 20% UNH (Semi-Works dissolved metal) fortified with plant UNH (60 to 85 days old metal) and with % concentrations of fission elements supplied by spiking with inactive isotopes. With the exception of pre-reduction, the extractions were carried out as outlined in the H.E.T. October 5th flowsheet. By-product precipitations comprised bismuth phosphate only. Reductions and product precipitations were made as outlined in the plant flowsheet, and the solubilizing agent was added at the beginning of the reduction. Generally fairly large extractions (2 to 3 liters) were made and the cycle carried through the by-product on the same scale. Aliquots of the oxidized effluent were then employed for comparative tests.

The sample of fluoboric acid was purchased from Pennsylvania Salt Co., had a density of 1.30, and assayed approximately 30% HBF_4 .

The sample of ammonium fluotitanate was prepared from TiO_2 by G. W. Sears in the H.E.T. laboratories.

Other fluo-derivatives were prepared from suitable compounds and HF.

Fluotitanic acid inhibits the precipitation of the bismuth phosphate product precipitate from process solutions. This precipitation is actually prevented at low concentrations of phosphoric acid. This is illustrated by the following data.

0.05% H_2TiF_6 Present

0.03% Fe; 2.5 g/l Bi; 1N HNO_3	
H_3PO_4 Concentration	Temperature Above Which No Crystallization Occurs
0.6%	55°C
0.8%	60°C
1.0%	65-70°C

Even though crystallization is initiated at the temperatures indicated, several hours aging at room temperature are required for complete precipitation to occur.

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SEP. ENG. -200 AREA TECH. DEPT.

B. F. Faris
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-4-

Table 1

Comparison of Other Complex Fluoro-Compounds with Ammonium Fluoroborate with Respect To Decontamination at the Product Precipitation Step

Added Agent	Decontamination Factor For Step	Decontamination Factor For Cycle	Decontamination Factor For Cycle Plus Extraction
None (Control)	4.5	17.1	111
.05M (NH ₄) ₂ SiF ₆	9	34.2	222
.05M HF	27.3	104	662
.01M HF	8.7	32.8	220
.05M Fluoroboric Acid (1)	11.4	43	291
None (Control)	6	28.8	182
.05M (NH ₄) ₂ SiF ₆	12.4	59.6	367
.05M HF	42.1	202	1320
None (Control)	2.6		
.05M (NH ₄) ₂ SiF ₆	6.3		
.01M (NH ₄) ₂ SiF ₆	6.9		
.025M (NH ₄) ₂ SiF ₆	5.4		
.05M (HF) ₂ SiF ₆	39.0		
0.1M (HF) ₂ SiF ₆	70.6		
None (Control)	4.0	19.2	129
.05M (NH ₄) ₂ SiF ₆	8.4	40.8	272
.05M Fluoroboric acid	84.4	407	2725
.05M Fluoroboric acid	37	176	1199
.05M Fluoroboric acid	3.2	15.4	105
.05M Fluoroboric acid	71.6	344	2300
.05M Fluoroboric acid	20.4	98	656
.05M Fluoroboric acid	21.8	105	704

Decontamination of Gamma activity only.

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-5-

Table II

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Tested Fluor Compounds Whose Properties
Prohibit Their Use

Agent Tested	Reason Why Cannot Be Used
.05M Fluocolumbic Acid	Hydrolyzes under flowsheet conditions
.05M Fluotungstic Acid	Hydrolyzes under flowsheet conditions
.05M Stannic fluoride	Hydrolyzes under flowsheet conditions
.05M Fluothoric Acid	Too insoluble
.05M Fluoplumbic Acid	Too insoluble

Table III

Agents Tested with Little or No Effect on
Decontamination in the Product Precipitation Step

Added Agent	Decontamination Factor For Step	Decontamination Factor For Cycle *
None (Control)	5.1	40.8
20 mg/liter LaF_3	5.6	44.8
0.05M $(\text{NH}_4)_2\text{SiF}_6$ (Control)	11	88
None (Control)	2.1	6.7
0.05M Chloroacetic acid	2.55	8.2
0.05M $(\text{NH}_4)_2\text{SiF}_6$ (Control)	7.5	22.6
None (Control)	2.5	15.7
0.01M HF	2.6	16.3
0.01M HCl	3.2	20.4
0.01M HBr	3.5	22.0
0.01M HI	4.8	30.2
0.05M Trichloroacetic acid	3.0	18.9
0.01M Trichloroacetic acid	3.0	18.9
0.05M Sodium 5-nitro 6-chloro toluene sulfonate	3.2	20.4
0.05M $(\text{NH}_4)_2\text{SiF}_6$ (Control)	12.9	87.6
None (Control)	5.1	34.2
0.01M HIO_3	3.8	25.5
0.05M Picric acid (not completely soluble)	2.2	14.7
0.05M Ammonium Vanadate	4.5	30.2
0.05M Sulfamic acid	8.2	55
0.05M $(\text{NH}_4)_2\text{SiF}_6$ + 0.01M HI	10	67
0.05M $(\text{NH}_4)_2\text{SiF}_6$ (Control)	14.8	99

* Overall gamma decontamination for by-product without scavengers and product precipitation steps.

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-8-

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Table IV

Complexing Agents in URE Product Extraction

Added Agent	Decontamination Factor
None (Control)	5.2
0.03M Oxalic acid	12
0.03M Tartaric acid	4.2
0.03M Citric acid	5.1
0.03M HF	5.4
None (Control)	7.1
0.1M Furfural	8.9

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