GENERAL ELECTRIC COMPANY

HW-35767

RICHLAND, WASHINGTON

HANFORD ATOMIC PRODUCTS OPERATION

This document consists of 10 pages; [redacted]

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F-10-P SOLUTION STUDIES

by

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March 14, 1955

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by the General Electric Company under Contract #W-31-109-Eng.-52

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INTRODUCTION

F-10-P solution must be filtered prior to further processing, to remove grease and plutonium-containing solids. The solids content of the solution is high enough that plutonium hold-up on the filters averages about six per cent of the through-put and necessitates frequent filter clean-outs. The desire to reduce the frequency of filter clean-outs has led to an experimental program to determine the composition of the solids in F-10-P and to find a means of preventing their formation. A limited study of the properties of the grease in F-10-P was also initiated, as a result of the proposals that F-10-P be processed in a solvent extraction plant (e.g. Recuplex or Redox). The work done on these problems is described in this report.

SUMMARY AND CONCLUSIONS

Plutonium-containing solids have been removed from F-10-P solution and analyzed, the results showing the solids to be variable mixtures of plutonium (IV) fluoride and phosphate. The relative quantities depend upon the original fluoride, phosphate, and hydrogen ion concentrations in the solution.

Investigation of the solubilities of these solids has shown that their formation in F-10-P solution can be prevented by increasing the acidity to three molar or more. In one experiment, the filtration of synthetic F-10-P equivalent to fifteen runs in the 231 Building, the hold-up from a solution containing 4.65 molar nitric acid was only three per cent as great as the hold-up from a solution containing only two molar nitric acid.

In view of these results, the feasibility of adjusting the process in the 224-T and 231 Buildings to permit the transfer and storage of F-10-P with as high an acidity as possible should be investigated.

The greases used in process equipment in the Concentration Building have been found to contain F-10-P-soluble, surface-active, organic compounds. The addition of these compounds to hexone-aqueous systems caused increased disengaging times. The compounds did not appear to affect the carbon tetrachloride-TBP system, beyond causing an increased entrainment of organic in the aqueous phase.

EXPERIMENTAL

The plutonium-containing solids were analyzed as follows: plutonium was determined by radio assay; fluoride analysis was made with a titrimetric method in the 234-5 control laboratory; and phosphate was determined gravimetrically as ammonium phosphomolybdate.

In the filtration experiments, the F-10-P was filtered through a one-inch pre-coat of filter aid. Most of the plutonium held up on the filter was removed with 13 molar nitric acid. Finally, the filter aid was destroyed

with hydrofluoric acid to obtain the remaining plutonium.

The effect of the grease was determined by contacting the solvent with successive, fresh samples of a synthetic, plutonium-free F-10-P solution.

RESULTS AND DISCUSSION

The investigation of grease and solids in F-10-P solutions developed along the following lines: 1) analysis of precipitates and of solutions in which the precipitates formed; 2) preparation of synthetic solutions and observation of their stability against precipitation; and 3) study of the properties of the grease found in F-10-P solution.

Tables I - III show the results of analyses of solutions and precipitates. The fluoride and phosphate contents of F-10-P solution have normally ranged from 0.5 to 1 gram per liter, although higher concentrations of both have been observed [1, 2, 5]. (The presence of these ions presumably results from incomplete metathesis of the lanthanum fluoride product cake in the 224 Building.) Solids removed from F-10-P solution, either as received or after storage, have been found to range in empirical composition from $Pu(PO_4)_{.7}$ to $PuFPO_4(1-3)$.

The precipitates obtained on storage of F-10-P solutions which had been spiked with various amounts of phosphoric and hydrofluoric acids, contained plutonium (IV), fluoride, and phosphate, the fluoride and phosphate content depending upon the fluoride, phosphate, and hydrogen ion concentration in the original solutions. The solids which were high in phosphate were more granular and dissolved readily in strong nitric acid. The solids having a high fluoride content were finely divided and were only slightly soluble in hot, concentrated nitric acid, but dissolved in aluminum nitrate-nitric acid mixtures. X-ray diffraction patterns of the solids gave no conclusive results. The analyses of the solids are given in Table I.

Storage tests were made with synthetic F-10-P solutions of various acidities, with phosphate and fluoride ion concentrations of one and one to two grams per liter, respectively. When the acidity was greater than three molar, no precipitate was formed in one to five months. A solution containing 4.65 molar acid (tested because of its suitability for use as feed to Recuplex) dissolved plutonium phosphate and freshly-prepared lanthanum plutonium fluoride, to the extent of 5.8 and 10 grams per liter, respectively.

Filtration experiments were carried out with synthetic F-10-P solutions which contained one gram per liter phosphate, two grams per liter fluoride, and either 2 or 4.65 M HNO_3. With the 2 M HNO_3, the plutonium retention by the filter amounted to 1.9 per cent (equivalent to a hold-up of 85 grams on the H-1 filter in the 231 Building after the filtration of 15 runs). With 4.65 M HNO_3, the plutonium hold-up was only 0.05 per cent (Table V).

Investigation of three lubricants used in the Concentration Building showed that, when these oils were added to synthetic F-10-P solution, a surface-active component dissolved in the F-10-P. This surface-active component caused increased disengaging times on contacting with hexone, but did not affect a carbon tetrachloride-TBP system beyond causing an increase in entrainment of organic in the aqueous phase. This component could not be removed by washing with sodium carbonate. In order to use F-10-P in a hexone system, an inert solvent wash is needed, in addition to filtration of the F-10-P. Table VI gives the data obtained on contacting the F-10-P with hexone and carbon tetrachloride-TBP.

(1) Harmon, K. M., Separations Technology Sub-Section, Plant Processes Unit, 234-5 Development Sub-Unit Progress Report for August, 1954, HW-33156. September 23, 1954.

(2) Cooper, V. R., Separations Technology Unit Process Assistance Progress Report for April, 1952, HW-24426.

(3) Hill, O. F., Separations Technology Sub-Section, Plant Processes Unit, Process Technology Progress Report for October, 1954, HW-33817. November 15, 1954.

(4) Cooper, V. R., Separations Technology Unit, Process Assistance Progress Report for May, 1952, HW-24682.

(5) Cooper, V. R., Separations Technology Unit, Process Progress Report for November, 1951, HW-23015.

(6) Harmon, K. M., Separations Technology Sub-Section, Plant Processes Unit, 234-5 Development Sub-Unit Progress Report for October, 1954, HW-34072. November 10, 1954.

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TABLE I

ANALYSIS OF SOLIDS FROM F-10-P SOLUTION

Solution Run Number	Solution Composition(g/l) Pu	H^+	$PO_4^{\equiv}$	F^-	Composition of Air Dried Precipitate Weight(g)[a]	Wt.Pu(g)	Wt.$PO_4^{\equiv}$(g)	Wt. F^-(g)	Empirical Formula
T-11-12-D-50	10.4	1.63		0.98					$PuFPO_4$
T-54-01-45		3.0	0.83	0.13		0.15	0.04	0	$Pu(PO_4)_{.7}$
T-54-01-45(b)		3.0	1.33	0.13	14.7	5.9	1.84	0.2	$PuF_{.43}(PO_4)_{.78}$
T-54-01-45(b)		3.0	1.33	0.38	14.7	8.7	0.59	1.8	$PuF_{2.5}(PO_4)_{.17}$
T-54-01-45(b)		3.0	0.83	0 60	4.0	2.5	0.23	0.13	$PuF_{.69}(PO_4)_{.22}$
T-54-01-45(b)		2.0	0.55	0.09	3.3	1.7	0.11	0.27	$PuF_{1.9}(PO_4)_{.16}$

(a) Amount of precipitate from one liter of solution.

(b) Run T-54-01-45 was spiked to the fluoride and phosphate concentrations which are shown.

TABLE II

ANALYSIS OF SOLIDS ON N-1 FILTER
in 231 Building (3)

	Solid Composition - Wt. Per Cent
Plutonium	15
Fluoride	3.67
Phosphate	5.57
Lanthanum	3
Empirical Formula	$PuF_{.55}(PO_4)_{.94}$

TABLE III

ANALYSIS OF F-10-F SOLUTIONS (5)

Run Number	Pu (g/l)	La (g/l)	F^- (g/l)
B-11-10-F-24	11.55	42.89	.86
B-11-10-F-25	12.02	48.36	.85
B-11-10-F-26	12.08	65.57	1.06
T-11-10-DR-18	11.82	56.83	.74
T-11-10-DR-19	11.57	42.07	.87
T-11-10-DR-20	12.42	70.99	.42

TABLE IV

DEPENDENCE OF SOLIDS - FORMATION UPON ACIDITY AND ALUMINUM CONCENTRATION

Run Number	Solution Composition					Storage Time Days	Precipitate Formation
	Pu(g/l)	H^+(g/l)	F^-(g/l)	$PO_4^{\equiv}$(g/l)	Al(M)		
T-54-01-45(a)	12	2	1	1	0.0	30	Yes
T-54-01-45(a)	12	2	1	1	0.4	30	Yes
T-54-01-45(a)	12	4	1	1	0.0	30	No (Possible Trace)
T-54-01-45(a)	12	4	1	1	0.4	30	No
1 (b)	9.8	4.65	2	1	0.35	138	No
2 (b)	9.8	4	2	1	0	110	No
3 (b)	9.8	3	2	1	0	110	No
4 (b)	9.8	2	2	1	0	110	Yes

(a) Run T-54-01-45 was spiked to the indicated H^+, F^-, $PO_4^{\equiv}$, and Al^{+++} concentrations.

(b) Synthetic F-10-P. The solution also contains 0.43 M La^{+3}.

TABLE V

FILTRATION OF SYNTHETIC F-10-P SOLUTIONS

Plutonium Hold-up

Operation[a]	Plutonium on Filter[b] After Filtration (g)	After Clean-out (60% HNO_3) (g)	(%)
Filtration of F-10-P (c)	85	2.6	2
Filtration of F-10-P, followed by filtration of modified F-10-P (d)	13	0.14	1
Filtration of modified F-10-P	2.4	0.07	1

(a) Filtration through filter-aid pre-coat, one inch thick: 1.64 liters solution filtered per square inch of filter area, corresponding to filtering 15 runs through the N-1 filter.

(b) Equivalent to hold-up on N-1 filter after 15 runs.

(c) F-10-P composition: 2 M H^+; 0.53 M La^{+3}; 0.16 M K^+; 12.5 g/l Pu; 1.0 g/l PO_4^{-3}; 2 g/l F^-.

(d) Modified F-10-P composition: 4.65 M H^+; 0.43 M La^{+3}; 0.35 M Al^{+3}; 0.16 M K^+; 9.8 g/l Pu; 1 g/l PO_4^{-3}; 2 g/l F^-.

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TABLE VI

EFFECT OF GREASE UPON DISENGAGING TIMES

Contact No.(a)	Disengaging Time, Seconds	
	Hexone	15% TBP - CCl_4 (b)
0 (No Grease)	12	29
1	13.5	37
2	15.0	33
3	16.0	34
4	17.0	
5	16.0	

(a) The solvent was contacted successively with samples of fresh, synthetic F-10-P filtrate. (The solution contained no plutonium. Grease had been added as follows: 1 ml/liter A-4 oil; 1 ml/liter A-18 oil; and 1 g/liter A-06 grease.)

(b) Entrainment of aqueous in the organic phase increased with successive contactings.

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