August 29, 1972

THE CONVERSION OF PLUTONIUM OXIDE TO PLUTONIUM
TETRAFLUORIDE WITH FLUORINE IN
A FLUID BED REACTOR

PART II: DEMONSTRATIONS RUNS: A COMPARISON OF THE
FLUORINE PROCESS WITH THE HYDROFLUORINATION PROCESS

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Abstract. A series of 82 1-kg-batch pilot plant runs was made to demonstrate the potential of a process using fluorine and a fluid-bed reactor to convert plutonium oxide (PuO_2) to plutonium tetrafluoride (PuF_4). A comparison of this process with the rotary hydrofluorination process, currently used to generate PuF_4 in the Rocky Flats plutonium recovery plant, indicated that replacement of the existing process would result in a number of significant improvements.

Properly designed, a fluid bed-fluorine system should reduce the radiation exposure rate presently experienced by the hydrofluorination process operators by a factor of 10. This reduction in exposure would result from the smaller inventory of PuF_4 and the relative ease of remote operation of the fluid bed-fluorine process.

Use of the fluorine process would eliminate the generation of approximately 10,000 gallons/month caustic waste solution containing an average of approximately 170 grams plutonium. This waste stream, with the contained plutonium, must be processed for water removal, and ultimately, shipped off-site for burial.

The fluorine process should reduce the quantity of plutonium recycled by: (1) reducing the quantity of impure PuF_4 and (2) improving the yield of plutonium metal in the calcium reduction operation. Approximately 95% of the

recycle from these sources should be eliminated. Based on an average recovery rate of 400-kg plutonium metal per month and a recycle processing cost of \$1,000-per-kilogram plutonium recycled, cost calculations show a potential savings of approximately \$1.25 million/year by replacing the present hydrofluorinators with a fluid bed-fluorine system.

The demonstration runs indicate that because of reduced corrosion and the use of multiple small reactors, dependability and maintenance requirements appear more favorable with the fluid-bed fluorine process. No significant disadvantages were apparent during this series of demonstration runs.

INTRODUCTION

Previous investigative work indicated that a process for converting plutonium oxide (PuO_2) to plutonium tetrafluoride (PuF_4), using fluorine (F_2) and a fluid bed reactor, offered certain advantages compared to the hydrofluorination process currently used in the Rocky Flats plutonium recovery facility for PuF_4 generation.¹ To adequately demonstrate the fluid-bed fluorine process as a practical production operation, and to provide a valid comparison of significant factors (i.e., radiation exposure, reliability, product quality, quantities of wastes and residues generated, and operating costs), more extensive

data were needed. To provide this information, a total of 82 1-kg-batch pilot plant runs were made, generating a total of 88 kg of PuF_4 , which was subsequently reduced to plutonium metal. The only significant process change made during this series of runs was the addition of a pneumatic transfer system to permit charging and unloading the reactor remotely. The remote operation of the process would minimize the exposure of operators to radiation from PuF_4 , one of the primary problems with the current hydrofluorination process. Although totally remote operation of the pilot plant was not feasible without major modifications, the addition of the transfer system facilitated the testing of all the components necessary for a remotely operated system.

Because the pilot plant was not designed to process large quantities of materials continuously (i.e., small-scale equipment, few automatic or remote controls, and a minimum of radiation shielding), the actual unit operating labor requirements and radiation exposure levels determined for the pilot plant operation could not be compared directly with data for the production hydrofluorination process. Estimates of operating labor and radiation exposure were made for a production-scale fluid bed-fluorine system with the same capacity as the hydrofluorinator, based on time study and radiation data obtained from the pilot plant operation. Adequate instrumentation and shielding, with remotely located controls, were assumed in making these estimates. All other pilot plant data collected were assumed to be directly comparable with data from the present production operation.

EXPERIMENTAL

Description of Equipment and Procedure:

As in the earlier feasibility studies¹ components of a pilot plant system, designed originally for volatile fluoride process development,² were used. The 82 batch runs were made in three continuous operating periods. During the first operating period, which consisted of six 1-kg-batch runs, the PuO_2 feed was simply poured into the reactor through a port in the top. The reactor was then sealed before starting each run. Product removal was effected by inserting a tube, connected to a vacuum source, into the reactor

after completing each run, and sucking the product PuF_4 into a collection container.

Prior to the second series of runs, a pneumatic transfer system was installed. Although the PuO_2 charging system worked well, the presence of the product withdrawal tube, using the arrangement shown in Figure 1, caused erratic performance of the fluid bed, resulting in incomplete conversion to PuF_4 in some cases, and the formation of lumps of PuF_4 in the reactor in a number of the runs. The formation of lumps caused plugging of the product withdrawal tube, preventing complete product removal. When this condition occurred, it was necessary to remove the reactor base to recover the residual PuF_4 . The resulting spillage and exposure of residual PuF_4 to external contamination by impurities generated undesirable quantities of impure PuF_4 . Several changes in the diameter and depth of immersion of the product withdrawal tube were made during this series of runs. Some improvement in performance was attained but it became evident that the presence of the withdrawal tube in the reaction zone of the fluid bed created an unstable condition. Prior to the last eight runs of this series, the product withdrawal tube was removed and product removal procedure used in the first series was resumed.

Before beginning the third series, which consisted of 24 runs, the pneumatic transfer system for product removal was revised. The revised arrangement was entirely satisfactory and the final 24 runs were made, without interruption, and the results were favorable.

The sequence of operations for a complete cycle is shown in Figure 2. Also shown are the approximate times required and the gas flow rates at various points in the system during each operation. Typical operating temperatures for the components which operate above ambient temperature are shown also.

A predicted, or calculated, overall material balance is shown in Figure 3. These values are based on 1000 grams contained plutonium per batch, and a stoichiometric fluorine efficiency of 67%. The stoichiometric efficiency used was verified experimentally with highly reactive PuO_2 . With less reactive PuO_2 slightly lower efficiencies result, as shown by the actual fluorine usage during the demonstration runs.

FIGURE 1. Pneumatic Transfer System for Product Removal (Initial Design).

Figure 4 is a simplified diagram of the pneumatic transfer system used for feed introduction during the second and third series of runs. The vacuum system shown was fabricated from 3/8-in. tubing and was used to transfer PuO_2 approximately 20 feet from the feed preparation glovebox to the reactor. As a safety feature, the transfer line was encased in a jacket of 3/4-in. pipe. This system was trouble free during the entire operating period. Because of the limited pressure differential available with a vacuum system, a pressurized transfer system would probably be preferable for longer distance transfers.

The final pneumatic transfer system for removing PuF_4 from the reactor is shown in Figure 5. This system eliminated the problems associated with the original product transfer system shown in Figure 1.

The material balance data, obtained individually for each of the 82 runs, included: weight and plutonium assay of the feed and product, weight and plutonium assay of any impure PuF_4 generated, fluoride and sulfate analyses of the feed and product, and fluorine usage. The quantities of sodium fluoride and charcoal used, and the quantities of PuF_4 deposited on the sodium fluoride, and the quantities retained in the reactor, were determined as totals for each of the three series of runs because the quantities of these materials used in a single run were too small to measure accurately.

Because the quantity of PuF_4 needed for a standard calcium reduction charge (approximately 2000 grams) was double the quantity of PuF_4 produced during each pilot plant batch run, two consecutive batches of PuF_4 were combined for each reduction. The data obtained for each of the reductions included: the yield of plutonium metal, analyses of impurities in the plutonium metal, and notations of any abnormalities (i.e., high pressure, evidence of excessive splattering in the reduction vessel) which occurred during the reductions.

Time study and radiation exposure data were collected during the third series of runs, after the transfer system problem had been corrected. The quantities of recycle and waste, and all interruptions and repairs, were recorded for all three operating periods.

Operation

- 1 Transfer PuO₂ to Reactor
- 2 Exothermic Reaction Period
- 3 SO₄ = Removal Period
- 4 Purge Reactor
- 5 Transfer PuF₄ to Receiver
- 6 Blowback Receiver Filter
- 7 Dump PuF₄ Receiver
- Total Time/Cycle

Time (Min)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
5	2	0.5	—	—	—	—	—	—	—	2.5	—	0.5	2.5	—	1.0	1.0	—	1.0	2.5	2.5	2.5	—	—
98	—	—	.08	.02*	—	—	—	—	.06	—	—	1.08	1.06	1.0	1.0	1.0	1.0	—	.06	.06	.06	—	—
100	—	—	.03	.02	—	—	—	—	.05	—	—	1.03	1.03	1.0	1.0	1.0	1.0	—	.05	.05	.04	—	—
20	—	1.0	—	.02	—	—	—	—	1.02	—	—	1.0	1.02	—	1.0	1.0	—	1.0	1.02	1.02	1.02	—	—
5	—	1.0	—	.02	—	—	—	—	1.02	—	—	—	1.02	—	1.0	1.0	—	1.0	1.02	1.02	1.02	1.02	1.02
0.05	—	1.0	—	—	5.0	—	—	—	6.0	—	—	6.0	6.0	—	1.0	1.0	—	1.0	6.0	6.0	6.0	-5.0	—
5	—	0.5	—	—	—	—	—	—	0.5	0.5	-0.5	0.5	—	—	1.0	1.0	—	1.0	0.5	0.5	0.5	—	—
233	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

*Reactor Filter Blowback — 4 scfm — 2 sec Duration at 5 min intervals Throughout Run; — Ave rate = 0.25 scfm

FIGURE 2. Process Sequence and Flows.

Material In (Grams)

Material	Stream							Total
	1	2	3	4	5	6	7	
PuO ₂	1101							1101
Pu(SO ₄) ₂	52							52
F ₂			525					525
C							78	78
NaF						3		3
AR	506	1520		226	13			2265
Total	1659	1520	525	226	13	3	28	3974

Material Out (Grams)

Material	Stream					
		8	9	10	11	Total
PuF ₄					1314	1314
PuF ₄ 2NaF		7				7
O ₂			145			145
CF ₄			206			206
SF ₆			37			37
AR			1506	759		2265
Total		7	1894	759	1314	3974

FIGURE 3. Calculated Overall Material Balance. Basis: 1000 g Pu/batch, F_2 efficiency = 67%, SO_4 content of PuO_2 feed = 2.0% by weight.

Samples from each batch of PuO_2 , PuF_4 , and Pu metal were analyzed for the common cation impurities, as an aid in determining increases occurring during the fluorination process. However, as was found in the earlier work, the results for individual batches correlated poorly, probably because of nonrepresentative sampling or inaccuracies in the analytical results for the PuO_2 and PuF_4 samples. Historically, through the use of standard check samples, impurity results obtained for plutonium metal samples have been found more reliable than for samples of PuO_2 or PuF_4 . Because of the poor correlation found between corresponding PuO_2 , PuF_4 , and plutonium metal samples, the PuO_2 and PuF_4

impurity results were not used in comparing the quantities of impurities introduced by the fluid bed-fluorine and hydrofluorination processes. Instead, a direct comparison of the average impurity levels of the product plutonium metal from both processes, produced during the same time periods, were made. Because the fluid bed-fluorine pilot plant equipment was fabricated from either nickel or Monel 400® (primarily a copper-nickel alloy) copper and nickel were the impurities of major concern.

The three series of runs were made as continuous, around-the-clock, operations. Two operators per 8-hour shift, working on a three-shift basis,

PuO₂ Transfer Procedure

1. Maintain fluidizing argon flow of 0.5 scfm throughout transfer to prevent plugging of fluidizing gas inlet line.
2. Evacuate reactor to 300mm absolute pressure.
3. Open ball valve and immerse transfer line in PuO₂ until transfer is completed.
4. Close ball valve and vacuum source.
5. When reactor and traps are pressurized, vent the traps to the atmosphere.

*Argon purge at pressure higher than reactor operating pressure is maintained to prevent F₂ leakage during fluorination period.

FIGURE 4. Pneumatic Transfer System for Feed Introduction.

provided continuous coverage. Single-operator coverage was maintained during lunch and rest periods. To ensure nitrate and moisture-free feed, all batches of PuO₂ were recalcined on a hot plate before use in the pilot plant. Approximately one-half of the PuO₂ batches evolved copious quantities of NO during the recalcining operation.

Because the pilot plant was located remotely from the production area, it was necessary to remove all PuO₂ and PuF₄ batches from

gloveboxes before and after processing. A cart, provided with radiation shielding, was used to transport material to and from the pilot plant area. This procedure, which would not normally be used for a routine production operation, was responsible for most of the radiation exposure incurred by the operators. The estimate of radiation exposure for a production-scale fluid bed operation did not include this source, assuming the use of pneumatic transfer equipment.

FIGURE 5. Pneumatic Transfer System for Product Removal (Final Design).

DISCUSSION OF RESULTS

The factors considered pertinent in comparing the fluid bed-fluorine process with the hydrofluorination process are discussed below. Based on estimates of the differences in operating cost factors for the two processes, an estimate of the cost savings potential of the fluid bed-fluorine process was made. A discussion of these calculations is included in this section.

Material Balance Data:

The material balance data for the three series of runs is summarized in Table 1. A complete tabulation of the material balance data for all 82 runs is shown in the Appendix A. The plutonium balance for the 82 runs averaged 99.6%.

Appreciable quantities of PuF_4 were retained in the process equipment during each of the three series of runs (123 grams in series 1, 761 grams in series 2, and 741 grams in series 3). This material was removed at the end of each series by partially dismantling the reactor. It should be noted, however, that the quantities retained during series 2 and series 3 were almost the same even though the amount of material processed during series 2 was more than twice as much as in series 3. This indicated that once the void spaces in the reactor had been filled, no further significant retention of material occurred. With the proper design of equipment (eliminating all unnecessary void spaces) the retention of PuF_4 could be reduced appreciably.

The relatively large ratio of recycle material generated during series 2 (2.5%) was due,

TABLE 1. Material Balances and Efficiencies

	Series 1	Series 2	Series 3	Total
(1) Total Pu in (g)	4848	45807	21179	71834
(2) Total product Pu out (g)	4786	45666	21115	71567
(3) % Balance (2) ÷ (1)	98.72	99.69	99.70	99.63
(4) Pu as impure PuF ₄ (g)	11.4	933.5*	21.2	966.1*
(5) Pu on NaF (g)	19.8	195.3	93.0	308.1
(6) Total Pu Recycle (g) (4) + (5)	31.2	1128.8	114.2	1274.2
(7) Pu Recycle ratio (6) ÷ (1) (g/g)	0.0064	0.0246*	0.0054	0.0177*
(8) NaF Used (g)	61	522	358	941
(9) NaF Ratio (8) ÷ (1) (g/g)	0.0126	0.0114	0.0169	0.0131
(10) Charcoal Used (g)	390	4019	1927	6336
(11) Charcoal Ratio (9) ÷ (1) (g/g)	0.0804	0.0877	0.0910	0.0882
(12) F ₂ Used (g)	2202	19848	11116	33166
(13) F ₂ Ratio (12) ÷ (1)	0.454	0.433	0.525	0.462

* Abnormally high impure PuF₄ produced in Series 2 was due to problems with pneumatic transfer system. This was corrected before Series 3.

entirely, to the problems with the pneumatic PuF₄ removal system used during this series. Very little impure PuF₄ was generated during the other runs. The efficiencies and ratios for the runs (shown in Table 1) generally agreed well with the calculated material balance figures shown in Figure 3. The exceptions were the usages of sodium fluoride and charcoal. The average usage of NaF was approximately 15 grams per kg of plutonium processed compared to an ideal usage of 3 grams per kilogram. This was probably owing to the removal of only partially depleted

NaF from the trap. The actual average charcoal usage ratio was 0.0882 grams/gram plutonium processed compared to a stoichiometric ratio of 0.028 grams/gram. The cost comparison calculations were based on the actual usages of NaF and charcoal.

Equipment Reliability and Maintenance:

The only interruptions in operation or maintenance required occurred during the second series of runs, and resulted from the unstable fluid bed performance caused by the pneumatic product withdrawal tube used during this series. The formation of lumps of PuF₄ in the reactor prevented complete product withdrawal after five of the runs in this series. It was necessary to remove the bottom flange from the reactor and manually clean the system before operation could be resumed. Approximately 4 hours downtime resulted each time this cleaning operation was necessary. Some lump formation was evident in several of the other runs made during this series, but the lumps were small enough to pass out through the withdrawal tube without plugging. After revising the product withdrawal system, prior to the third series of runs, no interruptions or equipment malfunctions occurred, and no lumps of PuF₄ were observed. A detailed inspection of all the equipment was made after completing the third series of runs and no evidence of deterioration of any of the equipment was found. A thin deposit of PuF₄ on the surfaces of the compressor valves, caused by the decomposition of PuF₆, was noted after the first series of runs. However, an examination of the valves after the third series showed no significant increase in the quantity of PuF₄ deposited and no problems with the performance of the compressor occurred. Corrosion, a serious problem with the hydrofluorination system, was not evident in any of the fluid bed-fluorine equipment. The recalcining of all PuO₂ feed before charging the reactor, to ensure nitrate-free feed, and the moisture-free nature of the fluorine process appeared to provide a much less corrosive environment than is present with the production hydrofluorination process. Because of the limited duration of the fluid bed-fluorine runs, no quantitative determination of the improvement in equipment life and maintenance requirements could be made. In making the operating cost comparison for the two processes it was assumed that there would be no difference in maintenance costs.

The radiation exposure calculations shown in Appendix B indicate that a properly designed fluid bed-fluorine system, with the same throughput capacity (approximately 36 kg/day plutonium) as the hydrofluorinator could reduce the operator exposure levels by at least a factor of 10. This level would permit operation of the process within the 3 rem/year limit without the rotation of operators. It should be emphasized that without proper design most of the advantages of the fluid-bed-fluorine system are lost and little improvement would be attained. A conceptual layout of a production fluid bed-fluorine system, with the same capacity as the hydrofluorinator, designed for minimum exposure is shown in Figure 6. The radiation exposure calculations are based on an arrangement providing this degree of protection. The radiation exposure calculations compare

average film badge results for the hydrofluorinator operators with calculated exposures using a fluid bed-fluorine system, based on radiation readings taken during the pilot runs. (See appendix B.) The estimated exposures for the fluid bed-fluorine system were based on the following assumptions:

1. Three 2-kg-batch reactors, requiring 4 hours/batch, will process 36-kg/day plutonium. Production reactors with twice the batch capacity of the pilot plant reactor would be required. One additional spare reactor is recommended.
2. Individual reactors are isolated with sufficient shielding so that an operator would not receive exposure from adjacent reactors while working in a reactor cell.
3. No more than 1-kg residual plutonium (as PuF_4) will be present in each reactor cell. By designing the reactors with minimum void spaces where material can be trapped, and by using small, easily cleaned reactor gloveboxes with a minimum of auxiliary equipment present in each glovebox, this requirement can be met. The auxiliary equipment should be located in a glovebox outside the shielded area, as shown in Figure 6.
4. Shielding, 4-in. thick, will be installed on the operating side of each reactor glovebox.
5. The three reactors will be operated by two operators per shift. Each operator will spend no more than an average of 30-minutes per day, working through gloves in the reactor cell area. These assumptions are supported by time study data taken by the Industrial Engineering Department⁴ during the pilot plant runs. They are based on the use of remotely operated pneumatic transfer equipment for loading and unloading the reactors. Based on the pilot plant results, the 30-minutes per day allowed for in-glove operations appears conservative.
6. All routine operations will be performed remotely from a well-shielded control-room area, so that operators receive no significant radiation in normal operation.

By implementing the fluid bed-fluorine process, along with comparable improvements in PuF_4 handling techniques in the calcium reduction

process, radiation exposure from PuF_4 could be reduced to acceptable levels.

Generation Rates for Recycle Material and Plutonium-Contaminated Waste:

The hydrofluorination process generates large quantities of: (1) impure PuF_4 , which requires reprocessing through the complete recovery system, and (2) plutonium contaminated caustic waste solution, which is processed for water removal and eventually shipped off-site for burial. The fluid bed-fluorine process has the potential of substantial reductions in the quantities of both categories of material generated. The quantities of impure PuF_4 and plutonium-contaminated caustic waste solution generated by the hydrofluorination process from September through November 1971 is shown in Appendix C. The fluid bed-fluorine process routinely generates no discardable waste comparable to the caustic waste solution from the hydrofluorinator. The quantity of impure PuF_4 generated during the pilot plant fluid bed-fluorine runs (excluding the runs in which the first pneumatic PuF_4 removal system caused plugging problems), was very low. Based on the material balance data shown in Table 1, the total plutonium recycle ratio anticipated for the fluid bed-fluorine process is approximately 0.006-gram plutonium (as recycle) per gram plutonium (as PuF_4 product). This includes both impure PuF_4 and PuF_4 -NaF residue generated in the sodium fluoride trap. This compares to a ratio of 0.148-gram plutonium (as impure PuF_4) per gram plutonium (as PuF_4 product) for the hydrofluorinator for September through November 1971. The quantity of spent NaF residue averaged 0.013-gram per gram plutonium in the feed. The total monthly quantities of residues (PuF_4 and NaF) anticipated for a production-scale fluid bed-fluorine system, based on an average feed rate of 400 kg/month PuO_2 , would be 5.75-kg NaF combined with 2.65-kg plutonium (as PuF_4). Sodium fluoride, which is soluble in water, presents no special recovery problems.

Product Quality:

Although a number of direct analyses of the PuF_4 provide useful process control information, the results obtained in the calcium reduction operation provide the ultimate tests for

satisfactory PuF_4 quality. The standard analyses obtained for each batch of PuF_4 included % F^- , % SO_4^{2-} , and the levels of the cation impurities. Although unsatisfactory results will generally be obtained in the calcium reduction process if the results of these analyses are not acceptable, acceptable levels do not necessarily ensure satisfactory PuF_4 quality, probably because of other unmeasured variables. Because changes in parameters in some of the other process steps have an effect on the reduction results, it is difficult to correlate directly the performance of the fluorination or hydrofluorination operations with reduction results. However, by comparing a large number of reduction results obtained from hydrofluorinator-produced PuF_4 with PuF_4 obtained from the fluid bed-fluorine process during the same operating periods, any differences in the effects of variables in the other process steps should be minimal. Tables 2 and 3 show the comparable reduction yields and cation impurity levels for plutonium metal produced from PuF_4 from the two processes. These data show that the reduction yields from fluid bed-fluorination-produced PuF_4 averaged approximately 97.5% (excluding the reductions of PuF_4 produced during the series 2 runs, when problems with the product removal system were encountered). This compares to an average reduction yield of 89.0% for hydrofluorinator-produced PuF_4 during the same time period.

The average reduction yield for all fluid bed runs, including Series No. 2, was 95.1 wt%. This was well above the yields obtained from the hydrofluorinator-produced PuF_4 for the same period.

A comparison of the average impurity levels shows no significant difference between the two processes. Since the fluid bed-fluorine equipment

is composed entirely of nickel and a copper-nickel alloy, with no iron present, the iron contamination of the product plutonium was probably not increased significantly in either PuF_4 production operation.

The primary benefit of better yields of plutonium in the calcium reduction operation is the resulting reduced quantity of plutonium in the slag. Any plutonium in the slag must be recovered and recycled through the purification process.

Direct Labor Requirements:

Time-study data collected during the third series of runs by the Industrial Engineering Department⁴ indicated that the operating labor requirements would be the same for both processes (two operators/shift). This estimate was based on a system similar to that shown in Figure 6. The labor requirements shown were based on liquid fluorine supply system. Some additional labor would be required if gas cylinders are used. It was estimated that supplemental labor requirements, including maintenance, analytical laboratories, and health physics support, would also be approximately the same for both processes.

Cost Savings Calculations:

The cost-savings calculations (appendix D) indicate that the fluid bed-fluorine process offers a potential savings of about \$1.25 million per year. This savings would primarily result from the much lower generation rates of plutonium-contaminated waste and recycle, predicted for the fluid bed-fluorine process. (The cost of processing the recycle material was estimated to be \$1000

TABLE 2. Reduction Data for Hydrofluorinator-produced PuF_4 During the Period of Fluid Bed-fluorine Runs

Period	Pu Metal Produced (kg)	Average Reduction Yield (%)	Average Impurities in Plutonium Metal (ppm)					
			Al	Cr	Cu	Fe	Ni	Si
June 1971	177	90.4	55	36	8	263	31	12
August 1971	281	89.1	42	39	10	369	46	22
September 22 to October 1, 1971	130	90.0	35	35	35	412	113	26
October 11 to October 25, 1971	241	87.4	47	65	10	476	115	78
Total Weighted Average	829	89.0	45	45	13	384	73	22

TABLE 3. Reduction Data

Run	PuF ₄ Analyses		Reduction Yield (%)	Impurities in Plutonium Metal (ppm)						Remarks
	%F	%SO ₄		Al	Cr	Cu	Fe	Ni	Si	
Series 1 (May 1971 to June 1971)										
1-2	23.4	<0.1	97.5	95	32	50	316	80	30	
3-4	23.5	<0.1	97.1	95	38	50	309	88	23	
5-6	23.4	<0.1	98.5	72	32	40	306	62	28	
Avg.	23.4	<0.1	97.7	87	34	47	310	77	27	
Series 2 (August 1971 to September 1971)										
7-8	24.1	<0.1	92.8	41	35	22	623	145	10	Splattering, high pressure
9-10	24.3	<0.1	94.0	96	35	10	283	63	17	
11-12	23.3	<0.1	89.9	52	39	9	330	63	17	Splattering, high pressure
13-14	23.4	<0.1	96.4	31	47	6	270	56	28	
15-16	18.9	<0.1	92.6	47	30	12	265	54	16	
17-18	23.2	<0.1	90.7	57	33	11	240	53	48	High pressure
19-20	23.7	<0.1	98.2	54	42	11	259	46	49	
21-22	23.6	<0.1	92.7	47	26	4	230	48	24	Splattering, high pressure
23-24	24.2	<0.1	99.8	57	24	7	233	46	21	
25-26	23.1	<0.1	98.8	19	29	5	274	40	22	
27-28	23.0	<0.1	88.4	93	32	2	287	64	10	High pressure
29-30	23.7	<0.1	97.8	27	30	3	223	49	35	
31-32	23.5	<0.1	97.3	31	28	6	260	55	22	
33-34	23.4	<0.1	98.3	31	48	5	406	67	21	
35-36	21.6	<0.1	97.5	46	52	22	538	83	30	
37-38	22.1	<0.1	97.7	45	59	9	468	83	37	
39-40	21.5	<0.1	97.9	48	60	19	456	103	37	
41-42	22.0	<0.1	93.4	62	59	16	472	86	26	
43-44	23.0	<0.1	98.4	18	37	11	448	89	13	
45-46	22.8	0.6	97.6	41	57	20	536	85	67	Splattering, high pressure
47-48	24.0	<0.1	97.3	40	38	12	377	66	30	
49-50	23.7	<0.1	97.8	37	37	9	357	59	44	
51-52	22.8	<0.1	88.1	40	25	12	571	27	25	Splattering
53-54	23.7	<0.1	97.3	20	23	6	295	31	28	
55-56	23.6	<0.1	86.1	35	57	10	1170	140	25	Splattering
57-58	23.9	<0.1	96.6	33	21	7	321	34	25	
Avg.			95.1	44	39	10	392	67	28	
Series 3 (September 1971 to October 1971)										
59-60	23.1	<0.1	97.9	27	13	6	187	37	30	
61-62	22.2	<0.1	98.6	26	13	8	205	54	13	
63-64	23.2	<0.1	99.0	17	13	11	215	43	14	
65-66	23.9	<0.1	98.2	34	15	11	193	39	14	
67-68	23.7	<0.1	98.0	37	19	6	181	35	17	
69-70	23.9	<0.1	96.9	43	19	16	167	32	17	
71-72	23.9	<0.1	98.0	30	16	7	180	35	7	
73-74	24.0	<0.1	87.9*	19	11	33	159	34	25	
75-76	23.4	<0.1	97.1	41	16	6	157	35	31	
77-78	23.5	<0.1	**							
79-80	23.5	<0.1	97.5	18	15	7	147	37	11	
81-82	23.4	<0.1	**							
Avg.			97.9	29	15	11	179	38	17	
Avg. All Runs			96.1	43	32	13	331	60	25	

*Crucible failure occurred during reduction—not related to properties of the PuF₄.**PuF₄ was used for other experimental work.

per kg of plutonium processed.) The higher raw material cost for the fluid bed-fluorine process—as a result of the high cost of fluorine—is almost insignificant. The other cost factors should be approximately the same for the two processes.

Safety

Although fluorine, potentially, is a very hazardous material because of its extreme toxicity and reactivity, the safety experience at Rocky Flats and at other industrial locations using fluorine, has been excellent. No accidents or injuries involving fluorine have occurred during 5 years in which fluorine has been used at Rocky Flats. It should be emphasized, that because of the potential hazard, complete training of

operators in the safe handling and use of fluorine is essential before they are exposed to processes using fluorine.

Fluorine is presently supplied to the pilot plant system from gas cylinders containing 4-1/2 pounds of fluorine per cylinder. The process of changing the cylinders presents the greatest single hazard in using fluorine. Bulk liquid fluorine should be considered for process fluorine use. Not only should this system be safer but it would be much cheaper, eliminating the cost of handling large numbers of fluorine cylinders. In addition to the handling cost, the approximate cost of bulk liquid fluorine is \$8 per pound compared to a cost of about \$14 per pound for fluorine in gas cylinders.

Appendix A

MATERIAL BALANCE DATA

Run No.	PuO ₂ In (g)	Pu/PuO ₂ (g/g)	Total Pu In (g)	PuF ₄ Product (g)	Impure PuF ₄ (g)	PuF ₄ on NaF (g)	PuF ₄ Retained	Total PuF ₄ out (g)	Pu/PuF ₄ (g/g)	Total Pu out (g)	F ₂ Used (g)	Charcoal Used (g)	NaF Used (g)
Series 1													
1	926			928									
2	924			1024									
3	1009			1073									
4	1008			880									
5	898			1180									
6	938			1040									
Total	5703	.8501 (Avg.)	4848		15	26	123	6289	0.761 (Avg.)	4786	2202	390	61
Series 2													
7-8	2065			2035	125*						791		
9-10	2100			2218							715		
11-12	2075			2308							740		
13-14	2100			2139	184*						820		
15-16	2085			2348	100*						765		
17-18	2063			2263							765		
19-20	2069			2349							790		
21-22	2078			2347							765		
23-24	2040			2258							765		
25-26	2066			2291							740		
27-28	2077			2290							790		
29-30	2058			2313							740		
31-32	2048			2298							740		
33-34	2060			2227							740		
35-36	2060			2286							740		
37-38	1984			1999	189*						740		
39-40	2036			2157	88*						765		
41-42	2042			1699	518*						765		
43-44	2058			2002							765		
45-46	2030			2305							791		
47-48	2073			2249							765		
49-50	2068			2311							765		
51-52	2074			2220							791		
53-54	2067			2098							765		
55-56	2043			2421							765		
57-58	2056			2178							765		
Total	53575	.8551 (Avg.)	45807	57609	1224	256	761	59850	0.7627 (Avg.)	45666	19848	4019	522
Series 3 (September, 1971)													
59-60	2084			2255							943		
61-62	2049			2256							943		
63-64	2031			2241							918		
65-66	2100			2231							918		
67-68	2138			2334							943		
69-70	2123			2317							918		
71-72	2074			2229							943		
73-74	2060			2261							918		
75-76	2017			2182							918		
77-78	1971			2221							918		
79-80	2036			2287							918		
81-82	2085			2224							918		
Total	24768	.8551 (Avg.)	21179	27038	28	123	741	27930	0.7560 (Avg.)	21115	11116	1927	358

* Abnormally high impure PuF₄ produced in Series 2 was due to problems with pneumatic transfer system. This was corrected before Series 3.

Appendix B

RADIATION EXPOSURE OF PERSONNEL

EXPOSURE FROM OPERATION OF
HYDROFLUORINATOR

	Neutron (mrem)	Gamma (mrem)	Total (mrem)
Average 2-week penetrating radiation for hydrofluorinator operators for August and September 1971 (film badge results)*	358	82	440

Basis: 2 operators/shift, 3 shifts/day, 36 kg/day PuO_2 processed.

$$\text{Average hourly exposure} = \frac{440 \text{ mrem}}{80 \text{ hr/2 weeks}} = 5.5 \text{ mrem/hr}$$

$$\begin{aligned} \text{Unit exposure rate} &= \frac{24 \text{ hr}}{\text{operating day}} \div 36 \text{ kg/day} \times 2 \text{ operators} \times 5.5 \text{ mrem/hr} \\ &= 7.33 \text{ mrem/kg PuO}_2 \text{ processed} \end{aligned}$$

*Personal communication, R. E. Hayne, Health Physics Unit Supervisor, Rocky Flats Division, Dow Chemical, U.S.A.

ESTIMATED EXPOSURE FOR FLUID
BED FLUORINE PROCESS

Calculated exposure while operator is working, through gloves, in reactor glovebox
(based on pilot plant operation).**

7.0 mrem/hr

Assumptions:

1. 2 kg PuF_4 in reactor
2. 1 kg PuF_4 residual in glovebox
3. 4-in. neutron shielding on glovebox exterior

**Personal communication, C. G. Haynes, Health Physics, Rocky Flats Division, Dow Chemical, U.S.A.

UNIT EXPOSURE RATE

Additional Assumptions:

1. 2 operators per shift will operate three reactors
2. 3 reactors will process 36 kg/day PuO_2
3. Controls will be located in well-shielded control room
4. Adequate space and/or shielding between reactors will prevent significant cross radiation
5. Each operator will spend no more than an average of 30 minutes per day in close proximity to equipment containing PuF_4 (manual operations performed through gloves;

$$\begin{aligned} \text{Unit exposure rate} &= \frac{7.0 \text{ mrem}}{\text{hr}} \times \frac{0.5 \text{ hr}}{\text{operator-day}} \times 6 \text{ operators} \div 36 \text{ kg/day PuO}_2 \\ &= 0.6 \text{ mrem/kg PuO}_2 \text{ processed.} \end{aligned}$$

Appendix C

**RECYCLE AND PLUTONIUM CONTAMINATED WASTE
FROM PRESENT HYDROFLUORINATION PROCESS**

	Sept. 1971	Oct. 1971	Nov. 1971	Total
1. Pu in PuO ₂ charged to hydrofluorinator (kg)	368.9	338.3	550.8	1258.0
2. Pu in PuF ₄ product (kg)	344.8	286.8	463.9	1095.5
3. Pu as impure PuF ₄ (impure recycle, waste, or retained in hydrofluorinator glovebox) (kg)	24.1	51.5	86.9	162.5
4. Potassium hydroxide solution used for HF removal (gal)	8600	11000	7860	27460
5. Plutonium in spent potassium hydroxide solution (to waste disposal) (g)	216	171	131	518

Assuming that all material loss in the hydrofluorinator (item 3; above) is eventually recovered and recycled through the process, the plutonium recycled per kg of Pu as PuF₄ product is:

$$\frac{162.5}{1095.5} \times 100 = 14.8\%$$

Potassium hydroxide usage and spent KOH generated:

$$\frac{27,460 \text{ gal}}{1095.5} = \frac{25.5 \text{ gal KOH}}{\text{kg Pu as PuF}_4 \text{ product}}$$

Plutonium to waste disposal in spent caustic:

$$\frac{518 \text{ grams}}{1095.5 \text{ kg}} = \frac{0.473 \text{ g Pu}}{\text{kg Pu as PuF}_4 \text{ product}}$$

Appendix D

INCREMENTAL OPERATING COSTS

The following comparison of operating costs considered only the factors which reflect differences in operating costs for the two processes. The factors considered are as follows: (1) raw material costs, (2) cost of reprocessing residues, (3) waste disposal cost, and (4) value of plutonium lost in waste streams. All other cost factors were assumed to be the same for both processes. (A discussion of the other cost factors is given in the Results-Discussion section.)

ASSUMPTIONS:

1. Residue processing cost \$1,000 per kg plutonium contained in residue
2. Plutonium value \$40 per gram*

*AEC Appendix 1701, Part IV, Pricing, p 20.

HYDROFLUORINATION PROCESS

(Basis — 1 kg Pu metal produced)

Plutonium (as PuO_2) to hydrofluorinator:

$$1 \text{ kg Pu metal} \div \text{reduction efficiency} \times 1.148 \frac{\text{Pu to hydrofluorinator}}{\text{Pu out hydrofluorinator as PuF}_4 \text{ product}} \\ = 1.275 \text{ kg Pu to hydrofluorinator per kg Pu metal produced.}$$

Raw Material Cost

Anhydrous hydrogen fluoride:

$$200 \text{ lb per day HF} \times \frac{\$33.03}{100 \text{ lb}} \div 36 \text{ kg per day} \times 1.275 = \$ 2.34$$

Potassium hydroxide solution:

$$\frac{25.5 \text{ gal KOH}}{\text{kg Pu as PuF}_4 \text{ product}} \div 0.90 = \frac{28.3 \text{ gal}}{\text{kg Pu metal}} \\ 28.3 \times 10 \text{ lb per gal} \times \frac{\$3.90}{100 \text{ lb}} = \$ 1.10$$

Total Raw Material Cost \$ 3.44

Waste Disposal Cost

$$\frac{28.3 \text{ gal KOH}}{\text{kg Pu metal}} \times \$.50 \text{ per gal (disposal cost)} = \$ 14.15$$

Cost of Reprocessing Residues

$$\frac{0.275 * \text{kg Pu recycled}}{\text{kg Pu metal produced}} \times \frac{\$1000}{\text{kg Pu as residues}} = \$275.00$$

Value of Plutonium in Spent Caustic

$$\frac{0.473 \text{ g Pu to waste}}{\text{kg Pu as PuF}_4 \text{ product}} \div 0.90 \times \$40 \text{ per gram} = \$21.02$$

Total Incremental Cost \$313.61

FLUID BED-FLUORINE PROCESS

(Basis - 1 kg Pu metal produced)

Plutonium (as PuO_2) to fluorination:

$$\begin{aligned} & 1 \text{ kg Pu metal} \div 0.975 \text{ reduction efficiency} \times 1.006 \frac{\text{Pu in PuF}_4 \text{ product}}{\text{Pu charged as PuO}_2} \\ & = \frac{1.031 \text{ kg Pu to fluorination}}{\text{kg Pu metal produced}} \end{aligned}$$

*This includes residues recycled from hydrofluorinator and reduction slag at reduction yield efficiency of 90%.

Raw Material Cost

Fluorine:

$$\$14.00 \text{ per lb} \times \frac{2.2 \text{ kg}}{\text{lb}} \times \frac{0.525 \text{ kg F}_2}{\text{kg Pu}} \times (1.031) = \$16.70$$

Sodium Fluoride:

$$\$7.50 \text{ per lb} \times \frac{2.2 \text{ kg}}{\text{lb}} \times \frac{0.017 \text{ kg NaF}}{\text{kg Pu charged}} \times (1.031) = .28$$

Charcoal:

$$\$0.45 \text{ per lb} \times \frac{2.2 \text{ kg}}{\text{lb}} \times \frac{0.091 \text{ kg charcoal}}{\text{kg Pu charged}} \times (1.031) = .09$$

Total Raw Material Cost \$17.07

Cost of Reprocessing Residues

$$\frac{0.031 * \text{kg Pu recycled}}{\text{kg Pu metal produced}} \times \frac{\$1000}{\text{kg Pu as residues}} = 31.00$$

Total Incremental Cost \$48.07

Differential Cost $\$313.61 - \$48.07 = \$265.54$ kg Pu metal produced

With a monthly average plutonium metal production rate of 400 kg:

The potential monthly savings for the fluid bed-fluorine process is:

$$400 \text{ kg} \times \$265.54 = \$106,200.00$$

The potential yearly savings would be: $\$106,200 \times \frac{12 \text{ mo}}{\text{yr}} = \$1,274,000.00$

*This includes residues recycled (NaF and impure PuF_4) and reduction slag at reduction yield efficiency of 97.5%

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3. Personal communication, R. E. Hayne, Health Physics Unit Supervisor, Rocky Flats Division, Dow Chemical, U.S.A.
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