[redacted] DECLASSIFIED
(CLASSIFICATION)

BEST AVAILABLE COPY

GENERAL ELECTRIC

HANFORD ATOMIC PRODUCTS OPERATION – RICHLAND, WASHINGTON

DOCUMENT NO.
HW-81662

SERIES AND COPY NO.
[redacted]

DATE
May 1, 1964

☒ [redacted]CTED DA[redacted]
THIS D[redacted] CONTAINS [redacted]D DATA A[redacted]
DEF[redacted]N THE ATO[redacted]RGY ACT O[redacted]
[redacted]NSMITTAL [redacted] DISCLOSURE [redacted]
[redacted]TENTS IN [redacted]NER TO AN UNA[redacted]ED
[redacted]ERSON IS [redacted]ITED.

TITLE

ANALYSIS OF ALTERNATIVES: PLUTONIUM BUTTON-LINE IMPROVEMENTS

☐ OTHER OFFICIAL CLASSIFIED INFORMATION
THIS MATERIAL CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECS. 793 AND 794, THE TRANSMISSION OR REVELATION OF WHICH IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

AUTHOR
B. M. Johnson
V. W. Smith
E. O. Swain
M. J. Szulinski
L. L. Zahn

ISSUING FILE

THIS DOCUMENT [redacted]T BE LEFT UNATTEN[redacted]HERE AN UNAUTHORIZ[redacted]N MAY HAVE A[redacted] TO IT. WHEN [redacted]SE, IT MUST BE S[redacted]AN APPROVED LOCKE[redacted]TORY WITHIN AN [redacted]VED GUARDED [redacted] WHILE IT IS YOUR[redacted]SION AND UNTIL YOU [redacted]TAINED A SIGNED R[redacted] FROM CLAS[redacted]FILES, IT IS YOU[redacted]NSIBILITY TO KEEP I[redacted]TS CONTENTS WITHIN[redacted]IMITS OF TH[redacted]JECT AND FROM AN[redacted]THORIZED PERSON. ITS[redacted]MITTAL TO, AND STO[redacted] YOUR PLACE [redacted]SIDENCE IS PRO[redacted] IT IS NOT TO BE D[redacted]TED. IF ADDITIONAL [redacted]S ARE REQUIRED, [redacted]AIN THEM FROM [redacted]ELATED ISSUING FILE. [redacted]RSONS READING THIS DOCU[redacted]NT ARE REQUESTED [redacted]O SIGN IN TH[redacted]PROVIDED BELOW.

ROUTE TO:	PAYROLL NO.	LOCATION	FILES ROUTE DATE	SIGNATURE AND DATE
300 Files				

REFERENCE COPY
RECEIVED 300 AREA
JUN 24 1964
RETURN TO
TECHNICAL INFORMATION FILES

THIS DOCUMENT IS PUBLICLY AVAILABLE

~~THIS DOCUMENT HAS BEEN SCANNED AND IS STORED ON THE OPTICAL DISK DRIVE~~

[redacted] N

[redacted] Y

[redacted]

DECLASSIFIED

54-3000-340 (3-57) AEC-GE RICHLAND, WASH.

[redacted]
(CLASSIFICATION)

DECLASSIFIED

[redacted]

HW-81662

This document consists of
24 pages. [redacted]

ANALYSIS OF ALTERNATIVES:
PLUTONIUM BUTTON-LINE IMPROVEMENTS

By

B. M. Johnson - Research and Engineering
V. W. Smith - Weapons Manufacturing
E. O. Swain - Facilities Engineering
M. J. Szulinski - Research and Engineering
L. L. Zahn - Facilities Engineering

CHEMICAL PROCESSING DEPARTMENT

May 1, 1964

Classification Cancelled and Changed To
DECLASSIFIED
By Authority of RM Iten
CG-PR-2, 4-13-94
By J E Savely 4-16-94
Verified By Jerri Maley, 4-18-94.

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract #AT(45-1)-1350
between the Atomic Energy Commission and the General Electric Company

[redacted]A

[redacted] manner to an unauthorized person [redacted].

[redacted]

[redacted]

[redacted]

THIS DOCUMENT IS
PUBLICLY AVAILABLE

DECLASSIFIED

[redacted]

[redacted]

[redacted]

[redacted]

Distribution

1. R. A. Connell
2. J. B. Fecht
3. W. S. Frank
4. W. J. Gartin
5. M. K. Harmon
6. W. M. Harty
7. H. H. Hopkins, Jr.
8. B. M. Johnson
9. B. F. Judson - J. B. Kendall
10. P. H. Reinker
11. H. P. Shaw
12. V. W. Smith
13. R. E. Smith
14. A. E. Smith
15. R. J. Sloat
16. M. J. Szulinski
17. R. E. Tomlinson
18. J. H. Warren
19. L. L. Zahn
20. 300 Files
21. Record File
22. Extra
23. Extra

The following data are based on the existing General Electric organization, and no provision or consideration has been given to transfer operations which will take place within this period of time. Similar data prepared by other contractors may differ widely, based on assumptions used.

[redacted]

[redacted]

ANALYSIS OF ALTERNATIVES: PLUTONIUM BUTTON-LINE IMPROVEMENTS

INTRODUCTION

Reduction of plutonium nitrate solution to metal in the 234-5 Building is accomplished in a processing complex, the button line portion of the Remote Mechanical Line (RMC), which (a) converts the nitrate solution to an oxide via precipitation of the Pu(IV) oxalate followed by calcination, (b) hydrofluorinates the oxide to PuF_4, and (c) reduces the tetrafluoride to metal with calcium metal. These steps are designated as Tasks I, II, and III, respectively. The present facility and its predecessor, the RMA Line, have contributed very significantly to Hanford's ability to produce plutonium metal from nitrate solution at a unit cost below that of any other AEC site because of the high capacity and continuous mode of operation in Tasks I and II.

Although the performance of the processing complex has been acceptable, several areas of deficiency are evident in the facility:

(1) Maintenance costs have more than doubled over the three years of operation, principally as the result of process and equipment difficulties in the Tasks I and II operations. The heavier maintenance load, in addition to raising costs, increases the risk of plutonium contamination and deposition in personnel through accidental contact, contaminated injuries, and inhalation.

(2) Criticality control within the Task I operation is satisfactory but heavily dependent on administrative controls. Complete physical containment of plutonium with the process equipment cannot be assured, and spills cannot be easily controlled.

(3) Purity of the plutonium metal has been intermittently below specifications. The principal sources of difficulty have been carbon contamination,carried over from the oxalate precipitation step,and inadequate feed purity because recycle of plutonium scrap has been handled by improvised procedures since the April, 1962, criticality incident in the reclamation facility.

(4) Radiation exposure is an area of concern. While the established dosage limits do not require the use of larger numbers of operators than necessary to man the work stations, the processing to metal of plutonium irradiated to much above the present level would require additional operators to avoid overexposing any individual.

It is anticipated that within the next three years these deficiencies must be corrected in order to maintain continuity of operation.

[redacted]

Research and development on a new reduction process has been in progress over the past three years. The process embraces the direct calcination of plutonium nitrate to plutonium dioxide, the chlorination of the plutonium, and its reduction to the metal by electrowinning. Based on the assumption that the present button line would have to be replaced within the relatively near future because of the limited equipment life anticipated under the very corrosive processing conditions, the development of a new technology as a basis for building a replacement facility could potentially further improve Hanford's ability to produce metal at the minimum unit cost.

In December, 1963, a study was undertaken to define and evaluate the operational and economic parameters pertinent to the decision to improve or replace the present button line. Several factors prompted this study: (1) Experience with the operation of the button line indicated that CPD should adhere to the goal to correct the deficiencies of the facility during FY 1966. Tentative plans had been made to budget for construction of a new line in that year, and the timing of the development program was aimed at providing the necessary technology for that schedule. (2) A change in procedure of budgeting for capital facilities required that detailed design criteria of the project be prepared prior to budgeting. This change necessitated the criteria to be established before June, 1964, and consequently required a speed-up in the schedule of providing technological data. In view of the early need date for the project scope, it was also necessary to evaluate whether or not the development program had progressed sufficiently to allow budgeting for a new line in FY 1966. (3) Announcement of a cutback in plutonium production at Hanford indicated that a new line would be more difficult to justify because the reduced throughput would result in (a) a greater impact of amortization on the unit cost of plutonium and (b) a reduced need for the higher operating efficiency anticipated in a new line.

This paper serves to document the study and to present the conclusions and recommendations that ensued.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Optimum Process

The relative merits of process steps for converting plutonium nitrate to metal were systematically considered. Exhaustive comparisons were made, principally between those process steps currently in use at Hanford and those under development for the new line. Processes that are used for plutonium reduction operations at other AEC sites were considered in less detail and rejected either because of throughput limitations or incompatibility with preceding process steps in the Purex and Redox plants.

The task force concluded that, if the detailed design criteria of a new button line must be established at this time for inclusion in the FY 1966 capital facilities budget, the optimum process on which to base the design is one involving direct calcination of plutonium nitrate to the oxide, in

[redacted]

a screw calciner; fluorination to PuF_4 in either a stirred-bed reactor or a stirred-fluidized-bed reactor; and reduction to the metal with calcium in a bomb. This process differs from the existing one principally in the Task I operation; direct calcination would be used in place of oxalate precipitation and calcination. The principal benefits offered by direct calcination are complete containment of process materials with a resultant increase in nuclear safety and decrease in radiation exposure. Other advantages are lower anticipated operating cost of $75,000 annually and a capital cost saving of $140,000. The principal disadvantage is that calcination, although it introduces no carbon into the system (a notable advantage), has no capability for decontaminating the plutonium from metallic impurities and consequently requires a higher purity feed.

A comparison of the present bomb reduction of PuF_4 with electrowinning from a chloride melt indicated that although both were technically feasible the former should be used for scope design of a new line at this time. The capital costs of an electrowinning facility would be $180,000 more than those for installation of bomb reduction; moreover, electrowinning would require an additional $100,000 capital expenditure in the reclamation facility to accommodate the chloride recycle. However, these cost increments would be partially offset by lower anticipated operating costs for the new process (electrowinning); the difference was estimated to be about $55,000/year on the line and $50,000/year in the reclamation facility due to a lower quantity of recycle. The decisive factor in the rejection of electrowinning was the consensus that the process required at least an additional year of development, involving expenditures up to $150,000. Thus, scope design would have to be delayed a year or face what was estimated to be a 25 percent chance of having to undergo a major, and perhaps very costly, revision.

The comparison of fluorination with chlorination of the oxide, assuming the halogen compound would be reduced with calcium metal in a bomb in either case, led to the conclusion that fluorination is the preferable operation. Chlorination offered the advantages of (1) potentially lower radiation (considerably less alpha-n reaction), (2) a smaller volume of recycle (higher solubility of chloride slag), and (3) some decontamination from metal contaminants. However, these advantages were more than offset by (1) the nuclear and chemical safety problem introduced by the hygroscopic nature of the plutonium chloride and by (2) the requirement of higher conversion during halogenation to attain satisfactory yield during reduction. Cost comparisons showed no appreciable difference in the capital cost of a new button line but pointed up the need with chlorination for an additional $250,000 expenditure in the reclamation facility to handle the large (as compared with electrowinning) volume of chloride recycle. Over-all operating costs (line and recycle) of the two alternatives appear to be approximately comparable, the lower recycle operating cost associated with chlorination being nearly offset by higher anticipated maintenance costs on the line.

The conclusion that direct calcination should be adopted in place of oxalate precipitation is contingent upon the feasibility of obtaining pure plutonium

[redacted]

nitrate from the separations plants and reclamation facility; the feed material to the calcination step must be sufficiently free of metallic impurities to eliminate the need for further decontamination in the button line. Personnel of Purex Process Engineering and Plutonium Process Engineering studied the feasibility of establishing such a feed purity specification and concluded that a capital expenditure of $45,000 in Purex and $10,000 in the reclamation facility would probably enable those facilities to produce nitrate solution of sufficient purity at little or no additional operating cost.

The study also considered the alternatives of constructing a new button line or of extensively renovating the existing line. Renovating would involve the replacement of hoods containing the Tasks I and II operations, the installation of a new direct calciner and a new fluorinator, and the provision of auxiliary and supporting equipment as required. Such a facility would correct essentially all the deficiencies of the present line. Complete containment of process materials would be assured, thereby eliminating the nuclear safety problem associated with oxalate filtration and decreasing markedly the radiation exposure. The improvement in operation anticipated in the renovated line should result in over-all operating costs which are within $50,000 of those for a completely new line. Capital cost estimates of the two alternatives were $1,900,000 for a new facility and $445,000 for a revamped line; hence, the payoff period for a new line vs a revamped line would probably be in excess of 20 years.

The ensuing recommendations of the study were that construction of a renovated line using direct calcination, fluorination, and reduction with calcium metal in a bomb be undertaken. As a corollary, a recommendation was made that development work on chlorination be stopped. Work on electrowinning could profitably be diverted to electrorefining, a non-aqueous electrolytic dissolution-deposition process for purifying plutonium metal. Electrorefining would provide a backup route for obtaining high purity metal and would use most of the technology developed for electrowinning.

Premises

In the absence of specific information on the future commitments for producing plutonium metal at Hanford, the following premises were used to guide the estimation of required button line capabilities.

1. The need for weapons-grade plutonium within the AEC complex will continue at a rate at least one-half that at present, and purity requirements will become more stringent.

2. The business scope of Hanford will probably include one of the following: (a) continued fabrication at about the current rate, (b) expanded fabrication, including retrofit, and (c) shipment of Hanford product as buttons.

e. Need will develop for U-233 at 250 to 1250 kg/year.

[redacted]

DECLASSIFIED

4. Hanford will be designated to receive and store plutonium nitrate or oxide from Nuclear Fuels Service. Hanford must be capable of shipping oxide and of recovering Am-241 from the stockpile.

Based on the above premises, the following assumptions were made regarding the capacity and flexibility needed in the new or improved button line facility.

a) The need to produce plutonium metal irradiated to levels above 1400 MWD/T is remote; above this level, interest will probably be limited to producing plutonium oxide except for isolated requests. These small orders can be handled in the special handling facility (Room 179-B) in the 234-5 Building if this facility is authorized.

b) Capacity requirements for producing metal will not be markedly less than the current level of production.

c) The facility requirements for handling U-233 is dependent on the size of program that develops but has relatively little impact on the alternatives involved in choosing the optimum process or the selection of a new line vs. a renovated line. The small initial quantity (25 kg) of U-233 metal involved in the proposed test program will be handled in the 179-B facility. If a decision is made to engage in a large-scale program of U-233 production, a separate production line would be required within 234-5. Consequently, very little weight was put on the possible interaction of the U-233 program with the study of the plutonium button line.

d) Specifications on allowable metallic impurities in plutonium metal will probably become more stringent than those currently in effect. Even greater significance will be attached to the necessity of producing a product that is "in control", i.e., one in which the variation in impurities is small.

PRESENT STATUS OF BUTTON LINE(1)

The present RMC Line for plutonium reduction has evolved from the initial RG Line (rubber glove) installed in 1949, through the first remote mechanical line, RMA, installed in 1955. The improved and shielded RMC Line was placed in operation in 1960. Capital expenditure was $1,845,000 for the button line portion, and capital improvements have averaged about $90,000 per year following the first year of operation.

DECLASSIFIED

[redacted]

Operating costs have steadily increased since the RMC Line was put into service, primarily due to the increasing maintenance costs which are shown in Figure I. Task III maintenance costs have been essentially constant while those of Task I and Task II have increased sharply. The general pattern shown in Figure I also approximates the previous expense performance of the RMA Line. The high failure rate in equipment is not unexpected in view of highly corrosive and abrasive materials being handled (anhydrous HF, oxalic acid, plutonium nitrate and several solid compounds of plutonium). Experience at all AEC sites has shown that thus far no button line has been operated beyond about seven years.

Two principal operating deficiencies are inherent in the design of the line, high radiation exposure and uncertain criticality control. In addition, the purity of the metal product has intermittently been below specification.

The exposure of operating personnel to ionizing radiation is an important factor to be evaluated. Both gamma and neutron radiation are of concern; the gamma originates from decay of plutonium and its daughters, and the neutrons are produced both by spontaneous fission of plutonium and the alpha-n reaction of the fluorine atoms in PuF_4. Measurements of radiation levels near the Task I and Task II hoods have led to the estimation that powder distributed about the hood due to incomplete containment is the source of more than 80 percent of the radiation. Considerable effort has been expended to reduce personnel exposure by shielding portions of the line but has not been completely effective because:

(1) The hood design presents large expanses of hard to clean hood surfaces resulting in work stations with high ambient radiation.

(2) The design also limits the extent to which additional weight and thickness of shielding materials can be added.

(3) The plutonium fluoride intermediate is the source of neutron radiation which is virtually unaffected by shielding.

The annual exposure limitation is currently not the controlling factor in operating personnel requirements, but on occasion the daily exposure limits have imposed scheduling problems for maintenance operations. Higher reactor exposure levels would result in higher group exposure rates. Studies indicate that annual exposure will be a controlling factor at the level of 1400 MWD/T anticipated for N-Reactor product, and an additional eight operators over and above those normally required to man the work assignments will be required.

Criticality control is of considerable concern. The large quantities and high densities of the fissile materials processed require that primary reliance be placed on shape and spacing for control measures. Process vessels and equipment are designed with a maximum size limitation wherever possible and are placed at distances calculated to essentially eliminate neutron interaction. Plutonium outside process vessels is minimized by strict but difficult administrative procedures. The oxalate process requires the continuous filtration and subsequent transfer of plutonium oxalate, a wet, sticky material. The system presents a

[redacted]

problem of physical containment since both physical and visual access to the filter must be provided for process control. The material must then be moved from a vacuum drum filter through an open feed hopper to a continuous calciner. Because of the vertical hood arrangement, spills at this point land near the hydrofluorinator which is in the hood directly below. Frequent inspection and immediate cleanup are used as control measures, but these activities are hampered by the radiation field and the limited visibility into the hood. Although criticality control is currently being maintained by strict administrative procedures, the task is becoming increasing difficult because of continuing deterioration of hood panels (visibility) and equipment (increasing exposure). Eventually production rates will be affected.

Carbon contamination in the plutonium metal has been an intermittent and unpredictable source of difficulty. Presumably the result of incomplete decomposition of the oxalate anion, the impurity has run as high as 750 ppm for an extended period of time and then drifted back to well within the recently established limits of 600 ppm maximum on individual buttons and 350 ppm average. Within the periods of high carbon contamination, it has been estimated that up to 60 percent of the buttons might have been rejected by the new specifications.

COMPARISON OF ALTERNATIVE PROCESS STEPS

Anticipated Performance and Development Status

All plutonium conversion processes now in use or under study are composed of two distinct operations:

(A) conversion of the plutonium nitrate to a halide, and

(B) reduction of the halide to metal.

Several processes have been developed or studied for preparation of the plutonium halide from the nitrate:

(1) precipitation of plutonium peroxide followed by halogenation;

(2) precipitation of plutonium trifluoride, which can be reduced to metal or oxidized to a mixture of tetrafluoride and oxide;

(3) precipitation of $CaPuF_6$, which is equivalent to the tetrafluoride and may be reduced directly;

(4) precipitation of Pu(III) oxalate, followed by calcination and halogenation;

[redacted]

(5) precipitation of Pu(IV)oxalate followed by calcination and halogenation; and

(6) direct calcination to plutonium dioxide, followed by halogenation.

The critical comparison of processes for preparation of the plutonium halide was limited to the last two listed. Number (5) is the existing process in the button line, and number (6) is the process under development. The precipitation of plutonium peroxide was formerly used as a batch process at Hanford and is currently used as a continuous process at Rocky Flats. It was not considered exhaustively as it appeared to offer the same approximate decontamination potential as the oxalate precipitation, with the exception that no carbon is introduced, and introduces the added safety hazard associated with handling hydrogen peroxides. The precipitation of trifluoride was given relatively little consideration because it possesses no outstanding advantages. This process requires plutonium to be in the plus three state; in the Savannah River button line, the trivalent form exists in the solution obtained from a cation exchange concentration step. Decontamination is markedly less than is capable with the present button line process, the mode of operation is batchwise, and further development would be required to provide the throughput desired. Processes (3) and (4) have not been developed extensively and consequently were not considered in the study.

An exhaustive study$^{(2)}$ was made of the status of the development effort at Hanford on the so-called chloride process which consists of direct calcination of the nitrate to plutonium dioxide, chlorination with phosgene (or possibly CCl_4) to form $PuCl_3$, and electrowinning (electro-deposition) of the metal from a mixed lithium-potassium chloride bath containing about 25 percent $PuCl_3$. The information brought together by this study was used along with the accumulated operational experience with the present button line process to form the basis of a comparison of expected performance for each individual process step. The comparisons are summarized below. Following this section, expected performances are translated into estimated operating cost differentials, and capital costs are estimated for each of the alternative steps. These costs, together with comparisons of such intangible considerations as development status and inherent safety hazards, are used to arrive at a semiquantitative assessment of the relative merits of the alternatives.

Direct Calcination vs Oxalate Precipitation and Calcination

A comparison of the anticipated operational characteristics of a direct calcination step with the known characteristics of oxalate precipitation and calcination points out several marked advantages for the former. The design of the direct calciner results in a compact, completely contained system throughout the conversion of nitrate to halide as opposed to the

[redacted]

large filter and open feed hopper arrangement inherent in the precipitation process. Spills and inadvertent dispersal of powder have been a source of concern in the present line, both from the standpoint of a criticality hazard and the buildup of powder on the hood faces with the resultant increase in radiation exposure. Although some improvement would certainly be realized in a new design of the precipitation process, it would not be possible to achieve containment and compactness to the degree possible with direct calcination. Capital cost and maintenance requirements for direct calcination are thus expected to be much less because of the greater simplicity of the process and equipment.

Direct calcination does have an important drawback when compared to oxalate precipitation; essentially no decontamination from metallic impurities is achieved so that feed of much higher purity is required in order to meet the button specifications. This drawback is somewhat offset by the fact that no carbon is introduced into the system. A disadvantage of lesser importance is the low reactivity to subsequent halogenation exhibited by the oxide from direct calcination. The addition of 0.5 mole fraction of sulfate to the nitrate solution results in a powder of satisfactory reactivity. The effect of the sulfate on subsequent reduction steps has not been fully defined. However, experience at Rocky Flats has indicated that sulfate is not a problem in bomb reduction of the fluoride if the sulfate concentration is kept below a level which is easily achieved by the anticipated mode of operation.

In order to assess the feasibility of obtaining plutonium nitrate from the Purex Plant of sufficient purity to allow utilization of direct calcination, Purex Process Engineering was asked to estimate the costs involved. Table I(3) lists the proposed button specifications(4), the present purity of the L-10 (plutonium product) solution, and two suggested purity goals (the second more stringent than the first). Also tabulated are the estimated capital costs and incremental increases in operating expense.

The changes that would be required are (1) a new resin movement system for N-Cell to provide improved decontamination factor (df) for fission products, aluminum, uranium, volatiles (Ca, Hg, etc.), and corrosion products (Fe, Ni, Cr); (2) use of distilled water for the XAS and XCX streams in N-Cell for improved silica, carbon, volatiles and corrosion product purity; (3) insertion of tantalum equipment (N6 loop, set of downcomer screens, and possibly a tube bundle) to reduce titanium and corrosion products; and (4) modification of the operation of the 1BS and 2B columns to provide adequate uranium df. In addition, it may be necessary to add a zirconium complexant to the HAF for additional ZrNb df, and perhaps to replace the present IBS system with a new column to achieve improved uranium scrubbing without loss of plutonium. Since it is not precisely known if all of these steps would be required, the costs are listed in varying degrees of probability. The large jump in estimated cost listed for Case II represents the possible insertion of a new 1BS Column and tantalum tube bundle.

[redacted]

[redacted]

TABLE I

HIGH-PURITY PLUTONIUM NITRATE REQUIREMENTS FOR DIRECT CALCINATION

	Proposed Button Specifications(4) ppm	Purex Performance - Plutonium Product (L-10) Purity*, ppm		Desired (L-10) Purity, ppm 95% Confidence Level	
		95% Confidence Level	50% Confidence Level	Case I	Case II
Fe)	< 1000	1 330	380	500	150
Cr)		620	160	100	30
Ni)		120	45	50	< 20
C	< 500	Not available			
Stabilizers**	< 100				
(Weighting Factor)					
Al 1.0		60	20	25	15
Ce 0.2					
Dy 0.2					
Er 0.2					
Hf 0.2					
In 0.2					
Lu 0.2					
Mo 0.3					
Si 1.0		40	25	25	15
Sc 0.6					
Sn 0.2					
Tb 0.2					
Ti 0.6		25	10	40	25
Tl 0.1					
Tm 0.2					
U 0.1		450	200	250	100
Zr 0.3					
Volatiles					
(Ca,Mg,Li,Zn,Na)	< 750	1 700	750	< 750	< 750
Fission Products					
ZrNb-95 (G/AT)		1.0×10^{-11}	2.0×10^{-11}	1×10^{-11}	5×10^{-12}
Ru (G/AT)		3.0×10^{-12}	5.5×10^{-12}	4×10^{-12}	2×10^{-12}

* Based on Oct., Nov., Dec., 1963, operation of Purex.
** Sum of weighted analyses.

[redacted]

[redacted]

DECLASSIFIED

TABLE I, cont'd

Probability that Indicated Costs Will Be Required	Purex Costs Required to Meet Desired Purity			
	Case I		Case II	
	Operating	Capital	Operating	Capital
Certain	$ 5 300	$26 000	$ 5 500	$ 45 000
Medium	5 500	33 000	13 800	146 000
Low	9 800	45 000	13 800	164 000

A similar survey of the plutonium reclamation facility's ability to meet the same purity goal, Case II, indicated that the addition of a heat exchanger following the final product evaporator (for an estimated $10,000) should result in a comparable impurity level. Uranium decontamination is the principal uncertainty, but it was felt that occasional changes in the solvent extraction flowsheet would satisfactorily reduce any uranium buildup in the recycle system. The addition of a partitioning facility for separation of thorium, uranium, and plutonium that has been requested in connection with a scrap recovery program at Hanford would also provide the ability to prevent continuous buildup of uranium.

The decision was made to proceed with the alterations obtainable with the $45,000 capital expenditure in Purex and the $10,000 expenditure in the reclamation facility, irrespective of the choice between direct calcination and oxalate precipitation for the button line.

Chlorination vs Fluorination

The principal reason for initiating research and development in the field of chloride chemistry was the virtual elimination of neutron radiation currently originating from the alpha-n reaction in the fluorine nucleus. It had been reasoned that in order to process high-exposure plutonium (> 2000 MWD/T) neutron radiation would have to be greatly reduced. Three other advantages are also associated with the chloride process: (1) chlorination of plutonium oxide gives the potential for some purification from metallic impurities because of relatively high volatility for a number of metal chlorides; (2) a process for the purification of metal scrap by direct chlorination without dissolution and aqueous reprocessing appears feasible; and (3) the quantity of aqueous waste from dissolution of chloride slag from bomb reduction is somewhat less than in the case of fluoride reduction because of higher solubility. The latter two characteristics opened the possibility of marked reduction in the volume of solution handled through aqueous processing steps.

The two principal disadvantages of chlorination are the lower heat of reaction during reduction to metal and the hygroscopic character of the

DECLASSIFIED

[redacted]

[redacted]

plutonium chloride. The lower heat of reaction dictates a requirement for higher conversion to the halide and the use of greater quantities of iodine booster than is required for the reduction of plutonium fluoride. The need for high conversion during halogenation ($> 95\%$) would result in control difficulties on the button line where at present the requirement of $> 80\%$ conversion can be monitored simply by the color of the powder. The high iodine requirement would present processing difficulties in the reclamation facility. The hygroscopic chloride powder could be handled in a button line provided with an atmosphere having a dewpoint of -20 °C or lower. Above this humidity, the powder would pick up sufficient moisture to present both a serious corrosion problem and a chemical hazard during bomb reduction of moist powders. The greatest source of concern resulting from this hygroscopic nature, however, is in the storage of chloride waste materials. Inadvertent exposure to moist air could change the Pu:H ratio sufficiently to present a nuclear hazard.

The present state of development may be summarized as follows. The ability to chlorinate direct-calcined oxide to 95% $PuCl_3$ in batch equipment has been demonstrated. Df's of from 2 to 10 have been demonstrated for iron and chromium, but no conclusive data are available on other impurities. Metal chlorination has not been studied. Further effort is needed on design of a reactor for chlorination of the oxide. Early work indicated the vibrating tube concept does not work as satisfactorily as with fluorination; lumping and poor flow of powder through the tube, perhaps due to localized overheating, led to the decision to develop either a stirred-bed or stirred-fluidized-bed reactor. As yet, a satisfactory design has not been demonstrated for either type.

Electrowinning vs Bomb Reduction

The principal advantage of electrowinning is the continuous mode of operation as compared with the batch operation inherent in bomb reduction, and consequently the greatly reduced quantity of slag and crucible solids that has to be processed for plutonium recovery. Performance of the two processes is estimated to be comparable with respect to purification of the metal, the manpower requirements for operation, and the maintenance requirements on that portion of the line. Initially, the neutron radiation associated with electrowinning was expected to be lower than that with bomb reduction of PuF_4 because of the absence of fluoride. However, present development has shown a need for the use of lithium chloride as one of the molten salt constituents, and the alpha-n reaction with lithium is approximately one-fourth that with fluorine.

Nuclear safety is an item of concern with electrowinning because existing designs that are capable of achieving the desired processing rates are not critically safe by geometry. Consequently, the operation would have to be subject to administrative batch control, backed up by instrumentation to detect off-standard operation.

[redacted]

[redacted]

The laboratory development of electrowinning has resulted in some significant contributions to the understanding of molten-salt electrolysis in general and plutonium non-aqueous chemistry in particular. Several ingenious design innovations were introduced to solve the difficult problems of achieving satisfactory current efficiency and continuously withdrawing the molten product from the cell; good progress was being made in this very difficult field of high-temperature operations under very corrosive conditions. However, there were several aspects of the development that had not progressed to the extent that one could assure satisfactory design at this time. It was estimated that another year would be required at the present level of effort to obtain the required information and experience. If detailed scoping were attempted at this time, there exists a 25% probability that a major change in design would be required as the result of information obtained during the next year. The following are some of the uncertainties that exist. (1) A reasonable cell life and absence of gradual buildup of deleterious effects from side reactions have not been demonstrated. Further work is needed on cell design and materials of construction. (2) The cell off-gas contains a significant amount of volatilized electrolyte which condenses in the off-gas system. A system must be developed to handle these solids in a trouble-free manner or the volatilization of the electrolyte must be eliminated. (3) Systems need to be developed to control the feed rate, electrolyte addition and product discharge, and to provide alarms for low current efficiency and off-standard operation.

COST COMPARISONS - NEW LINE

Capital Costs

Table II is a summary of capital cost estimates made by Facilities Engineering personnel. The design concept for a new button line based on the existing process is that developed in the engineering study of a high-level plutonium button line.(5) Since the original document included costs for the entire line, it was necessary to prorate some of the costs of supporting services between steps in a somewhat arbitrary fashion. The estimates for the new process steps are based on an engineering study of a new button line using the chloride process.(6) The figures listed for recovery facilities represent additional capital expenditures that would be required to handle the chloride recycle by converting it to the nitrate form before running it through the reclamation facility. This expense is less in the case of electrowinning (as compared with bomb reduction) because of the quantity of solids originating from used electrolytic cells is very much less than that originating from slag and crucible wastes; the smaller volume could probably be handled with small, batch-type dissolvers and boil-down equipment.

[redacted]

[redacted]

TABLE II

SUMMARY OF CAPITAL COSTS

Liquid-Solid Conversion		Halogenation		Reduction		Recovery(1)	
Direct Cal.	480,000	Chlorination	350,000	Electrowinning	1,090,000	Electrowinning	100,000(2)
Oxalate ppt	620,000	Fluorination	350,000	Bomb Reduction	910,000	Bomb (Chlorides)	250,000(3)
						Bomb (Fluoride)	None

Equipment estimates for oxalate precipitation, fluorination, and bomb reduction are for a design concept as developed in HW-64156(5).

The design concepts used in estimating costs for direct calcination, chlorination and electrowinning are as outlined in HW-77233(6), Engineering Study - New Button Line - 234-5 Building.

(1) Includes capital costs required to allow recycle material to be handled in 880 Facility.

(2) $100,000 for new chloride dissolver hood with two small dissolvers.

(3) $250,000 to replace two S&C dissolvers and scrubbers for chloride dissolution and provide distillation facilities for chloride separation.

[redacted]

Direct Operating Costs

Incremental differences in yearly operating costs were estimated for each alternative step and are briefly explained below. These estimates were made with the assumption that the variations in operating costs would be affected only by differences in personnel, chemicals, and maintenance requirements. Other costs, such as quality control, analytical, and monitoring services as well as overhead assessments, were assumed to be the same in each case. Manpower costs were set at $10,000 per man-year. The contribution of each of the three areas of possible cost difference are indicated below, but little attempt is made to discuss in detail the breakdown within each area.

The operating cost of direct calcination was estimated to be $75,000 per year less than that of oxalate precipitation plus calcination. Personnel requirements were assumed to be the same, chemical costs were estimated to be $5,000 per year less for direct calcination, and maintenance was $70,000 per year less. This last contribution was based on the following reasoning. Task I and II maintenance and yearly capital improvement charges have averaged about $200,000 per year, and from a survey of work orders, it was estimated that about two-thirds of these costs were incurred by Task I operations. Finally, it was judged that due to the simplicity of design and operation of the continuous calciner, maintenance costs would be reduced by at least 50 percent.

The operating cost of chlorination was estimated to be $25,000 per year more than that of fluorination. This figure too was based heavily on judgment. Chemical costs were calculated to be $5,000 per year higher. A reduction of five men in personnel requirements (i.e., $50,000 per year) was assumed to be directly attributable to the choice of chlorination rather than fluorination. The savings do not occur just in the operation of the Task II or chlorination step; rather, the savings are distributed throughout the button line and are the result of lower neutron radiation exposure. This conclusion is based on the assumption that plutonium will be irradiated to 1400 MWD/T, and that under these conditions, personnel requirements for a button line using fluorination would be determined by allowable radiation exposure. The analysis of the effects of radiation exposure is discussed below. Maintenance costs were judged to be about $70,000 per year higher for chlorination than fluorination. Again, as in the case of personnel savings, this increased cost would not occur just in the maintenance of Task II operations but throughout the line as the result of the corrosive character of hydrated $PuCl_3$ (i.e., corrosive conditions in Task III as well as Task II in the event of failure in the dry atmosphere system). Within Task II itself, corrosion would also be increased due to the use of phosgene rather than anhydrous HF. Present charges for maintenance and capital replacements are approximately $100,000 per year, and it was judged reasonable to assume that the total increase attributable to chlorination would be about 70 percent of this value. While it might be argued that the assumed values for manpower savings and maintenance increases are very speculative, it was felt that the directions of most likely error

[redacted]

were such that they would compensate, i.e., the assumed savings in manpower may be too optimistic and the assumed penalty in maintenance may be too pessimistic. Thus, the conclusion of $25,000 per year higher operation cost for chlorination is believed to be reasonable.

Comparing electrowinning and bomb reduction, the task force concluded operating costs would be approximately $75,000 less for electrowinning. This saving is directly attributable to savings in chemical costs, primarily crucibles. No change in manpower or maintenance needs were foreseen.

The analysis of the impact of radiation on manpower requirements on the button line is summarized in Table III. This information is based largely on a study of the present button line made by V. W. Smith.(1) The last column on the right indicates the number of men required for button line operation over and above the number required to man the operating stations in order to obtain an average radiation dosage of 3.2 rem/man-year. Thus, the estimated savings due to using a combination of processes based on chloride chemistry is $50,000 (five men) assuming astute design would result in a line (using either process) requiring only eight operator assignments rather than the present eleven assignments.

Recycle Costs

The new high-capacity reclamation facility is designed to handle a wide variety of plutonium-bearing waste streams. The impact of a reduced load of slag and crucible solids on the operating cost of this complex, while significant, would not be in seeming proportion to the reduction in solution volume from the dissolvers because of the interrelations in the flowsheet between this and other intermediate process streams. Comparing the alternatives of electrowinning, bomb reduction of plutonium chloride, and bomb reduction of plutonium fluoride one concludes the following: Bomb reduction of plutonium chloride will result in a markedly smaller volume of solution from the slag and crucible dissolvers and may allow a reduction of one shift (one operator) on the solvent extraction section. This, together with an accompanying reduction in essential materials cost, would result in a savings of from $20,000 to $30,000 per year. Electrowinning would virtually eliminate this stream and would reduce the manpower needed for dissolution; consequently, it is estimated a savings of from $40,000 to $60,000 would result.

[redacted]

[redacted]

TABLE III

ANALYSIS OF BUTTON LINE RADIATION

Operating Assumptions	Gamma Exposure r/yr	Neutron Exposure rem/yr	Total Exposure rem/yr	Manpower(1) Required by Radiation	Manpower(2) Required by Assignments	Radiation "Overhire"
Present Conditions	49(3)	46(3)	95	30	33	-
Present Process and Equipment at 1400 MWD/T	78(4)	53(5)	131	41	33	8
Present Process with new line and improved powder containment at 1400 MWD/T	39(6)	53(5)	92	29	24	5
Chloride process with improved powder containment at 1400 MWD/T	39(6)	21(7)	60	19	24	-

(1) Average rem/man-year not to exceed 3.2.

(2) Assumes present number of work stations (11) reduced to 8 by astute design.

(3) 1962-63 averages.

(4) Calculated factor of 1.6, based on an assumed isotopic distribution of 89.8% Pu-239, 8.4% Pu-240, 1.6% Pu-241.

(5) Calculated factor of 1.15, based on the above isotopic distributions.

(6) Assumes 50% reduction for hood cleanliness.

(7) Assumed 60% reduction net (approxi. 62% reduction in alpha-n).

[redacted]

[redacted]

Summary and Conclusions from Process Comparisons

In summarizing these various findings, the comparisons and conclusions were considered in reverse order so as to reduce the interaction with subsequent selections. Even so, consideration of electrowinning necessitates concurrent consideration of chlorination so that the first comparison is between bomb reduction with preceding fluoriation and electrowinning with preceding chlorination. The second comparison is between chlorination and fluorination with the assumption in both instances that the halide will be reduced in a bomb. Lastly, direct calcination and oxalate precipitation are compared.

Electrowinning has the following advantages and disadvantages compared with bomb reduction:

a) Lower operating cost on the button line - $55,000/yr.

b) Lower operating cost due to recycle - $50,000/yr.

c) Higher capital cost in the button line - $180,000.

d) Additional capital cost in the reclamation facility - $100,000.

e) Additional development costs - $100,000 - $150,000.

f) A year's delay in the completion of a scope design or a 25 percent chance of a major scope change.

g) The need for administrative criticality control of plutonium in the electrolytic cell.

The decision was made within the Research and Engineering Operation as a result of these findings that electrowinning is not ready for scope design at this time and should be dropped from consideration as the principal reduction process for the next button line. However, because of the similarity between it and electrorefining, which has previously been under development at Hanford as a method of obtaining pure metal from scrap, effort of the latter should be reinstated and directed toward a possible metal recycle step and a means of achieving high-purity metal.

Chlorination has the following advantages and disadvantages compared with fluorination (assuming subsequent bomb reduction):

a) Higher operating cost on the button line - $25,000/yr.

b) Lower operating cost due to recycle - $25,000/yr.

c) Additional capital cost in the reclamation facility - $250,000.

d) Lower radiation exposure to personnel.

[redacted]

e) Some decontamination capability.

f) A chemical and nuclear hazard associated with hygroscopic plutonium trichloride.

g) The need for higher conversion of oxide to chloride and more iodine to achieve satisfactory yields in bomb reduction.

The decision was made that fluorination was better adapted to plant use and that development work on chlorination should be terminated.

A similar comparison between direct calcination and oxalate precipitation followed by calcination indicates the former has:

a) A lower operating cost - $75,000/yr.

b) Lower capital cost - $140,000.

c) Greater nuclear safety and lower radiation field.

d) No decontamination capability (but carbon is not added).

A choice of direct calcination would necessarily be contingent on the ability to obtain a higher purity plutonium nitrate from the separations plants. The tentative decision was to plan for incorporation of direct calcination in the new or revised line on the premise that the required purity of feed will be obtained by the changes being effected in Purex and recovery facilities.

Thus, the optimum process for a new button line, if it is to be designed at this time, involves direct calcination, fluorination and bomb reduction.

IMPLEMENTATION

The preceding discussion dealt with the choice of the optimum process for a new button line and concluded that it would differ basically only in the Task I operation. This decision, together with the changing business climate, provoked consideration of the alternatives of building a new button line or extensively renovating the existing line. Discussions among operating, maintenance, project, research and engineering, and process design personnel associated with the Z Plant Facility resulted in the formulation by Facilities Engineering Operation personnel(7) of a concept for line renovation which consisted of replacement in the RMC Button Line of the process hoods associated with solution makeup and Tasks I and II operations and construction of hoods into which one direct calciner and one new fluorination unit would be installed.

This alternative corrects essentially all of the deficiencies of the existing RMC Line.

(1) Incorporation of direct calcination would permit nearly complete containment and more convenient housekeeping, thereby essentially eliminating the criticality hazard.

(2) A major source of radiation exposure (loose powder on hood faces) would be markedly reduced.

(3) Operating efficiency of the renovated line would be markedly better than the existing line.

Comparing a renovated line and a new line, the study group concluded that:

(1) Operating costs of a renovated line would be no more than $50,000 per year higher than those of a new line.

(2) Capital cost for the renovated line would be $1,450,000 less.

Experience on the present button line points out that failures in Task I and II continuous operations have been the principal cause of forced down time. Figure 1 shows that maintenance costs of Task III have been essentially constant, while those of Tasks I and II have risen sharply. Since the first two operations would be essentially new for either alternative, and since maintenance costs of a new Task III could not be expected to be much lower than at present, total maintenance costs of the two should be comparable. Although it is possible that a new Task III could be designed to require less personnel, the maximum saving obtainable in total operating costs is estimated to be $50,000 per year.

The preliminary estimate of the capital cost for the renovated line is $445,000 as compared with $1,900,000 for a new line. A significant cost reduction is realized in renovating through the use of existing services and supporting facilities, instrumentation lines, ventilation, etc.

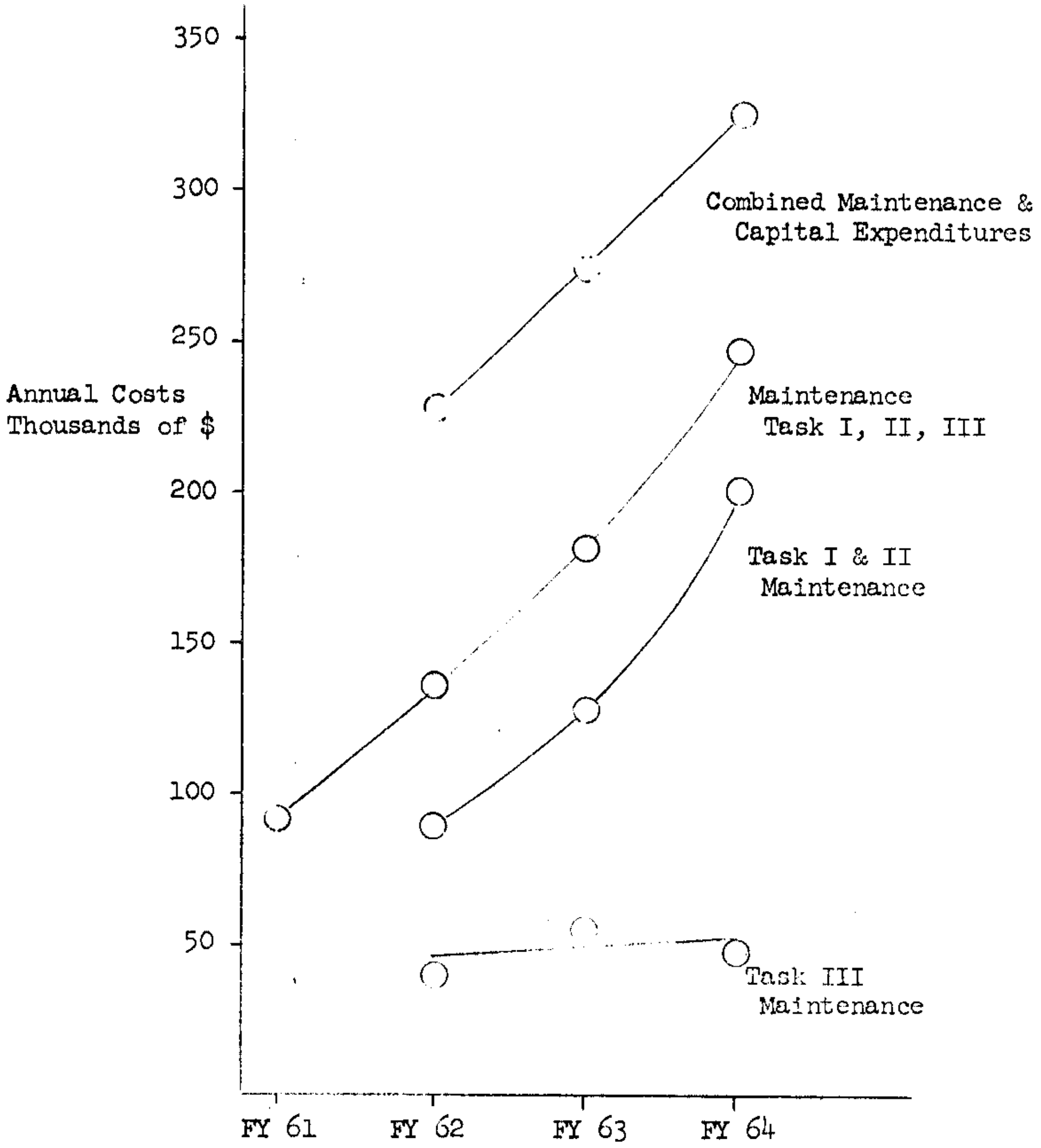
As a result of these considerations, the recommendation was made by the study group that, with an apparent pay-off period of greater than twenty years, construction of a new line rather than renovation of the existing RMC Line was not justified. Subsequently, the decision was made by the CPD General Manager to budget for extensive renovation of the RMC Line in FY 1966.

[redacted]

DECLASSIFIED

FIGURE 1

CAPITAL & MAINTENANCE COSTS - RMC LINE



DECLASSIFIED

[redacted]

REFERENCES

1. V. W. Smith, Maintenance and Operational Experience of Plutonium Reduction Equipment. HW-79636. December 16, 1963. (SECRET)

2. B. M. Johnson and M. J. Szulinski, Study of the Status of the Chloride Process for Plutonium Metal Production. December 6, 1963. (CONFIDENTIAL UNDOCUMENTED)

3. J. B. Kendall, Private Communication, January 24, 1964.

4. R. E. Van der Cook, Button Specifications. HW-81242. March 9, 1964. (not issued)

5. H. J. Bellarts and J. W. Kolb, Design Study - Interim Report, RMA Button Line Radiation Reduction. HW-64156. April 1, 1960 (SECRET)

6. R. A. Ciccarelli, Engineering Study - New Button Line - 234-5 Building. HW-77233. April 15, 1963. (SECRET)

7. R. A. Ciccarelli, Budget Facility Description - Button Line Equipment, 234-5 Building. HW-81535. March 31, 1964. (UNCLASSIFIED)