MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0059196 4

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

2

ORNL-3977
UC-10 – Chemical Separations Processes
for Plutonium and Uranium

OXIDATION AND CHLORINATION OF UO_2-PuO_2

K. S. Warren
L. M. Ferris

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price $2.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Virginia 22151

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-3977

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

OXIDATION AND CHLORINATION OF UO_2-PuO_2

K. S. Warren

L. M. Ferris

JULY 1966

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0059196 4

CONTENTS

Page

ABSTRACT 1

INTRODUCTION 2

APPARATUS AND PROCEDURE 2

RESULTS 4

Oxidation of UO_2-PuO_2 Pellets 4

Selection of Chlorinating Agent 9

Summary of Previous Work 9

Experimental 9

Chlorination of Uranium-Plutonium Oxides with 85% Cl_2--15% CCl_4 11

Chlorination of UO_2-PuO_2 Pellets 11

Chlorination of U_3O_8-PuO_2 Powders 17

DISCUSSION AND CONCLUSIONS 21

REFERENCES 24

APPENDIX I 27

OXIDATION AND CHLORINATION OF UO_2-PuO_2

K. S. Warren

L. M. Ferris

ABSTRACT

Oxidation and chlorination of UO_2-PuO_2 was studied on a laboratory scale. High-density pellets of UO_2-PuO_2 that contained less than about 20% PuO_2 usually could be converted to U_3O_8-PuO_2 powder by reaction with oxygen at 600°C. The UO_2 in pellets containing 20% or more PuO_2 could be partially oxidized; however, oxidation was always incomplete even on extended exposure to oxygen at 800°C. No powdering of the high-PuO_2-content pellets was observed.

After limited experimentation, 85% Cl_2--15% CCl_4 was selected as a practical chlorinating agent. In the temperature range of 450 to 550°C, the rates of conversion of uranium oxides to volatile chlorides (UCl_5 and UCl_6) were about the same for small, high-density UO_2-PuO_2 pellets containing 5% PuO_2 or less as those obtained with U_3O_8-PuO_2 powders produced by oxidizing pellets. Uranium from pellets of higher PuO_2 content was chlorinated less readily. Uranium chlorination efficiency was unaffected by changes in PuO_2 content (0 to 20%) of U_3O_8-PuO_2 powders. At 550°C, complete conversion of uranium oxide to volatile chlorides required 3 to 5 hr in an excess of chlorinating agent. Liquid oxychlorides formed at temperatures above about 550°C.

The amount of plutonium oxide converted to volatile $PuCl_4$ was proportional to the amount of chlorine passed through the system. This behavior was predictable from the equilibrium constant for the reaction $PuCl_{3(s)} + 1/2Cl_2 \rightleftharpoons PuCl_{4(g)}$. Large amounts of chlorine were required to volatilize plutonium. At 500 to 600°C, about 10^4 moles (about 10^5 liters) of chlorine were required to volatilize one mole of $PuCl_4$.

It was concluded that chloride volatility processes for recovering uranium and plutonium from nuclear reactor fuels are not technically attractive.

1. INTRODUCTION

Chloride volatility processes for recovering uranium and plutonium from spent nuclear reactor fuels have been studied by several groups throughout the world.[1-25] The processes generally involve chlorination of the fuel followed by fractional distillation or sublimation of the resultant chlorides to isolate and purify the uranium and plutonium. Most of the processes investigated related to uranium-bearing fuels, with only a small effort being devoted to recovery of plutonium by chloride volatility. The purpose of this investigation was to evaluate the possibility of utilizing a chloride volatility process for UO_2-PuO_2 fuels having PuO_2 concentrations of up to about 35%. The mixed oxide is of special interest because of the widespread use of low-enrichment UO_2 power reactor fuels (which contain up to about 1% Pu after irradiation) and because UO_2-PuO_2 is a prime candidate for a fast reactor fuel.

In general, UO_2 is chlorinated more slowly than U_3O_8 in the temperature range of 400 to 600°C. Therefore, most chloride volatility schemes for processing oxide fuels involve oxidation of the UO_2 to U_3O_8 prior to chlorination. Consequently, a study of the oxidation behavior of UO_2-PuO_2 fuel pellets was included in this study. The effects of PuO_2 content, type of chlorinating agent, reaction temperature, and amount of chlorine required in the chlorination of the oxidized products were then evaluated. The results obtained here on the oxidation of UO_2-PuO_2 are applicable not only to chloride volatility processes but also to processes involving oxidation of oxide or carbide fuels in a fluidized bed of inert alumina followed by either fluorination[26,27] or acid leaching[28] to recover the uranium and plutonium.

Acknowledgment. - The authors thank J. W. Ullmann and R. H. Rainey for obtaining the UO_2-PuO_2 samples used in this study. Chemical analyses were provided by the ORNL Analytical Chemistry Division under the supervision of J. H. Cooper and C. E. Lamb.

2. APPARATUS AND PROCEDURE

All work with plutonium compounds was conducted in a standard Kewaunee glove box. The chlorination vessel consisted of a 43-cm-long, 2.5-cm-diam quartz tube which rested in a Nichrome-wound clam-shell

furnace 30 cm long. Glass-wool traps were provided at the exit end of the quartz tube to catch condensed chlorides of uranium and plutonium. These traps consisted of 24-mm-ID Pyrex tubes filled with glass wool and were coupled to the quartz tube by means of a 34/45 standard-taper ground-glass joint, using tapered Teflon sleeves as lubricating seals for the joints adjacent to the furnace. The exit gases from the glass-wool traps were bubbled through 5 M NaOH, which completely absorbed CO_2 and excess chlorinating agent.

The gases required for this investigation (Cl_2, CO, CO_2, CH_4, and $COCl_2$) were drawn from commercial cylinders, bubbled through concentrated sulfuric acid, and passed through a glass-wool filter prior to admittance to the quartz reaction tube. In most experiments, gaseous chlorine was saturated with CCl_4 vapor at 25°C by bubbling it through liquid CCl_4. The composition of the mixture was about 85% Cl_2--15% CCl_4.

A pellet of a desired UO_2-PuO_2 composition was weighed in a quartz boat and either chlorinated directly or first oxidized to U_3O_8-PuO_2 in oxygen at elevated temperatures. Weights of samples (and residues) were obtained with a Torsion balance and were accurate to ± 0.01 g. In some cases the pellet was ground by hand in a mortar to pass through a 100-mesh sieve, and the powder chlorinated after reweighing. The powdered sample was not admitted to the hot reaction zone until the air in the tube had been displaced with chlorinating agent.

The temperature of the furnace could be varied by a Variac connected to the furnace heating elements. A Chromel-Alumel thermocouple was inserted in the furnace adjacent to the quartz tube and was connected to a Simplytrol. The temperatures read on the Simplytrol were calibrated against a second thermocouple inserted directly into the reaction zone of the quartz tube before inserting the sample. The temperatures recorded throughout this report are those measured in the reaction zone.

At the end of a chlorination experiment, each glass wool trap and the tube were leached with 2 M HNO_3 to dissolve condensed compounds for analysis. Any residue remaining in the quartz boat was weighed and analyzed for uranium and plutonium. A sample of the alkali trap was analyzed for chloride ion to measure the total chlorine throughput. Material balances for uranium and plutonium were ± 10% in each experiment.

3. RESULTS

3.1 Oxidation of UO_2-PuO_2 Pellets

Since chlorination of U_3O_8 is rapid between 400 and 550°C, oxidation of UO_2 (and UO_2-PuO_2) is recommended as the first step in a chloride volatility process.[2] Oxidative powdering of UO_2-PuO_2 also will probably be essential if fluidized-bed volatility processes[26,27] or alternative oxidation-leach processes[28] are to be feasible. In these processes, the UO_2-PuO_2 would be converted to U_3O_8-PuO_2 powder by reaction with oxygen (or HF-O_2) in a fluidized bed of inert alumina with the U_3O_8-PuO_2 powder being dispersed homogeneously throughout the alumina. Uranium and plutonium can be recovered from the product bed as their respective hexafluorides (by fluorination) or as solutions of aqueous nitrates by leaching the bed with nitric acid. Because of its general interest, the oxidation behavior of UO_2-PuO_2 pellets that contained up to 35% PuO_2 was studied briefly. The UO_2-PuO_2 pellets were obtained from a variety of sources, with the fabrication conditions usually being different for each batch of pellets (Table 1).

The results of this study showed that, in general, pellets containing up to about 20% PuO_2 could be oxidized to U_3O_8-PuO_2 powder whereas pellets of higher PuO_2 content were partially oxidized, but did not powder, in oxygen at high temperatures. Pure UO_2 pellets were readily converted by oxygen to U_3O_8 powder in about 0.5 hr at temperatures as low as 400°C (Table 2). In experiments with pellets containing up to 20% PuO_2, rapid oxidation of the mixed oxide was achieved at temperatures of 500 to 600°C (Table 2). Based on visual examination and weight increases, it was shown that pellets containing up to 18% PuO_2 could be practically completely converted to U_3O_8-PuO_2 powders in 3 hr or less at 600°C (Table 2). Particle-size distribution of the powdered oxidation products was not determined in most cases. The product from a 99% UO_2--1% PuO_2 pellet was sieved, however, and gave the following approximate size distribution:

Table 1. Composition and Fabrication Conditions of UO_2-PuO_2 Pellets Used in This Study

Pellet Batch No.	Fabricator	PuO_2 Content of Pellet (%)	Fabrication Conditions: Blending	Pelletizing Pressure (tsi)	Sintering in 94% N_2--6% H_2: Temp. (°C)	Time (hr)	Pellet Density (% of theoret.)	References
Hanford	Hanford[a]	1	M.B.[b]	--	1500	12[c]	--	29
NUMEC 14A	NUMEC[d]	5	Copptn.[e]	12.7	1600	1	95	30,32
NUMEC Pu17	NUMEC	17.8	Copptn.	21.2	1600	16	93	31,32
NUMEC MBR-17	NUMEC	17.8	M.B.	13.4	1600	16	80	32
NUMEC Pu13	NUMEC	20	Copptn.	11.7	1300	2	87	32,33
Vallecitos 2-C-4	GE-VAL[f]	20	Copptn.	6-12	1600	4-5	90-96	34
NUMEC Pu19	NUMEC	35	Copptn.	11.7	1600	16	88	35
PuO_2	NUMEC	100	---	31.7	1600[g]	1	86	32

[a]Hanford pellets were 1.43-cm high, 1.27-cm diam.

[b]Mechanical blending of UO_2 and PuO_2 powders.

[c]Fired in pure hydrogen.

[d]Nuclear Materials and Equipment Corporation; all pellets fabricated by NUMEC were 0.69-cm diam, 0.55-cm high.

[e]Continuous coprecipitation of $Pu(OH)_4$ and $NH_4U_3O_7$.

[f]General Electric Company, Vallecitos Atomic Laboratory; GE-VAL pellets were 0.653-cm high, 0.546-cm diam.

[g]Fired in air instead of hydrogen-nitrogen mixture.

Table 2. Results of Oxidation Studies with UO_2-PuO_2 Pellets

Expt.	Pellet Batch No.	PuO_2 Content of Pellet (%)	Oxidation Conditions Temp. (°C)	Oxidation Conditions Time (hr)	Wt. Increase (%) Theoret.[a]	Wt. Increase (%) Found	UO_2 Converted to U_3O_8 (%)	Remarks
1	UO_2-1	0	400	0.5	3.95	3.85	97	Pellet Powdered
2	UO_2-1 wafer	0	550	1.0	3.95	4.06	103	Wafer Powder
3	UO_2-1	0	600	0.5	3.95	3.86	98	Pellet Powdered
4	UO_2-1	0	600	2.0	3.95	3.8	96	Pellet Powdered
5	Hanford	1	600	1.5	3.91	4.0	102	Pellet Powdered
6	Hanford	1	600	2.0	3.91	3.92	100	Pellet Powdered
7	NUMEC 14A	5	500	1.3	3.75	3.8	102	Pellet Powdered
8	NUMEC 14A	5	650	1.75	3.75	4.0	107	Pellet Powdered
9	NUMEC Pu17	17.8	500	1.5	3.25	3.8	117	Pellet Powdered
10	NUMEC Pu17	17.8	650	1.3	3.25	3.8	117	Pellet Powdered
11	NUMEC MBR-17	17.8	600	3.0	3.25	4.0	123	Pellet Powdered
12	NUMEC Pu13	20	600	1.5	3.16	---	--	Partial Powdering
13	NUMEC Pu13	20	600	2.0	3.16	3.0	95	Partial Powdering
14	NUMEC Pu13	20	600	2.75	3.16	3.7	117	Pellet Powdered
15	NUMEC Pu13	20	600	3.3	3.16	2.6	82	Pellet Powdered
16	Vallecitos 2-C-4	20	650	19	3.16	0.94	30	No Powdering
17	Vallecitos 2-C-4	20	650	19	3.16	0.6	19	No Powdering
18	Vallecitos 2-C-4[b]	20	700	5	3.16	2.2	70	---
19	Vallecitos 2-C-4	20	800[c]	23	3.16	1.2	38	No Powdering
20	NUMEC Pu19	35	800[d]	16	2.57	1.4	54	No Powdering

[a]Based on conversion of UO_2-PuO_2 to U_3O_8-PuO_2.

[b]Sample was ground to -100 mesh prior to oxidation.

[c]This pellet had been previously heated in O_2 for 2 hr at 600°C.

[d]This pellet had been previously heated in oxygen for 23 hr at 650°C.

Sieve Size (mesh)	Amount of Powder in Size Range (% of Total)
+20	19.9
- 20+50	15.4
-50+100	15.0
-100	49.7

Although pellets from one batch of 80% UO_2--20% PuO_2 (NUMEC Pu13) were readily converted to U_3O_8-PuO_2 powder, oxidation generally was incomplete when the PuO_2 content of the mixed oxide was 20% or greater (Table 2). In these latter cases, no powdering of the pellet was observed, but 19 to 54% of the UO_2 was converted to U_3O_8, as indicated by the increase in weight (Table 2). In all cases where 80% or more of the UO_2 was oxidized to U_3O_8, crumbling of the pellet occurred. It should be noted that the 20% PuO_2--80% UO_2 pellets that did oxidize rapidly (NUMEC Pu13) were of somewhat lower density than those (Vallecitos 2-C-4) that did not oxidize as rapidly (Table 1). Lower density might also account for the higher percentage conversion of UO_2 to U_3O_8 in the pellets containing 35% PuO_2 (NUMEC Pu19) than in pellets from batch Vallecitos 2-C-4 (Table 2).

Increasing the surface area of the UO_2-PuO_2 can lead to an increase in the rate of oxidation. This is illustrated by the results of expt. 18 (Table 2). In this experiment, a pellet from the batch of 20% PuO_2--80% UO_2 pellets that was normally relatively inert to oxygen was ground to pass a 100-mesh screen and then was exposed to oxygen for 5 hr at 700°C. Reducing the particle size in this manner resulted in conversion of about 70% of the UO_2 to U_3O_8 (Table 2).

Our results are in qualitative agreement with those of other workers with respect to both the temperatures required for oxidation and the effect of PuO_2 on the oxidation rate. The Belgians[20-22] used powders of less than 0.07 mm particle diameter, obtained by grinding high-density (90 to 97% of theoretical) pellets. When the mixed oxide contained 10% or less PuO_2, nearly complete oxidation was achieved in air at temperatures of 375 to 475°C. However, the percentage conversion of UO_2 to U_3O_8 was only about 60 to 70% when the PuO_2 content of the oxide was 20 to 30%. They concluded that temperatures greater than 500°C would

be required for complete oxidation of the mixed oxides.

Gerrish,[36-38] who studied the diffusion of oxygen in UO_2-PuO_2 powders, also found that the rate of reaction was low at temperatures below about 500°C. His results also show that the presence of PuO_2 in the mixed oxide retarded the oxidation of UO_2 to U_3O_8, but that no simple relationship between the PuO_2 content and the rate of oxidation existed.

British workers[39] studied the oxidation of UO_2-PuO_2 solid solutions by air at 750°C, using compositions containing up to 80% PuO_2. The UO_2-PuO_2 used in these studies was fired in hydrogen, but the highest firing temperature was 1400°C. When the oxide contained 10% or less PuO_2, the oxidation products always had O/(U + Pu) ratios close to 2.67; their structures, as determined by x-ray diffraction analysis, were of the orthorhombic U_3O_8 type. Samples containing 10 to 40% PuO_2 generally gave two-phase (cubic + orthorhombic) oxidation products. The O/(U + Pu) ratios achieved varied considerably with the state of subdivision and composition of the material that was oxidized. The O/(U + Pu) ratio could not in itself be used to determine either the compositions or relative amounts of the two phases present since x-ray analysis did not show the presence of pure U_3O_8 and PuO_2. The overall reaction for oxides containing 10 to 40% PuO_2 was best represented by the general equation,

$$MO_{2(\text{cubic})} + \frac{(2 + x - y)}{2} O_2 \rightarrow M'O_{2+x(\text{cubic})} + M_3''O_{8-y(\text{orthorhombic})},$$

where M = U + Pu. When the starting material contained 40 to 80% PuO_2, the oxidation products had single-phase cubic structures. Assuming the plutonium to be tetravalent, the calculated valence of the uranium in the oxidation products was about 5, compared with a value of 5.33 expected for U_3O_8-PuO_2 mixtures. The former figure corresponds to the conversion of about 83% of the UO_2 to U_3O_8.

3.2 Selection of Chlorinating Agent

3.2.1 Summary of Previous Work

Chlorination of uranium and plutonium oxides has received some prior study.[2-25, 40-44] The chlorinating agents used most were CCl_4 and $COCl_2$, which generally did not give the most volatile chlorides as products. The main reactions involved are:

$$UO_2 + 2CCl_4 \rightarrow UCl_4 + 2COCl_2$$

$$U_3O_8 + 4CCl_4 \rightarrow 2UCl_5 + UCl_6 + 4CO_2$$

$$UO_2 + 2COCl_2 \rightarrow UCl_4 + 2CO_2$$

$$PuO_2 + CCl_4 \rightarrow PuCl_3 + CO_2 + 1/2Cl_2$$

$$2PuO_2 + 4CCl_4 \rightarrow 2PuCl_3 + 4CO + 5Cl_2$$

Chlorine reacts with uranium oxides forming initially mainly UO_2Cl_2[2,13,18,23,25] but has the capability[2,5,19,23,25,45] of converting UO_2Cl_2, UCl_4, and $PuCl_3$ to the more volatile species UCl_5, UCl_6, and $PuCl_4$. As might be expected, a mixture of chlorine and CCl_4 was selected as the best chlorinating agent by several investigators.[2,5,25,41] Other chlorinating agents studied were CO_2-CCl_4;[9] CH_4-Cl_2;[13] $CHCl_3$ and PCl_5;[43] and S_2Cl_2 and C_3Cl_6;[44] but these reagents did not appear to be as effective as Cl_2-CCl_4 mixtures.

The results of the previous studies indicate that, during chlorination, the presence of carbon-containing compounds is essential to the rapid removal of the oxygen in the oxide. Elemental carbon can be used but must be dispersed throughout the oxide to be effective. The oxide is released as CO_2, CO, and/or $COCl_2$, depending on the chlorinating agent used.

3.2.2 Experimental

Scouting experiments were conducted with both U_3O_8 and U_3O_8-PuO_2 powders to evaluate various chlorinating agents. The powders were obtained by oxidation of UO_2-PuO_2 pellets. Only carbon-containing reagents ($COCl_2$, 85% Cl_2--15% CCl_4, 15% CCl_4--85% N_2) were used in these tests. The latter two reagents were prepared by saturating chlorine and

nitrogen, respectively, with carbon tetrachloride at 25°C. The flow rate of the chlorinating agent was kept about the same in each experiment.

In agreement with the results of earlier workers,[2,5,25,41] a mixture of 85% Cl_2--15% CCl_4 appeared to be the most practical reagent tested for the following reasons: (1) It appeared to be more effective at lower temperatures. This is important since the upper temperature permissible for a chlorination process from a corrosion viewpoint is about 600°C.[1] (2) It is not as toxic as $COCl_2$. (3) The use of large amounts of inert gases such as nitrogen is avoided. In 6- to 7-hr reactions at 400°C, the amount of U_3O_8 converted to volatile chlorides (presumably UCl_5 and UCl_6) was about 10, 15, and 100% with $COCl_2$, 15% CCl_4--85% N_2, and 85% Cl_2--15% CCl_4, respectively (Table 3). Complete conversion of U_3O_8 to volatile chlorides could be achieved in 2 to 3 hr at 600°C with either $COCl_2$ or 85% Cl_2--15% CCl_4; a slightly longer chlorination period was required to achieve the same effect with 15% CCl_4--85% N_2, reflecting the lower instantaneous concentration of chlorinating agent in the latter reagent. Based on limited tests with 1% PuO_2--99% U_3O_8 at 550 to 600°C (expts. 27 and 31, Table 3), phosgene and 85% Cl_2--15% CCl_4 appeared to be about equally effective. This seems to conflict with some British work[40] and a statement made by Russian workers[14] who "established experimentally that at 700°C plutonium dioxide, contrary to uranium dioxide, does not interact with phosgene." Phosgene was ineffective at 300°C (Table 3). When oxygen gas was added to the Cl_2-CCl_4 mixture (about equal amounts of oxygen and CCl_4-Cl_2), volatilization of uranium chlorides was greatly reduced. For example, only 5% of the uranium was volatilized after 5 hr at 600°C when oxygen was present. In contrast, complete volatilization was achieved when the oxygen was absent. The 15% CCl_4--85% N_2 mixture was not tested with U_3O_8-PuO_2 samples. Other mixtures such as CO_2-CCl_4 and CH_4-CCl_4 were tested and were found to be relatively ineffective for chlorinating U_3O_8.

Table 3. Effect of Various Reagents on the Chlorination of U_3O_8 and U_3O_8-PuO_2 Powders[a]

Expt.	Composition of Oxide (%) U_3O_8	PuO_2	Chlorinating Agent	Temp. (°C)	Oxidation Time (hr)	Chlorination Time (hr)	Amount Volatilized[b] (%) U	Pu
21	100	0	Cl_2-CCl_4[c]	300	0.5	6.0	30	--
22	100	0	Cl_2-CCl_4	400	0.5	5.5	100	--
23	100	0	Cl_2-CCl_4	500	0.5	3.5	100	--
24	100	0	Cl_2-CCl_4	600	0.5	2.5	90	--
25	100	0	Cl_2-CCl_4	600	0.5	3.0	100	--
26	100	0	Cl_2-CCl_4	750	0.5	1.0	100	--
27	99	1	Cl_2-CCl_4	550	0.5	1.7	96	75
28	100	0	$COCl_2$	400	0.5	6.0	10	--
29	100	0	$COCl_2$	600	0.5	2.0	100	--
30	99	1	$COCl_2$	300	2.0	5.0	0.04	0.007
31	99	1	$COCl_2$	600	1.5	1.0	99.6	50
32	100	0	N_2-CCl_4[d]	400	0.5	7.0	15	--
33	100	0	N_2-CCl_4	600	0.5	2.0	76	--
34	100	0	N_2-CCl_4	600	1.0	2.0	60	--
35	100	0	N_2-CCl_4	600	0.5	4.5	100	--
36	100	0	N_2-CCl_4	750	0.5	2.0	85	--

[a]The powders were obtained by oxidizing UO_2 and UO_2-PuO_2, respectively.

[b]Defined as the amounts of uranium and plutonium found outside reaction boat (see Sect. 2).

[c]About 85% Cl_2--15% CCl_4; obtained by bubbling Cl_2 through CCl_4 at 25°C.

[d]About 15% CCl_4--85% N_2; obtained by bubbling N_2 through CCl_4 at 25°C.

3.3 Chlorination of Uranium-Plutonium Oxides with 85% Cl_2--15% CCl_4

3.3.1 Chlorination of UO_2-PuO_2 Pellets

Reaction with 85% Cl_2--15% CCl_4 of intact pellets and pellets ground to pass a 100-mesh sieve was investigated cursorily. In each experiment, more than 100 moles of chlorine were passed through the system for each gram-atom of uranium present. The average rate of volatilization of uranium as chlorides (presumably UCl_5 and UCl_6) was between 5 and 15 %/hr at 450 to 500°C with pellets containing up to 5 %

PuO_2 (Fig. 1, Table 4). Within experimental error, these rates were the same as those obtained with U_3O_8-PuO_2 powders produced by oxidation of UO_2-PuO_2 pellets (see Sect. 3.3.2, Fig. 3). With pellets of higher PuO_2 concentration, the rates of uranium chloride volatilization appeared to decrease with increasing PuO_2 content in the pellet (Fig. 1). At 500 to 550°C, for example, the rate decreased from roughly 10 to 2 %/hr as the PuO_2 concentration in the pellet increased from 5 to 35%. Since these rates appeared to be impractically low, no comprehensive study of the chlorination of pellets having high PuO_2 content was made.

High rates of conversion of UO_2 to volatile chlorides could be achieved, even with pellets of high PuO_2 concentration, when the specific surface area was increased by mechanically grinding the pellets to pass a 100-mesh sieve. The rate of uranium volatilization (as chlorides) from such powders at 500°C increased from about 30 to 50 %/hr as the PuO_2 concentration in the powder increased from 5 to 35% (Fig. 1, Table 4). These rates were as high as those obtained in the chlorination of U_3O_8-PuO_2 powders (see Sect. 3.3.2, Fig. 3).

In experiments with UO_2-PuO_2 pellets and powder at temperatures above 550°C, a liquid phase was noted in the reaction boat. The composition of this liquid was not determined but was probably mainly UO_2Cl_2, based on the results of other workers.[2,18,23] No liquid phase formed during chlorination of pure PuO_2 at 700 to 750°C.

It is difficult to correlate the rates of chlorination obtained in this study with data from other sources because of differences in type of sample and type of chlorinating agent. Perhaps the most analogous work was done at Argonne National Laboratory (ANL).[25] In the ANL work, 5/8-in.-long by 5/16-in.-diam UO_2 pellets were allowed to react with 33% Cl_2--33% CCl_4--33% N_2 at temperatures between 500 and 600°C. The rates of weight loss at 500 and 600°C were about 22 and 46 %/hr, respectively. It is interesting (and perhaps coincidental) that these values fall almost exactly on the rate curves shown in Figs. 1 and 3.

The rate of volatilization of plutonium chloride (or the amount volatilized during an experiment) was proportional to the amount of

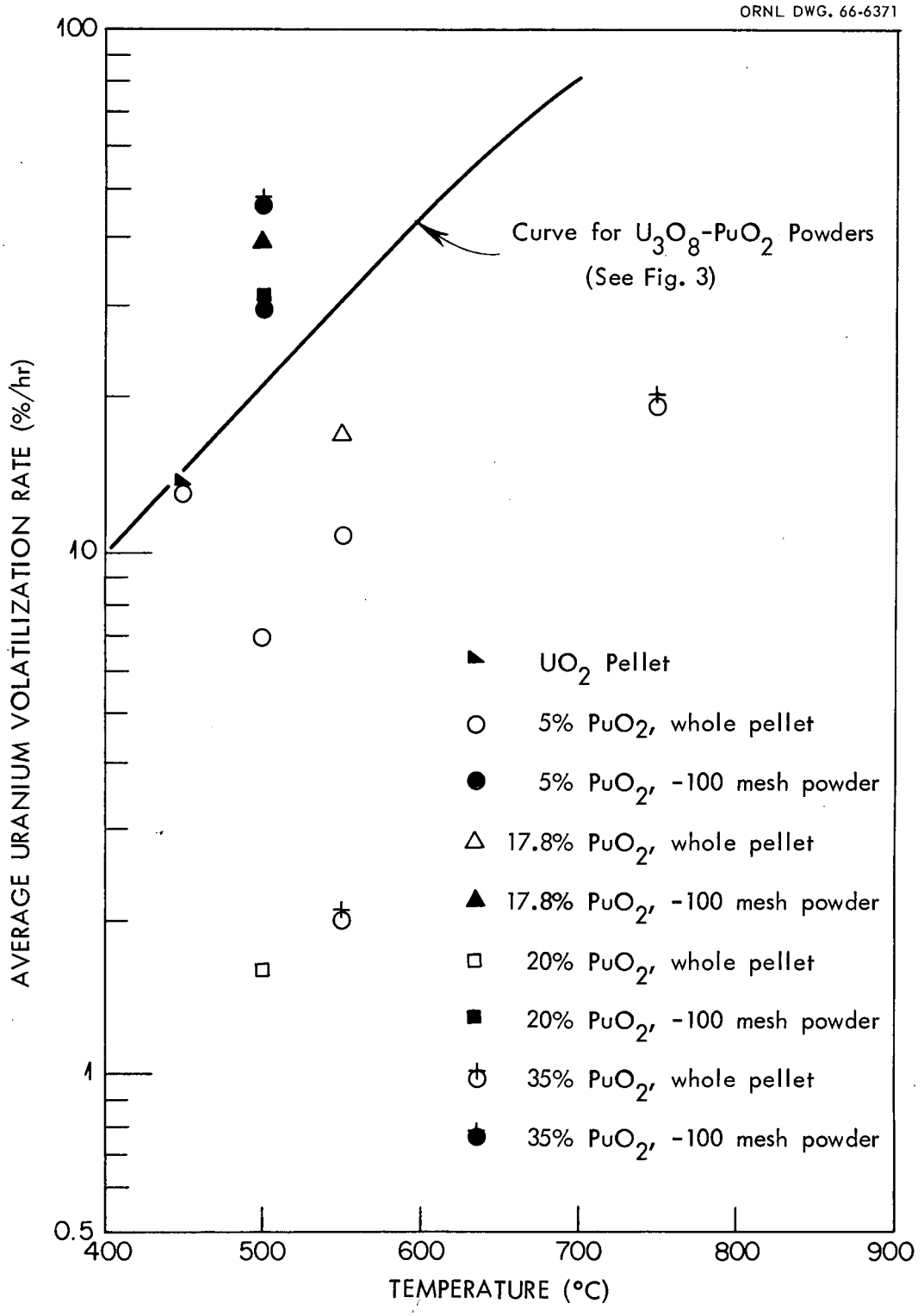

Fig. 1. Average Rates of Volatilization of Uranium Chlorides in Reactions of UO_2-PuO_2 Pellets and -100 Mesh Powder with 85% Cl_2--15% CCl_4.

Table 4. Reaction of 85% Cl_2--15% CCl_4 with UO_2-PuO_2 Pellets and Powder[a]

Expt.	PuO_2 in Mixture (%)	Chlorination Conditions: Temp. (°C)	Time (hr)	Average Chlorine Flow Rate[b] (g/hr)	Amounts Volatilized (%): U	Pu	Moles Chlorine per g-atom Pu Volatilized	K^c_{found}	K_{Benz} (ref. 45)
37	0	450	3	21.0	36	--	---	----	---
38	1	460	--	--	13	3.3	2.3×10^4	4.3×10^{-5}	0.9×10^{-5}
39	5	450	3	19.1	36	2.8	9.1×10^4	1.1×10^{-5}	6.5×10^{-4}
40	5	500	3	3.3	20	1.8	1.9×10^4	5.2×10^{-5}	3.5×10^{-5}
41[a]	5	500	1.4	17.1	41	11.0	8.3×10^3	1.2×10^{-4}	3.5×10^{-5}
42	5	550	2.5	27.2	26	4.0	7.0×10^4	1.4×10^{-5}	15×10^{-5}
43	17.8	550	2	12.0	27	1.0	2.6×10^4	3.8×10^{-5}	15×10^{-5}
44[a]	17.8	500	2	10.2	79	1.5	1.1×10^6	9.1×10^{-5}	3.5×10^{-5}
45	20	500	3	16.4	4	0.05	1.1×10^4	8.8×10^{-7}	3.5×10^{-5}
46[a]	20	500	3	12.1	94	2.1	1.7×10^4	6.0×10^{-5}	3.5×10^{-5}
47	35	550	2	21.8	4	0.5	4.3×10^3	2.3×10^{-5}	15×10^{-5}
48[a]	35	500	2	3.5	92	0.7	5.3×10^2	1.9×10^{-4}	3.5×10^{-5}
49	35	750	2	21.4	38	39.0	5.7×10^2	1.8×10^{-3}	15×10^{-3}
50	100	750	2	14.1	--	8.1	6.7×10^2	1.5×10^{-3}	15×10^{-3}

[a]Powder obtained by grinding pellets to pass a 100-mesh sieve.

[b]Calculated from reaction time and total chlorine found in caustic scrubbers.

[c]$K_{found} \cong \frac{\text{g-atoms Pu volatilized}}{\text{moles } Cl_2 \text{ passed through system}}$; see text.

chlorine passed through the system (Table 4, Fig. 2). This was not unexpected since volatilization of plutonium apparently proceeds mainly by the reaction $PuCl_{3(s)} + 1/2Cl_2 \rightleftharpoons PuCl_{4(g)}$ for which the equilibrium constant is very low, even at 500 to 600°C.[45] Since the equilibrium constant is low, large quantities of chlorine are required to drive the reaction and volatilize a significant amount of plutonium. If equilibrium were established, the number of moles of chlorine required to volatilize 1 gram-atom of plutonium at 500 and 600°C would be about 2.8×10^4 and 1.7×10^3, respectively.[45] To a reasonable approximation, the thermodynamic equilibrium constant K is equal to the number of gram-atoms of plutonium volatilized divided by the number of moles of chlorine passed through the system (see Appendix I). Values of K were calculated for each experiment from the amount of plutonium that volatilized and the total amount of chlorine that was passed through the system, neglecting the CCl_4 present (Table 4). These calculated values were then compared to the thermodynamic equilibrium constants[45] (Fig. 2). Very surprising results were obtained. At temperatures of 500°C and below, the calculated values of K generally were greater than the thermodynamic K, irrespective of the PuO_2 content of the pellet or the state of subdivision of the UO_2-PuO_2 (Fig. 2). This result was quite unexpected since, under the conditions of the experiments, very inefficient utilization of the chlorine would be anticipated. At temperatures of 550°C and above (where formation of a liquid phase in the reaction boat was generally noted), the calculated values of K were significantly lower than the thermodynamic K, as would be expected in tube-furnace experiments where gaseous reagent utilization generally is low. Although the results are not completely explicable, the fact remains that very large quantities of chlorine are required to volatilize small amounts of plutonium, in agreement with predictions made from the thermodynamic data.

During chlorination of UO_2-PuO_2 pellets with 85% Cl_2--15% CCl_4 the volatilized uranium chlorides generally passed through the exit end of the reaction tube and were condensed on glass-wool filters in sections of tubing located well outside the furnace. The color of these uranium chlorides was brown to brown-black, characteristic of UCl_5 and mixtures

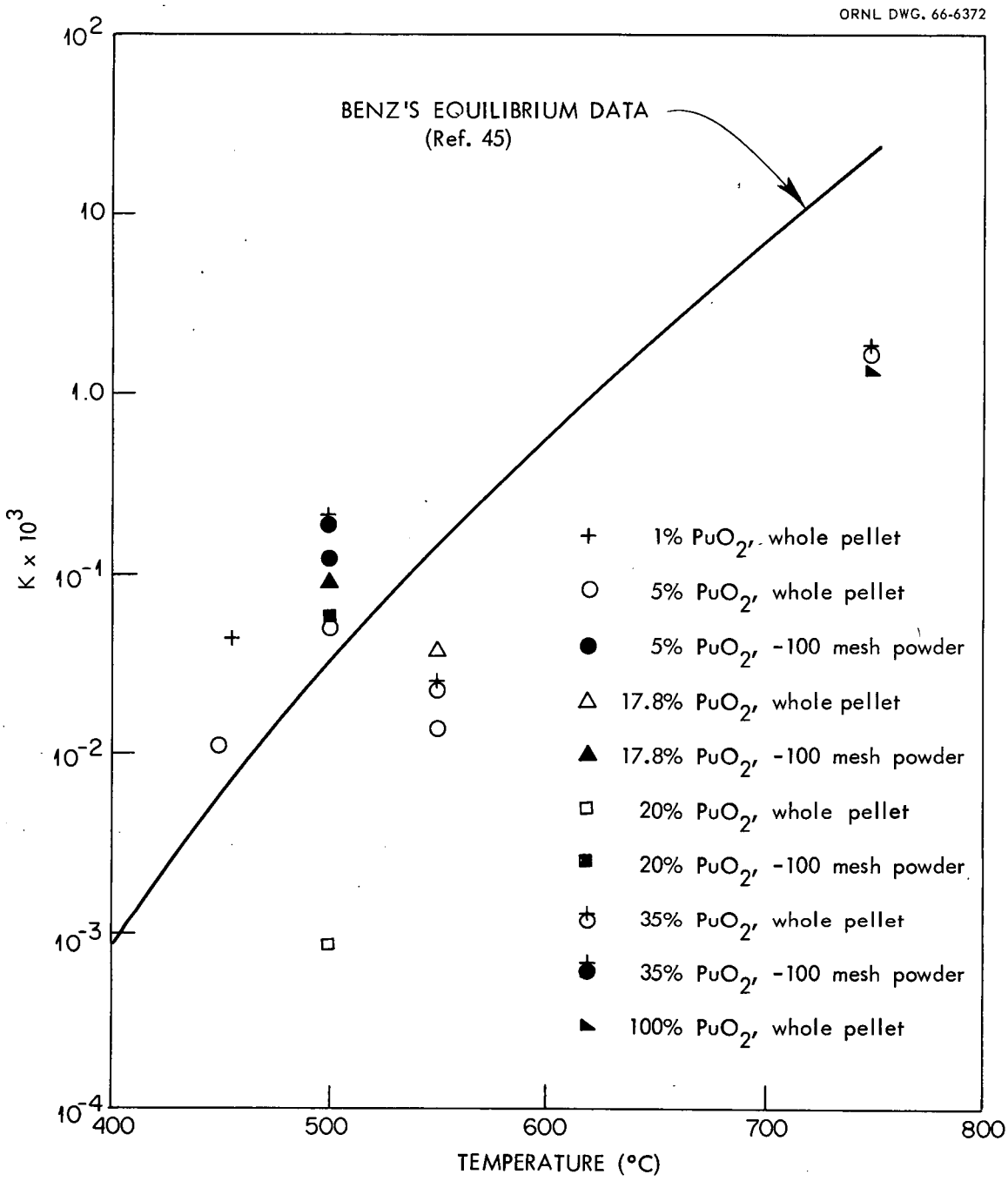

Fig. 2. Amounts of Plutonium Volatilized in Reactions of UO_2-PuO_2 Pellets and Powder with 85% Cl_2--15% CCl_4. The number of gram-atoms of plutonium volatilized per mole of chlorine would be approximately numerically equal to the equilibrium constant K if the chlorinating gas were saturated with $PuCl_4$ vapor.

of UCl_5 and UCl_6. In contrast, most of the volatilized plutonium chloride condensed as a blue band (presumably $PuCl_3$) on the wall of the reaction tube only 5 to 10 cm outside the furnace. These results show that the uranium chlorides are relatively more volatile than the plutonium chlorides. With the simple apparatus used in these experiments, quantitative separations of uranium and plutonium were not achieved; however, these results are in agreement with the fact that good separations are theoretically possible. Since the equilibrium constant for the reaction $PuCl_{3(s)} + 1/2Cl_2 \rightleftharpoons PuCl_{4(g)}$ decreases drastically with temperature,[45] it should be possible to condense solid $PuCl_3$ from a stream of chlorine at temperatures where UCl_5 and UCl_6 are still volatile.

3.3.2 Chlorination of U_3O_8-PuO_2 Powders

As shown in Sect. 3.1 (Table 2), not all UO_2-PuO_2 compositions could be oxidized to U_3O_8-PuO_2 powder. The chlorination experiments described in this section were conducted only with powders that were produced by oxidation of pellets; consequently, the highest PuO_2 concentration in the powder was 20%.

In general, the results obtained with the U_3O_8-PuO_2 powders were the same as those obtained with the UO_2-PuO_2 pellets. The rate at which the U_3O_8 was converted to volatile chlorides increased from about 4 to 50 %/hr as the reaction temperature was increased from 300 to 550°C, regardless of the PuO_2 content of the powder (Table 5, Fig. 3). There appears to be a decrease in reactivity between 550 and 650°C, but the data are too scattered to make this conclusion obvious. Interestingly, the apparent reduction in reaction rate occurs at about the temperature where formation of a liquid (probably UO_2Cl_2) was noted in the reaction boat.

Volatilization of plutonium was very nearly the same as that found for the pellets in that the amount converted to a volatile chloride was proportional to the amount of chlorine passed through the system (Table 5, Fig. 4). As with the UO_2-PuO_2 pellets, the calculated K was generally greater than the thermodynamic K at temperatures of 500°C and below, but less than the thermodynamic K at the higher temperatures where a liquid phase was present during chlorination (Fig. 4). It is

Table 5. Reaction of 85% Cl_2--15% CCl_4 with U_3O_8-PuO_2 Powder[a]

Expt.	PuO_2 in Mixture (%)	Chlorination Conditions: Temp. (°C)	Time (hr)	Average Chlorine Flow Rate[b] (g/hr)	Amounts Volatilized (%): U	Pu	Moles Chlorine per g-atom Pu Volatilized	K^c_{found}	K_{Benz} (ref. 45)
51	0	550	1.25	12.0	30[d]	--	---	---	---
52	0	550	2.0	11.1	8[e]	--	---	---	---
53	0	600	1.0	25.2	10[f]	--	---	---	---
54	1	300	4.75	8.8	14	5	2×10^6	5×10^{-7}	---
55	1	350	2.75	13.3	33	2	7×10^5	1.4×10^{-6}	---
56	1	400	1.5	15.9	11	6.4	9×10^4	1.1×10^{-5}	8×10^{-7}
57	1	450	3.67	11.5	>99	23	7×10^4	1.4×10^{-5}	6.5×10^{-6}
58	1	500	1.0	8.7	47	34	8×10^3	1.2×10^{-4}	3.5×10^{-5}
59	1	500	1.0	16.9	100	100	6.5×10^4	1.5×10^{-5}	3.5×10^{-5}
60	1	525	1.0	4.3	32	16	1×10^4	1×10^{-4}	7×10^{-5}
61	1	550	1.67	22.4	96	75	2×10^4	5×10^{-5}	15×10^{-5}
62	1	550	2.3	5.5	72	33	1.5×10^4	6.7×10^{-5}	15×10^{-5}
63	1	550	3.0	18.2	93	49	3.9×10^4	2.5×10^{-5}	15×10^{-5}
64[h]	1	555	1.0	15.4	11	11	5×10^4	2×10^{-5}	15×10^{-5}
65[h]	1	575	6.0	33.4	100	100	8.4×10^4	1.2×10^{-5}	28×10^{-5}
66[h]	1	650	5.0	14.7	99.4	90	3.1×10^4	3.2×10^{-5}	1.8×10^{-3}
67	5	500	1.42	21.5	99	6.9	6.7×10^4	1.5×10^{-5}	3.5×10^{-5}
68	5	500	8.5	25.0	100[g]	12	4×10^5	2.5×10^{-4}	3.5×10^{-5}
69	5	650	4.0	17.6	79	24	1×10^4	1×10^{-4}	1.8×10^{-3}
70	17.8	500	2.0	4.9	46	9.4	1.1×10^3	9.3×10^{-4}	3.5×10^{-5}
71	17.8	650	5.0	12.6	99	29	1.8×10^3	5.6×10^{-4}	1.8×10^{-3}
72	20	500	3.0	16.5	69	17	4.2×10^4	2.4×10^{-5}	3.5×10^{-5}
73	20	500	6.0	19.4	100[g]	5	4.8×10^4	2.1×10^{-5}	3.5×10^{-5}
74	20	650	5.0	9.6	72	17	2.7×10^3	3.7×10^{-4}	1.8×10^{-3}

[a]Powders produced by reaction of UO_2-PuO_2 pellets with oxygen.

[b]Calculated from reaction time and total chlorine found in caustic scrubbers.

[c]$K_{found} \cong \frac{\text{g-atoms Pu volatilized}}{\text{moles } Cl_2 \text{ passed through system}}$; see text.

[d]Formation of a liquid phase was noted in this experiment; the Cl/U ratio in the residue was 0.17.

[e]Formation of a liquid phase was noted in this experiment; the Cl/U ratio in the residue was 0.57.

[f]Formation of a liquid phase was noted in this experiment; the Cl/U ratio in the residue was 1.2.

[g]All the uranium was volatilized in the first 3 hr.

[h]Formation of a liquid phase was noted during chlorination.

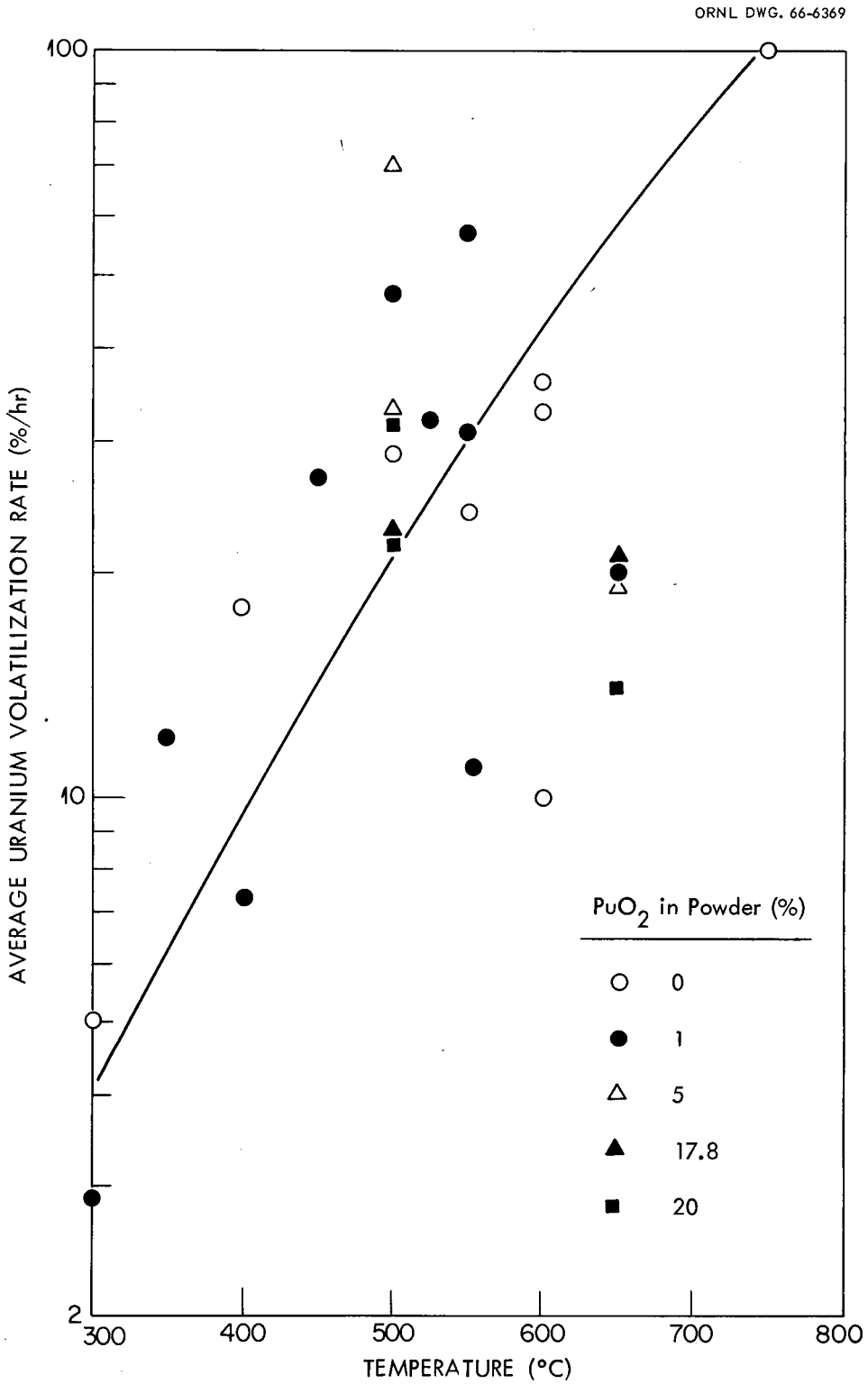

Fig. 3. Average Rates of Volatilization of Uranium Chlorides in Reactions of U_3O_8-PuO_2 Powders with 85% Cl_2--15% CCl_4.

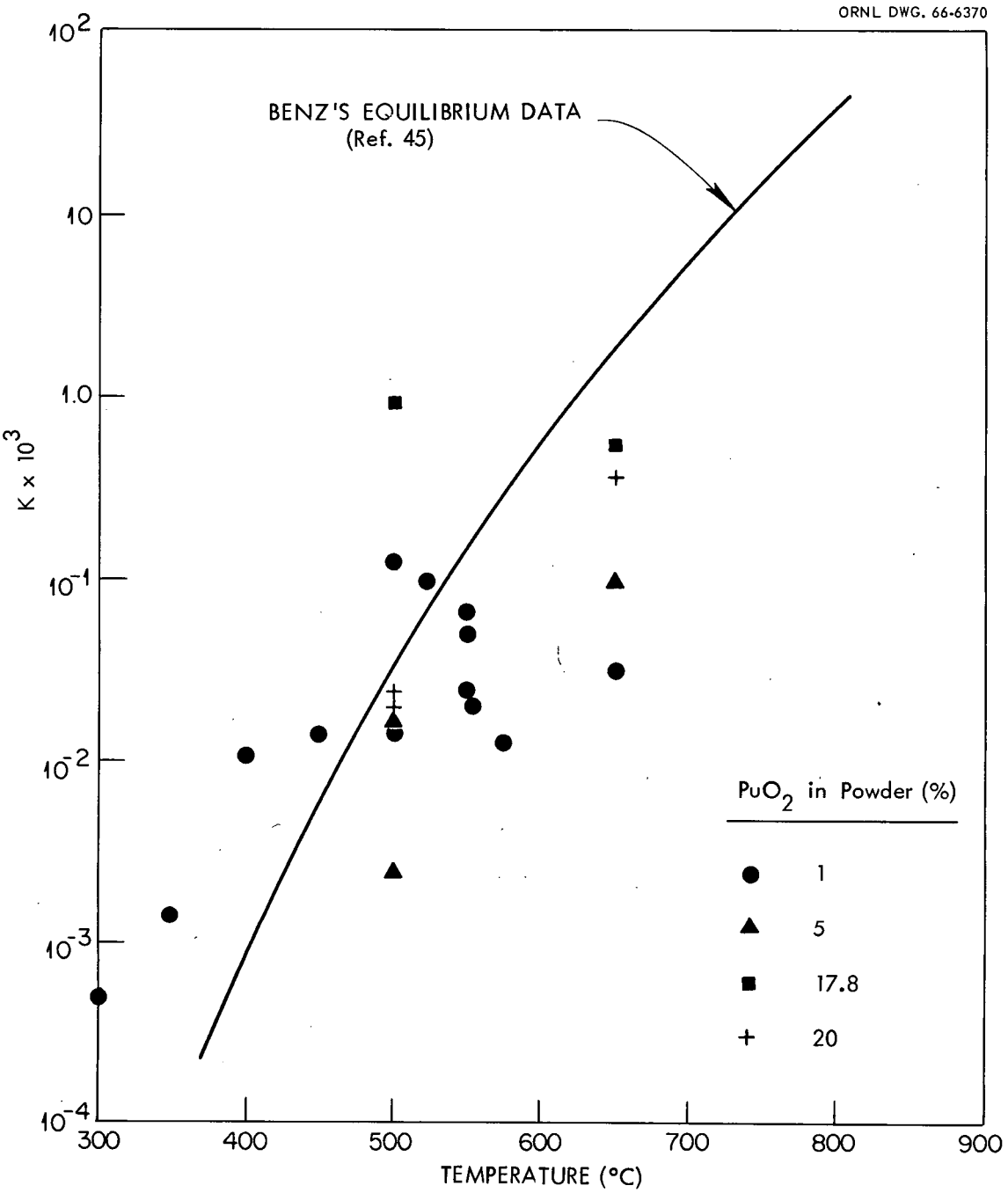

Fig. 4. Amounts of Plutonium Volatilized by Reaction of 85% Cl_2--15% CCl_4 with U_3O_8-PuO_2 Powders Produced by Oxidation of UO_2-PuO_2 Pellets. The number of gram-atoms of plutonium volatilized per mole of chlorine would be approximately numerically equal to the equilibrium constant K if the chlorinating gas were saturated with $PuCl_4$ vapor.

interesting to note that Naumann[9,10] obtained much more volatilization of $PuCl_3$ than expected from vapor-pressure data when he chlorinated irradiated UO_2 with a CO_2-CCl_4 mixture.

4. DISCUSSION AND CONCLUSIONS

The results obtained in this study on the oxidation of UO_2-PuO_2 pellets indicate that any process that depends on oxidative powdering of fuel having a PuO_2 concentration greater than about 20% would not appear feasible unless irradiation causes a marked effect on the oxidation behavior. This could be an important factor in the fluidized-bed processing of fast reactor fuels. If it is desirable to convert the UO_2 to U_3O_8 starting with UO_2-PuO_2 containing more than 20% PuO_2, the results show that mechanical pulverization prior to oxidation would permit more rapid and more complete oxidation. The results also show that oxidation of UO_2-PuO_2 containing less than about 20% PuO_2 probably can be achieved readily and that during oxidation a pellet is converted to a fine powder.

Based on scouting experiments, it was concluded that a mixture of chlorine and CCl_4 was the most practical chlorinating agent for UO_2-PuO_2 and U_3O_8-PuO_2. The carbon in the CCl_4 is useful in removing the oxygen from the oxide as CO and CO_2, and the chlorine provides a means for converting plutonium compounds to $PuCl_4$, which appears to be the most volatile plutonium chloride. A convenient chlorinating agent, and the one used in these studies, is 85% Cl_2--15% CCl_4, which is prepared merely by saturating chlorine gas with CCl_4 at 25°C.

Within the limits of experimental error, the rates of conversion of uranium oxides to volatile chlorides in the temperature range of 450 to 550°C were about the same for small, high-density UO_2-PuO_2 pellets and for U_3O_8-PuO_2 powder (produced by oxidation of UO_2-PuO_2 pellets) when the PuO_2 concentration of the mixed oxide was 5% or less. The efficiency of chlorination of uranium in U_3O_8-PuO_2 powders was not noticeably affected by changes in the PuO_2 concentration from 0 to 20%. At 550°C, complete conversion of the uranium oxide to UCl_5 and UCl_6 required about 3 to 5 hr. However, to obtain similar behavior with UO_2-PuO_2 pellets that contain 5% or more PuO_2, the pellets would

probably have to be mechanically pulverized prior to chlorination.

It appears from the results of this study that conversion of PuO_2 to $PuCl_3$ and the subsequent conversion of $PuCl_3$ to $PuCl_4$ are rapid reactions. The rate at which the $PuCl_4$ volatilizes from the system is dependent on the rate at which chlorine is passed through the system. Thus, the volatilization behavior of plutonium chloride is qualitatively the same as that expected from Benz's thermodynamic data.[45] Although the kinetics for the formation of $PuCl_4$ appear to be rapid, the fact remains that extremely large amounts of chlorine are required to volatilize plutonium as the tetrachloride. As noted in Sect. 3.3.1, about 10^4 moles of chlorine are required to volatilize one mole of $PuCl_4$ at 500 to 600°C. This corresponds to roughly 10^5 liters of chlorine per gram-atom of plutonium volatilized.

Based on this and other investigations, chloride volatility processes for the recovery of uranium, plutonium, and thorium from nuclear reactor fuels do not appear attractive. Hydrochlorination (reaction with gaseous HCl), on the other hand, could find application as a method for removing zirconium, niobium, or aluminum claddings from oxide fuels before the uranium, plutonium, and thorium are recovered by aqueous or fluoride volatility methods. Chloride volatility processes for recovery and decontamination of uranium, thorium and plutonium have the following, and perhaps other, disadvantages: (1) Temperature control appears to be extremely important. It would be desirable to operate at very high temperatures to achieve the benefits of higher reaction rates and minimization of the amount of chlorine required to volatilize $PuCl_4$. Unfortunately, formation of liquid oxychloride phases (that could produce deleterious effects on process operation) and high rates of corrosion of metallic materials of construction limit the upper operating temperature to about 550°C. (2) Plutonium can be volatilized at temperatures of 550°C and below only with vast excesses of chlorine. (3) Thorium can be volatilized only at temperatures above about 750°C, where the vapor pressure of $ThCl_4$ becomes appreciable.[46] (4) Uranium volatilizes not as a single species but as a mixture of UCl_5, UCl_6, and possibly other compounds, thus making it difficult to devise methods for separating the uranium

chlorides from other components of the fuel. (5) Remote refabrication of oxide fuels by a sol-gel process[47,48] is perhaps best accomplished starting with nitrate solutions. If this is proved correct, the products from a chloride volatility process would have to be converted to nitrates before fuel refabrication. It should be noted, however, that sol-gel methods utilizing chloride solutions as feeds also appear feasible.

5. REFERENCES

1. T. A. Gens, Chloride Volatility Processing of Nuclear Fuels, Chem. Eng. Progr. Symposium Series 60(47), 37 (1964).

2. T. A. Gens, Chloride Volatility Experimental Studies: The Reaction of U_3O_8 with Carbon Tetrachloride and Mixtures of Carbon Tetrachloride and Chlorine, ORNL-TM-1258 (Aug. 26, 1965).

3. H. S. Brown and G. T. Seaborg, Method of Separation of Uranium Values, Plutonium Values, and Fission Products by Chlorination, U. S. Patent 2,875,021 (Feb. 24, 1959).

4. J. H. Goode, A Laboratory Study of the Separation and Recovery of Uranium and Plutonium from Fission Products by Chloride Volatility, ORNL-TM-828 (April 2, 1964).

5. J. Schmets, et al., Retraitement des Combustibles Irradiés, EUR 82.f (1962).

6. Ph. Speeckaert, Processing of Irradiated Uranium by Sublimation of the Chlorides, BLG-38 (July 13, 1959).

7. Ph. Speeckaert, Processing of Irradiated Uranium Alloys by Fractional Sublimation of the Chlorides, CEN-R.1915 (Sept. 1, 1960).

8. D. Naumann, Kernenergie 5, 118 (1962).

9. D. Naumann, Kernenergie 6, 73 (1963).

10. D. Naumann, Kernenergie 6, 116 (1963).

11. D. Naumann, Kernenergie 6, 410 (1963).

12. D. Naumann, Kernenergie 6, 243 (1963).

13. G. Jangg, W. Ochsendeld, and A. Burker, Atompraxis 7, 332 (1961).

14. I. V. Budayev and A. N. Volsky, The Chlorination of Uranium Dioxide and Plutonium Dioxide by Carbon Tetrachloride, Proc. 2nd U. N. Conf. Peaceful Uses Atomic Energy, Geneva, Vol. 28, p. 316 (1958).

15. K. Iwamoto, F. Kobayashi, and J. Shimokawa, J. Atomic Energy Soc. Japan 5(7), 560 (1963).

16. T. Ishihara and K. Hirano, J. Atomic Energy Soc. Japan 5(7), 549 (1963).

17. T. Ishihara, K. Hirano, and T. Honda, J. Atomic Energy Soc. Japan 4(4), 231 (1962).

18. H. Parthey, Nukleonik 7(8), 473 (1965).

19. T. A. Gens, Thermodynamic Calculations Relating to Chloride Volatility Processing of Nuclear Fuels. II. The Capacity of Chlorine for Transporting Plutonium Tetrachloride Vapor During Reaction of U_3O_8-PuO_2 with Carbon Tetrachloride, ORNL-3693 (Oct. 1964).

20. J. Broothaerts, et al., Progres Récents Dans Le Domaine Du Retraitement Par Volatilisation, in "Aqueous Reprocessing Chemistry for Irradiated Fuels," ENEA-Eurochemic Symposium, Brussels, Belgium, (1963), p. 375.

21. J. Schmets, Reprocessing of Irradiated Fuels, Quarterly Report No. 11, Oct. 1 - Dec. 31, 1962, CEN, Belgium, Report No. 2211 (1963).

22. Reprocessing of Irradiated Fuels, Quarterly Report No. 20, January 1 - March 31, 1965, CEN, Belgium, EURAEC-1446 (1966).

23. Argonne National Laboratory Reactor Development for April - June 1961, ANL-6379 (Oct. 1961).

24. T. A. Gens, Thermodynamic Calculations Relating to Chloride Volatility Processing of Nuclear Fuels. IV. The Gas-Phase Reduction of Uranium Pentachloride and Hexachloride to Solid Tetrachloride with Carbon Monoxide, ORNL-TM-1340 (Oct. 14, 1965).

25. Argonne National Laboratory Reactor Development for Oct. - Dec. 1960, ANL-6287 (1961).

26. A. A. Jonke, "Reprocessing of Nuclear Reactor Fuels by Processes Based on Volatilization, Fractional Distillation, and Selective Adsorption," Atomic Energy Review, Vol. 3, No. 1, p. 3 (1965).

27. Chemical Technology Division Annual Progress Report for Period Ending May 31, 1966, ORNL-3945 (1966) (in press).

28. L. M. Ferris, Acid Leaching of Products from the Fluidized-Bed Combustion of Graphite-Base Reactor Fuels and the HF-O_2 Disintegration of Stainless Steel- and Zirconium-Clad Oxide Fuels, ORNL-3876 (Nov. 1965).

29. Letter, V. D. Donihee, HAPO, to H. F. Stringfield, ORNL, November 3, 1964.

30. Development of Plutonium-Bearing Fuel Materials, Progress Report for Period January 1 through March 31, 1962, NUMEC-P-100 (1962).

31. Development of Plutonium-Bearing Fuel Materials, Progress Report for Period April 1 through June 30, 1962, NUMEC-P-101 (1962).

32. C. S. Caldwell, NUMEC, personal communication to R. H. Rainey, ORNL, March 1963.

33. Development of Plutonium-Bearing Fuel Materials, Progress Report for Period October 1 through December 31, 1961, NUMEC-P-90 (1962).

34. F. J. Leitz, editor, Sodium-Cooled Reactors Program, GEAP-4080 (January 31, 1963).

35. Development of Plutonium-Bearing Fuel Materials, Progress Report for Period July 1 through September 30, 1962, NUMEC-P-102 (1962).

36. Development of Plutonium-Bearing Fuel Materials, Progress Report for Period January 1 through March 31, 1963, NUMEC-P-104 (1963).

37. Development of Plutonium-Bearing Fuel Materials, Progress Report for April 1 through June 30, 1963, NUMEC-P-105 (1963).

38. Development of Plutonium-Bearing Fuel Materials, Progress Report for Period July 1 through September 30, 1963, NUMEC-P-106 (1963).

39. N. H. Brett and A. C. Fox, Oxidation Products of Plutonium Dioxide—Uranium Dioxide Solid Solutions in Air at 750°C, AERE-R-3937 (April 1963).

40. D. Boreham, J. H. Freeman, E. W. Hooper, I. L. Jenkins, and J. L. Woodhead, J. Inorg. Nucl. Chem. 16, 154 (1960).

41. H. G. Rieber and N. A. Young, Vapor Phase Chlorination of Uranium Oxides, MDDC-1729 (1947).

42. R. J. Sorenson, A Thermobalance for Studying the Chlorination of Plutonium Dioxide with Phosgene, HW-79141 (October 1963).

43. V. V. Fomin, N. A. Dmitrieva, and V. E. Reznikova, Zhur. neorgan. Khim. III(9), 1999 (1958).

44. J. J. Katz and E. Rabinowitch, eds. "The Chemistry of Uranium," Natl. Nucl. Energy Series, Div. VIII, Vol. 5, McGraw-Hill, New York, 1951, p. 322.

45. R. Benz, J. Inorg. Nucl. Chem. 24, 1191 (1962).

46. F. L. Cuthbert, "Thorium Production Technology," Addison-Wesley, Reading, Mass., 1958, p. 167.

47. R. G. Wymer and D. A. Douglas, compilers, Status and Progress Report for Thorium Fuel Cycle Development for Period Ending December 31, 1964, ORNL-3831 (in press).

48. J. P. McBride, compiler, Preparation of UO_2 Microspheres by a Sol-Gel Technique, ORNL-3874 (February 1966).

APPENDIX I

Estimation of Equilibrium Constant for Reaction of $PuCl_3$ with Chlorine

As mentioned in Sect. 3.3.1, at equilibrium the number of moles of $PuCl_4$ (or gram-atoms of plutonium) volatilized divided by the number of moles of chlorine passed through the system is approximately numerically equal to the thermodynamic equilibrium constant, K, for the reaction

$$PuCl_{3(s)} + 1/2Cl_{2(g)} = PuCl_{4(g)} \cdot$$

That this approximation is valid is shown as follows:

$$K = \frac{p_{PuCl_4}}{p_{Cl_2}^{1/2}} = \frac{X_{PuCl_4} P_T}{X_{Cl_2}^{1/2} P_T^{1/2}} = \frac{N_{PuCl_4} P_T^{1/2}}{N_{Cl_2}^{1/2} N_T^{1/2}}$$

where the p's are the partial pressures of the indicated components, the X's are mole fractions of the indicated components, N's are moles of the indicated components, P_T is the total pressure of the system, and N_T is the total number of moles of gaseous components. Considering only the equilibrium above, $N_T = N_{Cl_2} + N_{PuCl_4}$. Since the number of moles of $PuCl_4$ is extremely small compared to the number of moles of chlorine, the approximation that $N_T = N_{Cl_2}$ can be made. Then,

$$K = \frac{N_{PuCl_4} P_T^{1/2}}{N_T} = \frac{N_{PuCl_4} P_T^{1/2}}{N_{Cl_2}}$$

When the total pressure of the system is one atmosphere,

$$\frac{N_{PuCl_4}}{N_{Cl_2}} = K \cdot$$

ORNL-3977
UC-10 — Chemical Separations Processes
for Plutonium and Uranium

INTERNAL DISTRIBUTION

1. Biology Library
2-4. Central Research Library
5. Reactor Division Library
6-7. ORNL — Y-12 Technical Library
Document Reference Section
8-37. Laboratory Records Department
38. Laboratory Records, ORNL R.C.
39. R. L. Beatty
40. J. E. Bigelow
41. R. E. Blanco
42. F. L. Culler
43. D. E. Ferguson
44. L. M. Ferris
45. H. A. Friedman
46. H. E. Goeller
47. R. L. Heestand
48. C. E. Larson
49. H. G. MacPherson
50. F. H. Patterson
51. J. T. Roberts
52. M. J. Skinner
53. K. S. Warren
54. A. M. Weinberg
55. R. G. Wymer
56. E. L. Youngblood
57. P. H. Emmett (consultant)
58. J. J. Katz (consultant)
59. C. W. J. Wende (consultant)
60. C. E. Winters (consultant)

EXTERNAL DISTRIBUTION

61. A. G. Blasewitz, Battelle Northwest Laboratory, Richland
62. O. F. Hill, Battelle Northwest Laboratory, Richland
63. L. Burris, Argonne National Laboratory
64. S. Lawroski, Argonne National Laboratory
65. M. Steindler, Argonne National Laboratory
66. R. C. Vogel, Argonne National Laboratory
67. C. E. Stevenson, Argonne National Laboratory, Idaho Falls
68. C. M. Slansky, Idaho Chemical Processing Plant
69. R. A. Pahler, Atomic Energy Commission, Washington
70. O. T. Roth, Atomic Energy Commission, Washington
71. H. Schneider, Atomic Energy Commission, Washington
72. J. A. Buckham, Idaho Chemical Processing Plant
73. K. L. Rohde, Idaho Chemical Processing Plant
74. A. R. Matheson, General Atomic
75. L. P. Hatch, Brookhaven National Laboratory
76. J. W. Morris, Savannah River Laboratory
77. J. Nehls, Atomic Energy Commission, Oak Ridge
78. J. A. Swartout, 270 Park Avenue, New York 17, New York
79. Research and Development Division, AEC, ORO
80-314. Given distribution as shown in TID-4500 under Chemical Separations Processes for Plutonium and Uranium category (75 copies — CFSTI)