MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL

UNION CARBIDE NUCLEAR COMPANY
DIVISION OF UNION CARBIDE CORPORATION

MEMORANDUM

EPS-X-342

AECU-3750

(KT-310)

January 24, 1958

TO: G.I. Cathers
FROM: T.R. Jaworowski and C.J. King, III
SUBJECT: Zircex Uranium Sublimate Loss

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

INTRODUCTION

The gas phase Zircex process, a head end process for converting fuel elements clad by zirconium to a chloride salt form by hydrochlorination with HCl gas, is currently under development at ORNL. During the hydrochlorination the volatile chloride salts are sublimed and swept from the reaction vessel. As the $ZrCl_4$ is more volatile than the uranium chlorides, the difference in volatilities may be utilized to effect a separation, and the valuable $ZrCl_4$ may be recovered. The uranium rich residue in the reactor may be treated to recover uranium from the fission products. The principal advantages as far as volatility processing is concerned are:

- 1) Recovery of zirconium for reuse after appropriate cooling times.
- 2) Reduction of HF requirements.

NOTE: This document contains information of a preliminary nature and was prepared primarily for internal use. It is subject to revision and/or correction, and does not represent a final report.

735 001

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

One of the essential limitations of the Zircex process to date is the large percentage loss of uranium which is carried off with the volatile ZrCl_4 . Since the ratio of uranium to zirconium in the fuel element is quite small ($< 1\%$), a large percentage of uranium loss can be caused by small amounts of uranium in the ZrCl_4 sublimate. For example, one mg of uranium present in 1000 mg of ZrCl_4 in the decublimator may result in a uranium loss of more than 20%. The uranium loss must be kept below 1% if the Zircex process is to be adapted to industrial scale reprocessing.

The zirconium is oxidized to the tetravalent state by the HCl upon reaction:

The uranium may be oxidized to either the trivalent or tetravalent states:

An equilibrium exists between solid and vapor phases of UCl_3 and UCl_4 and the HCl and H_2 in the vapor.

This equilibrium is developed and analyzed in Appendices A, B, and C.

APPARATUS

The fuel elements were processed in an inconel reactor of about 2 liters in volume (See Figure 1). The reactor was heated by two separate resistance wire heaters, one of which controlled the heat input to the bottom part of the reactor and the other the heat input to the top part. Two lines led into the reactor through the flange cover at the top, a 1/4-inch copper line which provided an inlet for the gas and an inconel line for outlet of the ZrCl_4 sublimate and other off-gases. The inconel line was heated by autoresistance to maintain it at a specified temperature. The inconel line was attached to a water cooled, nickel desublimator where solid ZrCl_4 was formed. The volume of the desublimator was 3.5 liters.

Copper tubing of 1/2 inch diameter led from the desublimator to a glass smoke trap, designated T_1 , whose volume was 10 liters. The use of the smoke trap was necessitated by the extremely small particle size of the solid ZrCl_4 formed in the desublimator. A glass HCl trap containing 2 liters of water, designated T_2 , was connected to T_1 by means of glass and rubber tubing. To insure complete solution of the HCl gas, the gas mixture from T_2 was led into a glass water bubbler. The off-gas escaped from the bubbler to the atmosphere through a wet test meter manufactured by the Precision Instrument Company.

On the inlet side of the reactor either HCl gas or N₂ gas was admitted by a needle valve through a Fischer and Porter thin-bore rotameter, which utilized a sapphire float, into the inlet tubing. A pressure gauge in the inlet line monitored the pressure at that point.

Temperature of the reactor, autoresistance inconel line, and desublimator were taken by means of four chromel-alumel thermocouples read by means of a Leeds and Northrup potentiometer. The temperature at the top and bottom of the reactor were taken by moving thermocouple No. 1 along the thermocouple well which ran the length of the reactor from the flange cover to within an inch of the bottom. The temperature at the inlet of the inconel line within the reactor was measured by thermocouple No. 4; the temperature at the approximate mid-point of the inconel line was measured by thermocouple No. 5; and the temperature at the exit of the inconel line within the desublimator was measured by thermocouple No. 3 (See Figure 1).

The temperatures at the bottom and at the top of the reactor and the temperature of the autoresistance line were regulated by three variacs in series with the heaters. The reactor was insulated with asbestos to minimize heat losses and allow steady state to be reached rapidly.

A photograph of the apparatus is shown in Figure 2.

PROCEDURE

Prior to the start of a run the reactor, desublimator, T₁, T₂, and the water bubbler, and all connecting lines were washed down with dilute HNO₃, water, and finally acetone, following which they were air dried. An STR fuel element section was weighed and positioned in the reactor about 2" from the bottom by fastening it to the end of the thermocouple well and the inlet gas line. The system was assembled and carefully examined for leaks by admitting a measured rate of N₂ into the reactor for some specified time and comparing this volume with the amount leaving the system through the wet test meter. When the entire system was leakproof the run was started.

After leak testing the reactor was heated to a temperature of 600°C at the bottom of the thermocouple well (where the fuel plate was fastened) and to a temperature of 330°C at the point 15 inches above the bottom of the well where the inlet of the inconel line was located during Runs 1 and 2. During the remainder of the runs the inlet of the inconel line was level with or about 1/4" above the bottom surface of the flange cover. The position of the inlet of the inconel line is considered in detail in Discussion of Results. The inconel line was maintained at a temperature of approximately 400°C during the run.

When the reactor top and bottom temperatures reached 330°C and ~600°C, respectively, the HCl flow into the reactor was started and maintained at the desired flow rate by the rotameter. During the run the temperatures were monitored and maintained at approximately the values given above. Readings

on the wet test meter were taken at five minute intervals to study the reaction rate from the amount of H_2 off-gas.

The effect of flow rate upon the percent of uranium lost was studied by means of six separate runs. Actually, only four different HCl flow rates were utilized: 1200 cc/min, 600 cc/min, 300 cc/min, and 150 cc/min, and a concerted effort was made to keep everything else constant, e.g., the top and bottom temperatures of the reactor, the inconel line temperature, the position of the fuel element in the reactor, and the amount of fuel element initially charged. Three runs were made at a flow rate of 600 cc/min because of experimental difficulties. During the first run at 600 cc/min extensive plugging took place and thereby necessitated dismantling the apparatus and finishing the run after a 69 hour downtime. On the second 600 cc/min run the reactor temperatures were abnormally low during part of the run, causing partial plugging and solidification of almost half of the $ZrCl_4$ on the reactor flange. The third 600 cc/min run was accomplished without any noticeable difficulties.

The run was considered to be completed when the rate of evolution of the H_2 off-gas as measured by the wet test meter fell to 10% or less of the rate of HCl inflow. This indicated that the HCl had already reacted with almost all of the zirconium and the additional HCl entering the system was going into solution in the HCl traps (T_2 and the bubbler) preceding the wet test meter. The flow of HCl gas was turned off at this point, and nitrogen gas was used to purge the system.

After the purge the apparatus was disassembled and the following materials were collected, weighed or measured for volume, and sampled for chemical analysis:

- 1) The solid $ZrCl_4$ removed from the desublimator through its bottom.
- 2) The solid $ZrCl_4$ shaken from the bottom of the smoke trap, T_1 .
- 3) The solid $ZrCl_4$ scraped from the crust on the underside of the flange.
- 4) Fuel element residue lying loose on the bottom of the reactor.
- 5) $ZrCl_4$ dissolved in a 0.5 M solution of HNO_3 , which was used to wash out the inconel line.
- 6) $ZrCl_4$ dissolved in a 0.5 M solution of HNO_3 which was used to wash out the reactor.
- 7) The HCl solution in the water trap, T_2 .
- 8) The HCl solution in the water bubbler.

All solid collections were ground or mixed to as great a homogeneity as possible before sampling. In like manner all liquid collections or washings were shaken well to achieve homogeneity. The results of the chemical analysis of these samples were used to determine the uranium lost to various parts of the apparatus and to determine the material balances for U, HCl, and Zr.

The uranium concentration in the reactor as a function of distance from the bottom was investigated in Runs 5 and 6. The thermocouple well which extends for 17⁺ inches into the reactor, from the flange to within an inch of the bottom, was arbitrarily divided into seven sections along its length. Each section was washed separately with the 0.5 M solution of HNO₃, and the washing was collected in a graduate. The volume was noted and a sample was taken for uranium analysis. The results from this analysis are given in the next section.

RESULTS

The results of the six runs are presented in summary form in Table I. The total uranium loss from the reactor residue varied from 7.1 to 17.7 percent. The material balances for uranium were between 91 and 113% for all but one of the runs. The material balances varied between 96 and 106% for the HCl and between 88 and 104% for the H₂. Sample calculations to arrive at the values in Table I are presented for Run 4 in Appendix E.

The results of the chemical analysis of the washings from the reactor thermocouple well are presented in Table II. Since washings of the thermocouple well were taken only for Runs 5 and 6, the first four runs are not included in this table. A temperature profile within the reactor is also presented in Table II for Runs 5 and 6.

DISCUSSION OF RESULTS

Reaction Rate

Figure 3 shows the variation of off-gas rate with respect to time, and is composed of contributions from the evolved hydrogen and the nitrogen initially in the system. If the initial rate is attributed solely to nitrogen purge and is extrapolated in the way shown so as to give an integrated volume of 18 liters under the curve, the difference between the observed rate and this curve is the rate of hydrogen evolution. This hydrogen evolution curve is denoted by "induction" in Figure 3.

The variation of reaction rate with respect to time shows an initial slow rate or induction period, followed by a rise to a maximum and then a decrease. The final decrease can be attributed to diminishing surface area as the fuel element disappears. The induction period is reputed (1) to be caused by the adsorption of an oxy- or hydroxy- film on the surface of the element before its introduction to the reactor. This is especially true for elements that have been exposed to high irradiation. Methods of circumventing this induction period, proposed by Savolainen (1) are either to introduce a small amount of chlorine gas or to utilize a catalyst of amino-aluminum chloride, a highly corrosive substance.

The reaction rate is therefore by no means constant with time; consequently, neither is the HCl efficiency. This fact may well account for the

TABLE I

SUMMARY OF RESULTS

<u>Item</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3^e</u>	<u>Run 4</u>	<u>Run 5</u>	<u>Run 6</u>
Fuel element weight, gm	174	84	85.7	44.2	37.0	29.3
HCl flow rate, cc/min	600	1200	600	300	600	150
Length of run, min	451 ^a	158	240	255	170	360
Total U loss, %	7.1	14.2	13-15	14.2	17.7	9.1
U loss in desublimator, %	2.9	9.4	5.9	3.7	7.1	2.8
U loss in Inconel line, %	3.2	3.6	unknown	6.1	7.4	1.8
U loss on flange cake, %	-	-	1.6	2.0	2.2	4.4
HCl efficiency, % ^b	65.7	47.2	59	60.5	37.4	52.0
HCl flow/fuel element weight cc/min-gm	3.45	14.3	7.0	6.8	16.2	5.1
Desublimator efficiency, % ^c	68	85.2	31 ^f	59.5 ^f	69.1 ^f	75.0
U balance closure, %	91	113	97.5	93	166	100
HCl balance closure, %	105	96	106	103	104	112
H ₂ balance closure, % ^d	101	104	102	93.5 ^g	95.5 ^g	88 ^g

^aRun interrupted with no flow for 69 hours.

^bDefined as $\frac{\text{HCl reacted}}{\text{HCl reacted} + \text{HCl passing through unreacted}}$.

^cDefined as $\frac{\text{weight in desublimator}}{\text{stoichiometric ZrCl}_4 \text{ formation}}$.

^dHigh values may result from inert and insoluble impurities in HCl.

^eAs of this run, take-off was from flange level rather than 2 in. below.

^fLarge portions of ZrCl₄ or ZrOCl₂ found on bottom of reactor flange.

^gOriginal N₂ apparently not completely purged from system by end of run because of low total off-gas rate and backmixing in vessels.

TABLE II

URANIUM CONCENTRATION AND TEMPERATURE PROFILE IN REACTOR

Location of Sample From Bottom of Thermocouple Well (inches)	Uranium Concentration (mg)		----- Temperature Profile -----			
			Run 5		Run 6	
	Run 5	Run 6	Temperature (°C)	Location (inches)	Temperature (°C)	Location (inches)
0 - 2	0.020	0.045	612	0	600	0
2 - 5	0.66	0.048	593	2	578	2
5 - 8	3.9	1.4	565	4	542	4
8 - 10	4.0	5.2	503	6	513	6
10 - 12	3.6	7.8	480	8	482	8
12 - 14	3.4	6.3	452	10	452	10
14 - 17 ⁺	2.8	3.9	418	12	416	12
			382	13.5	378	13.5
			348	15	346	15
					320	16
					296	17

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation

OFF GAS RATE HISTORY FOR RUN 2

DATE
1-23-58

DRAWN BY
CJK

FILE NO
EPS-X-342

FIG.
3

HCl input flow rate $\pm$ 1200 cc/min

discrepancies between results and the predictions of the Appendix.

HCl Utilization Efficiency

The low HCl efficiency of all the runs seems to have been caused by a high ratio of input HCl to fuel element surface area. The reaction is actually controlled by mass transfer to the surface or chemical reaction rate rather than by the rate of supply of HCl, as has been the case in previous investigations where much larger fuel elements have been used (2). From Table I, there is a good correlation of high values of this ratio with low HCl efficiency and vice versa. The lowest HCl efficiencies were attained in Runs 2 and 5 where the ratio was highest, and the highest HCl efficiency was found in Run 1 where the ratio was lowest.

Uranium Loss

Uranium loss from the reactor is due almost entirely to entrainment of solid uranium particles, mostly as UCl_4 , in the $ZrCl_4$ sublimate and off-gas. The uranium reacts with the hydrogen chloride to form UCl_3 and UCl_4 which, under the reactor conditions of high temperature ($600^\circ C$) and low uranium partial pressure, vaporize and diffuse away from the reaction surface into the gas stream. As these chlorides are swept upward through the reactor in the gas stream, the decrease in reactor temperature with height cools the gas. When the gas cools past about $483^\circ C$, nucleation of UCl_4 begins. At $433^\circ C$ about 90% of uranium chloride becomes desublimated to solid particles of extremely small size, unless there is a super-cooling, which is possible because of the low total uranium concentration. These particles are swept out of the reactor by the excess HCl, the H_2 off-gas, and the $ZrCl_4$ sublimate. The uranium chloride particles are deposited in various parts of the system, as is indicated in Table I by the location of the uranium losses. The reasons for the entrainment and subsequent loss of the uranium are given in detail in the following paragraphs.

Transpirational Vapor Loss. No more than 0.1% of the total uranium in the fuel element reacted leaves the reactor as uranium tetrachloride vapor for typical operating conditions. As is shown in Appendix A, for an exit vapor temperature of $350^\circ C$ and an average HCl utilization efficiency of 50%, the vapor pressure of UCl_4 is sufficiently low so that loss of uranium as UCl_4 vapor is small.

In application of this and the other analyses in the Appendix, it must be recalled that the HCl efficiency was not constant with respect to time and that the initial reaction is only that of zirconium, until the cladding has been penetrated to the point where the uranium alloy is located.

Phase of Uranium Chloride at $600^\circ C$. At the reaction temperature of $600^\circ C$, all uranium which forms chlorides as shown in Equations (2) and (3) exists in the vapor phase once it has diffused to the bulk reactor temperature. This calculation is shown in Appendix B and illustrates that the equilibrium weight

ratio of uranium (as a chloride) to zirconium at 600°C is 0.174, much higher than the ratio of uranium to zirconium (0.009) in the original fuel plate. Thus for very low concentrations of uranium, such as in an STR fuel element, the proportion of uranium chlorides vaporized at any temperature is much greater than in previous Zirce $\times$ studies where the uranium has been present to a degree of 10% or more in the element.

Incipient Nucleation. The temperature at which nucleation of the uranium chloride vapor begins is 483°C , for an HCl efficiency of 50% and a well-mixed reactor. This temperature corresponds to the limiting temperature for a weight ratio of uranium to zirconium of 0.009 to exist at equilibrium in the vapor. Details of deriving the temperature of incipient nucleation are given in Appendix C. Figures 4 and 5, which show the uranium concentration per unit height and temperature as a function of height for Runs 5 and 6, demonstrate that uranium particles begin to accumulate in the reactor below 500°C . The maximum uranium concentration occurred around 475° for Run 5 and around 435°C for Run 6. The discrepancies evident between Figures 4 and 5 and the theory of temperatures for incipient and complete desublimation are partly attributable to the assumption of uniform reaction rate.

Particle Size. The size of the uranium chloride particles is extremely small; the particles are therefore readily swept from the reactor with the ZrCl_4 sublimate, the off-gas, and any excess HCl. In Run 6 (150 cc/min) the upward velocity of the gas stream in the reactor may be on the order of the free sedimentation velocity of the UCl_4 particles, because of a distinct drop in entrainment loss from the 300 cc/min case. This 150 cc/min flow rate corresponds to an upward linear velocity of about 4.1 cm/min. A Stokes Law fall velocity of this magnitude corresponds to a particle size on the order of 2.8μ , or 2.8×10^{-4} cm (Appendix D). At this value for the diameter, the Brownian motion agitation velocity is only about 1% of the gravitational velocity (8).

Particle Growth. The growth rate in size for the uranium particles is small after their nucleation because of the very low concentration of the uranium in the ZrCl_4 vapor. The buildup of the size of the uranium chloride particles, being proportional in rate to the UCl_3 and UCl_4 concentration in the vapor, takes place at a very slow rate, which allows many of these particles to remain small and thus to be carried off.

Effect of Flow Rate. The uranium loss is decreased by the reduction of the HCl flow rate in Run 6 to 150 cc/min. Although the effect of flow rate upon uranium loss is none too clear, because of factors which interfered with the constant conditions for each run, nevertheless, a discontinuity for the uranium loss in Runs 2 through 6 appears in Run 6, the lowest flow rate used. If the uranium loss is due to entrainment, then lower flows should reduce the loss to a definite limit. The loss cannot be reduced below this limit, since it is determined by the percent of particles present of sufficiently small diameter to be suspended by Brownian motion.

UCL₃ = UCL₄ Equilibria Effect on Loss. As may be seen from reactions A-1 and A-2 of Appendix A, the presence of a large proportion of HCl in the atmosphere of the reactor will shift the UCL₃/UCL₄ vapor equilibrium to a lower value than encountered normally. Since UCL₄ is by far the more volatile chloride, the uranium chlorides will not tend to desublime as quickly upon lowering of temperature as they pass up the reactor. Hence there will be a lesser time for agglomeration and sedimentation before a particle is swept from the reactor after its nucleative birth, and losses may be expected to be higher. This corresponds well with the results. The high loss of Run 5 may especially be explicable by this, because of the low HCl efficiency of 37.4% encountered there.

Location of Uranium Loss. The location of the major part of the uranium loss varied in the runs. At a flow rate of 1200 cc/min in Run 2, 66% of the total uranium lost was present in the desublimator, 25% in the inconel line, and almost 10% in the trap T-1. In Run 5 (600 cc/min) 40% of the total uranium lost was found in the desublimator, 42% in the inconel line, and 12% on the flange. In Run 4 (300 cc/min) only 26% of the total uranium lost was present in the desublimator, but 43% was in the inconel line, and 14% was in the flange crust. In Run 6 (150 cc/min) 29% of the uranium lost was in the desublimator, 20% was in the inconel line, and 48% was in the flange crust. The location of the major portion of the uranium loss shifted from the desublimator for the run at 1200 cc/min to the inconel line for the run at 300 cc/min, and finally to the flange crust for the run at 150 cc/min. The uranium entrained in the gas flow collected in the sections of the apparatus progressively closer to the reactor for the low flow rates of 300 cc/min and 150 cc/min.

For Runs 1 and 2 the exit vapor stream was taken off from a point one inch below the reactor flange; however, a re-weld between Runs 2 and 3 put the take-off to the Inconel right at the reactor flange surface, thus allowing all vapor to strike the flange before leaving the reactor. This apparently accounted to a large degree for the caking of ZrCl₄ under the flange in the final four runs. In Run 6 the amount of ZrCl₄ deposited there was reduced by increasing the insulation over the top of the reactor. Uranium found in this cake was counted as loss.

The uranium loss in the inconel line was surprisingly high considering the small volume of the line. In Runs 4 and 5 about 42% of the total uranium lost was present in the inconel line. This suggests the possibility of trapping the uranium leaving the reactor in a line or very small desublimator, where a large percentage of uranium as compared with the total amount of desublimates could be obtained.

RECOMMENDATIONS

1) More runs at flow rates below 300 cc/min should be made to investigate the trend shown in Run 6 which indicated less entrainment loss at low flow rate.

2) Various filters should be tried at the start of the inconel line to trap the particles before they enter the line and the desublimator.

3) A Cottrell-type precipitator might be tried to eliminate the uranium particles from the off-gas and sublimate flow.

4) Fuel element surface should be kept large enough to maintain the HCl efficiency high and thereby minimize UCl_4 vapor formation as much as possible. This would give a longer growth time for UCl_4 particles after their formation and thus promote settling out of the particles from the vapor stream.

T.R. Jaworowski

C.J. King, III

APPENDIX

A. Possible Uranium Loss As Transpirational Vapor

Since the vapor pressures of UCl_4 and UCl_3 are quite small at the reactor draw-off temperature of 350°C , and since the proportion of uranium in the system is small enough for it to come to thermal equilibrium with its surroundings at all times and for it not to affect the environmental conditions of the system, the uranium loss possible in the vapor phase may be estimated by a technique analogous to the transpirational method of measuring small vapor pressures.

The equilibrium between UCl_3 and UCl_4 in the vapor at take-off may be ascertained from a knowledge of the ΔF° of the reaction:

at 350°C . Equilibrium constants for the reaction:

are available (5), giving by a small extrapolation a value of K_{ps} ($=P_{\text{HCl}}/P_{\text{H}_2}$) equal to 0.10 atm $^{1/2}$ at 350°C . For reaction (A-1) the K_{pg} would then be:

$$(K_{pg})_T = \frac{(P_{\text{UCl}_3})(P_{\text{HCl}})}{(P_{\text{H}_2}^{1/2})(P_{\text{UCl}_4})} = (K_{ps})_T \left(\frac{(\text{vapor pressure } \text{UCl}_3)_T}{(\text{vapor pressure } \text{UCl}_4)_T} \right) \quad (\text{A-3})$$

At 350°C the vapor pressure of UCl_3 is, again by extrapolation (4), 5×10^{-10} mm Hg and that of UCl_4 (4) is 0.00037 mm Hg. Therefore,

$$(K_{pg})_{350^\circ\text{C}} = 1.35 \times 10^{-7} \text{ atm}^{1/2} \quad (\text{A-4})$$

A typical atmosphere within the reactor corresponds to 50% HCl efficiency, or, on the assumption of a well mixed vessel, a vapor phase containing 0.143 atm ZrCl_4 , 0.286 atm H_2 and 0.571 atm HCl as major constituents. Equation (A-3) may then be solved for $P_{\text{UCl}_3}/P_{\text{UCl}_4}$, obtaining as a value 1.27×10^{-7} . The controlling vapor pressure will then be that of UCl_4 (since $vP_{\text{UCl}_4} \times (P_{\text{UCl}_3}/P_{\text{UCl}_4})_{\text{eq}} < vP_{\text{UCl}_3}$), and UCl_4 will be the solid phase present. Since the small vapor pressure of UCl_4 does not affect the large scale conditions, the mol ratio of U/Zr in the take-off vapor is $(0.00037 \text{ mm})/(0.143)(760 \text{ mm})$ or 3.4×10^{-6} , corresponding to a weight ratio of 8.8×10^{-6} , or a loss of 0.098% of the uranium in the fuel element, since it was present originally to an extent of 0.9%.

Thus the limitation placed on uranium loss as transpirational vapor is on the order of 0.1% for typical operating conditions.

B. Amount of Uranium Present in Vapor Phase Upon Initial Reaction at 600°C

The amounts of UCl_3 and UCl_4 vapor formed at 600°C upon reaction can be determined, again from a knowledge of the equilibrium of reaction (A-1). Again by a small extrapolation from the best available data (5), the value of K_{ps} at 600°C is $3.8 \text{ atm}^{1/2}$; K_{pg} is then, as before, given by Equation (A-3). At 600°C the vapor pressure of UCl_3 is $1.8 \times 10^{-4} \text{ mm Hg}$ (2) and that of solid UCl_4 about 26 mm Hg (6). $(K_{pg})_{600^\circ\text{C}}$ thus is $2.63 \times 10^{-5} \text{ atm}^{1/2}$.

Assuming the same average operating HCl efficiency as previously, the equilibrium $\text{PuCl}_3/\text{PuCl}_4$ is 2.47×10^{-5} . Now, since $(\text{vp}_{\text{PuCl}_4})(\text{PuCl}_3/\text{PuCl}_4)_{\text{eq}} > \text{vp}_{\text{PuCl}_3}$, any solid phase formed is UCl_3 and the vapor pressure of UCl_3 limits the proportion of uranium formed in the vapor phase.

Again, since the small pressures of UCl_3 and UCl_4 do not affect large-scale conditions, the mol ratio of U/Zr in the vapor phase can be

$$\frac{(1.8 \times 10^{-4} \text{ mm})}{(0.143)(760)} \cdot \frac{1}{2.47 \times 10^{-5}}$$

or 0.067, corresponding to a weight ratio of 0.174, or vaporization of all the uranium chlorides, since the original portion in the fuel element was 0.9%.

Thus all uranium forming the chlorides vaporizes upon reaction and is available for the nucleation and growth process described in Discussion of Results.

C. Temperature of Incipient Nucleation

The value of $\log (\text{PuCl}_3/\text{PuCl}_4)_{\text{equilibrium}}$ for a 50% HCl efficiency atmosphere may be considered linear in $1/T$, as may the values of $\log \text{vp}_{\text{PuCl}_3}$ and $\log \text{vp}_{\text{PuCl}_4}$. From the resulting three curves the solution of the previous sections may be made to obtain the temperature at which the weight ratio of U to Zr in the vapor at equilibrium is 0.009, corresponding to the limiting temperature at which all uranium chlorides are in the vapor phase. Such a point is then the temperature of incipient nucleation.

Such a solution gives the temperature of incipient nucleation as 483°C with the equilibrium solid phase being UCl_4 .

Similar calculations show that, if there is no sub-cooling, 50% of the chlorinated uranium will be desublimated to solid particles of UCl_4 at 470°C and 90% will be solid UCl_4 at 433°C.

Since no solid can be formed at temperatures above the point of transition (about 500°C) from UCl_4 solid equilibrium phase to UCl_3 solid, UCl_4 is the only solid phase ever actually formed once there has been original vaporization at

600°C, either at the reacting surface or after reaction products have diffused to the main gas stream.

D. Particle Size Estimation

An examination of the loss from Run 6 indicates that the linear upward velocity in the reactor for 150 cc/min HCl inlet flow may well be on the order of the Stokes free fall velocity. This input flow, for the 4 in. diameter reactor vessel, corresponds to a velocity of 4.1 cm/min when corrected for the molar decrease at 50% HCl efficiency and the average temperature of 475°C.

By Stokes' Law, the settling velocity is:

$$u_t = g_L D_p^2 \frac{(\rho_s - \rho)}{18\mu}$$

where g_L is the local acceleration due to gravity, D_p is particle diameter, ρ_s is the particle density, ρ is the fluid density, and μ is the fluid viscosity. Taking the particle density as 4.725 gm/cm³ (3) and the average viscosity of the gas stream as 0.03 centipoises (7), the particle diameter corresponding to 4.1 cm/sec is 2.8 μ .

E. Sample Calculations (Carried Through for Run 4)

1) Data

<u>Location</u>	<u>Volume or Weight</u>	<u>Concentration or %^a</u>	<u>mg Uranium</u>	<u>mol HCl</u>
Desublimator	67.4 gm	0.030% uranium	20.4	-
Smoke Trap	4.2 gm	0.087% uranium	3.7	-
Inconel Line ^b	37 ml	0.653 mg U/ml	24.4	-
Flange Cake ^c	31.1 gm	0.025% uranium	7.8	-
HCl Trap	2020 ml	0.63 N H ⁺	-	1.27
		0.000075 mg U/ml	0.15	-
Bubbler	74 ml	0.016 N H ⁺	-	0.0012
		0.00005 mg U/ml	0.0037	-
Reactor Residue	0 gm	-	-	-
Reactor Walls ^b	50 ml	6.25 mg U/ml	312	-

^aDetermined by G.R. Wilson, Analytical Chemistry Division, ORNL.

^bWashed with 0.5 M HNO₃.

^cScraped from directly beneath reactor flange.

Fuel element weight = 44.2 gm

Fuel element surface area = 8 sq in. (approximate)

Fuel element composition = 0.9% uranium ($\pm$ 0.1%)

HCl flow rate (from rotameter) = 300 cc/min*

Total insoluble off-gas (from wet test meter) = 40.2 liters

Length of run = 255 min

System volume: Reactor = 2.0 liters
 Desublimator = 3.5
 Smoke Trap = 10.0
 HCl Trap
     Above H₂O = 2.0
     Lines, etc. = 0.5
18.0 liters

2) Calculations

Total uranium in fuel element = 0.009 x 44,200 mg
 = 398 mg

Total uranium loss = 20.4 mg (desublimator)
                       3.7 (smoke trap)
                       24.4 (Inconel line)
                       7.8 (flange cake)
                       0.2 (HCl trap)
                       0.0 (bubbler)
56.5 mg

Percent uranium loss = $\frac{56.5}{398} \times 100 = 14.2\%$

Uranium balance closure = $\frac{\text{U loss} + \text{U in reactor}}{\text{U in fuel element}}$
 = $\frac{56.5 \text{ mg} + 312 \text{ mg}}{398 \text{ mg}}$
 = 93%

---

* All gas volumes at 20°C and atmospheric pressure.

$$\begin{aligned}\text{Moles Zr in fuel element} &= 44.2/91.2 \\ &= 0.485\end{aligned}$$

$$\begin{aligned}\text{HCl equivalent to Zr in fuel element} &= 4(0.485) \text{ moles} \\ &= 1.94 \text{ moles} \\ &= 47.4 \text{ liters}\end{aligned}$$

$$\begin{aligned}\text{H}_2 \text{ equivalent to Zr in fuel element} &= 2(0.485) \text{ moles} \\ &= 0.97 \text{ moles} \\ &= 23.7 \text{ liters}\end{aligned}$$

$$\begin{aligned}\text{HCl efficiency} &= \frac{\text{HCl reacted}}{\text{HCl reacted} + \text{HCl passing to trap}} \\ &= \frac{1.94 \text{ moles}}{(1.94 + 1.27) \text{ moles}} \\ &= 60.5\%\end{aligned}$$

$$\begin{aligned}\text{Total HCl fed} &= 0.300 \text{ liters/min} \times 255 \text{ min} \\ &= 76.5 \text{ liters}\end{aligned}$$

$$\begin{aligned}\therefore \text{HCl balance closure} &= \frac{\text{HCl reacted and HCl passing to trap}}{\text{HCl fed}} \\ &= \frac{47.4 \text{ liters and } 31.0 \text{ liters}}{76.5 \text{ liters}} \\ &= 103\%\end{aligned}$$

$$\text{Nitrogen removed through wet test meter (equivalent to system volume)} = 18.0 \text{ liters}$$

$$\begin{aligned}\therefore \text{H}_2 \text{ evolution} &= \text{wet test meter reading} - \text{N}_2 \text{ volume} \\ &= 40.2 - 18.0 \text{ liters} \\ &= 22.2 \text{ liters}\end{aligned}$$

$$\begin{aligned}\text{H}_2 \text{ balance closure} &= \frac{\text{H}_2 \text{ evolution}}{\text{H}_2 \text{ from Zr reaction}} \\ &= 22.2 \text{ liters}/23.7 \text{ liters} \\ &= 93.5\%\end{aligned}$$

$$\begin{aligned}\text{Moles ZrCl}_4 \text{ in desublimator} &= 67.4/233 \\ &= 0.289\end{aligned}$$

$$\begin{aligned}\text{Desublimator efficiency} &= \frac{\text{moles ZrCl}_4 \text{ in desublimator}}{\text{moles Zr in fuel element}} \\ &= 0.289/0.485 \\ &= 59.5\%\end{aligned}$$

F. Nomenclature (All in Consistent Units)

D_p = particle diameter

ΔF^0 = free energy of reaction from standard states

(g) = gaseous phase

g_L = local acceleration due to gravity

K_p = equilibrium constant in terms of pressures expressed in atmosphere

K_{pg} = equilibrium constant for gas phase reaction

K_{ps} = equilibrium constant for solid-gas phase reaction

$(K)_T$ = equilibrium constant at temperature, T

p = partial pressure, in atmospheres

p_{H_2} , etc = partial pressure of hydrogen

(s) = solid phase

u_t = terminal velocity of falling particle

vp = vapor pressure

μ = viscosity

ρ = density of fluid

ρ_s = density of solid

G. Literature Citations

1) Cathers, G.I., Personal Communication, Union Carbide Nuclear Company, ORNL, January 28, 1958.

2) Ibid., January 9, 1958.

3) Hodgman, C.D. (editor), "Handbook of Chemistry and Physics," 30th edition, 515, Ohio, Chemical Rubber Publishing Co., 1948.

4) Katz, J.J., and Rabinowitch, E., "The Chemistry of Uranium," 453, New York, John Wiley and Sons, 1951.

5) Ibid., p. 459.

6) Ibid., p. 476.

7) Perry, J.H. (editor), "Chemical Engineer's Handbook," 3rd edition, 371, New York, McGraw-Hill Book Company, Inc., 1951.

8) Ibid., p. 1020.