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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.

T. A. Gens

ABSTRACT

The equilibrium yields of solid uranium tetrachloride from the reduction of gaseous uranium pentachloride and hexachloride were calculated from literature free energy data as a function of temperature and the amounts of carbon monoxide, chlorine, and inert gases present. At temperatures as low as 470°K, the calculated yields were greater than 99% if more than 10 moles of carbon monoxide and less than 5 moles of chlorine were introduced with 2 moles of uranium pentachloride and 1 mole of uranium hexachloride. The yields decrease rapidly with increasing temperature. These calculations show that the proposed reduction process is thermodynamically feasible. A process proposal is briefly outlined.

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1. INTRODUCTION

This report is a continuation of thermodynamic calculations related to chloride volatility reprocessing of reactor fuels.[1,2,3] One of the methods being considered for recovering uranium from spent nuclear fuels involves chlorination of the fuel, followed by at least a partial separation of the volatile uranium chlorides from the nonvolatile chlorides of the fission products. If the volatile uranium chlorides are then selectively converted to a less volatile compound, they might be separated from co-volatilized fission-product chlorides. Accordingly, calculations were made to determine if the reduction of uranium pentachloride and uranium hexachloride vapors with CO to the relatively nonvolatile, solid uranium tetrachloride is thermodynamically possible. Determination of the effect of CO on uranium chlorides during chlorination of oxides (with CCl_4) was necessary, in any case, because CO is a by-product.

Although previous calculations[1] indicated that the reduction of higher-valent uranium chloride to solid UCl_3 with CO was not thermodynamically feasible, the calculations in this report indicate that reduction to the solid tetrachloride is thermodynamically possible under practical operating conditions. A temperature of only about 200°C must be used, and the concentration of chlorine must be kept low. The calculations indicate only that the proposed process is thermodynamically possible and which conditions of temperature and gas mixtures should produce the best yields. Laboratory experiments will be needed to determine if the reaction rates are high enough to make it possible to approach the favorable equilibrium yields under operating conditions. Based on the results of calculations in this report, a tentative process flowsheet for the purification of uranium chloride is presented.

2. CHEMICAL REACTIONS

As a starting point, it is assumed that the fuel under consideration is UO_2, one of the more important reactor fuels. The sintered oxide is first oxidized, forming U_3O_8 powder. The U_3O_8 is then converted to chlorides:

$$U_3O_8 + 4CCl_4 \longrightarrow 2UCl_{5(gas)} + UCl_{6(gas)} + 4CO_2 \ . \qquad (1)$$

Thus, the uranium chloride vapor to be reduced contains UCl_5 and UCl_6, in the molar ratio of 2:1. In other processes the molar ratio might be different, although it is likely that a mixture will always be present.

From Eq. (1) it is apparent that the uranium chloride vapor will be diluted with CO_2 and unreacted CCl_4. The effect of these, and any other diluent gases, must be considered in calculations of the yield of solid UCl_4. Therefore, gases which do not participate in the reactions discussed below are grouped together in an "inert gas" term in the equations derived in Sec. 5.

Three reduction reactions occur:

$$UCl_6 + CO \longrightarrow UCl_{4(solid)} + COCl_2 \ , \qquad (2)$$

$$UCl_6 + 1/2CO \longrightarrow UCl_5 + 1/2COCl_2 \ , \qquad (3)$$

$$UCl_5 + 1/2CO \longrightarrow UCl_{4(solid)} + 1/2COCl_2 \ . \qquad (4)$$

In addition, decomposition reactions to yield lower-valent chlorides occur to some extent and cannot be neglected:

$$UCl_6 \longrightarrow UCl_5 + 1/2Cl_2 \ , \qquad (5)$$

$$UCl_5 \longrightarrow UCl_{4(solid)} + 1/2Cl_2 \ , \qquad (6)$$

$$UCl_6 \longrightarrow UCl_{4(solid)} + Cl_2 \ . \qquad (7)$$

The decomposition of phosgene,

$$COCl_2 \longrightarrow CO + Cl_2 \ , \qquad (8)$$

must also be considered, since this reaction liberates CO, which has a favorable effect in reactions (2)-(4), and Cl_2, which has an unfavorable effect in reactions (5)-(7).

3. EQUILIBRIUM YIELDS OF SOLID URANIUM TETRACHLORIDE

Calculations were made to determine the effect of temperature and the amounts of Cl_2, CO, and inert gas introduced, relative to UCl_5 and UCl_6 vapor, on the yields of solid UCl_4 at 1 atm pressure.

At the lowest temperature investigated, 470°K, the calculations indicate that near-quantitative yields of solid UCl_4 can be obtained, even in the presence of a few moles of Cl_2, if 10 to 100 moles of CO are introduced with each 3 moles of uranium chloride vapor (Fig. 1). For example, when 10 moles of CO are introduced, over 99% of the UCl_5 and UCl_6 is converted, at equilibrium, to solid UCl_4, if less than 5 moles of Cl_2 are introduced; with 100 moles of CO, over 99% is converted if less than about 10 moles of Cl_2 are introduced (Table 1).

Table 1. Selected Equilibrium Yields of Solid UCl_4 at 470°K. 2 moles UCl_6, 1 mole UCl_5, and no inert gas

Moles Introduced		Yield of Solid UCl_4	
CO	Cl_2	(moles)	(%)
10	0.0	2.996	99.87
	0.1	2.995	99.83
	1	2.993	99.77
	2	2.989	99.63
	3	2.984	99.47
	4	2.9777	99.23
	5	2.965	98.84
	6	2.942	98.08
100	5	2.984	99.47
	10	2.974	99.13
	15	2.963	98.76
	20	2.950	98.35

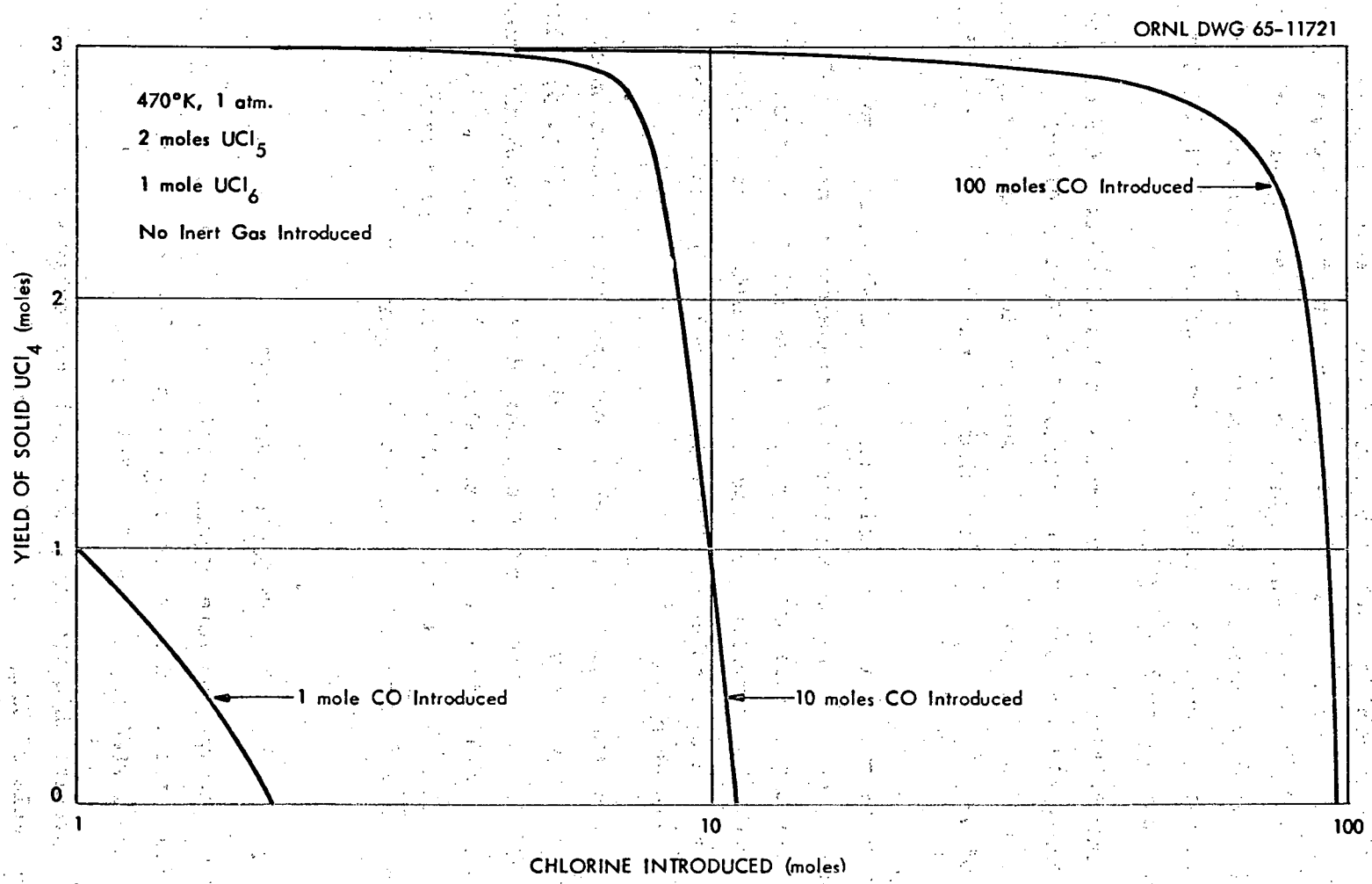

Fig. 1. At Temperatures as Low as 470°K, Near-Quantitative Yields of Solid UCl_4 Can Be Achieved, Even in the Presence of Several Moles of Cl_2, if 10 to 100 Moles of CO are Introduced with Each 3 Moles of UCl_5 Plus UCl_6.

However, the yields drop rapidly with increasing temperature. The near-quantitative yields obtained by introducing 10 moles of CO with 5 moles of Cl_2 at 470°K decrease to only 30% when the temperature is increased to 570°K (Fig. 2). In addition, at the higher temperature, the yields decrease more rapidly as the amount of Cl_2 is increased. It is apparent that the reduction cannot be carried out successfully at temperatures much in excess of 470°K.

The introduction of much more than 10 moles of CO at 570°K does not increase the yield, because of the unfavorable effect of dilution. Use of 100 moles of CO actually leads to a smaller yield of solid UCl_4 than does use of only 10 moles, when less than 5.5 moles of Cl_2 are introduced (Fig. 3).

This unfavorable effect of dilution on yield when large amounts of CO are introduced is of minor importance at temperatures below 500°K (Fig. 4). As the temperature is increased above 500°K, the effect of dilution becomes more pronounced. The maximum yields above 500°C occur when between 10 and 20 moles of CO are introduced with each 2 moles of UCl_5 and 1 mole of UCl_6.

As would be expected from the above results, the introduction of inert gas has only a very small effect on yields at 470°K (Fig. 5). However, at 570°K, when 10 moles of CO are introduced, increasing the amount of inert gas tenfold (from 10 moles to 100 moles) decreases the yield nearly fourfold. This unfavorable dilution effect at higher temperatures emphasizes the advantages of using as low a temperature as possible.

4. ASSUMPTIONS REQUIRED

Several assumptions were required before a solution to the problem of determining the yield of solid UCl_4 could be developed. These assumptions are listed and discussed in this section.

1. The uranium chloride vapor to be reduced contains 2 moles of UCl_5 per mole of UCl_6. This ratio is obtained from the stoichiometry of Eq. (1). Thus, the results given in Sec 3 apply to the off-gas

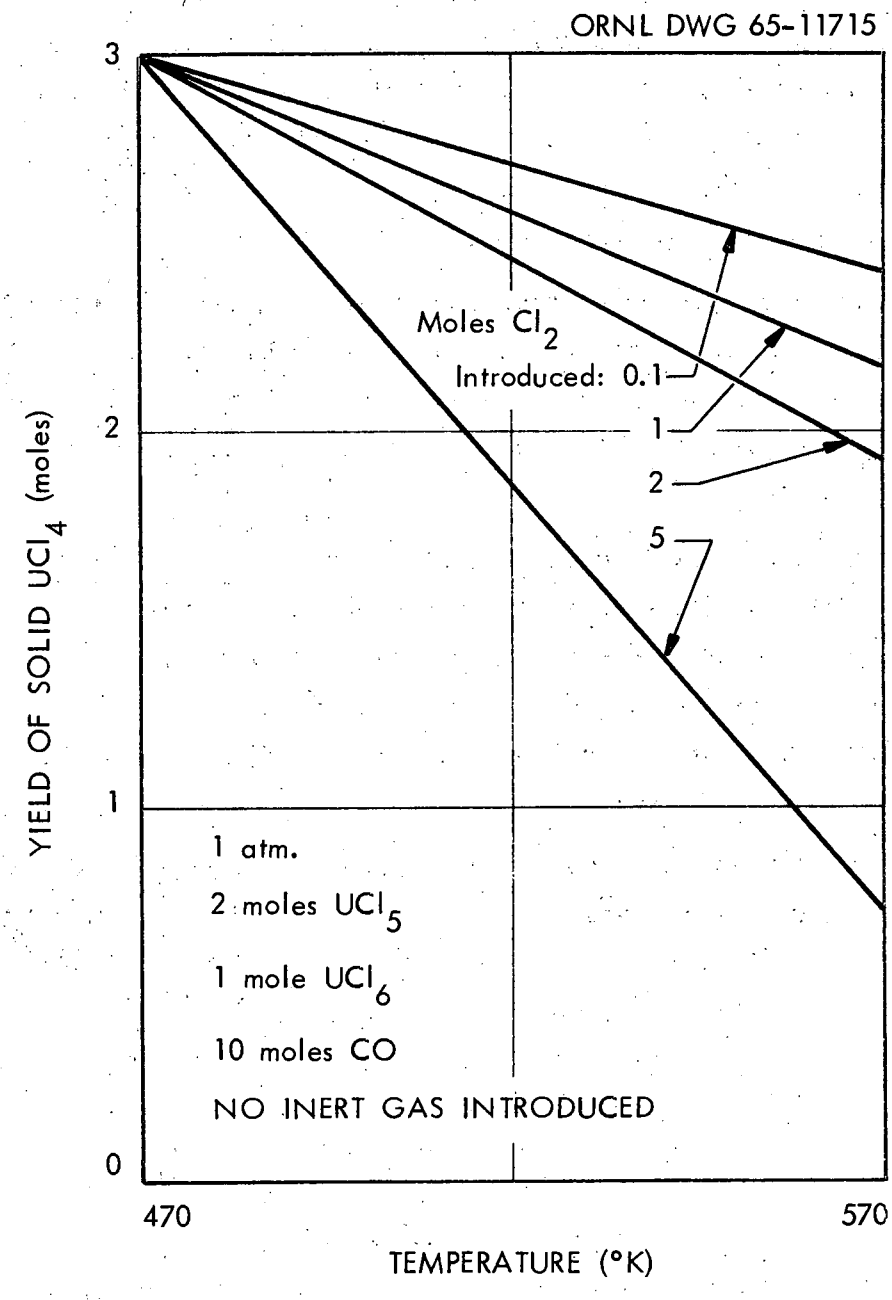

Fig. 2. Near-Quantitative Yields of Solid UCl_4 Can Be Achieved at 470°K, Even When up to 5 Moles of Cl_2 are Introduced with Each 3 Moles of UCl_5 Plus UCl_6, Using only 10 Moles of CO as the Reducing Agent. The yields decrease rapidly as the temperature is increased above 470°K.

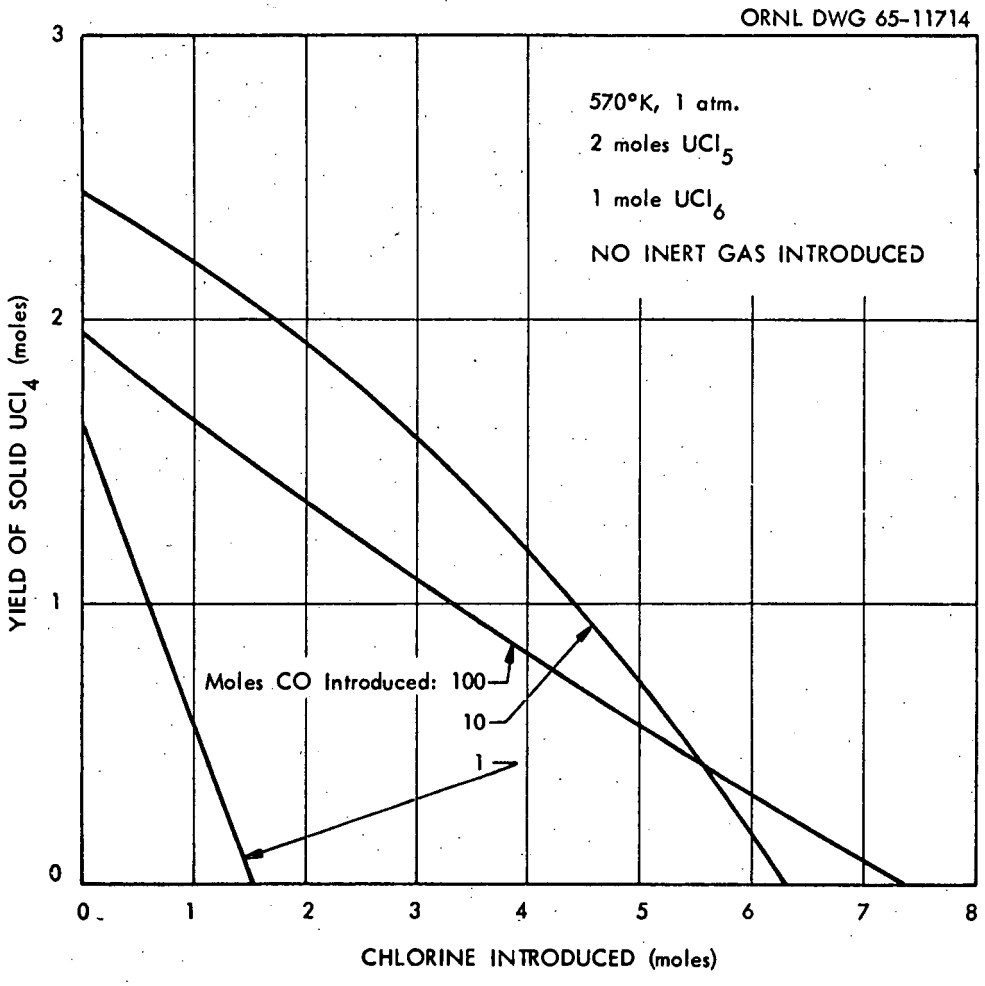

Fig. 3. Yields of Solid UCl_4 are Poor at Temperatures as High as 570°K, Even if Small Amounts of Cl_2 and Large Amounts of CO Are Introduced.

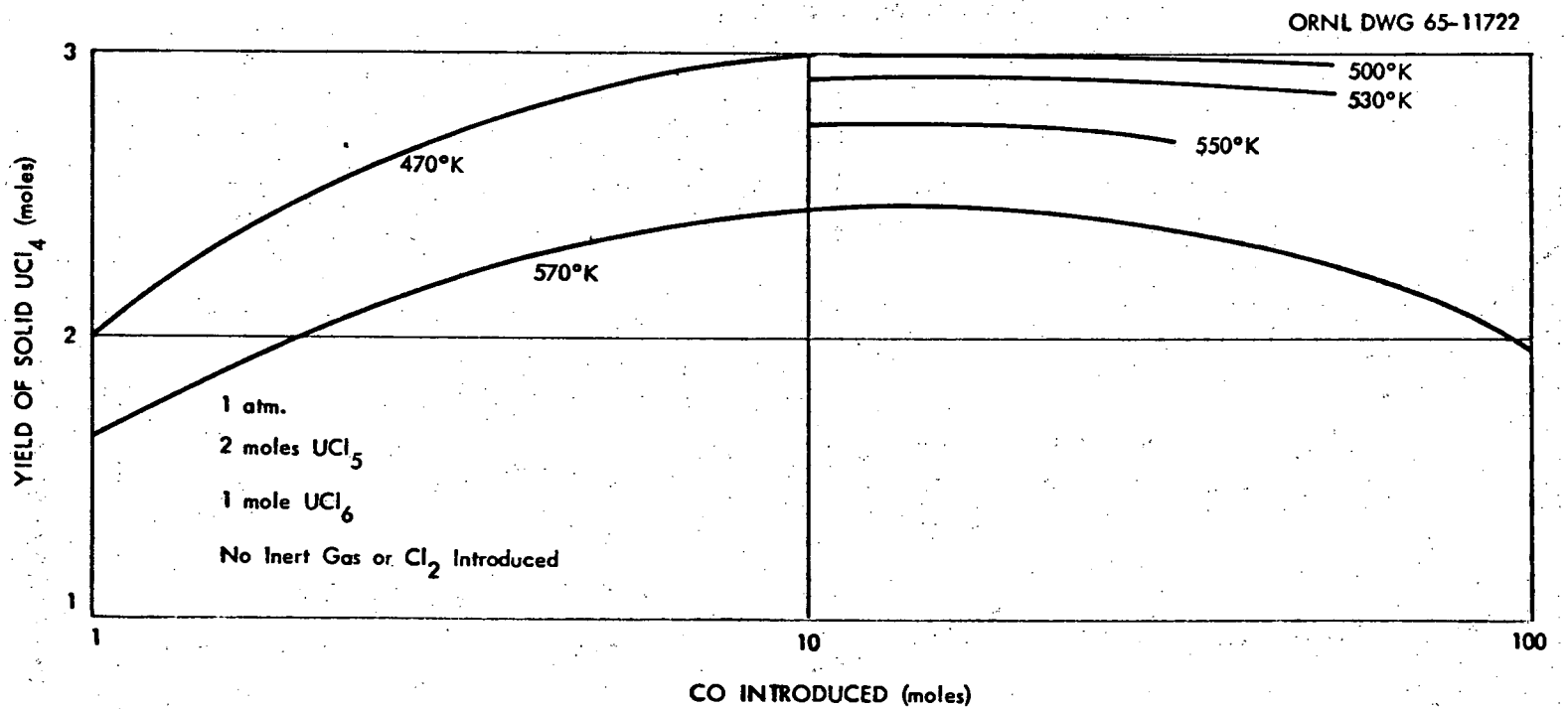

Fig. 4. While the Introduction of up to 100 Moles of CO with Each 3 Moles of UCl_5 Plus UCl_6 Increases the Yield of Solid UCl_4 at 470°K, the Introduction Over 20 Moles of Temperatures of 500°K or Above Reduces the Yield.

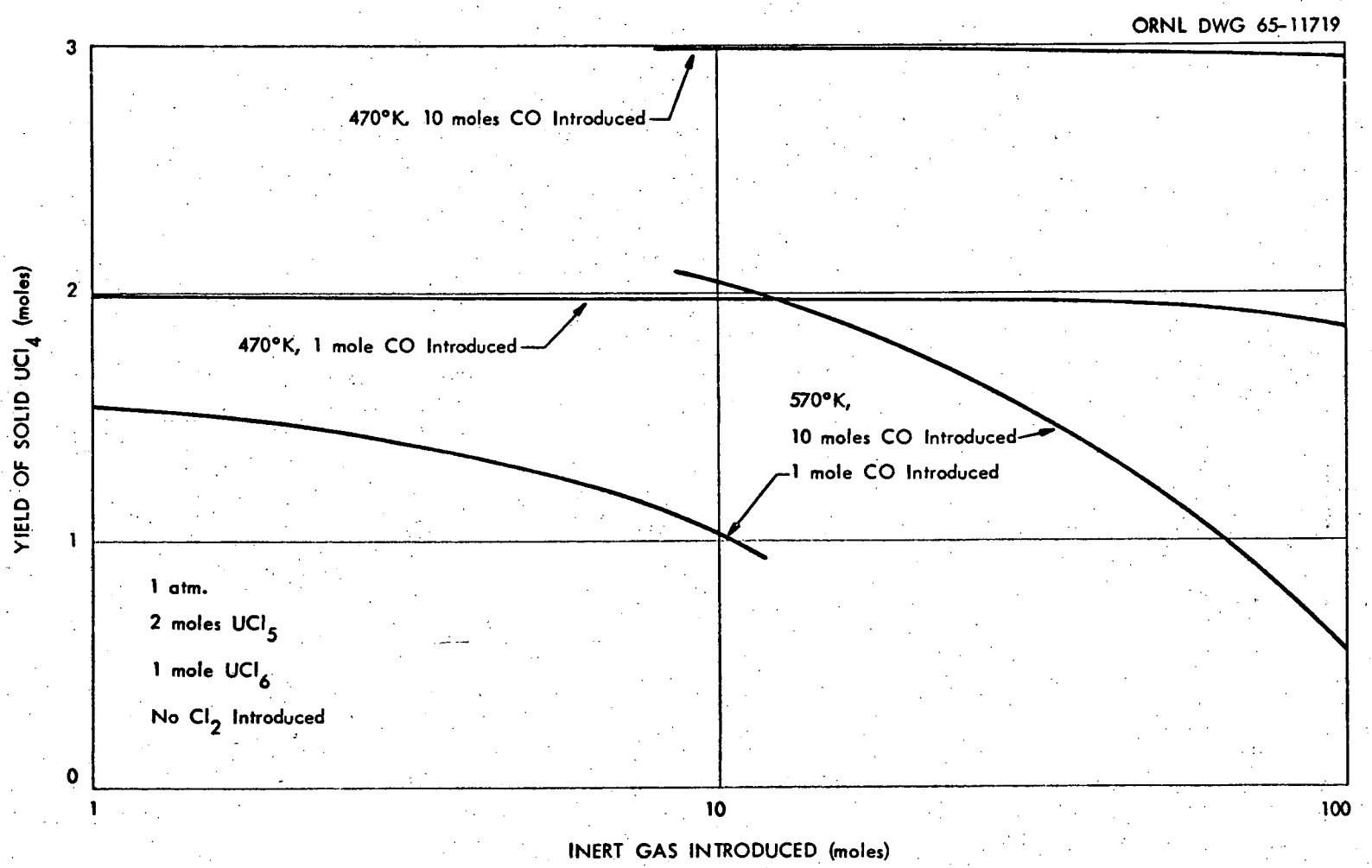

Fig. 5. Large Amounts of Inert Gas Severely Reduce the Yield of Solid UCl_4 at 570°K, but Have Only a Small Effect at 470°K.

from a process involving Eq. (1). Other ratios might well be encountered in chloride-volatility processes. For example, condensation followed by revolatilization of the UCl_5 and UCl_6 products of Eq. (1) would probably affect the ratio. This ratio has an effect on the amount of free chlorine at equilibrium, and therefore must be specified. The fact that the introduction of Cl_2 during the chlorination process [Eq. (1)] will decrease the ratio to below 2 moles of UCl_5 per mole of UCl_6 does not affect the calculation of equilibrium yields (that is, the starting ratio of 2 to 1 is still valid) as long as the number of moles of Cl_2 introduced per mole of uranium chloride vapor is known and included in the calculations.

2. Carbon tetrachloride and CO_2 do not react with UCl_6, UCl_5, UCl_4, $COCl_2$, Cl_2, or CO.

3. Literature estimates of the standard free energies of formation of UCl_5 and UCl_6 [1,4] are accepted as the best available data.

4. The equations for ΔF_f° of UCl_6 and UCl_5 vapors can be extrapolated from the minimum temperatures for which the equations were presented (550 and 690°K, respectively[4]) to 470°K, the minimum temperature used in the calculations below. These extrapolations can be justified if the partial pressures of UCl_6 and UCl_5 do not exceed their saturation pressures, that is, if none of the vapors condense.

5. No condensation of UCl_5 occurs. The vapor pressure of UCl_5 is lower than that of UCl_6; therefore the vapor pressure of UCl_5 is needed. Unfortunately, this vapor pressure is not known. However, in laboratory experiments, the mixed uranium chloride vapors have been observed to pass through tubes heated to about 470°K with very little condensation. If desired, diluent gas could be added to prevent condensation, since the calculations below show that diluent gas has a small effect on the yield of solid UCl_4 at temperatures as low as 470°K. In addition, if any chlorine is present, the partial pressure of UCl_5 will be reduced

due to the reverse of reaction (5). Although the calculations would be upset by the condensation of part of the UCl_5 vapor, it should be pointed out that such condensation should affect the yield of solid UCl_4 favorably, since solid UCl_5 decomposes rapidly to solid UCl_4 at 470°K. Thus, the least favorable case, that is, that no UCl_5 condenses, is assumed.

6. Total pressure is 1 atm.

5. DERIVING AND SOLVING THE EQUATIONS

Examination of Eqs. (2)-(8) shows that it is possible to obtain all seven equations from only three of the equations. Thus, all seven equilibrium constants can be obtained from K_2, K_5, and K_7 using the following relationships:

$$K_2 = K_3K_4 = K_7/K_8 = K_5K_6/K_8, \quad \text{and } K_4^{\,2} = K_2K_7/K_5^{\,2} .$$

Therefore, only the three independent equations (2), (5), and (7) need be considered in the calculations. The method used to obtain the equilibrium constants for these equations is described in Sec 6.

Equations (2), (5), and (7) contain six unknowns, the values of UCl_6, CO, UCl_4, $COCl_2$, UCl_5, and Cl_2. Therefore, three additional equations involving these unknowns are needed before the yield of UCl_4 can be calculated.

The number of moles of $COCl_2$ present at equilibrium will equal the amount of CO used in the formation of $COCl_2$:

$$N_{COCl_2} = N_{CO,i} - N_{CO} , \tag{9}$$

where N denotes number of molecules, and i denotes the amount introduced as contrasted to the amount present at equilibrium. The amount introduced is arbitrarily selected for each calculation.

The number of moles of Cl_2 present at equilibrium will equal the amount introduced, plus one mole for each mole of UCl_6 converted to UCl_4, and 1/2 mole for each mole of UCl_5 converted to UCl_4, minus the amount used in forming $COCl_2$:

$$N_{Cl_2} = N_{Cl_{2,i}} + (N_{UCl_{6,i}} - N_{UCl_6}) + 1/2(N_{UCl_{5,i}} - N_{UCl_5}) - N_{COCl_2} \quad (10)$$

The number of moles of UCl_6 and UCl_5 introduced was taken as 1 and 2, respectively, in all calculations, from the stoichiometry of Eq. (1).

The total number of moles of gas present at equilibrium, N_T, equals the number of moles of uranium chloride vapor introduced, $N_{U,i}$ (or $N_{UCl_{5,i}} + N_{UCl_{6,i}}$), minus the amount converted to UCl_4, plus the other gases present:

$$N_T = N_{U,i} - N_{UCl_4} + N_{Cl_2} + N_{CO,i} + N_{IG} , \quad (11)$$

where N_{IG} is the number of moles of "inert gas", and $N_{CO,i}$ is the sum of N_{CO} plus N_{COCl_2} [see Eq. (9)] .

The equilibrium-constant equations for Eqs. (2), (5), and (7) are:

$$K_2 = \frac{P_{COCl_2}}{P_{UCl_6} \; P_{CO}} , \quad (12)$$

$$K_5 = \frac{(P_{UCl_5}) \; (P_{Cl_2})^{1/2}}{P_{UCl_6}} , \quad (13)$$

and

$$K_7 = \frac{P_{Cl_2}}{P_{UCl_6}} , \quad (14)$$

where P denotes partial pressure. Considering that the partial pressure is the product of mole fraction times total pressure, when the total pressure is 1 atm Eqs. (12)-(14) become:

$$K_2 = \frac{N_{COCl_2} \; N_T}{N_{UCl_6} \; N_{CO}} , \quad (15)$$

$$K_5 = \frac{(N_{Cl_2})^{1/2} \, N_{UCl_5}}{N_{UCl_6} \, (N_T)^{1/2}} , \tag{16}$$

and

$$K_7 = \frac{N_{Cl_2}}{N_{UCl_6}} . \tag{17}$$

Thus, Eqs. (9)-(11) and (15)-(17) are the six equations needed to solve for yield of UCl_4. From considerations used in deriving Eq. (11),

$$N_{UCl_5} = N_{U,i} - N_{UCl_4} - N_{UCl_6} . \tag{18}$$

From Eq. (17),

$$N_{UCl_6} = \frac{N_{Cl_2}}{K_7} . \tag{19}$$

Giving $N_{U,i}$ the value of 3, substituting Eqs. (11), (18), and (19) in Eq. (16) and rearranging, one gets

$$K_5 = \frac{3 \, K_7 - K_7 \, N_{UCl_4} - N_{Cl_2}}{(N_{Cl_2})^{1/2} \, (3 - N_{UCl_4} + N_{Cl_2} + N_{CO_i} + N_{1G})^{1/2}} . \tag{20}$$

From Eq. (15),

$$N_{CO} = \frac{N_{COCl_2} \, N_T}{N_{UCl_6} \, K_2} . \tag{21}$$

Substituting Eqs. (9) and (19) in Eq. (21) and rearranging, one gets

$$N_{CO} = \frac{N_{CO_i} \, N_T \, K_7}{N_{Cl_2} \, K_2 + K_7 \, N_T} . \tag{22}$$

Substituting Eqs. (9), (11), (19), and (22) in Eq. (10), giving $N_{U,i}$ the value of 3, and rearranging, one gets

$$N_{Cl_2} = \frac{-B + \sqrt{B^2 - 4AC}}{2A} , \tag{23}$$

where

$$B = K_7(2K_7 + 1)(3-N_{UCl_4} + N_{1G} + N_{CO_i}) - K_2K_7(2N_{Cl_{2,i}} + 1 + N_{UCl_4} - 2N_{CO_i})$$

$$-K_7^2(2N_{Cl_{2,i}} + 1 + N_{UCl_4} - 2N_{CO,i}) - 2N_{CO_i} K_7^2 ,$$

$$A = (K_2 + K_7)(2K_7 + 1) ,$$

and

$$C = K_7^2 (2N_{Cl_{2,i}} + 1 + N_{UCl_4} - 2N_{CO_i})(3 - N_{UCl_4} + N_{1G} + N_{CO_i}) + 2N_{CO_i} K_7^2$$
$$(3 - N_{UCl_4} + N_{1G} + N_{CO_i}) .$$

Using Eqs. (20) and (23), the yield of UCl_4 can be calculated when temperature (that is, K_2, K_5, and K_7) and the amounts of Cl_2, CO, and inert gas introduced with each 2 moles of UCl_5 and 1 mole of UCl_6 are specified. Because these two equations are complicated, an iterative method must be used to solve them. The method used resembled that described in a previous report.[1] The Oak Ridge National Laboratory CDC-1604A computer was used in the calculations.

6. STANDARD FREE ENERGY CHANGES AND EQUILIBRIUM CONSTANTS

The standard free energies of formation of $COCl_2$, solid UCl_4, and CO have been given in a previous report, where the standard free energies of formation of UCl_4, UCl_5, and UCl_6 were displayed graphically.[1] The expressions for the standard free energies of formation of UCl_5 and UCl_6[4] are:

$$\Delta F_f^\circ\ UCl_5 = -228{,}270 + 5.2\ T \ln T - 0.6\times10^{-3}\ T^2 \frac{0.4\times10^5}{T} - 3.9T$$

and

$$\Delta F_f^\circ\ UCl_6 = -251{,}850 - 0.5\ T \ln T + 2\times10^{-3}\ T^2 - \frac{0.6\times10^5}{T} + 64.6T$$

The standard free energy changes in equations (2), (5), and (7) were obtained by subtracting the sum of the standard free energies of formation of the products in each equation from that of the reactants. The equilibrium constants were calculated from the relationship:

$$\Delta F^\circ = -RT \ln K_{eq}\ .$$

Values of the equilibrium constants and standard free energy changes in the temperature range of interest are listed in Table 2.

7. THE PROCESS PROPOSED FOR PURIFICATION OF URANIUM IN URANIUM OXIDE FUELS

Based on the results of calculations in this report, the conditions for efficient reduction of UCl_5 and UCl_6 vapors in a single-stage process would have to approximate those shown in Fig. 6. In order for such a process to work directly on the off-gas from the chlorination (with mixed CCl_4 and Cl_2) of U_3O_8 without a preliminary condensation and revolatilization of the uranium chlorides (to separate the uranium chlorides from the Cl_2, CO_2 and unused CCl_4), it would be necessary to operate the chlorination process with the minimum amount of Cl_2 in the mixed chlorinating reagent. In addition, it would be desirable to achieve higher efficiencies in the use of CCl_4 than the 20% efficiency observed in large-scale laboratory tests in order to keep the amount of "inert gas" (a term which includes unreacted CCl_4) at a minimum. The calculations show (sec 3) that the equilibrium yield of solid UCl_4 decreases only slightly as the amount of "inert gas" increases, but decreases rapidly as the amount of Cl_2 increases.

Actually, it has been shown in recent work that the addition of Cl_2 to CCl_4 is not necessary during the chlorination of U_3O_8 if the temperature is 550°C or higher.[5] However, there is considerable incentive for

Table 2. Standard Free Energy Changes and Equilibrium Constants

T(°K)	ΔF°_2	ΔF°_5	ΔF°_7	K_2	K_5	K_7
470	-6.149×10^3	7.336×10^3	4.936×10^3	7.245×10^2	3.868×10^{-4}	5.057×10^{-3}
500	-5.067×10^3	6.423×10^3	5.088×10^3	1.642×10^2	1.541×10^{-3}	5.961×10^{-3}
510	-4.709×10^3	6.131×10^3	5.136×10^3	1.044×10^2	2.353×10^{-3}	6.288×10^{-3}
520	-4.353×10^3	5.832×10^3	5.182×10^3	6.7641×10^1	4.644×10^{-3}	6.629×10^{-3}
530	-3.999×10^3	5.533×10^3	5.226×10^3	4.461×10^1	5.221×10^{-3}	6.985×10^{-3}
540	-3.646×10^3	5.234×10^3	5.269×10^3	2.992×10^1	7.601×10^{-3}	7.356×10^{-3}
570	-2.595×10^3	4.342×10^3	5.390×10^3	9.891×10^0	2.160×10^{-2}	8.562×10^{-3}
670	8.191×10^2	1.399×10^3	5.705×10^3	5.404×10^{-1}	3.495×10^{-1}	1.376×10^{-2}

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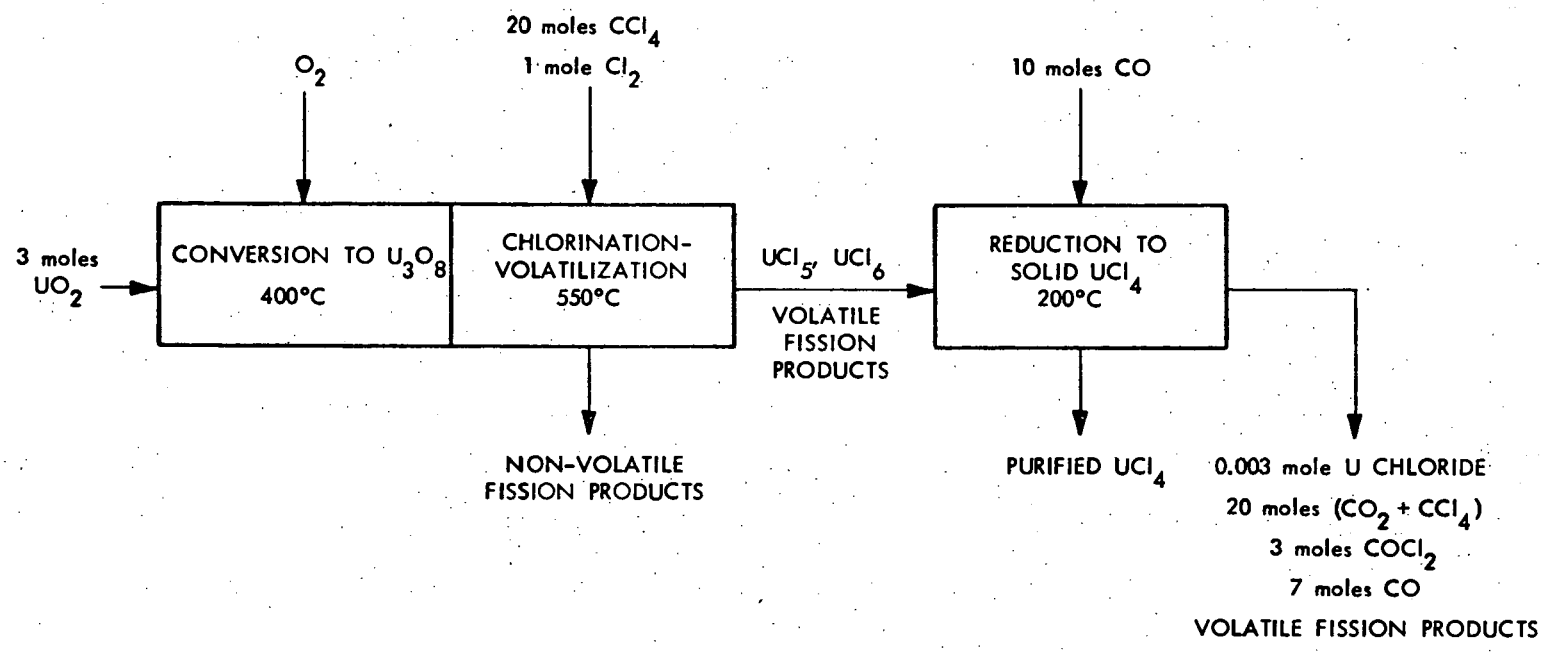

Fig. 6. Proposed Process for Purification of Uranium in Uranium Oxide Fuels. Conditions for the single-step reduction of UCl_5 and UCl_6 are based on Results of Equilibrium Calculations.

not increasing the chlorination temperature much above 550°C because the corrosion rates of the more suitable metallic construction materials, such as nickel, increase rapidly with temperature in this temperature range. Thus, Fig. 6 represents a compromise in that only 1 mole of Cl_2 is introduced for each three moles of uranium chloride formed in the chlorination process.

8. CONCLUSIONS AND DISCUSSION

The calculations in this report show that the single-stage reduction of UCl_5 and UCl_6 with CO to produce solid UCl_4 in good yields is thermodynamically possible at a temperature of about 200°C. It is not known whether equilibrium would be approached closely in all the reactions involved and under operating conditions. An excessively slow approach to equilibrium would not necessarily mean that yields would be lower than those calculated in this report. For example, the slow rate of decomposition of phosgene might actually be beneficial and cause experimental yields to exceed the equilibrium yields, since the Cl_2 liberated by decomposing phosgene decreases the yield in the equilibrium case. The decomposition rate of $COCl_2$ has been observed to be (very approximately) 1% per minute at 451°C in the presence of Cl_2, and slower in the absence of Cl_2.[6] The decomposition rate decreases with decreasing temperature.

The calculations indicate an equilibrium yield of 99.9% for the process outlined in Fig. 6. The uranium chlorides passing through the reduction chamber would be recovered in a cold trap, perhaps along with $COCl_2$ and unused CCl_4. A method of recycling this small amount of uranium chloride would have to be developed.

In a process for chlorinating uranium oxide fuel containing plutonium oxide, in which volatilization of both uranium and plutonium chlorides during chlorination is desired, it would be necessary to introduce condensation and revolatilization steps previous to the reduction step, in order to separate the uranium chlorides from large amounts of Cl_2. Previous calculations[2] indicated that at least 20 moles of Cl_2 per mole

of uranium would be required in such a chlorination process to ensure volatilization of the plutonium chloride. The calculations in this report show that the CO reduction process could not operate successfully with this much Cl_2 present.

The generally favorable results of the equilibrium calculations in this report suggest that the use of CO for reducing UCl_5 and UCl_6 to solid UCl_4 should be investigated experimentally. The conversion of uranium oxide to, first, volatile chlorides, and, second, to nonvolatile UCl_4 would bring about separation from both volatile and nonvolatile fission-product chlorides.

9. ACKNOWLEDGEMENTS

The services of A. Jenkins and G. Atta of the Mathematics Division in programming equations for the CDC-1604A computer are gratefully acknowledged.

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