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SUBJECT: Preparation, Purification, and Properties of the Uranium Chlorides: A Literature Survey

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FROM: H. A. Friedman

ABSTRACT

A literature survey of methods for preparing and purifying the uranium chlorides was made. Crystallographic, thermodynamic, and phase equilibrium data are included. The survey is current to July 1963.

CONTENTS

I. INTRODUCTION

The KCl-UCl_3 system is currently under investigation within the ORNL Reactor Chemistry Division as part of the continuing study of nuclear materials for a possible fuel in fast breeder reactors. The first major difficulty encountered in this investigation was in obtaining and maintaining anhydrous material; the various uranium chlorides are very hygroscopic. An extensive literature survey was initiated to find a possible solution to the problem. The different methods of preparation of the uranium chlorides, their reactions, properties, and structural materials for their containment are discussed in this report.

II. PREPARATION, PURIFICATION, AND DISPROPORTIONATION OF UCl_3

A. Preparation

1. With HCl

HCl gas at 250°C reacts with powdered uranium or UH_3[1-4] to produce UCl_3 that is green at room temperature, reddish-brown at 300°C, and purple at 450°C.[1]

2. By Reduction of UCl_4

a. With H_2. UCl_4 is reduced to UCl_3 at 450 to 575°C in a stream of H_2 gas at 7 atm pressure.[1,5,6] When UCl_5 is present, the chloride is heated in a stream of nitrogen; chlorine begins to be evolved at approximately 150°C and is complete at 350°C.[7,8] Reduction of the resulting UCl_4 with H_2 requires about 5 hr at a temperature of 500 to 525°C at atmospheric pressure.[1,7] If the material is heated much above 500°C, it melts and UCl_4 sublimes on the container wall. Redistilled UCl_4 is reduced more slowly than the product resulting from CCl_4 because of the crystalline character of the distilled UCl_4.[7] The reduction is best carried out at 500°C until most of the reaction is complete to prevent sintering, and then the temperature gradually raised to 650°C under 7 atm pressure.[1,6]

b. With HI. UCl_4 is reduced to UCl_3 at 300 to 350°C with HI. The UCl_3 would be contaminated with iodine but could be freed from the iodine by a stream of dry nitrogen at 200 to 300°C.[9]

c. With Metals. If a metal forms a volatile chloride, very good yield of crystalline UCl_3 can be obtained from the reduction of UCl_4. Metallic zinc is particularly suitable.[10,11] Good-quality UCl_3 was prepared by the reduction of UCl_4 vapors by metallic zinc. Zinc sublimes readily, continually exposing new surface for reaction, and zinc chloride is so volatile that it does not appreciably contaminate the UCl_3 produced.[11]

3. By the Oxidation of Uranium Metal with Metallic Salts

UCl_3 may also be formed by dissolving uranium in molten lead chloride[12-14] or $CdCl_2$ – alkali chloride melts.[4] Any excess cadmium can be plated out of solution by electrolysis. Cadmium is soluble in LiCl-KCl-UCl_3 melts to 100 ppm by weight.[4]

4. In Alkali Chloride Melts with Suspended UO_3

UO_3 suspended in liquid LiCl-KCl when chlorinated with chlorine in the presence of carbon is converted to UCl_4 which can be reduced with H_2 to give UCl_3.[4] Chlorine will also rapidly convert any hydroxide in the melt to the chloride.[15]

B. Purification

Uranium trichloride can be liberated from volatile materials including UCl_4 by heating to 770°C in a vacuum for several hours.[16] It can be purified further by converting it to UCl_3I, subliming the mixed halide, and decomposing the UCl_3I to regenerate UCl_3.[17-19] UCl_3 reacts in an iodine atmosphere at 500°C to form UCl_3I, which sublimes at this temperature. The UCl_3I decomposes to UCl_3 and I_2 under a high vacuum at a cooler part of the system (400°C).[17] UCl_3I is thermally unstable, losing iodine when heated in a vacuum at temperatures higher than 225°C.[17] If the I_2 pressure is maintained between 0.1 to 0.5 atm, a reddish-brown sublimate, UCl_3I, will deposit in the cool section of the system along with free I_2.[18]

C. Disproportionation

Uranium trichloride decomposes when heated in a vacuum to 840°C.[1,20,21] Evidence of decomposition can first be observed at 500°C.[20] The products of the disproportionation of UCl_3 which were measured at 10^{-5} mm H_2 at 750°C were determined to be UCl_4 and uranium metal.[22] UCl_3 in an NaCl-KCl melt is stable over temperature range of 690 to 810°C and from the heat of formation and entropy values should disproportionate only at a temperature above 5000°C.[23]

III. PREPARATION AND PURIFICATION OF UCl_4

A. Preparation

1. With Carbon Tetrachloride

Uranium tetrachloride can be prepared from uranium oxides with either the liquid or vapors of carbon tetrachloride under controlled conditions.[1,6,24-52] Numerous procedures have been reported for the chlorination of the oxides, but basically the majority of the methods are similar. A charge of uranium oxide is heated with liquid CCl_4 in an autoclave to an initial temperature of 120°C and to a final temperature of 140 to 160°C[24,25] while maintaining a pressure of 150 psi. Both UCl_4 and UCl_5 are formed as products. Complete conversion of UCl_5 to UCl_4 has been reported to occur when the UCl_5 is heated to 250°C[53] or 450°C[26] in a stream of N_2. Carbon tetrachloride reacts slowly with UO_2 or U_3O_8 at its boiling point (76.8°C) and atmospheric pressure--only 6% conversion with UO_2 and 31.5% completion with U_3O_8 after 24 hr.[51]

Carbon tetrachloride vapors may be passed over uranium oxide at 400 to 500°C with an inert gas such as CO_2 at atmospheric pressure to produce UCl_4 and higher chlorides. If $CHCl_3$ is mixed with the CCl_4 in a ratio of 1:3, pure UCl_4 uncontaminated by UCl_5 is obtained.[27] A mixture of chlorine and carbon tetrachloride vapor passed over uranyl formate heated to 400 to 600°C produces UCl_4 in almost quantitative yield.[28]

The state of the uranium oxide is very important with regard to the method of preparation and the valence of the uranium. Highly reactive UO_2 can be made by reducing UO_3 with CH_4 gas at 400 to 500°C,[42,43] or with ethyl alcohol at 290 to 350°C.[44] Highly reactive UO_3[45] can be formed by treating UO_2 with HNO_3 to form $UO_2(NO_3)_2$ which is treated with H_2O_2

to form $UO_4 \cdot 2H_2O$. Further treatment with NH_4OH changes the physical state of the $UO_4 \cdot 2H_2O$ through an unexplained mechanism.[45] This product, calcined to UO_3, reacts readily with CCl_4.[45]

The best manner for absorbing phosgene and chlorine,[25] the dangerous gaseous by-products of the chlorination of uranium oxide with CCl_4, is to conduct all bleed-off gases to an absorber that contains dilute caustic solution. Phosgene or chlorine can be detected with Harrison test paper, which is prepared by impregnating white filter paper with an alcoholic solution of para-dimethyl-amino-benzaldelhyde and diphenylamine. If either gas is present, the color changes from white to yellow.[25]

2. With Hexachloropropene

Uranium tetrachloride has been prepared from the higher valent uranium oxides with hexachloropropene (b.p. 210°C[54]) vapors and liquid.[55-59] Liquid hexachloropropene is heated with the oxide at 180 to 190°C and in some cases refluxed. When the reaction is completed (approximately 1 to 2 hr), the reaction mixture is cooled and filtered through a sintered glass funnel. The resulting filter cake is washed with CCl_4 to remove unreacted hexachloropropene. The sample is degassed by heating under a pressure of 5 to 15 mm Hg for about half an hour at 300 to 350°C. Hexachloropropene will chlorinate $UO_2Cl_2 \cdot H_2O$,[59] $UO_2Cl \cdot HCl$,[60] but not UO_2.[55,58] An atmosphere of hexachloropropene vapors at approximately 350°C easily chlorinates UO_3 or U_3O_8 into UCl_4 with substantially no formation of UCl_5. The speed of reaction is increased with rising temperature and/or pressure.[58]

3. With Thionyl Chloride

Thionyl chloride is a good chlorinating agent[40,50,56,57,61] for the conversion of uranium oxide to the chloride. The uranium oxides, with the exception of UO_2, react with the vapors of thionyl chloride in the temperature range of 350 to 400°C to produce chlorides.[50,61] UO_3 and excess thionyl chloride at a pressure of 75 to 80 psi and a temperature of 100 to 125°C produce UCl_4 within 2 hr.[50,57] The method of manufacturing the oxide is important. Some oxides are more reactive than others. UO_3 from peroxide precipitation and oxide from the calcining of ammonium diuranate in a stream of dry air at 350°C react with $SOCl_2$ vapor at 350°C to produce good UCl_4.[50]

No evidence of reaction was observed when 20 g of either UO_3 or UO_2 was refluxed with thionyl chloride for 2 hr.[62]

4. With Sulfur Monochloride

Sulfur monochloride will convert uranium oxides to the chloride, but the main disadvantage to its use is the contamination of the final product with sulfur.[40,55] However, the use of chlorine can prevent the contamination.[55] Several methods have been reported for the chlorination of uranium oxides using S_2Cl_2.[6,7,26,51,55] The reactivity of S_2Cl_2 with oxides depends largely on the method of preparation and subsequent handling of the oxide. UO_3 prepared by heating $UO_4 \cdot 2H_2O$ at 325 to 350°C is very reactive. S_2Cl_2 and UO_3[26] in a ratio of 2.5:1 are boiled for at least 12 hr. The excess S_2Cl_2 is decanted off while still hot to eliminate as much sulfur as possible. The residual S_2Cl_2 is removed by distilling under vacuum and the residual sulfur distilled at 400°C in a stream of purified N_2 at a pressure less than 1 cm. The UCl_4 is further purified in a stream of purified N_2 at a pressure less than 5 mm at 600°C for an hour; then the temperature is raised over a period of 1.5 hr to 700°C where it will be held for 0.5 hr longer.[26] Less pure material is obtained from the reaction of S_2Cl_2 and UO_2 than with the other oxides, according to one report;[26] small amounts of UO_2 and $UOCl_2$ remain. Other investigators find UO_2 more reactive than either UO_3 or U_3O_8.[7,51] The methods of making the starting oxides could account for the difference.

Another procedure incorporated the use of chlorine in the reactor with sulfur monochloride.[57] UO_3, sulfur monochloride, and chlorine were charged into an autoclave in the ratio of 2:1:12 by weight; the pressure increased to 70 psi and the temperature rose from 25 to 40°C. The reactor was heated to 112°C during a 45-min period while an additional 250 g of chlorine was added. The temperature was raised to 150°C and held for approximately 4 hr. The pressure increased to 125 psi and then decreased to 65 psi. The final product was hydroscopic and appeared to contain UCl_5.[57]

5. With Cl_2

UCl_4 can be formed by direct reaction of uranium metal and chlorine and by the reaction of chlorine at red heat (1000°C)[40] with UO_2 plus carbon.[1] Contamination of the product with UCl_5 and phosgene ($COCl_2$) is at a minimum when using an oxide/carbon ratio of 0.6.[55,63] With a sodium uranate-lampblack mixture, the reaction proceeds at 600°C satisfactorily.[64] At 250°C, chlorine and methane in the ratio of 1:4 react with uranium oxide to produce UCl_4. Most chlorine[65] (0.3 vol % H_2O at 10 to 12°) can be dried by passing it through a tower containing activated Al_2O_3. When the Al_2O_3 nears saturation with moisture (18 hr), absorbed chlorine and part of the water are desorbed by stopping the chlorine flow and passing cool air up the tower. Later, air at $\overset{=}{<}$220°C is added to complete the desorption. The Al_2O_3 is then reused. Over 60 cycles are feasible.[65]

6. With Phosgene

Phosgene commences[55] to react with U_3O_8 at 450°C, and the conversion is complete at 900°C. The reaction takes place at a slightly lower temperature with UO_2.

7. With Trichloroacetyl Chloride

Boiling of the oxide for 2 hr with the reagent (b.p. 118°C) failed to give a reaction.[62] A violent reaction was observed on raising the temperature before the charge reached 180°C.[62] The products were UCl_4 (80%), UCl_5 (10%), and the rest a mixture of oxides and oxychlorides.[62]

UCl_4 can be prepared by heating UO_2, UO_3, or U_3O_8 with Cl_3CCOCl at atmospheric pressure and 135 to 225°C (preferably 180°C).[66] Cl_3CCOCl is swept over the heated uranium oxide by inert gas stream for 2 to 5 hr. UCl_4 is separated from other impurities by sublimation.[66]

8. With Miscellaneous Reagents

Tetrachlorethylene ($Cl_2C\text{-}CCl_2$, b.p. 121°C) failed to react with uranium oxide on prolonged boiling. When the charge reached nearly 400°C, its vapors reacted, but the final yield was low (calc. 50% chloride). There was some carbonization.[62]

Hexachlorethane (C_2Cl_6, m.p. 187°C) reagent tried both with and without tetrachlorethylene failed to react with the uranium oxide even on prolonged boiling.[62]

HCl (anhydrous), SO_2Cl_2, CH_3CCl_3 or $CHCl = CCl_2$ failed to convert UO_3 to UCl_4 when heated to temperatures up to 400°C.[50] Refluxing UO_3 with $SbCl_5$, C_4Cl_{16}, $C_6H_5CCl_3$, CH_3CCl_3, $CHCl_3$ or C_2Cl_6 in C_4Cl_6 failed to produce any UCl_4.[67]

B. Purification

Exceedingly pure uranium tetrachloride can be prepared by sublimation and fractional condensation of the vapors in glass apparatus.[68] UCl_4 can be sublimed near 650°C with only a small fraction appearing as higher chlorides.[4] Approximately 20 g of UCl_4 has been completely volatilized in 6 min at 3 to 5 mm and 600 to 650°C in a stream of N_2.[1] Residual loss can be avoided when subliming in an inert stream of nitrogen or helium at 3 to 5 mm Hg[53,55] by adding Cl_2 to the helium stream or CCl_4 to the nitrogen stream.[55]

Any UCl_5 may be decomposed by heating; its decomposition begins at 100°C and is complete at 250°C.[55] The volatility of UCl_5 and poor heat conductivity make it necessary to do the decomposition in a stream of nitrogen, carbon dioxide, or chlorine to recondense any sublimate and assist in heat transfer.[55]

IV. PREPARATION, PURIFICATION, AND PROPERTIES OF THE HIGHER CHLORIDES OF URANIUM

Uranium pentachloride may be prepared by the action of chlorine on the tetrachloride at 520 to 550°C[54,55] or the liquid-phase chlorination of uranium trioxide by carbon tetrachloride.[6,54] Carbon tetrachloride reacts with UO_3 at temperatures ranging from 100 to 160°C.[6] UO_3 prepared from the nitrate and ground to the proper size is reacted at 160°C in 1 hr. UO_3 prepared by calcining UO_4 at 350°C reacts with CCl_4 at 100°C in the course of approximately 2 hr. Conversion in either case is practically complete with impurities as low as 0.02%. Proper controls are necessary, as the temperature may increase rapidly as a result of exothermic reaction. Reaction temperature may be controlled by evaporation of the solvent.[6]

Mixtures of UCl_4 and UCl_5 can be converted to pure UCl_5 by the action of liquid chlorine at elevated temperatures and pressures.[69] A stream of chlorine at a temperature around 450°C converts UCl_4 to volatile UCl_5 and UCl_6.[53] UCl_6 can be removed by sublimation at 100 to 200°C in vacuum.[6,53]

UCl_6 is formed by the reaction of uranium oxide with a mixture of chlorine gas and CCl_4 vapors.[70] It may also be obtained by its sublimation from mixtures with lower chlorides. UCl_5[6] will be converted to UCl_6 by heating it in CCl_4 which has considerable amounts of Cl_2. Eighty per cent or more UCl_5 was converted to UCl_6 by heating at 100°C for 6 hr in in a mixture of 80% CCl_4 and 20% Cl_2. At 100°C, UCl_6 is produced from UCl_5 at a rate of 15 g per 100 g of CCl_4 per hour. This is for solvents containing 18% Cl_2.[6] UCl_6[55] may be prepared by reaction of Cl_2 with UCl_4 or UCl_5 at a temperature greater than 350°C, or by UCl_4 and Cl_2 in the liquid phase.

The density of UCl_5 has been reported as 3.81 g/cc and that of UCl_6 as 1.56 g/cc.[71]

V. VARIOUS PROPERTIES AND REACTIONS OF THE URANIUM CHLORIDES

The density of UCl_3 measured by displacement of CCl_4 has been reported as 5.35 g/cc while the density determined by calculation from x-ray data as 5.51 g/cc.[1] X-ray measurements show UCl_3 to have a hexagonal structure with the following constants: $A_o = 7.428 \pm 0.003$, $c_o = 4.312 \pm 0.003$[1,72,73] with 2 moles per unit cell,[72] $d_{calc} = 5.51$, $d_{exprt} = 5.44$; space group is $C6_3/-m(C_{6h}^2)$. There are 2 U in ± (1/3, 2/3, 1/4) and 6 Cl in ± (x, y, 1/4)

$(\bar{y}, x-y, 1/4)$, $(y-x, \bar{x}, 1/4)$; $x = 0.375 \pm 0.014$, $y = 0.292 \pm 0.014$. Each uranium atom is bonded to 3 Cl atoms with U - Cl = 2.95 A and to 6 Cl atoms with U - Cl = 2.96 A. The closest approach of 2 Cl atoms is 3.45 A. UCl_3 has coordination type of structure; U-Cl bonds are predominantly ionic in character.[72] The upper limit of the vapor pressure of the solid has been set by experiments as 0.0035 mm Hg at 750°C and 0.011 mm Hg at 820°C.[21] The estimated value for the heat of sublimation is 5 kcal/mole.[21]

The melting point of UCl_3 has been reported as 842 ± 5°C[1] and 830°C.[29] It is unstable in CCl_4, acetone, chloroform, or ether.[1]

UCl_3 reacts smoothly with chlorine gas at 250 to 300°C,[1,3] but the reaction becomes vigorous at higher temperatures. It reacts rapidly with oxygen at 150 to 200°C. The products are UO_2Cl_2 and Cl_2 with pure UO_2 resulting from overheating.[1] UCl_3 is less hygroscopic than other uranium chlorides. No absorption occurs if $P_{H_2O} = 2.4$ mm Hg; slight absorption occurs when $P_{H_2O} = 3.4$ mm.[53] When 600 mg of UCl_3 was placed on a watch glass exposed to atmosphere, the gain in weight was 2 mg in the first 4 min and 1.2 mg in the next 3, with an average increase in weight of 0.1%/min.[20] In an N_2 stream containing water vapor at a P_{H_2O} of 9 mm Hg, UCl_3 deliquesces to form a purple solution which slowly evolves hydrogen. In moist air with $P_{H_2O} = 9$ mm Hg, UCl_3 does not deliquesce but rapidly hydrolyzes and simultaneously oxidizes to $UOCl_2$.[54] The rate of reaction of UCl_3 with moisture varies with its preparation.[74] Reaction is less rapid at 0°C than at room temperature. At 0°C, UCl_3 can be kept in saturated aqueous solution in contact with a solution of the salt with little oxidation for a considerable time. HCl increases the rate of oxidation of UCl_3.[74] The amount of H_2 evolved in the reaction of the trichloride with water corresponds closely to that required for oxidation of the uranium to the tetravalent state.[74]

UCl_3 can be reduced with sodium metal.[6]

UCl_3 has been reported to form a compound with KCl ($2KCl \cdot UCl_3$, m.p. 625°C). It forms simple eutectic systems with NaCl and $CaCl_2$.[1] Phase equilibrium studies in systems containing UCl_3 with LiCl, NaCl, KCl, RbCl, CsCl, KCl and LiCl,[75] KCl and CuCl, and UCl_4[76] have been conducted at this Laboratory.

The crystal structure of UCl_4 has been determined from powder diffraction photographs as a body-centered tetragonal lattice with space-group symmetry D_{4h}^{19} - I 4/amd that has 4 molecules in the unit cell: $a_1 = 8.296 \pm 0.009$ A; $a_3 = 7.487 \pm 0.009$ A.[1,77] Each metal atom is coordinated to 8 chlorines; 4 chlorines are at a significantly smaller distance than the remaining 4, indicating bonds tend toward covalence.[77] Elson[78] in agreement reports for UCl_4 $\alpha_1 = 8.303 \pm 0.001$ A and $\alpha_3 = 7.483 \pm 0.001$ A. The density (calc.) is found to be 4.87 g/cm^3.[1,77] The density measured has been reported to be 4.88 g/cc.[1,71]

Solid UCl_4 has been found to have a transition at 506°C,[21] and 543°C.[1,21] The melting point (calc.) has been reported as 589.4°C,[21] 590 ± 1°C,[21,29] and 588 ± 5[1] with the triple-point pressure as 18.4[72] and 19.5 mm Hg.[68,77] The addition of 10% UCl_3 lowers the melting point of UCl_4 by 14°C.[1] The boiling point has been measured at 802°C[1] but extrapolated from vapor curves as 878°C[1] and 792°C[29,68] at 760 mm. The estimated critical temperature is 1325°C.[68]

UCl_4 reacts with moisture as low as 2 mm H_2O pressure.[1]

UCl_4 does not lend itself to reduction with metallic sodium,[6] partly because of low melting point and high volatility and partly because sodium does not wet the surface of UCl_4 crystals. Reactions with sodium metal are initiated at 500°C and are quite violent. However, the reduction is not complete.[6]

Uranium tetrachloride forms a compound with KCl ($2KCl \cdot UCl_4$, m.p. 650°C) and with NaCl ($2NaCl \cdot UCl_4$, m.p. 430°C). It forms simple eutectic systems with LiCl, $BaCl_2$, and $CHCl_2$.[1] Phase studies of UCl_4 with KCl,[76,79-81] TlCl,[80] LiCl,[80] KCl and LiCl,[75,80] CsCl,[75,81] CuCl,[81] and NaCl and LiCl,[75] and RbCl[75] have been done at this Laboratory.

Heat capacities, enthalpies of UCl_3 from 0 to 725°C and of UCl_4 from 0 to 425°C,[80,81] heats of formation of the chlorides,[23,85] the vapor pressure of UCl4 with ΔH, ΔF, and ΔS values[21,53,86-88] have been reported.

VI. OXYCHLORIDES

A number of oxychlorides exist. A controversy exists on the temperatures at which oxygen and UCl_4 react and the final products at the various temperatures. UCl_4 reacts extremely slowly at 125°C with oxygen to form UO_2Cl_2 according to some investigators,[21] but others report oxygen in dry air is inert to UCl_4 up to 225°C[89] with 230°C as the lowest temperature for measurable reaction.[54,55] At 235°C the rate of reaction is appreciable and is about 10^2 greater at 306°C.[89] Some reports state that oxygen reacts with UO_2Cl_2 to form U_3O_8 and Cl_2 at 250°C,[54,55] but others report that at 300 to 320°C UCl4 reacts with oxygen to form UO_2Cl_2 with UO_2 and Cl_2 formed at higher temperatures.[1]

There is evidence that a mixture of oxychlorides, $UOCl_3$, $UOCl_4$, and UO_2Cl_2, is formed with UCl_5 and UCl_6 when UO_3 and UCl_5 react with CCl_4 at its normal boiling point.[29] On testing $UOCl_4$, it appears to lose chlorine to form $UOCl_3$ and finally $UOCl_2$.[29] When $UOCl_2$ is heated in the presence of UCl_5 in an autoclave at 170°C, conversion to UCl_4 is obtained.[55]

UOCl, a dark-red crystal, was formed in small amounts during distillation at 1000°C under 10^{-4} to 10^{-5} mm pressure of UCl_3 contaminated with UO_2.[90] UOCl is insoluble and stable in water, ethyl alcohol, and carbon tetrachloride. It decomposes at room temperature in dilute H_2SO_4 and in HCl with evolution of H_2. UOCl is tetragonal with lattice constants: $a = 4.001$, $c = 6.85$ A.[90]

$UOCl_2$ decomposes in a stream of N_2 to UO_2 and Cl_2 above 400°C.[71] In vacuum the decomposition begins around 300°C. UO_2Cl_2 melts in a stream of Cl_2 near 500°C to a reddish-brown liquid. As the temperature is increased to 700°C, decomposition to UO_2 and Cl_2 occurs along with sublimation of UO_2Cl_2 and reaction to form a small amount of higher uranium chlorides.[71] The black crystalline residue of UO_2 by x-ray studies is slightly different from ordinary UO_2.[71]

All uranium polychlorides are hygroscopic,[29] their reactivity to water vapor decreasing in the order from UCl_6 to UCl_3.[29] UCl_6 is hydrated to $UOCl_4$,[21,29] then UO_2Cl_2, and finally UO_2Cl_2 hydrate.[21] UCl_5 is converted to a product having a composition between UCl_6 and UCl_4.[29] UCl_4 forms the hydrate, $UCl_4 \cdot H_2O$, then $UOCl_2$, and finally $UOCl_2$ hydrate.[21] $UOCl_3$ is less hygroscopic than UCl_4.[21] UCl_4 and UCl_3 dissolve in water to yield respectively a green solution of uranous ion and a purple solution of U^{+3} ions. The uranous solution is slowly oxidized by oxygen to form yellow uranyl ions and U^{+3} reduces water to yield H_2 and is oxidized to the uranous state.[21]

When heated in a vacuum, UO_2Cl_2 decomposes completely to UO_2 and Cl_2 at about 750°C, $UOCl_2$ above 500°C.[21,29]

VII. STRUCTURAL MATERIALS

Various structural materials have been reported in the literature to be used in apparatus containing uranium chlorides. Some investigators report stainless steel 316 and 304 was the best material in the construction of reactor vessels used with CCl_4 to make UCl_4.[47,86] Stainless steel 18-8 is satisfactory structure material for conversion of U_3O_8 to UCl_5 by means of CCl_4.[7] Other investigators[1] found that UCl_4 showed no chemical attack on graphite, fused quartz, refractory porcelain, or Alundum at 465°C in 3 hr; Ni, Ta, Monel, and stainless steel lost 0.5 mg/cm^2 under the same conditions. At 600°C, Inconel and Chromel metal are least attacked. Some investigators[1] report that UCl_4 liquid and vapor attack both Pyrex glass and quartz, but pure UCl_4 has been prepared by sublimation and condensation of the vapors in glass apparatus.[68] This attack may have been caused by moisture contamination in the starting material. S_2Cl_2 vapors (used to convert the oxide to UCl_4) corrode Ni (500°C) but attack Chromel A only slightly.[51]

All fused-salt mixtures containing UCl_4 with NaCl and $CaCl_2$ corroded stainless steel.[55] Chromel A is satisfactory.[7,51] In general, fused-salt mixtures containing uranium tetrachlorides attack stainless steel,[91] including 18-8 stainless steel.[7] Aluminum and its alloy and magnesium are completely corroded.[87] Molten UCl_4 goes through carbon.[91] Molybdenum followed by Hastelloy D and Hastelloy C were best material[91] to contain molten chloride salts.

Ni was found to be more susceptible to mass transfer in a 100-hr nonisothermal dynamic corrosion system than was Inconel when exposed to $NaCl-MgCl_2-UCl_3$ (50-33.3-16.7 mole %) melt both at a hot zone temperature of 1800°F.[92] No Ni mass transfer occurred in a 500-hr test at 1350°F, but Inconel showed some attack under these conditions. Inconel mass transfer was observed in both tests, being more severe at higher temperatures.[92]

Ni and alloys of Ni containing at least 65% Ni, e.g., Monel, Inconel, and Nichrome, were found to be resistive to the effect of UCl_6 at 100°C and 10^{-4} mm for 24 hr.[93]

VIII. DISCUSSION

A number of methods for the preparation of the different chlorides of uranium have been described. Of the various chlorides, only UCl_3 and/or UCl_4 are of possible use in a reactor fuel. High yields of uranium tetrachloride can be obtained by the chlorination of the proper uranium oxide with carbon tetrachloride, hexachloropropene, thionyl chloride, sulfur monochloride, or chlorine using the appropriate procedure. The UCl_4 can be purified, if necessary, by fractional sublimation.

UCl_3 can be made by the direct reaction of dried HCl gas on either uranium metal or hydride, or from the reduction of UCl_4. It can be purified by converting the UCl_3 to UCl_3I and then subliming and decomposing the mixed halide.

Extreme precautions should be taken to dry all gases used in making any of these chlorides and to exclude any moisture from the products, as they are hygroscopic. They will also react with oxygen if heated in the air. There are conflicting data on the final oxidation products and the exact temperature at which oxidation commences. This conflict could be caused by the length of time the different investigators held the chlorides at temperature, the longer time the greater chance for reaction. Both UO_2 and U_3O_8 have been reported as the final products for the reaction of the chlorides or oxychlorides with air at relatively low temperatures (approximately 250 to 320°C), but at these temperatures and conditions UO_3 is the equilibrium form of uranium oxide. Except for minor discrepancies in the temperatures of various reactions and the final products (some mentioned above), the different reports and articles reviewed in this report are in fair agreement on reactions involving the uranium chlorides.

IX. REFERENCES

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