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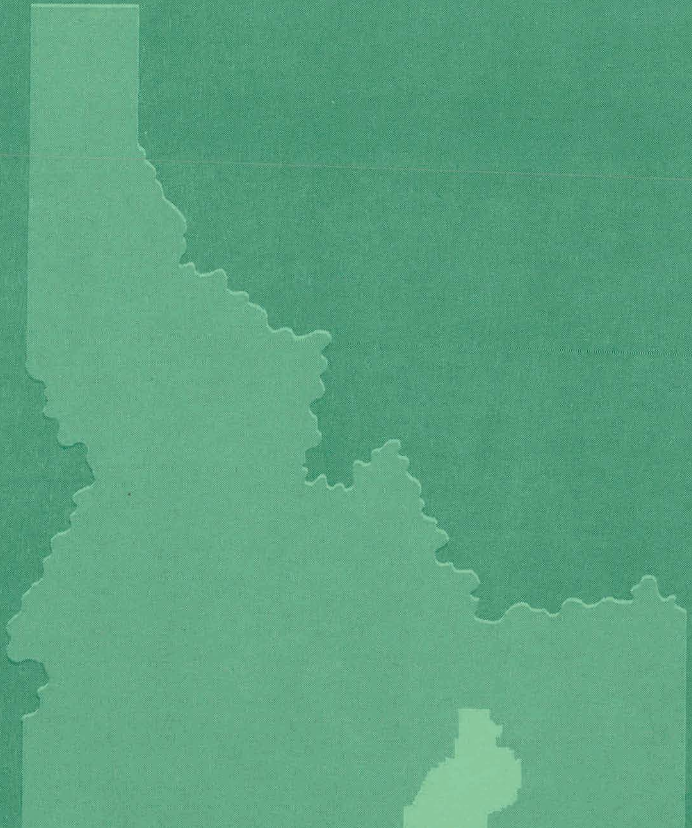
SALT PHASE CHLORINATION OF REACTOR FUELS
III - CATALYZED DISSOLUTION OF URANIUM DIOXIDE IN LEAD CHLORIDE - CHLORINE SYSTEMS

E. M. Vander Wall
D. L. Bauer
H. T. Hahn

February 5, 1962



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III - CATALYZED DISSOLUTION OF URANIUM DIOXIDE IN LEAD CHLORIDE-CHLORINE SYSTEMS

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ABSTRACT

The rapid dissolution of uranium dioxide is described, wherein copper is added to molten lead chloride at 550°C, and chlorine is passed through the melt. The integral dissolution of zirconium-clad uranium dioxide fuels is also described. The dissolution rate of uranium dioxide is directly proportional to the concentration of cuprous chloride if an excess of chlorine is used; the value for the rate constant is approximately 100 mg (UO_2) cm^{-2} min^{-1}/(CuCl molality). The uranium dioxide is converted to water soluble uranyl chloride. The dissolution rate can be controlled by three factors: (1) the copper concentration, (2) the flow rate of chlorine, and (3) the surface area of uranium dioxide. Scoping work indicates that iron chloride may be as effective catalytically as copper chloride for uranium dioxide dissolution in the lead chloride-chlorine system at 550°C; thallium chloride is not as effective.

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I - SUMMARY

The ARCO Process(1) has been demonstrated to provide a feasible dissolution medium for several potential fuel-cladding materials such as stainless steel, chromium, niobium, zirconium and its alloys, and aluminum, and for fuel materials such as uranium and thorium.(3) In this report, the rapid dissolution of uranium dioxide is described, wherein copper is added to the molten lead chloride at 550°C, and chlorine is passed through the melt. The integral dissolution of zirconium-clad uranium dioxide fuels is also reported.

The dissolution rate of uranium dioxide is directly proportional to the concentration of CuCl if an excess of chlorine is used; the value for the rate constant is approximately 100 mg (UO_2) cm^{-2} min^{-1}/(CuCl molality). The uranium dioxide is converted to water-soluble uranyl chloride. The active chlorinating agent in the system is cupric chloride. The dissolution rate can be controlled by three factors: (1) the copper concentration, (2) the flow rate of chlorine, and (3) the surface area of the uranium dioxide. The dissolution rate of uranium dioxide in molten lead chloride alone is $< 10^{-3}$ mg (UO_2) cm^{-2} min^{-1}; in the lead chloride-chlorine system, the dissolution rate is proportional to the flow rate of the chlorine and the rate constant is $(3.4 \pm 0.8) \times 10^{-3}$ mg (UO_2) cm^{-2} min^{-1}/mg (Cl_2) min^{-1}.

Scoping work indicates that iron chloride may be as effective catalytically as copper chloride for uranium dioxide dissolution in the lead chloride-chlorine system at 550°C; thallium chloride is not as effective.

II - INTRODUCTION

The ARCO Process employs molten lead chloride as a solvent for reactor fuel alloys.(1) Zirconium and aluminum alloys dissolve readily in the molten salt, and the respective chlorides are volatilized; uranium and thorium(2) also dissolve readily but exhibit no volatility; stainless steel dissolution requires the addition of chlorine to the melt.(3) This lead chloride-chlorine system also dissolves chromium and niobium at reasonable rates. Since uranium dioxide is a reactor fuel of increasing importance, the demonstration of its dissolution in this system would further establish the versatility of lead chloride as a solvent. For this purpose, then, a catalytic reagent was sought which would yield reasonable uranium dioxide dissolution rates at 500-550°C in the lead chloride-chlorine system. The reagent is copper or one of the copper chlorides; the dissolution product is uranyl chloride. The resulting system, lead chloride-copper-chlorine, can be used for integral dissolution of zirconium-clad uranium dioxide fuel as well as several other metallic-clad uranium oxide fuels.

III - EXPERIMENTAL

A. Apparatus

Since all the reactions investigated in this study required elevated temperatures, a 5-inch crucible furnace was used as the heat source. A temperature controller was used to maintain the furnace at 550 ± 10°C.

Experiments in which no gaseous reagents were used were usually performed in stoppered Pyrex glass tubes. Reactions occurring above 550°C were carried out in analogous Vycor glass equipment.

Experiments which required chlorine as a reagent were performed in an apparatus as shown in Figure 1. Pyrex glass frits (medium porosity) were found to be suitable supports for molten salt reagents and also served to disperse the chlorine as it entered the molten salt. Any excess chlorine passed into a scrubbing column through which a slightly acidified potassium iodide solution was recycled. The chlorine was converted to the chloride, and the iodine produced was titrated with a standard thiosulfate solution. To provide a large surface area, the column was filled with glass beads. A peristaltic pump was used to circulate the scrub solution.

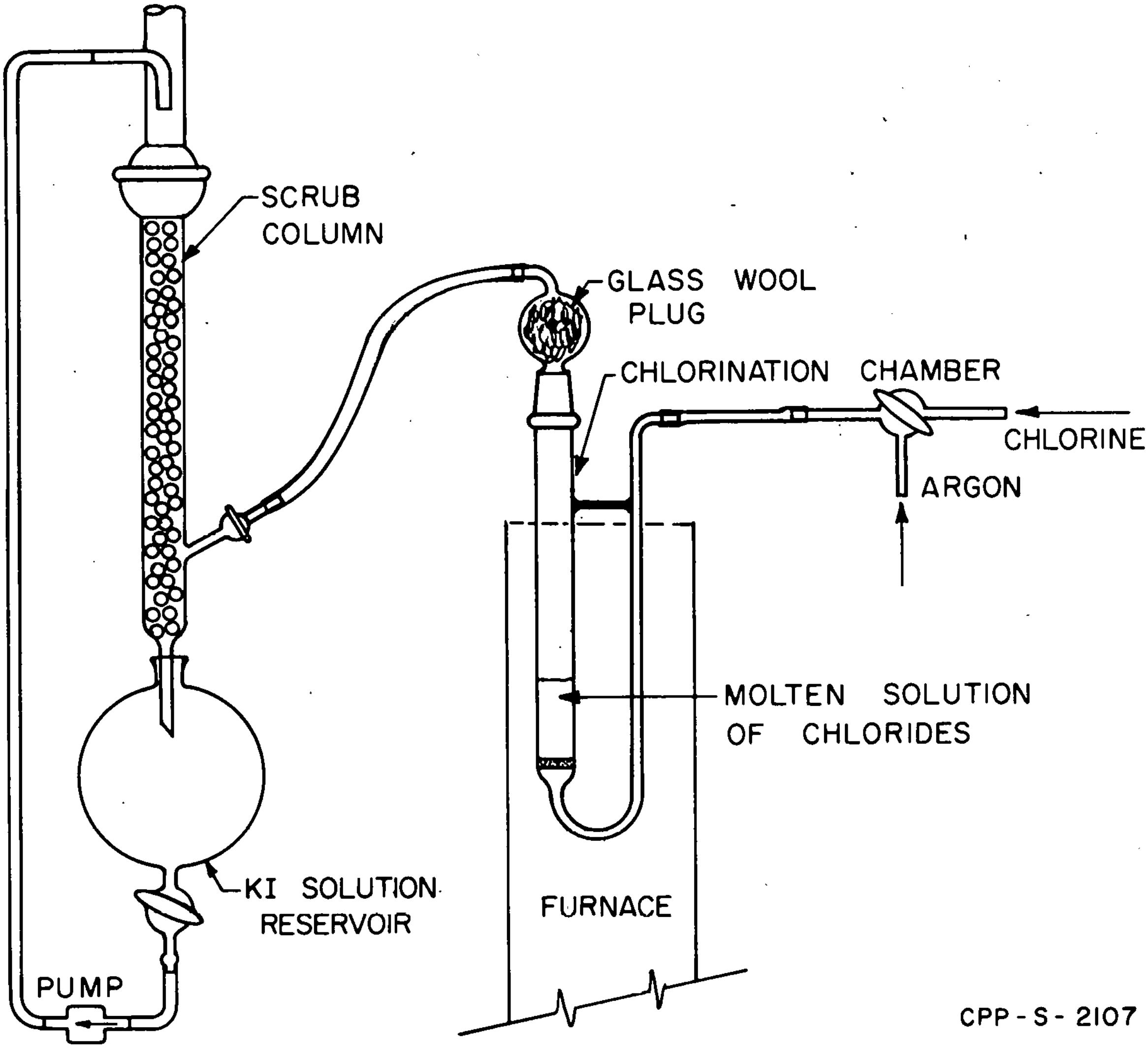

Figure 1

Experimental Apparatus for Study of the Dissolution of Uranium Dioxide in Molten Chlorides

B. Materials

The uranium dioxide used in these experiments was of two types: cylindrical pellets (0.9 cm diameter and 0.9 cm high, density = 10.28 g/cc) from PWR fuel elements, and material which was between 30-40 mesh (U.S. Standard Sieve) and had an average density of 10.18 g/cc. Attempts to measure the surface area of the latter material by the Brunauer-Emmett-Teller method were unsuccessful. Therefore, surface areas used in this report are calculated on the basis of particle dimensions.

Anhydrous cuprous chloride was prepared by reduction of hydrated cupric chloride with sulfite.(4) Typical chloride analysis of the product was 35.7% compared to a theoretical 35.8%. Anhydrous cupric chloride was prepared by passing anhydrous hydrogen chloride through hydrated cupric chloride at 150°C for several hours. The product had a 52.6% chloride content compared to a theoretical value of 52.7%.

All other chemicals required for these experiments were commercially available and were used as received.

C. Procedures

Utilization of chlorine was determined by two methods. Originally, the amount of chlorine used was determined from the flow rate. Any excess chlorine was absorbed by an acidic potassium iodide solution in the scrub column. Due to fluctuations in the flow rates, this method was not entirely satisfactory. In later experiments, the chlorine was transferred to a small cylinder which weighed 124 g and held 14 g of chlorine, and the amount of chlorine used was determined by direct weighing on an analytical balance. The excess chlorine was again absorbed in the scrub column. The chlorine actually consumed by the reaction could be calculated readily.

The reaction products were poured out of the reactor chamber, and after cooling were dissolved in hot water. The resulting solution was filtered to remove any finely divided uranium oxide residue. The filtrate was then converted to a nitrate system with concentrated nitric acid. In the latter system, lead could be retained in solution at reasonable concentration levels and the conversion step insured that all elements present were in their highest oxidation state.

To determine if any uranium oxide would dissolve prior to analysis in this procedure, parallel experiments were performed with one of the reaction product mixtures in contact with the various solutions for days, compared to a few hours for the other. There was no significant difference in the uranium analysis. As an additional check, the melts in some experiments were filtered through a Pyrex glass frit to remove the undissolved uranium dioxide from the molten salt solution. The results obtained in this manner were comparable to the experiments in which the entire mixture was dissolved in water. This assured the validity of the procedure for sample preparations.

The uranium and other cations were analyzed by the CPP Analytical Branch. Chloride analyses were conducted using a potentiometric method. Iodine analyses were made by titrating with standard thiosulfate solutions and using starch as the end point indicator.

IV - RESULTS AND DISCUSSION

A. Dissolution of Uranium Dioxide in Molten Lead Chloride

The reaction of uranium dioxide pellets (5.8 g, 3.82 cm^2) with molten lead chloride (10.0 g) was investigated from 500 to 800°C. After being in contact for an hour, all the pellets gained slightly in weight (1 to 4 mg). Since no appreciable reaction had occurred, only three of the resulting melts were analyzed for water-soluble uranium. The combined data from two experiments at 750°C for an hour and one experiment at 800°C for five hours gave an average dissolution rate of 4.4×10^{-4} mg (UO_2) cm^{-2} min^{-1} in the lead chloride melt. This negligible dissolution rate of uranium dioxide indicates that zirconium alloy cladding could be readily removed from uranium dioxide fuels at 500-520°C without any appreciable uranium dioxide losses due to dissolution in the lead chloride melt.

B. Dissolution of Uranium Dioxide in the Lead Chloride-Chlorine System

Uranium dioxide pellets (5.8 g, 3.82 cm^2) were immersed in molten lead chloride (20.0 g, 550°C) through which chlorine was passed. The typical apparatus used in these experiments is shown in Figure 1. The flow rates of chlorine ranged from 19 to 80 mg min^{-1}; the dissolution period varied from 30 to 60 minutes; and the dissolution rates of uranium dioxide ranged from 0.24 to 0.93 mg min^{-1}. The resultant rate constant, k, for the expression

$$-\frac{d(UO_2)}{dt} = k\ (Cl_2\ \text{flow})$$

is $(1.3 \pm 0.3) \times 10^{-2}$ mg (UO_2) min^{-1}/mg (Cl_2) min^{-1}. Since the pellets all shattered to some extent during the dissolution, one can only calculate the upper limit of the dissolution rate based on the area. Using the initial area of 3.82 cm^2, the rate constant, k′, for the equation

$$-\frac{d(UO_2)}{dt} = k'\ (UO_2\ \text{area})(Cl_2\ \text{flow}),$$

is $(3.4 \pm 0.8) \times 10^{-3}$ mg (UO_2) cm^{-2} min^{-1}/mg (Cl_2) min^{-1}.

C. Dissolution of Uranium Dioxide in the Lead Chloride-Cuprous Chloride-Chlorine System

To obtain practical dissolution rates in the lead chloride-chlorine system, a catalyst is necessary. Any compound which is soluble in molten lead chloride and which can add and lose chlorine readily might serve as a suitable catalyst. Cuprous chloride was a likely candidate in view of its ready reaction with zirconium, a potential cladding material. It is soluble in molten lead chloride, and at temperatures above the melting of lead chloride (500°C), the cupric chloride is thermodynamically less stable than cuprous chloride. Experiments have established the effectiveness of cuprous chloride as a catalyst in this system.

The effect of cuprous chloride on the dissolution rate of uranium dioxide in the lead chloride-chlorine system was investigated at 550°C. The experiments were performed with the apparatus shown in Figure 1.

Throughout this series of experiments the initial amount of lead chloride was 20.0 g; an excess of chlorine was used in all experiments; cylindrical pellets of uranium dioxide were used (3.82 cm^2, 5.8 g); and the concentration of cuprous chloride ranged from 0.0041 to 0.671 molal. Molality was used because it defines the concentration of cuprous chloride uniquely in reference to the solvent, lead chloride.

The data obtained are plotted in Figure 2. The scatter in the plot is probably caused by the shattering of the pellets during dissolution, which results in a large variation in the surface area available for reaction. Only one pellet remained intact during the dissolution. Since the plot of dissolution rate vs cuprous chloride concentration has a slope of 1, the following rate equation results:

$$-\frac{d(UO_2)}{dt} = k_1(CuCl).$$

The rate constant $k_1 = 453 \pm 62$ mg (UO_2) min^{-1}/CuCl molality. An upper limit of the dissolution rate involving area can be obtained by consideration of the initial pellet area and assuming that the area function is first order. This yields the rate equation

$$-\frac{d(UO_2)}{dt} = k_2(CuCl)(UO_2 \text{ area}),$$

where $k_2 = 119 \pm 16$ mg (UO_2) cm^{-2} min^{-1}/CuCl molality. In the experiment in which the pellet remained intact, the rate constant based on the initial pellet area was 81. Since the area of this single piece decreased during the dissolution, the value for the rate constant based on the true area must be approximately 100 mg (UO_2) cm^{-2} min^{-1}/CuCl molality.

Another series of experiments was conducted similar to the preceding series except that the uranium dioxide used was 35 to 40 mesh material. In each experiment 5.0 g of uranium dioxide was used. The data obtained from these experiments are plotted in Figure 3. The resulting rate equation is:

$$-\frac{d(UO_2)}{dt} = k_3(CuCl),$$

and the rate constant $k_3 = 1336 \pm 52$ mg (UO_2) min^{-1}/CuCl molality. There

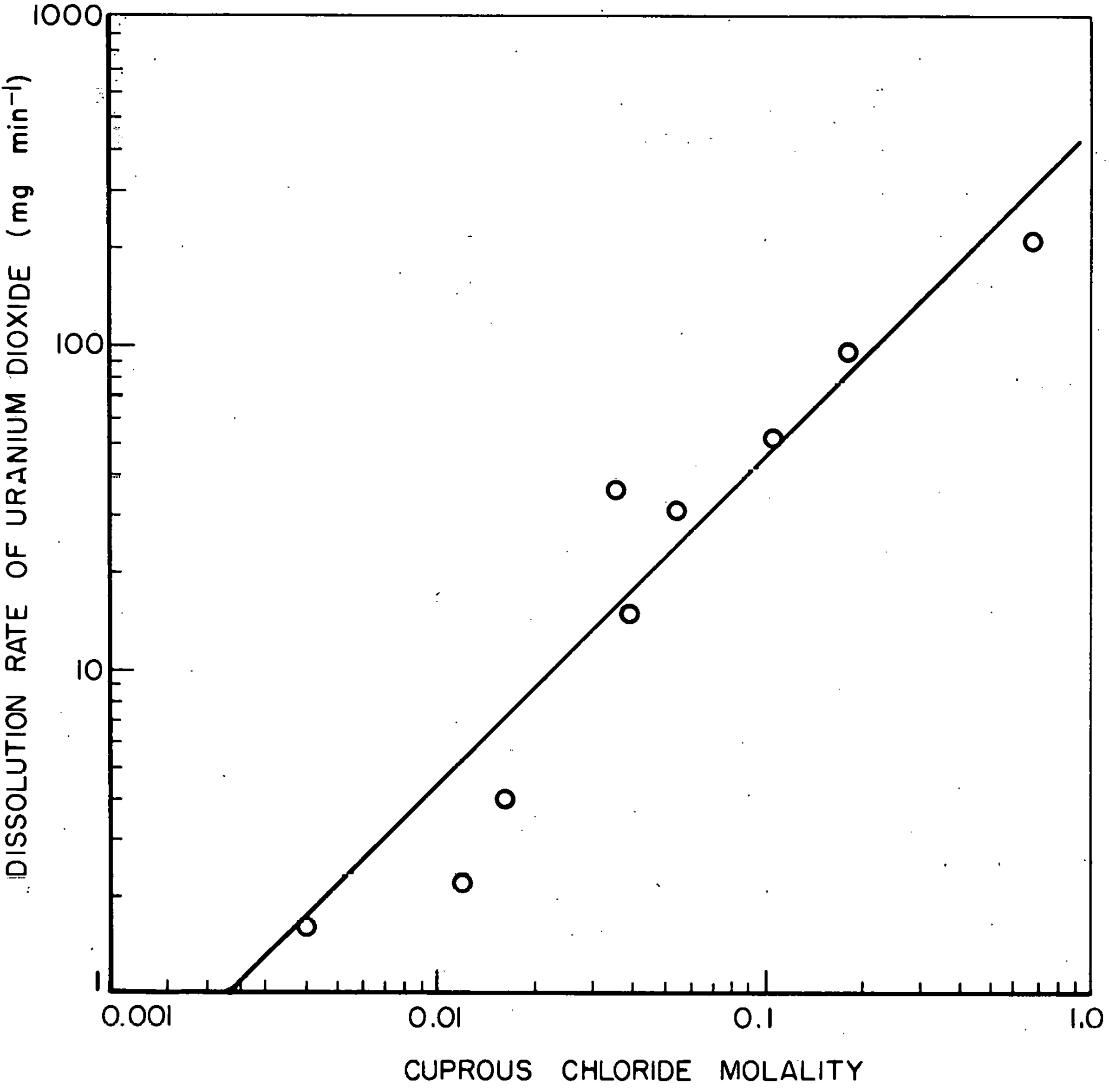

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Figure 2

Effect of the Initial Concentration of Cuprous Chloride on the Dissolution Rate of Uranium Dioxide in the Lead Chloride-Chlorine System at 550°C (UO_2 pellets)

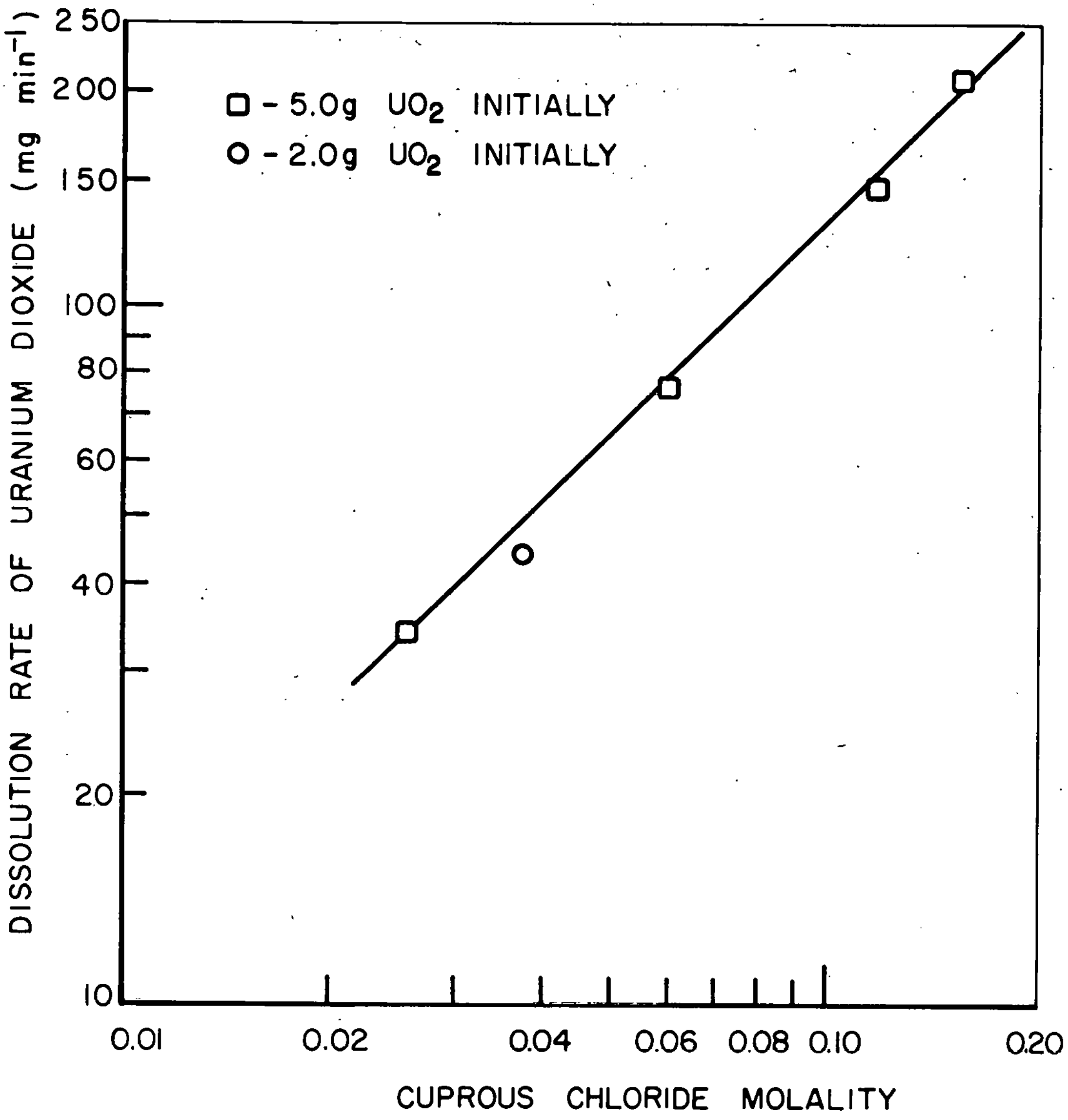

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Figure 3

Effect of the Initial Concentration of Cuprous Chloride on the Dissolution Rate of Uranium Dioxide in the Lead Chloride-Chlorine System at 550°C (UO_2 material 30-35 mesh) is much less scatter of data points in this plot. This is probably due to the large surface area available for reaction (calculated area = 64.0 cm^2). To confirm this, an experiment was performed in which only 2.0 g of uranium dioxide (30-35 mesh) was used; this gave a calculated surface area of 21.5 cm^2. The rate constant obtained in this experiment was 1182. Thus, a 66% reduction in area caused only a 12% reduction in the rate constant, indicating that the dissolution rate in this series of experiments is not sensitive to the area change and that with this large surface area available, the area of the uranium dioxide is not a rate-limiting factor.

On the basis of the preceding data, it is evident that the dissolution of uranium dioxide can be controlled by three factors: the copper concentration, the surface area of the uranium dioxide, and the flow of chlorine. In the lead chloride-chlorine system, the dissolution rate of uranium dioxide was directly proportional to the flow rate of chlorine through the dissolver, since the surface area was maintained as constant as possible. However, when copper is added, the dissolution rate of uranium dioxide is determined by the copper concentration as long as there is an excess of chlorine and the available surface area of the uranium dioxide is large. If the chlorine is completely utilized, then the flow of chlorine and the surface area available are the important rate-controlling factors. A series of experiments was performed in which copper was immersed in molten lead chloride and chlorinated with an excess of reagent to produce solutions which were 0.4 molal in copper chlorides. One pellet of uranium oxide was added to each melt, and the flow rate of chlorine varied from 34 to 79 mg min^{-1}. These rates afforded essentially complete chlorine utilization and the data are plotted in Figure 4. The curve turns upward slightly with increasing flow rate, but it is difficult to attach any theoretical significance to this phenomenon because of the variables involved.

The identity of the uranium species produced by dissolution of uranium dioxide in the system - lead chloride-cuprous chloride-chlorine - must be determined by indirect means, since direct analyses are ambiguous unless

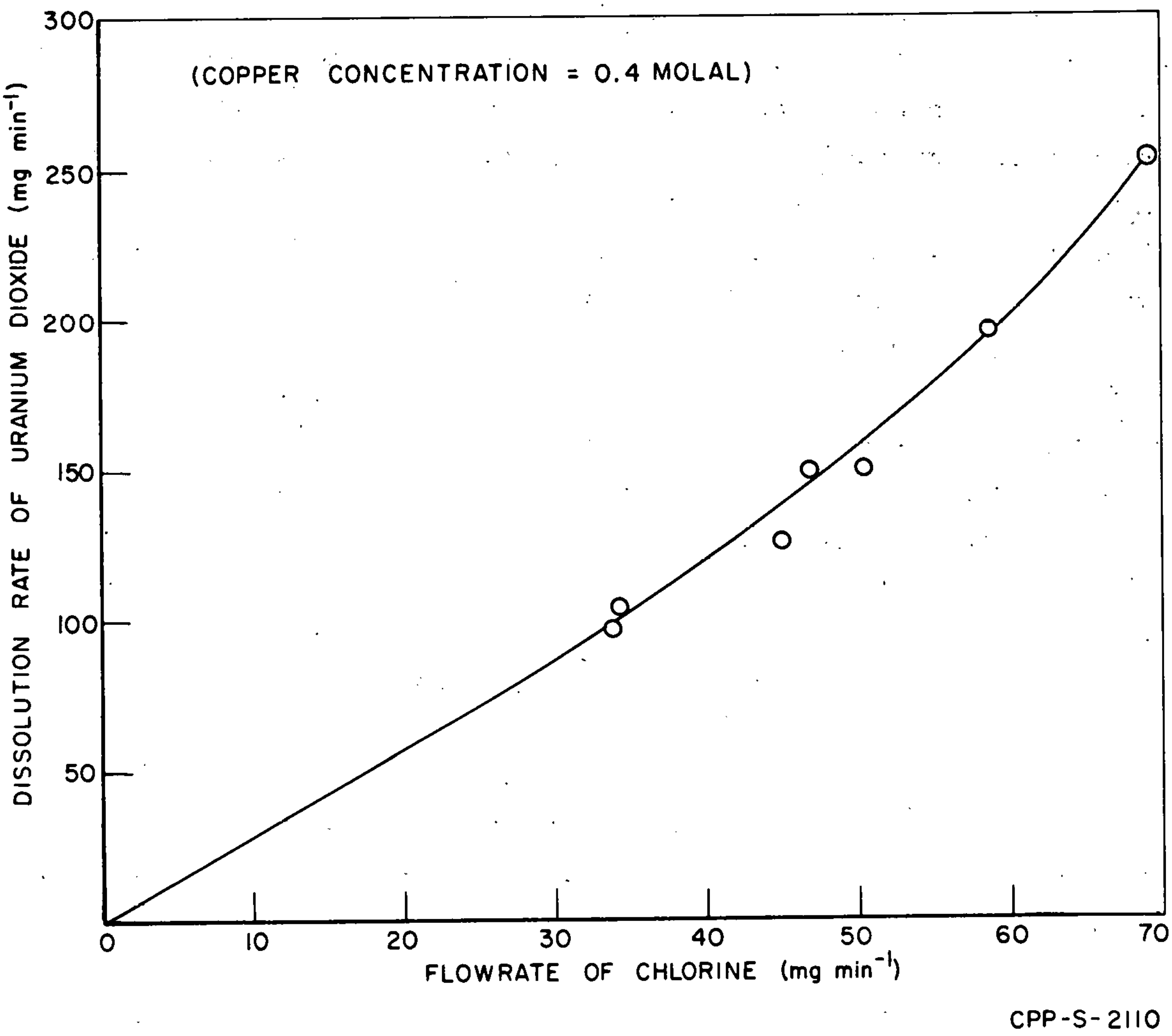

Figure 4

Effect of the Flow Rate of Chlorine on the Dissolution Rate of Uranium Dioxide in Lead Chloride-Copper Chlorides-Chlorine System at 550°C the cupric to cuprous ratio in the system is known. Some information regarding the equilibrium ratio of cupric to cuprous chloride at 550°C in this system was obtained in duplicate experiments in which a mixture of copper (1 g) and lead chloride (10.0 g) was chlorinated for three hours with a large excess of chlorine. The product melts were analyzed for total chloride. If one uses 2.00 as the chloride to lead ratio, the chloride to copper ratio is 1.44 ± 0.05 and the cupric to cuprous chloride ratio is 0.79. In a similar experiment, the copper was chlorinated for three hours and then the melt was maintained in 550°C for an additional two hours. The final chloride to copper ratio in this instance was 1.28. This indicates that the chloride to copper ratio will vary as experimental conditions change, and conceivably the ratio can range from 1.0 to 2.0. As described in a succeeding paragraph, chlorine solubility in lead chloride does not seem to be responsible for the variation.

The product resulting from a 30-minute dissolution of uranium dioxide in a melt prepared by chlorinating copper (0.99 g) in lead chloride (20.00 g) was analyzed for total chloride and water-soluble uranium. The products were analyzed similarly from two additional experiments in which uranium dioxide was dissolved in lead chloride (20.00 g) containing copper (0.06-0.07 g) and through which chlorine was passed for several hours. Using the value 1.44 for the chloride to copper ratio and the value 2.00 for the chloride to lead ratio, the average chloride to uranium ratio is 1.91 ± 0.05. Since it appears that there are two chlorides per uranium and since this reaction is performed in an oxidizing medium, the product is probably uranyl chloride. In several other experiments, on the basis of uranyl chloride being the uranium product, the chloride to copper ratio varied considerably but was found to range between limits of 1 to 2.

A few additional experiments were conducted to determine the final chloride to lead ratio when lead chloride is chlorinated alone at 550°C. Titration of total chloride gave a chloride to lead value of 2.02 compared to 2.00 obtained prior to passage of chlorine through lead chloride. Under the experimental conditions used, it would not be determined if this "apparent solubility" existed when copper and uranium dioxide were present in the system.

To determine which copper chloride species catalyzed the dissolution of uranium dioxide in the lead chloride-cuprous chloride-chlorine system, both the lead chloride-cuprous chloride and lead chloride-cupric chloride systems were investigated. In a lead chloride-cuprous chloride solution which was 0.38 molal cuprous chloride, the average dissolution rate without chlorine during a 90-minute period was 4.6×10^{-3} mg (UO_2) cm^{-2} min^{-1}. These rates are an order of magnitude greater than the dissolution rates of uranium dioxide in lead chloride alone.

Several experiments involving the dissolution of pellets of uranium dioxide in the lead chloride-cupric chloride system were conducted at 550°C. The data obtained from these experiments are given in Table I. Rates obtained at less than two minutes were not considered significant because the pellets of uranium oxide were at room temperature when introduced into the melt. The rates obtained in the lead chloride-cupric chloride system are 4 to 5 orders of magnitude greater than those obtained in lead chloride alone, and 3 to 4 orders of magnitude greater than obtained with cuprous chloride. Therefore, it appears that cupric-chloride is the actual chlorinating reagent in the lead chloride-copper-chlorine system.

Table I

Dissolution of Uranium Dioxide in the
Lead Chloride-Cupric Chloride System at 550°C

Dissolution Period (minutes)	$CuCl_2$ Concentration (molality)	Average Dissolution Rate (mg (UO_2) cm^{-2} min^{-1})
2	1.21	11
2	1.18	15
30	0.15	0.11
60	0.24	0.92
60	0.37	1.1
60	0.71	1.1
60	0.88	1.6
60	1.98	2.3
80	0.15	0.26

The instantaneous dissolution rate of uranium dioxide in the lead chloride-cupric chloride system initially is larger than any value reported in Table I. To establish the initial dissolution rate of uranium dioxide with a fixed concentration of cupric chloride (0.39 molal) in lead chloride and with a constant surface area of uranium dioxide, five experiments were performed in which a pellet of uranium dioxide (5.8 g, initial calculated surface area = 3.82 cm^2) was immersed in the melt at 550°C for various periods of time ranging from 2 to 45 minutes. The total amount of uranium dioxide dissolved in each experiment was plotted vs time. The initial slope divided by the initial area was 18 mg (UO_2) cm^{-2} min^{-1}. This corresponds to a dissolution rate about five-fold less than one would expect based on the data from the lead chloride-cuprous chloride-chlorine system. The expected rate was calculated on the following basis: since the average equilibrium value for the cupric to cuprous chloride ratio in the lead chloride-copper-chlorine system was found to be 0.79, a 0.39 molal cupric chloride solution would be 0.88 molal in total copper. Using a rate constant value of 100 mg (UO_2) cm^{-2} min^{-1}/CuCl molality, the dissolution rate would be 88 mg (UO_2) cm^{-2} min^{-1}. However, the flow of chlorine stirs the melt in the lead chloride-cuprous chloride-chlorine system, while the lead chloride-cupric chloride must depend on diffusion alone for mixing. Under equivalent conditions, these rates could conceivably be comparable.

As an additional step in clarification of the dissolution mechanism, the rate of formation of cupric chloride from cuprous chloride and chlorine in the lead chloride system was checked. A 1.17 molal solution of cuprous chloride in lead chloride was chlorinated with an excess of reagent for a two-minute period, using the chlorination apparatus illustrated in Figure 1. The total chloride content of the melt was used as a measure of the amount of cupric chloride present. The rate of formation of cupric chloride based on this experiment was 0.473 mole min^{-1}/1000 g $PbCl_2$. In 20 g of lead chloride, such a rate would make it possible to convert 1.28 g of uranium dioxide per minute to uranyl chloride. This compares favorably with the rate of 1.56 g (UO_2) min^{-1} calculated from the rate constant obtained in the lead chloride-cuprous chloride-chlorine system where a large excess of chlorine was used and the surface area necessary for reaction was also in excess.

Therefore, it appears that in the situation where the surface available for reaction is in excess, the rate of formation of cupric chloride from cuprous chloride is the rate-controlling step. If only a limited surface is available for reaction, the decomposition of cupric chloride is probably the rate-controlling factor.

As a laboratory-scale demonstration of the integral dissolution of zirconium-clad uranium dioxide fuel, a small segment (6.2 g Zr, 10.4 g UO_2) of a PWR fuel rod was dissolved at 550°C in a melt initially containing 35 g lead chloride and 1.4 g copper. Chlorine was passed through the system at a rate of 110 g min^{-1}; the rod was immersed slowly with no more than 1/4 inch submerged at any time. The zirconium volatilized from the reaction chamber as zirconium tetrachloride. The dissolution was stopped by solidification of the melt. The melt composition at this point was 20.6 mole per cent uranyl chloride, 11.8 mole per cent copper chloride, and 67.6 mole per cent lead chloride. (This gives some indication of the solubility limits in the system; however, a melt which contained 43.7 mole per cent uranyl chloride, 0.8 mole per cent copper chloride, and 55.5 mole per cent lead chloride showed no signs of solidification at 550°C.) The overall reaction was completed within four hours with 44% utilization of chlorine. This dissolution rate could have been accelerated considerably by an increase in the fuel immersion rate.

D. Dissolution of Uranium Dioxide in Other Molten Chloride Systems

1. Lead Chloride-Cadmium Chloride-Copper-Chlorine System

To determine the importance of temperature on the dissolution rate of uranium dioxide, a solution (20.00 g) which was 30.75 mole per cent cadmium chloride in lead chloride was heated to 430°C, well above the eutectic point. To this solution, 0.823 g copper was added and chlorinated until it completely dissolved. A pellet of uranium dioxide was then added and chlorine was passed through the melt for 30 minutes. The average dissolution rate based on the initial pellet area was 18.4 mg (UO_2) cm^{-2} min^{-1}. In the same melt without copper added, the average dissolution rate for a 30-minute period was 6×10^{-2} mg (UO_2) cm^{-2} min^{-1}, indicating that the cadmium chloride does not dissolve or catalyze the dissolution of any appreciable amount of uranium dioxide. Considering the cadmium chloride-lead chloride as the solvent, the copper concentration was 0.65 molal. At 550°C under similar experimental conditions in the lead chloride-copper-chlorine system, the average dissolution rate of uranium dioxide would be approximately 40 mg (UO_2) cm^{-2} min^{-1}. So a 120°C reduction in temperature reduced the dissolution rate of uranium dioxide by approximately one-half. Therefore, the reaction is not sensitive to small changes in temperature in this system with the experimental apparatus used. Also, this experiment establishes the feasibility of uranium dioxide chlorination at temperatures below 500°C.

2. Lead Chloride-Thallous Chloride-Chlorine System

Another likely candidate for a catalyst for dissolution of uranium dioxide in the lead chloride-chlorine system is thallous chloride. The higher chloride of thallium, $TlCl_3$, is unstable compared to TlCl at higher temperatures and could therefore serve as the chlorinating agent. It had been reported that thallous chloride was a satisfactory catalyst in a molten potassium chloride-chlorine system at 650°C(5) for dissolution of uranium dioxide. In this laboratory, two experiments were performed at 550°C in the lead chloride-chlorine system using thallous chloride. The average dissolution rate of uranium dioxide at 550°C, for a melt which was 0.196 molal thallous chloride, during a 30-minute period was 9.86×10^{-1} mg (UO_2) cm^{-2} min^{-1}. Under the same conditions, using 2.22×10^{-2} molal thallous chloride, the dissolution rate was 3.14×10^{-1} mg (UO_2) cm^{-2} min^{-1}. These rates are considerably slower than those obtained if copper is used in the system.

3. Lead Chloride-Iron-Chlorine System

A scoping experiment was conducted in which 1.375 g of pure iron wire was dissolved in molten lead chloride (20.0 g) by passing a large excess of chlorine through the melt at 550°C. This yielded a 1.23 molal solution of iron chloride in lead chloride. A pellet of uranium dioxide (5.28 g) was introduced while the flow of chlorine continued, and was found to have dissolved completely within a 15-minute period. This dissolution rate is comparable to that experienced when copper is dissolved with an excess of chlorine in the lead chloride-chlorine system and the uranium dioxide then introduced.

The implication of dissolution of uranium dioxide catalyzed by the presence of iron chloride in the lead chloride-chlorine system is that integral dissolution of stainless steel-clad uranium dioxide fuels is possible without introduction of other reagents. Since the volatilization of iron from these melts has been shown to be incomplete(6), such a reaction would be autocatalytic.

V - CONCLUSIONS

1. An integral dissolution of zirconium-clad uranium dioxide fuels is possible in the lead chloride-copper-chlorine system at 550°C. The uranium product is apparently uranyl chloride. In the absence of copper and chlorine, uranium dioxide dissolves at a negligible rate, so that zirconium cladding could be removed without any appreciable dissolution of uranium.

2. Stainless steel-clad uranium oxide fuels can be dissolved integrally; copper may not be needed, since iron will catalyze dissolution of uranium dioxide in the lead chloride-chlorine system.

3. The dissolution rate of uranium dioxide is directly proportional to the concentration of cuprous chloride if chlorine is in excess.

4. The dissolution rate of uranium dioxide can be controlled by three factors in this system: the copper concentration, the flow of chlorine, and the surface area.

5. The active chlorinating agent in the lead chloride-copper-chlorine system is cupric chloride.

6. The dissolution rate is not strongly temperature-dependent. This permits feasible dissolution rates of uranium dioxide in chloride systems at 430°C or less.

VI - REFERENCES

(1) H. T. Hahn and E. M. Vander Wall, Salt Phase Chlorination of Reactor Fuels, I. Dissolution of Zirconium Alloys in Lead Chloride, IDO-14478 (1959).

(2) J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, IDO-14567, April-June 1961, page 46.

(3) E. M. Vander Wall, H. T. Hahn and D. L. Bauer, Salt Phase Chlorination of Reactor Fuels, II. ARCO Process Definition and Scoping Studies, IDO-14525 (1960).

(4) W. C. Fernelius, Inorganic Synthesis, Vol. II, page 1, McGraw-Hill Book Co., New York (1946).

(5) W. H. Reas, Ed., HW 66237 C, July 1960 (Classified).

(6) J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, IDO-14560, January-March 1961, pages 86-87.

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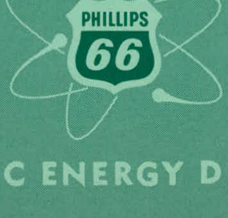

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