

Solubility of Uranium Oxides in Fluoride Salts at 1200 °C

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Data were collected for the solubility of uranium oxides in UF_4 and mixtures of fluoride salts at 1200 °C. These solubilities are important to an electrolytic production of uranium metal by a process similar to the Hall-Heroult process for aluminum. Data reported in the technical literature were supplemented by new measurements. The solubilities of UO_2 are low at low UF_4 concentrations and are approximately proportional to UF_4 concentrations for the 0.02–0.5 mol fraction UF_4 range of interest for electrolytic cell operation. New data for $CaF_2 + LiF + UF_4$ over this range show solubilities of 0.11 mol of UO_2 /mol of $UO_2 + UF_4$ as compared to about 0.07 mol of UO_2 /mol of $UO_2 + UF_4$ for $BaF_2 + LiF + UF_4$. Our data did not show the anomalous increase in UO_2 solubility for decreasing UF_4 concentration that had been reported for $CaF_2 + LiF + UF_4$ mixtures.

Introduction

One process for production of uranium metal is an electrolysis of UO_2 dissolved in halide salts (1, 2). Temperatures above the melting point of uranium (1132 °C) would allow operation similar to the Hall-Heroult process for aluminum. The alkali-metal and alkaline-earth-metal fluorides have the chemical stability and low vapor pressure necessary for this type of electrolysis process (1, 2). Mixtures of salts are probably desirable to give lower melting points. Good (high) solubilities of UO_2 are desirable. The objective of this study was to collect and complete a set of data for the solubility of UO_2 in such fluoride salt mixtures at temperatures above the melting point of uranium.

The development programs reported in the literature for electrolytic reduction of uranium oxides to metal have included measurements of the solubilities of uranium oxides. These measurements are scattered through a number of reports of limited availability. Also, some salt compositions of importance for use of the "frozen crust sidewall" as used in aluminum production cells were not adequately studied. New measurements were made and were correlated and compared with literature data using adjustments to a common temperature of 1200 °C. Correlations based on the amount of UF_4 as the principal variable gave simplified and more consistent results.

Experimental Methods

The basic concept was to equilibrate a molten fluoride salt mixture with an excess of uranium oxide (usually at 1200 °C) and then take a filtered sample to exclude the undissolved uranium oxide. Graphite crucibles were used to contain the salt without reaction or contamination. An argon atmosphere inside a dense Al_2O_3 tube was used to prevent oxidation of the graphite. The sampler was a graphite tube with a replaceable porous plug in the bottom end and a metal connector to the top end. An argon pressure difference was used to force the salt sample through the porous plug. The apparatus was disassembled to allow batchwise addition of charge powders and removal of the filtered sample and the frozen button from the crucible.

Two similar sets of apparatus were used, with the major difference being a factor of 2 in diameter and 8 in sample size. Only the larger set is described here. The schematic flow sheet is shown in Figure 1. The tubular furnace had a 6.3-cm i.d. and 35-cm heated length and was rated to operate at 1325 °C maximum. The test temperature was indicated by a

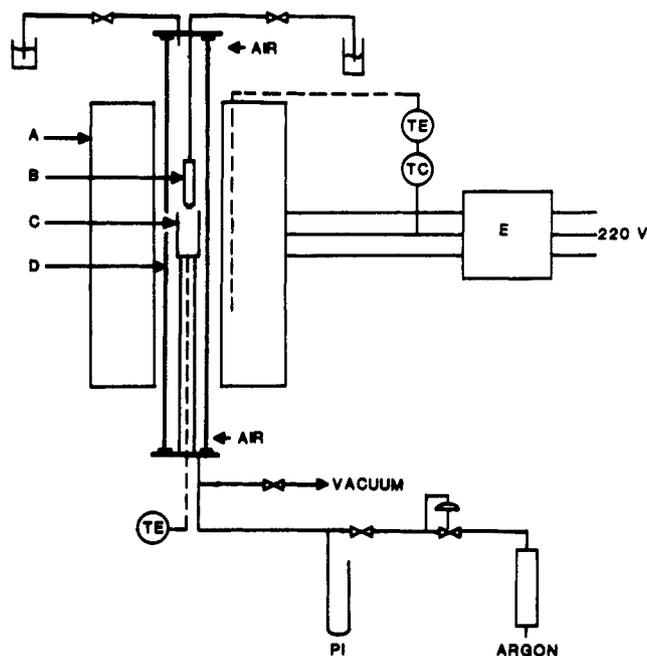


Figure 1. Molten salt solubility apparatus: A, Marshall tubular furnace; B, filter stick sampler; C, graphite crucible; D, alumina furnace tube; E, transformer; TC, temperature controller; TE, thermocouples; PI, manometer.

thermocouple at the bottom of the graphite crucible. The furnace controller was set at a higher temperature determined by trial to give the desired test temperature. The alumina tube (5.7-cm o.d., 5.1-cm i.d., 76-cm length) and stainless steel end flanges with seals were catalog items (McDaniel Refractory Co., Beaver Falls, PA) with 1/4-in. tubing fittings welded to the flanges. The fitting for the sampler tube was drilled to an easy slip fit and used with a Viton O-ring seal. The graphite crucible was supported from the bottom flange by a mullite tube with a 3.2-cm o.d. and 30-cm length. A manometer was used to indicate the gas pressure and bubblers on the exit lines to check gas flows. The plug for sampling the molten salt was machined from a porous carbon reported to have an average pore diameter of 60 μm .

The CaF_2 , BaF_2 , and LiF were reagent grade chemicals. The UF_4 was a pure feed material from an Oak Ridge U.S. Department of Energy plant supply. The uranium oxide was UO_3 with ceramic grade properties calcined to U_3O_8 in air

(average true particle size of 3- μm mean diameter and Brunauer-Emmet-Teller surface area of 7 m^2/g). The uranium oxide would be all UO_2 at the solubility test conditions (1200 $^\circ\text{C}$ in graphite crucibles).

The powders were weighed separately, mixed by stirring, and charged to the crucible at room temperature. The system was assembled and evacuated to about 30 kPa while heating to about 300 $^\circ\text{C}$. Argon was then admitted, and a controlled positive pressure of argon was maintained for the remainder of the tests, including the cooling to room temperature.

Salt equilibration was achieved by holding the crucible at test temperature (usually 1200 $^\circ\text{C}$) for 1 h before sampling. Previous studies elsewhere have shown high initial UO_2 concentrations followed by equilibrium concentrations after only a few minutes (3, 4). The high initial concentrations were probably UO_2 fines that recrystallized or settled to leave the soluble UO_2 in the melt. Our sampling procedure placed the porous sampler plug near the settled excess UO_2 without ever showing any noticeable errors in the form of inconsistent high results. Dependable and reproducible sampling required some trial and error practice and careful control of the gas pressures. The amounts of UF_4 and UO_2 in the sample were determined separately after selective dissolution of the UF_4 (see Appendix A).

Results

A literature search resulted in data for about 70 measurements of UO_2 solubilities in fluoride salts (3-5). These data as published were not adequate for application to the electrolysis cell conditions of interest to our program. The limitations were the following: (a) More than 10 different sets of units were used. As an example, some melt compositions were given as weight percent additions of UF_4 to mixtures of two other fluoride salts on a mole basis. The UO_2 solubilities were given in many combinations of weight, mole, and volume units. (b) The three principal sets of data were at three different primary temperatures (1150, 1200, and 1250 $^\circ\text{C}$). (c) Individual measurements appeared to show limited accuracy or large errors. (d) There was little data for some salt compositions of greatest interest while many measurements were with compositions of little interest. (e) One set of data for a composition of greatest interest ($\text{CaF}_2 + \text{LiF}$) showed unusual and anomalous solubilities which were inconsistent with some single data points and with the behavior of solubilities for other compositions.

The earliest studies of electrolytic preparation of uranium were made without any measurements of UO_2 solubilities. Two measurements made at KAPL were interpreted as showing upper solubility limits of 2 mass % UO_2 (6). The first values reported using the filtered sample procedure were by the U.S. Bureau of Mines (5). The Mallinkrodt Chemical Works pilot plant cells were operated with $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ (usually with a BaF_2/LiF ratio of about 1 (mol/mol)). They reported solubilities at 1150 $^\circ\text{C}$ for this ratio of BaF_2/LiF and 0-45 mass % UF_4 and for single compositions using a number of other fluoride salts with UF_4 (4).

The widest range of conditions was for solubility studies reported by Greenfield and Hyde (3). They show good data for $\text{BaF}_2 + \text{UF}_4$ and $\text{LiF} + \text{UF}_4$ for 50-100 mol % UF_4 and 1000-1300 $^\circ\text{C}$. They also show data for LiF , BaF_2 , and $\text{BaF}_2 + \text{LiF}$ mixtures at 1200 to 1300 $^\circ\text{C}$ and 10-30 mol % UF_4 . They report several values for other ternary mixtures at 1200 $^\circ\text{C}$.

Our first work was to make the maximum use of the published data and to identify where additional measurements were needed. Calculations were made to convert all the data to a single set of units. Then the data for other temperatures were adjusted to 1200 $^\circ\text{C}$, using empirical corrections based

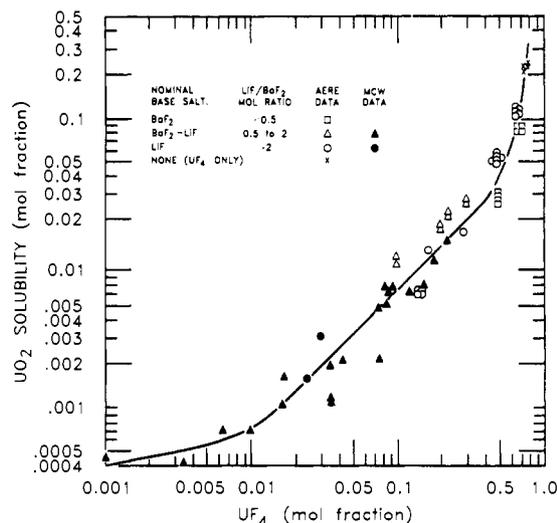


Figure 2. Solubility of UO_2 in $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ melts at 1200 $^\circ\text{C}$.

on temperature data for $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ (see Appendix B). For most of the salt compositions, experimental results were reported at 1150, 1200, and 1250 $^\circ\text{C}$, and the errors for temperature corrections were small.

The published data after conversions of units and adjustments for temperature effects to 1200 $^\circ\text{C}$ were examined for correlations. The principle experimental variables for which measurements are reported include the following: (1) the composition of the fluoride base salt before addition of UF_4 or uranium oxides (the base salts were either single metal fluorides or binary mixtures of fluorides), (2) the amount of UF_4 added to the base salt, (3) temperature, (4) properties of characteristics of the uranium oxide that is added to the fluoride salts.

The literature results indicated that the chemical composition or physical form of the uranium oxide did not affect the solubility after equilibration (3, 4). All other forms of uranium oxide are converted to UO_2 in the molten salt containing UF_4 at 1200 $^\circ\text{C}$. This result would be expected theoretically and was not studied as an experimental variable at Oak Ridge National Laboratory (ORNL). A UO_2 of fine particle size rapidly recrystallizes to a coarser and denser form of UO_2 . Several pairs of data at two temperatures with the same composition showed good agreement with the empirical temperature correlation for $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ compositions. This confirmed that the empirical adjustments for the effects of temperature on UO_2 solubility were useful for the other fluoride salts.

The data clearly show that the amount of UF_4 in the melt is the controlling or most important variable for UO_2 solubility. The amounts of compositions of the other fluorides have small effects with only a few exceptions. This correlation is made apparent if the UO_2 solubility is plotted versus the amount of UF_4 using the same units for both. If the solubility and the amount of UF_4 are given in different units (for example, weight percent UO_2 versus mole percent UF_4), then different fluoride salts with different densities or molal volumes appear to give significant differences in UO_2 solubilities.

A large amount of the published data is for BaF_2 , LiF , or $\text{BaF}_2 + \text{LiF}$ mixture as the base salts. These also represent some extremes of salt properties. The LiF fluoride is an alkali-metal fluoride with a density of 1.63 g/cm^3 and a molal volume of 15.9 cm^3/mol at 1200 $^\circ\text{C}$ while BaF_2 is an alkaline-earth-metal fluoride with a 4.30 g/cm^3 density and 40.7 cm^3/mol molal volume at 1200 $^\circ\text{C}$. The UO_2 solubility data for $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ melts is shown with log scales to expand the low concentrations (Figure 2). A 45 $^\circ$ line is reasonable for the

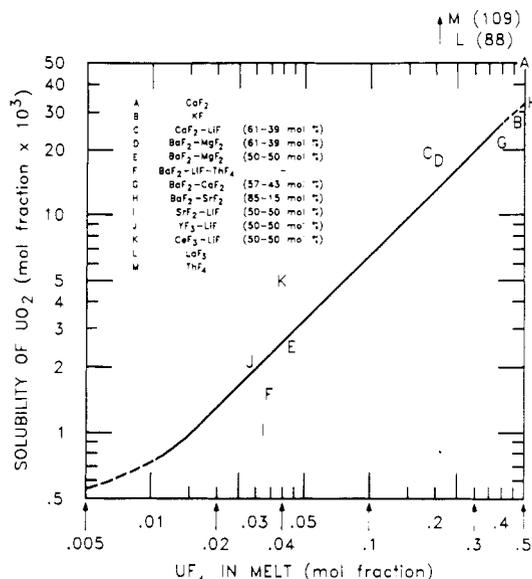


Figure 3. Solubility of UO_2 at 1200 °C for varied base salts.

0.02–0.5 mole fraction UF_4 concentrations of most interest for electrolysis cells. For low UF_4 concentrations, the UO_2 solubilities level off to the low values of about 0.0003 mole fraction UO_2 for melts without UF_4 . The UO_2 solubilities for more than 0.5 mole fraction UF_4 increase to much higher values than those indicated by the 45° line.

The formation of complexes in the melt is probably important to the UO_2 solubility behavior. The controlling effect of the UF_4 concentration seems to indicate a complex of UO_2 and UF_4 . The phase diagram for UO_2 and UCl_4 shows formation of UOCl_2 equivalent to up to 13 mol % UO_2 in the liquid phase (8). A similar formation of either UOF_2 , or $\text{U}_2\text{O}_2\text{F}_4$ has been suggested, but has not been proven, for UO_2 and UF_4 . Fluoride salt complexes such as K_2UF_6 or $2\text{KF}\cdot\text{UF}_4$ have been observed and would affect the activity of UF_4 in the melt. The solubility results seem to indicate that the complexes of UO_2 with the UF_4 have more effect than the complexes of UF_4 with other fluoride salts.

A high solubility of UO_2 was important to operation of electrolysis cells. The search for high solubilities resulted in solubility measurements for many other base salt compositions. These are shown (Figure 3) as a plot that includes the line from Figure 2 for BaF_2 , LiF , or $\text{BaF}_2 + \text{LiF}$ base salts. Considering the limited accuracy of single measurements, all the alkali-metal and alkaline-earth-metal base salt mixtures are reasonably close to the line for $\text{BaF}_2 + \text{LiF} + \text{UF}_4$. Data for La , Ce , and Th fluorides are much higher than the line. Perhaps these fluorides also complex the UO_2 similar to the reported complexes with UF_4 .

A $\text{CaF}_2 + \text{LiF}$ base salt is of particular interest because it would allow formation of a frozen salt sidewall similar to the operation of frozen sideledge cells for aluminum. Piper demonstrated much higher cell current efficiencies for operation with a frozen sidewall and a $\text{CaF}_2 + \text{LiF}$ melt (1). Piper also reported UO_2 solubility measurements that show increasing UO_2 solubilities in $\text{CaF}_2 + \text{LiF}$ as the UF_4 concentration decreased (1). These solubility results are anomalous and inconsistent with the behavior for other base salts (Figure 4).

The ORNL data for $\text{CaF}_2 + \text{LiF}$ show UO_2 solubilities that are higher than those reported for $\text{BaF}_2 + \text{LiF}$ mixtures, but an increase at low UF_4 contents was not seen (Table I and Figure 4). The slope of the straight line (Figure 4) gives a solubility of 0.11 mol of UO_2 /mol of $\text{UO}_2 + \text{UF}_4$. The values at low UF_4 contents are from analyses for total uranium in the samples and are more certain than the indirect procedures

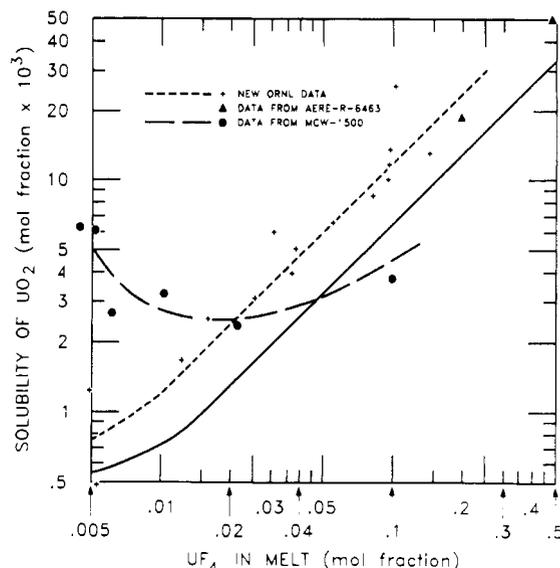


Figure 4. Solubility of UO_2 at 1200 °C in $\text{CaF}_2 + \text{LiF} + \text{UF}_4$.

Table I. ORNL Data for UO_2 Solubility in CaF_2 or $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ Melts

LiF/ CaF_2 or BaF_2 (mol/mol)	UF_4 mole fraction	UO_2 mole fraction	UF_4 to UO_2 conversion (ppm U)	UO_2 solubility (mol of UO_2 /mol of $\text{UO}_2 + \text{UF}_4$)
CaF ₂ + LiF + UF ₄ at 1200 °C				
0.75	0	0.000 20	no UF ₄	1.00
	0	0.000 34	no UF ₄	1.00
	~0	0.000 25	4100 (all)	1.00
	~0	0.000 24	4100 (all)	1.00
	<0.0002	<0.000 5	>20 000	0.71
	<0.0002	<0.000 6	>20 000	0.75
	0.0032	0.001 27	26 000	0.28
	0.0033	0.000 60	est 25 000	0.15
	0.0050	≤0.000 2	est 25 000	0.04
	0.0121	0.001 69	26 000	0.122
	0.0250	0.003 12	36 000	0.111
	0.0547	0.006 68	45 000	0.109
0.45	0.0939	0.010 1	est 30 000	0.097
	0.0941	0.011 9	34 000	0.112
	0.1422	0.013 2	29 000	0.085
	0.0373	0.005 11	28 800	0.120
2.00	0.1002	0.025 8	45 500	0.205
	0.0300	0.006 03	14 800	0.167
	0.0807	0.008 72	17 100	0.098
CaF ₂ + LiF + UF ₄ at 1280 °C				
0.75	0.0157	0.003 10	22 500	0.165
	0.0365	0.005 10	20 500	0.123
	0.0908	0.016 3	41 900	0.152
BaF ₂ + LiF + UF ₄ at 1200 °C				
1.00	0.0346	0.003 02	31 000	0.080
	0.0380	0.005 51	25 000	0.127
	0.0883	0.008 96	21 000	0.092
	0.1815	0.023 7	31 000	0.115

required when significant amounts of UF_4 are present. The MCW results (1) are by analyses for oxygen. We suggest that the anomalous MCW results for $\text{CaF}_2 + \text{LiF}$ of low UF_4 contents are caused by oxygen impurities; that is, the increase in oxygen content as the UF_4 concentration decreased was not from an increase in UO_2 solubility. The molten salts at test conditions generally contained about 0.3 mass % oxygen as impurities. The analyses determined these oxygen impurities, and the results were interpreted as being UO_2 —much higher UO_2 contents than the true UO_2 solubility for low UF_4 contents. When UF_4 was added, the oxygen impurities reacted with UF_4 to form additional insoluble UO_2 , thus reducing the oxygen content of filtered samples. For additions of more than 0.02 mole fraction UF_4 , the oxygen impurities were removed completely enough to give approximately correct

Table II. UO_2 Solubilities for 0.02–0.5 Mole Fraction UF_4 in Other Fluoride Salts^a

base salt	original data		calculation from	UO_2 solubility (mol of UO_2 /mol of $\text{UF}_4 + \text{UO}_2$)
	organization ^b	ref		
$\text{BaF}_2 + \text{LiF}$	MCW	1, 4	Figure 2	0.055
	AERE	3	Figure 2	0.086
	U.S. Bureau of Mines	5	single value	0.071
	ORNL	7		0.100
LiF	MCW	4	Figure 2	0.078
	AERE	3	Figure 2	0.055
BaF_2	AERE	3	single value	0.059
CaF_2	AERE	3	single value	0.097
$\text{CaF}_2 + \text{LiF}$	AERE	3	single value	0.089
	MCW	1	<0.005 mol of UF_4 /mol	>0.50
	MCW	1	>0.05 mol of UF_4 /mol	<0.10
	ORNL	7	Figure 4	0.109
$\text{BaF}_2 + \text{CaF}_2$	U.S. Bureau of Mines	5	single value	0.051
KF	AERE	3	single value	0.055
MgF_2	AERE	3	single value	0.124
$\text{BaF}_2 + \text{MgF}_2$	MCW	4	single value	0.057
	AERE	3	two values	0.086
$\text{BaF}_2 + \text{SrF}_2$	U.S. Bureau of Mines	5	single value	0.058
$\text{SrF}_2 + \text{LiF}$	MCW	4	single value	0.030
$\text{YF}_3 + \text{LiF}$	MCW	4	single value	0.064
$\text{CeF}_3 + \text{LiF}$	MCW	4	single value	0.112
LaF_3	AERE	3	single value	0.162
ThF_4	AERE	3	single value	0.196

^a Basis: UO_2 solubility proportional to UF_4 concentration. Temperature: 1200 °C. ^b ORNL indicates authors of this paper; otherwise, see references for full names.

values for the UO_2 solubility. This explanation is in excellent agreement with the conversions of UF_4 to UO_2 seen in ORNL tests (7) and with the postulated reaction of UF_4 with oxides. The ORNL test commonly showed about 0.03 g of U/g of salt (30 000 ppm U) conversion of UF_4 to UO_2 (Table I).

Most of the 40 new measurements of UO_2 solubility at ORNL were with the $\text{CaF}_2 + \text{LiF}$ UF_4 melts (Table I). In addition to the correction and explanation of the anomalous solubility results for $\text{CaF}_2 + \text{LiF}$ base salt, the ORNL results showed the following: (1) The effect of the Li/Ca ratio on the UO_2 solubility was small or insignificant. (2) Data for $\text{CaF}_2 + \text{LiF} + \text{UF}_4$ at 1280 °C showed a temperature effect that agreed with the empirical temperature correction for $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ (Appendix B). (3) The ORNL results for $\text{BaF}_2 + \text{LiF} + \text{UF}_4$ showed somewhat higher UO_2 solubilities than the most complete previous results (4). The MCW results (4) were usually somewhat lower than the other results for all salt compositions where comparisons were possible.

For melt concentrations of 0.02–0.5 mole fraction UF_4 (the range of interest for electrolytic cell operation) the UO_2 solubilities appear to be directly proportional to the UF_4 concentrations. This proportionality seems consistent with a number of different sets of data (Figures 2–4). The UO_2 solubilities as mole fraction UO_2 based on total uranium were calculated for 45° lines for these sets of data and for single points or small sets of data by assuming the same proportionality (Table II). All the salt mixtures that are practical for electrolytic cell operation showed experimental UO_2 solubilities of 0.06–0.11 mole fraction UO_2 (based on total uranium). The higher values are for $\text{CaF}_2 + \text{LiF} + \text{UF}_4$ as compared to melts without CaF_2 and for ORNL or AERE (5) results as compared to MCW (4) results. The overall results do not clearly prove any differences for the different alkali-metal and alkaline-earth-metal fluorides or mixtures. The limited accuracies of single points and the difference between studies may account for the whole 0.06–0.11 mol of UO_2 /mol of $\text{UO}_2 + \text{UF}_4$ range of variation. Some fluorides of higher valence such as ThF_4 and LaF_3 (Table II) show higher solubilities of UO_2 , but the salts are not practical for production electrolytic cells. The solubilities of UO_2 at electrolytic cell conditions in units of moles of oxygen per liter are less than one-tenth of the solubilities of Al_2O_3 at

Hall–Heroult cell conditions. The lower solubilities would be expected to result in lower current density limits and lower cell capacities for uranium as compared to aluminum.

Appendix A. Analyses for Uranium Oxide

The frozen samples removed from experimental tests are particles of UO_2 finely dispersed in mixtures of solid fluoride salts. Most of the compositions of interest include UF_4 , and simple analyses for uranium content do not provide useful measures of UO_2 content in the presence of UF_4 . The UO_2 solubilities are about one-tenth of the UF_4 concentrations for the most important salt compositions. Oxide impurities react with UF_4 so that the sample UF_4 concentrations are always lower than those calculated from the charge makeup. Therefore, UO_2 contents determined by determination of total U and subtraction of UF_4 concentration calculated from the charge makeup are valid only for zero concentrations of UF_4 .

For the three useful sets of UO_2 solubilities in the published literature, the UO_2 concentrations were determined using an inert gas fusion procedure to evolve the oxygen as CO . Other analytical procedures that have been used for oxides in fluoride salts are treatment with HF to evolve H_2O and treatment with F_2 or other fluorinating agents to evolve O_2 . All of these procedures assume that all the oxygen in the sample is present as UO_2 . This is a reasonable assumption for samples with moderate or high UF_4 concentrations as the oxide impurities all react with UF_4 at 1200 °C to give fluorides and UO_2 .

For our samples with UF_4 in the salt, the UO_2 was determined using an analytical concept that has been applied to determine the unreactive uranium (that is, uranium oxides) in UF_4 feed materials. This procedure starts with the selective extraction of UF_4 in a solution that leaves uranium oxides as an insoluble residue. Separate analyses of uranium contents give data that allow calculation of the UF_4 and UO_2 contents in the initial sample. The solution used for our samples was 5% Na_2EDTA (disodium ethylenediaminetetraacetic acid)– H_3BO_3 . The CaF_2 is not soluble in the solution, and the completeness of UF_4 removal from CaF_2 solids is an important uncertainty. Good separations were demonstrated, and the analytical procedure was verified by the analyses of a series of unfiltered melts of known compositions (9). The procedure

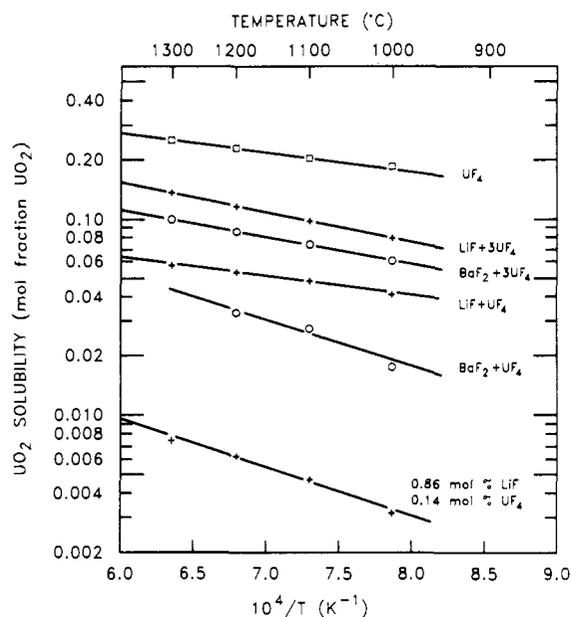


Figure 5. Solubility of UO_2 versus temperature.

developed by Batiste and Lee is given in more detail in the ORNL report (7).

Appendix B. Temperature Dependence of UO_2 Solubility

Information on the UO_2 solubility as a function of temperature was important in two ways. Temperature is an important variable for the molten salt electrolysis. Three previous studies of UO_2 solubilities used three different primary temperatures (1150, 1200, 1250 °C). Adjustments for the temperature effects were needed to allow comparisons of otherwise similar data. We chose 1200 °C as a reasonable operating temperature to prepare molten uranium (melting point of 1132 °C) and as a middle temperature that would minimize the temperature adjustments for comparisons of data.

The effects of temperature on UO_2 solubilities for a number of binary mixtures of fluoride salts are reported by Greenfield and Hyde (3). Their data show straight lines of similar slopes

when log solubilities are plotted versus (temperature, K)⁻¹ (Figure 5). We used a set of curves to provide temperature corrections with 1200 °C as the standard or no correction value. The UO_2 solubilities on the abscissa were plotted versus the UO_2 solubility at 1200 °C for the same sample compositions. Lines were drawn for points at the same temperature, and these lines were used to adjust data for that temperature to 1200 °C. This procedure should be considered as an approximation to be used when exact experimental data are not available, but the errors are probably no larger than the uncertainties of the individual experimental points. The correction curves should have small errors for a difference of 50 °C (that is, to make temperature corrections of 1150 or 1250 to 1200 °C). Corrections of 1000 °C or less to 1200 °C are less dependable. The experimental data of Figure 5 are for UF_4 or $\text{UF}_4 + \text{BaF}_2 + \text{LiF}$ mixtures. Our experimental data confirm this temperature correction for $\text{CaF}_2 + \text{LiF} + \text{UF}_4$ at 1280 °C, but use for other salt compositions is an additional extrapolation.

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