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SPRAY FLUORINATION OF FUSED SALT
AS A URANIUM RECOVERY PROCESS

A Preliminary Feasibility Study

by

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ABSTRACT

Spray fluorination may be used to recover uranium as the volatile hexafluoride from molten fluorides by spraying the salt into a fluorine atmosphere. This dropwise liquid-gas contacting system was considered as a step in the fused-salt fluoride volatility process applied to zirconium-matrix fuels, with the possible advantage of avoiding corrosive conditions involved in sparging. Experimental equipment was developed and tests were made for heat and mass transfer. From the data obtained, process design calculations indicated that a satisfactory equipment design is possible.

SUMMARY

Uranium can be recovered from zirconium-matrix fuels by dissolving the alloy in a fused salt mixture of sodium and zirconium fluorides and sparging the melt with fluorine to volatilize uranium as the hexafluoride. Spraying fused NaF-ZrF₄ containing dissolved uranium tetrafluoride into an atmosphere of fluorine to recover uranium hexafluoride was conceived as an alternative to sparging fluorine in a vessel containing the fused salt. This dropwise fluorination was proposed as a means of avoiding the corrosive combination of the fused salt and fluorine encountered in the fused salt process for recovering uranium from spent zirconium-matrix fuels.

Equipment development was an essential part of this program. Heat transfer data were determined from experiments with fused salt spray in air and were found to be in good agreement with the following correlation:*

$$hD/k = 0.37 (Dv\rho/\mu)^{0.6}$$

The rate of uranium removal from the salt was found to be controlled by chemical kinetics rather than by a process of diffusional mass transfer. In the experimental range of data it was found that uranium removal could be correlated by either of the following equations:

$$\% \text{ Uranium removal} = 1246 (1/r) \ln (T_1 - T_s) / T_2 - T_s$$

or

$$\ln (C_0/C) = 13.74 (1/r) \ln (T_1 - T_s) / T_2 - T_s$$

*Nomenclature given in the Appendix, page 27.

Design calculations in which the experimental data were extrapolated to higher per cent removals by the latter equation (this has more theoretical justification) indicate that four stages of 10-ft towers would be required to avoid an impractically large single-spray tower. These results indicated that this method of fluorination would be too complex to justify its use in a fused salt volatility process.

INTRODUCTION

In the fused salt volatility process for the recovery of uranium from zirconium-matrix fuels, the alloy is dissolved in a fused salt mixture of zirconium fluoride and sodium fluoride and then the uranium is volatilized as the hexafluoride by contacting with fluorine. The simplest concept for the fluorination step is a fluorine sparge in a vessel containing the fused salt. However, because the combination of fused salt and fluorine is corrosive to metals, an alternative means of contacting, i.e., spraying the salt into a fluorine atmosphere, was considered.

Corrosion can be eliminated in the dissolution step by using a graphite vessel as a container for the fused salt. The fuel element is put into solution by reaction with a hydrogen fluoride sparge to form zirconium tetrafluoride and uranium tetrafluoride. In the spray fluorination process for removal of the uranium from the salt, the fluorine reacts with the uranium tetrafluoride to form uranium hexafluoride at the surface of the spray droplet. The salt is formed into small drops by a nozzle at the top of a tower filled with fluorine. The uranium hexafluoride diffuses into the gas phase, and more uranium tetrafluoride diffuses to the surface of the drop from within the liquid phase. Operating conditions can be adjusted so that after a sufficient amount of uranium was removed the salt drop would solidify before it contacted the metal at the bottom of the column.

During the course of this experimental program, heat transfer from the drops and the controlling mechanism of uranium removal were investigated. Equipment design and development to ensure a process that is operationally feasible were also an important part of the project to be studied.

I. APPARATUS AND PROCEDURE

Figure 1 shows schematically the equipment used for the salt spray tests. The salt-melting furnace was constructed from 2-inch nickel pipe and welded to the top of the drop contactor. The spray nozzle was a Spraying Systems Co. $\frac{1}{4}$ LN3 hollow-cone single-phase nozzle. The nozzle was constructed of Monel. The spray contactor was made of stainless steel and was 30 inches in diameter. The nozzle was 4 feet above the nickel collection pans at the bottom of the vessel. All gasketing was either of copper or of Teflon.

FIGURE 1
SCHEMATIC DIAGRAM OF DROP-FLUORINATION APPARATUS

The salt-melting furnace and the walls of the vessel were heated by electrical resistance heaters. A thermowell in the salt indicated the salt temperature, and a thermocouple on the wall of the vessel was used to control the wall temperature.

The fluorine was introduced at the top of the vessel and was heated by the walls of the vessel. A nitrogen cylinder pressurized the salt through the spray nozzle. The fluorine and reaction products were evacuated through a line at the bottom of the vessel into a scrub tower.

Two mechanical methods were used to prevent salt from entering the nozzle before spraying. A nickel stopper rod was inserted from above into the nozzle coupling on the salt side of the nozzle, and a nichrome wire was inserted into the nozzle orifice from the discharge side of the nozzle. Both of these devices were operated through gas seals.

Before the salt was sprayed it was pretreated by a sparge of hydrogen fluoride, hydrogen, and helium, as a purification step. In this series of runs 40 mol per cent zirconium tetrafluoride-60 mol per cent sodium fluoride salt was used. It was supplied by the General Chemical Company and contained less than 2000 ppm metal impurities other than alkali metals. Major impurities in the salt as received were potassium (about 1 atom per cent) and oxygen (equivalent to about 5 per cent of the zirconium as zirconium dioxide). To prevent oxidation of salt by leakage from the salt furnace into the nozzle during the hydrogen fluoride pretreatment, the vessel was evacuated of air and then filled with nitrogen to 3 psig. Oxidized salt would have a higher melting point and could have plugged the nozzle. The nitrogen was subsequently evacuated, and fluorine was introduced into the vessel.

For the heat transfer tests a Spraying Systems Company full-cone spray nozzle ($\frac{1}{8}$ G3001.4) was used. This nozzle had a 0.026-inch orifice and was constructed of Monel. The salt was sprayed in air and samples were collected in $1\frac{1}{8}$ -inch copper cups.

II. HEAT TRANSFER TESTS

Determinations of the heat transfer coefficients between the spray droplets and the gas were made from measurements of the time required for solidification of droplets of various sizes. Solidification time was determined from measurements of the distance traversed by the spray droplets before solidifying, together with the calculated velocity of the droplets.

A. Velocity of Fused Salt Discharged from Nozzle

Tests were made to determine the volumetric discharge rate and linear velocity of the droplets at the nozzle. In two tests with the solid cone nozzle under 40 psig gas pressure, the salt collected during a measured portion of the spray period was weighed. The volumetric flow rate for the 0.026-inch orifice was 242 ml/min.

For comparison, the discharge rate of tetrabromoethane was measured under the same conditions. The density of tetrabromoethane is about 10 per cent lower than the 200-lb/cu ft density of the salt. Also, for reference, the theoretical velocity was calculated assuming complete conversion of the gas pressure (40 psig) into salt velocity head (neglecting friction). These results, given in Table 1, show that the discharge velocity is approximately 40 ft/sec.

Table 1

FULL-CONE SPRAY NOZZLE DISCHARGE RATES

Measured Fused Salt Volumetric Discharge Rate

Run	Wt Collected (g)	Time (sec)	Volumetric Flow (cc/min)
1	259.0	20	242
2	192.6	15	241
Average			242

Discharge Velocity of Nozzle

Basis	Discharge Velocity (ft/sec)
NaZrF ₅ salt tests	38.8
Tetrabromoethane	41
Calculated from pressure head	43

B. Determination of Droplet Size and Solidification Point

Three spray tests were made in which droplets at various distances from the nozzle were collected and their sizes measured by observation with a microscope. The salt was heated to 650 C and sprayed into air at 20 C. The results of these tests are presented in

Figure 2, in which the relative frequency of given drop sizes, in per cent, is plotted against drop size in microns for six distances from the nozzle ranging from 15 to 40 inches. The number of droplets measured for each distance ranged from 100 to 393.

A substantial portion of the salt had not solidified at each point of collection, as indicated by the fact that not all the material was in the form of discrete droplets. Measurements were made only on the drops collected as spheres. Figure 3 shows the type of solidified salt that was measured. The solidified product particles are nonporous spheres; they have the desirable feature of being free-flowing.

Figure 2 shows an increase in the relative number of larger drops with increasing distance

from the nozzle, indicating that larger droplets take longer to solidify. For purposes of calculation the largest or critically sized droplet which just solidified before striking the collection cup was taken as the size below which 90 per cent of the particles were found in a given collection. At 15 inches from the nozzle, droplets smaller than 100 microns were solid, while at 40 inches droplets of over 200 microns had solidified. The size

Figure 3
PHOTOGRAPH OF SOLIDIFIED DROPS

distributions in Figure 2 also show a fairly flat distribution of droplet sizes with the solid-cone nozzle from diameters of about 30 to over 200 microns.

C. Cooling Time and Heat Transfer Coefficients for Spray Droplets

From the data on solidification obtained in the above spray tests, times for droplets to cool to the freezing point and of the corresponding heat transfer coefficients were calculated as follows:*

1. From the basic law of motion for droplets slowed by air friction, the relation between distance travelled in a given time was found as a function of drop size and initial velocity. The determination of distance travelled before solidification as a function of drop size and of initial velocity was described above; this allowed the solidification time to be calculated.

2. Knowledge of the heat capacity of the molten salt and of the latent heat of freezing of the salt allowed the average total heat loss to be determined. From this, the heat transfer coefficients for various drop

*Consult the appendices for further details.

sizes were calculated. Radiation losses were minor and were neglected. It was assumed that the heat transfer coefficients for both loss of sensible heat down to the melting point and latent heat removal were equal. The solidification time was taken as the sum of the time for these two steps.

The results of these calculations of the heat transfer coefficients are summarized in Table 2; values ranged from 72 to 144 Btu/(hr)(sq ft)(F) for the measured conditions. The Nusselt numbers, hD/k , based on droplet diameter, D , and air conductivity, k , compare favorably with the correlation

$$hD/k = 0.37 (Dv\rho/\mu)^{0.6} ,$$

where v is taken as average particle velocity, and ρ and μ are the density and viscosity of air, respectively. In Figure 4 these heat transfer data are plotted with data from other workers on the heat transfer of spheres to air. The spray droplet data extend the data range to spheres of smaller size than those used in any previous study. The measure of agreement tends to confirm the general analysis adopted for heat transfer and solidification time in spray fluorination.

Table 2

SOLIDIFICATION TIMES AND HEAT TRANSFER COEFFICIENTS
FOR FUSED-SALT DROPLETS

Initial velocity: 38.8 ft/sec
Initial temp: 650 C (T_1)
Final temp (mp): 505 C (T_2)
Room temp: 20 C (T_s)

Distance from Nozzle (in.)	Drop Size (microns)	Solidifi- cation Time (sec)	h [Btu/(hr)(sq ft)(F)] ^b	Calculated Values of hD/k	Average Velocity (ft/sec)	Avg N_{Re}	Predicted ^a Values of hD/k
15	100	0.08	95	2.2	15.5	32.2	2.9
18	133	0.07	144	4.5	20.4	56.0	4.1
21	133	0.10	101	3.2	17.6	47.3	3.8
24	133	0.133	76	2.4	14.1	38.7	3.3
27	142	0.15	72	2.4	14.7	43.1	3.5
40	217	0.165	100	5.1	20.2	90.4	5.5

^aFrom $hD/k = 0.37 N_{Re}^{0.6}$

^bCalculated by equations on p. 33 and 44.

III. RESULTS OF URANIUM REMOVAL TESTS

Measurements were made of the fraction of uranium removed by spraying fused salt containing uranium tetrafluoride into a fluorine atmosphere. Results were correlated in terms of the temperature of the fluorine and the drop size.

FIGURE 4
CORRELATION OF DATA ON HEAT TRANSFER FROM SPHERICAL PARTICLES TO GAS

Six runs, in which fused salt consisting of one w/o uranium tetrafluoride was sprayed into a fluorine atmosphere, were made. The salt temperature was brought to 760 C for spraying and duplicate runs were made with fluorine at 20, 100, and 200 C. Nitrogen at 40 psig was used to force the molten salt through the single-phase hollow cone nozzle.

The salt was given a sparge pretreatment before spraying in order to mix the uranium tetrafluoride and to fluorinate oxides. The sparge gas was a mixture of helium, hydrogen, and hydrogen fluoride. It was thought that any oxides present might react initially with the fluorine and delay the formulation of uranium hexafluoride from the uranium tetrafluoride.

A. Size Distribution of Salt Spray

Weight fractions of various droplet sizes of the sprayed material from Run 1 are shown at the top of Figure 5. The sample of material collected was screened with 40, 60, 80, 100, and 200 mesh sieves. A frequency distribution based on microscopic measurements of a sample of 100 particles from the unscreened material is also shown for comparison at the top of Figure 5. Because the weight of the drop is proportional to its diameter cubed, a small number of large drops would constitute a considerable proportion of the weight. Average droplet diameters are given in terms of the specific surface average size on a number basis, $\sum D^3 / \sum D^2$, a measure of the ratio of the volume to surface area of the particles. The average diameter for the as-sprayed material was 164 microns.

The particle size distribution of the five screened fractions are also shown in Figure 5. These distributions are based on microscopic measurements of 100 particles. Average diameters and mesh sizes are indicated. The dotted lines indicate the limits of the screen openings.

FIGURE 5
DROP SIZE DISTRIBUTION IN FLUORINATION TESTS
(Dotted lines refer to screen opening)

B. Uranium Analysis

These fractions were analysed for uranium to determine the effect of drop size on uranium removal. The per cent of uranium removal was determined by an X-ray spectral analysis. The results were based on the ratio of the intensity of the uranium emission line of the material before spraying to the intensity in a sample representative of a particular screened fraction. The results are summarized in Table 3.

IV. MECHANISM OF URANIUM REMOVAL

The removal of the uranium content from the droplet by fluorination depends on liquid and gas-phase diffusion and on kinetics of the chemical reaction. The controlling step in uranium removal can be determined from the sizes and properties of the spray droplets and from the time available before solidification.

Table 3

RESULTS OF DROP FLUORINATION RUNS

Salt Composition: Approx 40 m/o ZrF_4 -60 m/o NaF
with one w/o UF_4 added

Conditions	Mean Drop Diam of Fraction (Microns)	Spray Parameters				Measured % U Removed			Predicted % U Removed	
		$\dot{Y}$, avg ^a	hD/k^b	h^c	Cooling time (sec)	1	2	Avg	Film Resistance Controlling	UF_4 Diffusion Controlling
Gas temp: 200 C(T_s)	62.13	7.70	2.00	154	0.037	11.8	9.8	10.8	100	95.7
mp: 508 C (T_2)	118.2	7.57	2.13	86.3	0.13	8.5	8.7	8.6	100	94.4
Salt temp: 765 C(T_1)	157.7	8.57	2.71	82.5	0.18	6.9	7.5	7.2	100	90.6
	215.2	9.83	3.56	79.0	0.25	6.7	5.7	6.2	100	84.7
	307.9	11.5	4.84	75.0	0.38	6.7	3.8	5.3	100	78.0
Gas temp: 100 C(T_s)	62.13	6.96	2.00	187	0.036	16.4	26.4	21.4	100	95.7
mp: 505 C(T_2)	118.2	7.02	2.00	98.2	0.13	12.9	18.5	15.7	100	94.4
Salt temp: 765 C(T_1)	157.7	7.13	2.00	73.4	0.23	9.4	14.8	12.2	100	94.3
	215.2	7.74	2.24	60.5	0.39	5.7	10.9	8.3	100	93.0
	307.9	10.2	3.28	61.8	0.54	2.3	8.3	5.3	100	85.8
Gas temp: 200 C(T_s)	62.13	6.22	2.00	224	0.039	21.0	29.3	25.2	100	95.7
mp: 505 C(T_2)	118.2	6.20	2.00	118	0.14	7.6	15.0	11.3	100	95.4
Salt temp: 765 C(T_1)	157.7	6.25	2.00	86.2	0.26	5.7	10.7	8.2	100	95.8
	215.2	6.73	2.00	64.8	0.47	3.9	8.5	6.2	100	95.5
	307.9	8.98	2.25	51.0	0.85	2.0	3.1	2.6	100	93.9
Purified	62.13	6.22	2.00	224	0.038	18.7	11.7	-	100	95.7
Salt	118.2	6.20	2.00	118	0.14	18.6	5.8	-	100	95.4
Gas temp: 20 C(T_s)	157.7	6.40	2.00	86.2	0.25	29.3	8.2	-	100	95.4
mp: 523 C(T_2)	215.2	6.78	2.00	64.8	0.46	25.7	-	-	100	95.3
Salt temp: 800 C(T_1)	307.9	9.03	2.25	51.0	0.83	24.4	-	-	100	93.5

^aUnits are ft/sec^bDimensionless^cUnits are Btu/(hr)(sq ft)(F)

A. Solidification Time

As was described previously, calculations of solidification times were made from values of drop sizes, initial velocities, distances traveled before solidification, and operating temperatures. It was found that the heat transfer coefficient, h , agreed quite well with a previous correlation.

The amounts of heat involved in sensible and latent heat changes were very nearly equal and, therefore, the times for each of these steps were approximately equal. Although it is possible that freezing the drop might initially form a shell, so that only a fraction of the time is available for diffusion transfer, the effect of supercooling and shrinkage of salt upon freezing would tend to delay the formation of an impervious shell of this sort.

Measurements of the volumetric salt flow obtained for the hollow cone nozzle are summarized in Table 4. The calculated initial velocity, based on full flow through the orifice, was one-half that of the solid-cone nozzle used for heat transfer tests.

Table 4

HOLLOW-CONE SPRAY NOZZLE DISCHARGE RATES

Run	Wt Collected (g)	Time (sec)	Volumetric Flow (cc/min)
1	101.0	15	136
2	105.4	15	142
Average			139

Initial velocity: 19.1 ft/sec

B. Predicted Uranium Removals Compared with Experimental Results

In Table 3 are shown the calculated times for solidification of the salt drops of the different diameters and the various experimental fluorine temperatures. Also shown are the predicted uranium removals for the cases in which mass transfer is controlled by gas-film resistance and fused salt diffusion, based on the calculated solidification times. The purpose of these calculations was to indicate a basis for interpretation of the experimental results. From the values shown in Table 3, it appears that diffusion mass transfer is not controlling, but that kinetics is. In nearly every case the actual uranium removed is but a small fraction of that which would be predicted by mass-transfer mechanisms.

C. Fluorination of High-purity Salt

Two runs were made in which high-purity salt was pretreated with a fluorine sparge to see if salt impurities had an inhibiting effect on the conversion of the uranium tetrafluoride to the hexafluoride. Fluorine is a much stronger fluorinating agent than hydrogen fluoride. The fluorine was sparged at an excess of a bubble per second for a half hour. After the fluorine sparge, uranium tetrafluoride was added to the molten salt and mixed with a helium sparge. A high-purity salt made by the Kawecky Chemical Company with the following composition was used:

44.2 m/o ZrF_4
 55.8 m/o NaF
 (mp: 523 C)

The impurity assay in weight per cent was as follows:

Fe	0.020	Ni	0.001
S	0.0004	Ti	0.001
B	0.002	Mn	0.001
Si	0.005	Al	0.025
Cr	0.001	O	0.0001

Operating difficulties were encountered in the attempts to spray fluorinate this salt. Four runs were required before two samples suitable for uranium analysis could be obtained, in contrast with the previous six runs which had been successfully accomplished without any operational difficulties. The main problem was good nozzle operation. On two occasions the spray did not leave the nozzle straight but sprayed against the wall on one side. This resulted in an insufficient sample for analysis in the collection pans at the bottom of the vessel. This faulty operation may be due either to wear on the nozzle or to the fact that the melting point of this salt is higher and could more easily cause the nozzle to be partially plugged. There were also several failures of Teflon gaskets during the course of these runs. These failures occurred in part because of overheating of the seal flange by the misdirected salt spray.

In the first fluorine pretreatment run with the high-purity salt, a maximum uranium removal of 29.3 per cent was indicated, which is the same maximum value as obtained for the previous hydrogen fluoride pretreated salt at the same temperature. However, unlike the previous runs, the per cent removal was about the same for various drop sizes. The absence of impurities might be used to account for better uranium removal in the larger droplet sizes, but the fact that no fraction showed maximum removal higher than in the previous runs leaves the issue somewhat in doubt as to the overall effect of impurities.

The second fluorine pretreatment run failed to duplicate the first, as can be seen from Table 3. Also, this run did not produce the usual drop size distribution, but showed a larger fraction of fines and very little of the coarser droplets. This presumably resulted from uneven spraying. Further, a question about the validity of the data for this run is posed by a lack of reproducibility of samples of the unsprayed salt. In every run an initial sample of the salt was taken before spraying to be used as a reference to determine the per cent uranium removal. A sample was also taken of the unsprayed salt left behind in the salt reservoir after the bulk of the salt was sprayed. The reproducibility of these samples, expressed as the ratio of the latter to the former, is shown in Table 5. An exact check would be indicated by a ratio of unity; variations could be due to lack of mixing and/or removal of uranium from the salt in some manner before spraying and/or error variance in analysis.

Table 5

DUPLICATE SAMPLES OF UNSPRAYED SALT
AT BEGINNING AND END OF OPERATION

Type	Run	<u>Relative Uranium Concentrations</u>	
		<u>Beginning</u>	<u>End</u>
HF pretreatment	No. 2 at 100 C	1.000	0.982
HF pretreatment	No. 2 at 200 C	1.000	1.012
F ₂ pretreatment	No. 2 at 200 C	1.000	0.874

V. PROCESS DESIGN

In order to evaluate the process, a preliminary design of equipment was developed on the basis of the results obtained for removal of uranium by spray fluorination.

A. Equipment Lifetime

The recommended material of construction for a spray fluorinator vessel is nickel, which appears from corrosion tests to have the best high-temperature resistance to fluorine (less than 60 mils/year below 600 C). Monel and copper have good resistance to fluorine also. The vessel lifetime would be greatly reduced if molten salt contacted the walls; this can be prevented by proper design and operation. (In the present feasibility tests fluorine temperatures were limited to 200 C because of the use of an available stainless steel vessel; corrosion of this vessel was evident.)

Both Teflon and copper gaskets were used in the fluorine tests with satisfactory results. Teflon should, however, not be used in contact with fluorine much above room temperature; severe attack was noted in one case at above 100 C. Copper would be usable with fluorine to a high temperature.

Plugging of the spray nozzle by the fused salt was an initial operational difficulty. This difficulty was overcome by improving the heating of the nozzle and by the technique of using a wire inserted in the nozzle orifice to keep it clear until spraying was desired. The wire was withdrawn through a packing gland. This wire technique is not suitable for operation with radioactive material, where remote operation is required. It is believed that an improved nozzle-heating system would take care of this problem. A promising method is electrical autoresistive heating, which is used on fused-salt transfer lines and connections in connection with other fused-salt process studies at ANL. No plugging has been encountered with this system, even when used with water-cooled flanges.

The hollow-cone Monel nozzle used in the spray tests was removed and inspected. It had been used for twenty batch sprayings, half of which were with fluorine. The fluorine gas temperature in the vessel never exceeded 200 C, but the salt sprayed was heated as high as 800 C. The general condition of the outside and inside of the nozzle was good, but the orifice had enlarged from 26 to 32 mils; this amounts to an area increase of about 50 per cent. This situation indicates that fairly frequent nozzle replacement would be necessary.

B. Correlation of Rate Data

The equipment design shown here is based on the data from those runs with hydrogen fluoride pretreatment, because this case probably simulates more closely the type of salt that would be used in the process, and also the more conservative results would allow for a safety factor in the design.

The first step in the design calculations was to deduce a reasonable method for extrapolating the data to higher uranium removals. The data indicate a strong dependence of uranium removal on drop size and on fluorine temperature. It did not appear possible to form a correlation involving the calculated solidification times and uranium removal. However, a plot of either per cent uranium removal or of $\ln(C_0/C)$ versus $(1/r) \ln[(T_1 - T_S)/(T_2 - T_S)]$ have a set of points which apparently could be approximated by a straight line. These correlations are plotted in Figures 6 and 7, respectively.*

Table 6 shows the solution for the data. It is difficult to distinguish empirically at the lower removals whether % U removal or concentration ratios from $\ln(C_0/C)$ would be expected to provide the driving forces in

*They were developed by a least-squares method outlined in Appendix 7.

kinetics or diffusion. The concentration ratio is also the more conservative parameter for design purposes, since it involves an asymptotic approach to complete removal of uranium. This difference in parameters is important when extrapolating to higher per cent removal, as indicated in Figures 6 and 7.

Table 6

LEAST-SQUARES ANALYSIS OF DATA

$T_1 = 765 \text{ C}; T_2 = 505 \text{ C}$
(D and r are in microns)

Drop Diam D (microns)	T_s (C)	$\frac{100}{r} \ln \frac{T_1 - T_s}{T_2 - T_s}$	Avg U Removed (%)	Avg $\ln(C_0/C)$	Drop Diam D (microns)	T_s (C)	$\frac{100}{r} \ln \frac{T_1 - T_s}{T_2 - T_s}$	Avg U Removed (%)	Avg $\ln(C_0/C)$
62.1	20	1.379	10.8	0.114	157.7	100	0.628	12.2	0.129
118.2	20	0.715	8.6	0.090	215.2	100	0.461	8.3	0.087
157.7	20	0.543	7.2	0.074	307.9	100	0.322	5.3	0.055
215.2	20	0.398	6.2	0.064	62.1	200	1.980	25.2	0.290
307.9	20	0.278	5.3	0.054	118.2	200	1.042	11.3	0.121
62.1	100	1.592	21.4	0.243	157.7	200	0.781	8.2	0.086
118.2	100	0.837	15.7	0.171	215.2	200	0.574	6.2	0.064
					307.9	200	0.400	2.6	0.026

$$\sum X^2 = \sum \left(\frac{100}{r} \ln \frac{T_1 - T_s}{T_2 - T_s} \right)^2 = 12.99$$

$$\text{For \% U removed } \sum xy = 161.97$$

$$S_b^2 = 0.635$$

$$\hat{b} = 12.46 \pm 1.71$$

$$\text{For } \ln(C_0/C) \sum xy = 1.786$$

$$S_b^2 = 0.0000806$$

$$\hat{b} = 0.1374 \pm 0.0193$$

C. Fluorination Column Design

Figure 8 gives a comparison of expected removal for a 25-micron radius drop and a 50-micron radius drop. In order to obtain a drop size distribution of 100 microns maximum diameter, a smaller nozzle and higher pressures would be required than were employed in the present tests.

The height of the spray fluorination column was based on a maximum drop radius of 50 microns. The heat transfer coefficient was determined from the terminal velocity of the droplet. The column height was calculated by multiplying the time for solidification by the terminal velocity and allowing two feet for the drop to slow down from its initial velocity at the nozzle to the terminal velocity. The terminal velocity was calculated by using the intermediate law equation⁽⁹⁾

$$U_t = \frac{0.153 g_L^{0.71} D_p^{1.14} (\rho_s - \rho)^{0.71}}{\rho^{0.29} \mu^{0.43}}$$

Tables 7 and 8 give a summary of the calculations.

Consideration was also given to the diameter of the column. From knowledge of the spray pattern and the initial droplet velocity, it is estimated that the droplets would have little horizontal travel.

Table 7

COLUMN DESIGN CALCULATIONS

$$\% \text{ U Removed} = 12.46 \frac{1}{r} \ln \frac{T_1 - T_s}{T_2 - T_s} \times 100$$

Conditions: $r = 50$ microns
 $T_1 = 800$ C
 $T_2 = 505$ C (melting point)
 $hD/k = 2.00$

T_s (C)	$\ln \frac{T_1 - T_s}{T_2 - T_s}$	$\frac{100}{r} \ln \frac{T_1 - T_s}{T_2 - T_s}$	% U Removed	h	Solidification Time (sec)	Terminal Velocity (ft/sec)	Column Height (ft)
20	0.465	0.930	11.6	91.4	0.105	1.86	2.2
100	0.546	1.092	13.6	113	0.126	1.77	2.2
200	0.675	1.350	16.8	138	0.161	1.67	2.3
300	0.893	1.787	22.2	163	0.227	1.59	2.4
350	1.065	2.03	25.3	175	0.287	1.56	2.4
400	1.338	2.68	33.4	187	0.399	1.55	2.6
450	1.850	3.70	46.1	198	0.686	1.52	3.0
475	2.38	4.76	59.3	202	1.148	1.50	3.7
480	2.55	5.10	63.6	205	1.345	1.50	4.0
490	3.03	6.06	75.5	207	2.11	1.50	5.2
495	3.42	6.84	86.4	204	3.04	1.49	6.5
500	4.09	8.18	100.2	210	5.78	1.49	10.6
501	4.31	8.62	~100	210	7.15	1.49	12.7
502	4.60	9.20	~100	210	9.45	1.49	16.1
503	5.00	10.00	~100	211	13.90	1.49	22.7
504	5.69	11.37	~100	211	27.30	1.49	42.7

Table 8

COLUMN DESIGN CALCULATIONS

$$\text{Basis: } \ln \frac{C_0}{C} = 0.1374 \frac{100}{r} \ln \frac{T_1 - T_s}{T_2 - T_s}$$

where r = drop radius in microns

C_0 = initial concentration

C = final concentration

Design based on these conditions:

$r = 50 \mu$

$T_1 = 800$ C

$T_2 = 505$ C = T_{mp} (melting point)

T_s (C)	$\frac{100}{r} \ln \frac{T_1 - T_s}{T_2 - T_s}$	$\ln \frac{C_0}{C}$	% U Removal	% U Removal for $r = 25 \mu$	$T_{mp} - T_s$ (C)
20	0.930	0.1278	11.9	22.5	485
100	1.092	0.1500	14.0	26.0	405
200	1.350	0.1856	16.8	31.0	305
300	1.787	0.245	21.7	38.7	205
350	2.03	0.279	24.4	42.7	155
400	2.68	0.368	30.7	52.1	105
450	3.70	0.508	39.8	63.8	55
475	4.76	0.655	48.0	73.1	30
480	5.10	0.701	51.8	75.4	25
490	6.06	0.834	56.5	81.2	15
495	6.84	0.940	60.9	84.7	10
500	8.18	1.123	67.5	89.5	5
501	8.62	1.183	69.4	90.7	4
502	9.20	1.264	71.8	92.6	3
503	10.00	1.374	74.7	93.6	2
504	11.37	1.560	79.0	95.6	1
504.9	16.00	2.20	88.9	98.8	0.1

However, to allow for drifting of the spray, it would probably be wise to have a vessel at least 5 ft in diameter, based on experience with a 30-inch diameter vessel.

Since from a corrosion viewpoint it is necessary to prevent molten salt from contacting the wall, both the wall temperature and the temperature of the fluorine atmosphere must be less than the melting point of the salt. The length of the tower must be sufficient to allow the drop to fall freely for a long enough time to cool to the solidification point. Where the temperature difference $T_2 - T_s$ is small, a longer time is required. These effects are shown in Figure 8. The column height in the figure is calculated for the case of $r = 50$ microns; for the case of 25 microns, the equivalent minimum height is about 45 per cent of that shown.

From this figure it appears that impractically high towers are required for uranium removal of as high as 95 per cent in a single pass. One method might be to allow four passes, each with a 10-foot tower. The removal in each pass for a drop of 100-micron diameter is 67 per cent. The uranium remaining after four passes is then $C_4 = (0.33)^4 C_0 = 0.012 C_0$, or 1 per cent remaining. The removal is thus 99 per cent. Temperature control to within 5 degrees C of the melting point of the salt is required for each stage, as well as a spray nozzle delivering 100 per cent of the droplets of less than 100-micron diameter.

For such a process to work, adequate means of recycle of fluorine and salt is required also. The fluorine system would require pumps and uranium hexafluoride cold traps. The solid separation and transfer systems would require cyclones and/or filters for each stage. The fact that the solidified droplets are free-flowing spheres promises to make solids handling fairly easy. All of these steps are considered technically feasible.

In the interest of serving as a basis for process comparisons, a conceptual plant schematic diagram is shown in Figure 9 for a two-stage spray unit. Since it would be expected that even a small single nozzle could handle 100 to 200 pounds of salt per hour, the nominal salt capacity of the plant is 200 lb/hr or 4800 lb/day. If the uranium content of the salt was one wt per cent in uranium the equivalent processing rate for uranium is 20 kg/day. Probably multiple nozzles would be used together with batch handling of salt.

D. Further Development Studies

In order to make more accurate process design, further development work would be required. The following is an outline of suggested points for further study.

1. Investigate effects of concentration on uranium removal by varying initial concentration of uranium tetrafluoride in the salt. This would help to determine the validity of design extrapolations from data based on lower per cent removals.

2. Investigate different nozzles and effects of higher pressures in an effort to achieve finer sprays.

3. Improve on data of effect of impurities in the salt on uranium removal. It would be interesting to see what effect no salt pretreatment sparge would have on uranium removal.

4. Design and demonstrate a nozzle-heating system so that mechanical stopper plugs would be unnecessary for fully controlled operation. If the nozzle heating system were properly designed, the unheated nozzle could act as a freeze valve.

In other fused-salt process studies, autoresistively heated salt transfer lines have proved very successful. A suggested design of an autoresistively heated nozzle is shown in Figure 10.

5. Construct and operate a 10-foot spray tower of suitable materials to test actual process conditions.

FIGURE 10
CONCEPTUAL DESIGN OF AUTORESISTIVELY
HEATED FUSED-SALT SPRAY NOZZLE ASSEMBLY

VI. CONCLUSIONS

A spray-fluorination process for the recovery of uranium as the hexafluoride from fused salt appears technically feasible from preliminary experimental tests. The method would apply to schemes in which the uranium is present in the tetrafluoride in a fused fluoride mixture. The possible advantages of this system for fluorinating fused salt is in avoiding high corrosion rates encountered in the simultaneous exposure of metal to fused salt and fluorine. The disadvantages of the method are (1) the probable requirement of frequent nozzle replacement and (2) the probable requirement of recycling the fluoride salt through as many as four batch stages to get uranium recoveries of better than 99 per cent. It is believed that the complexity of a process requiring this many stages would outweigh the advantages to be gained.

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*Student Aides

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APPENDIX

A. Nomenclature

- a = surface area of drop
- C = final average UF_4 concentration
- C_0 = initial UF_4 concentration
- C = drag coefficient
- C_p = heat capacity of drop
- D = diameter of drop
- D = liquid diffusivity
- D_v = gaseous diffusivity
- g = gravitational constant
- h = heat transfer coefficient
- H = heat of fusion
- k = thermal conductivity
- K_g = mass transfer coefficient
- N = moles of UF_6
- N_{Re} = Reynolds number
- p = partial pressure of UF_6 in F_2
- p_i = vapor pressure of UF_6
- P = vapor pressure of pure UF_6
- q = rate of heat flow
- r = radius of drop
- t = time
- T = mean temperature of drop
- T_1 = initial temperature of drop
- T_2 = final temperature (freezing point) of drop
- T_s = temperature of surroundings
- v_0 = initial velocity
- x = mole fraction of UF_6 at drop surface
- y = distance
- $\dot{y}$ = velocity

$\ddot{y}$ = acceleration

$$\alpha = CN_{\text{Re}} \cdot \frac{3}{4} \frac{\mu}{D^2 \rho}$$

ϵ = emissivity

μ = viscosity of resisting medium

ρ = density of drop

ρ_m = molar density of drop

σ = Stephan-Boltzman constant

B. Theory

A brief discussion of the theory of processes involved in spray contacting is necessary as a basis for quantitative analysis of experimental data and their interpretation in process design.

1. Heat Transfer

An important part in the operation of the spray fluorinator is the control of the time for the salt drop to solidify. The solidification of the salt occurs in two steps: removal of the sensible heat from the initial temperature to the melting point and removal of the latent heat at the melting point. Control of the solidification time would depend upon the initial temperature of the salt, temperature of the surroundings, and the physical properties of the salt (such as melting point, heat of fusion, and heat capacity). The heat would be removed by gas convection and radiation. The spraying conditions also determine the solidification time through variation of drop size and velocity.

a. Removal of Sensible Heat

Let it be assumed that temperature gradients within the drop are negligible (this is demonstrated below).

The conditions of heat balance in an increment of time for unsteady state lead to the equation

$$\left(\frac{4}{3} \pi r^3\right) (\rho) \left(C_p\right) \frac{dT}{dt} = -h(4\pi r^2) (T - T_s) - (4\pi r^2)(\sigma \epsilon)(T^4 - T_s^4) .$$

Rearrangement yields the equation

$$dt = -\frac{r}{3} C_p \rho \frac{dT}{\sigma \epsilon (T^4 - T_s^4) + h(T - T_s)}$$

Integrating, there is obtained

$$\Delta t = -\frac{r}{3} C_p \rho \int_{T_1}^{T_2} \frac{dT}{\sigma \epsilon (T^4 - T_s^4) + h(T - T_s)}$$

If it may be assumed that the radiation loss is negligible,

$$\Delta t = -\frac{r C_p \rho}{3h} \ln \frac{T_2 - T_s}{T_1 - T_s}$$

b. Removal of Latent Heat

$$\left(\frac{4}{3}\pi r^3\right) (\rho) (-\Delta H) = \left[-h(4\pi r^2) (T_2 - T_s) - 4\pi r^2 \sigma \epsilon (T_2^4 - T_s^4) \right] \Delta t$$

Rearrangement gives

$$\Delta t = \frac{\Delta H \rho r}{3} \left[\frac{1}{h(T_2 - T_s) + \sigma \epsilon (T_2^4 - T_s^4)} \right]$$

If radiation loss may be assumed to be negligible,

$$\Delta t = \frac{r(\Delta H) \rho}{3h(T_2 - T_s)}$$

c. Temperature Gradient within Drop

The temperature gradient within a cooling drop varies with the ratio between the radius r and the coefficient of thermal conductivity k . The Gurney-Lurie chart for thermal diffusion in spheres shows a temperature gradient of practically zero for cases in which the parameter k/rh exceeds 6.⁽¹⁾ Typical values of this parameter for drop-lets encountered by spraying were of the order of 100, indicating a negligible temperature gradient within the drop.*

2. Mass Transfer

An estimation of the rate of uranium removal is necessary for equipment design. In estimating the rate of removal of uranium it is helpful to determine which mechanism is responsible for the uranium removal. A simplified picture of the mass-transfer mechanism is as follows: (1) uranium tetrafluoride diffuses from within the drop to the surface of the drop; (2) the tetrafluoride reacts with fluorine at the surface of the drop to form the volatile hexafluoride; and (3) finally the uranium hexafluoride diffuses from the drop surface into the gas phase.

For the first step involving liquid diffusion in a spherical drop, the rate equation is⁽²⁾

$$\frac{C_0}{C} = \frac{6}{\pi^2} \left(e^{-\pi^2 Dt/r^2} + \frac{1}{4} e^{-4\pi^2 Dt/r^2} + \frac{1}{9} e^{-9\pi^2 Dt/r^2} + \dots \right),$$

*An alternate demonstration for a particular case is given in Appendix C.

where

C_0 = initial UF_4 concentration

C = final average UF_4 concentration

D = liquid diffusivity

r = radius

t = time.

The next step at the surface of the drop is not easily predicted. The uncertainty of the reaction velocity constant and the possibility of complicating intermediate reactions would make any theoretical prediction uncertain.

In the third step, the diffusion rate equation for uranium hexafluoride removal through the gas film resistance would be

$$\frac{dN}{dt} = K_g a (p_i - p) \quad ,$$

where

N = moles of UF_6

K_g = mass transfer coefficient

a = surface area of drop

p_i = vapor pressure of UF_6

p = partial pressure of UF_6 in F_2 .

Assuming the validity of Raoult's law,

$$p_i = Px$$

where

P = vapor pressure of pure UF_6

x = mole fraction of UF_6 at drop surface.

By substitution and integration of the above rate equation, there is obtained

$$\ln \frac{x_1}{x_2} = K_g \frac{3P}{r \rho_M} t \quad ,$$

where ρ_M is the molar density of salt, 2.16 moles/cu ft.

In a process such as this, which involves several mechanisms, in general only one stage is rate controlling. The rate-controlling step is found from experimental results and by calculations with known physical constants. After the rate-controlling mechanism is established, design parameters can be calculated.

3. Drop Motion: The Distance-Time Relation

Droplets emerge from the nozzle with an initial velocity v_0 and are slowed by air resistance. The basic differential equation is

$$\ddot{y} = g - \alpha \dot{y}$$

where

$$\alpha = C N_{Re} \cdot \frac{3}{4} \frac{\mu}{D^2 \rho} .$$

For the boundary conditions:

$$\text{at } t = 0, y = 0 \text{ and } \dot{y} = v_0 .$$

The solutions of the equation for distance and velocity are

$$y = \left(\frac{g}{\alpha^2} - \frac{v_0}{\alpha} \right) e^{-\alpha t} + \frac{1}{\alpha} \left(gt - \frac{g}{\alpha} + v_0 \right)$$

$$\dot{y} = \left(v_0 - \frac{g}{\alpha} \right) e^{-\alpha t} + \frac{g}{\alpha}$$

The drag coefficient is a function of the Reynolds number and changes with decreasing drop velocity. The equation may be solved by an incremental method.

C. Miscellaneous Calculations and Correlations

1. Distance Traveled by Spray Droplet Slowed by Air Friction

The solution for the equation of motion of a droplet slowed by air friction was given in Appendix B:

$$y = \left(\frac{g}{\alpha^2} - \frac{v_0}{\alpha} \right) e^{-\alpha t} + \frac{1}{\alpha} \left(gt - \frac{g}{\alpha} + v_0 \right) .$$

$$\dot{y} = \left(v_0 - \frac{g}{\alpha} \right) e^{-\alpha t} + \frac{g}{\alpha} .$$

These equations relate distance and velocity to time. Since the drag coefficient is a function of the Reynolds number, α changes with decreasing drop velocity. The equations were, therefore, solved by an incremental method. Table 9 gives an example of the type of calculation made. Figure 11 shows the change of drop velocity with time.

Table 9

DISTANCE TRAVELED BY SPRAY DROPLET SLOWED BY AIR FRICTION

Air temperature: 20 C
Drop diameter: 100 microns
Cup distance: 15 in. or 1.25 ft

Time (sec)	$\dot{y} = \left(v_0 - \frac{g}{\alpha} \right) e^{-\alpha t} + \frac{g}{\alpha}$	N_{Re}	CN_{Re}	α	$y = \left(\frac{g}{\alpha^2} - \frac{v_0}{\alpha} \right) e^{-\alpha t} + \frac{1}{\alpha} \left(gt - \frac{g}{\alpha} + v_0 \right)$
0	38.8	80.5	94.2	39.2	0
0.01	27.0	56.0	80.1	33.3	0.331
0.02	20.2	41.9	71.2	29.7	0.576
0.03	15.6	32.4	63.0	26.2	0.754
0.04	12.5	26.9	58.7	24.4	0.893
0.05	10.2	21.2	51.5	21.4	1.005
0.06	9.36	19.5	51.1	21.3	1.099
0.07	7.19	14.9	49.0	20.4	1.178
0.08	-	-	-	-	1.245

FIGURE 11
CHANGE OF DROP VELOCITY WITH TIME

2. Calculation of Heat Transfer Coefficients

The heat transfer coefficient from drop to gas was calculated for the two stages of heat removal, i.e., cooling to the melting point and

removal of the heat of fusion. For the first stage, cooling from 650 C to the salt melting point (505 C), the following equation applies:

$$h = \frac{1}{t_1} \frac{\rho c_p r}{3} \ln \frac{T_1 - T_s}{T_2 - T_s} .$$

Heat transfer by radiation was assumed to be negligible, thereby greatly simplifying the solution of the equations. Calculations were made in which there was assumed an emissivity of 0.9; an approximately 10 per cent error in the heat transfer coefficient at 100 Btu/(hr)(sq ft)(F) was found. However, it is expected that the emissivity for the fused salt is much lower than 0.9, since the absorption factor for CaF_2 and other halogen salts is very low.⁽³⁾ This greatly reduces any possible error in neglecting radiation losses.

For the second stage, removal of the heat of fusion at the freezing point, the following equation applies:

$$h = \frac{1}{t_2} \frac{\rho \Delta H_f}{3} \left(\frac{1}{T_2 - T_s} \right) .$$

It was assumed the heat transfer coefficients for both stages were equal and that the total solidification time, determined by the time for the drop to traverse the distance from the nozzle to the cup, was equal to t_1 plus t_2 .

The results are summarized in Table 3. The calculated heat transfer coefficients ranged from 72 to 144 Btu/(hr)(sq ft)(F). The Nusselt number (hD/k) compared favorably with that predicted from the correlation.⁽¹⁾

$$hD/k = 0.37 (N_{Re})^{0.6} .$$

Figure 5 shows how these heat transfer data compared with a correlation of data by other workers. The fused-salt data extend the range of data to smaller size spheres than used in any previous study.

3. Demonstration of Negligible Temperature Gradient within the Drop

The overall rate of heat transfer from the drop to the gas is given by the equation

$$q = \frac{4}{3} \pi r^3 \rho C_p \frac{\Delta T}{\Delta t} .$$

This is equal to the flow at the surface of the drop:

$$q = k \ 4 \ \pi r^2 \left(\frac{dT}{dr} \right) .$$

The gradient is thus

$$\frac{dT}{dr} = \left(\frac{r}{3} \right) \left(\frac{\rho C_p}{k} \right) \left(\frac{\Delta T}{\Delta t} \right) .$$

When typical values for the parameters are inserted, values for the temperature drop can be approximated:

$$r = 1.67 \times 10^{-4} \text{ ft}$$

$$\rho = 200 \text{ lb/cu ft}$$

$$C_p = 0.25 \text{ Btu/(lb)(F)}$$

$$k = 1.5 \text{ Btu/(hr)(sq ft)(F/ft)}$$

$$\Delta T = 1.8(700 - 500) = 360 \text{ F}$$

$$\Delta t = 0.08 \text{ sec} \times (1/3600)(\text{hr/sec}) = 2.2 \times 10^{-5} \text{ hr}$$

$$\begin{aligned} \frac{dT}{dr} &= \left(\frac{1.67 \times 10^{-4}}{3} \right) \left(\frac{200 \times 0.25}{1.5} \right) \left(\frac{360}{2.2 \times 10^{-5}} \right) \\ &= 3 \times 10^4 \text{ F/ft} . \end{aligned}$$

The temperature drop across the radius is approximately

$$\Delta T = (dT/dr) \Delta r = (3 \times 10^4 \text{ F/ft}) (1.67 \times 10^{-4} \text{ ft}) = 5 \text{ F or } 3 \text{ C} .$$

Thus the temperature within the drop is nearly uniform.

4. Calculation of Solidification Time

1) Velocity was plotted against time for the spray droplets, using small increments of time from the frictional drag equation:

$$\dot{y} = \left(v_0 - \frac{g}{\alpha} \right) e^{-\alpha t} + \frac{g}{\alpha} .$$

An example of solidification time calculations is shown in Table 10.

2) The plot of the velocity equation was then graphically integrated to obtain the average velocity between $t = 0$ and $t = t$.

Table 10

VELOCITY OF SPRAY DROPLET SLOWED BY FLUORINE FRICTION

F₂ temperature: 20 C
Drop Diameter: 62.1 microns

Time (sec)	Velocity (ft/sec) $\dot{y} = \left(v_0 - \frac{g}{\alpha}\right)e^{-\alpha t} + \frac{g}{\alpha}$	NRe	CNRe	α	Average Velocity (ft/sec)	Average NRe	hD/k	$\frac{h}{[Btu/(hr)(sq ft)(F)]}$
0	19.1	24.5	55.5	76.0	-	-	-	-
0.01	9.98	12.8	43.8	60.0	14.6	18.7	2.15	166
0.02	5.93	7.61	37.9	51.9	11.3	14.5	2.00	154
0.03	3.87	4.96	34.4	47.1	9.17	11.8	2.00	154
0.04	2.72	3.49	32.0	43.8	7.70	9.89	2.00	154
0.05	2.04	2.62	30.4	41.6	6.64	8.52	2.00	154
0.06	1.62	2.08	29.4	40.2	5.85	7.52	2.00	154
0.07	1.35	1.73	28.5	39.7	5.23	6.70	2.00	154
0.08	1.19	1.53	27.9	38.2	4.71	6.04	2.00	154
0.09	1.08	1.39	27.6	37.8	4.31	5.52	2.00	154
0.10	1.01	1.30	27.3	37.4	3.98	5.11	2.00	154
0.11	0.96	1.23	27.1	37.1	3.71	4.76	2.00	154
0.12	0.93	1.19	27.0	37.0	3.48	4.47	2.00	154
0.13	0.91	-	-	-	3.28	4.21	2.00	154

3) The heat transfer coefficient was calculated on the basis of the average velocity from the correlation

$$hD/k = 0.37 (Dv\rho/\mu)^{0.6}$$

It should be noted that the theoretical minimum value for hD/k , i.e., in a stagnant medium, is 2.0.

4) The solidification time was then calculated from the equation

$$t = \frac{\rho C_p r}{3h} \ln \frac{T_1 - T_s}{T_2 - T_s} + \frac{\rho r (\Delta H)}{3h} \frac{1}{T_2 - T_s}$$

This is a trial and error solution. The value t calculated from the heat transfer equation must agree with the value of t upon which the average Reynolds number is based.

Using the results from Table 10, a sample calculation is as follows:

$$t = \frac{(200)(0.25)(62.1)}{(3)(154)(2 \times 25,400 \times 12)} \ln \frac{(765 - 20)}{(505 - 20)} + \left(\frac{(200)(62.1)(111.5)}{(154)(3)(2 \times 25,400 \times 12)} \right. \\ \left. \times \frac{1}{1.8(505 - 20)} \right) (3600) = 0.037 \text{ sec.}$$

The cooling time thus calculated is about 0.04 second for a heat transfer coefficient of 154 Btu/(hr)(sq ft)(F). A check with Table 10 to see if the heat transfer coefficient for average velocity conditions is in agreement with the heat transfer coefficient on which t is based shows that the two heat transfer coefficients are the same.

5. Calculation of UF₆ Removal Rate through Film Resistance

As previously described in Appendix B, the rate equation for the diffusion of UF₆ through the gas film resistance is:

$$\frac{dN}{dt} = K_g a (p_i - p)$$

The partial pressure of uranium in contact with fused NaF-ZrF₄ was 250 mm, and the uranium content of the fused salt was 50 ppm.⁽⁴⁾

$$p_i = P x(\text{Raoult's law})$$

$$\frac{250}{760} = P (50 \times 10^{-6}) \left(\frac{100}{352} \right)$$

$$P = 2.3 \times 10^4 \text{ atm}$$

Thus

$$p_i = 2.3 \times 10^4 \frac{N}{(\pi/6)D^3 (\rho/92.08)},$$

where the average molecular weight of the salt is 92.08.

It is assumed that the partial pressure of UF₆ in the fluorine atmosphere is zero. The mass transfer coefficient, K_g , was taken from a plot of $K_c D/D_v$ versus $(D_v \rho / \mu)(\mu / \rho D_v)^{2/3}$ for spheres.⁽⁵⁾ The diffusivity was estimated by the Hirschfelder equation:⁽⁶⁾

$$D_{12} = \frac{0.001858 T^{3/2} [M_1 + M_2] / M_1 M_2^{1/2}}{P \sigma_{12}^2 \Omega_D}$$

An estimation of the diffusivity of UF₆ in F₂ at 20 C from this equation gives $D_v = 0.07$ sq cm/sec. This was checked by the Arnold equation and the agreement was within 2 per cent.⁽⁶⁾

Integration of the rate equation yielded

$$\ln \frac{x_1}{x_2} = K_g \pi D^2 \frac{2.3 \times 10^4}{(\pi/6) D^3 (\rho/92.08)} t$$

$$= K_g \frac{6 \times 92.08 \times 2.3 \times 10^4}{D \times 200} t$$

In sample calculation, the following values were selected:

$$D = 62.1 \text{ microns}$$

$$t = 0.04 \text{ second}$$

$$D_v \rho / \mu = 4.84$$

$$T = 20 \text{ C}$$

From a plot, $K_g = 9.34 \text{ lb moles}/(\text{hr})(\text{sq ft})(\text{atom})$. Thus

$$\ln \frac{x_1}{x_2} = 9.34 \times \frac{6 \times 92.08 \times 2.3 \times 10^4}{(62.1/25,400 \times 12) \times 200} \times \frac{0.04}{3600}$$

$$= 3.24 \times 10^3 = 3240 \text{ or } 100\% \text{ removal.}$$

6. Calculation of UF_6 Removal with UF_4 Diffusion Controlling

The diffusion equation is

$$\frac{C_0}{C} = \frac{6}{\pi^2} \left(e^{-\pi^2 Dt/r^2} + \frac{1}{4} e^{-4\pi^2 Dt/r^2} + \frac{1}{9} e^{-9\pi^2 Dt/r^2} + \dots \right)$$

Using the following values in a sample calculation:

$$r = 62.1/2 = 31.1 \text{ microns}; \quad D = 6.5 \times 10^{-5} \text{ sq cm/sec}^{(7)}$$

$$t = 0.04 \text{ second}$$

there is obtained

$$\frac{\pi^2 Dt}{r^2} = \frac{(3.14)^2 (6.5 \times 10^{-5}) (0.04)}{(31.1)^2 (10^{-8})} = 2.66$$

$$\frac{C_0}{C} = \frac{6}{(3.14)^2} (0.070) = 0.043 \text{ or } 95.7\% \text{ removal.}$$

7. Alternative Correlation of Uranium Removal by Least Squares

The slope of the lines in Figures 6 and 7 was determined by a least-squares approximation thus:

$$\frac{\partial F}{\partial b} = \min \sum [y_i - \hat{b} x_i]^2$$

$$\frac{\partial F}{\partial b} = 2 \sum [y_i - \hat{b} x_i] (-x_i) = 0$$

$$\hat{b} = \frac{\sum x_i y_i}{\sum x_i^2}$$

$$s_y^2 = \frac{\sum (y_i - \hat{b} x_i)^2}{N-1} = \frac{\sum (y_i^2 - 2\hat{b} x_i y_i + \hat{b}^2 x_i^2)}{N-1}$$

$$= \frac{y_i^2 - \hat{b} \sum x_i y_i}{N-1}$$

$$s_b^2 = \text{var} \frac{\sum x_i y_i}{\sum x_i^2} = \frac{s_y^2}{\sum x_i^2}$$

8. Estimation of the Horizontal Travel of a Spray Droplet

The differential equation for drop movement in the horizontal direction is

$$\ddot{x} = \alpha \dot{x}$$

At $t = 0$ and $x = 0$, the initial velocity is $\dot{x} = v_0$. Further

$$\alpha = \frac{3}{4} \frac{CN_{Re}\mu}{\rho D^2}$$

The solution of the differential gives

$$x = (v_0/\alpha)(1 - e^{-\alpha t})$$

At an infinite time,

$$x = v_0/\alpha$$

From a calculation of α on the basis of the terminal velocity to give the smallest possible value of α with an initial velocity of 27.5 ft per sec, it was found that x equals about 0.70 ft. This indicates that the spray would have little horizontal travel. This result was considered in estimating the diameter of the spray tower.