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FISSION PRODUCT RELEASE FROM
ALUMINUM-BASED FUEL MELTS (U)

BY

L. Baker, Jr., W. Gunther, A. Sharon, B. Bonomo
J. K. Fink, M. Hutcherson, and R. P. Stein

Argonne National Laboratory

and

P. Ellison, P. Monson, D. Leader, and D. K. Allison
Westinghouse Savannah River Company

August 1992

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Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29803

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APPROVALS

<u><i>Davis K. Allison</i></u>	<u>8-11-92</u>
D. K. Allison, Author	Date
<u><i>M. L. Hyder</i></u>	<u>8/18/92</u>
M. L. Hyder, Technical Reviewer	Date
<u><i>S. B. Whitfield</i></u>	<u>8/21/92</u>
S. B. Whitfield, Technical Editor	Date
<u><i>L. A. Wooten</i></u>	<u>10/19/92</u>
L. A. Wooten, Manager, SAES	Date
<u><i>M. B. Hitchler</i></u>	<u>10/26/92</u>
M. B. Hitchler, Manager, STS	Date

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Argonne National Laboratory

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P. Ellison, P. Monson, D. Leader, and D. K. Allison

Westinghouse Savannah River Company

ABSTRACT

An experimental program on the release and transport of fission products from aluminum-based fuel melts was initiated at the Argonne National Laboratory. The program included the development of an apparatus to melt and heat up to 1400 K and 750 g of aluminum-uranium alloy containing inactive fission product elements. Helium gas flowing across the melts carried vapors and aerosols into a system of thermal gradient tubes, filters, and bubblers. Two experiments were completed and supported by chemical analyses of the deposits. Two other experiments with uranium-containing melts and several calibration tests with pure metals were also performed. Thermodynamic analyses of the melts and calculations of the expected release rates are reported.

The experimental results have provided tentative data on the activity coefficients of strontium and barium in the melts. Observations on the behavior of released cesium metal and cesium iodide are described. Results indicated that tellurium may be retained in the melt because of liquid phase reactions. The elements molybdenum, cerium, zirconium, and uranium were included but not released from the melts.

PREFACE

This report describes experiments performed at Argonne National Laboratory for the Severe Accident Group at WSRC. The intent of the experiments was to study the release of fission products from molten pools of aluminum-uranium as might obtain during a severe accident in one of the production reactors at the Savannah River Site. This program concentrated on the long term release of the less volatile fission products such as: Cs, I, Te, Sr, Ba, Mo, Zr, and Ce. The evolution of simulated fission products from melts prototypic of an SRS reactor (at 30% burnup) was measured experimentally and calculated using the SOLGASMIX-PV code.

Because of funding reductions only four experiments, in addition to calibration runs, were performed. Also because of funding reductions, only limited chemical analysis of material deposited on surfaces and filters during the experiments was permitted. However, the feasibility of the approach was demonstrated and the initial results were promising.

Knowledge of the evolution of fission products during each phase of a severe accident is critical for the complete analysis of the accident. The prevention of fission product release to the environment is, after all, the primary reason for undertaking the analysis. The data base regarding aluminum based fuels such as SRS fuel is sparse and data such as this program was intended to generate are very valuable.

Furthermore, a knowledge of fission product evolution affects the design of release mitigating systems such as the filter systems. The nature of the confinement system of an SRS reactor puts much importance on maintaining the integrity of the filter system. The characteristics of material reaching the filters must be known to ensure that filter integrity is not compromised during an accident. The release of iodine during an accident, for example, is directly related to the iodine loading of the charcoal filters. The loading of the filters determines to a great extent the timing of filter failure if failure occurs. Data generated during this project is, therefore, important, for predicting radioactive releases to the environment during certain severe accidents.

Because the present program never got beyond its initial stages, the quantity of information generated by the program is not great.

However, preliminary information regarding the release of several fission product species important to SRS reactors was produced.

1. INTRODUCTION

This report summarizes the results of an experimental program on the release of fission products from aluminum-based fuel melts. The Production Reactors located at the Savannah River Site are fueled with aluminum-uranium alloys. Analyses of postulated severe accidents for this type of reactor require an understanding of the rates of release of the radiologically important fission products from the fuel during fuel heating and melting transients. Many test reactors such as ATR, HFIR, and HFBR have aluminum based fuel systems, with either uranium aluminide or oxide dispersed in aluminum. Information is needed on releases during the initial phase of fuel melting and for later phases where relatively deep pools of melt might exist for extended periods of time. This work was directed primarily toward the latter need, ie., the long-term release of the less volatile fission products from melt pools.

Rates of fission product release may depend on many factors, including the vapor pressures of the fission product elements, their solubilities in molten aluminum, the thermal-hydraulic condition of the melt, etc. For example, release rates would tend to be increased for a pool undergoing vigorous gas bubbling or convective stirring relative to a quiescent pool. Models describing release from pools under various conditions of agitation have been developed by Ades, Ellison, and Hagrman [1] and by McClure, Leonard, and Ellison [2]. However, the models cannot be fully implemented until the solubilities, vapor pressures, chemical forms, and other basic properties of the fission product elements are known. The primary purpose of this study was to obtain the data needed for the implementation of deterministic models.

Previous studies of fission product release employed irradiated fuel in the form of thin plates. The available data were summarized in a recent paper by Taleyarkhan [3]. Shibata, et al [4] showed that there was negligible release of fission gas below 773 K for aluminide fuel. Significant release occurred coincident with blistering of the cladding at 834 K. The next major release began at the solidus temperature for the cladding alloy. A further release occurred at the eutectic temperature of the aluminum-uranium alloy, 923 K. Most of the xenon and krypton were released on heating to 973 K which is about 40 K above the melting point of pure aluminum. However, less than 0.01% of the iodine and cesium were released in one-half hour at 973 K.

Fission product release from aluminum-uranium alloy fuels was studied at Oak Ridge by Parker, et al [5,6] at temperatures from 1023 to 1373 K. Plate fuel samples were exposed to helium, air, or steam for periods of 2 minutes or 30 minutes. Releases of krypton/xenon, iodine, cesium, tellurium, and ruthenium were measured. Rare gas release was rapid and complete in all of the experiments in agreement with the Shibata results. Iodine release was typically one-half complete in 2 minutes at 1023 K and substantially complete in two minutes at 1173 K. Cesium releases were quite different from iodine releases. Cesium release in 2 min. was less than 10% in air or in steam at temperatures below 1273 K and less than about 40% at 1400 K. Cesium releases in helium were about twice those in air or steam. Tellurium releases were less than 10% in air and steam below 1273 K, but reached values from 40 to 80% at temperatures of the order of 1400 K. Tellurium release in helium was no more than about 5% over the entire temperature range from 700 to 1400 K. Ruthenium releases were less than 1% over the 700 to 1400 K range.

A series of fission product release experiments were carried out at the Hanford Engineering Development Laboratories [7]. The experiments employed Savannah River fuel samples exposed for two minutes in flowing argon, air, and steam environments. Iodine release results were generally similar to the Oak Ridge results, although HEDL results indicated between 20 and 70% release at 973K while ORNL data indicated only a 50% release at 1023K. Shibata's data indicates that iodine release for aluminide fuel is much less than for alloy fuel. Cesium releases, measured at HEDL, were much greater than those measured at Oak Ridge. Cesium releases were of the order of 20% at 923 K and ranged from 40 to 80% at 1100 K and higher. Cesium releases were relatively independent of the environment. Only a few results were reported for tellurium release. The limited results indicated that release was greater in air or steam than in inert gas in agreement with the Oak Ridge results.

The increased releases of cesium in the HEDL experiments relative to those of the ORNL experiments were attributed by Taleyarkhan [3] to the greater burnup of the fuel used in the HEDL experiments, 52%, over that used in the ORNL experiments, 24%. This explanation is attractive but not well established. The available data base is deficient in many other respects as well. The experiments employed thin fuel samples; no pools of significant depth were studied. No data were obtained for barium, strontium or other important elements of intermediate volatility. Also, the chemical forms and behavior of the released elements were not determined. Because of these deficiencies, the ANL program was initiated.

2. SUMMARY

An experimental program on the release and transport of fission products from aluminum-based fuel melts was initiated at the Argonne National Laboratory. The experiments were designed to determine the basic physical properties needed for the implementation of deterministic models of the release and transport from melt pools. In each experiment, about 750 g of a molten aluminum-uranium alloy containing inactive fission product elements were melted, heated to a maximum of 1400 K, and exposed to a flow of helium gas. The flowing gas carried vapors from the melt into a system of thermal gradient tubes, filters, and bubblers. Subsequent analyses of the deposits and bubbler solutions were designed to determine the quantities and chemical forms of the released vapors and aerosols.

Thermodynamic analyses were performed using the SOLGASMIX-PV Code and available data compilations. The calculations indicated that the principal vapor species would be the elements, cesium, strontium, and zinc and the compound cesium iodide. The zinc is considered a likely impurity in the aluminum. In addition, the calculations indicated that tellurium is combined with uranium as a telluride and the low vapor pressure of barium would prevent these elements from having a vapor phase presence.

The experimental melts included the fission product elements molybdenum, zirconium, and cerium. These elements, while not volatile themselves, might be expected to interact with the more volatile elements and affect their behavior. In addition, strontium and barium were included in the preparation of the alloys to be used in the experiments. Volatile fission products, including, iodine in the form of either cesium iodide or aluminum iodide, elemental tellurium, and cesium metal were added to the melt crucibles just prior to the experiments. The overall compositions closely simulated those expected for a postulated severe accident in a Savannah River Reactor core at near end-of-life conditions. The melts were contained in tantalum crucibles to avoid contamination by carbon or oxygen which might have resulted from the use of graphite or ceramic crucibles.

Calculations were performed to estimate the rates of release expected from the melts for several postulated rate-limiting processes. Rates based on (1) vapor sweepout from the nominal 1.5 cm. space above the melt pool, (2) gas phase diffusion from the melt surface, (3) Langmuir, limiting vaporization rates, and (4) liquid phase diffusion from the bulk of the pool to the surface. Langmuir vaporization rates were found to be very fast and thus not limiting. Gaseous diffusion rates were found to be 5 - 10 times greater than vapor sweepout rates so that it was expected that vapor sweepout, controlled by the vapor pressures of the elements and compounds, would be the operative process. Thus, it would be possible to infer vapor pressures, and, indirectly, activity coefficients, from the measured releases. Liquid phase diffusion could become limiting under certain conditions. Because of this possibility, it was necessary to adopt experimental procedures to both minimize this potential limitation and test for its presence.

The results of the release rate calculations based on the assumption of ideal solution behavior indicated: (1) rapid and complete releases of cesium iodide would occur at 1000 K if there were no solubility in the melt, but, in the event of complete solubility, releases would be very small, even at 1400 K, (2) cesium release would be rapid whether the cesium is soluble in the melt or not, (3) tellurium is known to be soluble so that significant tellurium releases

should occur only above about 1200 K, unless liquid phase reactions prevent releases entirely, (4) strontium is soluble in aluminum so that significant releases would occur only at about 1400 K or higher, (5) barium and aluminum releases would be negligible.

The experimental apparatus included 6 identical gradient tube, filter, and bubbler trains. By rotating the lower part of the apparatus which contained the melt crucible, the vapor space above the melt could communicate with one train at a time. The operating sequence was to provide flow through gradient tube 1 during the initial heatup period, to obtain duplicate exposures at constant temperature for Tubes 2 and 3, to increase the temperature to a new level while in contact with Tube 4, to obtain duplicate exposures for Tubes 5 and 6, and, finally to return to Tube 1 for cooldown. Each gradient tube was lined with thin foils of tantalum or stainless steel which were removed and weighed to determine weight gains after each experiment. Filter elements as well as other liners were also removed and weighed after each experiment. A personal-computer based data acquisition system enabled frequent recordings of melt and gradient tube temperatures, filter pressure drops, and helium flow rates. An averaging process was developed to characterize conditions during each sampling period.

Two calibration experiments were performed with melts of pure bismuth. The results of the calibrations indicated that there was a very low background of aerosol in the system and that the deposit masses were proportional to helium flow rates, exposure times, and the known vapor pressures of bismuth as expected from prior analyses. The results of the bismuth experiments were analyzed to determine a calibration constant relating the calculated and observed deposit masses for use in the experiments with melts having unknown vapor pressures.

Calibration experiments with pure aluminum were conducted. An attempt to use a zirconium crucible to contain the melt showed that aluminum reacted vigorously with the zirconium to destroy the crucible. Tantalum crucibles were found to contain the melts satisfactorily. The tests with aluminum with a nominal purity of 99.99% yielded liner weight gains up to 40 mg in 30 min. The composition of the deposits responsible for these unexpected weight gains could not be determined because of resource limitations. Calibrations with other pure metals such as zinc were needed but could not be included in the limited program.

Four experiments were performed with aluminum-uranium alloy melts. The first experiment was performed without added volatile elements. Following the experiment, the gradient tube liners were leached with aqua regia and elemental (ICP) analyses were performed on the solutions. In all cases, the element masses determined by analysis were significantly less than the weight gains. Significant quantities of strontium and barium were released at 1324 K while the quantities released at 1102 K were negligible. The barium and strontium deposits were found toward the hot end of the liners. Other elements found included aluminum and traces of molybdenum, the elements of stainless steel, and impurity elements, calcium, copper, magnesium, and zinc.

In the second experiment, cesium iodide and tellurium were added. The gradient tube liners showed a series of distinct deposit morphologies. Chemical analysis showed that cesium and iodine were the principal constituents of two distinctly different and separated deposits. The measured ratio of cesium to iodine in the deposits decreased in going from the hot to the cold end of the liner suggesting that some decomposition occurred along the gradient tube. Only

a trace of iodine, but no cesium, was found in the bubbler solution. No tellurium, uranium, cerium or zirconium were detected in any of the deposits.

The apparent vapor pressures and activity coefficients of the released species were calculated from the analytical results. From two measurements, the apparent activity coefficients were for barium, 5 and 15, and for strontium, 0.10 and 0.25. These results must be considered very tentative in light of the many experimental uncertainties.

Two more experiments were performed in which cesium metal along with tellurium and iodides were added to the melt. Following the tests, the liners showed a rapid pickup of water from the atmosphere indicating that large releases of metallic cesium had occurred. No quantitative data were obtained because resources were not available to conduct chemical analyses.

The limited program provided a sound basis for a more comprehensive program. Several needed apparatus improvements were identified which should be readily achievable. Although the number of experiments and the number of chemical analyses were very limited, the results should be useful in future assessments of fission product behavior for aluminum based fuel systems. Tentative conclusions and observations are summarized as follows:

Strontium: The experimental data, supported by literature studies, indicates that the vapor pressure of strontium is significantly less than predicted for ideal solution behavior.

Barium: The experimental data indicate that the vapor pressure of barium may be greater than predicted for ideal solution behavior.

Iodine: Calculations indicate that cesium iodide is the likely chemical form for iodine. Experimental observations indicate that cesium iodide is not soluble in aluminum melts so that rapid and extensive release is likely.

Cesium: Cesium release was observed to continue throughout the experiments. More chemical analyses would be needed to determine if cesium solubility in the melt is significant or not.

Tellurium: The apparent absence of tellurium in the deposits indicates that the tellurium may be chemically stabilized within the melt as predicted by thermodynamic analysis.

Molybdenum, cerium, uranium, and zirconium: Only traces of molybdenum were found in the deposits, while no cerium, uranium, or zirconium were found, indicating that these elements are not volatile, as expected.

3. THERMODYNAMIC ANALYSES

A series of thermodynamic analyses were performed to determine the most likely chemical forms of the fission products. The mixtures to be studied were based on composition data provided by the Westinghouse Savannah River Co. The ratios of fission product elements to uranium in spent fuel corresponding to about 30% burnup were chosen for study. The ratio of aluminum to uranium was selected on the basis that the fuel cladding and some additional aluminum from structural material would be present in the fuel melt. The composition chosen for study is listed in Table 1.

Table 1. Composition Selected for Study

<u>Element</u>	<u>Weight %</u>	<u>Mole Fraction</u>
Al	87.5	0.9807
U	10.1	0.0128
Cs	0.373	0.00085
I	0.022	0.00005
Te	0.046	0.00011
Sr	0.174	0.00060
Ba	0.178	0.00039
Mo	0.355	0.00112
Zr	0.516	0.00171
Ce	0.766	0.00165
Total	100.0	1.0000

The quantity of cesium listed above includes the cesium expected in spent fuel in addition to the expected quantity of rubidium. It was assumed that rubidium would behave like cesium. Similarly, the cerium content was increased to represent the total expected quantities of yttrium, lanthanum, and the rare earth elements. Ruthenium was not included because it was expected to be non-volatile and relatively inert.

For the thermodynamic calculations, a small quantity of zinc (mole fraction 0.0003) was included to represent the likely impurity in the aluminum. The calculations were made using the SOLGASMIX code [8]. Free energy data from major compilations [9,10,11] for known compounds among the elements listed above were input to the code. The code minimizes the total Gibbs free energy of the system. Argon is included in the list of elements in order to achieve a total pressure of one atmosphere. It is necessary to prescribe the number of condensed phases and to assume that the condensed phases are perfect solutions. The vapor species calculated to be present on the assumption of a single condensed phase are shown in Figure 1. Cesium, zinc, strontium, and cesium iodide were the only vapor

Major Vapor Species

1 Condensed Phase in Melt

Figure 1. Major Vapor Species (One condensed phase assumed to be present)

phase species. Calculated results when two condensed phases are assumed are shown in Figure 2. The second phase was a salt phase which included the iodides of cesium, barium, and strontium as well as uranium, zirconium, and cesium tellurides. The metallic phase included aluminum, uranium aluminides, cerium aluminide, zirconium, and molybdenum. The vapor phase species included barium and strontium iodide as shown in Figure 2.

Several significant results emerged from the thermodynamic analysis:

1. The predominant form of iodine is expected to be cesium iodide in the condensed and in the vapor phase.
2. The predominant form of cesium is as metallic cesium.
3. There is no tellurium in the vapor phase; it is combined with uranium as a telluride. Smaller amounts are combined with zirconium and cesium.
4. Elemental strontium has a significant vapor phase presence while barium does not.

Major Vapor Species

2 Condensed Phases in Melt

Figure 2. Major Vapor Species (Two condensed phases assumed to be present)

4. EXPERIMENTAL APPROACH

The primary purpose of the study is to understand the release process of fission product elements from melt pools. To develop a fully prototypic melt would require the use of irradiated fuel material. However, a program of studies with irradiated material would have required more time and resources than were available. It was believed that molten pools prepared with inactive fission product elements would be sufficiently representative of the real case, at least for the less volatile elements such as strontium and barium. Moreover, it was believed that the behavior of the volatile fission products, iodine, cesium, and tellurium, could be deduced from their observed behaviors after their addition to the melt during an experiment.

One feature of the program was to include non-volatile fission product elements which probably would not be released themselves but which might associate with more volatile elements and affect their behavior. Accordingly, molybdenum, zirconium, and cerium were included in the melts. Another feature was to use metallic crucibles to contain the melts to avoid possible contamination by oxygen or carbon.

The principal factor affecting release is probably the vapor pressure of the elements above the pool. This assumes that the release occurs in elemental form. For an ideal solution, the vapor pressure is the product of the vapor pressure of the pure element and the mole fraction of the element in solution. However, metallic solutions are rarely ideal. To describe non-ideal behavior, an additional factor, the activity coefficient, is included. Activity coefficients must be determined experimentally. One commonly used method to determine vapor pressures and activity coefficients is the Knudsen Effusion Method. This method involves the use of a small evacuated cell with only a single hole in the top. The hole is sized to provide an equilibrium pressure within the cell but allow a measureable leak rate. The method is ideal for pure materials or simple mixtures with relatively low vapor pressures. The use of the method was rejected because of the complexity of the mixtures to be studied and the wide range of likely vapor pressures.

The method chosen was to establish melt pools having significant depths and cross-sectional areas. One method considered was to analyze the concentration of vapors above the pools by an in-place method such as atomic absorption. This method appeared to require considerable apparatus development and calibration. Moreover, the method applies only to elements and not to compounds. Instead, it was decided to continuously sweep the space above the pool with inert gas and pass the gas through thermal gradient tubes, filters, and bubblers. In this way, the vapors would be sampled and to some degree classified by the location of condensed material in the gradient tubes. This method has been used extensively in studies with irradiated fuels at ORNL [12].

Calculations were performed to predict the behavior of the fission product elements released from the melt pools to provide a basis for the analyses of the measured results. Four processes which might limit the release rates were considered: (1) the rate at which an inert gas would sweep vapors into a thermal gradient tube assuming that an equilibrium vapor pressure is established above the pool, (2) the rate of gaseous diffusion of the fission product vapors from the surface of the pool assuming that the sweep gas completely removes the vapors at a short distance above the pool surface, (3) the limiting rate of vaporization

from the pool given by the Langmuir equation, and (4) the rate of liquid phase diffusion which transports the fission product elements to the surface for release.

Vapor Sweepout - It is assumed that the vapors in the space above the pool maintain an equilibrium partial pressure. The rate of sweepout is obtained from the perfect gas law. The volume used in the calculation is the gas flow rate times the time of flow so that the release is:

$$W = \frac{P F t M}{R T} \quad (1)$$

Where: W = Mass of Vapor Released
P = Vapor Pressure of Species
F = Flowrate of Sweep Gas
t = Time
M = Molecular Weight of Species
R = Gas Constant
T = Temperature

Vapor pressures for the elements and compounds of interest were calculated from standard compilations of Gibbs free energy [9,10,11].

Gaseous Diffusion - The diffusion coefficients for the species were calculated using the Chapman-Enskog theory and characteristic Leonard-Jones energy and length values as outlined in standard texts [13,14]. The energy and length values for helium are well established. The corresponding values for the fission product vapors were estimated using the methods outlined by Svehla [15]. Each diffusion coefficient was calculated as though the species were a binary mixture with helium using the usual combining rules [13]. The releases which occur per hour were calculated from the diffusion coefficients as follows:

$$W = \frac{P D A M}{X R T} \quad (2)$$

Where: D = Diffusion Coefficient
A = Pool Surface Area
X = Diffusion Distance

Langmuir Vaporization - The maximum rate of free vaporization into a vacuum is described by an equation from the kinetic theory of gases. The equation is given in the text by Glasstone [16]. The calculations for the vapors of interest showed that the rates were several orders of magnitude greater than those calculated for gaseous diffusion or vapor sweepout. It was concluded that Langmuir vaporization will not limit release rates in the experiments.

Liquid Phase Diffusion - The ability of dissolved species to diffuse from the bulk of the melt to the surface depends strongly on the internal convection process within the melt pool. The most limiting situation would occur for a stable pool, ie., where the temperature within the pool is lowest at the bottom and increases vertically upward. In this case, the upward motion of dissolved

species would occur by diffusion alone. The following equation would apply assuming that the concentration at the upper surface is maintained at zero:

$$Fr = \frac{2 \sqrt{D t}}{L \sqrt{\pi}} \quad (3)$$

Where: Fr = Fraction Released
D = Diffusion Coefficient
L = Pool Depth
t = Time

Diffusion coefficients for liquids are relatively independent of the nature of the liquid. High temperature diffusion coefficients can be estimated at 10^{-4} cm²/s. Using this value and assuming a pool depth of 5 cm., the release at 1/2 hour would be 9.6 % and at 1 hour would be 13.5 %. The release rate decreases with the square root of time. However, if the pool is not stable and vigorous natural convection occurs, the rate would stabilize at a constant value after the initial, more rapid transient. Three experimental requirements resulted from considerations of liquid phase diffusion: (1) An effort would be made to concentrate the heating toward the bottom of the crucible to promote convective mixing, also, measurements would be made of the temperature profiles within the pool, (2) At least two periods of sample collection would be carried out at each temperature to determine if the release rate were decreasing with time, and (3) experiments would be performed with two pool depths.

Calculations were performed assuming that liquid phase diffusion is not limiting. The calculations were to evaluate the expected release rates based on two different assumptions: (1) the fission product species form a separate phase from the melt and (2) the fission product species form an ideal solution in the melt. In the former case, the species exerts its normal vapor pressure. In the latter case, the vapor pressure is reduced in proportion to the mole fraction of the species. The results of calculations for the vapor sweepout and the gaseous diffusion processes are shown in Table 2. The parameters used in the calculations were those expected to be used in the experiments.

The results of the calculations, shown in Table 2 indicate the following:

1. The potentials for release from the pool by gaseous diffusion are consistently greater than vapor carry-out quantities by factors of from 5 to 10 or more. Thus it is likely that the vapor pressures of species above the pool could maintain near equilibrium conditions in spite of the continuing carry-out by the sweep gas.
2. Rapid and complete releases of cesium iodide could be expected at 1000 K or higher if there is little or no solubility in the melt. If there is significant solubility, releases would be very small even at 1400 K.
3. Cesium release is likely to be relatively rapid whether the cesium is soluble in the melt or not.

4. Tellurium is known to be soluble in molten aluminum. Thus, significant releases are likely to occur only at temperatures above about 1200 K.
5. Strontium is known to be soluble in molten aluminum so that significant releases could occur only at about 1400 K or higher.
6. Barium is also soluble in molten aluminum. The vapor pressure is low so that very little release is expected even at 1400 K unless the activity coefficient is significantly greater than unity.
7. No significant release of aluminum should occur even at 1400 K.

Table 2. Calculated Values of One Hour Releases
(Pure Phases and Ideal Solutions)

Surface area = 55.2 sq cm
Diffusion Distance = 1.5 cm
Sweep Gas Flowrate = 1000 cc/min
Pressure = 1 atm He

Temperature, K	Vapor Pressure, atm	One Hour Releases, g	
		Flow into Gradient Tube	Diffusion from Surface
Cesium Iodide - Mole Fraction = 1			
900	0.000219	0.046	0.213
1000	0.00159	0.302	1.66
1100	0.00803	1.39	8.94
Cesium Iodide - Mole Fraction = 0.00005			
1100	0.000000	0.0000	0.0000
1200	0.000000	0.0002	0.0018
1300	0.000005	0.0007	0.0061
1400	0.000013	0.0018	0.0169
Cesium - Mole Fraction = 1			
900	0.685	74	374
1000	1.62	--	--
Cesium - Mole Fraction = 0.00085			
900	0.00058	0.063	0.318
1000	0.00138	0.134	0.809
1100	0.0028	0.247	1.75
1200	0.00504	0.408	3.33
Tellurium - Mole Fraction = 1			
900	0.0144	1.49	8.87
1000	0.0532	4.96	35.3
Tellurium - Mole Fraction = 0.00011			
900	0.000002	0.0002	0.0010
1000	0.000006	0.0006	0.0039
1100	0.000017	0.0014	0.0121
1200	0.000042	0.0032	0.0312
1300	0.000089	0.0064	0.0700
1400	0.000167	0.0113	0.140

Table 2. Continued

Temperature, K	Vapor Pressure, atm	One Hour Releases, g	
		Flow into Gradient Tube	Diffusion from Surface
Strontium - Mole Fraction = 1			
900	0.00016	0.0115	0.0752
1000	0.00112	0.0717	0.562
1100	0.00547	0.318	2.93
1200	0.0205	1.09	11.6
Strontium - Mole Fraction = 0.00060			
1000	0.000001	0.0000	0.0003
1100	0.000003	0.0002	0.0018
1200	0.000012	0.0007	0.0070
1300	0.000038	0.0019	0.0226
1400	0.000098	0.0045	0.0618
Barium - Mole Fraction = 1			
900	0.000009	0.0010	0.0059
1000	0.000070	0.0070	0.050
1100	0.000378	0.0344	0.288
1200	0.00154	0.129	1.25
Barium - Mole Fraction = 0.00039			
1200	0.000000	0.0001	0.0005
1300	0.000002	0.0002	0.0017
1400	0.000006	0.0004	0.0049
Aluminum - Mole Fraction = 1			
1400	0.000004	0.0001	0.0013

5. SIMULATED FUEL MATERIALS

The desired composition of the melts was given in Table 1. The experimental melts were prepared by melting together an ingot containing the uranium and two disks of pure aluminum. The ingots were prepared at the Savannah River Laboratory Fabrication Lab. and included quantities of the less volatile fission products. The disks were prepared from 99.99% aluminum which was obtained commercially. The impurities were stated to be about 30 ppm each of Cu, Fe, and Si and 5 ppm Mg. This approach provided flexibility in that experiments could be performed with the desired mixture by dilution with aluminum or they could be performed with two ingots in a larger crucible at twice the concentrations of uranium and fission products.

The ingots were prepared in two batches but had very similar compositions. Ingot compositions were determined both at Savannah River and at Argonne. Typical composition results are shown in Table 3.

Table 3. Average Composition of Savannah River Ingots

<u>Element</u>	<u>Weight Percent</u>
Al	79.0
U	18.2
Ce	1.15
Mo	0.47
Ba	0.30
Sr	0.30
C	0.27
O	0.23
Zr	0.08

The ingots were prepared in graphite crucibles which accounts for the quantity of carbon present. It was not possible to include the desired quantities of molybdenum or zirconium in the ingots. Each ingot weighed about 410 g. In the experiments, they were melted with about 335 g of aluminum. A typical melt composition, including the added aluminum, is compared with the desired composition in Table 4. Quantities of zirconium, iodine, cesium, and tellurium to be added to the ingots to produce the final melts are included in Table 4. The actual composition was somewhat low in cerium and molybdenum, but, this was not considered significant.

The use of ceramic or graphite crucibles was avoided to minimize further contamination of the melts with oxygen or carbon. Tantalum crucibles were obtained commercially and performed satisfactorily. The tantalum crucibles were 8.4 cm inside diameter and 6.35 cm deep which corresponds to a volume of 352 cc. The room temperature densities of the ingot and the added aluminum are estimated at 3.2 g/cc and 2.7 g/cc, respectively. Thus, the melt volume is about 260 cc at room temperature. Allowing for a 13% expansion on heating through melting yields a melt volume of 294 cc. Thus, the melt occupies about 84% of the crucible leaving a freeboard of slightly more than 1 cm. This made it possible to limit the vapor space above the melt to no more than about 1.5 cm.

Table 4. Desired and Actual Melt Compositions

Element	Desired Composition Weight %	Typical Composition Used in Experiments	
		Mass, g	Weight %
Al	87.5	658.9	87.55
U	10.1	74.6	9.91
Ce	0.766	4.72	0.63
Zr	0.516	*4.33	0.58
Mo	0.355	1.93	0.26
Ba	0.178	1.23	0.16
Sr	0.174	1.23	0.16
Cs	0.373	*3.0	0.40
Te	0.046	*0.40	0.053
I	0.022	*0.17	0.023
C		1.11	0.15
O		0.94	0.12
Total	100.0	752.6	100.0

*4 g zirconium, 3 g cesium, 0.4 g tellurium, 0.17 g iodine were added to the ingot and the aluminum disks before melting in particular experiments.

The crucible was loaded first with an aluminum disk about 1.3 cm in thickness, then with the uranium-containing ingot, and finally with another, somewhat thinner aluminum disk. The fission product elements to be added were placed in one or more of four holes drilled partly through the lower disk as indicated in Figure 3. The cesium was loaded from a medicine dropper in an inert glovebox; the hole was then sealed with a small aluminum cover which was hammered into the top of the hole. Aluminum iodide was loaded in a similar way except that the cover was provided with a small hole to avoid a buildup of pressure during heating. Cesium iodide and elemental tellurium were added without seals. Zirconium was added either as zirconium aluminide or as zirconium metal and was placed either in the holes or between the disk and the ingot. The disks and the ingots were made with a 6.4 mm center hole. A tantalum tube, sealed on the bottom, was inserted through the assembly to serve as a thermocouple well. Additional thermocouples were inserted directly into the melt in some of the experiments.

Figure 3. Drawing of Lower Aluminum Disk used to Load Volatile Fission Products into the Melt Crucible

6. APPARATUS AND TEST DESCRIPTION

6.1 Apparatus Design

The apparatus was designed to provide the features indicated in Figure 4. The melt crucible, 8.4 cm diameter, is surrounded by a heavy stainless steel enclosure. The enclosure serves as a susceptor for induction heating and provides a region of relatively constant temperature. A continuous flow of pure helium enters at the bottom of the enclosure, flows across the surface of the melt, and exits through the thermal gradient tube. It was desired to have several different thermal gradient tubes available during a single experiment. Accordingly, the lower portion of the structure, shown in Figure 4, was designed to rotate, allowing the gas flow to enter each of six gradient tubes in succession. Inlet and outlet flows are controlled and metered separately. The outlet flow results from the application of a vacuum on the discharge side of the gradient tube, filter, and bubbler train. The inlet flow is driven by an external positive pressure. It was found to be difficult to make the internal system perfectly leak tight and to balance the the inlet and outlet flows. Thus, a leak path was introduced deliberately at the seal between the enclosure and its cover. In this way, the internal system was maintained at the same, slightly positive pressure, as the external system. Most of the helium sweep gas was heated by passing through the area between the ceramic melt catcher and the enclosure before contacting the melt surface. At most, a small quantity entered through the radial leak path. The melt catcher served as a safety feature in the event of a crucible failure incident.

The thermal gradient tubes were made from stainless steel tubing, 1.0 cm inside diameter and 46 cm long. Thin tantalum or stainless steel sheet material, 0.051 mm, was inserted into the steel tubing to form liners. New liners were used for each run and they were weighed before and after each run. The HEPA filters were 2.5 cm diameter commercial units with mineral fiber filter sections of the type used in Savannah River reactor filter banks. The sides and top of the enclosure were also lined with metallic sheets. These were also weighed and either replaced or cleaned between experiments. The melt crucible was weighed before and after each experiment. The bubblers contained water in most of the experiments, but, a solution, containing 3.17 g sodium sulfite per liter of water, provided by the Argonne Analytical Chemistry Laboratory, was used in experiments involving iodine to facilitate collection and analysis. One or more thermocouples were inserted into the melt through the central, stationary steel tube. Another thermocouple, entering through the central tube, was located in the gas space above the melt. The vertical height of the gas space was maintained at about 1.5 cm.

The entire assembly of the melt enclosure and the gradient tubes was contained within a nominal 15 cm fused silica tube as shown in Figure 5. The glass tube was sealed to the bottom support plate by a rubber gasket and sealing wax. The top of the tube was sealed with a greased "O" Ring which allowed for the differential expansion of the heated metal structure relative to the glass tube. The gradient tubes were fastened to the upper stationary plate and to the system top plate using Conax fittings. Each gradient tube was instrumented with three Chromel-alumel thermocouples. A shroud tube surrounded each gradient tube. A 3 liter/minute helium flow passed through the annulus between the shroud and the outside of the gradient tubes. This flow was calculated to improve the linearity of the temperature gradient along the gradient tube. The helium flow

Figure 4. Schematic of the Internal Portion of the Fission Product Release Apparatus

exited through a small tube in the base of support plate which was provided with a silicone oil bubbler. The bubbling action indicated that a positive pressure was being maintained within the apparatus. The gradient tubes and the central thermocouple tube extended upward beyond the inerted system. The upper ends of the gradient tubes were terminated with in-line filters which remained close to room temperature at all times. The pressure drops across each filter were measured and recorded. The lower ends of the gradient tubes terminated at the plane of rotation of the assembly which was at a temperature only slightly below that of the melt. The upper end of the central tube was sealed during experiments.

The lower part of the apparatus, shown in Figure 5, provided the capability to rotate the enclosure containing the melt. Indentations in the bottom of the support plate, combined with a spring system, allowed the rotation to be indexed so that the single hole in the rotating plate was always aligned with one of the six holes leading to a gradient tube in the stationary plate. The rotation was done manually using a handle located near the floor of the laboratory. The lower end of the apparatus was terminated in a final melt catcher.

A water-cooled induction coil was located outside of the glass tube. The induction heater had a capacity of 100 kW and operated at 450 kHz. The experimental apparatus was enclosed in a Lucite and aluminum box as indicated in Figure 6. The pressure in the box was monitored and alarmed to assure a slightly negative pressure. The box exhausted through HEPA filters to the building exhaust. The bubblers were preceded by small check valves to prevent the back diffusion of water vapor into the system through inactive gradient tubes. The three helium flow systems were controlled by precision flow controllers and the flow rates were recorded continuously.

A data acquisition system was built around a 386-33 MHz personal computer. A Hewlett-Packard system converted the thermocouple, flowmeter, and pressure difference signals for recording on the computer. There was significant interference in the thermocouple readings by the induction field. To avoid this interference, the plate current of the induction generator was turned off momentarily every few minutes while a complete set of temperature and flow data were recorded. The induction power was also turned off briefly while the system was rotated to align a new gradient tube. This was done to ensure personnel safety. A Pascal program was developed to record and display the data in real time on the monitor.

6.2 Test Sequence

The upper, stationary assembly, including the gradient tubes, the upper plate, and the in-line filter housings were assembled permanently. To begin an experiment, the gradient tube and the other liners were degreased and weighed. The tube liners were coiled and slipped into the steel tubes. The spring action caused the liners to seat firmly against the tubes. The filter elements were weighed and loaded into the housings. The volatile fission product simulants were loaded into the lower aluminum disk. This was done in an inert atmosphere box for cesium and aluminum iodide. The aluminum disks were weighed before and after each material was added. The uranium-containing ingot, along with the two aluminum disks, were loaded into the crucible and weighed. The crucible was then mounted into the lower, rotating section of the apparatus. The enveloping glass

Figure 5. Schematic of Fission Product Release Apparatus

Figure 6. Schematic of Fission Product Release Apparatus Showing the External Support System

tube was installed and the upper assembly put in place, carefully seating the large, greased O-ring between the upper section and the glass tube. The bubblers were connected to the filters with Tygon tubing. The upper plate was fastened to flexible steel braces which allowed up and down movement but prevented rotational motion. After checking all of the connections, a helium flow of about 400 cc/min was initiated and allowed to continue overnight.

On the day of the test, each gradient tube was flushed with helium. The three helium flows were set to the desired flowrate. The Data Acquisition System was activated and tested. With gradient tube number 1 in place, the induction power was turned on to heat the crucible and the enclosure to a predetermined temperature. As soon as the desired temperature level was reached, the lower assembly was rotated to isolate Tube 1 and transfer the flow to Tube 2. After a predetermined period of time, the flow was moved to Tube 3. After another period of time, the flow was moved to Tube 4, and the power was increased to reach a higher temperature level. After achieving a relatively constant temperature, Tubes 5 and 6 were exposed in succession for periods of time. To conclude an experiment, Tube 1 was exposed to the flow during the melt cooldown. In this way, duplicate samples at each of two temperatures were obtained. Deposits in Tubes 1 and 4 occurred over wide ranges of temperatures and were not expected to provide important data.

Following the cooldown, the system was dismantled and the liners, filters, and crucible were weighed. The bubbler solutions were collected. The system was decontaminated and cleaned in preparation for the next experiment.

In some of the experiments, the filters began to plug and in some, plugged completely. The pressure drop data, displayed on the monitor, provided the first indication of filter plugging. As the pressure drop increased, a point was reached when the controller could no longer maintain the desired flow and the flowrate began to decrease. In some cases, this made it necessary to switch to the next tube even though the desired temperature conditions had not been achieved.

7. SHAKEDOWN AND CALIBRATION TESTS

A series of shakedown tests were performed to discover and correct operating problems with the apparatus. Calibration tests were planned with several pure metals having known vapor pressures. With a single component melt, there would be no limitation to release caused by liquid phase diffusion. Tests were planned with bismuth, zinc, and aluminum. However, only two tests with bismuth and several tests with aluminum were performed because of limitations on program resources.

7.1 Tests With Bismuth

The tests were performed with 99.99% bismuth granules obtained from Johnson Matthey Co. The granules were loaded into a stainless steel beaker and melted in a muffle furnace. The oxide formed on the surface of the melt was removed by machining. The upper portion of the beaker was removed by sawing to form a crucible with a freeboard of about 1.0 cm. This made it possible to load the crucible into the apparatus so that the melt surface was no more than 1.5 cm from the top of the crucible enclosure. The gradient tubes were lined with stainless steel sheet for the bismuth calibration tests.

The Data Acquisition System records a complete set of data on command. A number of data sets were recorded during each period for which flow passed through one of the gradient tubes. Included in each data set are the melt temperature, the flow rate, and the time at which the data were recorded. A method was developed to obtain a representative test temperature, flow rate, and duration. The method uses the fact that vapor pressures can usually be represented by the following equation:

$$P = A \exp(-E/T) \quad (4)$$

Where: P = Vapor Pressure
 T = Temperature
 A and E are Constants
 E = 22,000 K for bismuth

Three sums were calculated as follows:

$$\sum_{i=1}^{\mu} \Delta t_i, \quad \sum_{i=1}^{\mu} F_i \Delta t_i, \quad \text{and} \quad \sum_{i=1}^{\mu} F_i \Delta t_i \exp(-E/T_i) \quad (5)$$

Where: Δt_i = Time interval
 F_i = Flow rate during each recording interval
 T_i = Melt temperature during each recording interval

The duration of flow for a given gradient tube is the first sum; the flow rate is the second sum divided by the first; and the temperature is obtained from the third sum divided by the second by evaluating the exponential for the temperature. The derived values for the bismuth calibration tests are listed in Table 5:

Table 5. Bismuth Calibration Tests

Test	Gradient Tube	Duration of Flow, min.	*He Flow Rate cc/min.	Melt Temperature K
1	2	63.6	500	930.3
1	3	59.7	500	933.7
1	5	30.0	500	990.4
1	6	30.1	500	1004.0
2	2	63.0	500	1102.9
2	3	32.2	1000	1084.7
2	5	20.1	1000	1162.9
2	6	23.3	1000	1163.1

*The flow rate refers to helium at 300 K and was maintained constant during each test.

The expected transport of bismuth vapor into each gradient tube was calculated from the perfect gas law as follows:

$$W = \frac{P M F t T}{R T T_0} \quad (6)$$

Where: W = Bismuth transported into gradient tube
M = Molecular weight
F = Helium flowrate measured at T_0
t = Time
T = Melt temperature
R = Gas constant

Bismuth vapor pressures were calculated from free energy data given in Ref. 11. Separate calculations were made for monatomic and diatomic bismuth and the calculated masses were added together to obtain a total. The calculated masses passing into the gradient tubes are compared with measured weight gains in Table 6.

The weight gains from Test 1 are in the few milligram range and indicate that the aerosol background in the system is very small. The ratios of measured weight gains to the calculated masses of bismuth entering the gradient tubes are very consistent and independent of flow rate over the range studied. Considering only the larger deposits, ie., from Test 2, the average ratio is 0.41. The lack of an effect of flow rate suggests that an equilibrium is obtained between the helium gas and the bismuth vapor. However, the fact that the ratios are considerably less than unity suggests either that the gas flowing over the melt

Table 6. Comparison of Calculated and Measured Weight Gains in the Gradient Tubes

Test	Temperature, K	Flowrate cc/min	Weight Gains, g			Ratio Meas./Calcd.
			Calculated	Measured Gradient Tube	Filter	
1	930.3	500	0.0034	0.0019	0.0001	0.588
1	933.7	500	0.0035	0.0018	0.0003	0.600
1	990.4	500	0.0069	0.0026	-0.0003	0.377
1	1004.0	500	0.0093	0.0040	-0.0002	0.430
2	1102.9	500	0.1429	0.0503	0.0054	0.390
2	1084.7	1000	0.1040	0.0396	0.0026	0.406
2	1162.9	1000	0.2582	0.1052	0.0049	0.426
2	1163.1	1000	0.3003	0.1183	0.0020	0.401

is at a significantly lower temperature than the melt or that the gas does not equilibrate with the vapor. Tests with other melts such as zinc would be required to resolve the issue. However, program resources were insufficient to permit further calibration testing.

7.2 Tests with Aluminum

An initial test with a melt of pure aluminum (99.99 %) was performed using a zirconium crucible. The pure aluminum cylinder, placed in the crucible, was not provided with a center hole in the same way as the uranium-containing disks. It was planned to lower the melt thermocouple into the melt just after melting. During the test, it was found that the melt thermocouple could be lowered too far into the crucible, indicating that the crucible had failed. The test was terminated and the crucible removed after cooling. It was apparent that the aluminum had reacted with the zirconium producing a annular region of a solid compound, probably $ZrAl_3$, which was attached to the unreacted upper portion of the zirconium crucible. The lower portion of the crucible had disappeared completely. Most of the melt had relocated to the ceramic melt catcher just below the crucible. It was concluded that zirconium crucibles could not be used.

A second test was performed with pure aluminum. In this test, a tantalum crucible was used. It was found, once again, that the thermocouple could be lowered too far into the crucible. The test was terminated and the crucible removed after cooling. The tantalum crucible was found to be intact but the tantalum shield on the thermocouple had dissolved. It was then decided to use a fairly thick walled tantalum tube, crimped at the bottom, as a thermocouple well. The 6.4 mm tube would be installed into a center hole in the solid ingots during the apparatus assembly. The melt thermocouple would be lowered into the thermocouple well.

A third test with pure aluminum was performed using a tantalum crucible and the thermocouple well. This test was continued for 5 hours at temperatures as high as 1360 K. On disassembly, it was found that about half of the aluminum had crawled up the side of the crucible and overflowed into the melt catcher below. It was determined that the melt level at the maximum temperature would have been

within about 2 mm of the top of the crucible. Because of the high degree of wetting of the tantalum by the aluminum, the meniscus reached above the crucible lip so that a siphon flow was initiated. It was expected that this type of overrunning would not occur if more freeboard were provided.

It was expected that the deposit masses on the liners and the filters would have been negligible for the pure aluminum test. However, this was not the case. Liner deposits ranged from 17 to 30 mg and the filter deposit for the initial heating period was 30 mg. Filter deposits for the subsequent periods were negligible. The compositions of the deposits were not determined. It was concluded that the experimental procedures were sufficiently developed to begin tests with uranium-containing melts.

Following the completion of the four experiments with uranium-containing melts, described in the next Section, a final calibration test was performed with pure aluminum. The melt temperature history during the test is shown in Figure 7. The Figure shows clearly the thermal halts corresponding to melting and freezing of the aluminum and provides meaningful temperature calibrations. Several times during the test, a multi-junction thermocouple was thrust into the melt. The readings indicated that the melt is about one degree cooler near the bottom and the top with a uniform temperature in the bulk.

In the final calibration test, the aluminum melt was initially heated to about 1120 K during a 40 min. period. The filter on Tube 1, exposed during the heating period, gained 23 mg and plugged. The liner also gained 23 mg. The melt was then held at 1120 K for two periods of 30 min. The filter weight gains were small, but, the liners gained 39 and 25 mg. Following these exposures, the melt temperature was increased to 1310 K during a period of 45 min. The filter gained 18 mg and the liner gained 28 mg during this period. Finally, the melt was maintained at 1310 K for two periods of 20 min. The liners gained 26 and 19 mg during these periods. In this test, four of the six liners were stainless steel and two were tantalum.

Limited examination of one of the tantalum liners by scanning electron microscopy showed the presence of iron but did not indicate the presence of foreign materials in the quantities necessary to account for the large weight gains produced in tests with nominally pure aluminum. Oxidation of the liners could be a major factor in the weight gains although there was no apparent effect of liner material. More experimentation would be required to determine the causes of the unexpected weight gains. Experiments using getters to vary the trace levels of oxygen and water vapor are needed.

Figure 7. Melt Temperature History for Pure Aluminum Calibration Test

8. EXPERIMENTAL RESULTS

Four experiments were performed with the uranium-containing ingots. One ingot was used in each test along with two aluminum disks. Tantalum crucibles were used in the tests. The melt masses were about 750 g. The melt pools were 5.3 cm deep with a top surface area of 55.2 sq cm. The experiments are described in the following sections.

8.1 Experiment B1

The only material added to the ingot and the aluminum disks was 8.0 g of a commercially obtained zirconium aluminide. The material was in the form of a black powder. The powder was compressed into the 4 holes in the lower aluminum disk. It was expected that the material would become dispersed in the melt, thus providing the required quantity of simulated fission product zirconium. After the experiment, the 4 disk shaped compacts of black powder were found intact on top of the frozen melt. Thus, the zirconium aluminide did not dissolve in the melt and simply floated to the top.

The surface of the melt was dark colored but not heavily oxidized. A small quantity of greenish-gray powder was on the surface of the melt. Chemical analysis showed the presence of aluminum, aluminum oxide, tantalum oxide, barium, and strontium in the powder. It was likely that enough air or water vapor was present to oxidize a small quantity of the released barium and strontium along with some aluminum and tantalum from the crucible.

The melt temperature, time, and flowrate data were averaged in the same way as for the bismuth calibration tests, described in Section 7.1, except that the constant used in the exponential term was 18,000, which was consistent with the temperature dependence of the barium and strontium vapor pressures. The derived data for B1 are listed in Table 7:

Table 7. Experiment B1
(Helium flow rate 1000 cc/min)

Gradient Tube	Duration of Flow, min.	Melt Temperature, K	Measured Weight Gains, mg	
			Liner	Filter
1	51.0		12.9	*21.2
2	39.9	1101	**12.0	1.8
3	40.1	1104	36.6	- 0.2
4	33.0		35.6	1.1
5	30.4	1333	40.6	0.0
6	29.9	1334	33.3	2.4

*Filter plugged

**A small piece of the tantalum liner was lost

The filter on Tube 1 plugged during the initial heatup period. As a result, the flowrate decreased to very low values just before switching to Tube 2. Chemical analyses were performed on the liner and filter from Tube 1 to determine what

caused the filter to plug. The results were inconclusive because of the many elements present in the mineral wool of the filter. The only material found in significant quantity above the blank analysis was about 2 mg of zinc. The liners were leached with aqua regia and the elemental composition of the solutions were determined by ICP. Liner 1 was analyzed as a unit. Liners 2 and 3 were cut in half. The hot ends of Liners 2 and 3 were combined for a single analysis. The cooler ends were also combined for a single analysis. The same procedure was used for Liners 5 and 6. The results of the analyses are given in Table 8, where the results for Liners 2 and 3, and 5 and 6 were combined. Cerium, uranium, and zirconium were below detection limits.

The total quantities of materials found by chemical analysis are much less than the weight gains. Some of this discrepancy probably resulted from the limited oxidation of tantalum and from the pickup of some oxidized stainless steel from the heavy-walled tubes in contact with the tantalum liner. However, the major cause of the discrepancy could not be determined from the limited analytical chemistry that could be carried out. Also, it could not be determined how much of the iron, chromium, nickel, and manganese might have entered the tubes as vapor and how much became attached because of contact with the steel tubes. It was tentatively assumed that the aluminum, the fission product elements, Ba, Sr, and Mo, and the impurity elements Ca, Cu, Mg and Zn entered as vapor. The apparent vapor pressures of these elements were calculated when there was a significant deposit mass. The method of calculation used an inversion of Equation 6 including the empirical correction factor of 0.41, determined from the bismuth calibrations.

$$P = \frac{W R T_o}{0.41 M F t} \quad (7)$$

W = Element mass
R = Gas constant
T_o = 300 K
M = Atomic weight
F = Flowrate
t = Time

The apparent vapor pressure values obtained from the calculations will be presented along with those calculated from Experiment C1 in the next Section.

As noted previously, the upper sections and the lower sections of the liners were analyzed separately, thus providing an indication of whether the deposits were located in a high temperature or a low temperature region of the gradient tube. The temperature gradients recorded during the early, (Tube 2 and 3) portion of the test are shown in Figure 8. The liners were cut in half so that deposits on the lower end were formed above about 700 K and deposits on the lower end were formed below about 700 K. Barium and strontium were deposited almost entirely above 700 K. Aluminum, magnesium, zinc, and molybdenum were concentrated in the lower temperature region. Calcium and copper were more evenly distributed.

Table 8. Analytical Chemistry Results for Experiment B1

Uranium-containing Ingot
Pure Aluminum Disks
Zirconium Added as $ZrAl_3$
No Volatiles FPs Added

Helium Flow Rate through
gradient tubes: 1000 cc/min

Gradient Tube Liners	1	2 + 3	4 + 5
Melt Temperature, K	300-1102	1102	1324
Time, min	51	80	60.2
Analytical Results, mg			
Al	0.160	0.063	0.393
Ba	0.016	0.004	1.649
Sr	0.0	0.0	0.427
Mo	0.005	0.002	0.013
Ca	0.146	0.150	0.233
Cu	0.200	0.051	0.212
Mg	0.015	0.012	0.275
Zn	6.83	0.777	1.858
Fe	0.790	1.252	13.34
Cr	0.119	0.038	0.435
Ni	0.052	0.031	0.068
Mn	0.031	0.006	0.342
Ce, U, Zr	Below detection limits		
Total	<u>8.368</u>	<u>2.390</u>	<u>19.248</u>
Weight Gains			
Liners	12.9	*73	73.9
Filters	21.2	1.6	2.4

*Estimated; Liner 3 was 36.6 mg; a small piece of tantalum was lost from Liner 2

Figure 8. Temperature Profile along the Gradient Tube for Experiment B1

8.2 Experiment C1

In this experiment, 0.68 g of cesium iodide and 0.41 g of elemental tellurium were added to melt by placing them in the holes in the lower aluminum disk. Also, 4 g of metallic zirconium in sheet form were placed between the lower disk and the ingot although it was expected that the zirconium would not dissolve uniformly in the melt. The 3.17 g/l sodium sulfite solution, in place of water, was loaded into the bubblers to trap any iodine which passed through the filters.

The averaged temperature, time, and flowrate values for the experiment and the weight gain values are ~~are~~ listed in Table 9.

Table 9. Experiment C1
(Helium flowrate 1000 cc/min)

Gradient Tube	Duration of Flow, min.	Melt Temperature, K	Measured Weight Gains, mg	
			Liner	Filter
1	49.8		21.3	14.3
2	30.6	1020	64.0	68.5
3	30.7	1021	41.9	16.7
4	17.5		30.2	18.7
5	30.2	1189	35.1	4.4
6	32.8	1188	21.1	3.2

The melt temperatures and the pressure drops across the filters are plotted in Figure 9. The pressure drop curves indicate that filter 1 was very close to plugging when the switch to Tube 2 was made. However, the flow control system was able to maintain full flow in spite of the increased pressure drop. The temperature curves show the two stage melting of the ingot at about 926 K and the melting of the aluminum disks at 933 K and the freezing of the melt at an indicated temperature of about 918 K. Tube 4 was used for the cool down.

The deposits obtained during the period when Tube 2 was active were subjected to a relatively complete chemical analysis. The results are shown in Table 10. The bubbler solution was analyzed for cesium and iodine. A trace of iodine was found, but the cesium was below detection limits. The filter contained rather large amounts of cesium and iodine. The ratio of cesium to iodine deviated significantly from the value for the compound CsI. Liner 2 was sectioned into 3 pieces; each was analyzed separately. The analytical results are shown in Table 11:

Table 10. Analytical Chemistry Results for Experiment C1

Uranium-containing Ingot
 Pure Aluminum Disks
 Metallic Zirconium Added
 Cesium Iodide and Tellurium Added

Helium Flow through Gradient
 Tubes: 1000 cc/min

Gradient Tube	Bubbler #2	Filter #2	Liners		
			2	3	5
Melt Temperature, K			1020	1021	1189
Time, min			30.6	30.7	30.2
Analytical Results, mg					
Cs	<0.003	27.0	20.0	11.8	10.6
I	0.006	33.8	13.9	9.74	13.6
Al			0.065	0.036	0.031
Ba			0.005	0.006	0.550
Sr			0.0	0.002	0.117
Mo			0.0	0.008	0.012
Ca			0.079	0.059	0.032
Cu			0.072	0.072	0.053
Mg			0.015	0.010	0.009
Zn			0.046	0.021	0.121
Fe			0.526	0.288	0.436
Cr			0.022	0.012	0.014
Ni			0.058	0.019	0.033
Mn			0.008	0.004	0.023
Te, Ce, U, Zr			Below detection limits		
Total			34.80	22.08	25.63
Weight Gains					
Liners			68.5	41.9	35.1
Filters			64.0	16.7	4.4

Figure 9. Melt Temperature History and Filter Pressure Drops for Experiment C1

Table 11. Analytical Results for Cesium and Iodine for Tube 2, Experiment C1

	Liner Temperature Range, K	Quantity, mg		Ratio Cs/I
		Cesium	Iodine	
Bubbler		<0.003	0.006	0
Filter		27.0	33.0	0.82
Liner, 28-45 cm	300 - 550	4.00	3.62	1.10
Liner, 7-18 cm	730 - 900	15.8	10.2	1.55
Liner, 0-7 cm	900 - 1000	0.235	0.087	2.7
Total		47.04	46.91	1.00
Ratio for CsI				1.05

The temperatures along gradient Tube 2 are shown in Figure 10. The results in Table 11 indicate that CsI was probably evolved as a compound, but may have undergone some decomposition along the gradient tube. There were distinct differences in the visual appearances of the deposits along the liner. The hot end, 0-7 cm, had a uniform light gold appearance. The portion from 7 to 18 cm from the hot end was covered with a speckled gray deposit which was crystalline under the microscope. There was no apparent deposit between 18 and 28 cm. From 28 cm through to the cold end, there was a white deposit. Most of the other elements were distributed more or less uniformly along the liner, except for zinc which was concentrated at the cold end. A similar speckled deposit was located at the same place in tube 3 although no chemical analyses were performed. The speckled deposit was found between 17 and 21 cm on the liner from Tube 5. This corresponded to 800-990 K which was about the same temperature range where the deposit was found in Tubes 2 and 3. The speckled deposit was less apparent in Tube 6.

The whole of Liners 3 and 5 were analyzed as indicated in Table 10. Tellurium, cerium, uranium, and zirconium were below detection limits. The apparent vapor pressures were calculated from the chemical analyses in Table 10 for cases when the deposit mass was considered significant. The results of the calculations of apparent vapor pressures from Experiments B1 and C1 are presented in Table 12.

The apparent vapor pressures of aluminum are much greater than the known values for the pure metal. This could have been caused by the presence of small quantities of oxygen in the system, giving rise to the formation of AlO and Al₂O which would transfer some aluminum into the gradient tubes. Also, there could have been a small quantity of finely divided aluminum oxide transported into the gradient tubes as an aerosol.

Significant quantities of barium and strontium were found only in the two experiments at the highest melt temperatures. The apparent vapor pressures of barium exceeded those expected for an ideal solution while the apparent vapor pressures for strontium were less than those for an ideal solution. Thus, the apparent activity coefficients for barium were 5 and 15, and for strontium were 0.10 and 0.25. The low values for strontium are consistent with results reported by Srikanth and Jacob [17].

Figure 10. Temperature Profile along the Gradient Tube for Experiment C1 with Tube 2 Active

Table 12. Apparent Vapor Pressures Calculated
from the Analytical Chemistry Results

(Includes results from Exp. B1, Tubes
2+3, 4+5 and C1, Tubes 2, 3, and 5,
neglecting element masses below about
0.01 mg)

Element (or Compd.)	Temp. K	Element Mass, mg	Vapor Pressure, atm.			Apparent	
			Apparent	Pure Element	Ideal Soln.	Activity Coeff.	Concn. Mole Frac.
Al	1020	0.065	0.0047	0.00000	--	>10,000	--
	1021	0.036	0.0026	0.00000	--	> 6,000	--
	1102	0.063	0.0018	0.00000	--	340	--
	1189	0.031	0.0023	0.00005	--	44	--
	1324	0.393	0.0145	0.00104	--	14	--
Ba	1189	0.550	0.0079	1.338	0.00052	15.2	--
	1324	1.649	0.0120	6.59	0.00257	4.67	--
Sr	1189	0.117	0.0027	17.9	0.0108	0.25	--
	1324	0.427	0.0049	80.0	0.0486	0.10	--
CsI	1020	94.7	0.715	2.25	0.00024	--	--
	1021	38.2	0.288	2.29	0.00025	--	--
	1189	28.6	0.219	27.0	0.0029	--	--
Ca	1020	0.079	0.0039	0.327	--	--	0.012
	1021	0.059	0.0029	0.333	--	--	0.009
	1102	0.150	0.0028	1.37	--	--	0.002
	1189	0.032	0.0016	5.06	--	--	0.0003
	1324	0.233	0.0058	27.3	--	--	0.0002
Mg	1020	0.015	0.0012	18.5	--	--	0.00007
	1021	0.010	0.0008	18.7	--	--	0.00004
	1102	0.012	0.0004	57.9	--	--	0.00001
	1189	0.009	0.0007	164	--	--	0.00000
	1324	0.275	0.0113	626	--	--	0.00002
Zn	1020	0.046	0.0014	146	--	--	0.00001
	1021	0.021	0.0006	147	--	--	0.00000
	1102	0.777	0.0089	361	--	--	0.00003
	1189	0.121	0.0037	825	--	--	0.00000
	1324	1.858	0.0283	2400	--	--	0.00001

The results of Experiment C1, Tube 2, for cesium iodide indicated that significant quantities passed through the gradient tube into the filter, but, very little reached the bubbler. The filters from Tubes 3 and 5 were not analysed. An estimate of the quantities of cesium iodide for Tubes 3 and 5 were obtained by assuming that the entire filter weight gains were cesium iodide. The results indicated that the cesium iodide vapor pressures were much greater than ideal solution values but less than values for pure cesium iodide.

The calculated vapor pressures of calcium, magnesium, and zinc were used to estimate concentrations based on ideal solutions. The calculated quantities of calcium were badly scattered and not consistent with an impurity level likely to be in the melt. No calculations were performed for copper because of its extremely low volatility. Thus, the quantities of calcium and copper found in the deposits cannot be accounted for on the basis of the available data. The apparent vapor pressures of magnesium and zinc, although scattered, are consistent with impurity levels of about 20 ppm of each in the melts.

8.3 Experiment D1

The additions to the ingot and the aluminum disks included the same quantities of zirconium, 4 g, cesium iodide, 0.68 g, and tellurium, 0.42 g, that were added in Experiment C1. One more element was added in Experiment D1, namely, 2.7 g cesium metal. The averaged temperature, time, and flowrate values are listed in Table 13:

Table 13. Experiment D1

<u>Gradient Tube</u>	<u>Duration of Flow, min.</u>	<u>Melt Temp.</u>	<u>Flow Rate cc/min</u>	<u>Weight Gains, mg</u>	
				<u>**Liner</u>	<u>***Filter</u>
1	21.5		1000	6.4	* 51.9
2	5.0	919	916	16.2	*160.4
3	17.6	946	1002	54.7	*427
4	13.7	986	925	6.8	* 60.5
5	24.2	977	1002	7.6	40.1
6	30.6	985	1002	14.5	41.8

*Filter plugged

**Weight gain after water washing and drying

***Weighings made while samples were absorbing water

It was apparent during the experiment that cesium was evolving even before the aluminum was melting. The filters on Tubes 1 and 2 had plugged very quickly. The filters on Tubes 3 and 4 plugged more slowly. Meaningful weighings of the filters were not obtained because of the rapid absorption of water which began as soon as the filters were exposed to laboratory air. All of the liners were also gaining weight during the initial weighing process. Each liner was rinsed in distilled water and dried. The liner weight gains given in Table 13 refer to the dried liners. The wash water and the liners were retained for future chemical analysis, however, no analyses have been carried out.

The rapid absorption of water vapor from the air for all of the filters and the liners indicated that elemental cesium was evolving throughout the experiment. This behavior suggests that the cesium is not dissolving rapidly in the melt. It was likely that some cesium would escape before the aluminum melted, however, subsequent release should have been greatly reduced had solution occurred. Analyses of the frozen melt would be needed to determine if some of the cesium had dissolved in the melt. Possibly, an experiment reusing the melt would have clarified the solubility question.

8.4 Experiment E1

In Experiment E1, the same quantities of zirconium, tellurium, and cesium were added as in Experiment D1. The only difference was the substitution of 0.36 g of aluminum triiodide for the cesium iodide. The filter on Tube 1 was removed to avoid rapid plugging from the initial release of some of the iodide and the cesium. The melt temperature, time, and flowrate were averaged and the results are listed in Table 14.

Table 14. Experiment E1

<u>Gradient Tube</u>	<u>Duration of Flow, min.</u>	<u>Melt Temp. K</u>	<u>Flow Rate cc/min.</u>	<u>Weight Gains, mg</u>	
				<u>Liner</u>	<u>Filter</u>
1	24.3		1000	161	* -
2	5.2	930	497	115	**105
3	19.4	992	424	67.8	39.8
4	31.1	988	414	41.1	9.4
5	30.4	***1175	431	125	159
6	31.1	1180	439	72.6	68.5

*No filter present

**Filter plugged

***Tube 2 was in place during the temperature increase

It appeared that large amounts of cesium and aluminum iodide evolved during the initial heating period. The released material affected the exit flow controller so that the flow during the remainder of the experiment was reduced and somewhat erratic. However, the measurement of flow rate is believed to be accurate. None of the remaining filters plugged. The liner and filter weights were taken immediately on disassembly of the apparatus to minimize the effects of water absorption. However, it is likely that the weight gains were increased somewhat by the cesium oxidation and hydration. No chemical analyses were performed although the filters and the liners have been preserved.

9. DISCUSSION AND CONCLUSIONS

The program of fission product mass transfer experiments was limited to 2 calibration tests with bismuth, several calibration tests with pure aluminum, four experiments with uranium-containing melts, and a very limited series of chemical analyses of deposits. The results of the program have provided a sound basis for a more comprehensive program. The results have indicated directions for further apparatus improvements as well as pointing to the need for specific experiments. However, the results of this limited program are considered significant and should contribute importantly to future analyses of radiological source terms for reactors using aluminum-based fuel systems. The results of the program are discussed in the following paragraphs.

9.1 Apparatus Performance

The mechanical aspects of the apparatus performed well. Early difficulties in rotating the lower part of the apparatus were overcome satisfactorily. Early difficulties in sealing the glass enclosure to the metal system were largely overcome before experimentation was begun. However, further improvement is needed to improve the atmosphere within the glass system. The effects of internal getters, such as exposed zirconium in the inner cell region, should be investigated to determine possible effects of atmosphere purity on results. Also, gas sampling and analyses of the atmosphere are needed. Modifications to the exit gas system are needed to avoid even moderate flow transients in the system when changing to another gradient tube after a filter plugging event.

The initial bismuth calibration test indicated a very low level of background aerosol from sources other than the melt. However, tests with aluminum resulted in excessive weight gains on the liners and filters. Clearly, analyses of the aluminum are needed to verify the stated purity of 99.99%. Also, some complete analyses of liners involving the total dissolution of the tantalum liners are needed to positively identify the source of weight gains. Clearly, calibrations with other pure metals, such as zinc, are needed to verify system behavior. Experiments are needed using double tantalum liners to eliminate pickup of stainless steel elements from the structure of the gradient tubes.

The type of filters used in the experiments should be changed. Larger filters with increased capacity should be used to avoid plugging. Also, an organic filter media should be used which does not contain any of the elements of interest in the program.

It must be emphasized that the improvements noted above should be readily achievable. No unresolved problems concerning the feasibility of the method were encountered.

9.2 Barium and Strontium

Significant deposits of barium and strontium were found only in two cases, at the highest melt temperatures studied, 1189 and 1324 K. This finding, that significant releases occur only at the higher temperatures, is an important qualitative result of the program. The measured activity coefficients for barium

of 5 and 15 and for strontium of 0.01 and 0.25 must be considered very tentative. For barium, it suggests that the release rates may be greater than estimated on the basis of ideal solution behavior. The opposite is true for strontium. Support for a low activity coefficient for strontium is provided by the results of a recent study of the aluminum-strontium system [17]. An activity coefficient of 0.024 was reported for a 0.17 mole fraction mixture of strontium in aluminum and 0.005 for a 0.091 strontium mole fraction. The authors noted that strontium is strongly stabilized in solution by the formation of Al_2Sr .

The activity coefficients noted above for barium and strontium are based on the assumption that the releases occurred by vaporization from the melt surface. An alternate process of release should be considered. Barium and strontium could have been oxidized at the surface to form a finely divided powder which could have been transported into the gradient tubes as an aerosol. This could have occurred only if sufficient oxygen were present. Thus, there is a need for experiments where the oxygen level in the system is varied. It should be noted that powder containing barium and strontium was found on the surface of the frozen melt in Experiment B1. However, the fact that the barium and strontium deposits were concentrated at the high temperature ends of the gradient tubes indicates that transport probably occurred as a vapor.

9.3 Iodine

The observed behavior when cesium iodide was added to the mixture to be melted indicated, tentatively, that the cesium iodide was not soluble in the melt. It was expected that significant release would begin even before melting, but, if solubility occurred, the release rate would reduce to very low levels. Instead, release continued for over an hour at a rate, corresponding to an apparent vapor pressure much greater than that expected for a solution. Analyses of the frozen melts for cesium and iodine would be key to an assessment of the solubility and possible decomposition behavior of the cesium iodide.

The behavior of the cesium iodide in the gradient tubes was complex. The bulk of the deposits occurred in the temperature range 730-900 K and appeared as fine crystalline deposits. Oak Ridge investigators reported collocations of cesium and iodine deposits in the 600-800 K range in experiments with irradiated LWR fuels [12]. In this study, powdery white deposits containing important quantities of cesium and iodine were also found at locations corresponding to gradient tube temperatures less than ~~than~~ 550 K. The deposits, at 730-900 K and at 300-530 K, were very distinct and separated spatially. As shown in Table 11, the ratios of cesium to iodine varied significantly along the gradient tube. Also, a trace of iodine, but no cesium, was found in the bubbler solution. Clearly, more experimentation is needed to understand the behavior of cesium iodide.

In one experiment, the iodine was added as aluminum iodide. The high volatility of aluminum iodide probably resulted in the loss of most of the material before aluminum melting occurred. However, no analyses of deposits were performed so that behavior was uncertain. Again, analyses of the melt residue would establish if any iodine had gone into solution. For future experiments, it is recommended that iodine be added as uranium triiodide. This form of iodine was shown to be stable at the temperatures used in this study in experiments

with uranium fuel melts used in metal fuel reprocessing [18]. A significant effort would be required to prepare the compound for use.

9.4 Cesium

The addition of cesium metal to the crucible charge proved to be very simple. The boiling point of cesium is only slightly higher than the melting point of aluminum. Thus, some loss of cesium was expected before melting. However, cesium release continued during the experiments. Because of the significant vapor pressure of cesium, even as a solution, (see Table 2), it was not clear whether cesium was dissolving in the melt or not. Cesium was readily volatilized from irradiated uranium melts in melt refining studies [19]. Also, the release experiments at Hanford [7] indicated rapid release of cesium from aluminum fuel melts, although the ORNL studies showed a more delayed release [5,6]. Analyses of the frozen melts would be key to the determination of cesium solubility.

The method of washing the liners immediately after the tests to collect the cesium and other soluble deposits seemed satisfactory. This ensured no loss of material from the wet liners. Further experiments combined with chemical analyses of the wash solutions and the dried liners would clarify the release behavior of cesium.

9.5 Tellurium

Deposits were analyzed for tellurium in only one experiment. No tellurium was found in the deposits. This is considered a significant finding of the program. SOLGASMIX analysis, Chapter 3, showed that tellurium should be stabilized in solution by the formation of UTe_2 and possibly other tellurides. Studies of the melt refining of irradiated uranium indicated that tellurium formed rare earth tellurides which prevented significant volatilization [20].

The absence of tellurium in deposits, although considered significant, should be verified by the complete dissolution and analysis of one or more liners. This would establish whether tellurium was released from the melt, but formed deposits on the tantalum liners which were insoluble in the aqua regia used to remove deposits from liners.

9.6 Molybdenum, Cerium, and Uranium

No cerium or uranium were found in the deposits, consistent with their very low vapor pressures. These findings suggest that little transport occurred by mechanical means, ie., by the transport of solid oxide particles from the melt surfaces. Very small quantities of molybdenum were found in the deposits. Molybdenum transport could have resulted from the formation of trace quantities of volatile molybdenum oxides. Studies of the melt refining of irradiated uranium also indicated that molybdenum and cerium were not volatilized from melts [19,20].

9.7 Zirconium

The solubility of zirconium in molten aluminum is reported to be 0.11% at the aluminum melting point [21]. Thus, it was considered likely that zirconium crucibles could be used for the experiments. However, it was observed that zirconium reacts vigorously with aluminum, probably to form ZrAl_3 , which appeared to be insoluble in the melts. Thus, it was not possible include zirconium in the original preparation of the ingots. Zirconium was included in the crucible charge in each experiment. Its disposition during and after melting was not determined. No zirconium was found in the deposits.

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