Treatment of Off-Gases from Melting Reactor Fuel (U)

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Introduction

The "Melt-Dilute" process has been studied as a method for preparing spent highly enriched reactor fuels for repository disposition.[1] In this process the fuels in question, which are fabricated from aluminum intimately mixed with uranium or its compounds, would be melted together with depleted uranium metal to form a homogeneous material of low ^{235}U enrichment. This material would be of no concern for illegal diversion, and would present acceptably low risk of accidental nuclear criticality. Aluminum melts near 650 °C, and process temperatures near 850 °C are expected.

Spent fuels are contaminated with fission products, some of which are volatile at anticipated melting temperatures. However, as the fuels in question would be cooled for several years, only a few volatile radioisotopes would remain. The most important of these are ^{85}Kr and ^{137}Cs. Krypton, a noble gas emitting weak beta radiation, was shown by radiological calculations to be of no health concern. However, the cesium isotope is a major concern because of its high abundance, long half-life (30.2 y), and its intense gamma radiation.[2] The study reported here was undertaken to determine the behavior of cesium under projected process conditions, and to investigate techniques for its recovery and disposition.

Discussion

Background

Cesium is an alkali metal similar to potassium in its chemistry. In the elemental form it is the most volatile alkali metal, boiling at the relatively low temperature of 671 °C.[3] Elemental cesium is highly reactive with many other materials, especially air and water. With air it reacts to form a series of oxides with compositions between Cs_2O and CsO_2. The reaction of Cs with water produces hydrogen and CsOH, which volatilizes without decomposition at temperatures above about 1000 °C. Cesium oxide is readily incorporated into aluminosilicate compounds, and the resulting materials are stable towards heating. This stability of cesium in silicate structures is exploited in the fixation of nuclear waste, by incorporating radiocesium into stable glass.

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The release of cesium from melting irradiated fuel has been investigated in studies of possible reactor accident scenarios. The review of these studies by Taleyarkhan[4] shows only a fraction of cesium being emitted from molten uranium-aluminum alloy fuel at temperatures below 1000 °C. Inasmuch as elemental cesium is the most likely form of the element in a molten metal environment, this is a somewhat surprising result. Cesium boils at temperatures well below this.

In irradiated fuel, ^{137}Cs is produced along with stable ^{133}Cs and long-lived ^{135}Cs. The 137 isotope constitutes a bit less than a third of total fission product cesium. A small part of this cesium may form compounds with other fission products, including iodine. Cesium iodide, which might amount to a few per cent of fission product cesium, is stable at temperatures below 1000 °C, and is only slightly volatile at 900 °C.

Experimental Procedures

The reactivity of elemental cesium with air and other oxidizing chemicals makes it difficult to prepare non-radioactive simulants of spent fuel for laboratory study. Molten uranium-aluminum fuel contains fission products, including cesium, in an intimate dispersion throughout the metallic lattice. Exact simulation of this process was not possible because cesium-aluminum alloy is not available. (Again, the problem is that cesium boils at temperatures near the melting point of aluminum.) However, at temperatures above ca. 400 °C, cesium oxides begin to decompose and generate elemental cesium.[5] Also, anhydrous cesium carbonate decomposes to carbon dioxide and cesium oxide when heated above about 600 °C. These properties were exploited in this work to generate elemental cesium by thermal decomposition of the monoxide (Cs_2O) or carbonate. The release of cesium from a melt was studied by putting cesium metal, oxide, or carbonate into a cavity in the center of a cylindrical metal (aluminum or U-Al alloy) block, which was then closed with an aluminum screw (Figure 1).

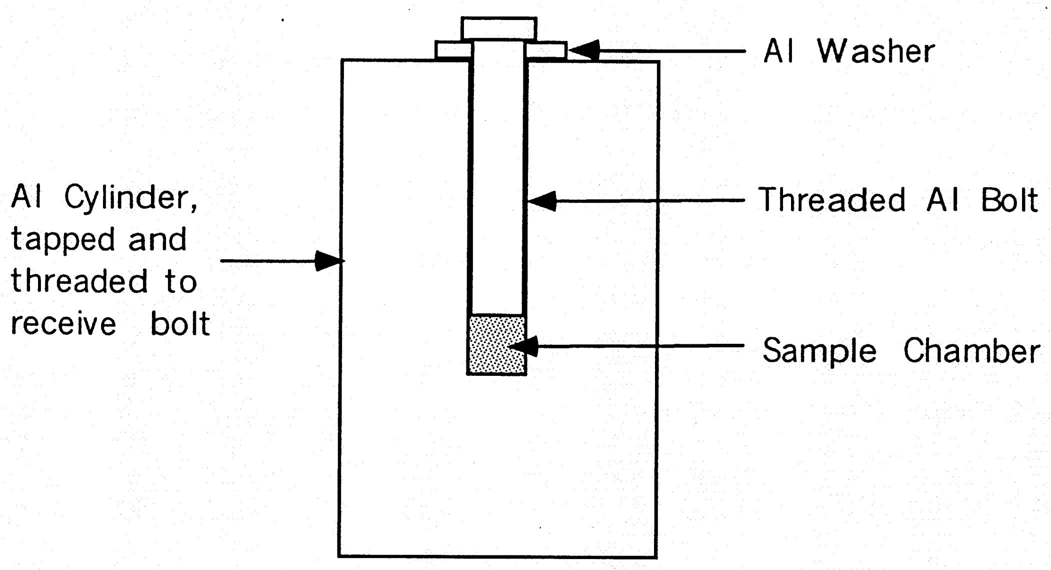

Figure 1: Sample Capsule

On melting of the block, the cesium vapor formed in the cavity will bubble out along with air (or inert gas) from the cavity. This is similar to expected conditions in the molten fuel, in which bubbles will also be generated by the release of noble gas fission products. This simulation proved adequate to provide significant insights concerning the behavior of cesium in the molten metal environment.

The apparatus used in this experiment is shown schematically in Figure 2. The material of interest is inserted into a graphite or steel crucible, which is then placed in a steel outer vessel (the "retort"). The retort is fabricated from two inch (ca. 5 cm) carbon steel pipe, and is about 30 cm long. The portion of the retort containing the crucible is inserted into a Lindbergh resistance furnace. Air is pumped through the retort via an inlet port entering just above the crucible. The flow rate is 2.0 to 2.5 standard cubic feet per hour (scfh) (about 20 mL/sec). Air exiting the retort is passed through an offgas system that typically includes two beds of particulate media, in some cases a thickness of HEPA filter media, and a water scrubber. The superficial velocity through the bed at 2.5 scfh is 1.9 ft/min (0.0097 m/sec).

After some preliminary experiments, a standard heating protocol was developed and used consistently through the remaining studies. This protocol was designed to provide temperatures similar to those that are expected in the melt-dilute process, although time at temperature is less than that anticipated in larger equipment. The retort was heated to a temperature of 850 °C, as measured by a thermocouple located inside the retort just above the crucible. This required about forty-five minutes. The temperature was then maintained at 900 ± 50 °C for about 20 minutes before cutting off the power and allowing the apparatus to coo. Maximum temperatures above 900 °C were always reached. Airflow was maintained for at least 30 minutes during cooldown. This regimen approximates the conditions expected during actual fuel melting, which is expected to require a longer melting time (about an hour) at a slightly lower temperature (ca. 850 °C).

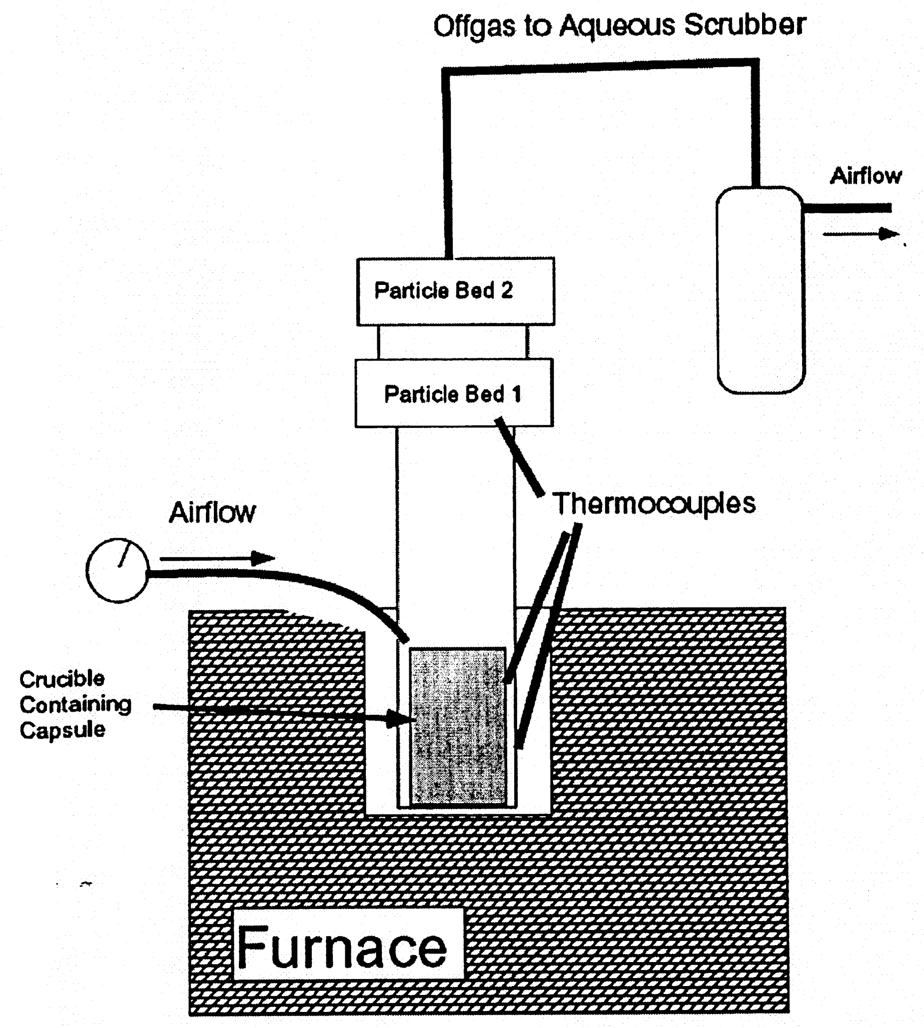

Figure 2: Schematic drawing of experimental arrangement.

Two main types of experiment were conducted. One, which was devised for comparing techniques for retaining cesium, involves introducing a quantity of cesium carbonate at the bottom of a crucible, with no molten metal present. This was intended to provide a reproducible source of cesium vapors. In the other, cesium or one of its compounds is placed into the cylindrical metal capsule shown in Figure 1, and this is then sealed with the screw plug, placed in a crucible and inserted into the retort. (When cesium or cesium oxide was used, this operation was done in a dry argon atmosphere in an inerted box.) Following the experiment, the individual components of the system were recovered and washed with water or dilute acid to recover cesium. Washings were typically taken from the retort, each of the particle beds and their chambers, the retort head above the particle beds, the plastic line leading to the scrubber, and from the crucible. The scrubber water was also sampled. When metal was melted in the crucible, a washing was taken from the combined ingot and crucible unless the ingot could be removed from the crucible. In the latter case, each was washed separately. When HEPA filter material was in line, it was also washed. The washings were made to known volume, sampled, and analyzed for cesium by standard methods.

It quickly became apparent from material balances that not all cesium was being recovered in washes. Qualitative analysis techniques, including x-ray fluorescence, x-ray diffraction, and electron microprobe methods, were used to locate cesium in solid samples. These techniques provided important confirmation that cesium was being fixed in some of the materials under study.

In several studies materials were added to the crucible to decrease the release of cesium. These included glass frit, activated alumina, and zeolite-based molecular sieves. The activated alumina and molecular sieves were also evaluated for retaining cesium in the off-gas train.

The glass frit used was type 165-A. This is a relatively low-melting frit used during startup of electrolytic melters. In physical form it is a gray powder, mainly free-flowing but with some tendency to cake. Although the temperatures reached in this study are below its melting point, it was found to sinter into a semi-transparent glassy mass upon being subjected to the experimental heating cycle.

Two types of activated alumina were used. One was 8x14 granular type A material obtained from Kaiser Chemical or its successor company, LaRoche Chemicals. The other was cylindrical (1/8 in. diameter by 1/8 in. long) activated alumina pellets manufactured for use as a catalyst support. This material was obtained from Alfa Aesar Chemicals. Both kinds were visually unchanged after heating to 900 °C, although the literature indicates that heating to temperatures >400 °C causes the surface area of activated alumina to decrease.[6]

It was found that when activated alumina was used in the offgas train, considerably more cesium could be leached from its surface with dilute (0.075 M) nitric acid than with water. This suggests chemical binding of cesium with the alumina. The dilute acid was routinely used to leach alumina and molecular sieve beads.

Molecular sieves used were Kemp type K-4, obtained as spherical beads of about 1/8 inch diameter. Again, no change of appearance from heating inside the crucible was noted, but in the presence of cesium some beads change color. This color change was found to be associated with cesium uptake, with the lighter colored beads being heavily loaded with cesium. This cesium was not leachable, even with dilute nitric acid. (Unheated molecular sieve was found, in fact, to take up cesium from water solution.) X-ray diffraction analyses showed that the heating cycle converts the molecular sieve to anhydrous aluminosilicates, as suggested by the literature. Molecular sieve beads in the off-gas train close to the retort are probably partially dehydrated, as the temperatures in this area were found to exceed 200 °C. (The first molecular sieve bed was much closer to the top of the furnace than indicated in the schematic drawing in Figure 2, and insulation not shown in that figure was used on the top of the assembly to minimize heat loss from the furnace.)

In one experiment a liner made from "Fiberfrax"® paper was placed inside the crucible, between the graphite wall of the crucible and the Al capsule. ("Fiberfrax" is a trademark of the Carborundum Co.) The purpose was to determine if this liner would protect the crucible from chemical attack, and perhaps also take up cesium into its structure. The liner protruded from the crucible about a half inch, permitting the addition of a bed of molecular sieve beads above the capsule.

Cesium compounds used in these experiments were reagent grade. Cesium metal and oxide (Cs_2O) were obtained from Alfa Inorganics sealed in glass, and were opened in a dry box for loading into capsules. Anhydrous cesium carbonate, a hygroscopic material, was loaded in air with the minimum practical exposure to air to avoid moisture uptake.

A few experiments were made with fission product simulant compacts, in order to evaluate the possible effects of fission products on cesium release and retention. These were of two types; the first consisted of cesium (as carbonate) and other fission products pressed into a cylindrical aluminum pellet. This pellet was roughly ¾ inch (about 2 cm) in diameter and height. Unfortunately, these pellets tended to swell and crack on standing before use. In the second type cesium carbonate was loaded into an aluminum tube which was then pressed flat to form a wafer slightly over an inch in width and four to five inches in length. This arrangement proved stable. Tests with either sort of package involved adding extra aluminum as aluminum rod. The rod sections were placed on top of the cylindrical capsule, or to either side of the wafer.

Results

Major findings in this study include the following. These are discussed below in greater detail.

1. In experiments in which no molten metal was present, most of the cesium remained in the crucible. Typically, less than 0.1 per cent of cesium was recovered from outside the crucible. Inasmuch as both the literature[5] and the evidence of other experiments indicate that a substantial amount of cesium ought to have vaporized, this result indicates that the conditions inside the crucible limit transport of the vapors. This may be partly the result of cesium-crucible chemical interactions, and partly the result of stagnant conditions inside the crucible.
2. In the experiments in which cesium was originally contained in an aluminum (or U-Al alloy) capsule, much of the cesium was released in a form that could be recovered by water washing. Most of the remainder appears to have been concentrated in the oxide layer on the surface of the metal melt. Little cesium remains in the bulk metal. Again, most of the cesium remained inside the crucible. The releases outside the

crucible from this type of experiment were ten or more times higher than in those experiments in which cesium compounds were placed in the bottom of the crucible. The reasons for this may be geometric effects, transport of cesium in gas bubbles, or both.

3. Glass frit, molecular sieve beads, and activated alumina added to the crucible reduce the release of cesium. The lowest levels of leachable cesium were found in those samples containing glass frit, probably because the frit sinters to form an impermeable mass. Cesium is taken up into molecular sieve beads and leached with difficulty; there is also evidence that activated alumina strongly retains cesium. Crystalline silico-titanate does not retain cesium effectively.
4. Scouting experiments showed that CsI vaporized significantly only at temperatures of about 1000 °C. In these experiments silica was present in the heated zone, and it reacted with CsI to release elemental iodine.
5. Very little cesium was released for the experiment with the Fiberfrax® liner. There was no evidence of cesium carbide formation; but the liner adhered to the crucible.

Taken together, these findings suggest that the amount of cesium released to the atmosphere is determined by geometric and mixing factors. In a static system cesium does not migrate very far, even though the majority of the cesium is released from the bulk metal.

The findings from these studies were used to design pilot scale equipment in which a thick heated bed of granulated molecular sieve is used to retain vaporized cesium.

Detailed Observations

Control Experiments. Table I summarizes the results of control experiments in which cesium carbonate was heated in the bottom of the retort without a billet present. Carbonate was used in this experiment because it is less reactive or deliquescent than other cesium compounds that might be selected. (One experiment used cesium oxide.) With the exception of one anomalous experiment, little cesium was recovered outside the crucible. When other materials ("flux") were added to the crucible, a little cesium was still emitted but overall recovery of cesium was quite poor, indicating that it became tied up with the flux material.

The reason for the anomalous sample is unknown, but may be a confusion of analytical samples or a mechanical transfer of cesium during handling. (Experiments 2-19 and 2-26 essentially replicate the conditions of 2-18, placing the results from that experiment in question.)

Most of the small amount (less than 0.1 per cent of total cesium) released from the crucible in each experiment was found on the walls of the retort.

The small amount of material released is attributed to the distance (about 8 cm) from the top of the cesium carbonate bed to the top of the crucible. Apparently, even though cesium carbonate is decomposed, the resulting vapors and aerosols do not move very far before being fixed on the wall of the crucible.

The volatilization of cesium from the carbonate under these conditions was confirmed in an experiment in which a stainless steel (SS) vacuum retort was used instead of the carbon steel equipment used in the remaining experiments. Cesium carbonate was placed in the bottom of the SS retort, and the unit was evacuated before being subjected to the same heating cycle used in other experiments. Following cool-down and reopening, cesium compounds and cesium metal were recovered from the cooler upper section of the retort. (Cesium metal was identified by probing the deposits, which sparked spontaneously.) This confirmed that the rate of cesium release was significant under vacuum conditions, and the small releases from the crucible tests in air were the result of limited cesium diffusion rates in air.

The experiments with other materials in the crucible provide additional insights on cesium behavior. The glass frit used in experiment 2-19 essentially sealed the cesium in the bottom of the crucible in a solid mass, from which less than 1% could be leached by a water wash. Crystalline silico-titanate (02-17) appeared to decompose at the temperature of the experiment, and had only a small effect on the leachability of cesium. On the other hand, both activated alumina and molecular sieve took up most of the cesium, and only a part of the total cesium could be recovered from these by leaching. Microprobe analysis of the molecular sieve beads showed that cesium had been incorporated into the material structure. These data suggest that the presence of zeolites in the crucible reduced the release of cesium from the crucible. The glass frit appears to tie up cesium remaining in the crucible in an unleachable form.

Table I: Volatility of Cesium from Cesium Carbonate

Expt #	Flux	Crucible	Cs in Crucible, %	Cs ex crucible, %
01-8	None	Graphite	40.6 (Oxide)	0.02
02-15	None	Steel	89.4	0.11
02-16	165 Frit	Steel	0.43	0.06
02-17	CST	Steel	68.1	0.09
02-18	None	Steel	0.58	81.4
02-19	None	Steel	80.2	0.05
02-20	zeolite	Steel	0.48 (+12.4)*	0.01
02-21	AA	Steel	0.96 (+53.9)**	0.07
02-23	None	St. Steel	90.0	0.01
02-26	None	Steel	97.8	0.05

*Recovered by leaching molecular sieve beads.
**Recovered by leaching activated alumina particles

Abbreviations: CST = Crystalline silico-titanate; AA= Activated alumina

Capsule experiments. Table II summarizes a wide variety of experiments performed using the capsules and apparatus pictures in Figure 2. The poor material balances for cesium reflect the problems in trying to recover the solidified metal "billets" formed when the aluminum capsule melted and consolidated in the bottom of the crucible.

A major problem was removing the metal billet from the crucible. In most cases the billet could be recovered only with difficulty, i. e., by pounding on the crucible, and some material was lost in this process. Some billets could not be separated from the crucible. In several such cases the crucible was cut apart with a saw. Some Cs could be leached from the resulting fragments, but could not be quantitatively recovered. The cesium appeared to concentrate at the interface between billet and crucible, as anticipated.

It is known that cesium can react with graphite to form cesium carbide, and this happened in some experiments that used graphite crucibles. Bubbles of acetylene were observed on washing the crucible with water. This was of some concern, as an induction furnace with a graphite crucible was to be used with actual fuel. A coating ("Mold wash") was applied to the crucible in several experiments to minimize this reaction.

It is important to note that the fraction of cesium found outside the crucible was much higher in these experiments than in those with no metal capsule. This is attributed to cesium transport by the air present in the chamber containing cesium at the time of melting. In addition, the cesium starts out higher in the crucible and closer to the moving air stream.

In one experiment a capsule made from uranium-aluminum alloy was used. The uranium had no significant effect.

Table II: Data Obtained from Capsule Experiments

Expt.#	Crucible	Capsule	Cs Form	Additive	Cs in Crucible,% (+Billet)	Cs ex Cruc., %
01-7	Graph.	Al	CsI	None	0.4	0.04
02-1	Graph.	Al	Oxide	None	32.8	1.49
02-3	Graph.	Al	Oxide	None	34.1	0.78
02-4	Steel	Al	Carb.	None	33.0	0.37
02-5	Steel	Al	Carb.	Frit	2.1	0.75
02-6	Steel	Al	Metal	None	55.3	2.5
02-7	Steel	Al	Metal	Frit	4.2	1.10
02-8	Steel	Al	Oxide	None	10.5	0.82
02-9	Steel	Al	Oxide	Frit	0.0	0.18
02-12	G, MW	Al	Oxide	None	38.6	4.48
02-13	S, MW	Al	Oxide	None	43.3	0.69
02-14	S, MW	Al	Oxide	CST	32.4	1.79
02-24	Graph.	Al	Carb.	None	NR	0.13
02-27	Steel	Al	Carb.	Z	2.8(+4.5)	0.07
02-28	Graph.	U-Al	Carb.	None	67.0	2.7
02-33	G, lined	Al	Carb.	Z	46.8	0.10

Abbreviations: Graph. or G = Graphite; MW = Aluminum oxide Mold Wash applied to crucible; S = Steel; U-Al = Depleted uranium-aluminum alloy; Oxide = Cs_2O; Carb. = Cs_2O_3; Frit = 165A glass frit; CST = crystalline silico-titanate; Z = Zeolite molecular sieve beads; NR = Not recovered.

Fission Products. Experiments with fission product simulants present are summarized in Table III.

The composite buttons in tests 2-22 and 2-25 contained cesium carbonate and other fission product simulants pressed into a small Al cylinder. The total weight of each button was about 20 g. Unfortunately, these two composites were cracked upon receipt, and it appeared that some material had been lost from them. The material balance from the experiment was therefore uncertain. Following the experiment these compacts essentially maintained their original sizes and shapes. This is attributed to the aluminum oxide distributed throughout the compact (which was formed from pressed Al powder), and to the presence of refractory fission product simulants. As in other experiments in which cesium compounds were heated at the bottom of the crucible, little cesium was lost from the crucible following the heating cycle.

In experiments 2-29 and 2-30 cesium carbonate and other fission product simulants were encapsulated in flat rolled wafers as previously described. These were long enough to protrude from the crucible by several cm. Pieces of aluminum tubing were placed in the bottom of the crucible to hold this wafer in a vertical position. After the heating cycle it was found that the wafer remained in its original shape and position, though it was mostly oxidized. The oxidized wafers were brittle and crumbly. In experiment 2-30 the molecular sieve beads in contact with the plate had turned white, perhaps from taking up cesium. The aluminum spacers in the bottom of the crucible appeared to have melted into a pool, and no longer retained their original shapes. Perhaps the reaction of the cesium compounds with aluminum thickened and toughened the oxide in the pressed piece. Because the wafer containing the cesium actually protruded from the crucible, the amount of cesium recovered outside the crucible was also larger than had been seen before.

These experiments show the difficulty of simulating the fission product content of irradiated fuel, and also suggest that the presence of fission products may somewhat affect the behavior of the fuel on melting.

Table III: Simulant Fuel Studies (Abbreviations as in Table II)

Test #`	Material	Conditions	Cs in Crucible, %	Cs ex Crucible, %
02-22	Composite	G	1.2	0.14
02-25	Composite	G, U-Al*	0.0	0.00
02-29	Pressed	S	9.7	12.2
02-30	Pressed	S, Z	13.9**	0.23

*A piece of uranium-aluminum alloy, weighing 158.6 g, was loaded into the crucible on top of the button

**Includes 3.4% of cesium leached from molecular sieve beads in crucible.

Particle Bed Effects. Evaluating the effectiveness of the particle beds in retaining cesium was complicated by two factors. First, the amount of cesium recovered downstream of these beds was always very low, of the order of 0.01 per cent. Second, it was determined that the cesium was strongly retained on the particles, and the simple leaching techniques used almost certainly underestimated this retention. Data suggested that a decontamination factor between 20 and 100 was obtained, but these numbers are almost certainly too low. A more realistic estimate would be a DF of 100 or more.

Miscellaneous Observations

A complication in working at this scale is the relatively high strength of the oxide layer on the outside of aluminum. Although usually quite thin, this layer is tough enough to contain tens or hundreds of grams of molten aluminum and prevent it from bursting through under its own weight. Remarkably, for a ceramic material, this outside layer can deform and sag while containing the liquid aluminum.

This tough oxide layer has led to some interesting observations. In early experiments in which the aluminum was heated to a somewhat lower temperature than the standard protocol, the aluminum melted, but the aluminum screw only deformed and could be clearly discerned in a cut section. In another experiment a piece of uranium-aluminum alloy was placed in a crucible on top of a bed of molecular sieve beads. After heating to above 900 °C it was found to have sagged down on top of the beads, but not to have flowed through them. The beads were intact. As previously noted, pressed pieces containing cesium and other fission products apparently form a particularly thick and strong oxide layer, and tended to retain their original shape.

This behavior of small melted aluminum pieces emphasizes the importance of doing tests on a larger scale prior to startup of hot tests. On a larger scale the aluminum can more easily break through the oxide skin and flow downwards.

Implications of this work

As noted above, larger equipment designed for melting simulated or actual fuel was designed around an induction furnace with a graphite crucible. The induction process stirs the melt, and this may promote the release of cesium from the melt. From the observations in these studies, a separately heated particle bed was designed for the off-gas stream to trap and hold cesium vapors or aerosols emitted from the heating chamber. A limited number of larger-scale simulation experiments suggest that this is very effective.

Acknowledgments

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