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**VAPORIZATION OF ELEMENTAL MERCURY
FROM POOLS OF MOLTEN LEAD AT LOW CONCENTRATIONS**

by

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ENERGY SCIENCES AND TECHNOLOGY DEPARTMENT

**Brookhaven National Laboratory
Brookhaven Science Associates
Upton, Long Island, New York 11973**

**Under Contract No. DE-AC02-98CH10886 with the
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ABSTRACT

Should coolant accidentally be lost to the APT (Accelerator Production of Tritium) blanket and target, and the decay heat in the target be deposited in the surrounding blanket by thermal radiation, temperatures in the blanket modules could exceed structural limits and cause a physical collapse of the blanket modules into a non-coolable geometry. Such a sequence of unmitigated events could result in some melting of the APT blanket and create the potential for the release of mercury into the target-blanket cavity air space. Experiments were conducted which simulate such hypothetical accident conditions in order to measure the rate of vaporization of elemental mercury from pools of molten lead to quantify the possible severe accident source term for the APT blanket region. Molten pools of from 0.01% to 0.10% mercury in lead were prepared under inert conditions. Experiments were conducted, which varied in duration from several hours to as long as a month, to measure the mercury vaporization from the lead pools. The melt pools and gas atmospheres were held fixed at 340°C during the tests. Parameters which were varied in the tests included the mercury concentration, gas flow rate over the melt and agitation of the melt, gas atmosphere composition and the addition of aluminum to the melt. The vaporization of mercury was found to scale roughly linearly with the concentration of mercury in the pool. Variations in the gas flow rates were not found to have any effect on the mass transfer, however agitation of the melt by a submerged stirrer did enhance the mercury vaporization rate. The rate of mercury vaporization with an argon (inert) atmosphere was found to exceed that for an air (oxidizing) atmosphere by as much as a factor of from ten to 20; the causal factor in this variation was the formation of an oxide layer over the melt pool with the air atmosphere which served to retard mass transfer across the melt-atmosphere interface. Aluminum was introduced into the melt to investigate its effect upon the mercury vaporization rate in simulation of the aluminum structure in the APT blanket. No effect at all was observed for a case with an argon atmosphere. This suggests that there are no chemical effects of the aluminum on the vaporization kinetics. With an air atmosphere, the presence of aluminum in the melt reduced the mercury vaporization by a factor of six in comparison to the identical test but without aluminum present. This suggests that aluminum in the lead/mercury melt retards the vaporization of mercury by creating a surface oxide layer in addition to the lead-oxide layer which increases the mass transfer resistance.

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INTRODUCTION

The primary contributors to the accident source term for APT come from the proton-irradiated tungsten spallation target and the surrounding lead/aluminum blanket. From the tungsten spallation target, the principal spallation products that are considered in accident analyses are activated isotopes of tungsten which could be released by oxidation and subsequent vaporization in steam should temperatures in the target exceed 700°C. From the blanket, the principal spallation products that are considered in accident analyses are isotopes of mercury produced in the lead which could be released by vaporization should temperatures in the blanket exceed the lead melting temperature of 327°C. The present investigation attempts to quantify the release of elemental mercury from the APT blanket under severe and unmitigated accident conditions in which temperatures in excess of the lead melting temperature are achieved and maintained in the lead blanket.

Activated isotopes of mercury would be produced in the APT lead blanket as a result of nuclear reactions in the lead with protons and neutrons emanating from the tungsten spallation target. Calculations indicate that in the highest power regions of the blanket, the concentration of mercury in the lead could approach 0.012% by weight after one year of operation at full accelerator power (170 MW) and availability (75%). The mercury concentration after five years of service would be approximately 0.06% [1]. These isotopes of mercury would have little or no mobility and would remain in the bulk of the lead and pose no corrosion or health problems as long as normal operating conditions were maintained in the blanket. Although concentrated mercury has a high vapor pressure and would rapidly vaporize at temperatures characteristic of normal operating conditions of the APT blanket, no vaporization of mercury from the lead blanket would be expected in APT under normal operating conditions because the mercury would be at low concentrations in a matrix of solid lead which would retard mass transfer and the entire structure would be encapsulated in an aluminum-clad structure and be cooled by flowing water.

Should coolant accidentally be lost to the APT blanket and target and the decay heat in the target be deposited in the surrounding blanket by thermal radiation, temperatures in the blanket modules could exceed structural limits and cause a physical collapse of the blanket modules into a non-coolable geometry. Such a sequence of unmitigated events could result in some melting of the APT blanket and create the potential for the release of mercury from the damaged modules into the target-blanket cavity air space. The prevailing hypothetical accident conditions which could be expected would be temperatures close to the lead melting temperature (327°C), an air or air/steam atmosphere, upper-limit mercury concentrations of 0.012% by weight, and aluminum in the melt pool from the blanket structures. It is necessary to be able to estimate the extent of the mercury release from the lead for purposes of safety analyses and estimates of environmental impacts. The series of experiments which will be discussed provide an empirical basis from which such estimates may be made and parametric variations considered. The test parameters which will be examined are intended to permit direct comparison of the experimental data to possible APT severe accident conditions and to support the determinations of functional [2] and hazard classifications [3] of the facility and safety systems.

EXPERIMENTAL APPARATUS

The apparatus used in this study was designed and constructed to incorporate features that enhance its safety, reliability, and ease of use. The entire apparatus was constructed on a lab rack in a stainless steel secondary containment pan mounted on a test stand in a large lab fume hood. The pan provided protection from potential spills or leaks of mercury, and the fume hood provided protection from mercury vapors in the event of the failure of a cold trap. The apparatus was robustly constructed from commercial off-the-shelf hardware and labware incorporating standard tapered joint connections for the glass components, facilitating fast servicing. A schematic of the experimental apparatus is shown in Figure 1.

The melt vessel was assembled using a 316 stainless steel hemispherical reaction flask with a four inch neck opening (Ace Glass Inc. p/n 6497-12) and a Pyrex three-neck reaction flask head (Ace Glass p/n 6486). The inside diameter of the stainless steel reaction flask measured at the surface of a typical molten pool was 4.29 inches. Both pieces were mounted to the test stand as a single unit using a quick release design clamp (Ace Glass p/n 6496) and flat Teflon gasket. A heavy-duty hemispherical heating mantle was mounted immediately below the reaction flask. This heating mantle was equipped with several type-K thermocouples, a temperature controller, and a supplemental insulation package to provide stable control of the melt temperature. The left-hand neck of the flask top was connected to a gas supply system capable of delivering heated air or argon to the vessel via mass flow controllers. The center neck of the flask top was equipped with a Trubore® stirrer assembly (Ace Glass p/n 8064) driven by a remotely mounted variable speed motor via a flexible shaft. The stirrer blade is a chordal segment of a circle with radius 1.75 inches and a chord length of 2.792 inches; the blade's thickness is 0.129 inch. The right-hand neck of the flask top was fitted with a Pyrex "transfer line" leading to the cold trap. This transfer line, shaped like an inverted U, provided approximately eight inches of lateral separation between the reaction flask and the cold trap. To prevent unwanted condensation of mercury vapors, this line was trace heated with a heating tape and equipped with type-K thermocouples and a temperature controller to maintain a wall temperature of about 100°C. A series of U shaped cold traps were fabricated from Pyrex to be installed as required on the end of the transfer line. A Dewar flask containing a slurry of dry ice and acetone was raised up around the cold traps after they were installed on the transfer line to cause the mercury vapors in the flowing gas stream to condense. All glass joints were sealed with standard Teflon tapered joint sleeves. All glass surfaces and gas supply lines were either heavily insulated or trace heated to prevent accidental mercury condensation.

EXPERIMENTAL PROCEDURES

The following procedure was employed to conduct the mercury vaporization tests. An initial charge of about 2.5 kg of lead strip was cut for loading. The lead was weighed on a Sartorius electronic top loading balance to a precision of 0.1 gram. The reaction flask was heated to approximately 350°C and an argon cover gas flow was established through the apparatus. The stirrer assembly normally

installed in the center neck of the flask was removed and the center neck used to introduce the lead to the flask. Lead strips were continuously added to the flask as they melted into the pool. When all of the lead was melted into the pool, it was stirred manually and skimmed of slag. This slag was collected and weighed and the mass of slag subtracted from the initial charge of lead to give the mass of the pool. The temperature of the pool as well as the temperature of the cover gas and transfer line were adjusted and stabilized at the desired set points. The stirrer assembly was then installed in the center neck and set to stir the pool in preparation for mercury injection.

To introduce the mercury into the pool, a hypodermic syringe with a long spinal needle was used. The syringe and needle were tare weighed using a Sartorius analytical balance capable of weighing to a precision of 0.1 mg. The balance calibration was frequently checked using both its internal 100 g standard mass and an external 50 g standard mass. An amount of mercury appropriate to give the desired mercury concentration was taken up in the syringe and the syringe reweighed. The transfer line was temporarily disconnected from the flask and, with vigorous stirring, the mercury was injected into the bulk of the pool to achieve the desired mercury concentration. Post injection mass measurement of the syringe was recorded to calculate the actual mercury concentration. The transfer line was then reconnected and a tare weighed set-up collection trap installed on the end. A Dewar flask containing a slurry of crushed dry ice and acetone was elevated around the sample collection trap. This slurry maintained the trap at about -80°C , a temperature at which mercury has virtually no vapor pressure [4]. Stirring, gas species temperature and flow rate, pool temperature, dry ice replacement and trap change outs were attended to as prescribed in run sheets prepared for each test. The lead temperature and gas atmosphere were measured and controlled with standard type-K thermocouples, each with an uncertainty of 2.5°C . The gas flows were calibrated by using a "soap bubble flow meter" to time the delivery of a fixed volume of gas. The flow meter is constructed from a standard 100 ml. laboratory burette which has a volume tolerance of 0.2 ml. For the 200 ml/min flow setting, the uncertainty in the calibration is estimated to be 6%; for the 750 ml/min setting, the uncertainty in the calibration is estimated to be 2%. As traps were changed out, they were placed in a desiccator prior to weighing to remove atmospheric moisture that condensed on their cold (-80°C) surfaces. The uncertainty in elapsed time was negligible. When dry, the traps were weighed and their masses compared to pre-run masses to determine the mass of mercury collected. The masses of mercury injected into the melt as well as the masses of mercury collected in the cold traps were measured to an accuracy of ± 0.5 mg.

Upon completion of a test, the following procedure was used for recovery. A waste trap was installed on the transfer line. The stirrer was elevated without removing it from the apparatus so that it would not freeze in the pool. The pool heat was turned off and the pool was allowed to solidify. After the pool had cooled, all other heat was turned off and the glass components were allowed to cool. The reaction flask top was removed, the stainless steel flask lifted from the mounting ring and heating mantle, and the solidified lead/mercury slug removed and stored for proper disposal. All glassware was cleaned in nitric acid to remove any traces of mercury, and the acid was stored for proper disposal.

CONDUCT OF EXPERIMENTS

A series of tests was executed to quantify the effects of several dominant parameters upon the rate of vaporization of elemental mercury from pools of molten lead to simulate postulated severe accident conditions in the APT blanket regions. The matrix of parameters which was considered for these tests included variations in melt temperature (low/high), melt composition (Pb, Pb/Hg), gas composition (air, argon), gas flow rates (low/high), aluminum in the melt and circulation of the melt. All of the parametric variations were investigated with the exception of the high temperature melt cases, which were omitted for programmatic reasons. The experimental uncertainties of these parameters are listed in Table 1. A discussion of each of the tests and their results is given below. The reader will note that there is no test designated as Hg-Pb/07. This test failed during execution and the run number was not recycled. Several tables which summarize the test parameters and results have been provided for the readers' reference. Table 1 provides a listing of the nominal test parameters and their ranges. The specifications for the individual tests are provided in Table 2. Table 3 provides a comprehensive listing of the experimental results of the ten tests.

Hg-Pb/00

This test was the first in the series and was conducted primarily to provide a shakedown test of the experimental apparatus. All the features of the apparatus were exercised including the melt, gas, and trace heaters, as well as the dry-ice/acetone cold trap for condensation and collection of mercury vapors. The heating systems achieved and maintained pre-established set points after several modifications to the heater configuration and insulation packaging. A second objective of the test was to address an issue which was raised during the review process, and this was the possibility of lead being carried over from the melt crucible into the heated gas-discharge plumbing and deposited in the cold traps, thus affecting the mercury mass measurements. The concern was whether the mass collected in the cold traps would be all mercury or would it be a lead/mercury mixture requiring complex post-experiment chemical analyses. The results of the experiment conclusively demonstrated that there was no measurable increase in the mass of the cold traps after more than 24 hours of service at the prescribed nominal test conditions of 340°C for both melt and flowing gas. These results confirmed our assumptions during the design phase that only volatile components in the melt would accumulate in the cold traps and that, if high-purity lead sheet material were used for the melt preparation, the collection of other volatile or semi-volatile contaminants could be eliminated as well. The use of a set-up cold trap for the melt preparation stage of the experiments also helped to capture volatile contaminants prior to the actual start of the timed experiments, after steady state conditions had been achieved.

Hg-Pb/01

The second test in the series, designated as Hg-Pb/01, was conducted to evaluate mercury injection and mixing techniques, the cold trap collection efficiency, and initial mercury vaporization results for a case with a grossly bounding concentration, in this case 1% mercury by weight. This experiment helped to finalize procedures and techniques for the mercury injection and mixing (by

means of a submerged stirrer) which allowed us to optimize the mixing and avoid excessive mercury loss through unwanted vaporization during the injection period. The dry ice/acetone cold trap technique for condensing and collecting the mercury vapors which were released from the molten pool worked as intended. All the mercury was found to condense in the U-tube at the dry ice/acetone interface in small droplets on the inside of the glass tube. These droplets were easily agglomerated into a larger droplet by mechanical agitation of the U-tube and able to be returned to the mercury inventory after the gravimetric analysis had been completed, thus reducing the waste stream. Mercury vapor dosimetry and detection equipment were used to sniff the gas discharge from the cold traps to the breathing zone to measure any possible vapor discharge. None was measured. Since this experiment employed the highest mercury concentration expected in any of the future tests, it was concluded that the cold trap technique would be 100% efficient at condensing and collecting mercury vapors.

The mercury concentration was established at 1% by weight for this test, 83 times greater than the maximum concentration expected in the APT blanket after one year of irradiation and 17 times greater than the maximum five-year concentration. This gross upper bound concentration was established for this test in the expectation that no vaporization of mercury would be measured, thus simplifying the remainder of the series needed for the accident source term assessment to a variation in pool agitation and possibly aluminum in the melt. This expectation was immediately dispelled by the results. Vaporization of mercury from the molten lead pool at this high concentration was immediate and excessive. Greyish deposits of mercury formed on all the glass surfaces immediately and, over a period of two hours, nearly 5% of the mercury in the lead was collected in the cold trap. The average mercury release, extrapolated to a 24-hour period, was calculated to be 56% per day. The test was terminated and it was decided to restrict the mercury concentration in the lead to a maximum of 0.1% for future tests, with some tests conducted at 0.01% to evaluate the scaling of mercury concentration on the vaporization rate. These two concentrations are consistent with the 5-year and 1-year maximum concentrations in the APT blanket, respectively.

Hg-Pb/02a, b

The first quantitative test in the series was Hg-Pb/02. The parameters of this test were as follows: lead pool 2.5 kg (nominally identical for all tests), mercury concentration 0.11% and an argon cover gas. There was no melt agitation during the test, gas flow was low (200 ml/min) and there was no aluminum added to the melt. This test was inadvertently performed in two stages. Hg-Pb/02a consisted of three sequential cold trap changes over an elapsed time of eight hours. The power to the melt heater was turned off after this elapsed time and the melt was allowed to solidify. The three cold traps were desiccated to remove all moisture as was the procedure with all cold traps and then weighed to determine the cumulative mass release of mercury over the eight hour period. It was immediately observed from the results that the mercury release was still continuing after eight hours; as a result, the test was resumed with the designation Hg-Pb-02b, using the same melt charge and the test was run out to a total duration of 48 hours. The combined results of Hg-Pb/02a and Hg-Pb/02b are shown in Figure 2. The total mass of mercury released after 24 hours was found to be 0.33 grams out of an initial inventory of 2.83 gm, a release fraction of 12%. This release fraction,

when averaged to a 24-hour period, was found to be 5.9% per day on average. (Note: in a later comparison of results, Hg-Pb/02 will be superseded by Hg-Pb/11 which was a repeat of Hg-Pb/02 but was uninterrupted over a period of seven days.)

Hg-Pb/03

The parameters for this test were identical to those for the previous test with the exception of the mercury concentration. The mercury concentration for this test was reduced by a factor of ten to 0.012% to provide a comparison to the results of Hg-Pb/02 on the basis of initial mercury concentration. All other parameters including argon cover gas were unchanged. The mercury concentration of 0.01% is nearly equal to the maximum calculated mercury concentration in the APT blanket after one year of operation. This test, building on the lessons from the previous test, was set up to run for seven days. The results of this test are shown in Figure 2 along with the previous test (Hg-Pb/02). The total mass of mercury released from the melt was found to be 10.2% over a period of nearly seven days. This computes to an average release fraction per day of 1.5%. The average mass flux per unit area is 2.2×10^{-6} gm/cm² hr. However, it is more reliable to compare the results to Hg-Pb/11 instead of Hg-Pb/02 for reasons already discussed. The average mass flux per area for Hg-Pb/11 was 4.2×10^{-5} gm/cm² hr. This comparison shows that the release rate scales nearly linearly with concentration. The concentration ratio for Hg-Pb/03 to Hg-Pb/11 is about 8.6 while the vaporization mass flux/unit area ratio is about 19.3, about a factor of two different as could be expected. The mercury release fraction for Hg-Pb/03 when normalized to a 24-hour period, was found to be 1.5% per day, a little less than half of the value for Hg-Pb/11 of 3.43% per day.

Hg-Pb/04

The primary purpose of this test was to examine the effect of mass transfer resistance in the gas phase on the rate of vaporization of mercury from molten pools of lead. The mercury concentration was established at 0.11%, the gas and melt temperatures were set to 340°C as in all the other tests, and the test was begun with the nominal low argon gas flow rate of 200 cm³/min. After 26 hours (1583 minutes), the gas flow was increased to 750 cm³/min, and after 43 hours (2588 minutes) the gas flow was reduced back to 200 cm³/min. The data are shown in Figure 3 along with the data for Hg-Pb/05 (which examined the effects of mass transfer in the melt). It is clear from Figure 3 that although the gas flow was increased by almost a factor of four in the middle of the test, there is no apparent change in the rate of mercury vaporization from the melt. It was concluded from this test that gas phase mass transfer is not a significant resistance to the vaporization rate and, thus, not a significant parameter to consider. The fractional mercury release per day was measured to be 2.7%, comparable to tests Hg-Pb/02, 03, 10 and 11.

Hg-Pb/05

The primary purpose of this test was to examine the effect of the mass transfer resistance in the condensed phase (melt pool) on the rate of vaporization of mercury from molten pools of lead. Once

again, the mercury concentration was established at 0.11% and the gas and melt temperatures were held at 340°C. The cover gas was argon and the flow was set to 200 cm³/min (this is the default gas flow rate for all the tests). The glass stirrer which was used to initially mix the mercury in the melt was left submerged during the experiment. For the approximate time period 1200 to 2700 minutes (24.5 hours), the stirrer was turned on in the melt at a rate of approximately one rpm. After 2700 minutes, the stirrer was once again turned off. The data are shown in Figure 3 along with the data for Hg-Pb/04. The vaporization rate began at a low rate but was observed to suddenly increase dramatically until, at about 2700 minutes, the release rate once again flattened to a low value. The release fraction during the melt stirring period was found to be nearly 21% per day. For the times prior to stirring and after stirring, the normalized fractional mercury releases were 0.25% per day and 2.1% per day, respectively. It was concluded that enhanced mass transfer in the lead pool would significantly increase the mercury vaporization rate above the stagnant case. Fortunately, an accident in the APT blanket would be expected to involve a stagnant pool of lead at a temperature close to its freezing point; since the surface of the lead would be hotter than the bottom, the pool would be stably stratified and no buoyancy-driven convection would be expected. Thus, enhancement of mercury vaporization by condensed phase mass transfer would not occur. Instead, the release of mercury from the molten lead pool would be a transient diffusion process in which the surface concentration would be continuously depleted due to vaporization; steady state would only be achieved if thermal convection in the pool could replenish the surface depletion of mercury.

Hg-Pb/06

All the experiments through Hg-Pb/05 used argon for the cover gas although, for the APT accident case, the atmosphere would be air with some steam. To examine the effect of an oxidizing atmosphere instead of an inert gas atmosphere, a set of experiments were conducted with air. The first test in this set was Hg-Pb/06, which had the default set of test parameters (200 ml/min gas flow, no melt agitation, 0.10% mercury concentration) with the exception that an air atmosphere was used instead of argon. Melt and gas temperatures were set to 340°C as usual. The rate of mercury release was relatively high at the beginning of the test for the first collection period of 15 hours. After the initial collection period, the cold traps were replaced on 24-hour intervals to a total elapsed time for the test of 14 days. After the first mass collection, the collected mass decreased over the remainder of the 14 days by a factor of from 10 to 50, due to a lead oxide film which formed on the surface of the pool. Whereas the mass collected in the first 24-hour period was 86 mg, in the second 24-hour period only 5 mg were collected and, in the 14th day, less than 2 mg was collected. The results of this test are shown in Figure 4 and again in Figure 5. Whereas for the earlier tests with an argon atmosphere the average daily mercury release fractions were in the range 3-6% per day (for an initial mercury concentration of 0.1%), for Hg-Pb/06 the average daily release fraction was only 0.3%, a reduction in the vaporization rate by a factor of 10-20 due to the oxidizing atmosphere effect.

Hg-Pb/08

This test was conducted to reproduce the conditions of test Hg-Pb/06 with the one exception that the mercury concentration was reduced to 0.011% to examine the effect of concentration in the presence

of an oxidizing (air) environment. This mercury concentration is a factor of ten less than Hg-Pb/06. This permits a comparison of the effects of initial mercury concentration just like with the two tests with argon, Hg-Pb/02 and 03 which are shown in Figure 2. Once again, the gas flow and temperature settings were nominal. The overall duration of this test was increased from 14 days to 27 days in light of the low concentration of mercury and the previous observation that the release rate would be roughly proportional to changes in the concentration of mercury in the pool. The mass of mercury collected in the first 48 hour period was only 2.4 mg, compared to 86 mg of mercury collected in the first 24 hours of Hg-Pb/06. Only 8.5 mg more were collected over the remaining 25 days, less than 0.4 mg/day on average. At the end of 27 days, a total of 10.9 mg of mercury had been collected during this test and the mercury release rate had decreased essentially to zero. This compared to a total of 112 mg released in Hg-Pb/06, a factor of ten more at a mercury concentration a factor of ten more than this test. The results of Hg-Pb/08 are shown in Figure 4 along with the results of Hg-Pb/06 for comparison. The conclusions from this test are that the mercury release rate does indeed scale with mercury concentration and the formation of a surface oxide layer due to an oxidizing atmosphere presents a significant resistance to vaporization over the case with an unoxidized surface. The combination of factors in this test, air atmosphere and 0.01% mercury concentration, contributed to reducing the mercury vaporization rate by nearly two orders of magnitude below Hg-Pb/02 and Hg-Pb/11 (argon atmosphere, 0.1% mercury).

Hg-Pb/09

This test was a repeat of all the test parameters from a previous test (Hg-Pb/06: air atmosphere and 0.1% mercury) with the addition of a new test parameter, the addition of aluminum to the molten lead pool. The proposed APT blanket region is an extensive structure of lead columns which surround the tungsten spallation target. These columns of lead are enclosed in thin-walled aluminum cans and it has been postulated that upon melting, aluminum could become dissolved in the molten lead. Although the solubility of aluminum in lead at 340°C is extremely slight (only 0.04% at 500°C), the effects upon vaporization and oxidation reactions can, in principle, be strongly affected by a minor melt constituent which has a strong effect upon the oxygen potential of the melt, such as aluminum. Therefore, the presence of aluminum was included in the test matrix to determine what effect, if any, it would have on the rate of vaporization of mercury from the pool.

The approach which was taken to introduce aluminum into the melt was rather simple, although not quantitative. The stirrer mechanism which was used to mix the mercury as it was injected into the pool had a glass paddle which was replaced by one made out of aluminum. In earlier experiments, the pool was stirred after the mercury injection for approximately two hours. In order to allow time for aluminum to dissolve into the melt from the stirrer paddle, this stirring period was increased from two hours to more than six hours. Afterwards, the aluminum stirrer was left submerged in the melt for the duration of the test to allow for continued dissolution.

Hg-Pb/09 was run for a total duration of 14 days. Gravimetric analyses of the cold traps indicated that out of a total mercury release of 16.5 mg in 14 days, 5.7 mg was collected in the first 16 hours; the remaining 11 mg was released at a continuously decreasing rate for the duration of the 14-day

test. The overall mercury release fraction for this test was 0.7% at a daily average release rate of 0.05% per day. These results are a factor of six less than the same results from Hg-Pb/06 indicating a retarding effect of aluminum in the melt on the mercury vaporization rate with an air (oxidizing) atmosphere. These results are shown in Figure 5 which is a comprehensive compilation of four tests, Hg-Pb/06, 09, 10 and 11.

Hg-Pb/10

The conclusion from Hg-Pb/09 was that an aluminum oxide film might form over the surface of the pool with aluminum in the melt and an air atmosphere. This would be in addition to the lead oxide film that was customarily observed with air. In order to test this obvious conclusion, Hg-Pb/10 was conducted to repeat the conditions of Hg-Pb/09 but with an argon atmosphere instead of air, thus eliminating oxidation reactions from consideration. If there were no effects of aluminum in the melt on mercury vaporization, the results should agree with Hg-Pb/11 (the replacement test for Hg-Pb/02). If the effects of the aluminum are similar to those in Hg-Pb/09, then the results should lie below Hg-Pb/11. The melt preparation procedures for Hg-Pb/10 were identical to Hg-Pb/09; however, after the mercury mixing and melt stirring period (at the start of the test), the gas flow was left on argon instead of changing to air. The test was conducted for seven days for direct comparison to Hg-Pb/11. Gravimetric analysis of the cold trap masses revealed a surprisingly close agreement between the two tests, with many of the data points lying over one another as shown in Figure 5. The pool surface was observed to remain shiny for the entire test, indicating that there were no oxidation reactions occurring with either the lead or aluminum. The masses and release fractions for Hg-Pb/10 and Hg-Pb/11 were nominally identical, indicating that there was no effect of aluminum in the melt with an inert (argon) atmosphere. The conclusion that is drawn here is that there is no effect of dissolved aluminum in a pool of molten lead (at 340°C) on the vaporization of mercury from the pool without an oxidizing atmosphere. However, with an oxidizing atmosphere, the effect of aluminum in the melt is to retard the vaporization. The mechanism is attributed to the formation of an aluminum oxide film over the pool which presents an additional resistance to mass transfer across the interface; no enhancing effect of aluminum on the vaporization of mercury from the melt was found.

Hg-Pb/11

The last test in the series was Hg-Pb/11 which has been previously discussed out of order because it was intended to use these results to replace Hg-Pb/02 for reasons already discussed. This test was conducted under better experimental control than Hg-Pb/02 and ran smoothly for seven days. The details will not be repeated here; the parameters are listed in Table 3 and the results are shown in Figure 5. It is clear from Figure 5 that Hg-Pb/11 and Hg-Pb/10 are in remarkable agreement, supporting the earlier stated conclusions.

DISCUSSION OF RESULTS

Experiments were conducted to measure the vaporization of mercury from pools of molten lead with APT-prototypic mixtures of lead and mercury, on the order of 0.01% to 0.10% by weight, to span the possible APT blanket service lifetime of from one to five years. Melt and atmosphere temperatures were controlled at 340°C to represent the low temperatures expected in the APT blanket in the event of an accident. It was found that the vaporization rate of mercury from the molten lead pool scaled roughly linearly with the mercury concentration. In other words, a reduction in the mercury concentration by a factor of ten resulted in a reduction in the mercury vaporization rate by about a factor of ten. This was found to be the case with both argon and air atmospheres over the melt pool. The rates of mercury release were found to be insensitive to changes in the gas flow rates, indicating that the limiting resistance to mass transfer was on the condensed phase side of the melt-atmosphere interface, not in the gas phase. A subsequent test in which the melt was agitated by a stirrer confirmed this observation; the stirring at one rpm increased the mercury vaporization rate by approximately a factor of ten over the identical case without stirring the melt. This result is fortunate because although the melt is not expected to be undergoing convection (mass transfer in the melt will be limited by diffusion), the results indicate that it is not necessary to consider complex flow fields in the gas phase because the vaporization rate is insensitive to the gas phase mass transfer coefficient. It appears that there is little resistance to mass transfer in the gas phase even at the lowest gas flow rate tested. An argon gas atmosphere was always used to prepare the melts and maintained while the prescribed test conditions were being established. For the early tests (up to Hg-Pb/05), argon was used for the gas phase atmosphere over the melt during the test in order to avoid the complications that might be manifested with air, while investigating the parametric effects of mercury concentration and mass transfer on the mercury vaporization rates. However, commencing with test Hg-Pb/06 through Hg-Pb/09, air was used for the atmosphere over the molten lead-mercury pool to examine its parametric effects. The application of air as the atmosphere over the melt instead of inert argon demonstrated an order of magnitude reduction in the mercury vaporization rate, attributed to the formation of a lead oxide layer over the melt which retarded vaporization through the layer. Subsequent tests which had a reduced mercury concentration with air demonstrated a corresponding reduction in the mercury vaporization rate. The addition of aluminum to the melt was investigated to determine its effects with the argon and air atmospheres. Although no effect on the mercury vaporization rate was observed in the test with argon (Hg-Pb/10) as compared to its counterpart test Hg-Pb/11, a significant reduction in the mercury vaporization was observed in the identical test with air (Hg-Pb/09) as compared to its counterpart test Hg-Pb/06.

Remarkably, the rate of mercury vaporization in Hg-Pb/10 with argon and 0.10% mercury was found to be two orders of magnitude greater than Hg-Pb/09 which had a comparable mercury concentration but an air atmosphere. The test which is considered to be most representative (in a generic sense) of expected mercury vaporization from a damaged (molten) APT blanket module after one year of operation is Hg-Pb/09.

The average mercury release rate in the Hg-Pb/09 was measured to be 0.58 $\mu\text{g}/\text{cm}^2\cdot\text{hr}$ over a two-week period. If one assumes the mercury concentration is one-tenth of that in the experiment, then

the mercury release rate would scale down to about $0.06 \mu\text{g}/\text{cm}^2\cdot\text{hr}$ or $1.5 \text{ mg}/\text{cm}^2\cdot\text{day}$. Allowing for a melt surface area of 2 m^2 , the average daily release rate would be $30 \text{ mg}/\text{day}$. Integrating this result over three days and normalizing by the one-year total mercury inventory of 4 kg , the release fraction so estimated would be 2.5×10^{-5} . For the APT Environmental Impact Statement [5,6], a mercury release fraction of 2% was postulated based upon earlier experimental results [7,8,9] and the published values in the PEIS [10,11]. This illustration suggests that the PEIS and EIS values for mercury release are bounding. However, detailed accident analyses are recommended.

CONCLUSIONS

The integrated release of elemental mercury from pools of molten lead was measured under a variety of fixed and variable parameters, including mercury concentration, lead pool and atmosphere temperatures, atmosphere composition and aluminum in the melt. In addition, variations in the rates of mass transfer in the gas phase and condensed phase were investigated. A total of eleven tests were conducted. The purpose of these tests was to provide well-characterized empirical data to allow estimates of the fractional release of mercury produced by nuclear spallation in the APT blanket which could be expected under severe accident conditions in which the lead/aluminum blanket would become molten and remain in such a condition for a prolonged period of time. Estimates of the mercury source term in the APT EIS were made, based upon results from earlier experiments and analyses in support of the SILC target APT design [7,8,9], which demonstrated that mercury release from droplets of molten lead would be negligible. The actual release fraction used in the APT PEIS [10,11] for a beyond-design-basis-accident in the SILC target was 2%. The same estimate was used in the APT EIS [5,6] based on arguments that this estimate would be bounding. However, verification that this estimate is bounding was needed. The following results were obtained from these experiments.

1. Mercury vaporization rates were measured to scale roughly linearly with the initial mercury concentration for concentrations in the range 0.01% to 0.10% by weight.
2. Variations in the atmosphere gas flow rates across the surface of the molten lead pool had no measurable effect on the mercury vaporization rate, indicating that the mass transfer resistance in the gas phase could be neglected.
3. Variations in the melt pool agitation did have a significant effect upon the mercury vaporization rate, indicating that experimenters should take great care not to arbitrarily enhance the mercury vaporization rate by agitation of the melt.
4. Experiments in which air was used for the atmosphere over the melt instead of inert argon gas demonstrated an order-of-magnitude reduction in the mercury vaporization rate due to the formation of an oxide film on the lead surface which did not form when argon was used.

5. The addition of aluminum to the melt was examined for its effect on the mercury vaporization rate. The presence of aluminum in the melt had no apparent effect on the mercury vaporization rates in experiments with an argon atmosphere; however, a significant reduction in the mercury vaporization rate was measured in experiments with an air atmosphere with the addition of aluminum to the melt compared to the identical experiment with air but without aluminum in the melt.

REFERENCES

1. Los Alamos National Laboratory Memorandum, E. Pitcher to G. A. Greene, "Mercury Concentration in Lead [in the APT Blanket After One Year and Five Years of Full Power Operation]" (April 10, 1998).
2. "Functional Classification Report," Accelerator Production of Tritium Project Report PPO-P00-S-FCD-X-00001, Rev. A (1998).
3. "Hazards Analysis Report," Accelerator Production of Tritium Project Report PPO-P00-S-PHA-X-00001, Rev. A (1998).
4. CRC Handbook of Chemistry and Physics, 71st Ed., David R. Lide, editor (1990).
5. Edwards, J., L. A. Miller, R. Lowrie and G. A. Greene, "APT Accident Analysis for the Environmental Impact Statement," APT-110-1997-40, LAUR 98-251 (1998).
6. "Environmental Impact Statement, Accelerator Production of Tritium at the Savannah River Site," DOE/EIS-0270D (1997).
7. Tutu, N. K. and G. A. Greene, "Vaporization of Mercury From Molten Lead Droplets Doped With Mercury: Pb/Hg Source Term Experiment for the APT/SILC Target," BNL Formal Report 52449 (1994).
8. Tutu, N. K., G. A. Greene and R. W. Youngblood, "Analysis of an Unmitigated Large Break Loss of Coolant Accident (LBLOCA) with the Non-Mechanistic Failure of Passive Cooling for the APT Spallation Target," BNL Formal Report 52451 (1995).
9. Van Tuyle, G. J., et al., "Preconceptual Design of the Spallation-Induced Lithium Conversion (SILC) Target for the Accelerator Production of Tritium (APT)," ATD/APT 94-0013 (1995).
10. Miller, L. A., G. A. Greene and B. E. Boyack, "Accelerator Production of Tritium Programmatic Environmental Impact Statement Input Submittal," SAND 93-2094 (1996).
11. "Final Programmatic Environmental Impact Statement for Tritium Supply and Recycling," DOE/EIS-0161 (1995).

Figure 1. Schematic of the Experimental Test Facility.

Figure 2. Cumulative Mercury Release From a Molten Lead Pool vs. Mercury Concentration with an Argon Atmosphere: Hg-Pb/02 vs. Hg-Pb/03.

Figure 3. Cumulative Mercury Release From a Molten Lead Pool as a Function of Gas Phase and Condensed Phase Mass Transfer Enhancements: Hg-Pb/04 vs. Hg-Pb/05.

Figure 4. Cumulative Mercury Release From a Molten Lead Pool vs. Mercury Concentration with an Air Atmosphere: Hg-Pb/06 vs. Hg-Pb/08.

Figure 5. Comparison of the Cumulative Effects of Mercury Concentration, Atmosphere Composition and Aluminum in the Melt on the Rate of Vaporization of Elemental Mercury From Molten Lead Pools: Hg-Pb/06, Hg-Pb/09, Hg-Pb/10, Hg-Pb/11.

Table 1

Ranges of Nominal Test Parameters

Parameter	Nominal Value and Uncertainty
Lead Mass	2.5 kg
Lead Surface Area	93.3 cm ²
Mercury Concentration (weight)	0.01%, 0.10%, 1.0%
Lead Temperature	340°C ± 2.5°C
Atmosphere Temperature	340°C ± 2.5°C
Gas Flow Rate	200 ml/min ± 6%, 750 ml/min ± 2%
Atmosphere Composition	argon, air
Melt Stirring Rate	none, 1 rpm
Aluminum in Melt	yes, no

Table 2

Specifications for Individual Tests

Test (-)	Hg (wgt%)	Cover Gas	Gas Flow	Pool Agitation	Aluminum in Melt	Purpose/Comments
00	0.0	argon	low	no	no	Shakedown test, measure of the lead carryover.
01	1.0	argon	low	no	no	Effect of very high mercury concentration.
02	0.1	argon	low	no	no	Bounding (5-year APT) mercury concentration.
03	0.01	argon	low	no	no	Nominal (1-year APT) mercury concentration.
04	0.1	argon	high	no	no	Effects of changes in the gas flow rate.
05	0.1	argon	low	yes	no	Effects of agitation of the melt pool.
06	0.1	air	low	no	no	Effects of an oxidizing air atmosphere.
08	0.01	air	low	no	no	Effects of air at nominal mercury concentration.
09	0.1	air	low	no	yes	Effects of aluminum in the melt with air.
10	0.1	argon	low	no	yes	Effects of aluminum in the melt with argon.
11	0.1	argon	low	no	no	Repeat of Hg-Pb/02 with improved procedures.

Table 3

Cumulative Average Mercury Release Results

Test (-)	Cover Gas	Initial Hg Mass	Mercury Concentration	Mercury Released	Duration of Test	Mercury RF	Release Rate, Average	Average Daily Release
01	argon	28.01 gm	1.14 %	1.310 gm	2.0 hr	4.7 %	6.99E-3 gm/cm ² ·hr	56.4 %
02	argon	2.83	0.11	0.330	48.0	11.7	8.02E-5	5.85
03	argon	0.31	0.01	0.031	165.0	10.2	2.19E-6	1.48
04	argon	2.79	0.11	0.155	50.4	5.6	3.57E-5	2.67
05*	argon	2.75	0.11	0.569	24.5	20.7	2.69E-4	20.3
06	air	2.58	0.10	0.112	336.0	4.4	3.86E-6	0.31
08	air	0.27	0.01	0.011	643.6	4.1	1.96E-7	0.15
09	air	2.51	0.10	0.017	328.9	0.7	5.82E-7	0.05
10	argon	2.41	0.09	0.626	163.9	26.0	4.43E-5	3.81
11	argon	2.55	0.10	0.596	163.6	23.4	4.22E-5	3.43

* Data shown are for the 24.5 hour period of melt agitation only. The time during which the melt was not being stirred has been excluded.

Table 4

Integrated Mercury Mass Released vs. Elapsed Time: Tests Hg-Pb/02 and Hg-Pb/03

Test Hg-Pb/02		Test Hg-Pb/03	
Elapsed Time (min)	Cumulative Release (g)	Elapsed Time (min)	Cumulative Release (g)
120	0.0444	310	0.0039
240	0.071	1290	0.0039
253	0.0787	1775	0.0039
480	0.1015	2685	0.0062
1140	0.1816	3155	0.0096
1595	0.21	9900	0.0312
2880	0.3321		

Table 5

Integrated Mercury Mass Released vs. Elapsed Time: Tests Hg-Pb/04 and Hg-Pb/05

Test Hg-Pb/04		Test Hg-Pb/05	
Elapsed Time (min)	Cumulative Release (g)	Elapsed Time (min)	Cumulative Release (g)
143	0.0085	595	0.0058
398	0.0398	835	0.0945
643	0.0561	1113	0.1848
1133	0.0757	1415	0.3357
1583	0.097	2065	0.5745
2048	0.1153	2575	0.633
2588	0.1312	4000	0.7358
2800	0.1398	5395	0.7464
3024	0.1553	6923	0.7678

Table 6

Integrated Mercury Mass Released vs. Elapsed Time: Tests Hg-Pb/06 and Hg-Pb/08

Test Hg-Pb/06		Test Hg-Pb/08	
Elapsed Time (min)	Cumulative Release (g)	Elapsed Time (min)	Cumulative Release (g)
936	0.0811	2925	0.0024
1410	0.0856	5415	0.0036
2860	0.0906	8610	0.0060
4320	0.0939	21570	0.0082
5660	0.0972	30260	0.0097
7090	0.0996	38617	0.0109
8575	0.1009		
10015	0.1028		
11440	0.1049		
12940	0.1064		
14200	0.1078		
15671	0.1088		
17090	0.1097		
18390	0.1105		
20160	0.1123		

Table 7

Integrated Mercury Mass Released vs. Elapsed Time: Tests Hg-Pb/06 and Hg-Pb/09

Test Hg-Pb/06		Test Hg-Pb/09	
Elapsed Time (min)	Cumulative Release (g)	Elapsed Time (min)	Cumulative Release (g)
936	0.0811	979	0.0057
1410	0.0856	2432	0.0081
2860	0.0906	4184	0.0104
4320	0.0939	5322	0.0107
5660	0.0972	6884	0.0119
7090	0.0996	8159	0.0123
8575	0.1009	11019	0.0126
10015	0.1028	14224	0.0146
11440	0.1049	16824	0.0149
12940	0.1064	19734	0.0165
14200	0.1078		
15671	0.1088		
17090	0.1097		
18390	0.1105		
20160	0.1123		

Table 8

Integrated Mercury Mass Released vs. Elapsed Time: Tests Hg-Pb/10 and Hg-Pb/11

Test Hg-Pb/10		Test Hg-Pb/11	
Elapsed Time (min)	Cumulative Release (g)	Elapsed Time (min)	Cumulative Release (g)
930	0.2296	1125	0.2558
1402	0.3076	1525	0.3179
2370	0.412	2495	0.4248
2835	0.443	2915	0.4454
4080	0.5015	4160	0.4962
6990	0.5683	5600	0.5294
9835	0.6264	7060	0.5552
		8480	0.5765
		9815	0.5955