

Mobilization measurements from Flibe under argon and air flow

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Abstract

Flibe a molten salt consisting of 2LiF:BeF₂ has interest as cooling and tritium breeding media in both magnetic and inertial fusion. Key safety issues are the mobilization of vapors and aerosols from accidental introduction of air, moist air, or steam to the molten salt. Mobilization tests were performed with argon, air and moist air using a classical transpiration apparatus designed for vapor pressure determinations. Vapor pressures determined between 500 and 800 °C in flowing argon, assuming BeF₂ and LiBeF₃ as the vapor species, are 2–3 times lower than those predicted by recent vapor pressure models. Mobilization rates were comparable in all environments. Some lithium-bearing species provides an increasing contribution to the overall mobilization with temperature and a greater role in mobilization in the air environments. Estimates of mass flux values (kg/m² s) are obtained and assessed with regard to relevance for safety assessments of molten salt breeder blanket designs.

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1. Introduction

Flibe of the 2:1 mol% composition was studied extensively and used as the coolant salt in the Molten Salt Reactor Program during the 1960–1970s. Vapor pressures determined by Oak Ridge National Laboratory (ORNL) studies were at temperatures of above 1000 °C [1]. Current applications of this salt in fusion energy devices are around 600 °C. Recent models [2,3] have been developed to express vapor pressures for temperatures more applicable to fusion energy applications. Olander et al. [2] compared the extrapolation of ORNL data with a model utilizing selected activity coefficients from various studies and prominent vapor species as identified by mass spectroscopy by Büchler and Stauffer [4]. The latter authors reported BeF₂ and LiBeF₃ as the dominant vapor species above the LiF–BeF₂ system. These two

species were found to exist in a ratio of 10:1 above a LiF saturated solution on 74%LiF–26% BeF₂ at 600 °C. The two models [2,3] provide essentially the same pressure for BeF₂ that is about 60% below the extrapolated ORNL data. The models differ only by the minor contribution attributed to lithium-bearing species. The current study was undertaken to provide experimental confirmation of vapor pressures at the lower fusion-relevant temperatures and to determine influences of different environments, e.g., argon, dry air, and moist air or steam possibly encountered during an accident. Another goal was to obtain mass flux measurements from conditions approximating saturation to provide a basis for comparison with LOVA safety studies addressing blanket design concepts for APEX [5].

2. Experimental methods

The salt was prepared from reagent grade chemicals. Both the BeF₂ and LiF were listed as 99.9% pure based

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Table 1
Impurities in ingredients and final salt

| | O (ppm) | C (ppm) | N (ppm) | Fe (ppm) | Ni (ppm) | Cr (ppm) |
|------------------|---------|---------|---------|----------|----------|----------|
| BeF ₂ | 5700 | <20 | 58 | 295 | 20 | 18 |
| LiF | 60 | <20 | 78 | 100 | 30 | 4 |
| Flibe | 560 | 10 | 32 | 260 | 15 | 16 |

upon the metals content. Internal analyses provided impurity levels shown in Table 1. Oxygen and nitrogen analyses were made with a LECO® Model EF-400/TC-436 instrument. Carbon levels were determined with a LECO® TC-436 instrument. Metals analyses were by inductive coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-MS (mass spectroscopy). The powders were dried and weighed to provide the mole ratio of 2:1 and then purged with helium and melted. The salt was then purged with gas mixtures of He, H₂ and HF at 520 °C to reduce inherent oxides. The salt was then passed through a 60- μ sintered stainless steel filter into another vessel. The impurities in the final product used for the mobilization tests are given in Table 1. Measurements of beryllium and lithium in the final product ranged from 8.3 to 8.5 wt% and 13.06 to 13.2 wt%, respectively. Although these are lower than the theoretical values of 9.04 and 14.14 wt%, the lithium to beryllium mole ratios of 2.01–2.06 are close to the targeted composition. This suggests that the weight-based discrepancies might be due to absorbed water or analytical biases.

Mobilization tests of the salt were performed in a transpiration setup similar to that described by Sense et al. [6] for vapor pressure measurements. A schematic of the test system set up in an inert gas glove box is shown in Fig. 1. The test chamber made from 3/4-in., Schedule 40, nickel pipe had a 2.09 cm ID \times 51 cm length and was heated in a 36 cm long resistance heated muffle furnace. Flibe samples were contained at the center of the hot zone in different types of crucibles depending on the test environment. An Inconel 600 tube with a 3.35 mm ID was used for the probe through which vapors were transported by the gas flow. This probe was situated either over or just behind the molten salt. A thermo-

couple clad with Inconel 600 was located at the front of the crucible. Temperature profiles confirmed that the 7.6-cm zone containing the specimens was always within +10 °C of targeted temperatures. Temperature gradients between the test region and the ends of the furnace were rather steep. The probe was attached to 1/2-in. stainless steel tubing with a region of packed quartz wool to assure the collection of mobilized products. The test gases of argon and dry air were preheated to 350 °C in a small resistance heated furnace prior to being introduced to the test chamber. Moist air was generated by flowing the gas over a water bath maintained at 40 °C in the preheat furnace. Saturation at this temperature provided air with a water vapor content of 5 vol.%. The gas lines to the test chamber were heat traced to maintain temperatures and prevent condensation. The moist air exiting from the stainless steel collector flowed through a water-cooled condenser to remove the moisture. A quadruple mass spectrometer (QMS) located downstream was used to verify that the test system was leak tight prior to test initiation.

Weights of the Flibe samples, the crucibles containing the salt and surrogate crucible material were recorded before and after tests. Nickel crucibles were used for tests performed in argon. Air exposures oxidized the nickel crucible negating weight change data. Surface interaction between the salt and the nickel crucibles, including those lined with platinum foil increased in air. This higher wettability allowed salt to flow out of the crucible and contaminate the probe and the internal surfaces of the test chamber. Glassy carbon crucibles (GCCs) were subsequently used for air and moist air tests. The GCCs contained the salt but underwent significant oxidation losses. Weight change therefore could only be obtained for the argon tests in nickel crucibles. The probe and associated stainless steel collection tube were removed after each test. These components were cleaned with 10% nitric acid and the solutions analyzed for beryllium and lithium by ICP-AES. Measurements obtained from the internal surface of the probe were used for vapor pressure calculations. Deposits recovered from the external surfaces of the probes were used to compare the amounts and ratios of beryllium to lithium on internal and external probe deposits. The test chamber surface was also cleaned after selected test series. Measurements from the test chamber were used to check beryllium to lithium ratios and to correlate with weight losses incurred during argon tests.

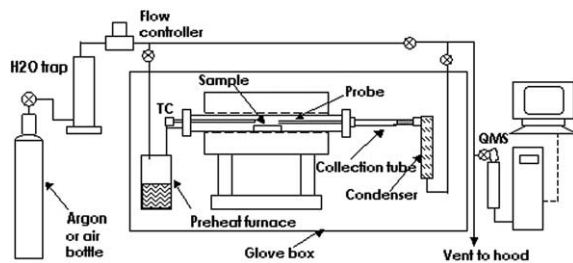


Fig. 1. Transpiration test setup.

3. Experimental results and discussion

Some initial tests with pure LiF in the system showed good correlation of vapor pressures obtained for this salt with those reported in the literature. An integrated test (6-h periods with 50, 100 and 200 sccm argon) at 875 °C yielded a vapor pressure of 6.7 Pa. Data from Sense et al. [7] and Kubacshewski et al. [8] indicated vapor pressures of 9.5 and 5.0 Pa, respectively. A 6-h test at 1000 °C with a flow rate of argon 50 sccm showed a vapor pressure for LiF of 78 Pa. Vapor pressures from the previous authors were 90 and 58 Pa, respectively. The data from Kubacshewski et al. [8] were derived from pressure measurements. Sense et al. [7] used a transpiration method similar to the one used in this study. Pressures are derived assuming monomer LiF molecules. The differences between the two referenced studies are the influence of polymerization. Since pressures obtained from the current study are within 30% of those reported by Sense et al. [7], the test geometry and flow rates appear to provide conditions close to saturation.

Flibe salt was tested in argon at temperatures of 500, 600, 700, and 800 °C with flow rates of 25, 50 and 100 sccm. Nickel crucibles were used for most tests, however, some tests were also run in GCCs. Tests with dry air were run at these four temperatures with flow rates of 25 and 50 sccm. Tests in moist air were run at 600, 700, and 800 °C with flow rates of 25 and 50 sccm.

The test parameters, amounts of beryllium and lithium recovered from the inside and outside of the probe, and weight losses for the argon tests in nickel are given in Table 2. All of the vapors transported into the probe were deposited in this component and no beryllium or lithium was found in the downstream stainless steel tubes or filters for any of the tests. The moles of beryllium and lithium recovered from the inside of the probe for each test are listed in Table 2. Relative abundance in mole percent of beryllium to (Be + Li) is also shown. The ratios of these elements of 9:1 to 4:1 at 600 °C agree quite well with the relative abundance of BeF₂ to LiBeF₃ of 10:1 reported from the mass spectroscopy [4] study at a similar temperature. Partial pressures have been calculated for BeF₂ and LiBeF₃ assuming that these are the two primary compounds. Calculations for BeF₂ in argon have been adjusted for the moles of beryllium, i.e., the equivalent moles of lithium, associated with the LiBeF₃ species. The relative abundance of the lithium-bearing species increases at 700 and 800 °C for the argon tests. In fact, the moles of lithium exceeded those of beryllium for many of the tests performed in air. This suggests that some lithium-bearing species besides LiBeF₃ may be involved in the volatilization process. Pressures for BeF₂ in air and moist air were therefore calculated from the total moles of beryllium. Pressures of some lithium-bearing species, assuming a single lithium atom, were calculated from the moles of lithium.

The pressures for BeF₂ and LiBeF₃ from the argon tests in Table 2 are plotted in Fig. 2 along with those from the previous studies and models [1,2,4]. The plot shows excellent agreement between the 600 °C data from this study and that of Büchler and Stauffer [4]. The total pressures represented by Olander et al. [2], which are essentially equivalent to those of Zaghloul et al. [3], are about 60% lower than the extrapolated ORNL data [1]. Total pressures plotted for BeF₂ and LiBeF₃ from Table 2 are two to three times lower than predicted values. The increasing contribution from the lithium species in the INEEL data is apparent at 700 and 800 °C.

Partial pressures calculated for BeF₂ for all three test gases are shown in Fig. 3. The data for moist air parallels and are about one-half those measured for the argon tests. The reason for the lower datum points in the dry air tests at 700 and 800 °C is not known. This trend is based upon limited tests and some repeated tests would be needed to confirm this trend. The data did not show any markedly different volatilization rates in dry and moist air compared to those in argon.

Vapor pressures calculated, assuming a single lithium atom per molecule, e.g., LiF or LiBeF₃, are plotted for the various test gases in Fig. 4. No differences could be distinguished between the environments considering the scatter within the data. The data are slightly higher than pressure of LiBeF₃ indicated by Olander et al. [2] and that based on an extrapolation of the LiF data by Sense et al. [7] multiplied by 0.66 the mole fraction in Flibe to simulate ideal solution behavior. The latter extrapolation was from above the 845 °C melting point of LiF.

Mass comparisons using probe interior ICP-AES measurements and sample loss for the argon test series in the nickel crucibles showed that about 22% of the material was deposited in the probe. The remainder was deposited on the probe exterior and the walls of the test chamber. This reflects the diffusion and re-deposition of material down the temperature gradient. Mass flux calculation (kg/m² h) obtained by adjusting ICP-AES measurements for the 22% factor generally agreed within a factor of two of the mass loss determinations for individual tests. The model for safety assessments [5] addresses the evaporation process from molten Flibe, which becomes rate limited by diffusion through a boundary layer. The boundary layer mass transport coefficient K_m of 0.01–0.03 (m/s) derived for Flibe from this study was applied along with measured vapor pressures and mass based flux determinations to show that the vapor pressures for the argon tests were likely within 70% of saturation. This is in line with the comparison made with vapor pressures from the LiF study by Sense et al. [7]. Although the flow conditions within the test system are not specifically representative to the relatively placid conditions for a LOVA accident [5], the mass based flux values of 2.6×10^{-2} g/m² h at 500 °C, 7.7×10^{-2} g/m² h at 600 °C, 3.1×10^{-1} g/m² h at 700 °C

Table 2
Test parameters, mass recoveries, and pressure calculations

| Test ID | Gas | Temp. (°C) | Flow rate (sccm) | Time (h) | Mass loss (g) | Be IS probe (mole) | Li IS probe (mole) | Mole% Be inside probe | Pressure of BeF ₂ (Pa) | Pressure of Li-bearing species (Pa) |
|---------|--------|------------|------------------|----------|---------------|--------------------|--------------------|-----------------------|-----------------------------------|-------------------------------------|
| 1 | Ar | 500 | 25 | 24 | 0.0034 | <9.4E-9 | <2.9E-8 | n.a. | <5.87E-4 | <1.38E-3 |
| 2 | Ar | 500 | 50 | 24 | 0.0005 | <9.4E-9 | <2.9E-8 | n.a. | <2.93E-4 | <6.91E-4 |
| 3 | Ar | 500 | 100 | 24 | 0.0005 | <9.4E-9 | <2.9E-8 | n.a. | <1.47E-4 | <3.45E-4 |
| 4 | Ar | 600 | 25 | 24 | 0.0029 | 3.49E-7 | 3.89E-8 | 90 | 1.93E-2 | 2.42E-3 |
| 5 | Ar | 600 | 50 | 24 | 0.0015 | 1.38E-6 | 1.96E-7 | 88 | 3.68E-2 | 6.10E-3 |
| 6 | Ar | 600 | 100 | 24 | 0.0015 | 1.69E-6 | 3.84E-7 | 81 | 2.03E-2 | 5.92E-3 |
| 7 | Ar | 700 | 25 | 24 | 0.0071 | 9.40E-6 | 6.80E-6 | 58 | 1.62E-1 | 4.23E-1 |
| 8 | Ar | 700 | 50 | 8 | 0.0034 | 7.71E-6 | 4.50E-6 | 63 | 3.00E-1 | 4.20E-1 |
| 13 | Ar | 700 | 50 | 8 | n.d. | 9.8E-6 | 5.09E-6 | 66 | 4.44E-1 | 4.75E-1 |
| 17 | Ar | 700 | 50 | 8 | n.d. | 6.04E-6 | 4.46E-6 | 57 | 5.64E-1 | 4.17E-1 |
| 24 | Ar | 700 | 50 | 8 | n.d. | 8.39E-6 | 3.39E-6 | 71 | 7.83E-1 | 3.17E-1 |
| 9 | Ar | 700 | 100 | 8 | 0.0028 | 8.77E-6 | 6.74E-6 | 57 | 9.45E-2 | 3.15E-1 |
| 10 | Ar | 800 | 25 | 4 | 0.0085 | 2.71E-5 | 1.58E-5 | 63 | 4.22E+0 | 5.92E+0 |
| 11 | Ar | 800 | 50 | 4 | 0.0114 | 4.67E-5 | 2.92E-5 | 62 | 3.27E+0 | 5.45E+0 |
| 25 | Ar | 800 | 50 | 4 | n.d. | 8.73E-5 | 3.2E-5 | 73 | 1.63E+1 | 6.09E+0 |
| 12 | Ar | 800 | 100 | 4 | 0.0134 | 7.92E-5 | 3.99E-5 | 67 | 3.67E+0 | 3.72E+0 |
| 19 | Air | 600 | 25 | 4 | n.d. | 3.98E-8 | 4.47E-8 | 47 | 1.47E-2 | 1.67E-2 |
| 30 | Air | 600 | 25 | 4 | n.d. | 1.66E-8 | <2.9E-8 | n.a. | 6.21E-3 | <7.87E-3 |
| 32 | Air | 700 | 25 | 2 | n.d. | 1.78E-7 | 7.20E-8 | 71 | 1.33E-1 | 5.38E-2 |
| 28 | Air | 700 | 50 | 2 | n.d. | 1.11E-7 | 3.75E-7 | 23 | 4.14E-2 | 1.40E-1 |
| 33 | Air | 800 | 25 | 1 | n.d. | 3.33E-7 | 1.69E-6 | 16 | 4.97E-1 | 2.52E+0 |
| 29 | Air | 800 | 50 | 1 | n.d. | 1.49E-6 | 4.10E-6 | 27 | 1.11E+0 | 3.06E+0 |
| 35 | M. Air | 600 | 25 | 4 | n.d. | 4.27E-8 | 8.64E-8 | 33 | 1.60E-2 | 3.23E-2 |
| 34 | M. Air | 600 | 50 | 4 | n.d. | 1.78E-8 | 2.23E-8 | 44 | 3.31E-3 | 4.17E-3 |
| 36 | M. Air | 700 | 25 | 2 | n.d. | 4.63E-7 | 7.22E-7 | 39 | 3.45E-1 | 5.39E-1 |
| 37 | M. Air | 700 | 50 | 2 | n.d. | 9.56E-7 | 7.95E-7 | 55 | 3.57E-1 | 2.97E-1 |
| 38 | M. Air | 700 | 50 | 2 | n.d. | 9.08E-7 | 5.27E-7 | 63 | 3.39E-1 | 1.97E-1 |
| 39 | M. Air | 800 | 25 | 1 | n.d. | 4.48E-6 | 2.21E-6 | 67 | 6.69E+0 | 3.30E+0 |
| 40 | M. Air | 800 | 50 | 1 | n.d. | 6.22E-6 | 4.96E-6 | 56 | 4.64E+0 | 3.71E+0 |

Notes: (1) Test gases: Ar (argon), Air, and M. Air (moist air).

(2) ICP-AES detection limits for Be and Li are 0.085 μg ($9.4\text{E}-9$ mole) and 0.2 μg ($2.9\text{E}-8$ mole), respectively.

(3) Weight loss measurements could only be obtained from argon tests using nickel crucibles.

(4) Flibe surface area was $8.1\text{E}-4$ m² for 500 and 600 °C argon tests and $11.6\text{E}-4$ m² for 700 and 800 °C argon tests.

(5) Abbreviations: “n.d.” indicates not determined and “n.a.” indicates not applicable.

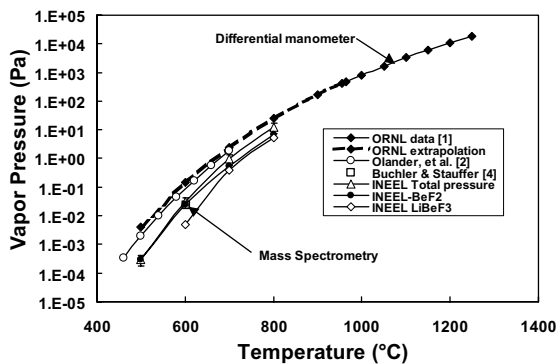


Fig. 2. Total pressure over Flibe.

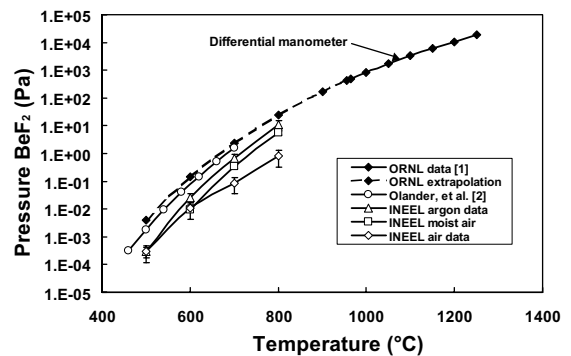


Fig. 3. BeF₂ pressure in various environments.

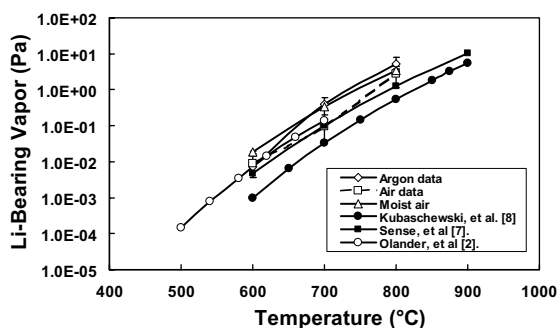


Fig. 4. Pressure of Li-bearing vapor over Flibe.

and 2.4 g/m² h at 800 °C could be used as a first order, conservatively high, approximations of evaporation rates.

4. Conclusions

Experimentally determined pressures for the beryllium-bearing vapor, presumably BeF₂, from this studies between 500 and 800 °C are 2–3 times lower than those extrapolated from higher temperature experiments or from recent models. Lithium as measured by ICP-AES for 600 °C argon tests agreed with the levels, and beryllium to lithium ratios, of a previous mass spectroscopy study. This would support the LiBeF₃ dimer as the secondary vapor after BeF₂. Relative levels of lithium to beryllium increased at 700 and 800 °C and in other environments. These levels were significantly higher than those indicated by the models and suggest that some other lithium-bearing vapor besides LiBeF₃ may be playing a role. Such behavior is not critical, however, since lithium is less of a safety issue compared to beryllium and the total vapor pressure remains less than those predicted by the models. No significant

influence of the test environment, i.e., argon, dry air and moist air upon volatilization rates were observed. The vapor pressure determined in this study appeared slightly less than saturation pressures, however, flux values given in the paper present conservatively high evaporation rates for molten Flibe with stagnant or low flow rate conditions.

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