Method for the Determination of Oxygen in FLiBe via Inert Gas Fusion

Nicholas J. Condon,* Susan Lopykinski, Francesco Carotti, Kaitlin E. Johnson, and Alan Kruizenga

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: In nuclear reactors that use molten fluoride salts, either as coolants or as the medium for the fuel, the purity of the salts is critical for controlling salt chemistry and mitigating corrosion. Water is a particularly important contaminant in this regard, as it participates in a number of important corrosion reactions, so the careful measurement of oxygen, which is principally present in the salts due to water contamination, is a critical step in salt characterization. Here, we present an analytical method for quantifying oxygen contamination in Li_2BeF_4 (FLiBe), a technologically important and suitably representative fluoride salt, with a detection limit of 22 μg of oxygen, or 110 ppm in a 200 mg sample. To test the method, four FLiBe samples from different batches were tested. Two of these showed oxygen concentrations below the method detection limit, while two showed concentrations above it. In particular, the difference in the oxygen concentration between purified and un-purified batches of material from Kairos Power showed the efficacy of this method in characterizing the degree of oxygen removal obtained from purification methods.
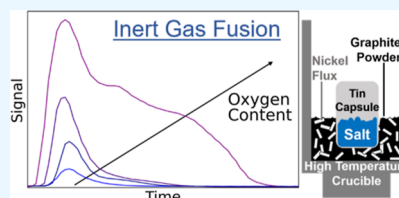
INTRODUCTION

FLiBe, nominally a 2:1 molar mixture of LiF and BeF_2, is selected to be used in several advanced nuclear reactor technologies; molten FLiBe is used as the coolant for solid fuel fluoride salt-cooled high-temperature reactors (FHRs), as the solvent salt for molten salt reactors (MSRs), and as the blanket fluid in high-magnetic field fusion systems.[1,2] FLiBe is thermodynamically compatible with metallic alloys used in engineering systems, and its corrosivity toward structural materials has been demonstrated to be negligible when impurity levels and redox potential are controlled throughout the reactor lifetime.[3,4]

Water and oxygen are the major external sources of impurities in molten fluoride salt engineering systems. They are entrained in the system gas phase and are present as contaminants in raw constituents. Oxides and hydroxides are introduced by oxygenated impurities in as-received LiF and BeF_2 and absorbed water from incomplete evaporation before co-melting. During FLiBe salt preparation, impurities are typically removed through a purification process that includes sparging FLiBe with a mixture of HF/H_2,[5] with HF reacting with oxides and hydroxides as in eqs 1 and 2 to produce water that can be removed from salt.

$$O^{2-} + 2HF \leftrightarrow 2F^- + H_2O \quad (1)$$

$$OH^- + 2HF \leftrightarrow F^- + H_2O \quad (2)$$

During reactor operations and maintenance, moisture and oxygen may leak into the inert gas phase and interact with FLiBe salt, causing undesired long-term degradation effects. Water ingress forces the reactions in eqs 1 and 2 from right to left and generates HF, a known strong corrosion agent for

metals. Oxygen gas oxidizes structural alloys, facilitating the dissolution of metals in molten fluoride salt and therefore accelerates the alloys' corrosion processes. Oxides in FLiBe solution are thermodynamically favored to form BeO, which has a solubility of about 200 ppm in FLiBe at 600 °C[6] and could therefore form solid particulates in the molten salt. Overall, the mechanisms of oxygen chemical interaction with FLiBe, their kinetics, and impacts on the redox potential and metal corrosion are not fully defined and are the focus of active research.[7−9]

An analytical method able to directly and efficiently measure the oxygen content in fluoride salt samples is critical to investigate oxygen interactions in fluoride salts, optimize purification processes, and monitor operating conditions of large engineering fluoride salt systems. Early measurements of oxygen in molten fluoride salts were accomplished through the use of extremely strong fluorinating agents, such as $KBrF_4$, to induce the release of oxygen,[10] reporting detection limits down to 0.02 mg of O with a recovery of 98%. In practice, this method is impractical due to the substantial safety hazards and specialized equipment required. Recently, the use of inert gas fusion to analyze FLiNaK salt has shown promising levels of oxygen recovery.[11] Beyond these, there are no reports in the literature of other convenient methods for the determination of

oxygen in these salts, pointing to the need for further research. Here, we present the development and calibration of an inert gas fusion analytical technique to measure the oxygen content at trace levels in FLiBe salt using a commercial instrument.

■ METHODS

Analyses were carried out on a LECO ON836 inert gas fusion analyzer. All crucibles, flux materials, sample capsules, and test standards were obtained from LECO Corporation.

Materials from four different batches of FLiBe were used in this work: one produced and purified by Oak Ridge National Laboratory (designated ORNL-P), one produced and purified at University of Wisconsin−Madison (designated UW-P), and two produced by Kairos Power—one sampled before purification (designated KP-U) and one after purification (designated KP-P). The ORNL material was used for initial experiments, while the UW-P FLiBe was used to construct the calibration curve.

All FLiBe manipulations were done in a glovebox or fume hood to prevent the transfer of potentially hazardous beryllium compounds to workers. The vials containing FLiBe were opened in a glovebox operating under a continuous purge of high-purity argon gas. The FLiBe chunks were ground to a coarse, granular consistency in the glovebox using an agate mortar and pestle. FLiBe samples with a mass of ∼0.1 g were loaded into low-oxygen tin capsules (obtained from LECO) (each with a mass of ∼0.28 g) in the glovebox and were crimp closed with tweezers. Due to the once-though nature of the glovebox and the lack of gas sensors, the purity of glovebox gases (oxygen and moisture content) during these operations could not be controlled.

For each analysis, a high-temperature (thick-walled) graphite crucible was used. The crucible was loaded with ∼0.9 g of nickel flux (from LECO) and ∼0.05 g of graphite powder (from LECO). The instrument outgassed the crucible, flux, and graphite powder for two cycles of 15 s each at 6000 W in a constant-power mode in an Ar atmosphere before sample analysis. The samples were then dropped into the crucible through the instruments purged sample introduction system, where they were analyzed for 110 s at a constant power of 2250 W (∼1900 °C).

Calibration Curve. In order to add oxygen to the UW-P FLiBe batch to develop a calibration curve, lithium oxide (Li_2O) was selected as the oxygen source. Simple thermodynamics calculations (using HSC Chemistry[12]) show that the oxygen is strongly favored to move from lithium to beryllium in FLiBe melts; thus, Li_2O additions are expected to be equivalent to adding beryllium oxide (BeO), without the hazard of handling BeO powders directly.

As an instrument blank, crucibles containing only the nickel flux and graphite powder were analyzed. To account for oxygen associated with the capsules themselves, empty capsules were analyzed alongside samples. The samples analyzed were each ∼0.1 g of FLiBe with 0−1000 μg of Li_2O added. As the conditions in the glovebox are not sufficiently stable to support a balance with 10 μg displayed precision, a balance with 100 μg precision was used to record the masses of the capsules as FLiBe and Li_2O were added. The reported oxygen concentrations were taken directly from the instrument, which based its value on the results of integrating the curve from the CO/CO_2 detection system.

The calibration samples were run in sets of six: one empty capsule, one capsule with FLiBe only, and four capsules with different amounts of Li_2O added. Five such sets of data were collected for each measurement series, and two full series were run. This provided a total of 10 empty capsule measurements and 50 measurements of FLiBe samples. These data were then used to construct the calibration curve.

FLiBe Comparison. As a test of the method, samples from the four batches of FLiBe (ORNL-P, UW-P, KP-U, and KP-P) were analyzed. Each analyzed sample was ∼0.1 g. The comparison samples were run in sets of five: one empty capsule, then one of each of the four FLiBe batches. Five such sets of data were collected, and the results of these five runs were averaged; 95% confidence intervals were then calculated from the standard deviations.

■ RESULTS AND DISCUSSION

Method Development. The method described above was arrived at after a series of experimental trials of other methods that produced inadequate results. Here, we will discuss the methods explored, the results from these methods, and our conclusions as to why they were unsuitable. This is relevant, as the insights gained informed about the development of the successful method.

The initial experiments in FLiBe analysis were performed (with the ORNL-P FLiBe batch) using nickel capsules and nickel flux, with Li_2O added as an oxygen spike. Experiments were performed over a wide range of temperatures using many possible temperature profiles, but the recovery of oxygen was always poor (∼50%) and was often highly inconsistent.

One possible issue was that of temperature: the boiling point of FLiBe is ∼1430 °C,[13] while the melting point of pure nickel is 1455 °C;[14] thus, to melt the nickel capsule and flux and allow it and the sample to react with the carbon in the crucible walls, it is necessary to raise the temperature high enough that FLiBe would vaporize very rapidly. This vaporization might compromise the accuracy of the analysis if the oxygen-containing material was carried out of the melt before it could sufficiently react with the carbon. To combat this, tin capsules and flux (which have a much lower melting point of 232 °C) were tried instead with much lower analysis temperatures. These experiments also produced inconsistent results, perhaps because tin, unlike nickel, does not form an alloy with beryllium.[14]

As tin and nickel form an alloy with each other with a melting point below that of nickel,[15] a tin capsule and nickel flux were tried together. The idea is that the tin capsule would melt, allowing the tin to alloy with the nickel flux; with 0.28 g of tin and 0.9 g of Ni, the resulting alloy of 13% Sn (by atom) and 87% Ni should have a melting point of ∼1240 °C. These experiments showed better recovery but were still inconsistent. Thus, to increase the speed of the reaction of carbon with the oxygen in the sample, graphite powder was also added to the capsule. This final mixture was tested at a range of analysis temperatures, and the maximum oxygen spike recovery was found to occur at a furnace setpoint of 2250 W, which corresponds to an analysis temperature of ∼1900 °C.

Analysis at this temperature resulted in fairly smooth and asymmetrical peaks in traces of oxygen signal versus time for relatively pure FLiBe, and spiking with Li_2O led to broad peaks with somewhat inconsistent profiles, as seen in Figure 1. This shape indicates that the reaction of the carbon contained in the crucible with the oxygen in the sample proceeds more slowly as the amount of Li_2O increases. The integrated areas of these peaks used by the instrument to compute the amount of
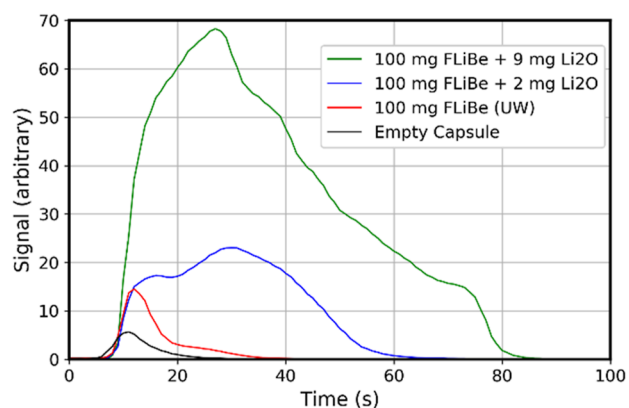
Figure 1. Plots of oxygen signal versus time from the LECO instrument with four different samples: one empty capsule, one unspiked sample of UW-P FLiBe, and two UW-P FLiBe samples spiked with Li_2O.

oxygen present, though, were quite consistent, with recoveries above 90%.

Calibration Curve Results. The tin capsules were selected to be lowest oxygen ones available commercially. However, each still showed a non-zero response when analyzed by the instrument, with an average response (when converted from percentage to mass of O) of 13 ± 7 μg. Using a Student's t-value to convert the standard deviation in measurement into a 99% confidence interval, this provides a measure of the method detection limit (MDL) of 22 μg. This would correspond to 220 ppm in a 0.1 g FLiBe sample. The use of a 0.2 g FLiBe sample (which the capsule will accommodate) would take this detection limit down to 110 ppm.

The results for the FLiBe samples were plotted separately for each experiment series and were found to provide statistically indistinguishable results. This confirms that the technique is repeatable from day to day and allows us to combine the two data sets when establishing a calibration curve. The combined results are plotted in Figure 2. The x-axis is the amount of oxygen added to each FLiBe sample, as converted from the measured Li_2O mass by multiplying by the fraction of the mass of Li_2O contributed by oxygen (~53.54%). The y-axis was
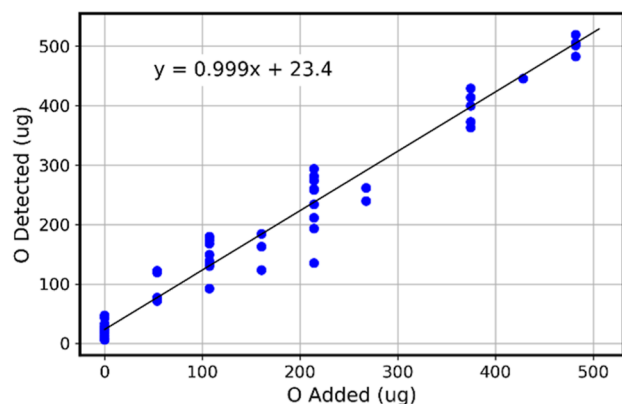
Figure 2. Measurement of detected oxygen in FLiBe as a function of the amount of oxygen added (as Li_2O). The equation for a linear fit, obtained via orthogonal distance regression (ODR) is shown on the plot, where x is the amount of oxygen added (in μg) and y is the amount of oxygen detected (in μg).

calculated by multiplying the reported oxygen percentage by the total mass of the capsule, FLiBe, and Li_2O.

The naïve linear fit using simple linear regression (SLR) is inappropriate for fitting a line to this data because SLR assumes that the x-axis values are exactly known. In many cases in experimental science, this is a reasonable approximation since the errors are very small compared to the values. However, here, we are measuring quantities of Li_2O of <1000 μg using a balance whose displayed precision is 100 μg, which means that there are substantial errors in both axes. While there are many errors-in-variables (EIV) fit methods available to address these situations, one of the simplest to implement is orthogonal distance regression (ODR). This method converges quickly to the correct value with an increasing number of samples, and for a linear fit on ~50 samples with errors that can be expected to be normally distributed, it is entirely appropriate. Here, the fit was accomplished in Python using the scipy.odr package (a Python wrapper for a well-established FORTRAN-77 implementation of ODR).[16,17]

The fit line in Figure 1 is the output of the ODR analysis. The slope is 0.999 ± 0.050, which indicates that the instrument is detecting 100% of the oxygen added to the FLiBe samples. The intercept is 23 ± 10 μg, which reflects the amount of oxygen in the capsule + FLiBe before the addition of any Li_2O. Subtracting the capsule oxygen mass gives an estimate for the amount of oxygen in the starting FLiBe of 17 ± 9 μg per ~0.1 g sample, or 170 ± 90 ppm. The intercept is barely above the MDL, so the value assigned to the concentration of oxygen in pure FLiBe should be considered to be a rough estimate at best; zero is within the 99% confidence interval (± 28 μg) for the measurement.

Recommended Measurement Method. To perform accurate oxygen analysis of FLiBe samples, the following steps are recommended as part of the analysis method. The LECO ON836 should be conditioned with a few surplus salt samples prior to calibration and sample analysis, as per manufacturer suggestion. If additional salt cannot be spared, a standard with a concentration near the lower end of the expected or estimated range of sample oxygen content is appropriate for use as a conditioner. A crucible containing ~0.9 g of nickel flux and ~0.05 g of graphite powder should be used as an instrument blank to account for oxygen not directly associated with samples. Empty tin capsules should be run with an equal number of replicates to that of the salt samples, and standards can be analyzed occasionally between measurements to insure efficacy of the overall analysis.

To calculate and report the actual O content in an unknown sample, one would carry out the measurement several times, subtract the O associated with the capsules (as well as the O from the crucible, flux, and graphite powder, if this has not already been accounted for), then divide the average of the results by the slope of the fit line, 0.999 ± 0.050. The 95% confidence interval can then be calculated via appropriate propagation of error and multiplication by a Student's t-value based on the number of measurements. To produce a good estimate of the value's distribution, the authors recommend 5–10 replicate measurements per sample, especially for samples whose O content might be near the MDL.

By handling samples in a glovebox environment that is actively maintained below 1 ppm of O_2 and H_2O, the authors were able to confirm further improvements to the method in terms of lower MDL and reduced the standard deviation between replicates. Other recommended strategies to improve

MDL are to increase the sample mass (fill capsules up to 0.2 g of salt) and double or triple crimped if prepared in a controlled inert glovebox. If samples are not prepared in a low-oxygen setting, leaving the capsules open may improve repeatability as atmospheric oxygen can be flushed from the capsule upon loading into the machine.

FLiBe Comparison Results. The results of the measurements on the four different batches of FLiBe are shown in Table 1. Two of the FLiBe samples, UW-P and KP-P, had

Table 1. Results from the Analyses of Oxygen Content in Samples from Four Batches of FLiBe

FLiBe batch	oxygen concentration (95% confidence interval)
Oak Ridge (ORNL-P)	330 ± 290 ppm (by mass)
UW−Madison (UW-P)	170 ± 120 ppm (by mass)
Kairos unpurified (KP-U)	740 ± 380 ppm (by mass)
Kairos purified (KP-P)	30 ± 80 ppm (by mass)

oxygen levels below the MDL of 220 ppm, though the latter was clearly further below this limit. The value for the UW FLiBe is also consistent with the estimate derived from the intercept of the calibration curve. The ORNL and KP-U samples were both above the MDL but had very broad 95% confidence intervals. In all cases, the confidence intervals were substantially broadened by the use of only five analyses per batch; had the material on hand permitted more analyses, the confidence intervals would likely have narrowed considerably. The difference between the purified and un-purified samples from Kairos was both clear and statistically significant, demonstrating that the method is effective in characterizing the FLiBe oxygen content in a range that is significant to purification processes and engineering systems operations.

CONCLUSIONS

Here, we have presented a method for the accurate determination of oxygen in lithium beryllium fluoride (FLiBe) salts via inert gas fusion. When added to a nickel flux and graphite powder, oxygen recovery of FLiBe samples in tin capsules reached 99.9%. The method was shown to be effective at characterizing the degree of oxygen removal in FLiBe samples that have undergone different purification processes and therefore can be used as a metric to evaluate fluoride salt purification procedures. This analysis technique is relevant for FLiBe fundamental chemistry studies and to characterize oxygen impurities level that are expected in FLiBe industrial-scale systems. In addition, we expect, based on its success and the success of a similar method in FLiNaK, that this technique could be extended to other fluoride salts in future work. The development of this technique will open the door to a deeper understanding of the oxygen chemistry behavior and solubilities in molten fluoride salts, which play an important role in salt systems' chemistry control and corrosion.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c04270.

Specific instrument parameters and settings for the LECO ON836 used for the final calibration and sample analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

Nicholas J. Condon − *Analytical Chemistry Laboratory, Chemical and Fuel Cycle Technologies Division, Argonne National Laboratory, Lemont, Illinois 60439, United States;* ⊙ orcid.org/0000-0001-5583-4852; Email: ncondon@anl.gov

Authors

Susan Lopykinski − *Analytical Chemistry Laboratory, Chemical and Fuel Cycle Technologies Division, Argonne National Laboratory, Lemont, Illinois 60439, United States*

Francesco Carotti − *Kairos Power, Alameda, California 94501, United States*

Kaitlin E. Johnson − *Kairos Power, Alameda, California 94501, United States*

Alan Kruizenga − *Kairos Power, Alameda, California 94501, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c04270

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Forsberg, C.; Zheng, G.; Ballinger, R. G.; Lam, S. T. Fusion Blankets and Fluoride-Salt-Cooled High-Temperature Reactors with Flibe Salt Coolant: Common Challenges, Tritium Control, and Opportunities for Synergistic Development Strategies Between Fission, Fusion, and Solar Salt Technologies. *Nucl. Technol.* **2019**, *206*, 1778−1801.

(2) Blandford, E.; Brumback, K.; Fick, L.; Gerardi, C.; Haugh, B.; Hillstrom, E.; Johnson, K.; Peterson, P. F.; Rubio, F.; Sarikurt, F. S.; et al. Kairos Power Thermal Hydraulics Research and Development. *Nucl. Eng. Des.* **2020**, *364*, 110636.

(3) Thoma, R. E. *Chemical Aspects of MSRE Operations*: United States, 1971.

(4) Zhang, J.; Forsberg, C. W.; Simpson, M. F.; Guo, S.; Lam, S. T.; Scarlat, R. O.; Carotti, F.; Chan, K.; Singh, P. M.; Doniger, W.; Doniger, W.; et al. Redox Potential Control in Molten Salt Systems for Corrosion Mitigation. *Corros. Sci.* **2018**, *144*, 44−53.

(5) Shaffer, J. H. *Preparation and Handling of Salt Mixtures for the Molten Salt Reactor Experiment*: United States, 1971.

(6) Baes, C. F. J. *Reactor Chemistry Division Annual Progress Report for Period Ending December 31, 1966*, 1967.

(7) Song, Y.; Shen, M.; Peng, H.; Wang, C.; Zhao, S.; Zuo, Y.; Xie, L. Solubility of Cr_2O_3 in Molten Fluorides with Different ZrF_4 Contents and Fluoroacidities. *J. Electrochem. Soc.* **2020**, *167*, 023501.

(8) Song, Y.; Shen, M.; Zhao, S.; Tang, R.; Xie, L.; Qian, Y. Interactions between Oxide and $LiF-BeF_2-ZrF_4-UF_4$ System through Electrochemical Techniques. *J. Electrochem. Soc.* **2021**, *168*, 036513.

(9) Goh, B.; Carotti, F.; Scarlat, R. O. A Review of Electrochemical and Non-Electrochemical Approaches to Determining Oxide Concentration in Molten Fluoride Salts. *ECS Trans.* **2018**, *85*, 2470.

(10) Goldberg, G.; Meyer, A. S.; White, J. C. Determination of Oxides in Fluoride Salts by High-Temperature Fluorination with Potassium Bromotetrafluoride. *Anal. Chem.* **1960**, *32*, 314−317.

(11) Sulejmanovic, D.; Kurley, J. M.; Robb, K.; Raiman, S. Validating Modern Methods for Impurity Analysis in Fluoride Salts. *J. Nucl. Mater.* **2021**, *553*, 152972.

(12) *HSC Chemistry*; Metso Outotec Oyj, 2021.

(13) Ingersoll, D. T.; Forsberg, C. W.; Ott, L. J.; Williams, D. F.; Renier, J. P.; Wilson, D. F.; Ball, S. J.; Reid, L.; Corwin, W. R.; Del Cul, G. D.; et al. *Status of Preconceptual Design of the Advanced High-Temperature Reactor (AHTR)*; ORNL/TM-2004/104: United States, 2004.

(14) Madelung, O. *Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys*; *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology-New Series*; Springer-Verlag Berlin, 1992.

(15) Okamoto, H. Ni-Sn (Nickel-Tin). *J. Phase Equilib. Diffus.* **2008**, *29*, 297−298.

(16) Virtanen, P.; Gommers, R.; Oliphant, T. E.; Haberland, M.; Reddy, T.; Cournapeau, D.; Burovski, E.; Peterson, P.; Weckesser, W.; Bright, J.; et al. SciPy 1.0: fundamental algorithms for scientific computing in Python. *Nat. Methods* **2020**, *17*, 261−272.

(17) Boggs, P. T.; Rogers, J. E. Orthogonal Distance Regression. *Contemp. Math.* **1990**, *112*, 183.