Revised Numerical Model for F_2 Bubble Breakdown in Molten FLiBe and its Economics in the Fuel Cycle

K. Seto
University of Ontario Institute of Technology, Ontario, Canada
kelvin.seto@uoit.ca

A PhD Level Submission

Summary

A one-dimensional numerical model of the breakdown for a fluorine bubble due to break-up and chemical reactions with dissolved UF_4 and PuF_4 in the molten salt reactor (MSR) volatilization process was revised. The updated model utilized a more realistic, 1.0 cm F_2 bubble to study the breakdown process in the idealized MSR fuel purification vessel. Although more accurate reaction interface and F_2 reactivity values were used, chemical reactions were still found to be the primary cause of bubble breakdown. The importance of efficiency in F_2 usage in the purification process on the economic and safety point of view was discussed.

1. Introduction

The fluoride volatility process is one of the methods that have been evaluated for the purification of the LiF-BeF_2 (FLiBe) eutectic used in MSR fuel cycle chemistry [1,2]. The MSR is a homogenous nuclear reactor that utilizes dissolved uranium (in the UF_4 form) to drive the fission reaction in molten LiF-BeF_2 salt, which also contains Pu fission products. The fused salt volatilization (purification) technique involves the fluorination of used MSR fuel via sparging with F_2 gas, in order to separate the resultant volatile compounds, such as UF_6, from non-volatile fluorides. The volatilization technique has a working temperature range of 500 – 550 °C [1,2], and follows the reaction [1-2]:

$$UF_4 + F_2 \rightarrow UF_6 \quad (1)$$

An alternative, F_2-bubbling technique is examined using a one-dimensional numerical model of the breakdown of a F_2 bubble was revised, utilizing more accurate bubble sizes and reaction rates to study the breakdown process. While excess F_2 is separated from the evolved fluorides in the off-gas and reused in the system, the chemical reactivity of F_2 results in unnecessary losses in the system. A brief examination of the economics of F_2 generation will be discussed in order to illustrate the importance of efficiency in the sparging technique.

2. Bubble-Breakdown Model

2.1. System Design

The fused salt volatilization technique involves the fluorination of used fuel in MSRs with F_2 gas and subsequent separation of the resultant volatile compounds; hexavalent compounds UF_6 and

PuF_6, from non-volatile fluorides UF_4, PuF_4, and other transition metal fluorides. Shear forces imparted by eddies within the FLiBe molten salt lead to the break-up of larger bubbles into smaller daughter bubbles. The processes being considered in this model are physical bubble break-up and chemical reactions between F_2 and the fluorinated compounds UF_4 and PuF_4 in solution. The height of the idealized reaction vessel is 10 m and divided evenly into 50 sections, with each section identified as a 'node'. The temperature and temperature-related physical characteristics were selected based on the typical working conditions of MSR reactors of 500 – 550 °C [1-3]. The revised initial bubble sizes were chosen based on more realistic bubble sizes expecting in bubbling systems.

Two of the major assumptions in the numerical model are:

1) breakdown or interaction (physical or chemical) of the daughter bubble with other species is not considered, because the focus is on the primary 'parent' bubble; and
2) only reactions of F_2 with UF_4 and PuF_4, are considered, with interactions between F_2 and container walls disregarded due to the unpredictable nature of molecular F_2.

Revisions to the previous model include:

1) 1 cm initial, and 3 mm daughter bubble diameter (vs. 4 cm and 4 mm);
2) F_2 reaction efficiency at 90% (vs. 60%); and,
3) only 0.1 mm of the outer bubble layer at the interface available to react in solution (vs. 1.5 mm originally).

The theoretical equation used to model bubble break-up is described below according to [4].

2.1.1. Bubble Breakage

The rate at which a bubble breaks-up is determined by the interaction of bubbles with turbulent eddies in solution. The bubbles are deformed against the interfacial forces, which eventually lead to break-up. The break-up probability, r_1, of bubbles of size v into bubbles of size v_d and $(v - v_d)$ can be calculated from:

$$r_1(v_d, v) = 1.5(1-\alpha_g)\,\frac{\rho_l^{11/5}\varepsilon^{9/5}}{\gamma^{11/5}}\frac{\hat{v}^{1/3}}{\hat{v}_d^{4/3}} \times \left(min\left(\hat{v}_d^{7/6}, \frac{1}{\hat{v}_d^{7/9}}\right) - \frac{1}{\hat{v}^{7/9}}\right) \quad (2)$$

A list of the variables that were used in the numerical model is provided in Table 1:

Table 1: Variables Set for System Characteristics

Property	**Variable**	**Value**	**Ref.**
Temperature	T	773 K [1]	[1]
Void fraction	α_g	5%	
Initial bubble diameter	Used to calculate v	0.01 m	
Diameter of daughter bubble	Used to calculate v_d	0.003 m	
Superficial bubble velocity	j_g	0.25 m/s	
Density of FLiBe (at 773 K)	ρ_{FLiBe}	2036 $Kg \cdot m^{-3}$	[3]
Surface tension of FLiBe (at 773 K)	γ_{FLiBe}	0.2050 $Kg \cdot s^{-2}$	[3]

Therefore, the decrease in bubble volume per second due to bubble break-up is:

$$V_{break} = \frac{1}{r_1} \quad (3)$$

2.1.2. Chemical Reactions

The reaction between F_2 with UF_4 and PuF_4 in molten FLiBe are assumed to go through the following overall chemical reactions [1], with their corresponding reaction rates, R_U and R_{Pu}:

$$UF_4 + F_2 \rightarrow UF_6 \qquad R_U = k_U[F_2][UF_4] \quad (4)$$
$$PuF_4 + F_2 \rightarrow PuF_6 \qquad R_{Pu} = k_{Pu}[F_2][PuF_4] \quad (5)$$

where, R_x is the reaction rate with a rate constant k_x for reaction x, $[F_2]$, $[UF_4]$, and $[PuF_4]$ represents the concentration of the reactants, with numerical values obtained from [2]. The maximum reaction rate may be determined by kinetic limits (sum of reaction rates between F_2 and UF_4 or PuF_4) or physical limits (availability of F_2 at bubble surface).

A list of the chemical constants that were used in the numerical model is provided in Table 2:

Table 2: Constants used for Chemical Characteristics at 773 K

Reactions	**Activation Energy**	**Arrhenius Factor**	**k**	**Ref.**
$UF_4 + F_2 \rightarrow UF_6$	64240 J/mol	221.4	1.01×10^{-2} $mol^{-1}s^{-1}$	[5,6]
$PuF_4 + F_2 \rightarrow PuF_6$	36000 J/mol	0.127	4.69×10^{-4} $mol^{-1}s^{-1}$	[7]
$[UF_4]$ = 0.496 mol/L		$[PuF_4]$ = 0.025 mol/L (assume 5% of $[UF_4]$)		

Finally, the total decrease in bubble volume is the sum of bubble losses based on Eqs. 2 - 5:

$$\Delta v = -(V_{break} + V_{rxn}) \quad (5)$$

3. Analysis and Discussion

This numerical analysis of F_2 bubble dissolution was conducted in MATLAB with physical and chemical properties of molten FLiBe obtained from various sources [1,2,5]. The boundary conditions were selected such that once the primary bubble had reached a size smaller than the minimum stable bubble size, d_{stable}, bubble break-up would not occur any further. In the ideal case, if the bubble fully dissolves near the top of the vessel, the bubble's efficiency is considered to be maximized, since a significant portion of the gas would not be removed by an off-gas stream. The revised model used an initial diameter of 1 cm to provide a more realistic bubble size that could form from a gas injection system, as opposed to 4 cm in the previous test case.

The relative contributions of volume loss (via break-up and reactions) were compared. Initial bubble volume loss was high, primarily because of the amount of surface area available for reactions to occur. The numerical model also indicated that volume loss by bubble break-up was very small compared to that of reactions. Figure 1 shows the relative contribution to volume loss by bubble break-up and reaction with UF_4 and PuF_4. Although the amount of F_2 available to

react was restricted to the 0.1 mm depth of gas/solution interface, reactions were still significantly higher than bubble break-up. Spontaneous bubble break-up, r1, remained low because they are highly dependent on solution properties (density and surface tension). Decreasing these values (to those of H_2O, for instance) had a positive effect on the break-up rate. In addition, an increase in the void fraction indicates more bubbles are present, and higher turbulence in solution resulting in higher rates of bubble break-up.

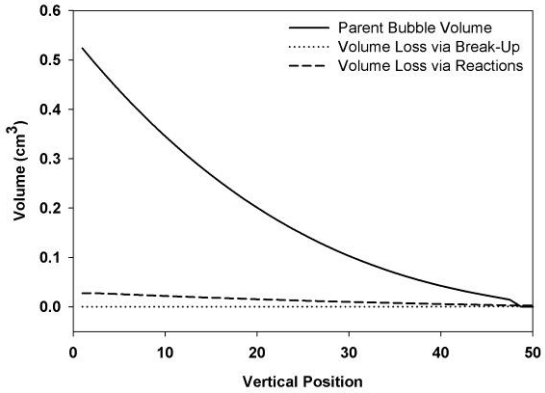

Figure 1 Overall contributions to bubble volume loss from bubble break-up and reactions as a function of node. Initial bubble size of 10 mm, daughter size of 3 mm.

This revised model using a 1 cm bubble still showed reasonable efficiency, dissolving near the top of the solution and thereby avoiding waste in the off-gas. Multiple gas streams should promote turbulent flow in the volatilization reactor and higher break-up rates, so larger initial bubble sizes may be required. In either case, the bubbling process should be more efficient than the existing sparging technique, by maximizing the contact time between F_2 and the solution. More work is required to build a better understanding of the mathematical model and the break-up phenomenon. Future work to increase complexity of the model, will include a distribution of bubble break-up sizes, a bubble coalescence step, and actively changing reactant concentrations. The validity of this model may be confirmed in future work.

The bubbling technique is proposed as an alternative to sparging in the fused salt volatilization technique. The evolved volatile fluorides, UF_6 and PuF_6, are captured and separated from excess F_2 in the off-gas, which is reused in the system. The high reactivity of fluorine results in numerous losses throughout the system as well as potential safety hazards. The cost to generate fluorine gas has decreased dramatically from ~ $20.6/kg in the early 70s [8] to $5 – 8/kg at the present date [9]. When one considers the difficulties in storage and handling of F_2 gas, the price can be multiplied by at least 10 to 100 times the original price when shipped in cylinders [1,2]. Thus, the bubbling technique seemingly appears to be a more efficient option to minimize the amount of waste and reprocessing required for purification of depleted FLiBe.

The cost breakdown for the long-term generation of fluorine gas (only considering inputs) is shown in Table 3. The overall cost of F_2 is highly dependent on the price of electricity if the price of the electrochemical cell, operational, and maintenance cost were disregarded. A

previous estimate placed the contribution of these three factors at 43% of the total cost for F_2-generation, while HF and electricity made up only 26% and 11% of the total cost, respectively [8].

Table 3: Sample Calculation for Fluorine Generation Price

	Amount	Price per	App. Total ($)	% of total
Electrode	32 blocks	$ 350/block	11 200	1
Electricity	3 000 000 kWh	6.5 cents/kWh	195 000	19
KF-HF	6 000 kg	$ 10/tonne	60	6
HF	150 000 kg	$ 5 000/tonne	750 000	74
SUM			**1 016 200**	**100**
Fluorine Generated (5-year period)			**152 000 kg**	
Price (per kg)			**$ 6.7/kg**	

For 6 kA operating current, 3.47 kg/h F_2-output in a single Union Carbide (USA) cell

4. Concluding Remarks

Chemical reactions were found to be the major contributing factor leading to breakdown of the fluorine gas bubble in solution. Small changes in the daughter (break-off) bubble size had minimal effect on the losses due to break-up. This was because the bubble break-up is dependent on the physical properties (density and surface tension) of the solution itself. The numerical model uses a number of assumptions for the size of the parent and daughter bubble sizes, superficial bubble velocity, and vessel height. The values used for calculations of chemical properties were obtained by interpolation of experimentally obtained data.

The economics of fluorine generation provide insight into F_2-bubbling as an alternative to the sparging technique used in the MSR experiments of the 70s for FLiBe purification. Maximizing contact between F_2 and the depleted salt will minimize the amount of potential waste and reprocessing required to reuse the F_2 capture in the off-gas stream during the volatilization technique.

5. References

[1] J. Uhlir, "Chemistry and Technology of Molten Salt Reactors – History and Perspectives", *Journal of Nuclear Materials*, Vol. 360, p. 6, 2007.

[2] P.N. Haubenreich, J.R. Engel, "Experience with the Molten-Salt Reactor Experiment", *Nuclear Applications and Technology*, Vol. 8, p. 118, 1970.

[3] S.J. Zinkle, "Summary of Physical Properties for Lithium, Pb-17Li, and $(LiF)_n \cdot BeF_2$ Coolants", APEX Study Meeting, 1998.

[4] F. Lehr, D. Mewes, "A Transport Equation for the Interfacial Area Density Applied to Bubble Columns", *Chemical Engineering Science*, Vol. 56, p. 1159, 2001.

[5] V.Y. Labaton, K.D.B. Johnson, "The Fluorides of Uranium – III. Kinetic Studies of the Fluorination of Uranium Tetrafluoride by Fluorine", *Journal of Inorganic Nuclear Chemistry*, Vol. 10, p. 74, 1959.

[6] T.A. O'Donnell, D.F. Stewart, P. Wilson, "Reactivity of Transition Metal Fluorides. II. Uranium Hexafluoride", *Inorganic Chemistry*, Vol. 5, no. 8, p.1438, 1966.

[7] M. Iwasaki, N. Ishikawa, A. Takahashi, T. Sakurai, "Fluorination of Plutonium Dioxide by Fluorine", *Journal of Nuclear Science and Techology*, Vol. 11, no. 9, p. 403, 1974.

[8] A.J. Rudge, "Production of elemental fluorine by electrolysis" in *Industrial Electrochemical Processes*, A.T. Kuhn (Ed.), Amsterdam, Chap. 1, p. 1, 1971.

[9] M. Jaccaud, R. Faron, D. Devilliers, R. Romano, "Ullman's Encyclopedia of Industrial Chemistry – Fluorine", Wiley VCH, Vol. 15, p. 381, 2012.