Computer Modeling for Lithium Safety in Fusion Systems: LINT and MELCOR

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Abstract

Accidents postulated to occur involving the chemical interaction of lithium with water and air are analyzed for the blanket test module (BTM) in ITER using two different computer models. The first model is a newly developed thermodynamic equilibrium computer model LINT. The second model uses the MELCOR systems code. The same basic logic used in LINT is incorporated into the MELCOR FDI package, though MELCOR allows for non-equilibrium conditions. This addition to MELCOR's capability allows MELCOR to be used in reactor systems analyses over a wide range of accident conditions; i.e., thermal-hydraulic events with chemical interactions involving molten metals. Pressure and temperature histories are predicted for a control volume in thermal equilibrium (LINT) or non-thermal equilibrium (MELCOR) in any accident scenario involving chemical interaction between lithium and water or air. These computational models are applied to postulated accidents for the ITER blanket test module.

In the ITER vacuum vessel, failure is not predicted to occur for lithium leaks from the BTM into water because of low lithium driving pressures resulting in self-limiting leaks. However, failure is predicted in minutes for a high pressure water leak into any amount of pre-existing lithium provided the pressure suppression system fails to work as designed. Assuming a 10 kg/s initial water leak rate, calculated failure times range from a maximum of 15 minutes with no lithium present to a minimum of less than two minutes for an initial lithium pool of 1300 kg.

For lithium leaks from the BTM into the ITER reactor vault containing pure air at atmospheric pressure, calculations predict failure if an adiabatic system is assumed, but not if heat loss to the surrounding cold structures is considered. Both pool and droplet configurations are considered for diffusional mass transfer calculations in determining chemical reaction rates, with droplet configurations inducing faster reaction rates and pressurization. Finally, pressure and temperature histories are predicted in the reactor vault for air ingress rates of 1, 10, 50, and 80 vol%/day into an argon atmosphere. Calculations show that this scenario poses no serious threat to the integrity of the reactor vault.
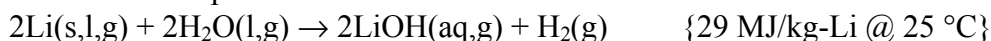
1 Introduction

The alkali metals have a long history of use in energy systems, particularly in nuclear power reactor design. These metals have excellent heat transfer characteristics and can be pumped easily either with conventional or electromagnetic pumps. For example, numerous fission reactors have been designed and built using sodium as a coolant [14]. Fusion reactor designs often use lithium for the dual purpose of coolant and tritium breeder. Specifically, several test modules using lithium or lithium-alloys will be tested in the International Thermonuclear Experimental Reactor (ITER). This reactor is now in the engineering analysis stage of its base design.

The ITER reactor design has some special lithium concerns since it is primarily a water-cooled reactor but also contains lithium coolant in some of its test modules. One of the primary concerns is that lithium is chemically reactive with both water and air. Therefore, special consideration must be given to potential lithium interactions in the ITER safety analysis for given abnormal events. This paper describes the various chemical interactions which lithium undergoes when exposed to water or air within a fusion system. The computer model LINT developed to calculate the interactions is described, and the new capabilities incorporated into MELCOR based on this model are discussed. These additions to MELCOR will extend its capabilities as a design analysis tool to fusion systems such as the ITER design. Finally, the principal reactions are outlined for two different sets of accident scenarios in ITER, and specific results are discussed.
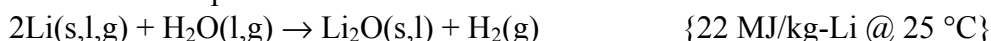
1.1 Li-H_2O interactions

When lithium reacts with water, two basic scenarios are possible. First, a relatively small amount of lithium may come in contact with an excess of water. This type of situation is possible if a pipe carrying liquid lithium coolant were to break, causing a stream of lithium to leak out and fall into a pool of water. Second, water may come in contact with an excess of lithium. This type of situation could occur if a high pressure water leak occurred near a lithium pool, or if cold water leaked into a volume containing lithium. The principal reactions are listed below [3,4,10,15]:

Reaction in the presence of excess water:
$$2Li(s,l,g) + 2H_2O(l,g) \rightarrow 2LiOH(aq,g) + H_2(g) \qquad \{29 \text{ MJ/kg-Li @ } 25 \text{ °C}\}$$

Reaction in the presence of excess lithium:
$$2Li(s,l,g) + H_2O(l,g) \rightarrow Li_2O(s,l) + H_2(g) \qquad \{22 \text{ MJ/kg-Li @ } 25 \text{ °C}\}$$

The hydroxide product is especially interesting because it can dissociate or reform from other products when thermodynamic conditions are favorable. This occurs during heating or cooling at temperatures in excess of the boiling point of the lithium hydroxide. Although the heats of reaction are endothermic from these phenomena and are much less in magnitude than the primary chemical reactions, they are important in that they take precedence over the exothermic

reactions at elevated temperatures. These dissociation reactions help to mitigate the pressurization of the vacuum vessel or reactor vault. Nevertheless, by this point temperatures are quite high and metal structures may have lost their integrity.

Lithium-hydroxide dissociation:
$$2LiOH(s,l) \rightarrow Li_2O(s) + H_2O(g) \qquad \{-1.1 \text{ MJ/kg-LiOH @ } 1312 \text{ °C}\}$$

Lithium-hydroxide formation:
$$Li_2O(s,l) + H_2O(g) \rightarrow (LiOH)_2(g) \qquad \{-2.6 \text{ MJ/kg-LiOH @ } 1312 \text{ °C}\}$$
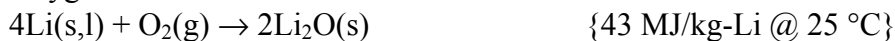
1.2 Li-air interactions

In air, lithium reacts with all the major gas constituents. Since nitrogen and oxygen compose over 98% of the molecules in air, these two major components are the only ones considered here. Air is assumed to consist of 79% nitrogen and 21% oxygen for analyses in this work. The chemical reactions between lithium, nitrogen, and oxygen are listed below. Dissociation of lithium nitride at high temperatures also needs to be considered in the case of chemical reactions extensive enough to elevate temperatures above 1000 K. In this case a similar mitigating effect on the pressurization of the reactor vault will occur due to the endothermic nature of the dissociation.

Nitrogen reaction:
$$6Li(s,l) + N_2(g) \rightarrow 2Li_3N(s) \qquad \{7.9 \text{ MJ/kg-Li @ } 25 \text{ °C}\}$$

Oxygen reaction:
$$4Li(s,l) + O_2(g) \rightarrow 2Li_2O(s) \qquad \{43 \text{ MJ/kg-Li @ } 25 \text{ °C}\}$$

Lithium nitride dissociation:
$$2Li_3N(s) \rightarrow 6Li(l) + N_2(g) \qquad \{-4.7 \text{ MJ/kg-Li}_3\text{N @ } 1088 \text{ °C}\}$$

Other lithium chemical interactions with minor gas constituents in air such as CO_2 are not considered in this paper [10].

2 Postulated ITER accident scenarios

The ITER fusion reactor safety analysis has two major accident scenarios regarding lithium. Due to the close proximity of water and lithium coolant channels in the lithium test modules of ITER, a postulated severe accident has the potential to release both lithium and water into the vacuum vessel. Similarly, in the reactor vault surrounding the lithium test module, a severe accident could cause both air and lithium to enter the vault [12]. Both of these situations could cause serious damage during the ensuing chemical reactions. A simple diagram (not to scale) of the ITER lithium test module setup is shown below in Figure 1.
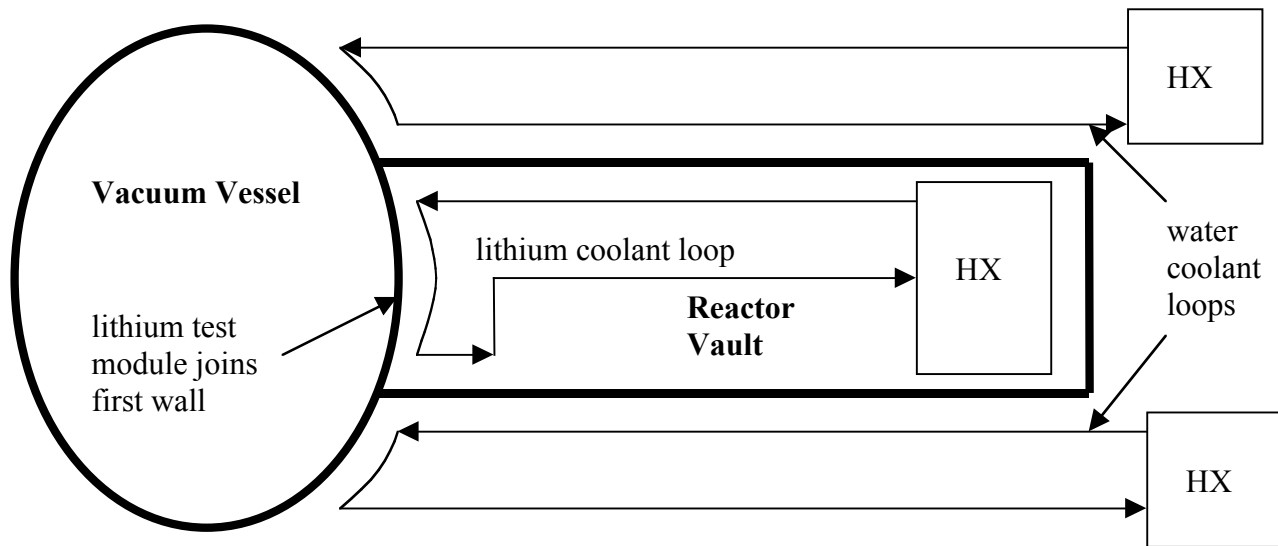
Figure 1

2.1 Li-H$_2$O interactions

The postulated accident for a lithium-water interaction in ITER occurs in the vacuum vessel (VV) of the reactor, which has a volume of 3800 m^3. The design of the lithium-vanadium ITER test modules (ITM's) specifies water coolant driven at around 50 bar and operating between 320 and 380 K, while the lithium coolant is driven at a relatively low 2 to 5 bar with exit temperatures between 600 and 800 K [9]. An accident involving an in-vessel pipe break of the ITM may lead to lithium and water coming into contact with each other [12].

Two possibilities exist in this scenario: first, a pre-existing pool of water could be present on the floor of the vacuum vessel with a subsequent lithium leak into the pool; and second, a pre-existing pool of lithium could be present on the floor of the vacuum vessel with a subsequent leak of steam or liquid water. In the first case, the reaction starts with a lithium leak into an excess of water. This results in the production of aqueous lithium hydroxide and hydrogen gas. In the second case, the reaction starts with a water or steam leak into an excess of lithium. This results in the production of solid lithium oxide and, again, hydrogen gas. The hydrogen gas production is a concern because of the potential for a hydrogen explosion to occur. Design limits require production of no more than 10 kg of hydrogen in any one accident scenario. Calculations were performed to determine pressure and temperature histories in the vacuum vessel for specified water or lithium flow rates given a driving pressure for the coolant pumping system. Hydrogen explosions were not modeled. Results from these calculations are discussed later in this report.

2.2 Li-air interactions

The second type of accident scenario postulated to occur in ITER is a lithium leak into the reactor vault outside of the lithium test module. This type of scenario involves chemical reactions with air. Normally, the 2150 m^3 area surrounding the vacuum vessel (the reactor vault, or RV) is flooded with inert argon cover gas. Since argon is heavier than air, retention of the

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cover gas is not a difficult problem. However, if cracks are present, air ingress is possible through the process of gaseous diffusion. Therefore, calculations were performed for a lithium leak into an air environment forming pools of 16.5 and 165 m^2 in surface area. Reaction rates are then dependent on the surface area of the lithium pool.

The case of lithium-air interactions considered here is generally one of lower concern than the lithium-water interactions for two reasons.   First, the heat of reaction for prevailing lithium-nitrogen combination is much lower than the Li-H_2O interactions. Since nitrogen is the major constituent in air, the relatively high heat of reaction with oxygen is offset. This means that temperatures are kept at more moderate levels in the Li-air case. Second, the product species produced from the Li-air interactions are less corrosive and do not include the potentially explosive hydrogen gas [10]. Nevertheless, if significant quantities of lithium react with either air or water, the resulting temperatures and pressures can be significant even for the relatively large volumes considered here.

3   Lithium interaction models

A rather simple conceptual geometry was used for the calculations discussed in this report. In both water and air interaction scenarios a single control volume with lithium, water, or air mass sources was defined. Pools of lithium and/or water are assumed to form on the floor of the volume in the Li-liquid H_2O case, while Li-steam/air interactions could occur with lithium droplets suspended in the atmosphere or from the surface of a pool formed on the floor. The different possibilities are shown in Figures 2 and 3.
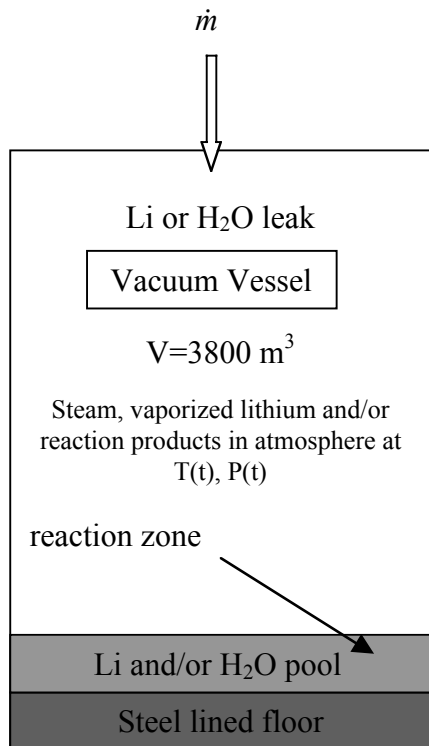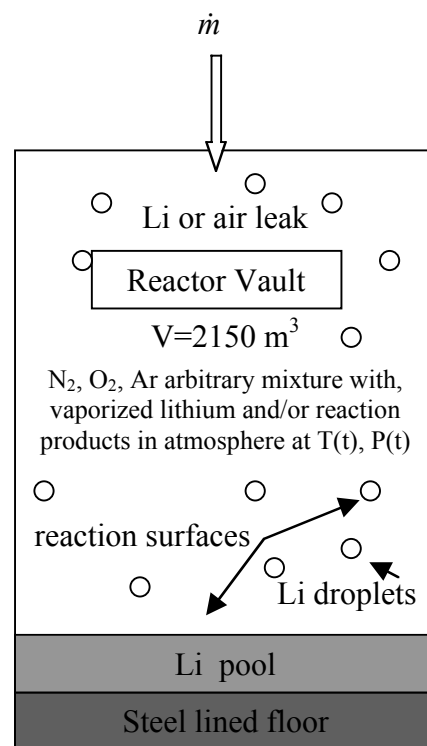

Figure 2

Figure 3

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The models shown here are similar to the one-cell option of the LITFIRE code as described by D.S. Barnett [17]. The LINT model is a bit simpler than LITFIRE's multi-node model in that the entire control volume is considered to be in thermal equilibrium. Conversely, MELCOR's capabilities include non-equilibrium conditions and arbitrary complex geometries. Thus, MELCOR can be used to model the two-cell or pan options in LITFIRE as well as other situations such as can be found in the complex geometry of ITER.

3.1 LINT computer model

A computer model, LINT (Lithium INTeractions), was developed to calculate results for each of the accident scenarios described above. This computer model was written using the FORTRAN90 language and run on a UNIX workstation. This model was developed as an outgrowth of an academic project. The purpose of the model was to provide bounded estimates on the MELCOR simulations of lithium air/water interactions which would follow.

The basic assumptions used in the model are as follows:
1. chemical reactions are instantaneous and stoichiometric
2. constituents in the control volume system are always in thermal equilibrium
3. gases behave as if they are ideal
4. liquids and solids are incompressible.

The assumption of instantaneous reactions means that all substances present together that can react, will react. This assumption is relaxed slightly for lithium interactions with air because a solid product layer will form a crust on the surface of the lithium liquid through which air must diffuse. This limits, in a sense, the amount of lithium and air present "together". All the gas molecules from the atmosphere that do penetrate this crust, however, are instantaneously reacted. Furthermore, the assumption that the entire lithium mass in the control volume is available for reaction if needed may be conservative and unphysical; especially when large volumes of substances are reacting in short times. This restriction will be lifted with future improvements on the model. The system control volume here consists of either the ITER vacuum vessel (for water interactions with lithium) or reactor vault (for air interactions with lithium).

The operation of LINT is essentially one of solving the time-dependent first law of thermodynamics in a chemically reactive open system. For such a system, the general form of the energy balance is as follows [6]:

$$\frac{dU}{dt} = Q - W + H_{in} - H_{out}.$$

(1)

This equation can be rearranged with $W=0$ and $U=\Sigma(n_i u_i)$ as

$$0 = \frac{d}{dt}\left[\sum_i (n_i u_i)\right] + Q + \sum_j (\dot{n}_j h_j).$$

(2)

Here n_i is the number of moles of species i already in the control volume with internal energy u_i, and n_j is the number of moles of species j leaking into the control volume with enthalpy h_j.

An initial amount of lithium, water, or air is defined to exist in the control volume and then a leak of either lithium or water is bled into the system based on an external pressure and an area through which the leaking fluid is allowed to flow. The leak is modeled based on Bernoulli's principle, which can be written for this simple case as follows:

$$\dot{n}_j = \frac{A_{leak}}{MW}\sqrt{\frac{2\rho\Delta P}{K}},$$ (3)

where A is the cross-sectional flow area, MW is the molecular weight of the substance, ρ is the density, P is pressure, and K is the discharge coefficient for the flow.

The leak is allowed to flow into the control volume at a constant rate for the duration of a single time step, at which point the flow rate will be readjusted for the next time step. During each time step, the appropriate chemical reactions are completed and a new condition of thermodynamic equilibrium is calculated iteratively by application of the first law of thermodynamics over that time period. The iterative routine used was taken from Press et al. [7]. Temperature dependent thermodynamic properties for each substance are built into the code [1,2,5,8]. Since pressure in the control volume will not reach very large values before failure, the equation of state for water is simplified to that at a constant pressure of one atmosphere. At low pressures, this assumption is reasonable. Both adiabatic and non-adiabatic calculations are made for comparison sake. The non-adiabatic systems are modeled as if the control volume walls are the surface of an infinite medium made of steel. Thus, heat transfer to the walls of the non-adiabatic system is given by $Q=hA\Delta T$ where the overall heat transfer coefficient h is found from the natural convection and conduction heat transfer coefficients. The heat transfer coefficient for conduction to the surface is found using the infinite medium approximation.

$$h_{tot}^{-1} = h_{nc}^{-1} + h_{cond}^{-1} \qquad \text{where} \qquad h_{cond} = \frac{k_w}{2}\sqrt{\frac{\pi\rho_w c_{p_w}}{k_w dt}}.$$ (4), (5)

LINT tracks the temperature and pressure histories for the control volume as well as the molar amount of each substance throughout a calculation. Lithium-air interactions are calculated on a more complex basis than lithium-water interactions. This is due to the formation of a product layer crust on the lithium surface. During the first time step in which chemical reaction occurs, all of the lithium injected into the system reacts. An initial product layer thickness is then calculated from the reaction in this time step. Subsequently, reaction products are added to the product layer as the nitrogen and oxygen gas phase reactants diffuse through to the fresh lithium inside. The reactant mass diffusing through the product layer is calculated using the following equation:

$$\dot{n}_{react} = K_{tot}A_{surface}(c_{atm} - 0).$$ (6)

where n is the molar diffusion rate, K_{tot} is the mass transfer coefficient, A is the product layer surface area, and c is the nitrogen or oxygen reactant concentration in the atmosphere of the chamber. The mass transfer coefficient, K_{tot}, is found from a combination of a gas reactant

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diffusing through the atmosphere to the product layer surface and then diffusing through the product layer crust to the fresh lithium underneath:

$$K_{tot}^{-1} = K_{atm}^{-1} + K_{crust}^{-1}. \tag{7}$$

The mass transfer coefficients are then found using formulations analogous to heat transfer with convection through the atmosphere to the product layer surface and conduction through the solid surface [13]:

$$Sh = \frac{K_{atm}L}{D_{o,atm}} \quad \text{where} \quad K_{crust} = \frac{D_{0,crust}}{t_{crust}}. \tag{8), (9}$$

Depending on the situation modeled, there are two possibilities for the Sherwood number:

i)   pool surface mass transfer mode $Sh = 0.13(GrSc)^{1/3}$ (10)
ii) stagnant droplet mass transfer mode $Sh = 2.$ (11)

The dimensionless groups in the above equations are the Sherwood, Grashof (for mass diffusion), and Schmidt numbers. These dimensionless groups are the mass transfer analogs of the Nusselt, Grashof, and Prandtl numbers in heat transfer. The Grashof and Schmidt numbers are defined as follows:

$$Gr = \frac{L^3 \rho^2 \varsigma g \Delta x}{\mu^2} \qquad\qquad Sc = \frac{\mu}{\rho D_{o,crust}}. \tag{12), (13}$$

where L is the characteristic length scale, ρ is the reactant density, ς is a quantity relating the reactants' molecular weight and concentration relative to the atmosphere, Δx is the difference in reactant mole fractions between the atmosphere and the product layer interior, and μ is the reactant viscosity. These are all known quantities at the beginning of a time step. Finally, the diffusion coefficients, $D_{o,crust}$ and $D_{o,atm}$, must be defined in order to solve for the mass transfer rate. These are temperature dependent quantities defined respectively for reactants diffusing through the product layer and through any argon/air mixture in the atmosphere:

$$D_{o,crust} = ae^{-\frac{b}{RT}} \qquad\qquad D_{o,atm} = \frac{T^c}{P}d. \tag{14), (15}$$

Here a, b, c, and d are constants, R is the gas constant, T the gas temperature, and P the gas pressure.

3.2 MELCOR code modifications

MELCOR is an integrated engineering level systems code developed for use in fission reactor safety studies. This work is part of an ongoing effort to modify MELCOR for use in fusion systems as well as fission systems modeling. Previously, the liquid metals gallium, lead, and lithium-lead were added as fusion materials by Gracyalny. These materials were then made

accessible by the Fuel Dispersal Interactions package (FDI) in MELCOR. Furthermore, the low pressure melt ejection model was made a "standalone" model [16].

The current work includes the addition of lithium and its related compounds formed from chemical interactions with water and air. These materials were added to the Materials Properties package (MP) of MELCOR. Also, the capability to simulate lithium chemical interactions has been added to MELCOR based on the LINT model. These lithium chemical reactions can occur with steam, nitrogen, or oxygen when lithium is either dispersed in the atmosphere of a control volume or deposited on the surface of a heat structure. Thus, the following chemical interaction capabilities have been successfully incorporated into MELCOR:

a) Li-H_2O reactions in a control volume atmosphere
b) Li-H_2O reactions on the surface of a heat structure
c) Li-air reactions in a control volume atmosphere
d) Li-air reactions on the surface of a heat structure
e) Settling of lithium and its reaction products from a control volume atmosphere to a heat structure.

Oxidation reaction rates and settling rates for fission materials are already included in MELCOR through user-defined time constants in the input to a problem. This model was extended to include lithium reaction rates. In this way, a consistent method is used for all chemical interactions currently included in MELCOR [11]. One "oxidation" reaction rate constant is defined for the atmosphere and one for each heat structure. A similar time constant must be defined for settling rates from an atmosphere to any heat structure defined as a deposition surface. It should be noted that the oxidation time constants referred to here are separate from oxidation time constants included in modifications made at the Idaho National Engineering and Environmental Laboratory (INEEL) for fusion applications. INEEL's modifications use internal oxidation time constants for steam reactions on heat structures made of beryllium, tungsten, and carbon.

Written in differential form, the rate of change of lithium mass in a control volume atmosphere is determined by

$$\frac{dm_{Li}(t)}{dt} = -\frac{m_{Li}(t)}{\tau_{so}} + S_{Li} \qquad \text{where} \qquad \tau_{so}^{-1} = \tau_{st}^{-1} + \tau_{ox}^{-1}. \qquad (16), (17)$$

Here τ_{so}, τ_{st}, and τ_{ox} are the time constants for simultaneous oxidation and settling, settling, and oxidation, respectively. S_{Li} is the lithium mass source term.

Similarly, the rate of change of lithium reaction product masses can be written as follows:

$$\frac{dm_i(t)}{dt} = -\frac{m_i(t)}{\tau_{st}} + R_i(t)\frac{m_{Li}(t)}{\tau_{ox}} + S_i. \qquad (18)$$

The subscript i represents a reaction product and R_i is the mass of product i formed per unit mass of lithium reactant. Since lithium has several possible reaction products, careful account of which products are being formed must be kept. To further complicate things, R_i for each

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reaction product is a time dependent quantity. This is because the relative abundance of the potential reactants H_2O, N_2, and O_2 changes as the reactions proceed.

In a single MELCOR time step, the amount of lithium available for reaction is first calculated using the equation

$$dm_{Li,react} = FRC \bullet m_{Li} + S_{Li}(dt - \tau_{so} \bullet FRC)\frac{\tau_{so}}{\tau_{ox}} \qquad (19)$$

$$\text{where} \qquad FRC = 1 - e^{-\frac{dt}{\tau_{so}}}. \qquad (20)$$

Next, the relative amounts of H_2O, N_2, and O_2 allowed to react with the lithium mass determined above are calculated using a scheme dependent on the relative molar amounts of each substance. First, the molar ratios of water to air and of oxygen to air are determined. The amount of lithium allowed to react with each substance can then be found using the calculated ratios:

$$dm_{Li-H_2O} = \frac{dm_{Li} \bullet R_1}{1 + R_1} \qquad\qquad dm_{Li-air} = dm_{Li} - dm_{Li-H_2O} \qquad (21), (22)$$

$$dm_{Li-O_2} = R_2 \bullet dm_{Li-air} \qquad\qquad dm_{Li-N_2} = dm_{Li-air} - dm_{Li-O_2} \qquad (23), (24)$$

$$R_1 = \frac{n_{H_2O} \bullet F}{n_{O_2} + n_{N_2}} \qquad\qquad R_2 = \frac{n_{O_2}}{n_{O_2} + n_{N_2}}. \qquad (25), (26)$$

The factor F in the equation for R_1 is a transition smoothing factor between water and air interactions. This factor represents the relative preference of the lithium-water reaction over lithium-air reactions seen in experiments [10]. A value of 1000 was chosen for F so that essentially all of the water present will react before the air reactions can begin to take over. Any water present in a control volume during an FDI event involving lithium is then 1000 times more reactive than air present in the same volume.

It should be noted that the term "water" interaction actually refers only to water vapor in the atmosphere of a MELCOR control volume. Future work may include liquid water and fog interactions with lithium. Also, current modifications apply only to the high pressure melt injection sequence in MELCOR. However, the lithium interaction additions made to the code can easily be extended to the low pressure melt injection sequence as well.

4   Results for lithium-water interactions

In the vacuum vessel, a failure is considered to occur if the pressure exceeds 5 bar. Temperature limits are not considered as a failure mode in this study. Since the coolant pressures driving liquid lithium are below 5 bar in a typical fusion reactor such as ITER, the vacuum vessel cannot exceed the 5 bar pressure limit because the lithium leak will asymptotically be choked off as the vacuum vessel pressure approaches that of the lithium coolant pressure. On the other hand, failure of the vacuum vessel can easily occur when a leak from the high-pressure water coolant

system enters the vacuum vessel provided the pressure suppression system fails to work as designed. Driving pressures of 50 bar are used for the water coolant system in calculations for this paper. This means the vessel could fail even without any lithium interaction provided the pressure suppression system fails to work as designed. Such a failure would be due to water flashing to steam and pressurizing the vessel beyond the 5 bar limit.

4.1 Lithium leak into pre-existing water

Figures 4 and 5 show pressure histories for a lithium leak into a water pool where the driving pressures are 5 and 2 bar, respectively. The initial, nearly linear, portions of the plots represent the heating to boiling and subsequent vaporization of the water pool present in the control volume at the beginning of the calculation. The sudden jumps at about 25 and 50 seconds in the two LINT plots are due to a modeling peculiarity. Although water is modeled to boil over a small finite temperature increment, the internal energy model rises suddenly at the true boiling point in the center of the phase transition temperature range. This is not the case for MELCOR, where a full EOS is included and all phase transitions are continuous and smooth. Once the water pool is vaporized, the pressure rise tapers off as the lithium leak is choked off and lithium flow rates into the volume are reduced eventually to zero.
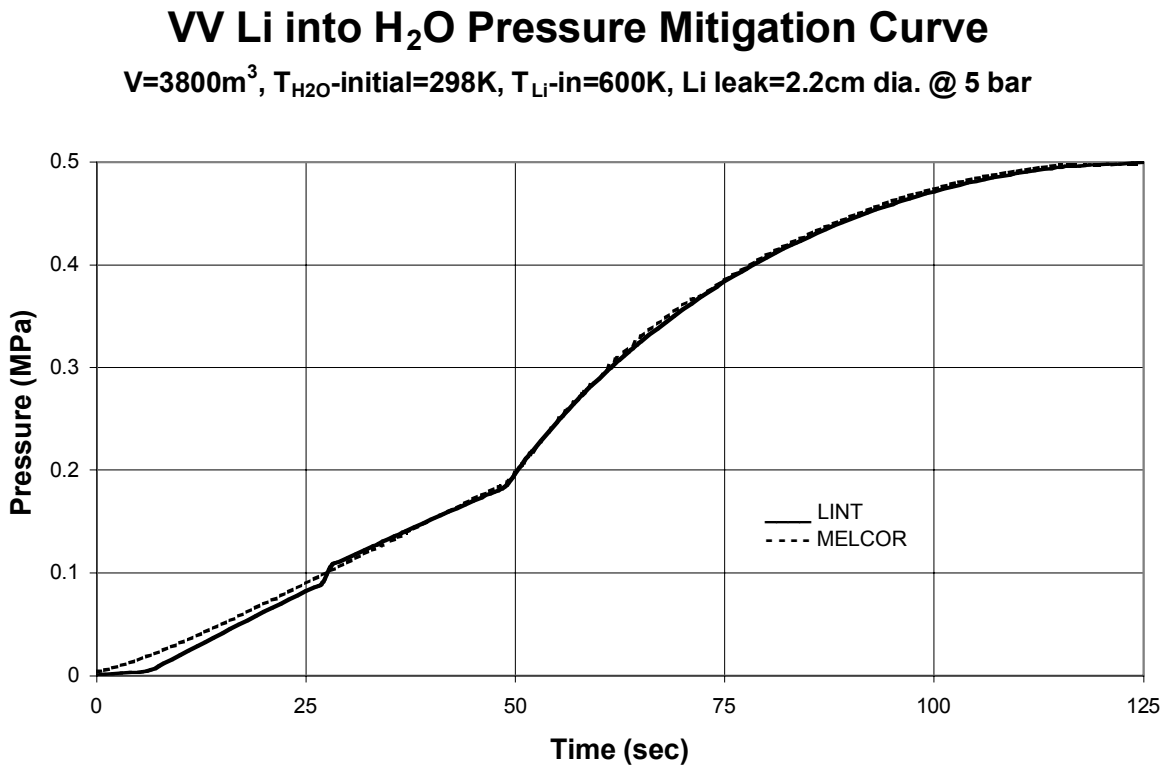

VV Li into H$_2$O Pressure Mitigation Curve

V=3800m^3, T$_{H2O}$-initial=298K, T$_{Li}$-in=600K, Li leak=2.2cm dia. @ 5 bar

Figure 4

VV Li into H_2O Pressure Mitigation Curve

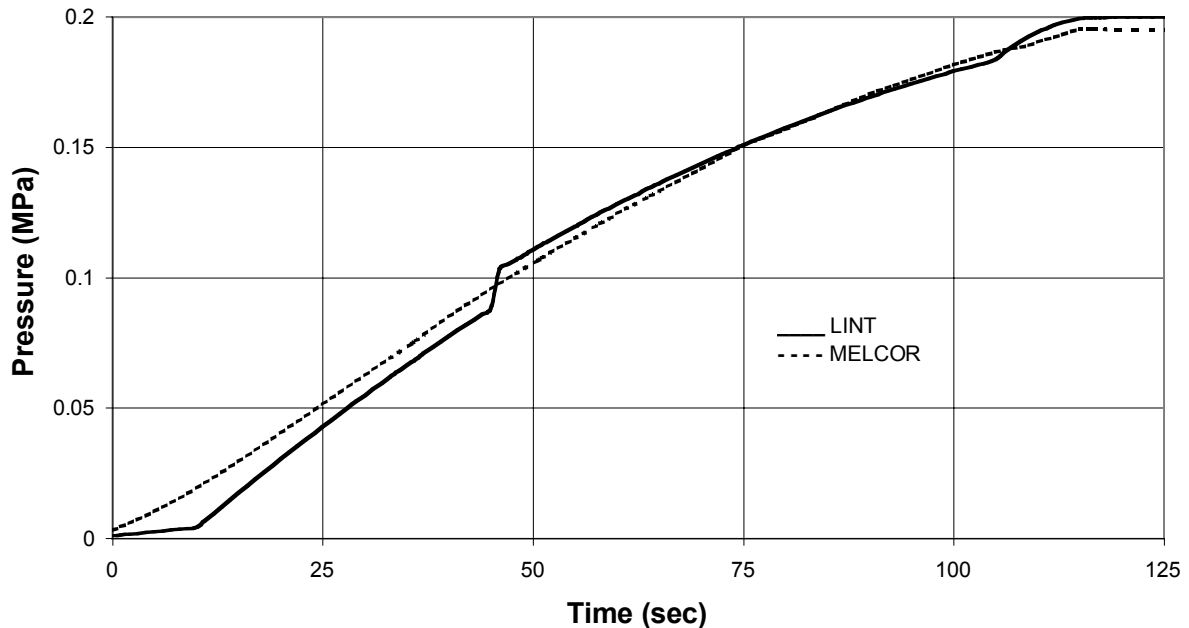### V=3800m^3, T_{H2O}-initial=298K, T_{Li}-in=600K, Li leak=2.2cm dia. @ 2 bar

Figure 5

4.2 Water leak into pre-existing lithium

A parametric study of failure conditions for a varying initial lithium pool mass is shown in Figures 6 and 7. Figure 6 shows the minimum water mass required to cause a pressurization failure for any given initial lithium pool mass. This calculation assumes that the rupture disk between the vacuum vessel and the suppression tank remains closed, thus allowing pressurization to continue indefinitely. At low lithium pool masses (under 240 kg), all of the lithium reacts before the design pressure is reached. This means that the water leak will continue without further chemical reaction until enough water has flashed into steam in the vacuum vault to cause a failure. Of course, higher initial lithium pool masses allow for more extensive exothermic reactions to occur. This results in higher temperatures and less required water to exceed the design pressure. Although no limit on temperature is given as a failure criterion, it should be noted that the temperature of the vacuum vessel atmosphere could reach 3000 K or more. Such extreme temperatures would almost certainly begin to melt any metal structure containing the reaction if conditions remained unchanged. In realistic situations, heat transfer out of the vacuum vessel would drastically reduce these temperatures.

Several interesting features in the safety curve of Figure 6 appear as the mass of the initial lithium pool increases. Above 250 kg of Li, significant amounts of LiOH have formed and the system temperature hovers around 1312 K, which is the boiling point of LiOH. This is the reason for the dip and subsequent plateau at 275 kg Li in the LINT results. Following this plateau, LINT shows a dropoff in the amount of water required to cause a failure. This is because vaporized LiOH contributes to the pressurization of the vacuum vessel. MELCOR, on the other hand, does not recognize LiOH as a vapor, resulting in lower pressures and thus more

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reactor water or steam in order to cause a failure. This is also the reason why MELCOR shows a long, slow increase in water mass up to about 1000 kg while LINT shows a gradual decrease.

Next, at just over 1000 kg Li for LINT and 900 kg Li for MELCOR, the point at which not all of the lithium reacts before failure is reached. This causes a change in the overall chemical makeup of the system and a drop in the required amount of water is observed. This drop is due to the relative ease of heating lithium as compared to heating water due to the difference in specific heats of the two substances.

Moving further along the curve, at about 1250 kg Li for LINT and 1000 kg Li for MELCOR, the system temperature is near the melting point of Li_2O. Here the effects of the heat of fusion for Li_2O are felt. Below about 1250/1000 kg Li the Li_2O is all liquid, while above about 1250/1000 kg Li the amount of melted Li_2O decreases and falls to zero leaving it as a solid. When the Li_2O mass remains as a solid the energy of the reaction is spent heating the reaction product gases rather than melting the Li_2O produced. This causes a rather large, sudden drop in the amount of water necessary to reach failure pressures. MELCOR displays a more precipitous drop in the amount of water required for failure than LINT does for this section of Figure 6. The explanation for this behavior is twofold. First, MELCOR is very sensitive to phase changes due to the way its EOS is calculated near melting points. Second, the "extra" energy available for sensible heating of lower heat capacity liquids and solids when Li_2O is not melting makes a greater difference in MELCOR than LINT because LINT includes reaction products as vapors while MELCOR does not.

VV H_2O into Li Interaction Safety Curve

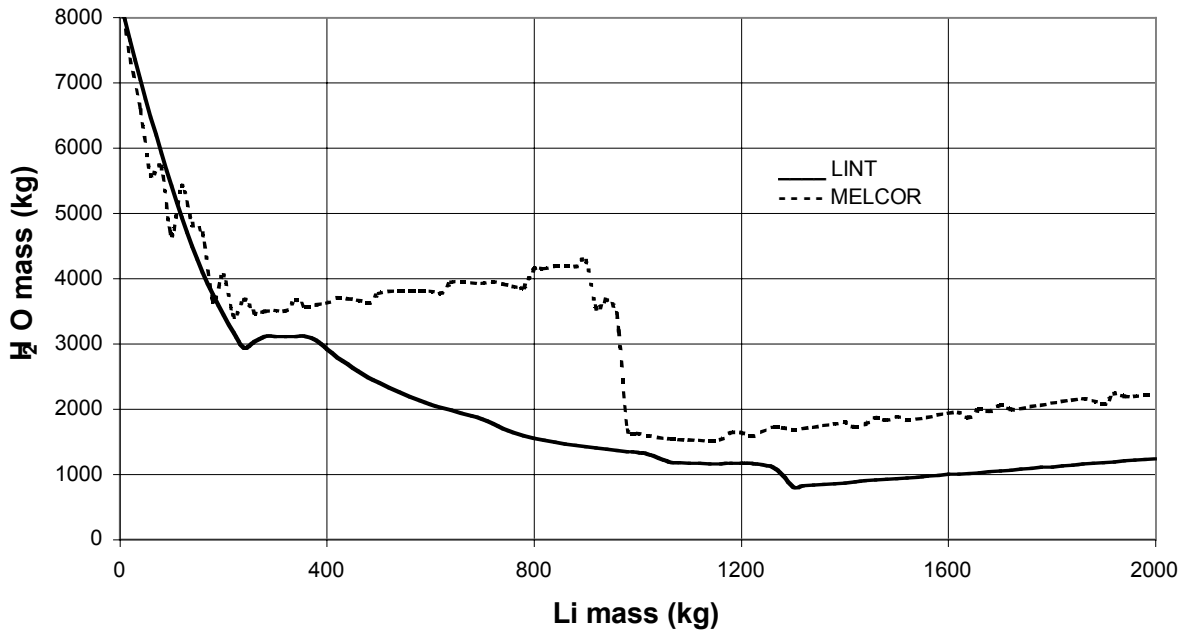**V=3800m³, T_{H2O}-in=380K, T_{Li}-initial=298K, H_2O leak=1.1cm dia. @50bar**

Figure 6

Finally, as more and more excess lithium is present in the system for very large initial lithium pool masses (above 1300 kg), the required water masses for failure gradually increase. This is because the thermal inertia of the system begins to overpower the effect of the chemical reaction.

Figure 7 shows the time to failure for the lithium and water quantities described in Figure 6 given an initial water leak flow rate of about 10 kg/s driven by a 50 bar pressure. Failure times are seen to be on the order of minutes for the entire range of initial lithium pool masses considered. Failure times are seen to correlate almost directly with the amount of water added to the system. This is due to the fact that the entire system is modeled as if it were in thermal equilibrium. LINT is by default a thermal equilibrium model, and MELCOR calculations were set up to approximate thermal equilibrium in order to match LINT more closely even though this is not necessary in general.

VV H_2O into Li Failure Time Curve

V=3800m^3, T$_{H2O}$-in=380K, T$_{Li}$-initial=298K, H_2O leak=1.1cm dia. @50bar
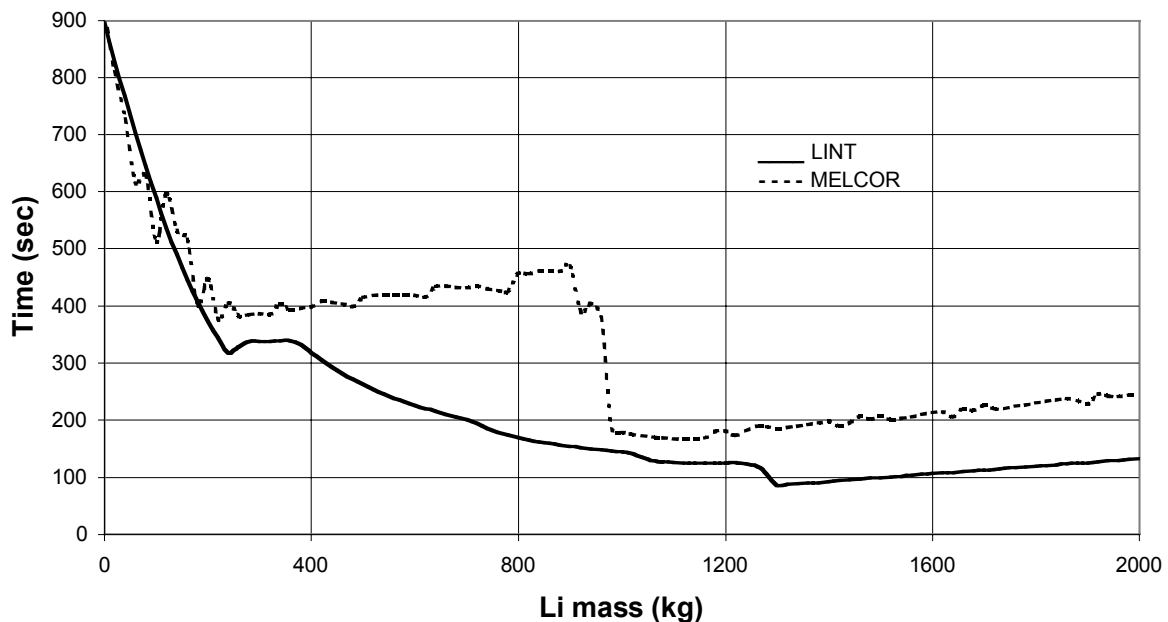

Figure 7

5 Results for lithium-air interactions

The ITER reactor vault has a lower pressure limit than the vacuum vessel, being set at 2 bar instead of 5 bar. An atmosphere at 1 bar consisting of any fraction of argon and pure air (79% N_2, 21% O_2) is considered to exist in the reactor vault before lithium begins to leak in. Leaks are allowed to enter either into the atmosphere or onto a surface where reactions take place. Failure of the reactor vault will occur due to Li-air interactions unless heat loss from the vault is considered. In general, the current method implemented in the MELCOR computer code using an oxidation constant predicts more severe consequences than the diffusion based model implemented in LINT.

Calculations were run with various amounts of pool spreading on the reactor vault floor using LINT and MELCOR, and for different diameter droplets in the atmosphere using LINT. Pool sizes were assumed to form on the floor with surface areas of either 16.5 or 165 m^2. These values were derived for the surface area of a square, six sided, 2150 m^3 room at full and one tenth coverage on the floor. In the pool case, the LINT calculations then proceed with an initial crust formation on the pool surface and subsequent diffusion through the product layer crust. A parametric study was performed for different initial air fractions in the RV atmosphere and for different lithium leak temperatures. One may expect that a pool of large surface area contacting a high initial air concentration will react much faster than a smaller pool area in contact with a low atmospheric air concentration. This is indeed borne out in the results from LINT. With MELCOR, surfaces of 16.5 and 165 m^2 area are defined as the destinations for the lithium leak and the oxidation rate constant for the lithium reaction is adjusted accordingly in order to match the LINT results as closely as possible. Two specific cases have been run to compare results.

In the case of lithium droplets dispersed in the atmosphere of the control volume, a parametric study for a lithium leak into an adiabatic system was conducted using LINT based on droplet size, mass diffusion rate, lithium temperature, and initial air fraction. Failure of the reactor vault occurred in two days or less for all cases except when the initial air fraction was at its smallest value of 1%. Calculations were also performed for varying air ingress rates with 35 kg of lithium droplets dispersed in the atmosphere and heat loss to the control volume walls taken into consideration. Failure did not occur in any of these cases even with 80 vol% per day air leaks and an 800 K initial lithium temperature used to represent a maximum expected temperature at the outlet from the blanket test module.

5.1 Lithium-air interactions, pre-existing air (LINT, MELCOR)

Table 1 shows a summary of the adiabatic results obtained from LINT for different pool and droplet cases all using 2000 kg of lithium. In general the spray, or droplet, mode is found to be more temperature dependent than the pool mode. One can see that no simple comparison between pool and droplet mode can be made. This is because both temperature and geometry effects must be taken into account when calculating the mass diffusion rate for the spray mode, while only temperature effects are important in the pool mode. One can, on the other hand, clearly see the effects of the lithium leak temperature. If hot lithium is used, failure times are on the order of a minute for any case. This is because the thermal energy carried by 2000 kg of lithium is enough to cause a failure even without a chemical reaction. The effects are similar even for a reduced total lithium mass of 350 kg. Finally, the faster failure times observed for lower air fractions seem counterintuitive at first. However, one must keep in mind that the argon cover gas used to fill the reactor vault has a smaller heat capacity than air. This results in higher temperatures when significant amounts of argon are present even though the rate of chemical reaction between lithium and air is reduced.

Failure Times for 2000 kg Li Leak into Reactor Vault with Air/Argon atmosphere (s)						
Air fraction in air and Ar atmosphere →			1%	10%	50%	100%
$Nu \propto (GrSc)^{1/3}$ (pool)	16.5 m^2 area	600 K Li	2,833,283	82,222	24,138	19,933
		800 K Li	56	60	76	97
	165 m^2 area	600 K Li	178,350	2,165	469	349
		800 K Li	56	58	61	68
Nu=2 (spray)	16.5 m^2 area	600 K Li	1,953,086	119,781	36,450	28,846
		800 K Li	56	60	77	98
	165 m^2 area	600 K Li	19,349	1,153	386	336
		800 K Li	54	51	55	64

Table 1

Figure 8 shows the pressure history up to failure for LINT and MELCOR (again assuming the pressure suppression system does not operate as designed) of the reactor vault for a 2000 kg lithium leak into pure air spreading to a pool of area 165 m^2. The steep gradient at the beginning of the leak is due to the assumption that the entire reactor vault is in thermal equilibrium throughout the calculation. Since air is not very dense, a small addition of hot liquid lithium can significantly heat the relatively small amount of air in the vault and cause the pressure to rise accordingly. At early times, the leaking lithium solidifies as it enters the chamber because of the thermal equilibrium restriction. However, at 50 seconds or so, the temperature in the system reaches the lithium melting point, and a discontinuity is observed in the pressure history due to the heat of chemical reaction with the air being applied to melting of the lithium. After approximately 310 seconds, all of the lithium in the ITER test module will have leaked into the reactor vault, so the flow stops. This explains the slight discontinuity in the slope of the pressure curve at that point. One can also observe that the time to failure for this case is rather long, taking about 350 seconds, even though this is the worst case scenario with a large pool surface area and atmospheric air without any argon in the vault. This sort of time scale would normally be plenty of time for operator intervention to take place in an effort to mitigate the effects of the accident.

RV Li into Air Diffusion Limited Failure Curve
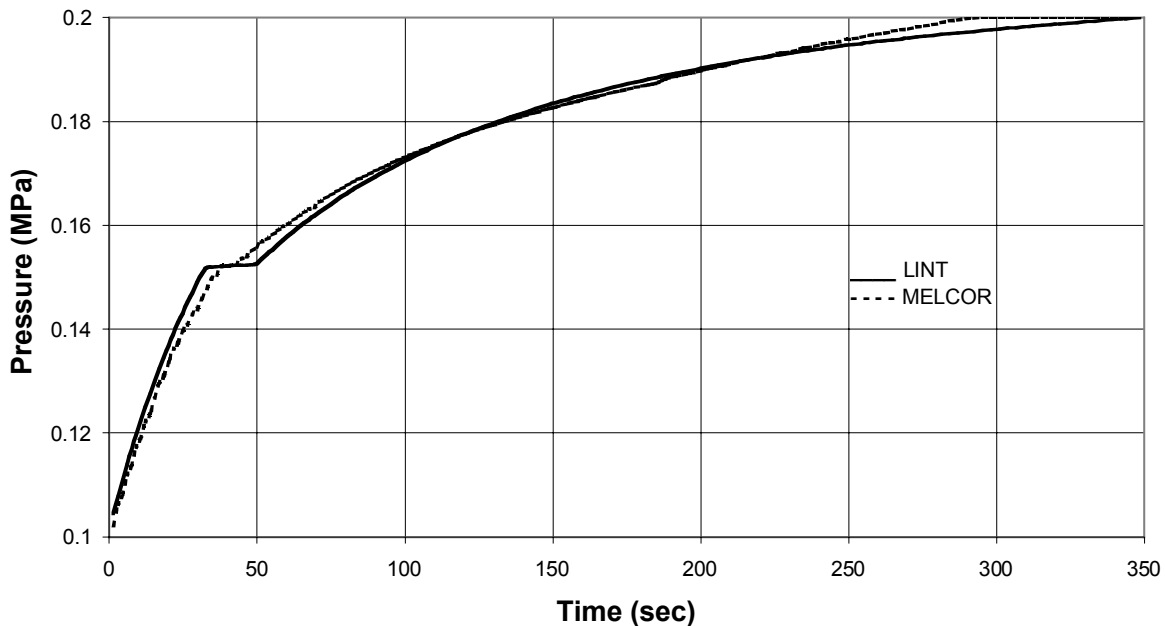### $V=2150m^3$, T_{air}-initial=298K, T_{Li}-in=600K, SA-pool=165m^2

Figure 8

The next figure (Figure 9) shows that a 16.5 m^2 pool does indeed take much longer to cause a failure since the surface area across which reactants can diffuse is restricted. All other parameters in the calculation are equivalent to those used for Figure 8. In Figure 8, results from LINT and MELCOR are shown to match quite closely. However, in Figure 9 MELCOR begins to diverge from LINT as time progresses. This is a numerical problem caused by the fact that when the oxidation constant for lithium reaction is increased beyond a value of 1.3e6 in the MELCOR calculation for this case single precision variables no longer suffice. The very large pool mass (~1000 kg) used in this calculation cannot be correctly tracked when sub-gram quantities of lithium are reacting. Thus, numerical limitations result in a maximum oxidation time constant or, equivalently, a minimum reaction rate. LINT is written using double precision variables and does not suffer from numerical limitation in this case.

RV Li into Air Diffusion Limited Failure Curve

V=2150m^3, T$_{air}$-initial=298K, T$_{Li}$-in=600K, SA-pool=16.5m^2
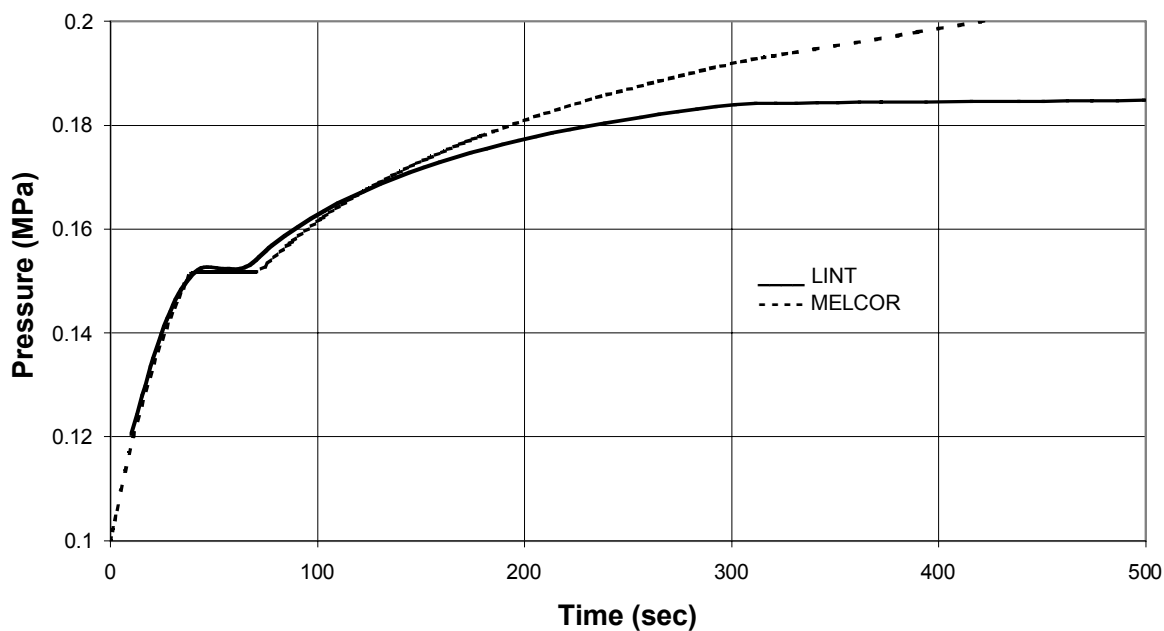

Figure 9

Both Figures 8 and 9 treat the reactor vault as an adiabatic chamber. Figure 10 shows results of the same accident scenario as Figure 9, but with heat loss through the walls of the vault to an infinite medium. As the figure clearly demonstrates, failure does not occur for this situation. At first, the pressure rises very quickly just as in Figure 6, but once the lithium leak stops at about 308 seconds, the heat loss to the walls begins to dominate. As the product layer crust thickens, the reaction slows and heat loss from the reactor vault to the steel lining is actually able to reduce the temperatures inside the vault even though chemical reactions are still occurring.

RV Li into Air Diffusion Limited w/ Heat Loss

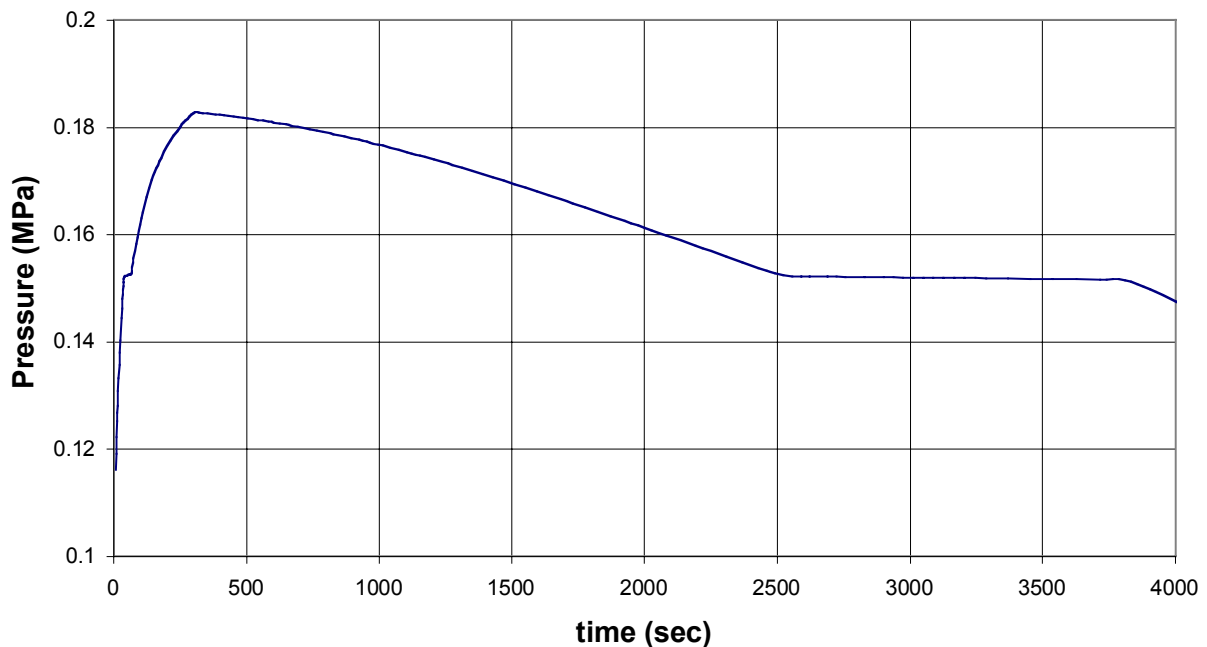$V=2150m^3$, T_{air}-initial=298K, T_{Li}-in=600K, SA-pool=16.5m^2

Figure 10

5.2 Lithium-air interactions, air ingress (LINT)

Figures 11 and 12 show the calculated results obtained in the reactor vault for varying air ingress rates with 35 kg of Li dispersed into the atmosphere as 2.8 mm droplets. This droplet size gives a total surface area equivalent to the 165 m^2 pool discussed earlier. As Figures 11 and 12 clearly demonstrate, even a maximum air ingress rate of 80 vol% per day into the reactor vault surrounding the lithium blanket test module poses no danger. Temperatures and pressures remain well within acceptable limits.

18

RV Pressure vs. Time (Spray Mode)

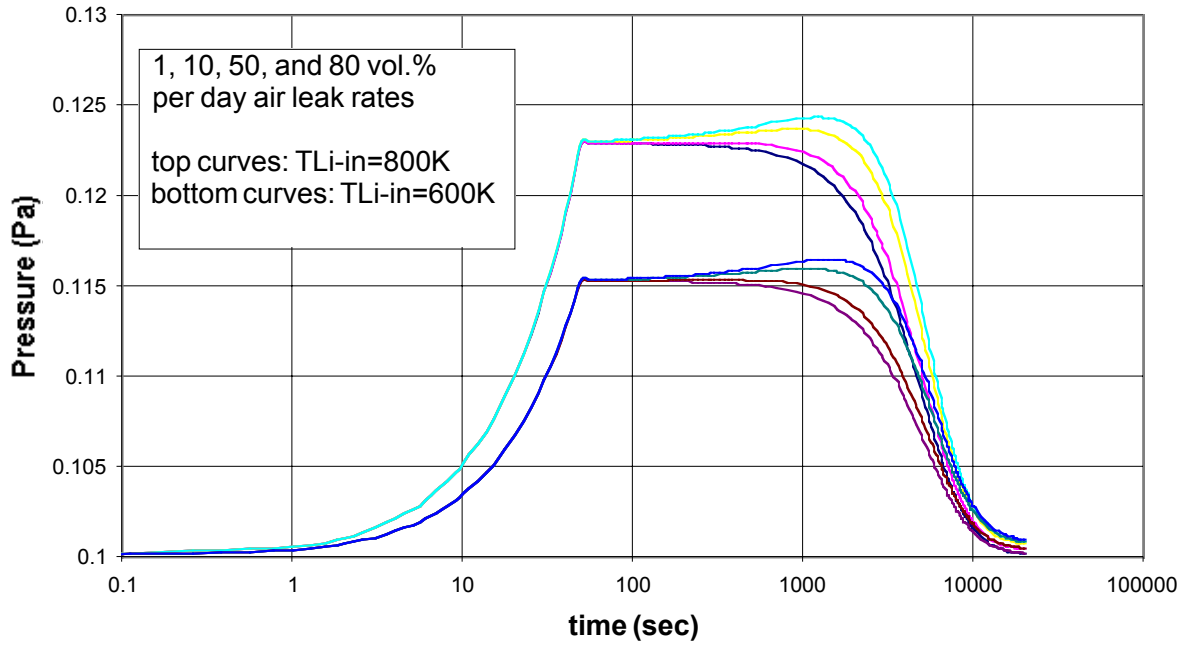Air Ingress, Heat Loss, SA=165m^2 (2.8 mm droplets)

Figure 11

RV Temperature vs. Time (Spray Mode)

Air Ingress, Heat Loss, SA=165m^2 (2.8 mm droplets)
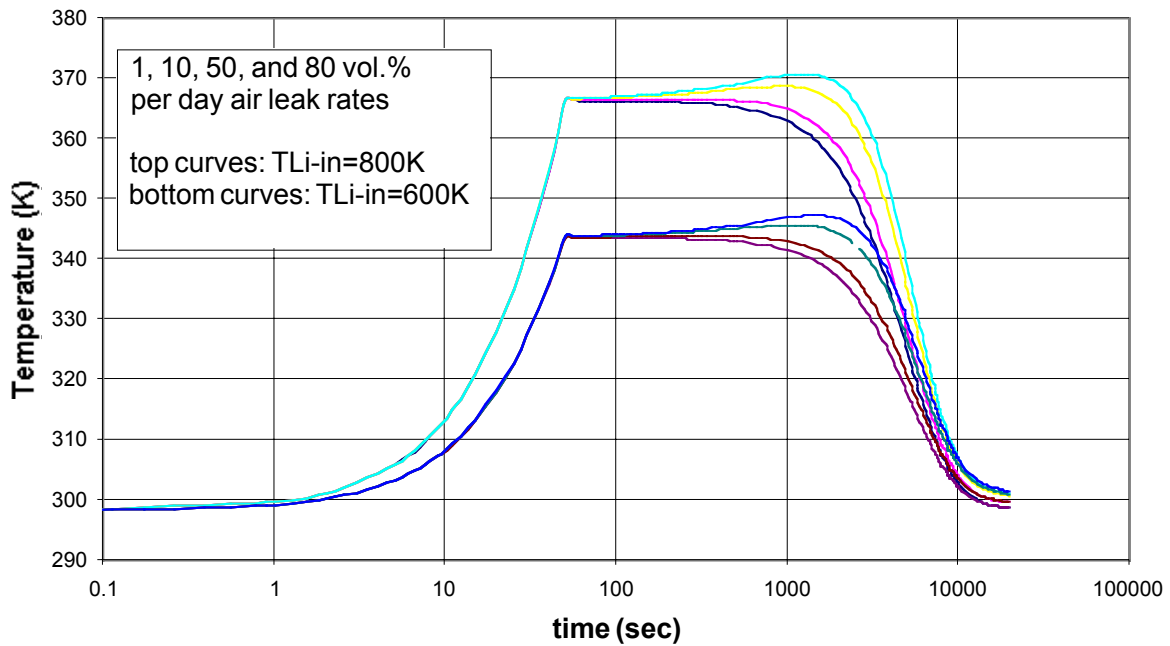
Figure 12

6   Conclusions

The results obtained from the LINT and MELCOR computer simulations show that the risks from lithium-water interactions exceed those from lithium-air interactions. Failure of the vacuum vessel occurs within a matter of minutes if a water leak into a pre-existing lithium pool occurs. Although failure of the vacuum vessel due to a lithium leak is not possible since driving pressures for lithium are low, the temperatures attained are high enough to warrant serious concern. Furthermore, hydrogen gas is produced in significant quantities for all lithium-water interactions. The limit of 10 kg of hydrogen produced can easily be exceeded if the amount of lithium is not limited. Reactions between lithium and air can cause temperatures exceeding 1000 K, but when heat loss from the control volume is considered failure due to overpressure is not a serious concern. Another preferable attribute of the lithium-air interactions as opposed to lithium-water interactions is that no hydrogen is produced in lithium chemical interactions with air.

7   Acknowledgements

NOMENCLATURE

A_{leak} cross-sectional area of leak
$A_{surface}$ surface area of Li pool or droplets
c_{atm} reactant concentration in atmosphere
$c_{p,w}$ heat capacity of system wall
$D_{o,atm}$ diffusion coefficient in atmosphere
$D_{o,crust}$ diffusion coefficient in product layer
F water/air transition smoothing factor
FRC reactant fraction
Gr Grashof number
H_{in} total enthalpy of material added
H_{out} total enthalpy of material removed
h_{cond} conduction heat transfer coefficient
h_j enthalpy of leak constituent j
h_{nc} natural convection heat transfer coefficient
h_{tot} total heat transfer coefficient
K discharge coefficient for leak
K_{atm} atmospheric mass transfer coefficient
K_{crust} product layer mass transfer coefficient
K_{tot} total mass transfer coefficient
k_w thermal conductivity of system wall

L mass transfer characteristic length
MW molecular weight
m_i mass of substance i
m_{Li} Li mass
m_{Li-H2O} Li reactant mass available for H_2O vapor
m_{Li-N2} Li reactant mass available for N_2
m_{Li-O2} Li reactant mass available for O_2
n_{H2O} moles of H_2O vapor
n_i moles of constituent i
n_j moles of constituent j
n_{N2} moles of N_2
n_{O2} moles of O_2
n_{react} moles of reactant
P system pressure
ΔP leak pressure difference
Q heat added to system
R gas constant
R_1 molar water to air ratio
R_2 molar oxygen fraction in air
R_i product to Li reactant mass ratio
Sc Schmidt number
Sh Sherwood number
S_i source term for substance i
S_{Li} Li mass source term
T system temperature
t time
t_{crust} thickness of product layer
U total internal energy
u_i internal energy of constituent i
Δx reactant mole fraction difference
W work
μ reactant viscosity
ρ density
ρ_w density of system wall
τ_{ox} oxidation time constant
τ_{so} simultaneous oxidation and settling time constant
τ_{st} settling time constant
ζ weighted reactant concentration relative to atmosphere

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