

# Web Substrate Heating and a Thermodynamic Calculation Method for Li Film Thickness in a Thermal Evaporation System

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## ABSTRACT

Substrate heating and deposition rate have been modeled for the thermal evaporation of Lithium in a vacuum web coating system. To aid in modeling the substrate heat load due to the Li deposition process a novel, self-consistent, thermodynamic model was developed that allows calculation of the deposition rate (for Li or any material) as a function of only evaporator geometry and temperature. Substrate heating due to both radiation and Li condensation are accounted for. With no free parameters, the self-consistent thermodynamic model predicts Li deposition thickness to within the 5% accuracy, at 10 micron film thickness, of our measurement technique. Input to the model is the measured liquid temperature, the measured temperature on the crucible at the point farthest from the liquid and geometrical characteristics of the crucible/substrate arrangement including the measured areas of the exposed substrate and reservoir-substrate gaps. The temperature rise of the substrate (Polyethylene Terephthalate, or PET) is then calculated based upon the Li flux, reservoir temperature and geometry, radiation heat load and the cooling drum temperature. Free parameters in this last step are the emissivity of the Li/PET surface and the heat transfer coefficient between the PET and the drum. The model predictions are compared to measurements.

## INTRODUCTION

Vapor deposited Li metal, on flexible polymer substrates, is of interest for use as anode material in a variety of batteries for commercial electronics, power tools or electric vehicles. However, the thickness of Li required is generally near, or in excess of, 10  $\mu\text{m}$ , with the precise thickness depending upon the specific operational requirements of the desired battery. To deposit such a thick Li film, at line speeds that would be commercially attractive, places a severe heat load on the polymer substrate. As rolled Li foil becomes thinner the surface roughness and oxidation increases and commercial foil at below about 35  $\mu\text{m}$  to 50  $\mu\text{m}$  is not available. Thus, vacuum deposition is required to meet both the thickness and quality requirements. For a variety of practical

reasons, the substrate of choice is presently Polyethylene Terephthalate, or PET. PET has a glass transition temperature of  $T_g=70\text{ }^\circ\text{C}$ <sup>1</sup>. Thus, in principle, when coating PET, the PET substrate can distort and undergo irreversible damage at temperatures as low as  $T_g$ . However, PET is found to retain its mechanical properties to as high as 120 C in some instances. The exact damage threshold can depend upon substrate gauge, tensioning, the length of time that the substrate is at temperature and, relative to the particular process/product, the definition of what actually constitutes damage. When depositing Li, if the film PET substrate distorts to the point where a wrinkle occurs, and any part of the substrate lifts from the cooling drum, the film burns through. It is therefore crucial to process the film under heat load conditions that do not exceed this point.

A first step in modeling the substrate heat load, in order to optimize the deposition rate and minimize the heat load to the substrate, is to understand the Li flux and thermal radiation emissions from the Li source. Our numerical model predictions agree extremely well with the thickness of Li deposited. As well, the model predictions appear to be quite reasonable, and qualitatively correct, for those parameters that we can estimate but cannot yet measure. Previously we presented the development of a general thermodynamic model for the calculation of evaporated flux from a thermal crucible that is central to the problem of modeling the heat load to the substrate during Li deposition<sup>2</sup>. This model for the thermal source will be summarized here and modeling of the thermal load to the substrate will be given greater attention. The general source model is tailored to the specific geometry of the Li evaporation source used in the R&D laboratory at Moltech. The salient features of the radiation emission, substrate heat load and substrate-to-drum heat transfer coefficient will be discussed, the relevant difference equations developed and the substrate heating model predictions will be presented and discussed and compared to the experimental data. We begin with the details of thermal evaporation model and our Li evaporation source and Li deposition experiments<sup>3</sup>.

## THE THERMAL SOURCE MODEL

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In a closed system, with isothermal walls, the relationships between the equilibrium vapor pressure, evaporation rate at the liquid surface and the temperatures of the liquid and gas have been studied for a large number of materials and most elements. The mathematical expression that relates the equilibrium mass evaporation rate to the liquid, or gas, temperature has a common functional form for most elemental liquids. This general mathematical expression is readily derived from the thermodynamic expressions for the enthalpy and free energy of the material<sup>4</sup>. The expression contains both material specific parameters (like molecular weight and Gibbs Free energy) for the particular element of interests along with some arbitrary constants and the liquid or gas temperature. The arbitrary constants are fitted through experimental measurements of temperature and vapor pressure. Scientific Foundations of Vacuum Technique, by S. Dushman and J.M. Lafferty<sup>5</sup> contains one such functional form for this expression for elemental liquids in equilibrium with their vapor along with a compilation of the fitted constants for most of the elements. Equation 1 is this functional relation for elemental Li where all of the material parameters and fitted constants have been combined and reduced to numbers to leave a functional form that appears to vary only with the temperature of the liquid, or gas. Thus, for liquid Li in equilibrium with its vapor<sup>5</sup>

$$W(T_{liq}) = 10^{\left[7.18 - 0.5 \text{LOG}(T_{liq}) - \frac{8070}{T_{liq}}\right]}, \frac{g}{cm^2 s},$$

**Equation 1**

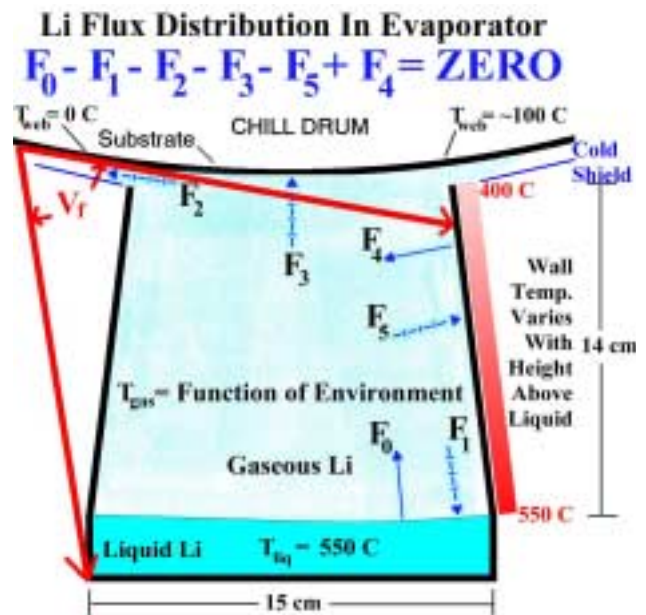
where, with liquid and vapor in thermal equilibrium at temperature  $T_{liq}=T_{gas}$ ,  $W$  is the mass flux of Li atoms leaving from (or returning to) the liquid Li surface per second per square centimeter of liquid Li surface. In Equation 1  $W$  depends only on  $T_{liq}$ , which is equal to  $T_{gas}$  due to the condition of equilibrium. The rate of this mass flux leaving/returning to the liquid surface, as given in Equation 1, must equal the mass impingement on, or emission from, on any other surface in the system as long as equilibrium conditions exist.

There are also well known equations, from the kinetic theory of gasses<sup>6</sup>, which relate the atomic/molecular constants, mean free path, pressure and temperature of a gas to the surface impingement rate. Thus, by equating Equation 1 to the kinetic impingement rate equation, one can also calculate the pressure of the Li gas.

The strict assumptions for the derivation of Equation 1 are that the liquid is contained in a closed volume and that the temperature of the walls, gas and liquid are all equal. The central assumption of our thermal source model is that Equation 1 still holds under a much broader range of conditions. Specifically, we assume that Equation 1 holds

under many circumstances when the system is not closed (flux may leave the system through gaps in the walls) and when the walls and gas are not at the same temperature as the liquid. Our relaxed conditions still require that the gas volume be approximately isothermal. Under these assumptions Equation 1 would describe the rate at which atoms are either emitted from *any* surface to, or impinge upon *any* surface from, the gas phase. With these assumptions, Equation 1 can then be used to calculate impingement and re-emission rates (i.e. effective sticking coefficients and, thus, deposition rates) at any surface in the system.

In other words, we postulate the following. When a liquid source is present somewhere in the system, Equation 1 will predict the emission and absorption rates at all surfaces in the system. This is regardless of whether the liquid and gas temperatures are equal or not ( $T_{liq}=T_{surface}=T_{gas}$  and  $T_{liq}\neq T_{surface}\neq T_{gas}$ ) and whether or not the *net* flux across the liquid-gas interface is zero or non-zero. The only constraint is that the gas volume be approximately isothermal.



**Figure 1.** A schematic representation of the steady state Li flux streams (the  $F_i$ 's) within our evaporator. Under steady state conditions, the number of Li atoms entering the gas phase must be identically equal to the number leaving the gas phase. Dashed and Solid lines represent Li flux leaving and entering the gas phase, respectively.  $V_f$  represents the view angle, from the web, of the evaporator.

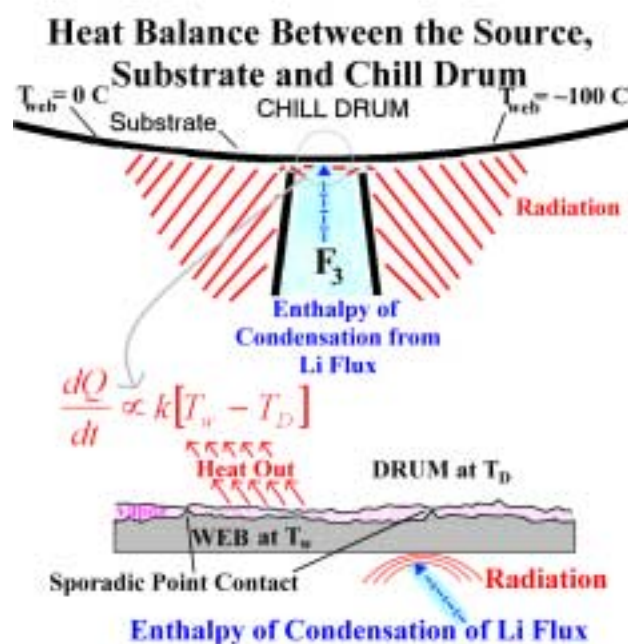
Such non-equilibrium conditions obviously exist in all thermal evaporation deposition processes since, by virtue of the very act of deposition, some species that leave the liquid can never return. As an example, Figure 1 is a

detailed process schematic of our Li evaporator. These authors have presented an equally detailed analysis of the evaporator depicted in Figure 1, accounting for all temperature gradients and non-equilibrium phenomenon<sup>2</sup>, and the deposition rate was found to agree to within the 5% accuracy of the measurements. We assume that, when only thermal processes are considered, all impinging atoms or molecules stick to the surface and that, independently of this impingement/sticking, other atoms and molecules are emitted from the surface. The modeled impingement and emission rates can then be calculated from Equation 1 where the gas and surface temperatures are not necessarily equal. The wall surfaces are found to be the largest Li flux sources in the system with the emission rate being a strong function of temperature and, thus, of wall position in Figure 1. Relatively small changes in the thermal profile produce very significant changes in the predicted Li thickness<sup>2</sup>. Further, the loss of the permanently deposited species, and the impingement and emission interactions of other species with various surfaces, must alter the gas temperature. For deposition, and for interactions with surfaces cooler than the liquid, the effect of these processes must be to reduce the temperature of the gas relative to the temperature of the liquid (i.e.  $T_{\text{gas}} < T_{\text{liq}}$ ). With a self-consistent mass balance relation, encompassing all of the flux streams and temperature gradients depicted in Figure 1, we have calculated the steady state gas temperature and, thus, the absolute impingement rate at any surface in the system<sup>2</sup>. If the wall gradients are not accurately accounted for, the gas temperature shifts significantly and the prediction for deposited Li thickness differs significantly from the measured values. The fact that we have no free parameters in this calculation, and it fits the data to within measurement error, further reinforces our belief in its applicability. Since the wall temperatures are everywhere above the melting point of Li, Li that accumulates on the walls eventually runs back down into the reservoir and is re-evaporated. The previous publication<sup>2</sup> also analyzes, and justifies, the isothermal assumption for our evaporator from the point of view of the kinetic theory of gasses.

### THE SUBSTRATE HEAT TRANSFER MODEL

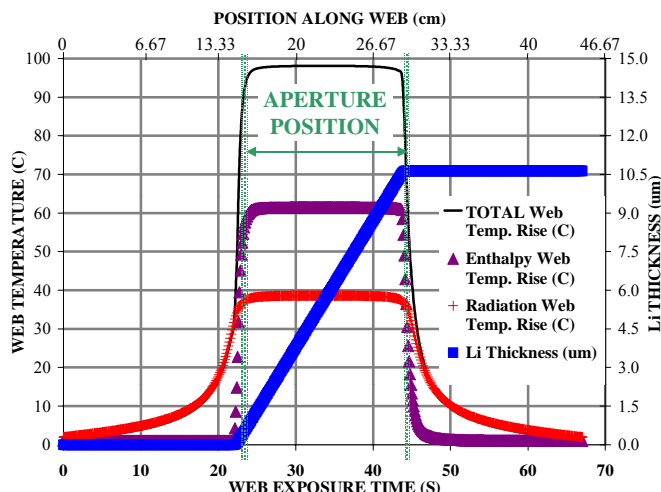
The web substrate can absorb energy from radiation incident upon its surface from the surroundings and from the enthalpy of condensation of the Li atoms deposited onto its surface from the gas phase. Energy may also leave the substrate as radiation as well as by conductive and/or convective transfer into the chill drum. The formulas for the radiative transfer of energy are easily found in the literature<sup>7,8</sup> and they depend on the temperatures and emissivities of the surfaces involved as well as the relative field of view that the surfaces have of each other. The enthalpy of condensation contribution

can be calculated directly from Equation 1, as detailed in previous work<sup>2</sup>, and the Latent Heat of Vaporization (LH) of Li ( $LH=2.13 \times 10^4$  J/g). To use the heat equation to calculate the heat flow into the chill drum it is necessary to know the thermal conductivity of the web<sup>9</sup> ( $Th_w$ ) and the heat transfer coefficient ( $KH_x$ ) between the drum and the web<sup>10</sup>. For PET<sup>1</sup>,  $Th_w=0.0017$  w/cm K. However  $KH_x$  depends on a number of factors and is highly process dependent as well as dependent upon the exact history of the PET. This is due to the fact that direct conduction proceeds only through a small fraction of the substrate area because the microscopically rough surfaces of the web and drum have very little actual contact area. A large contribution to  $KH_x$  is due to convection through vapors thermally released from the PET<sup>10</sup> during the deposition process. This PET outgassing rate is very sensitive to web temperature and to the amount of water and atmospheric gasses incorporated within the PET when the film was produced. Figure 2 is a schematic depiction of these heat transfer processes relevant to the temperature rise of the substrate.



**Figure 2.** Schematic depiction of the thermal flux streams to/from the web substrate in our Li deposition system.

An outline of the mathematical details of our numerical model for calculating the temperature rise of the substrate will be presented in the Appendix. At this time we present only the *results of the calculation* for modeling our standard run, with temperatures as depicted in Figure 1, at 0.4 m/min line speed and with the following **Figure 3.** Results from our mathematical model for substrate heating at 0.4 m/min line speed. The



substrate temperature profiles (total and individual contributions due to radiation and enthalpy of condensation), along with accumulated Li film thickness, as a function of position relative to the enclosure are shown. No variation of parameters was performed although emissivity was typical of metals with conductivity similar to Li metal and a reasonable literature value for the thermal conductivity of PET was used<sup>10</sup>. In these plots, the leading and trailing edges of the 14 cm long Li enclosure aperture are located at time indexes 22.5 s and 43.5 s, respectively. Thus, one sees the radiation heat flux becoming appreciable well before the web nears the box, and not vanishing until well after the web has left the area of the enclosure. Contrawise, the diffusion of Li flux out through the gaps only leads to deposition, and heat load, within 1-2 s of either edge.

assumptions. We have taken the emissivity of the growing Li film to be 0.15 and have used the value of 0.01 w/cm<sup>2</sup> K for KHx. The chosen emissivity of 0.15 is typical of metals with conductivity similar to Li metal and the heat transfer coefficient, KHx=0.01 w/cm<sup>2</sup> K, was a very typical *measured* value from the literature<sup>10</sup>. Figure 3 displays model predictions with only these 2 free parameters. From Figure 3 it is seen that the maximum temperature that the PET web is estimated to reach is about 98 C. This value is midway between PET's glass transition temperature of T<sub>g</sub>=70 C, and the maximum temperature, 120 C, at which PET can possibly retain its mechanical integrity. This value seems reasonable to us for two reasons. First, one would expect thermal substrate damage to begin to occur at a temperature in the vicinity of, but greater than, T<sub>g</sub>. Second, the reason that T<sub>liq</sub>=550 C is our standard run temperature is that 550 C is the highest temperature that we are able to run the liquid at, confidently, without damaging the substrate. NOTE that, for T<sub>liq</sub>=560 C (10 C above our standard run temperature), the model predicts a maximum web

temperature of 120 C. Thus, we know that the substrate temperature is very near the damage threshold (in theory and in fact), which should be above T<sub>g</sub> (70 C) and below 120 C. We also know that occasionally, if the web is tracking well and there are no other factors distorting the substrate, we can operate with the liquid temperature very slightly above 550 C without problems. Thus we are fairly certain that, with the liquid below 550 C, the web is safely below 120 C. Based on this information, the model prediction is not in conflict with the observations and it appears to be very reasonable.

It is also interesting to note that slightly more than 37% of the total heat load delivered to the substrate is due to radiation while the remainder is due to the enthalpy of condensation of the Li atoms. Further, for most of the 21 seconds that the web is exposed to the Li flux, thermally, the web is in steady state. The substrate temperature change, due to Li flux levels, is a rise from ambient to the maximum within 1-2 s on either side the leading edge of the evaporator aperture followed by a similarly swift fall back to ambient after passing the trailing edge. The radiation contribution to the temperature rise, on the other hand, is noticeable for more than 20 s before, and after, encountering the enclosure.

### THE ISOTHERMAL GAS ASSUMPTION RE-VISITED

In the work described here we have assumed, and previously justified<sup>2</sup>, that, in our evaporator, the gas temperature is approximately isothermal. With this justified assumption the mass balance relation<sup>2</sup> reduces to one equation with one unknown - the gas temperature T<sub>gas</sub>. We are satisfied that this approach is valid due to the good agreement with experiment. However, if the gas is not isothermal the model (i.e. Equation 1) may still be valid. In order to test this it would be necessary to set up a boundary value problem for the thermal flux, digitize the equations then iterate the equations until an unchanging temperature distribution results. If, at this point with a non-isothermal gas distribution, the assumption of Equation 1 still accurately predicts film thickness then the isothermal assumption can be discarded. However, it then becomes necessary to iterate the set of boundary value equations to find a temperature distribution as opposed to solving a single equation in a single unknown. We are presently developing an appropriate boundary value approach to test the isothermal assumption further. Therefore, the assumption of an approximately isothermal gas volume, which is justified for our Li evaporator, was actually for our mathematical convenience and may not really be required by the physics or the model - Equation 1.

## CONCLUSIONS

The thermodynamic model for calculation of evaporated flux works extremely well for Li and, based upon the general nature of its derivation<sup>2</sup>, the model should be applicable to all thermal sources. This model is extremely useful as a design tool for building thermal sources since it allows precise calculations of how all temperature gradients affect the deposition rate. Thus, measurements of the temperature gradients in the operating system can be used as feedback for process control to allow accurate deposition thickness control even when the system is still moving through quasi-steady states toward its final steady state operating conditions. The utility of the model stems from its ability to calculate, a priori, the sticking coefficients from known thermodynamic data<sup>5</sup> from the literature that, in turn, permits calculation of the deposition rate.

The accuracy of this flux model makes it an excellent starting point for the larger model that calculates the complete thermal flux to, and temperature rise of, the substrate during the deposition process. Once the source geometry is modeled so that the flux is accurately calculated, you automatically have the shape and temperature profile of the relevant radiation source as well. Thus, this thermodynamic source model produces all of the data necessary to calculate the total thermal input to the substrate. It then remains only to develop the model for the mechanisms that govern the thermal balance of the substrate. The results shown in Figure 3 indicate that our model for calculating the heat load to the substrate appears to work fairly well too. The model has shown us how to design more efficient sources that should provide higher and lower substrate heat loads.

## APPENDIX ON SUBSTRATE HEAT TRANSFER

The temperatures of all surfaces in the system (except for the web substrate) are known, as is the detailed geometry. The Li deposition flux is calculated from Equation 1 as detailed in previous work<sup>2</sup>, and this calculation also yields the temperature of the gas/walls associated with the Li evaporator. This is all of the heat load information required to calculate the rise in substrate temperature as the web passes the Li evaporator.

In order to set up our system of difference equations we will consider an elemental region of the web at distance  $S$ , along the drum, from the Li evaporator aperture. We consider unit cross-machine width of web so that, with a machine direction width of  $\Delta s$ , its area is  $\Delta s \text{ cm}^2$ . The equations are discretized in terms of a time increment  $\Delta t$ , whence the distance coordinate along the drum, after  $n$  time increments, becomes  $S_n = n \cdot \text{WebSpeed} \cdot \Delta t$ .

In terms of the above coordinates we are able to calculate a purely geometric view angle of the process zone from the point of view of the web,  $VF(S)$ . Correcting for emissivities<sup>8</sup> we find

$$\frac{1}{VF_e(S)} = \frac{1}{VF(S)} + \frac{1 - e_1}{e_1} + \frac{A_1}{A_2} \times \frac{1 - e_2}{e_2},$$

**Equation A1**

where  $A$ 's are areas (which may also contain a cosine factor for the angle of incidence relative to the surface normal),  $e$ 's are emissivities and subscripts 1 and 2 indicate web and Li source, respectively. Approximating  $e_2$  as 1 (a black body) and recognizing that the view factor from the web to the cold shield,  $VF_2(S)$ , is the compliment of the view factor from the web to the Li source, we find

$$VF_1(S) = \frac{e_1 \times VF(S)}{e_1 + VF(S) \times (1 - e_1)},$$

and

**Equation A2.1**

$$VF_2(S) = \frac{e_1 \times (1 - VF(S))}{e_1 + (1 - VF(S)) \times (1 - e_1)}.$$

**Equation A2.2**

We need to track the web temperature changes as the web passes by the hot Li source. The deposition of Li onto the web increases its thermal capacity and thus slows down the rate of rise of temperature. The heat transfer to the drum is important in determining the web temperature because almost all the heat load has to be taken away through that route in order to keep the web at a reasonable temperature. The speed at which the web is moving and gathering Li is a crucial factor. The emissivity of the Li as deposited is also important. In the example shown, the heat transfer through the thin web material, despite the fact that it is a good thermal insulator, is much faster than the transfer between web and drum. The equation set will therefore treat the lithium and web as a single layer.

To establish the changing temperature of the web, as it passes by the Li source, we set up a pair of ordinary simultaneous differential equations for the mass of Li accumulated by a representative point on the moving web and the corresponding temperature of the web with the independent variable being time. The inputs to this pair of equations are the visible radiation pattern seen by the web as it approaches the Li source, and the rate of deposition. We arrange for the speed of the web to determine how fast the pattern is applied to the heating and deposition. Thus, for example, if the web moves slowly, the total accumulation of Lithium is greater at any point in the progression past the box and the corresponding speed of response to heat load is reduced. The web has more time to equilibrate with the drum as far as temperature is concerned.

To estimate the deposition rate onto the web, the main contribution is from the more or less uniform rate of deposition as it passes over the open Li source. The geometry allows for the deposition rate to rise to this level as the web approaches the box, and decline similarly as it departs, due to gaps at the source/substrate interface. The total calculated deposition matches the measured level of deposition quite closely.

To estimate the radiation heat load, we have a geometric model that looks at the view of the open jaw of the hot Li source as seen by the web coming round on the drum. At first the Li source is below the horizon (as seen from the point on the web). First the Li source edge appears just slightly within view, as depicted by  $V_f$  in Figure 1. The view angle increases until, as the web passes over the edge of the Li source, the Li source radiation takes half the field of view. When the point on the web is over the middle of the Li source the whole view from horizon to horizon as seen by the web is looking into the hot Li source. We have used the fraction of the field of view, from the web, taken by the hot Li source as the view factor for a radiation calculation between hot Li source and web. This factor is adjusted to allow for emissivity and the complementary part of the field of view is used to define a view factor for radiation between web and the

surrounding cold shield and other external, cooler hardware in the vacuum chamber.

### Computational Sequence

First the radiation view factors and deposition rate patterns are converted to make them dependent on drum position, measured as distance round the drum,  $S_n$ , from a reference point above the center of the Li Source. Then the speed of the web is used to convert these patterns to functions of time, here represented by the index  $n$ . In the analysis described here, the drum speed is constant. The radiation view factor functions are obtained as discussed above. In the difference equations, the Lithium mass per unit area,  $L_n$ , builds up and its value is used to adjust the thermal capacity in the equation for web temperature,  $T_n$ .  $C_w$  is the thermal capacity of the web (Mass Density x Specific Heat x Thickness of web).  $Sp_{Li}$  is specific heat of Li,  $T_{Li}$  and  $T_{sh}$  are Li source (gas) temperature and cold shield temperature respectively.  $KHx$  is the heat transfer coefficient between web and drum,  $LH$  is the total latent heat of lithium, and  $\sigma$  is the Stephan Boltzman constant. Finally,  $F_n$  is the Li flux density at the drum position  $S_n$ .

Combining all of the above details, the coupled difference equations that we must increment and solve become:

$$\begin{pmatrix} L_{n+1} \\ T_{n+1} \end{pmatrix} = \begin{pmatrix} L_n + \Delta t \times F_n \\ T_n + \left( \frac{\Delta t}{C_w + Sp_{Li} \times L_n} \right) \times \left\{ (VF_{e_n} \times \sigma) \times (T_{Li}^4 + T_n^4) + (VF_{2_n} \times \sigma) \times (T_{Li}^4 + T_n^4) - KHx \times (T_n - T_{sh}) + F_n \times (LH - T_n \times Sp) \right\} \end{pmatrix}$$

Equation A3

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