

# MODELING AND VALIDATION OF TEMPERATURE AND CONCENTRATION FOR RAPID FREEZE PROTOTYPING

Frances D. Bryant and Ming C. Leu

Department of Mechanical and Aerospace Engineering  
University of Missouri-Rolla, Rolla, MO 65409  
{[fbryant@umr.edu](mailto:fbryant@umr.edu) , [mleu@umr.edu](mailto:mleu@umr.edu) }

Reviewed, accepted September 4, 2007

## ABSTRACT

Rapid Freeze Prototyping is a solid freeform fabrication process that uses water as the main build material in a cold environment to create three-dimensional parts. A eutectic sugar-water solution ( $C_6H_{12}O_6 - H_2O$ ) has been used as a sacrificial material in order to create complex 3D parts with features such as overhangs. A study of the interaction of the build and support materials is presented in this paper. The temperature of both materials during deposition and subsequent cooling is modeled using a semi-empirical model and a theoretical model. A concentration model is used to predict the concentration in the fabricated parts around the interface of the two materials with predicted temperatures as input. Experiments are conducted to validate both the temperature and concentration models.

## **1. Introduction**

Rapid Freeze Prototyping (RFP) is a solid freeform fabrication process that uses water freezing into ice to create multi-dimensional ice parts. The RFP process is conducted in a cold environment at a temperature below the freezing point of water. A sacrificial material has been recently incorporated into the build process in order to create geometries which require support, such as overhangs and internal voids. Bryant and Leu [1] previously discussed the properties of the support material, which is a eutectic sugar solution ( $C_6H_{12}O_6 - H_2O$ ). By using a cooling method in RFP to build parts, many advantages can be achieved. These advantages include using a clean material (i.e. water), an environmentally friendly process, relatively low energy consumption, good surface finish and low-cost equipment. Figure 1 shows a schematic of the RFP setup that is discussed in this paper. Figure 2 shows a photograph of the components used in RFP.

Existing literature in the area of predictive modeling for layer-by-layer manufacturing with consideration for support material is very limited. There has been an extensive study conducted on RFP in predicting the line width and layer height of water freezing into ice during the build process [3]. There has also been some work done in the area of thermo-mechanical models for a freeform fabrication process that has characteristics similar to RFP. Chin et al. ([9] and [10]) investigated the thermal and mechanical interactions between existing and new layers in Shape Deposition Manufacturing (SDM), which uses stainless steel for the build material and copper for support material. The model derived by Chin et al., however, only took into account the build material. Liu and Leu [12] considered the solidification time in RFP to understand the heat transfer that occurs during material deposition in RFP, but again the model only considered the build material, which is water.

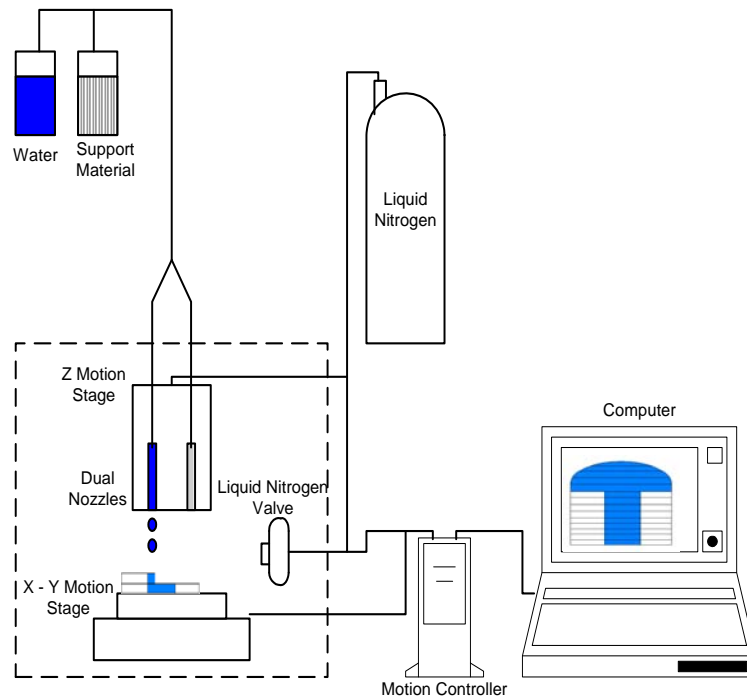


Figure 1. Principle of Rapid Freeze Prototyping

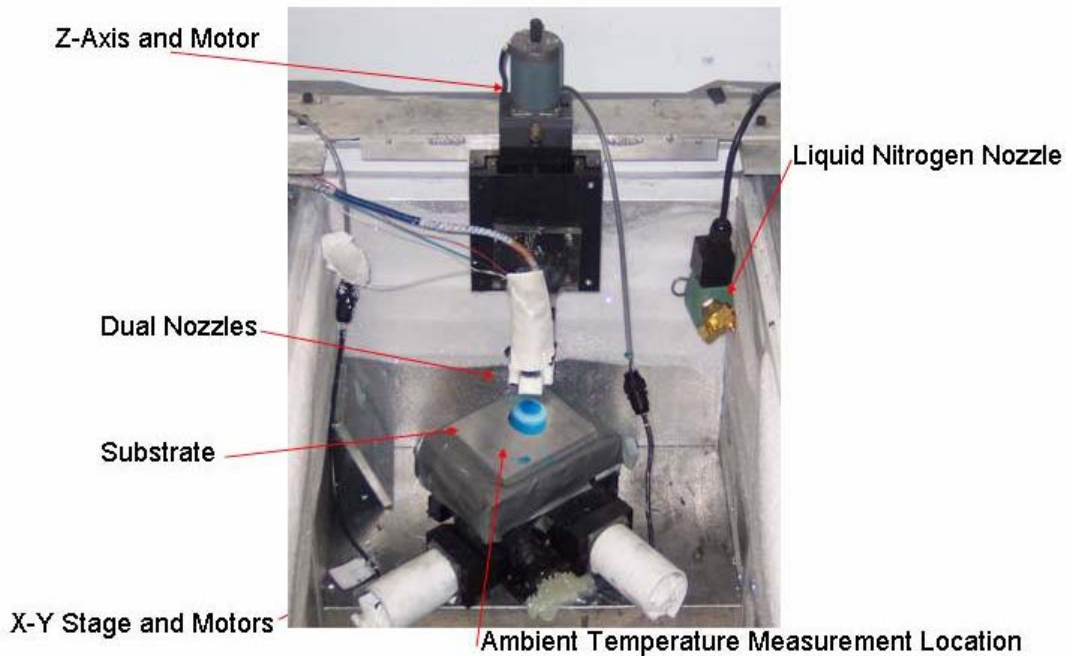


Figure 2: RFP Components

The objective of research presented in the present paper is to study the interaction between the build material (water) and the support material (eutectic sugar-water solution) during the RFP fabrication process, with temperature and concentration as the variables of concern. Temperature and concentration are modeled theoretically and semi-empirically and the

predicted results from these models are compared with experimentally measured results. The presentation of this paper is as follows. Section 2 discusses the temperature model. Section 3 discusses the concentration model. Section 4 presents predicted results from the temperature and concentration and their comparisons with experimental results. Section 5 concludes the paper.

## 2. Temperature Prediction Model

For a thin wall of ice and/or support material, a two-dimensional model can be considered because heat transfer through the thickness is much less than through the height and width dimensions[12]. Taking this into account, the temperature at any given location during the fabrication of a thin wall is governed by the two-dimensional heat conduction equation:

$$\frac{\delta T}{\delta t} = \frac{\lambda}{\rho c} \left( \frac{\delta^2 T}{\delta x^2} + \frac{\delta^2 T}{\delta y^2} \right) + q \quad (1)$$

where  $T$  is the temperature,  $t$  is time,  $x$  and  $y$  are spatial coordinates,  $q$  is the internal heat generation,  $\lambda$  is thermal conductivity,  $\rho$  is density, and  $c$  is specific heat. The values used for water are:  $\lambda=0.6 \text{ W/m}^2\cdot^\circ\text{C}$ ,  $\rho=1000 \text{ kg/m}^3$  and  $c = 4174 \text{ J/kg}\cdot^\circ\text{C}$ . The values used for support material are:  $\lambda=0.6 \text{ W/m}^2\cdot^\circ\text{C}$ ,  $\rho=1140 \text{ kg/m}^3$  and  $c = 2800 \text{ J/kg}\cdot^\circ\text{C}$ . Since the structure is built upon an aluminum substrate, which is much larger than the thin wall and acts as a heat sink, the temperature at the interface between the ice structure and the aluminum substrate can be considered to remain at the ambient temperature,  $T_{amb}$ .

The two side edges ( $x=0$  and  $x=L$ ), as shown in Figure 3 have a convective boundary condition, since these edges are exposed to the ambient. The convective heat transfer coefficient used is  $h = 6.7 \text{ W/m}^2\cdot^\circ\text{C}$ , which represents a free convection situation. The upper surface ( $y=H$ ) of an existing wall is exposed to a convective boundary condition until the new water droplets are deposited upon the existing wall. The new water droplets are deposited at a scan speed  $v$ , and modeled as a moving heat source. Finite element analysis is implemented to solve for the temperature at any given time and coordinate within the wall, using the boundary and initial conditions. The FEA program used in this analysis is ANSYS [16]. Specifically, the ANSYS Parametric Design Language (APDL) is utilized. The mesh size used is 0.1 mm, whereas a typical water layer height is approximately 0.2 - 0.3 mm.

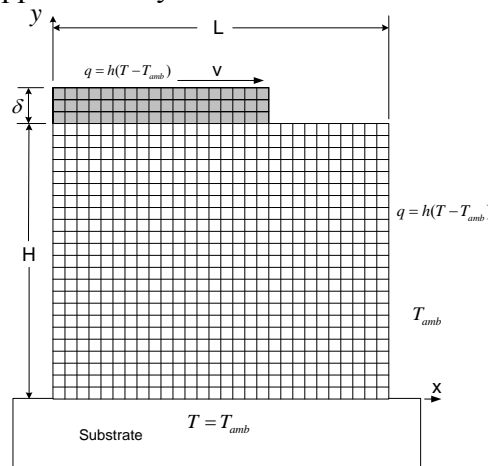


Figure 3: Two-dimensional wall of Support Material (white) and a layer of water (gray) for temperature analysis

Within the FEA program, the latent heat of each of the build and support materials is taken into account by defining the enthalpy of each material as a function of temperature in order to address the phase change from liquid to solid state. The temperature model predicts the length of time the build and support materials are in a liquid phase. The temperature and concentration are solved sequentially, with the output of the temperature model as an input to the concentration model.

Besides the above theoretical model, a semi-empirical model is also introduced, which is applicable to the physical setup used for this study. The semi-empirical model represents the heat source from the not-yet-frozen layers of water as a heat flux into the lower layers of frozen support material. The heat flux applied is a direct result of temperature measurements taken during the fabrication of thin walls for a range of realistic ambient build temperatures. While this semi-empirical model is not applicable to general applications, it serves very well in this study, since the temperature predictions will inherently be closer to the experimental results for a wider spectrum of ambient temperatures. This helps ensure that the concentration model has a solid foundation for the concentration value prediction. The schematic for the semi-empirical model is shown in Figure 4, along with the mesh and boundary conditions. The heat from the solidifying layers of water is noted as  $q_n$  in the figure.

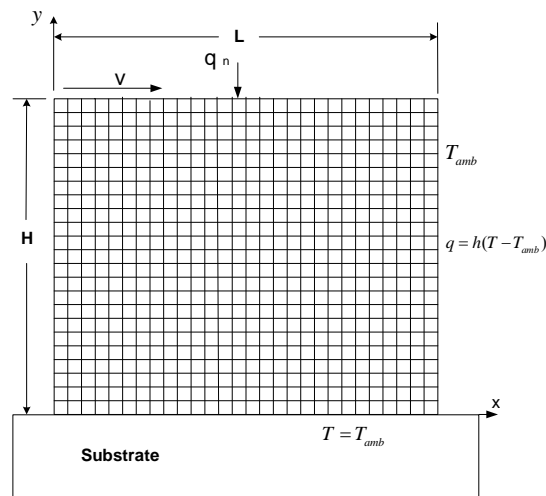


Figure 4: Schematic of semi-empirical thin wall temperature model

### **3. Concentration Model**

The concentration gradient in the near vicinity of the interface between the build and support materials within the thin wall is of special interest in the concentration model because the fabricated part is put in a kerosene bath to remove the sacrificial material once the entire ice part is fabricated. The support material used in the RFP process has a melting temperature of  $-5.6^{\circ}\text{C}$  [13, 14]. When the water and support material mix during fabrication, however, the melting temperature of the affected region is altered, due to the change in the composition where mixing occurred. Water has a higher latent heat than the support material, so when water is deposited onto already-frozen support material, there is a possibility for the support material to melt. The reverse scenario does not pose a problem, since the liquid support material does not melt the already-frozen ice layers due to its lower latent heat. When melting occurs, the water

and support material will mix, and then re-freeze due to the low ambient temperature. The mixing of the two materials during the liquid phase is the most important time to consider, since the diffusivity between two liquids is much higher than for a solid in contact with a liquid or a solid-to-solid contact [17]. In the concentration model, the time in which both materials are in the liquid phase is obtained from the temperature model. The direction of diffusion of the sugar molecules is from the support material to the water layers (i.e. from high sugar concentration to low sugar concentration).

The concentration as a function of time and location in a thin wall considered is governed by the following equation:

$$\frac{\delta C}{\delta t} = -D \left( \frac{\delta^2 C}{\delta x^2} + \frac{\delta^2 C}{\delta y^2} \right) \quad (2)$$

where  $C$  is the concentration,  $D$  is the diffusion coefficient,  $t$  is time, and  $x$  and  $y$  are spatial coordinates [7]. To solve for concentration finite element analysis is again utilized. The concentration model also has a moving source due to the finite deposition rate. The imposed boundary conditions are shown in Figure 5.

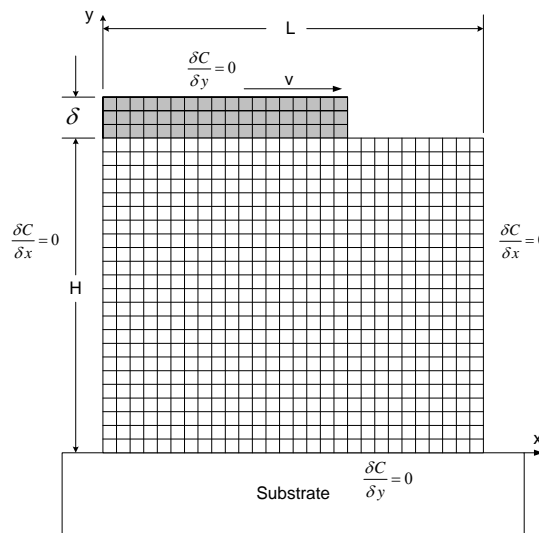


Figure 5: Concentration model mesh and boundary conditions

All the outer boundaries are considered to have a concentration flux of zero. The water and support material are in contact at the interface once deposition of the water has occurred. The temperature data from the temperature prediction model is used as an input to the concentration model. The temperature data is of importance to the concentration model because if the support material is melted at any point, diffusion will occur until the water is frozen.

#### **4. Experimental Results and Comparison with Model Predictions**

To compare the results of the temperature prediction models, thin walls were built in the RFP freezer and the temperature of the central interface location was monitored. Walls of support material had a length of 20 mm and a height of 10 mm. The ambient temperature, substrate temperature, the temperatures within the support material and at the central interface were monitored during the entire fabrication. The central interface location temperature is the

temperature used to compare to the experimental results with predictions. The water layer height was 0.2 mm, and the wait time between layers was 40 seconds. The measurements for three varying ambient temperatures (-24 °C, -13.7 °C, and -7.5 °C) and their comparisons with the semi-empirical model predictions are shown in Figures 6 – 8. It can be seen that the predicted temperatures have good agreement with the measured temperature for all their ambient temperatures.

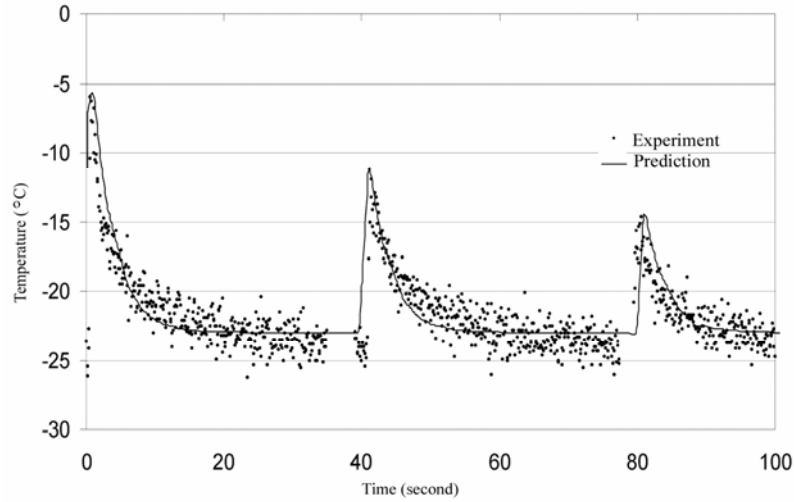


Figure 6: Experimental vs. predicted temperature data for an ambient temperature of -24°C

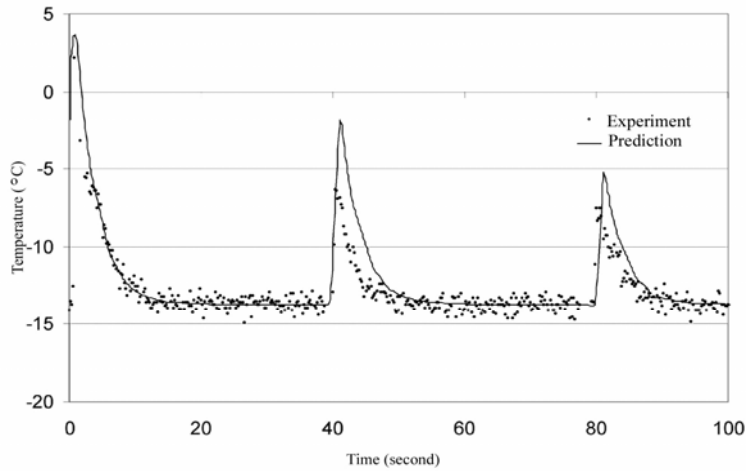


Figure 7: Experimental vs. predicted temperature data for an ambient temperature of -13.7°C

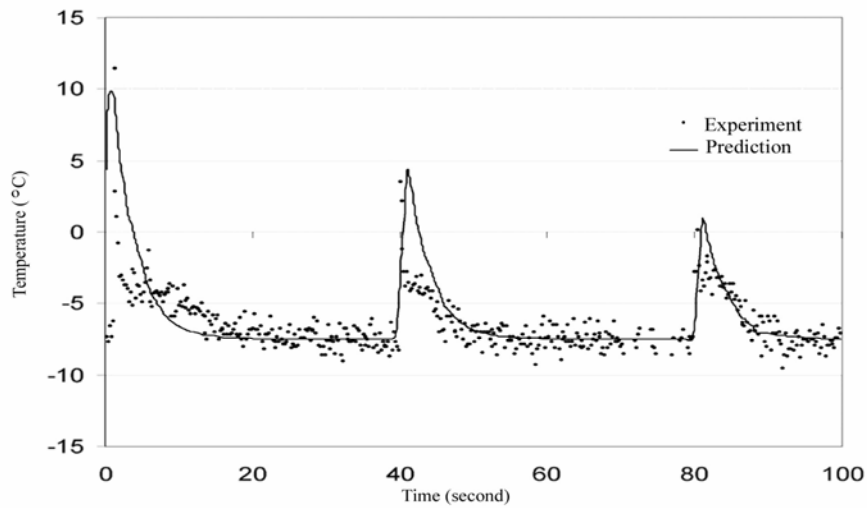


Figure 8 : Experimental vs. predicted temperature data for an ambient temperature of  $-7.5^{\circ}\text{C}$

The predictive temperatures from the semi-empirical model are very close to the measured temperature values. This is to be expected due to the nature of the semi-empirical model. In order to perform the research with a more scientific approach, the completely theoretical model predictions are shown in Figure 9 for the first temperature peak in an ambient temperature of  $-24^{\circ}\text{C}$ .

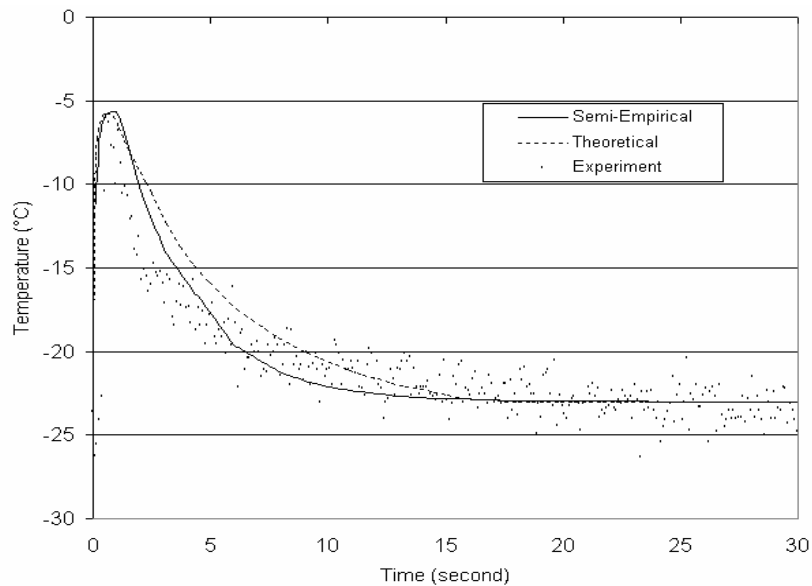


Figure 9: Theoretical, semi-empirical model, and measured temperature data for an ambient of  $-24^{\circ}\text{C}$ .

As can be seen in the figure, the temperatures by the theoretical model and by the semi-empirical model are very close in values. For the concentration model, which depends on the

accuracy of the temperature model, the semi-empirical result is utilized, since it more closely represents experimental data.

The concentration model is much harder to verify experimentally than the temperature model, since it is very difficult to measure concentration for any given point during the fabrication process. The concentration model predictions are shown in Figures 10 and 11. The data shown here considers a 10 mm high wall of support material with a length of 20 mm and a layer of water built upon the support material with a height of 2 mm. Figure 10 shows the concentration value at various heights of the fabricated wall as a function of time. At the top of the new layer of water ( $y = 2$  mm) the concentration level is near to that of pure water (0 %), whereas at a location lower into the support material ( $y = -2$  mm), the concentration is close to that of the original support material value (33%).

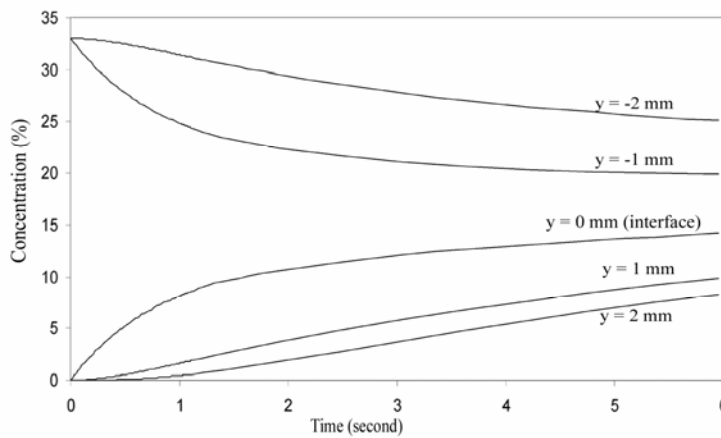


Figure 10 : Predicted concentration at different heights of the fabricated wall

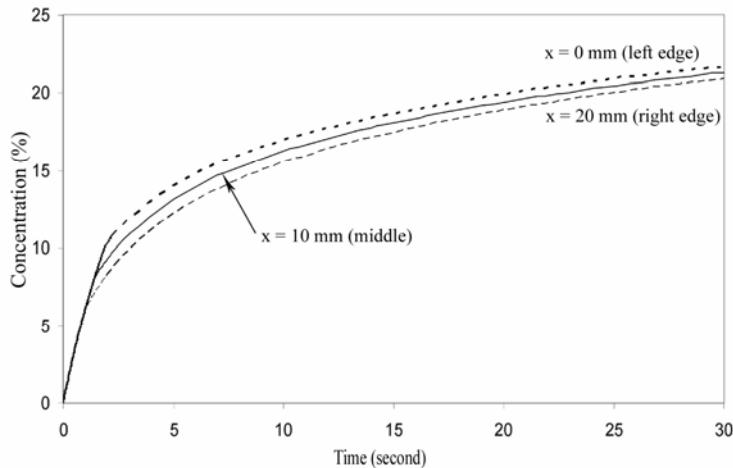


Figure 11: Predicted concentration at different values thru the left edge to the right edge on the x-axis

Figure 11 indicates that the concentration across the x-axis at the interface changes very little. The values shown in Figure 11 are computed with a scan speed of 20 mm/s. The small variance that is seen is due to the moving source because of finite deposition rate. The concentration values are within 4% of each other, even at the extreme time of 30 seconds. If the



scan speed is slower, the difference in the concentration value along the x direction will be larger. Typically, the scan speed used is 40 - 50 mm/s, so the difference in concentration along the x-direction in the actual fabrication of a thin wall will be smaller than that shown in Figure 11.

Since the support material is an organic mixture and not a pure substance, it takes on a semi-solid state in the vicinity of the melting point of the material. In order to remove the frozen support material from an ice structure, different methods of removal were attempted. Placing the frozen ice structure in the open ambient at a temperature of -5 °C resulted in a very uneven edge at the interface of the two materials and much of the support material could be visibly seen on the ice part. Figure 12 shows the uneven boundary in the middle of a cylinder where support material has been removed.

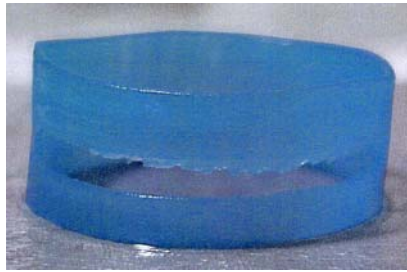


Figure 12: Cylinder with effects of diffusion shown on upper center section

To aid in the removal of support material, the parts are now placed in a kerosene bath at -5 °C and agitated until the support material is visibly removed. This method of removal especially helps when there are crevices in an ice part and support material is difficult to remove. In order to determine which concentration of the support material could be removed with the kerosene bath/agitation method, lines of support material at different concentrations of mixtures were created on a substrate. The concentrations ranged from 0.5% to 33 % for the amount of sugar in the solution. The lines were completely frozen in a -25 °C freezer, then placed in the -5 °C kerosene bath and agitated periodically for 30 minutes. The lines which had a composition of 1 % or more of sugar eventually broke down and were removed from the substrate during agitation due to the semi-solid state of the frozen support material. The lines with < 1% sugar all remained solid and adhered to the substrate. Since this test was done with thin lines, the results reported here are only applied to thin walled structures. Further tests will be conducted for other structures.

Thin walls of support material and then ice on top of it were built in varying ambient temperatures in order to validate the concentration model results. The support material region had a length of 20 mm and a height of 10 mm, and a 10 mm high wall of ice was built upon the wall of support material. Then the walls were transferred to a kerosene bath which had a temperature of -5 °C. In order to predict the height of the walls after the support material is removed, the time predicted for the interface of the two materials to be in liquid phase was first obtained from the temperature prediction for each ambient temperature build. Using the time value obtained, Figure 13 was used to predict how much of the wall would be affected up to the 1 % sugar concentration value.

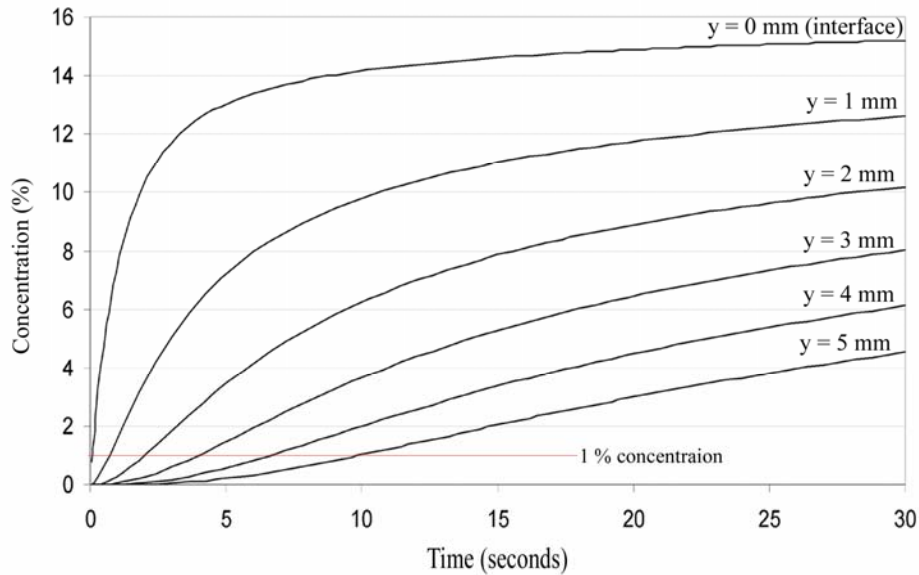


Figure 13 : Predicted concentration at different heights along the thin wall

Table 1 shows the ambient temperature for each build, the time predicted for both materials at the interface to be in the liquid phase, the predicted height of ice wall after support material removal, the measured height of ice wall after support material removal, and the % difference between the predicted and measured ice wall heights. The time predicted for both materials to be in the liquid phase at the interface, e.g. 3.1 seconds at  $T_{\text{ambient}} = -10\text{ }^{\circ}\text{C}$ , was used to calculate the height of ice wall affected up to 1 % sugar concentration. This is 2.5 mm from Figure 13, thus the predicted height of ice wall is 7.5 mm. Table 1 shows that the predictions and experiments agree within 2%.

Table 1: Comparison for ice part fabrication at four ambient temperatures after support material removal

$T_{\text{ambient}}$ ( $^{\circ}\text{C}$ )	Time (second)	$h_p$ (mm)	$h_m$ (mm)	% difference
-10	3.1	7.5	7.63	1.77%
-16	1.4	8.5	8.65	1.76%
-20	0	10	9.98	0.2%
-26	0	10	9.96	0.4 %

Figure 14 shows a fabricated ice part which requires support, built in a  $-8.5\text{ }^{\circ}\text{C}$  ambient. The area around the boundary of the two materials is very uneven and indicates that mixing has occurred. The part shown in Figure 15 was built in an ambient temperature of  $-23\text{ }^{\circ}\text{C}$ . Clearly, the part built in the cooler environment has a much sharper boundary as expected.

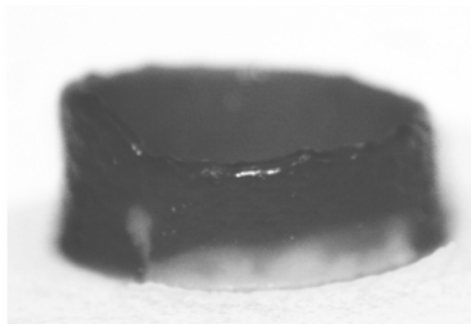


Figure 14 : Cylinder ice part with support region (white) built in  $-8.5^{\circ}\text{C}$  ambient



Figure 15: A cylinder built in  $-23^{\circ}\text{C}$  ambient, a) concept, b) before and c) after support material removal

## **5. Conclusion**

Semi-empirical and theoretical temperature models have been developed for use in processes which use two materials that are miscible. The two models agree well and also agree with experimental temperature data collected in the RFP setup. A concentration model has been developed to predict the total degradation due to the miscibility of the materials. The concentration model has predicted wall heights for thin walls built to within 2% error. Complex ice parts have been fabricated and they have been shown to have a marked improvement when fabricated in a lower ambient.

## **Acknowledgement:**

The authors graciously acknowledge the financial support of the study from the National Science Foundation Grants DMI-0321712 and IIP-0637556.

## **References:**

- [1] Bryant, F. and Leu, M. C., 2004, "Study on Incorporating Support Material in Rapid Freeze Prototyping", Proceedings of Solid Freeform Fabrication Symposium, University of Texas at Austin, Austin, TX.
- [2] Bryant, F., Sui, G., and Leu, M. C., 2003, "A Study on the Effects of Process Parameters in Rapid Freeze Prototyping", Rapid Prototyping Journal, Vol. 9, No. 1, pp 19-23.

- [3] Sui, G. and Leu, M.C., 2003, "Investigation of Layer Thickness and Surface Roughness in Rapid Freeze Prototyping", *ASME Journal of Manufacturing Science and Engineering*, Vol. 125, No. 3, pp 556-563.
- [4] Leu, M. C., Liu, Q. and Bryant, F. D., 2003, "Study of Part Geometric Features and Support Materials in Rapid Freeze Prototyping", *Annals of the CIRP*, vol. 52/1, pp. 185 – 188.
- [5] Leu, M. C., Zhang, W., and Sui, G., 2000, "An Experimental and Analytical Study of Ice Part Fabrication with Rapid Freeze Prototyping", *Annals of the CIRP*, vol. 49/1, pp. 147-150.
- [6] Ozisik, M. N., 1985, *Heat Transfer: A Basic Approach*, McGraw-Hill, Inc., New York
- [7] Crank, J., 1956, *The Mathematics of Diffusion*, Oxford at the Clarendon Press, London.
- [8] Lunardini, V. J., 1991, *Heat Transfer with Freezing and Thawing*, Elsevier, New York.
- [9] Chin, R.K., Beuth, J.L. and Amon, C.H., 2001, "Successive Deposition of Metals in Solid Freeform Fabrication Processes, Part 1: Thermomechanical Models of Layers and Droplet Columns", *Journal of Manufacturing Science and Engineering*, Vol. 123, pp. 623 – 631.
- [10] Chin, R.K., Beuth, J.L. and Amon, C.H. 2001, "Successive Deposition of Metals in Solid Freeform Fabrication Processes, Part 2: Thermomechanical Models of Adjacent Droplets", *Journal of Manufacturing Science and Engineering*, Vol. 123, pp. 632 – 638.
- [11] Vasinonta, A., Beuth, J.L. and Griffith, M.L., 2001, "A Process Map for Consistent Build Conditions in the Solid Freeform Fabrication of Thin-Walled Structures", *Journal of Manufacturing Science and Engineering*, Vol. 123, pp. 615-622.
- [12] Liu, Q. and Leu M.C., 2007, "Finite Element Analysis of Solidification in Rapid Freeze Prototyping", *ASME Journal of Manufacturing Science and Engineering*, Vol. 129, No. 3.
- [13] Jackson, R.F., Silsbee, C. G., 1922, *Scientific Papers National Bureau of Standards*, Vol. 17, No. 17.
- [14] Stephan, H. and Stephan, T., 1963, "Solubilities of Inorganic and Organic Compounds", Vol. 1, Pergamon Press, New York, page 108.
- [15] Rosenthal, D., 1946, "The Theory of Moving Sources of Heat and Its Application to Metal Treatments", *ASME Journal of Heat Transfer*, Vol. 123, No. 4, pp. 849-866.
- [16] ANSYS Thermal Analysis Guide, 2004, ANSYS release 9.0.
- [17] Bird, R.B., Stewart, W.E., and Lightfoot, E.N., "Transport Phenomena", 2<sup>nd</sup> Edition, John Wiley & Sons, Inc., Hoboken, NJ.