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ABSTRACT

A heat transfer model has been developed that mathematically describes the heating and calculates the thermal history of a gel particle in free-fall through the furnace. The model parameters that greatly affect the calculations have been found to be gel particle mass, geometry, specific heat, and furnace gas. Empirical testing of the model has commenced. The code calculations and the initial empirical testing results both indicate that the gel-to-shell transformation occurs early and rapidly in the thermal history of the gel particle, and that for current work the heat transfer rate is not a limitation in shell production.

Introduction

In the current method of Microshell[®] target production, uniform, hollow spherical glass shells are formed by dropping metal-organic gel powder into a drop tube furnace. The free-falling powder is heated by the hot furnace gas and transformed into hollow spheres. These shells usually have a wide distribution in size and quality, and are currently limited to sizes of less than 1 mm diameter for quality shells. It is the purpose of our current research to elucidate this gel-to-shell transformation, and ultimately to control and improve upon the size and quality of the product.

The research proposed for the current year is the development of a mathematical model that describes this transformation of gel powder to glass shells. We have initially concentrated on a portion of the general model, specifically the development and testing of a heat transfer code which models the heating of a gel powder (and a glass shell) particle as it drops through the furnace. This model was initially designed under the auspices of our DoE contract.

The present heat transfer code, termed GELSHEL, is a composite of two models:

- a) a particle displacement model that calculates, as a function of time, the position of a gel particle in a drop furnace, and
- b) a heat transfer model that describes the rate

of heat transfer from the furnace to the gel particle.

The GELSHEL code thus calculates the temperature of a gel particle (and the resulting shell) in free-fall as a function of its drop time and vertical displacement in the furnace.

The particle displacement model is based on Newton's Second Law and Stoke's Law. The displacement of the particle is found by integrating its velocity with respect to time of fall; its velocity is determined as a function of time from Newton's Second Law for a particle falling through a gas. The velocity of the particle is also a function of the particle shape and density, due to the effects of the drag and buoyancy forces of the furnace gas on the particle. These are satisfactorily described with Stoke's Law.

The displacement model that describes the particle position as a function of time of fall is summarized by

$$\frac{dU}{dt} = \gamma + \delta U \quad (1)$$

$$\frac{dS}{dt} = U \quad (2)$$

$$\gamma = g(1 - \alpha \rho_f) \quad (3)$$

$$\delta = -12.5 \mu_f \beta \quad (4)$$

where

U = particle velocity

S = particle displacement (distance of fall)

t = time

g = acceleration of gravity

ρ_f = density of the furnace gas

α = system parameter that is a function of particle mass, geometry, and density

$\alpha \rho_f$ = particle buoyancy term (coefficient)

μ_f = absolute viscosity of the furnace gas

β = system parameter that is a function of particle dimensions and mass

δ = velocity coefficient correcting for the drag force on the particle

The heat transfer model describes the rate of heating of the particle surface by the furnace, as the sum of both conductive heating by the hot furnace gas and radiative heating. The model is based on the fundamental heat transfer relationship

$$\frac{dQ}{dt} = \frac{mCdT}{dt} = h S_A (T_f - T) + \sigma \epsilon S_A (T_f^4 - T^4)$$

where

m = particle mass

C = specific heat of the particle

T = particle temperature

T_f = furnace temperature

t = time

S_A = particle surface area

h = convective heat transfer coefficient

σ = Stefan-Boltzmann constant

ϵ = emittance of the particle

This relationship has been refined to

$$\frac{dT}{dt} = Ak_f\pi(T_f - T) + B\sigma\epsilon\pi(T_f^4 - T^4)$$

where

A = convective heat transfer coefficient that is a function of particle mass, geometry, surface area, and specific heat

k_f = thermal conductivity of the furnace gas

B = radiative heat transfer coefficient that is a function of particle mass, geometry, surface area, and specific heat

The particle, as it drops through the furnace, changes in mass, size, geometry and specific heat. This evolution causes substantial changes in the heat transfer rate and particle velocity, as a consequence of the changing geometry, surface area and mass, and thus particle buoyancy and drag. To approximate these changes this complex particle history is simplified into three discrete regimes in the model, on the basis of particle temperature.

Particle characteristics are constant within a regime, but change from one regime to the next in a step-wise fashion. The temperature bounds (temperature switches) of the regimes and the particle characteristics within each regime are defined by the user. These regimes are:

- 1) gel pellet regime; mass, dimensions, and specific heat may be changed at the end of this regime,

but not pellet geometry

- 2) pellet sintering regime; at the end of this regime, mass and geometry are changed (from a cylinder to a sphere), and specific heat and emissivity may be changed within this regime
- 3) shell regime; emissivity may be changed within this regime, but mass, geometry dimensions and specific heat are constant for the glass shell.

This approach is based on these assumptions:

- 1) gel pellet characteristics change in a stepwise and not a continuous fashion
- 2) the geometry of the gel is a right cylinder
- 3) the geometry change from pellet to shell is instantaneous and
- 4) the heat transfer from the surface to the bulk, of both pellet and shell, is instantaneous, so there is no temperature gradient within the particle.

As the code for the model is presently formulated, the gel powder distribution is modeled by a gel pellet that is a right circular cylinder; the final product is a uniform hollow sphere. The code requires as input

- a) a correlated set of gel pellet and glass shell characteristics, i.e. mass, dimensions, specific heat, emissivity for each regime
- b) the furnace temperature, or a temperature profile

c) the values for the temperature switches, the particle temperatures at which the stepwise transformations occur which are listed in Table 1. The output of the code is a calculated thermal history of the particle, in the format of particle temperatures as a function of drop time and a function of particle displacement in the furnace (Figure 1). Given a set of gel and furnace parameters, the code cannot predict whether a particular gel will form a hollow shell but only whether the gel can reach the appropriate temperatures for that transformation, the rate at which that temperature is reached, and the residence time in the furnace.

Results

In modeling a shell blowing experiment for which furnace conditions were optimized, we have determined with the GELSHELL code that the gel is heated rapidly to the gel shell transformation temperature of 1000°C. In fact, for a gel pellet of 267 μm diameter and 240 μm length, 1000°C is reached with a drop time of 0.385 sec and a drop distance of 18.9 cm. This corresponds to an initial particle heating rate of 3400°C/sec, up to its melting range. Similar results have been obtained for calculations for other shell runs.

The GELSHELL code, in its present form, permits the variation of a number of gel, shell and furnace parameters for the study of the effects upon the thermal history of the particle. These code simulations were begun by

Table 1. Required Input Parameters for GELSHELL code

<u>Pellet</u>	<u>Shell</u>	<u>Temperature Switches</u>	<u>Furnace</u>
mass (MG1, MG2)	mass (MS)	mass loss (T1)	furnace gas choice
diameter (DG1, DG2)	diameter (DS)	geometry change (T2)	length (SMAX)
length (LG1, LG2)	glass density (RHOGLS)	specific heat change (T3)	temperature profile
specific heat (CPFAC1, CPFAC2)	emissivity (ALPHA 2)	emissivity change (T4)	
emissivity (ALPHA 1)			

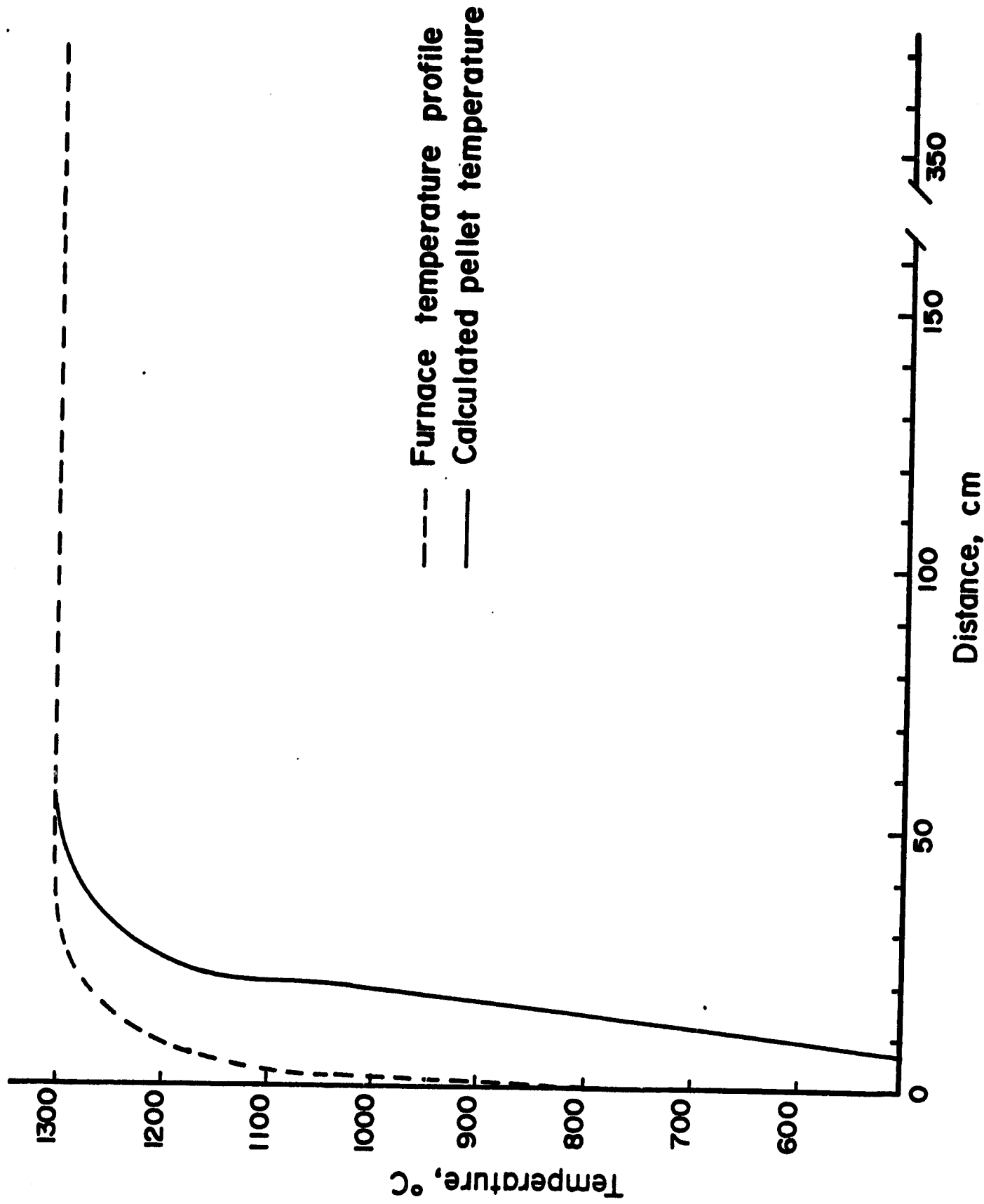


Figure 1. Normal Furnace Profile and Calculated Particle Temperature History

Table 2. Effect of Mass and Geometry on Particle Heating

Pellet ² Mass	Diameter ²	Length ²	D/L	Time, ¹ sec	Distance, ¹ cm	Length	Diameter	D/L	Time, sec	Distance, cm
m/2	$D\sqrt{2}$	L	$D/L\sqrt{2}$	0.216	8.4	L/2	D	2D/L	0.249	15.7
m	D	L	D/L	0.285	18.9	L	D	D/L	0.285	18.9
2m	2D	L	$D\sqrt{2}/L$	0.394	43.4	2L	D	D/2L	0.338	23.8
4m	$\sqrt{2}D$	L	2D/L	0.582	107.0	4L	D	D/4L	0.405	30.3
8m						8L	D	D/8L	0.477	37.3

¹ Time and distance of fall (into the furnace) required to heat the pellet to 1000°C.

² m = 17.6 µgm

D = 267 µm

L = 240 µm

selectively varying the parameters that we know we can control empirically or which are expected to have profound influence on the particle. The basic set of input data for these simulations was obtained from a shell run for which the parameters were optimized. The parameters

a) the mass, and consequently the dimensions of the

pellet and shell

b) specific heat of the gel

c) the temperature switches for the specific heat changes, emissivity changes, and geometry changes (cylinder to sphere)

d) the furnace gas

were varied to determine the effect on time and drop

distance required by the pellet to reach 1000°C. The results of these simulations are, briefly:

- 1) An increase in mass can decrease the particle heating rate rapidly. A four-fold increase in mass, to 70.4 μgm, can result in an increase in drop time and distance, required to reach 1000°C, to 0.58 sec and 107 cm respectively.
- 2) An increase in length, that is commensurate with an increase in particle mass, minimizes the free-fall velocity, maximizes the heating and results in faster particle heating in comparison to a comparable increase in particle diameter (Table 2, p. 6).
- 3) Despite its low gas density, helium is the best heat conducting furnace medium. Water vapor is second best, and the permanent gases as a group are third.
- 4) The specific heat of the gel and the values of the various temperature switches have only minor effects, not gross effects, in the temperature history of the gel particle.

Effect of Pellet Mass and Geometry

A difficulty with the parameter of particle mass is that it is directly related to particle volume by the particle density, which should be held constant. To vary the mass is to vary the volume, and consequently,

the length or diameter (or both) of the cylindrical gel pellet. For a cylinder, the volume increases proportionately and linearly with length, and with the square of the diameter. A variation in geometry can affect both the particle velocity and the heat transfer to the particle, as both are geometry-dependent.

The particle velocity is affected by the cylinder dimensions because the buoyancy and drag terms are geometry-dependent:

$$\alpha = \frac{D^2 L}{4m}$$

$$\beta = \frac{L}{m}$$

Thus a change in mass (m) with a commensurate change in length (L) will affect neither term, whereas a change in diameter (D) will affect β , the drag term. These considerations significantly complicate an analysis of the affects of pellet mass on the thermal history of the pellet.

The effect of increased pellet mass as a function of diameter and length of the pellet is tabulated in Table 2 (p. 6) as the drop time and distance required to raise the pellet temperature to 1000°C. For a given mass increase, the corresponding diameter increase, in contrast to the corresponding length increase, results in both a longer drop time and drop distance to reach 1000°C. For example, a pellet of 70 μgm mass (4M, Table 2) and diameter 535 μm (2D, Table 2),

drop-furnace heating method is theoretically capable of heating large pellets to the melting temperature. A 140 μm pellet (8M) requires only 0.48 secs and 37 cm of distance to reach 1000°C, the supposed gel-shell transformation point. More work remains to be done in this area. A more detailed analysis of the above calculations as well as further code calculations will follow in the next half of the contract.

Effect of Specific Heat

The specific heat of a metal-organic gel may differ substantially from that of the corresponding glass, primarily because of the reactivity of the organic residues of the gel system and the content of inorganic volatiles. In fact, by differential scanning calorimetry (DSC), the net gel reactivity is endothermic, and the specific heat of the gel is almost twice that of the glass. Since exact data (as a function of temperature) are known for glass but not for gels, the average specific heat for gels has been estimated from preliminary DSC work (as discussed in the May monthly progress report). It is expressed in the code as an additive factor of the specific heat of glass.

$$Cp_{\text{gel}} = Cp_{\text{glass}} + xCp_{\text{glass}}$$

The factor x is an input variable that determines the specific heat of a gel in terms of the specific heat of glass. It is a variable that can be stepped in value as

Table 3. Effect of Specific Heat on Pellet Heating

CPFAC 1	CPFAC 2	Time, sec ¹	Distance, cm ¹
0.0	0.0	0.195	10.8
0.5	0.0	0.216	12.8
1.0	0.0	0.237	14.8
2.0	0.0	0.280	19.1
1.0	0.0	0.237	14.8
1.0	0.5	0.261	16.9
1.0	1.0	0.285	18.9
2.0	1.0	0.326	23.1
2.0	2.0	0.371	27.0

¹ drop time and distance required to heat pellet to 1000°C

requires 0.58 secs and 107 cm to reach 1000°C. A particle of the same mass but of 960 μm length (4L) requires only 0.40 secs and 30.3 cm to reach 1000°C. These data reflect differences in heat transfer rates as well as particle velocities.

According to GELSHEL code calculations, the present

the gel passes from one temperature regime to the next. Thus, to account for the changing chemical and physical nature of the gel, the specific heat factor (CPFAC) is stepped twice:

- 1) at T1, from CPFAC 1 (regime 1) to CPFAC 2 (regime 2), to account for the mass loss by the gel, and
- 2) at T3, from the CPFAC 2 value to zero (which sets the specific heat to that of glass) to account for gel sintering and any further mass loss.

As can be seen in Table 3 (p. 8), without these factors, a pellet reaches 1000°C almost instantaneously. Changing CPFAC 1 from 0 to 1.0 increases the drop distance by almost 50%, from 10.8 cm to 14.8 cm. Additionally increasing CPFAC 2 from 0 to 1 almost doubles that drop distance, from 10.8 cm to 18.9 cm. These effects are significant if particle heating rates are critically important to shell formation (we have evidence to believe that this may be so). Otherwise, compared to the total furnace length (of 370 cm), or to gel mass and geometry effects, these are of modest significance. The effects become significant for CPFAC = 2, but these are unrealistically high specific heat values. Thus, errors in assessing the specific heats of gels will affect the temperature history of the gel only moderately.

Temperature Switches

The GELSHEL code has provisions for varying the temperatures at which chemical or physical changes are assumed to occur in stepwise fashion. These "switches" exist for the following:

- 1) end of the first thermal regime, which corresponds to a mass loss, and a specific heat change (T1 switch)
- 2) reversion of gel specific heat (CPFAC 2) to that of glass (T3)
- 3) gel to glass shell geometry transformation (T2)
- 4) reduction of the gel emissivity (ALPHA 1) to that of glass (ALPHA 2) (T4).

We have experimented only with the last three switches. The first switch, T1, has been maintained at 500°C since most of the gel mass loss occurs before that point.

The T3 switch, at which the specific heat of gel reverts to that of glass (CPFAC 2 → 0) was varied as shown in Table 4. The switch value has only a small effect on the heating rate, much like the effect of varying CPFAC 2 itself. Thus errors in assessing the exact temperature, or range of temperatures, over which the specific heat of the gel is reduced, will cause only modest errors in the temperature history of the gel.

The temperature at which the pellet is assumed to change, instantaneously, into a shell is 1000°, and is

distance. This code run did not use the "standard" set of gel-shell data used for previous sets, and therefore will be rerun.

Since ~70% of the heat transfer at the furnace equilibrium temperature is by the infrared radiation, the temperature switch T4, at which the gel emissivity changes from 1 to zero, is rather important. The value for this switch has normally been 1150°C, based on hot stage microscopy and furnace run observations. These indicate that carbon removal and thus a reduction in emissivity becomes appreciably fast only when the glass reaches ~1200°C-1300°C. Shells produced in dry air at 1300° still have high levels of carbon inclusions. The values for T4 were varied as shown in Table 6 (p. 12).

This set of calculations utilized an isothermal furnace temperature of 1305°, a hypothetical condition unlike the real furnace profiles used for all other calculations. The significance of the T4 switch, and of α for the gel (ALPHA 1), are illustrated by the results. The effects of T4 on the particle heating rate are significant only when T4 is set above 1150°; below this particle temperature, gel heating is primarily by gas conduction rather than by absorption of infrared radiation. The implication is that the choice of T4 does not affect the rate of gel heating to at least 1000°, but can dramatically affect the heating rate beyond that temperature.

Table 4. Effect of T3¹

<u>T3, °C</u>	<u>time, sec</u>	<u>distance, cm</u>
950	0.305	20.6
850	0.285	18.9
700	0.261	16.9
550	0.242	15.3

¹ drop time and distance to heat the pellet to 1000°C

a reasonable estimate based on hot stage observations and furnace work. This temperature is also a variable switch point in the program, but has not been investigated extensively. The results from this cursory work indicates this switch point does not have a very dramatic effect on the thermal history of the gel. This is summarized in Table 5 and in Figure 2, a plot of temperature vs. drop

Table 5. Effect of T2¹

<u>T2, °C</u>	<u>time, sec</u>	<u>distance, cm</u>
1200	0.479	37.4
1000	0.460	34.6
900	0.440	32.8

¹ drop time and distance to heat the pellet to 1000°C

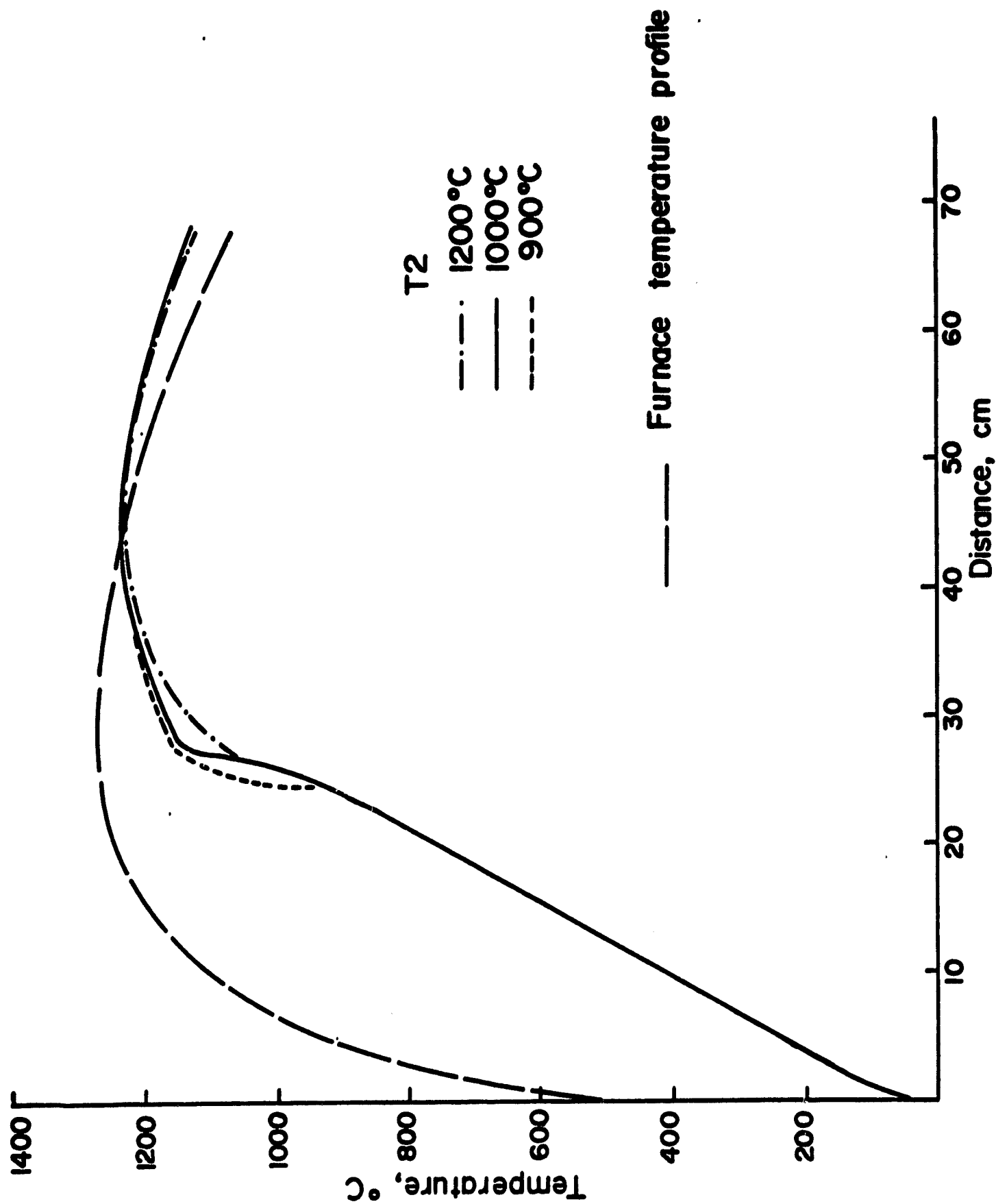


Figure 2. Effect of T2

Table 6. Effect of T_4^3

$T_4, ^\circ\text{C}$	1000°C^1		1300°C^2	
	Time, sec	Distance, cm	Time, sec	Distance, cm
1305	.204	11.1	.323	19.1
1150	.204	11.1	.520	31.0
1050	.204	11.1	.540	32.2
950	.214	11.9	.560	33.7
851	.230	13.2	.580	35.2

¹ drop time and distance to heat the pellet to 1000°C

² drop time and distance to heat the pellet to 1300°C

³ furnace is isothermal at 1305°C

Effect of the Furnace Gas

As seen in the previous discussion and Table 6, heat conduction by the furnace gas is the primary means of heat transfer, especially at temperatures lower than 1000°C . Not only does the heat conductivity of the gas determine its efficiency as a heat exchanger, but the gas viscosity and density affect the buoyancy and drag on the falling particle. These physical properties for several gases (at 1000°C and 1300°C) are given in Table 7 (p. 13), and the effects of the gases on particle heating are summarized in Table 8 (p. 13), again as the drop time and distance required to bring the particle

temperature to 1000°C . Helium, with a high thermal conductivity that outweighs its low gas density, is the best furnace medium, heating the gel to 1000°C in only 0.11 secs and 4.34 cm drop. Water vapor is surprisingly a distant second as a heat conduction, while the other gases rank third as a group.

Table 7. Physical Properties of Some Gases at Selected Temperatures

Gas	Density, 10^{-4} gm/cc		Viscosity, 10^{-4} gm/sec cm		Thermal Conductivity, 10^{-4} W/cmK	
	1000°C	1300°C	1000°C	1300°C	1000°C	1300°C
air	2.78	2.25	4.79	5.40	7.73	8.65
argon	3.74	3.04	6.45	7.38	5.03	5.76
carbon dioxide	4.12	3.35	4.65	5.35	8.32	9.45
nitrogen	2.63	2.13	4.55	5.24	7.42	8.51
oxygen	3.00	2.44	5.66	6.48	8.48	9.56
water	1.69	1.37	4.65	5.42	12.3	16.1
helium	0.375	0.305	5.56	6.44	43.4	50.3

Table 8. Effect of Furnace Gas

Gas	time, sec ¹	distance, cm ¹	Total residence time, sec ²
air	.285	18.9	6.13
argon	.352	20.6	8.23
carbon dioxide	.276	18.4	6.00
nitrogen	.291	19.9	5.88
oxygen	.278	16.6	7.26
water	.221	13.3	6.10
helium	.113	4.3	7.28

¹ drop time and distance to heat the pellet to 1000°C

² total time spent in the furnace

Experimental

Gel and Shell Characterization

The GELSHEL model was designed for maximum flexibility and usefulness, and thus requires as input data a number of correlated gel and shell characteristics and furnace parameters. For valid results, these parameters must be as realistic as possible. Therefore, gel has to be pelletized, fully characterized, formed into shells under optimized furnace conditions, and the resulting shells had to be fully characterized as well. A significant portion of this report period was consumed in developing a standard set of correlated input data for subsequent code simulation work.

Pelletization

In the heat transfer model, a right-cylindrical gel geometry was used to model the real gel powder, which has an irregular geometry, a highly variable surface area, and a wide size and mass distribution. Industrial particle pelletization techniques were adapted to press gel powder into such cylindrical pellets. This approach presented several advantages to the empirical aspects of the modeling work: accurate and reproducible control of gel mass and size; constant gel geometry; constant surface area/mass relationship within a particle population; and accurate correlation of the resulting gel and shell characteristics. Several pellet production runs have been completed; characteristics of these are summarized in Table 9. The mass and size distributions are quite narrow. Mass deviations from the

Table 9. Characteristics of Pellets from Several Runs

<u>Pellet Run</u>	<u>Mass, μgm</u>	<u>Diameter, μm</u>	<u>Length, μm</u>	<u>ρ, gm/cm^3</u>
1	14.9 \pm 1.3	259 \pm 1.6	225 \pm 4	1.27
2	12.5 \pm 1.4	259 \pm 1.6	225 \pm 4	1.06
3	15.8 \pm 1.7	250 \pm 2	237 \pm 5	1.35
4	14.1 \pm 1.1	250 \pm ?	252 \pm 5	1.15
5	17.6 \pm 1.5	267 \pm ?	240 \pm 9	1.31
6	21.6 \pm 0.8	272 \pm 5	245 \pm 8	1.52

mean were generally less than 10% and are due to variations in the particle packing efficiency of the powder fill step rather than abrasion or fragmentation of the resulting pellet. Presumably the efficiency and repeatability in the fill step can be improved upon by optimizing the particle size of the feedstock.

The pellet diameter is fixed by the aperture of the die plate to a nominal 250 μm . The pellet length is variable, and pellets of 50 to 450 μm length have been produced. However, for this work we have standardized to a nominal length of 250 μm .

Gel and Shell Mass Correlations

A gel-to-shell mass correlation was developed by characterizing individual pellet shell pairs. This entailed

- a) pellet mass and size determination
- b) formation of the shell from the pellet, one at a time, at 1500°C in dry air
- c) shell mass and size determination

These one-for-one correlations indicated a considerable variation in the pellet-to-shell mass losses, as shown in Table 10 (p. 16), and reflect the uncertainty in the weighings ($\pm 5\%$) as well as the actual mass loss variations. Analysis of these data indicated that statistical batch determinations of gel pellet and shell masses gave the same results statistically as the individual

correlations.

When the shells were formed in dry air, regardless of the furnace temperature the observed mass loss is similar to that observed by TGA (Table 11, p. 17). If the shells were formed in water vapor, the mass loss is significantly greater, probably due to some alkali loss from the glass, promoted by water. This phenomenon has been observed frequently before in the elemental analyses of gels and shells.

Specific Heat of Gel

The specific heat of gels is expected to be greater than the corresponding glass due to its content of organic residues and inorganic volatiles, which require additional heat input during pyrolysis. The specific heat, as a function of temperature, is available for glass, but not for gel. The average specific heat of gel pellets over the range of 20-600°C was determined to be 1.85 joules/gm^oK (for unhydrolyzed gel) by preliminary DSC work. This is twice the specific heat of glass in the same temperature range, which is 0.75-1.30 joules/gm^oK. Further DSC work is planned, specifically for generating accurate data of specific heat of pellets for various temperatures.

Effect of Pelletization on Shell Formation

The effects of gel pelletization on shell formation

Table 10. Pellet-to-Shell Mass Correlations

<u>Pellet</u>	<u>Mass, μgm</u>	<u>Shell</u>	<u>Mass, μgm</u>	<u>Mass Loss</u>	<u>% Mass Loss</u>
1	13.5	1	9.2	4.3	31.8
2	12.7	2	9.9	2.8	22.0
3	12.7	3	8.8	3.9	30.7
4	13.4	4	9.6	3.8	28.4
5	13.0	5	9.9	3.1	23.8
6	14.5	6	11.3	3.2	22.1
7	11.1	7	8.4	2.7	24.3
8	12.1	8	9.0	3.1	25.6
9	9.6	9	7.0	2.6	27.1

$$\bar{m}_p = 12.5$$

$$\sigma = 1.4$$

$$\bar{m}_s = 9.2$$

$$\sigma = 1.2$$

$$\bar{\Delta m} = 3.3$$

$$\sigma = 0.6$$

$$\bar{\Delta m} = 26.2\%$$

$$\frac{\bar{m}_p - \bar{m}_s}{\bar{m}_p} \times 100 = 26.2$$

Table 11. Pellet Mass Loss in Shell Runs

<u>Pellet Mass</u> <u>μgm</u>	<u>Shell Mass</u> <u>μgm</u>	<u>% Mass Loss</u>	<u>% Mass Loss</u> <u>by TGA</u>	<u>Furnace</u> <u>Conditions</u>
15.1 ± 1.1	9.5 ± 1.1	37.0	23.5	H ₂ O, 1500°
27.9 ± 1.1	18.6 ± 0.8	33.0	23.5	H ₂ O, 1500°
12.5 ± 1.4	9.2 ± 1.2	26.4	23.5	air, 1500°
17.6 ± 1.5	13.2 ± 1.0	25.0	21.2	air, 1300°
17.6 ± 1.5	12.8 ± 1.2	27.3	21.2	air, 1350°
17.6 ± 1.5	13.3 ± 1.0	24.4	21.2	air, 1400°

¹TGA mass loss was determined over 20-900°C rather than 100-900°C.

had to be ascertained if pellets were to model gel powder. While pelletization was advantageous in characterization and correlation work, we did not know whether the reduction in surface area/mass ratio or changes in the physical or chemical nature of the gel due to the local heating during compaction would affect the shell-blowing process. Accordingly, the sodium silicate gel powder and the corresponding pellets, closely matched in mass (Table 12), were blown into shells under identical furnace conditions. The resulting products were compared.

The differences in the product from the powder and pellets were slight. Nevertheless, the gel powder yielded

Table 12. Characteristics of Gel Powder and Pellets

<u>Gel</u>	<u>Mass, gm</u>	<u>Size, m</u>
Powder	16.4 ± 3.0	212-250 esd ¹
Powder	15.8 ± 1.7	250 ± 2 diameter 237 ± 5 length

¹esd = equivalent spherical diameter

a product that has

- a) a somewhat smaller average diameter and thicker walls
- b) less gas bubbles in the walls
- c) less elemental carbon inclusions in the glass
- d) less surface mottling

than the corresponding product from the pellets. These results suggest that the pelletization of gels slightly retards the shell-forming process. This is consistent with the lower surface area/mass ratio of the symmetrical, cylindrical pellet geometry, for which a reduced heat transfer rate is expected compared to the irregular powder particles. These differences, however, are not strong enough to invalidate the use of gel pellets to model gel powder.

Very large, thin-walled shells of 1 to 2 mm diameter were produced at 1400°C in a water vapor environment. While these conditions usually yield thin-walled shells, shells of such large size and thin walls have not been observed in our experiments before. They were extremely fragile and did not survive intact.

Optimum Furnace Condition

A furnace temperature study was conducted with pellets of unhydrolyzed gel to determine the optimum furnace conditions for shell formation. These experiments were run with dry air and with water vapor as the furnace gas.

With dry air as the furnace gas, the optimum temperature is 1300°C; a sharp reduction in yield of large thin-walled shells are observed at higher temperatures. A repetition of this experiment, with 50°C temperature increments between 1300° and 1400°C, confirmed this result, as a sharp drop in yield are observed beyond 1300°C. Unfortunately, these shells were still loaded with elemental carbon. The carbon, however, is not completely removed even at 1500°C, when the shells were well on the way to collapse to beads.

With water vapor as the furnace gas, the optimum temperature is 1400°C, at which large, uniform thin-walled shells were produced that were free of carbon. Lower temperatures yielded smaller shells, containing some carbon still, while higher temperatures resulted in a low shell yield. The results of these experiments corroborate earlier observations concerning the effect of water vapor upon shell yield and quality. High levels of water vapor in the furnace gas probably reduce the glass viscosity and increase the rate of gas permeability. Further, the water vapor probably enhances the rapid removal of carbon from the glass as a result of the water-carbon reaction



The decreased glass viscosity and the rapid formation of CO₂ gas may explain the production of larger and thinner shells in these conditions.

The modification of glass properties by water vapor is a complexity that we cannot describe yet. Therefore for simplicity in developing a set of standard input data correlations, the gel pellets were blown in dry gas, despite the problem of carbon inclusions in the glass.

To reduce these inclusions without the use of water vapor, the use of oxygen as the furnace gas was incorporated. As expected, the carbon inclusions in the glass were reduced in density, but not totally removed. An increase in furnace temperature from 1300° to 1400°C, with dry air, reduced the carbon levels more than using pure oxygen at 1300°C. Although the yields were not quantitatively nor statistically analyzed for size, no increase in diameter was apparent. Some increase was expected due to O₂ in permeation as well as increased CO₂ production.

In a final effort to reduce carbon inclusions in the shells, the behavior of pellets of hydrolyzed "organic-free" gel was compared to that of unhydrolyzed gel pellets. The pellets of hydrolyzed gel fragmented extensively upon injection into the furnace, as indicated by the much smaller average diameter and wider size distribution of the product. In general, pellets from hydrolyzed gel did yield a product of lower carbon content, but were also of poorer uniformity, lower average diameter and wider size distribution.

Model Verification

Further experiments were necessary to verify the validity of the model since it is based on several simplifying assumptions. After all, the model calculated some optimistically short drop times and distances required to melt gel pellets. These calculations indicated that the heat transfer from the furnace was not yet the limiting fact factor in shell production, even though good shells larger than 500 μm are not easy to produce.

The verification experiments consisted of a series of furnace experiments wherein the heated zone of the furnace was varied in length. For the initial "zoned furnace" experiment, only the top unit of the six stacked units was run at the operating temperature of 1300°C (nominally). To maintain the shortest length of "hot" zone possible, the remaining units were idled at 900°C. The resulting furnace temperature profile is shown in Figure 3. With each succeeding pellet-shell experiment, an additional unit was brought to 1300°C, so that the length of the operating zone, and thus the particle residence time in the hot zone, could be controllably increased. These experiments showed that the shortest zoned temperature profile was sufficient to transform the pellet to a black, opaque but hollow spheroid. As shown in Figure 3, this profile consisted of an initial temperature gradient of only 7.1 cm, and a hot zone length with only 70.8 cm at or above 1000°C; the maximum

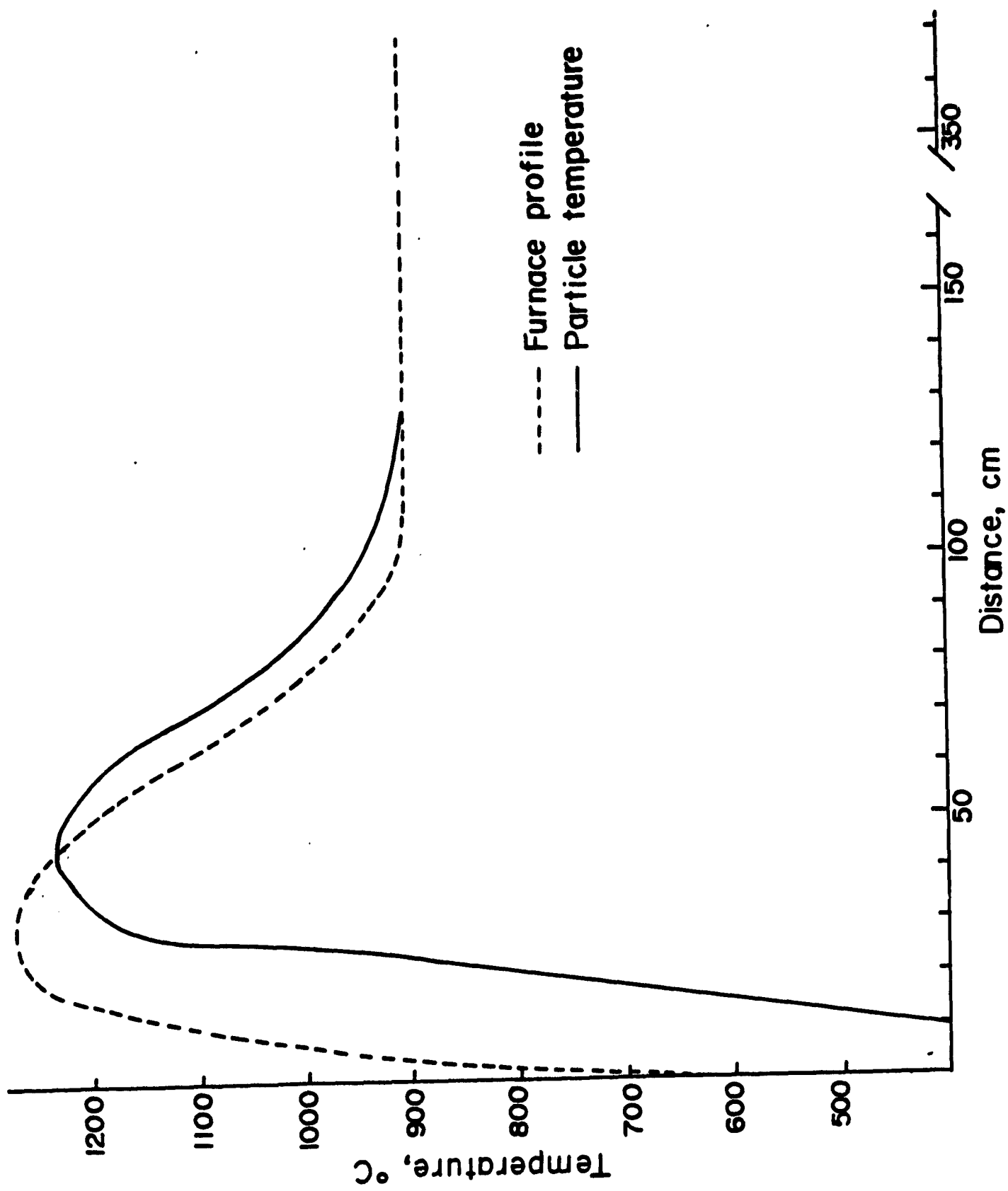


Figure 3. Zoned Furnace Experiment - Furnace Temperature Profile and Calculated Particle Temperature Profile.

addition, the gel-to-shell transformation, while not instantaneous, is completed fairly early in the blowing process. One furnace unit (with a 1250°C maximum) produced black, hollow spheroids that often had multiple rather than single voids. Two units, at 1300°C, produced good spheres with single voids and good uniformity, but much carbon inclusions in the walls. Additional furnace units, and consequently a longer residence time at temperature, yielded a reduction in the carbon levels in the glass, with only a slight increase in shell diameter. In fact, the shell diameter increased only 10%, from 360 μm to 407 μm , as the furnace zone length was increased from one to six units. These results imply that most of the spheridization and blowing of the pellets occurs very early, probably during the gel-glass transition state and not in the final glass state. From these results, it is evident that the heat transfer rate from the furnace to the pellet is not yet the limiting parameter for shell production.

Descriptions of Analytical Methods and Equipment

Mass Determination. The mass of gel pellets and shells was determined by weighing individuals rather than populations of known numbers. This permitted a statistical analysis of the pellet-shell transformation. Individual pellets and shells were handled with a vacuum chuck manipulator (Telvac Instrument Company, K-150) and

temperature was 1250°C. For this particular experiment, the GELSHEL code calculated a drop distance of only 25.5 cm for the pellet to reach a temperature of 1000°C. This calculated distance is comparable to the 18.9 cm calculated for a normal 1300°C furnace temperature profile (1300°C for 370 cm length). The fact that a hollow spheroid was formed in the above experiment is a verification of the validity of the model. The experiment showed that the pellet melted within a drop distance short enough that there was sufficient time at temperature for the spheroid to form. The calculated distances and the length of real temperature profile are in qualitative agreement.

These calculated results are further supported qualitatively by visual observations of pellet behavior upon injection into the furnace. A pellet will generally fall about 30-50 cm (1 foot) into the furnace before it is sufficiently incandescent to be seen easily. From hot stage microscopy observations, this indicates that a temperature of at least 1000-1100°C was reached.

Besides verifying the code calculations, these furnace experiments yielded further information. All of the particle mass loss occurred in the early portion of the thermal history, probably before the gel-glass transition. Regardless of the length of the hot zone, no significant differences in shell mass were observed; shells that experienced the shortest hot zone suffered as much mass loss as the shells from full-length furnace heating. In

weighed on a Cahn G-2 electrobalance. The electrobalance was calibrated with a 1 mg standard, significantly larger than the 10-20 μm weight of the samples. In this range, the error in accuracy was found to be less than 3-5%, determined by comparing the mass of a given shell population and the sum of the weights of individual shells in that population. The typical weighing error was \pm 3-5%, while the typical mass variations were \pm 5-10%.

Size. The diameter and length of the pellets and the outside diameter of shells, were determined by photomicrography, using a Vickers Photoplan microscope fitted with an optical standard supplied by American Optical Co. The maximum error in measurement was \pm 2%. The wall thickness of shells was determined for only one run, and was done by magnifying and measuring the wall image on an x-ray microradiograph.

Mass Loss. The mass lost by a gel particle during the shell-forming process was determined by thermogravimetric analysis (TGA) and the direct comparisons of pellet and shell masses. TGA analysis determined the mass loss between 20 and 1000°C, and was obtained with a Dupont 951 TGA module and a Dupont 990 Thermal Analyzer control unit.

Specific Heat. The average specific heat of gel was determined for powder and pellets using a Dupont Differential Scanning Calorimeter (DSC) controlled by the Dupont 990 control unit. Determinations were made in dry air over the range of 20-600°C.

Pellet Press. The gel powder was pelletized with a Pentronix Multipack No. 101 pellet press. The press produced pellets that were right circular cylinders. The length of these could be varied between 50 and 500 μm , but the diameter was fixed at a nominal 250 μm , the size of the aperture in the die plate of the press. For the current work, pellets nominally of 250 μm diameter, 250 μm length, and 15 μm mass have been made standardly. Volume variation was less than \pm 5%, and typically \pm 2%, while mass variation was typically \pm 5 to 10%.

Tower Furnace. Gel pellets were formed into shells by injection into a vertical Lindberg drop furnace (Figure 4). The furnace consists of six units stacked on top of each other, each unit with its own power control and three thermocouple temperature monitors. Updrafts and eddies in the furnace gas were minimized by an airtight seal at the bottom of the furnace, and an extension of the furnace liner beyond the heated zone at the top.

To maintain a dry air environment in the furnace the collection vessel was sealed to the bottom of the furnace tube. To generate a dry O_2 environment, a gas inlet collar was fabricated, sealed to the bottom of the furnace, and an oxygen flow was maintained at 5 l/min for 30 minutes to purge the furnace (21 liter volume) of air. Backflow at the top was minimized by covering the top of the furnace tube and venting the gas through a \sim 5 cm^2 vent in the cover.

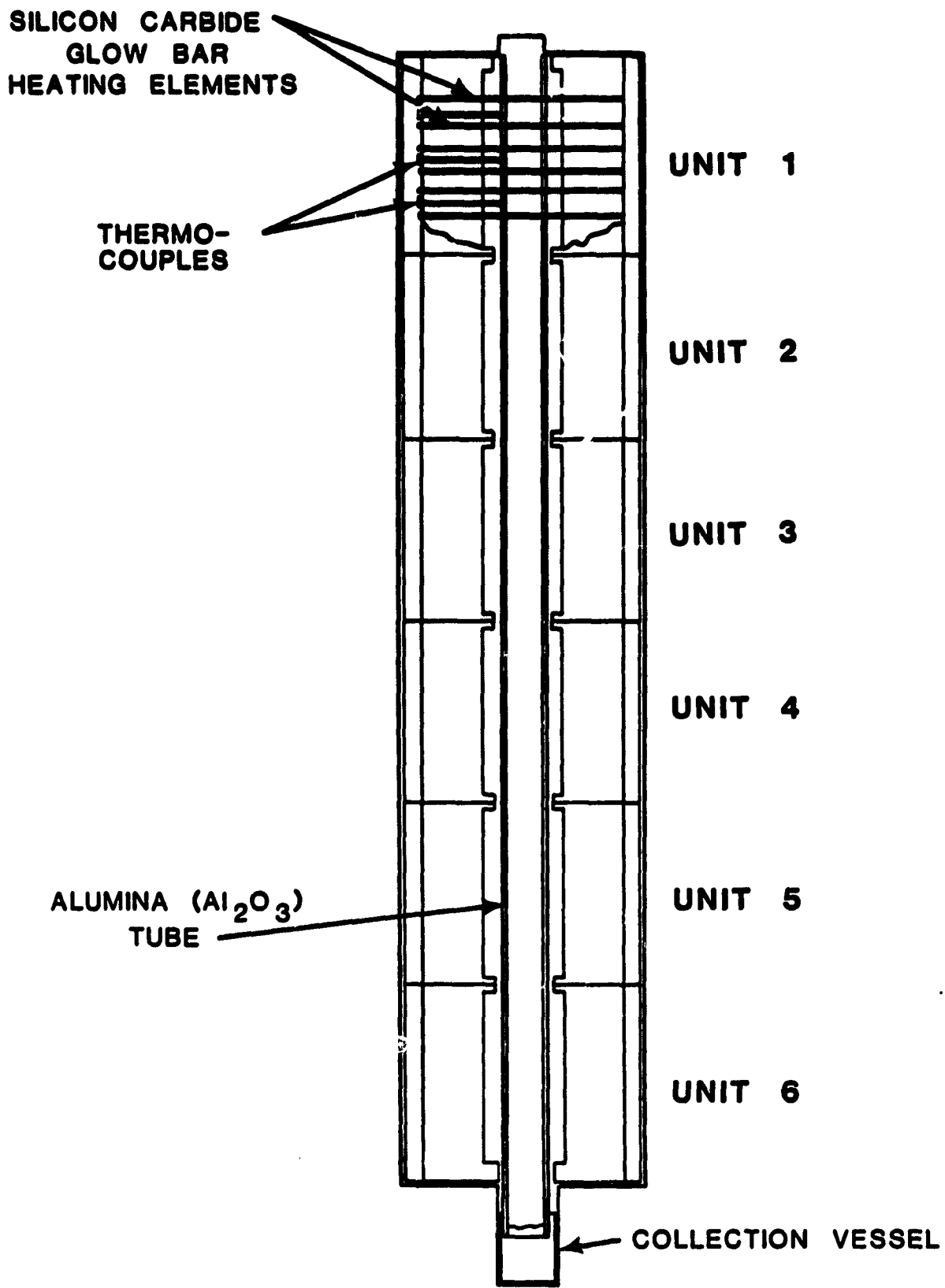


Figure 4. Schematic Diagram of the Drop Furnace

To generate a water vapor environment in the furnace, the furnace was hermetically sealed at the bottom, using a 1 liter beaker of boiling H₂O. The water was maintained at a vigorous boil for at least 10 minutes prior to a shell run, and during the whole run to ensure a water vapor environment. No means were available for assessing the concentration of H₂O in the furnace gas. The furnace temperature profile was obtained from the furnace thermocouples that measured the temperature of the furnace cavity and liner. These were calibrated against readings obtained with a thermocouple probe lowered to preset points in the furnace.

Conclusions

We have designed and developed a heat transfer model that describes the thermal history of a gel particle falling through the furnace. This model calculates that a very short drop time and distance is required to heat a gel particle to a melting temperature of 1000°C. These calculations specify a drop time and distance of 0.3 sec and 20 cm for a gel pellet that has a 267 μm diameter, 240 μm length and 17.6 μgm mass. The results of preliminary testing of the model agree with these calculations and support the validity of the model. The model code and computations have further determined that the parameters of greatest effect (on the particle heating rate) are gel particle mass, geometry and specific heat. Further

experiments addressing these parameters are planned for the next six-month period, and are necessary for full verification of the validity of the model.

As part of the empirical work fundamental to the development of the model and the empirical model verification, we have adapted and developed the method of pelletizing gel powder to form gel cylinders of uniform geometry and mass, as well as the analytical capabilities to measure these characteristics accurately.

As part of the model verification work, we have determined that the mass loss by the gel particle and the transformation of a gel particle to a glass shell occurs rather early and rapidly in the whole shell-blowing process. The particle spends the bulk of its residence time and travel distance in the furnace in the form of a glass shell; this time is necessary to reduce the carbon inclusions in the glass, but otherwise increases the shell diameter and quality only slightly. Thus heat transfer from the furnace to the pellet in current experiments is not a limiting factor in shell production.

Future Work

The work planned for the next six-month period consists primarily of the ground based experiments with levitation and heating of gels, conducted in conjunction with MSFC, and the further experiments with the heat transfer model. Our activities will primarily be involved

in ground based experiments at MSFC levitating gel and shells while heating. Preliminary experiments at MSFC look very promising and we will work closely with them to design some KC 135 flights. The proposed program plan is shown in Figure 5.

The planned modeling work consists primarily of empirical testing and refinement of the model. These activities include:

- 1) Detailed analysis of model simulation experiments already on hand
- 2) Accurate determination of the specific heat of gel pellets as a function of temperature, using the DSC, and incorporation of this data in the code.
- 3) Verification of the model predictions for gel particles of increasing mass (that is, determine and compare the real and calculated mass limits for the present furnace).
- 4) Verification of the model predictions for changes in gel particle dimensions (as mass is increased) comparing the effects of changing the length versus the diameter of a pellet for a given mass increase.
- 5) Verification of the model predictions for the effects of various furnace gases, such as helium, argon, CO₂, and possibly water vapor.

