MICROWAVE HEATING OF A FLOWING SLURRY

Mathematical models are constructed to investigate the use of microwaves to dissolve chemical crystals in a flowing solvent. The slurry is considered to be a Newtonian fluid in which the solvent is heated by microwaves. The solute crystals dissolve at a rate which depends strongly on temperature, and the dissolution has a profound effect on the viscosity of the slurry. Special consideration is given to crystal size and heating effects close to the walls containing the slurry.

A simplified version of the mathematical model is solved numerically, and the results lead to suggestions for improved design of the process. We also investigate the implications of non-Newtonian fluid models. The overall outcome of the work is a better understanding of the heat and mass transfer of the slurry, as well as recommendations on crystal size and design of the process.

1. Introduction

Kodak (Australasia) Pty Ltd is investigating a continuous process in which microwaves are used to heat a slurry consisting of chemical crystals in an organic solvent. The dissolved crystals form a solution which is then used in the manufacture of photographic products. At present, the crystals are dissolved in large tanks in a relatively slow batch process which is conducive to inter-batch variability.

Several features of the microwave process need to be taken into account. Firstly, the microwaves heat the solvent but not the crystals. The rate of dissolution of the crystals depends strongly on the temperature of the solvent. All the crystals need to be dissolved, so the slurry must remain in the microwave cavity for a sufficiently long time, although the slurry cannot be left too long in the microwave cavity since excessive heating causes degradation of the solution. Kodak therefore requested the Study Group to provide a better understanding of the microwave process, particularly of its heat and mass transfer and the effect of crystal size on the dissolution process. This improved understanding comes about through the development of mathematical models which incorporate known physical properties of the microwaves and the slurry. We also describe numerical and analytical solutions to the basic mathematical model, and we suggest how to incorporate modifications for non-Newtonian flow.

The proposed process is described in more detail in the next section. In Section 3, we then develop our basic mathematical model for heat and mass

transfer in the slurry as it passes through the microwave duct. The model is based on a Newtonian flow approximation with the viscosity of the slurry profoundly affected by the concentration of crystals. Dissolution of the crystals in the solvent requires a sub-model with strongly temperature-dependent solubility. The model is non-dimensionalised and we are then able to identify the important aspects and scales of the proposed process.

In Section 4, we describe the results of numerical computations on the model developed in Section 3. The numerical work forms the basis of a simulation model which could be used by Kodak to investigate design modifications to the proposed process. Section 5 contains comments on the significance of non-Newtonian flow effects in the proposed process.

The conclusions of the work are presented in Section 6. To highlight these:

- a mathematical model has been developed to describe the heat and mass transfer in the slurry as it passes through the microwave duct

- numerical methods can be used to investigate design improvements to the process

- the effect of crystal size is very important, and we recommend that Kodak use crystal particles less than 25 microns in radius

- slow flow near the walls of the tube leads to excessive heating and degradation of the mixture; this heat cannot be adequately removed by wall cooling

2. Details of the microwave process

The proposed process is illustrated in figure 1. At ambient temperature, the chemical slurry is a thick mixture of approximately equal portions by weight of solute crystals and solvent. The mixture, confined within a teflon tube which is transparent to microwaves, has the consistency of toothpaste when it enters the rectangular microwave guide. Microwave energy is predominantly absorbed by the solvent since the solute crystals are virtually transparent to the electromagnetic field. The rate of dissolution of the solute crystals increases rapidly as the solvent heats up. At the top of the duct, the temperature has reached about 150°C and dissolution of crystals is rapid; this produces a clear liquid which flows readily at Reynolds number of about 90. In fact, the viscosity of the mixture changes by nearly five orders of magnitude during the process so the Reynolds number at the inlet is very small. Further information on the rate

CYLINDRICAL
TEFLON INSERT

TEMPERATURE PROBE

RECTANGULAR WAVEGUIDE

MICROWAVE
ENERGY

HEATING ZONE

ELECTRIC FIELD
STANDING WAVE

EXPECTED SLURRY
FLOW PROFILE

DIRECTION OF SLURRY FLOW
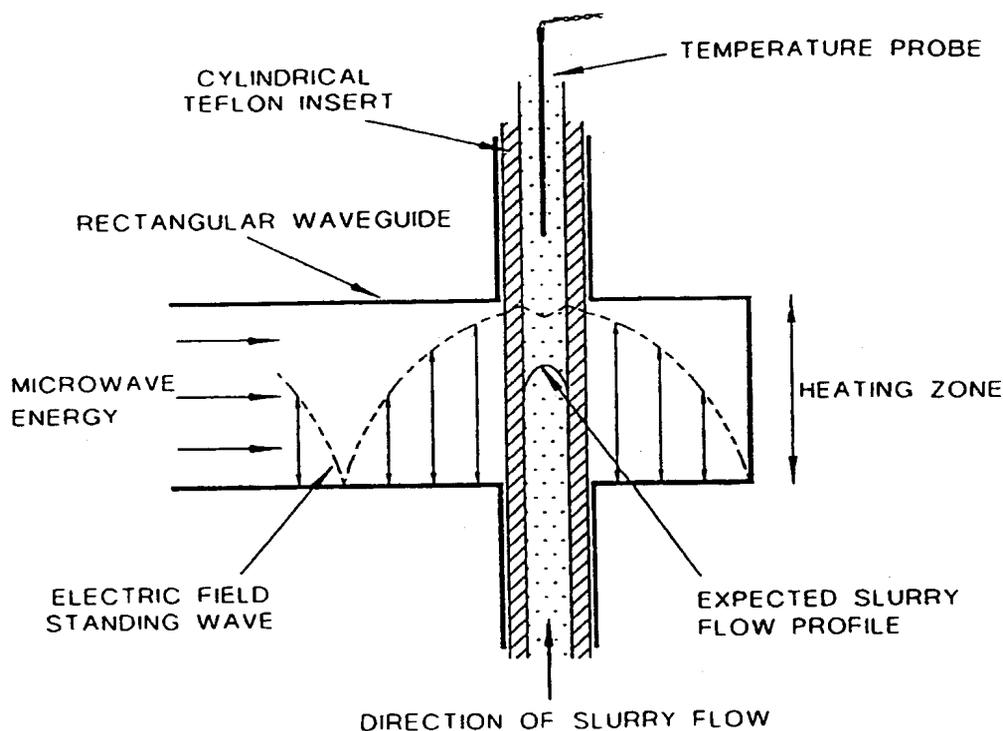
Figure 1: The microwave dissolution process of chemical slurries.

of dissolution of crystals and the viscosity of the solvent are given in the next section.

Control of the process is achieved by measuring the temperature of the mixture after it has passed through the microwave duct; if the temperature is too low, then greater microwave power is applied. To give an idea of the scales of the pilot process, the microwave duct is approximately 4.5 cm in height, the teflon tube is 6 mm in radius, and the heating and flow rate are such that the mixture passes through the vertical extent of the microwave guide in about 5 seconds. The cavity and microwave wavelength have been chosen so that the heating is approximately uniform in that part of the teflon tube in the duct.

The solute crystals at present have diameters generally distributed between 1 and 100 microns, although some crystals are as large as 1000 microns diameter. The most common crystal diameter is 20 microns. Big crystals take longer to dissolve than small crystals, and so a rate-limiting step is the time taken for all crystals to dissolve. This point is explored in detail in Section 3. The other

major complication is that the slurry in the teflon tube flows much more slowly close to the walls than in the middle. This means that greater heating of the slurry takes place near the walls. Unfortunately, too much heating will degrade the mixture, and so the heat transfer needs to be considered in detail.

3. The mathematical model and its non-dimensionalisation

After considerable discussion, the Group decided the most reasonable model to start with was steady, axisymmetric flow of an incompressible Newtonian fluid. The microwave heating causes uniform volumetric heating throughout the flow domain.

The viscosity of the fluid needs special consideration in that it varies throughout the flow domain with temperature, strain rate and with the concentration of solute crystals. The experimental evidence provided by Kodak suggested however that the dominant cause of variation in the viscosity was the solute concentration. Kodak's data suggest the empirical expression

$$\mu = 0.005 \times \exp(17.2 C^1) \text{ Pa.s} \tag{1}$$

where C^1 is the mass fraction of undissolved solute.

The mass fraction varies between about 0.5 at inlet and zero at outlet. Thus the viscosity can vary by a factor of more than 5000 throughout the flow domain. This exceptionally rapid variation indicates that we need a sub-model to account for solute concentration. In (7–8) below, we see that solute concentration is affected by the rate of solute dissolution which is, in turn, strongly temperature dependent. These rapid variations mean that zones of rapid changes should be expected in the flow solution; this will also cause difficulty in developing numerical methods to solve the model equations.

The equations for continuity, momentum and heat conservation in steady flow can thus be written

$$\nabla.\mathbf{u} = 0 \tag{2}$$

$$\rho\mathbf{u}.\nabla\mathbf{u} = -\nabla p + \nabla.\left(\mu(\nabla\mathbf{u} + \nabla\mathbf{u}^{\mathrm{T}})\right) \tag{3}$$

$$\rho C_p\mathbf{u}.\nabla T = k\nabla^2 T + Q \tag{4}$$

where $\mathbf{u}$ is the fluid velocity, ρ the density of the slurry, p the pressure, C_p the heat capacity, T the temperature, k the thermal diffusivity and Q the volumetric heating due to microwaves. In (3), $\nabla\mathbf{u}^{\mathrm{T}}$ denotes the transpose of $\nabla\mathbf{u}$.

The boundary conditions on $\mathbf{u}$ and T are straightforward. At the inlet, $\mathbf{u}$ and T are prescribed. For the numerical work in Section 4, $\mathbf{u}(r)$ was taken to

be a parabolic profile and T was a constant value (T_o). At the outlet, there will be zero stress and zero streamwise temperature gradient. At the walls of the teflon tube, $\mathbf{u}$ is zero and either $\partial T/\partial n = 0$ (for an insulating tube) or $\partial T/\partial n = H(T - T_w)$ (if wall cooling takes place).

We now develop a sub-model for solute concentration. Although the solute crystals have a range of sizes, many of them have a diameter of approximately 20 microns. We therefore make the simplifying assumption that all particles initially have the same radius R_0. The average concentration C of dissolved solute, equivalently the volume fraction of solute in liquid phase on a macro scale, can be written

$$ C = \frac{4}{3}\pi n_0 \left(R_0^3 - R^3 \right) \quad \text{[dimensionless]} \tag{5} $$

in which R_0 is the initial particle radius and n_0 is the initial number of particles per unit volume.

The solute particle size R is thus given by the equation

$$ \mathbf{u}.\nabla R = -f(T, C) \tag{6} $$

in which the function $f(T, C)$ is determined by considering the rate of dissolution of solute crystals into the solvent. On a microscopic scale (considering each solute particle to be contained by a bath of solvent), the local concentration S of solute in solvent satisfies an equation of the form

$$ \frac{\partial S}{\partial t} + \mathbf{q}.\nabla S = D\nabla^2 S $$

where $\mathbf{q}$ is the fluid velocity on a microscopic scale (*i.e.* driven by concentration gradients) and D the diffusivity of solute in solvent. Now the terms on the LHS are of $O(UR_0^2/DL)$ compared to the diffusion terms on the RHS. Here L, a typical length scale, is taken to be the height of the microwave duct, and U is the average flow velocity. If we use the values $U/L = 0.22$ s^{-1}, $D = 1.2 \times 10^{-10}$ m^{2}s^{-1} and $R_0 = 10^{-5}$ m, we find the LHS is about 1/5 of the RHS. We thus omit the terms on the LHS, which is equivalent to assuming the dissolution process is locally steady and driven by molecular diffusion alone; this leaves

$$ \nabla^2 S = 0. \tag{7} $$

The boundary condition at the surface of the crystal particle is that the solubility is strongly temperature dependent, that is

$$ S = S_0 \times \exp\left(a(T - T_0)\right) \tag{8} $$

in which data provided by Kodak suggests values of

$$S_0 = 0.53 \text{ weight percent}, \quad a = 0.0375 \,{}^{\circ}\text{C}^{-1}, \quad T_0 = 25 \,{}^{\circ}\text{C}.$$

Equation (7) needs another boundary condition to express the solute concentration far from each particle. Here we say that the dissolved solute in $r < r_s$ where $r_s^3 = 3/(4\pi n_0)$ comes from the particle under consideration. This gives

$$\int_R^{r_s} 4\pi\, r^2 S\, dr = \frac{4}{3}\pi(R_0^3 - R^3). \tag{9}$$

To complete the model, we observe that the function $f(T, C)$ in (6) is given by

$$f(T, C) = -D\left.\frac{\partial S}{\partial \xi}\right|_{\xi=R}. \tag{10}$$

Non-dimensionalisation

It is useful to non-dimensionalise the above equations in order to gain insight into the essential elements of the process and to facilitate further analytical and numerical work. Let L be the height of the microwave zone, U the mean velocity of the slurry, a suffix 0 denote conditions at inlet and a suffix L denote conditions at outlet. By conservation of heat, we see that

$$\overline{T}_L = T_0 + \frac{QL}{\rho C_p U} \tag{11}$$

where an overbar denotes the cross-sectional mean. We introduce non-dimensional quantities designated by dashes as follows:

$$(z, r) = L\left(z', r'\right); \quad (u, v) = U\left(u', v'\right); \quad t = Lt'/U$$

$$T' = \frac{T - T_0}{\overline{T}_L - T_0}; \quad p = p_0 + \frac{\mu_0 U}{L}p'$$

$$R = R_0 R'; \quad (C, S) = \frac{4}{3}\pi n_0 R_0^3 \left(C', S'\right); \quad \mu = \mu_0 \mu'.$$

Equations (2–4,6) therefore take the dimensionless form (in which the dashes are now omitted):

$$\nabla.\mathbf{u} = 0 \tag{12}$$

$$Re\ \mathbf{u}.\nabla\mathbf{u} = -\nabla p + \nabla.\left(\mu(\nabla\mathbf{u} + \nabla\mathbf{u}^{\mathrm{T}})\right) \tag{13}$$

$$\mathbf{u}.\nabla T = \delta\nabla^2 T + 1 \tag{14}$$

$$\mathbf{u}.\nabla R = \gamma\left.\frac{\partial S}{\partial \xi}\right|_{\xi=R^*/R}. \tag{15}$$

Re is the Reynolds number and R^* now denotes the dimensional radius of the crystals. The boundary conditions are as in Section 3.

Representative values of the various constants are as follows:

$\rho = 10^3 \, \text{kg.m}^{-3}$, $U = 10^{-2} \, \text{ms}^{-1}$, $L = 0.045$ m, $\mu_0 = 25$ Pa.s, $R_0 = 20 \times 10^{-6}$ m, $n_0 = 1.5 \times 10^{13} \, \text{m}^{-3}$, $k = 0.17 \, \text{Wm}^{-1 \circ}\text{C}^{-1}$, $C_p = 1.97 \times 10^3 \, \text{Jkg}^{-1 \circ}\text{C}^{-1}$, $D = 1.2 \times 10^{-10} \, \text{m}^2\text{s}^{-1}$.

In (12–15) the various dimensionless constants and their approximate numerical values are as follows

Re	$\rho U L / \mu_0$	0.018 at inlet
α	$\frac{4}{3}\pi n_0 R_0^3$	0.5
δ	$k/(\rho C_p L U)$	1.9×10^{-4}
γ	$D\alpha L/(U R_0^2)$	0.675

Equations (12–15) describe the basic model. The non-linear inertial terms in (13), characterised by the Reynolds number Re, are negligible at the inlet but might be significant near the outlet. The constant δ in (14) is small, which shows that the temperature is strongly dominated by volumetric heating rather than diffusion. We note that the crystal radius is given implicitly by the sub-model comprised of (7–9). The solution of (7) is

$$S(\xi) = A + \frac{B}{\xi} \qquad (16)$$

where A and B are found by applying conditions (8,9). If the temperature is known through (14), then (16) applied at the crystal radius as in (8) gives an implicit definition of the crystal radius at that point. The concentration C then follows from (5) and the viscosity from (1).

Effect of crystal size

In general, the model equations above require a numerical solution. It is possible however to draw immediate conclusions about the size of the crystals. Crystal dissolution is dominated by a diffusion process. The radius R_0 of the initial crystals should therefore be less than the length scale associated with diffusion, namely $(DL/U)^{1/2}$. For $D = 1.2 \times 10^{-10} \, \text{m}^2\text{s}^{-1}$ and $L/U = 5$ s, then $R_0 < 25\mu$. Other processes such as rolling, shear and physical degradation of the crystals might slightly extend this upper bound of crystal size, but we believe large crystals will never dissolve in the teflon tube during the time (approximately 5 seconds) that the slurry is exposed to microwaves. *We recommend that Kodak ensure that the crystal size be tightly controlled.*

4. Numerical results

Equations (12–14) were solved numerically in order to gain insight into the microwave heating process. The numerical model differed slightly from the equations presented in the previous section by virtue of the treatment of viscosity. In effect, the previous section established a link between temperature, crystal radius, concentration and then viscosity. For numerical purposes, it is equivalent to assume a direct empirical relationship such as

$$\mu(T) \;=\; \mu_0 e^{-\beta(T-T_0)} \tag{17}$$

between temperature and viscosity.

The computer package used for the numerical modelling was *Fastflo*. *Fastflo* was developed by CSIRO Division of Mathematics and Statistics; it is finite element-based and has the capability to deal with a range of element types on structured and unstructured meshes. It has sophisticated solvers for Computational Fluid Dynamics (CFD).

Within *Fastflo*, an Augmented Lagrangian scheme was set up to solve (12–14). The viscosity μ was set to be an exponential function of temperature as in (17), so that the system was fully coupled. An almost Newton-Raphson scheme was used (with some unimportant variations omitted from the Jacobian) to approach a converged solution.

The main numerical difficulty turned out to be the large viscosity variation. This leads to an unpredictable change in the spatial scales over which change occurs, and this cannot be anticipated with any reasonable meshing scheme. The inbuilt triangular mesh generator of *Fastflo* was used, which did enable concentration about some critical outlet points.

The computations were loaded according to the coefficient β in the viscosity relation (17), with suffix 0 denoting ambient temperature. That is to say, a solution was obtained for small β, and this was used as the starting point for a larger β, until convergence could no longer be achieved. Convergence failure generally happened when the ratio of maximum to minimum viscosity was in the range of 20–50, so the observed variations of several orders of magnitude could not be modelled.

This may not be important; the driving force for the flow is the applied pressure, and by the time the viscosity has reduced by a factor of 20 or so, there is very little pressure gradient remaining. So although large velocity gradients are possible and would occur in response to applied forces, there is not much applied force. To put it another way, almost all the energy is dissipated in the regime where the numerical solution is valid.
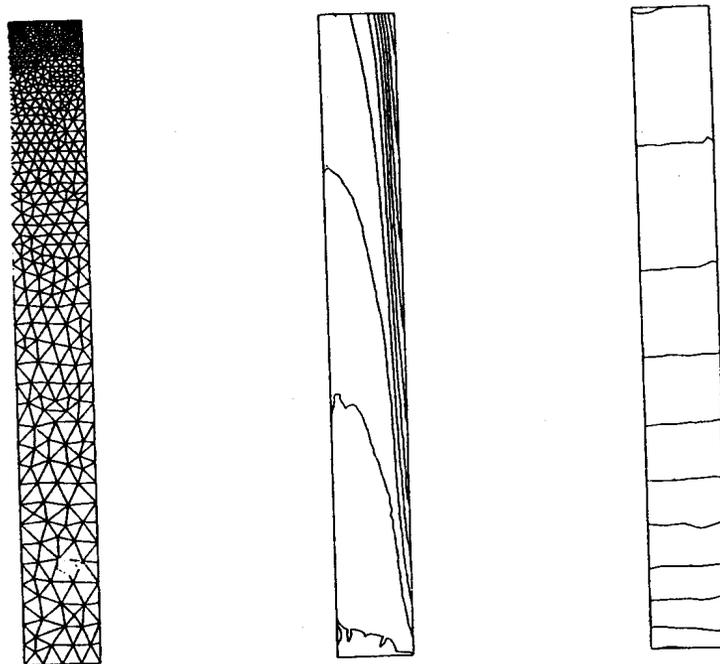
Figure 2: Computed results for microwave heating in an insulated tube. Left: the computational mesh; middle: temperature contours; right: pressure contours, shown for the half-tube.

A typical mesh for the suggested experimental configuration is shown in figure 2; there are 1881 nodes and 822 six-node triangular elements. With a reasonable loading sequence, a complete set of computations was done in about half an hour on a DEC alpha workstation.

Figure 2 also shows computed temperature contours for strong microwave heating in a microwave cavity 4.5 cm in length with an insulating boundary condition at the walls of the teflon tube. As mentioned above, it was not possible to achieve the wide range of viscosity that would take place in the industrial apparatus. Thus the results presented in this section have approximately a 30 fold variation in viscosity rather than the 5000 fold variation that would be experienced *in situ*.

The temperature contours in figure 2 would not be acceptable in practice because the mixture in the middle of the tube has not been sufficiently heated, whilst the mixture close to the edge of the tube has been heated as much as is possible without degradation taking place. Initially the Group thought that better results could be obtained by a judicious mixture of wall cooling and

stronger microwave heating. Thus the wall boundary condition was changed to $\partial T/\partial n = H(T - T_w)$. Here, H denotes a heat transfer coefficient to describe the flow of heat through the 1 mm thick teflon tube, and T_w denotes the temperature at the outside edge of the tube. Even when T_w was set to be $-190^{\circ}C$, the temperature of liquid nitrogen, the temperature contours do not look significantly different from those in figure 2. *The teflon tube does not allow sufficient heat transfer to take place even if the outside wall of the tube is maintained at very low temperatures.* It is difficult to replace the teflon tube with one giving better heat conduction because the tube material has to be transparent to microwaves, strong and chemically resistant.
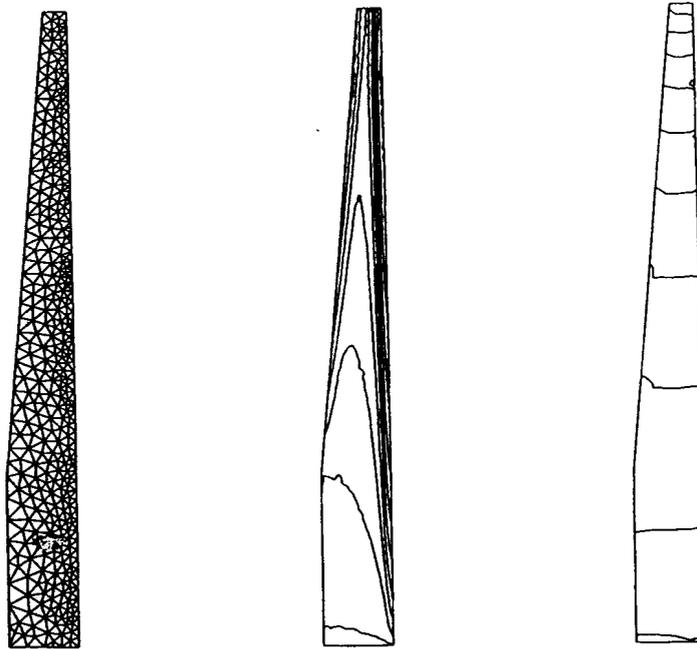
Figure 3: Computed results in a tube with a conical obstruction. Other details as in figure 2.

In view of the ineffectiveness of wall cooling, the Group then examined what would happen if island obstructions were placed in the teflon tube. A promising configuration is shown in figure 3 in which there is a conical island obstructing a significant part of the tube. The results are for insulated walls and the same heating conditions as figure 2. The conical obstruction, with a non-slip boundary condition on the flow, creates another region of slow flow in which high temperatures are reached. Also the mixture now has to pass through a relatively narrow annulus, and the exit temperature is more uniform and higher

than in figure 2. Even so, it is unlikely that one simple modification to the flow, as in figure 3, would be sufficient to produce sufficiently high and uniform temperatures as required for industrial application.

We feel that the numerical simulations can be used to design a better process in which microwave heating would produce uniformly high heating without degradation of the mixture at the walls due to excessive heating. Some options are described in Section 6.

5. Non-Newtonian flow

The region in which non-Newtonian effects are likely to be most important is the flow in the tube upstream of the waveguide. Evidence was presented by Kodak to suggest that the viscosity μ of cold slurry (in the "toothpaste" régime) was shear-thinning, *i.e.* μ is a decreasing function of shear rate. Suppose we have flow along a cylindrical pipe of radius a in which pressure depends only on distance z along the pipe, and all other variables are functions of r only, where (r, z) are cylindrical polar coordinates. Then in any cylinder coaxial with the pipe but inside it the viscous shear stress around the circumference must balance the pressure gradient in steady flow, so that

$$\pi r^2 \frac{\partial p}{\partial z} = 2\pi r \mu \frac{\partial v}{\partial r} \tag{18}$$

where μ is a function of $|\partial v/\partial r|$. Bird *et al.* (1960) treat problems of this kind. Equation (18) implies that

$$\frac{\mu}{r} \frac{\partial v}{\partial r} = \text{const} = \frac{1}{2} \frac{\partial p}{\partial z} = -c, \text{ say,} \tag{19}$$

so that we may write μ in terms of r and get

$$\frac{\partial v}{\partial r} = -\frac{cr}{\mu(r)} \tag{20}$$

and

$$v(r) = c \int_r^a \frac{r'}{\mu(r')} \, dr' \tag{21}$$

because $v = 0$ at $r = a$. The maximum value of v is $v_m = c \int_0^a r/\mu(r) \, dr$, and the volume flux Q along the pipe is $\int_0^a 2\pi r v(r) dr$, and so

$$Q = \pi c \int_0^a \frac{r^3}{\mu(r)} \, dr \tag{22}$$

after an integration by parts. There is some support from Kodak's data for the idea that their slurry is an Ostwald-de Waele power-law fluid (Bird *et al.*, 1960)

in which $\mu = m|\partial v/\partial r|^{n-1}$ where m, n are constants with n about 1.15 to 1.5, and so (20) gives

$$\mu = m \left(\frac{cr}{m}\right)^{1-1/n} \tag{23}$$

and

$$v = \left(\frac{c}{m}\right)^{1/n} (a^{1+1/n} - r^{1+1/n}). \tag{24}$$

Equation (24) can now be used as the upstream boundary condition for the heated region, in which variations of μ due to temperature and porosity dominate those due to non-Newtonian effects.

6. Conclusions

As a result of work on this topic, the Group developed a mathematical model to describe the heat and mass transfer in the mixture as it passes through the microwave duct. The mathematical model shows that it is important for Kodak to ensure that the solute particles be not too big. An upper limit of 25 microns radius is recommended.

The mathematical model was solved for a limited viscosity range using the CFD package *Fastflo*. This gave useful results on the temperature reached by the mixture, and it pointed out that excessive heating near to the wall is a problem which is not fixed at all by wall cooling and only partially fixed by placing obstructions in the flow.

The major challenge to be addressed is to obtain uniform heating of the mixture and to improve the numerical procedures. There are several promising lines of investigation:

- To investigate slower heating inside a much longer tube. Under these circumstances, cross sectional heat diffusion will play a role (as in the familiar Taylor (1953) shear dispersion theory) and we expect that a more uniform heat distribution will be obtained.

- To investigate slower heating in a series of passes through microwave cavities with some form of mixing to enable better heat transfer to take place. The mixing could be either active (*e.g.* stirring) or by flow through bends and obstructions.

- There is also a need for improved numerical work so as to capture the rapid viscosity changes that are expected to take place. Additional analytical

work on the thin transition regions is needed; matched asymptotic expansions may be useful here. We need to be able represent viscosity changes over more than 3 orders of magnitude, and, given that no obvious analytic approximations have been found, the only alternatives are adaptive meshing and large computations with very fine meshes.

Acknowledgements

References

W.B. Bird, W.E. Stewart, and E.N. Lightfoot, *Transport phenomena*, (Wiley, NY, 1960).

G.I Taylor, "Dispersion of soluble matter in solvent flowing slowly through a tube", *Proc. Roy. Soc.* A **219** (1953), 186–203.