

## NUMERICAL SOLUTION OF THE PROBLEM OF DIFFUSION OF A LOW-MOLECULAR WEIGHT SUBSTANCE IN A POLYMER MATERIAL WITH A MOVING PHASE BOUNDARY

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*A numerical solution of the problem of extraction of a low-molecular-weight solvent from a spherical polymer product with allowance for shrinkage is suggested. The solution is based on passage from a variable region to a fixed one using a difference scheme of a special form developed for the convective-diffusion equation in which the convection and diffusion terms vanish with time.*

Problems of heat and mass transfer in bodies with movable phase boundaries are among the most difficult ones. In solving the problems it is necessary to determine a function of the position of the phase boundaries along with a function of the concentration of the desired component. These functions are determined by a system of nonlinear differential equations. Since in this case the use of exact methods encounters difficulties, in solving practical problems with a movable phase boundary numerical methods are used.

A number of works are devoted to numerical methods of solving Stefan problems. Implicit difference methods with front capture at a grid node and with fractional steps of the fronts of an "extending grid" are a matter of sufficiently complete investigation [1].

In conformity with practical needs, in the majority of cases it is necessary to single out explicitly the moving boundaries. However, not every numerical method allows one to do this. For instance, algorithms based on an enthalpy formulation or "front smearing," determining the temperature field satisfactorily, give only a rough estimate of the position of the phase front. Voluminous literature, a brief survey of which is given, e.g., in [2], is devoted to methods with explicit singling-out of fronts. In developing this approach, recently several different versions of the method of finite elements with deformable calculation grids have been suggested for solution of problems in regions with unsteady boundaries. A common drawback of both these and previously suggested finite-difference methods is the fact that different numerical schemes describe heat and mass transfer inside a one-phase region and the law of front motion, with the order of accuracy of the latter schemes (in the vicinity of the front) being, as a rule, lower than that of the former. Along with the deterioration of the accuracy the heterogeneity of the calculation schemes results in complication of the algorithm of solution.

We suggest a numerical solution of the problem of solvent extraction from polymer particles in an aqueous medium involving solvent distillation out of the system. A special feature of the combined process under consideration is a simultaneous change in the composition of the interacting phases, their volumes, and the structure of the polymer material.

For systems with polymer particles the kinetics of mass exchange is determined by intradiffusional transfer. Here, concentration fields of low-molecular-weight components (solvents, moisture) with rather large gradients in the surface layer are observed in the particles.

The mathematical model of solvent extraction out of spherical polymer particles with allowance for their shrinkage can be written as [3]

$$\frac{\partial C_2}{\partial \tau} = -\frac{\partial}{r^2 \partial r} \left[ r^2 \left( C_2 v - D \frac{\partial C_2}{\partial r} \right) \right], \quad 0 < r < R(\tau); \quad (1)$$

$$D = D_0 C_2^k, \quad (2)$$

$$v(r, \tau) = \frac{dr}{d\tau} = \frac{1}{\bar{C}_2(r, \tau)} \left[ \left( D \frac{\partial C_2}{\partial r} \right) \Big|_{r=R(\tau)} - \frac{r d\bar{C}_2(r, \tau)}{3 d\tau} \right]; \quad (3)$$

$$\bar{C}_2(r, \tau) = \frac{1}{\frac{4}{3} \pi r^3(\tau)} \int_0^r C_2(r, \tau) 4\pi r^2 dr; \quad (4)$$

$$\frac{\partial C_2}{\partial r} \Big|_{r=0} = 0, \quad \left( D \frac{\partial C_2}{\partial r} \right) \Big|_{r=R(\tau)} = -\beta (C_1^* - C_1), \quad \tau > 0; \quad (5)$$

$$C_2(r, 0) = C_{2,0}(r), \quad 0 \leq r \leq R(0), \quad (6)$$

where  $C_2$  is the solvent concentration inside a particle at a distance  $r$  from its center at the instant  $\tau$ ,  $\text{kg}/\text{m}^3$ ;  $C_1$  is the solvent concentration in the liquid phase at the instant  $\tau$ ,  $\text{kg}/\text{m}^3$ ;  $D$  is the effective diffusion coefficient,  $\text{m}^2/\text{sec}$ ;  $D_0$  and  $k$  are constants;  $\beta$  is the mass-transfer coefficient,  $\text{kg}/(\text{m}^2 \cdot \text{sec})$ ;  $v$  is the velocity of particle shrinkage,  $\text{m}/\text{sec}$ ;  $R$  is the radius of the surface layer of the particle,  $\text{m}$ .

The first relation of the system differs from the ordinary diffusion equation in the term constituting the velocity of particle shrinkage, which is calculated by formula (3) obtained in [3]. The boundary condition on the particle surface relates the mathematical model of the process pertaining to a particle of the disperse phase to the description of the process of solvent extraction in the disperse phase as a whole.

A distinctive feature of the model is the presence of a movable boundary, which requires special methods of solution. The numerical solution suggested is based on passage from a variable region to a fixed one [4] and the use of a difference scheme of a special form.

The transition to the fixed region can be accomplished by means of the transformation  $x = r/R(\tau)$ ,  $C_2(r, \tau) = C_2(xR, \tau) \equiv C(x, \tau)$ ,  $0 \leq x \leq 1$ .

With regard for the rules of differentiation of a composite function the diffusion equation for the new function  $C(x, \tau)$  acquires the form

$$\frac{\partial C}{\partial \tau} = \frac{x}{R} \frac{dR}{d\tau} \frac{\partial C}{\partial x} - \frac{1}{Rx^2} \frac{\partial}{\partial x} \left( x^2 \left( Cv - \frac{D}{R} \frac{\partial C}{\partial x} \right) \right).$$

After transformation and reduction of like terms we arrive at the relation

$$\frac{\partial C}{\partial \tau} = \frac{1}{Rx^2} \frac{\partial}{\partial x} \left( x^2 \left( C \left( v - x \frac{dR}{d\tau} \right) - \frac{D}{R} \frac{\partial C}{\partial x} \right) \right) - \frac{3}{R} \frac{\partial R}{\partial \tau} C.$$

Similarly, we pass to the new variable  $x$  in the formula for the shrinkage velocity:

$$v(x, \tau) = \frac{1}{\bar{C}(x, R(\tau))} \left[ \left( \frac{D \partial C}{R \partial x} \right) - \frac{xR d\bar{C}(x, R(\tau))}{3 d\tau} \right].$$

Thus, the system becomes

$$\frac{\partial C}{\partial \tau} = \frac{1}{R x^2} \frac{\partial}{\partial x} \left[ x^2 \left( a \frac{\partial C}{\partial x} + b C \right) \right] + f, \quad 0 < x < 1, \quad \tau > 0, \quad a = \frac{D}{R} \left( 1 - \frac{C}{\bar{C}} \right), \quad b = - \left( W - x \frac{dR}{d\tau} \right),$$

$$f = - \frac{3}{R} \frac{dR}{d\tau} C, \quad W = - \frac{xR}{3\bar{C}(x, \tau)} \frac{d\bar{C}(x, \tau)}{d\tau}, \quad \frac{dR}{d\tau} = \frac{1}{\bar{C}(1, \tau)} \left[ \left( \frac{D\partial C}{R\partial x} \right)_{x=1} - \frac{Rd\bar{C}(1, \tau)}{3d\tau} \right], \quad (7)$$

$$D = D_0 C^k, \quad R(0) = R_0, \quad \bar{C} = (x, \tau) = \frac{1}{x^3 R^3(\tau)} \int_0^{xR} C(r, \tau) r^2 dr,$$

$$\left( \frac{D\partial C}{R\partial x} \right)_{x=1} = -\tilde{\beta}(\tau), \quad \tau > 0, \quad \tilde{\beta}(\tau) = \beta(C_1^* - \bar{C}_1),$$

$$\left[ a \frac{\partial C}{\partial x} + b C \right]_{x=0} = 0, \quad C(x, 0) = C_0(x), \quad 0 \leq x \leq 1.$$

As a consequence of passing from the variable to the fixed region, the diffusion equation in system (7) becomes more complicated: the additional term  $f$  appears in its right-hand side and the diffusion and convection terms of the equation are more complicated as well. Since the convection and diffusion terms vanish with time, it is necessary to use a difference scheme of a special type that ensures stable calculations.

The scheme is constructed on a grid that is uniform along the space coordinate  $\bar{W}_h = \{x_i = ih, i = \overline{1, N+1}, (N+1)h = 1\}$  and nonuniform along the time coordinate  $\bar{W}_\tau = \{\Delta\tau^{j+1} = \tau^{j+1} - \tau^j\}, j = \overline{1, M}$ .

The system of equations in finite-difference form is written as

$$\frac{C_i^{j+1} - C_i^j}{\Delta\tau^{j+1}} = \frac{1}{R^{j+1} h \bar{x}_i^2} \left\{ \hat{x}_i^2 \left[ \frac{1}{2h} (d_i^j + d_{i+1}^j) (C_{i+1}^{j+1} - C_i^{j+1}) + \left( \frac{1}{2} + \alpha_{+,i+1} \right) b_{i+1}^j C_{i+1}^{j+1} + \right. \right.$$

$$\left. + \left( \frac{1}{2} - \alpha_{+,i} \right) b_i^j C_i^{j+1} \right] - \hat{x}_{i-1}^2 \left[ \frac{1}{2h} (d_{i-1}^j + d_i^j) (C_i^{j+1} - C_{i-1}^{j+1}) + \left( \frac{1}{2} + \alpha_{+,i} \right) b_i^j C_i^{j+1} + \right.$$

$$\left. + \left( \frac{1}{2} - \alpha_{+,i-1} \right) b_{i-1}^j C_{i-1}^{j+1} \right] \right\} - \max(0, -\alpha_{-,i}) f_{i-1}^{j+1} - (1 - \max(0, -\alpha_{-,i}) - \max(0, -\alpha_{+,i})) f_i^{j+1} -$$

$$- \max(0, -\alpha_{+,i}) f_{i+1}^{j+1}, \quad 1 \leq i \leq N, \quad 0 \leq j \leq M, \quad C_i^j = C_{i,0}, \quad 1 \leq i \leq N+1,$$

$$\frac{D_{N+1}^{j+1} C_i^{j+1} - C_i^j}{R^{j+1} h} = -\tilde{\beta}^{j+1}, \quad D_i^j = D_0 (C_i^j)^k, \quad (8)$$

$$\frac{R^{j+1} - R^j}{\Delta\tau^{j+1}} = \frac{1}{\bar{C}_{N+1}^j} \left[ -\tilde{\beta}^{j+1} - \frac{R^{j+1} (\bar{C}_{N+1}^j - \bar{C}_{N+1}^{j-1})}{\Delta\tau^{j+1}} \right], \quad 1 \leq j \leq M,$$

$$d_i^j = \frac{D_i^j}{R^j} \left( 1 - \frac{C_i^j}{\bar{C}_i^j} \right), \quad f_i^{j+1} = - \frac{3}{R^{j+1}} \frac{R^{j+1} - R^j}{\Delta\tau^{j+1}} C_i^{j+1},$$

$$b_i^j = x_i \left( \frac{R^j}{3\bar{C}_i^j} \frac{C_{i+1}^{j+1} - C_i^{j+1}}{\Delta\tau^j} + \frac{R^{j+1} - R^j}{\Delta\tau^{j+1}} \right).$$

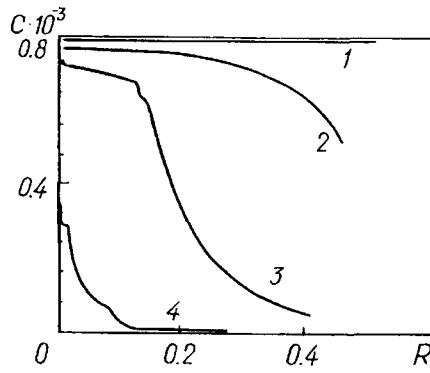


Fig. 1. Profile of the solvent concentration in a particle as a function of time ( $D_0 = 10^{-11}$ ;  $k = 2.5$ ;  $\bar{C}_0 = 792 \text{ kg/m}^3$ ): 1)  $\tau = 0$ ;  $R = 5 \cdot 10^{-4} \text{ m}$ ;  $C = 792 \text{ kg/m}^3$ ; 2) 26 min;  $4.58 \cdot 10^{-4}$ ; 663; 3) 54;  $4.1 \cdot 10^{-4}$ ; 159; 4) 157;  $2.67 \cdot 10^{-4}$ ; 10.  $R$ , mm;  $C$ ,  $\text{kg/m}^3$ .

To improve the accuracy and stability of the difference scheme, we introduced the following quantities:

$$d_+^{j+1} = \frac{1}{2} (d_i^{j+1} + d_{i+1}^{j+1}), \quad d_-^{j+1} = \frac{1}{2} (d_i^{j+1} + d_{i-1}^{j+1}), \quad q_{+,i} = \frac{hb_i}{2a_+}, \quad q_{-,i} = \frac{hb_i}{2a_-},$$

$$\alpha_{+,i} = \alpha(q_{+,i}), \quad \alpha_{-,i} = \alpha(q_{-,i}), \quad \alpha(q) = \frac{\rho(q) - 1}{2q}, \quad \rho(q) = \frac{3 + 3|q| + 3q^2 + 2|q|^3}{3 + 3|q| + 2q^2},$$

$$\alpha_{+i} = \frac{1}{2} (\alpha_{+,i+1} + \alpha_{+,i}), \quad \alpha_{-i} = \frac{1}{2} (\alpha_{-,i-1} + \alpha_{-,i}) = \frac{1}{2} (\alpha_{+i} + \alpha_{-i}),$$

$$\text{at } i > 1: x_{i+S} = x_i + Sh, \quad \hat{x}_i^2 = x_{i+\alpha_i} x_{(i+1)+\alpha_i}, \quad \bar{x}_i^2 = x_{i+\alpha_i}^2,$$

$$\text{at } i = 1: \frac{\hat{x}_i^2}{\bar{x}_i^2} = \frac{3h}{x_{(3/2)+\alpha_i}}, \quad x_{(3/2)+\alpha} = x_{(3/2)} + \alpha h, \quad x_{(3/2)} = (x_1 + x_2)/2,$$

where  $S$  is any real number.

In the suggested scheme the maximum principle is implemented, which means preservation of such properties of the solution as the monotonicity and nonnegativity of the solvent concentration.

In practice, the problem for the equation having different-scale coefficients in different regions is often subdivided into several problems and then the solutions obtained are "sewn." This approach is reasonable but it possesses certain difficulties in the case of nonlinear equations. On the other hand, its use is not always justified if there are numerical methods that can be adapted to the relevant situations. A scheme with a choice of weighting parameters for different coefficients provides the possibility of solving the problem using one and the same algorithm. In the scheme suggested the weighting parameters are chosen from the interval  $[-1/2, +1/2]$  in such a way that the scheme satisfies the maximum principle.

The scheme is a three-layer one with respect to time and a three-point one in relation to the space variable. It is known that for monotonic three-layer schemes the restrictions on the accuracy exist. With the aid of a Fourier transformation with respect to  $x$ ,  $\tau$  one could attain considerably better accuracy. Another possibility lies in the use of multigrid algorithms. However, three-layer schemes have their own advantages: simplicity, a high rate of calculation, small expenditures of computer memory. Using three-layer schemes, one can attain an accuracy of 2–3 orders relative to a step.

The scheme used is implicit and is solved by the factorization method. A linear analysis of the difference scheme shows that the scheme is absolutely stable. But since the system of equations is nonlinear, in choosing

the time step additional conditions are imposed, namely, at each time step the shrinkage velocity must be negative ( $v \leq 0$ ).

In performing the program a graph of the time variation of the total flow of solvent and a graph of its concentration distribution in the particles at each time step are made. Computer experiments make it possible to establish the influence of the main parameters on the kinetics of the process.

Two parameters,  $k$  and  $D_0$ , enter the formula for the diffusion coefficient. Calculations showed that with increasing  $D_0$  the process of solvent extraction out of particles is enhanced. By the prescribed time  $\tau^*$  the mass of the unextracted solvent in the particles is decreased. With increasing parameter  $k$ , the mass of the unextracted solvent in the particles increases by the fixed time  $\tau^*$  (i.e., the process slows down). In Fig. 1 the change in the profile of the solvent concentration inside the particles with time is shown. It is seen that in the course of the process a thin surface layer is formed near the phase boundary. The solvent concentration in it is close to zero, while inside the particles a slight change in the concentration of this component is observed. As a result of implementation of the numerical solution suggested, it is possible to trace the quality of the product obtained in a computer experiment upon a change in the input characteristics and optimization of the process. The adequacy of the model was determined from the calculated and experimental kinetic curves of the total solvent flow versus time using the method of least squares. The maximum deviation was 9.6%.

## REFERENCES

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