

MATHEMATICAL ANALYSIS OF SINGLE-WELL TRACER TEST

SUPRI TR-57

**By
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W. E. Brigham**

July 1987

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**Stanford University
Stanford, California**

FOSSIL FUELS



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ABSTRACT

Single-well tracer test as a means of evaluating reservoir *in-situ* fluid saturation has attracted many interests in recent years. The hydrodynamics of single-well tracer test is based on the radial flow of a tracer which can partition in the fluid saturations within the reservoir. At the same time, the tracer is mildly reactive with the mobile phase fluid saturation. This mild, irreversible chemical reaction results in the formation of another tracer species called secondary tracer. The secondary tracer is different from the parent tracer in its partition and chemical reaction characteristics. Typically, the secondary tracer is not reactive with, and has a near-zero partition coefficient with the immobile phase fluid saturation.

The hydrodynamics of the above tracer system is described by a Radial-Diffusion-Convection-Reaction (R-D-C-R) type second order differential equation. The use of this equation to analyze single-well tracer test has, in the past, largely been through the application of numerical techniques. Since these techniques may suffer from inaccuracies due to adverse numerical dispersion or the problem of uniqueness arising from fitting many unknown parameters, there is a need to develop an exact analytical solution to the R-D-C-R type differential equation for accurate single-well tracer test analyses.

This research work reexamines the R-D-C-R system of differential equations as it applies to single-well tracer tests, and obtains an exact analytical solution which heretofore has been considered impossible. Even though the exact solutions are based on a linear equilibrium adsorption isotherm model for tracer partitioning, it is shown that a solution based on the linear nonequilibrium adsorption model could also be obtained without much additional mathematical difficulties.

Using the exact analytical solution as our basic tool, the hydrodynamic models describing all phases of the single-well tracer test were solved analytically.

Graphs showing the tracer concentration profiles for each of the phases of the single-well tracer test were constructed.

1. INTRODUCTION

Tracer studies are important techniques for reservoir characterization, particularly in such specialized areas of studies as oil reservoir engineering (Baldwin, 1966; Abbaszadeh-Dehghani and Brigham, 1983), hydrology (Rubbin and James, 1973; Sauty, 1980), and in recent years geothermal engineering (Vetter, 1981; Fossum, 1982).

In reservoir characterization studies, suitable tracers, be it radioactive or chemical are flowed through the reservoir. Quantitative or qualitative information can then be deduced from the nature of the tracer breakthrough concentration profiles at the observation wellbore. This constitutes the basic principles of the two-well tracer test technique.

A version of the above two-well (well-to-well), single tracer technique is the dual tracer (Cooke, 1971) test. While the single tracer, well-to-well tracer test (Abbaszadeh-Dehghani and Brigham, 1983) yields information in respect of reservoir heterogeneity, dual tracer tests can be designed for information on *in-situ* fluid saturations. The dual tracer technique relies on the ability of the input tracers to partition in formation fluids at different rates. If therefore, we have a system where, for example, the oil saturation is immobile, while the water saturation is mobile or vice versa, the tracer which preferentially dissolves in the immobile fluid phase suffers a chromatographic retardation as it moves through the reservoir. On the other hand, the other tracer which preferentially dissolves in the mobile fluid phase suffers no retardation and therefore propagates through the reservoir at the same velocity as the mobile fluid phase. As a consequence of this difference in the propagation velocities of the two injected tracers, a time lag exists in the arrival times of the tracers at a designated observation wellbore. Such time lags provide the means of evaluating the *in-situ* fluid saturations (Cooke, 1971) of the reservoir.

An interesting variation of the dual tracer, well-to-well, tracer test is the single-well tracer test (Deans, 1971; Tomich, 1973). In this test, a chemical tracer, capable of reacting irreversibly with one of the formation fluids to form a second tracer which is substantially different from the original (primary) tracer in its partitioning characteristic, is used. The irreversible chemical reaction ensures that the formation of the second (secondary) tracer is never reversed during the test so that the chromatographic retardation which the primary tracer would suffer as it is pushed deep into the reservoir is not annulled when the tracer's flow is reversed for production at the wellbore. Here again, as in the case of the dual-tracer test, the time lag in the arrival times of the primary and secondary tracers provides the means of evaluating *in-situ* fluid saturations.

In this study, the single-well chemical tracer test is the preferred option for fluid saturation evaluation largely because of the convenience of operation and also because of the economic consideration of using only one test well rather than two. The primary objective of this work therefore is to model the single-well tracer test analytically and obtain an exact solution to such an analytical model. It is hoped that the exact analytical solution so obtained can be used in subsequent tracer test designs.

2. LITERATURE REVIEW

The literature on single-well tracer tests is rather sparse. The first known reports were as recent as 1971, in two separate patents claimed by Cooke (1971) and Deans (1971). These patents described techniques for evaluating residual oil saturation from single-well tracer tests. In the same year, Chase (1971) presented a finite element simulation model for analyzing test data; while in 1973, Tomich *et al.* presented a finite difference simulation model. These simulation models are unfortunately prone to error arising from attendant numerical dispersion. They also suffer from the problem of uniqueness arising from having to fit several unknown parameters during the simulation run. A comprehensive analysis of the above four reports is contained in a previous SUPRI report (Antunez and Brigham 1984).

Apart from Antunez, no known reports have shown an attempt to solve the governing equations of the single-well tracer test analytically. Indeed, no exact solution of the Radial-Diffusion-Convection-Reaction (R-D-C-R) type differential equation which governs the single-well tracer hydrodynamics is known to have been reported anywhere in the literature. The rest of this section will therefore be devoted to examining some of the known previous attempts to solve the R-D-C-R class of second order differential equations.

R-D-C-R equations have wide applications in many specialized fields of study such as petroleum engineering (Tomich, 1973), hydrology (Sauty, 1980), ecological studies (Saffman, 1962), oceanographic and limnological diffusion studies (Okubo, 1962) to mention a few. In general, R-D-C-R system of differential equations can be written in the form:

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C}{\partial r} \right] - v(r) \frac{\partial C}{\partial r} - S(C) = v \frac{\partial C}{\partial t} \quad (1)$$

where v is a constant, $S(C)$ is a source or sink term which can account for such phenomena as chemical reactions, adsorption processes, physical loss or addition of chemicals, etc. $v(r)$ and $D(r)$ are the radius dependent convection velocity and hydrodynamics dispersion function, respectively.

For the simple cases where $v(r)$ and $D(r)$ are constants, and $S(C)$ is either zero or directly proportional to C , a Fickian solution to Eq. 1 is easily obtained (Carslaw and Jaeger, 1959; Skellam, 1951). However, where $D(r)$ is radially distributed, no exact analytical solutions to Eq. 1 has been reported in the literature.

An attempt to obtain approximate solutions for the radially distributed $D(r)$, R-D-C-R system of second order differential equations was probably first reported in 1958 by Joseph and Sendner (See Okubo, 1980, p. 22-24) who presented a solution in terms of a *diffusion velocity* P in the form

$$C = \frac{M}{2\pi h P^2 t^2} \exp \left[- \frac{r}{Pt} \right] \quad (2)$$

In the same year, Ozmidov (1958) presented another approximate solution in terms of an *energy dissipation parameter* γ of the form

$$C = \frac{M}{6\pi h \gamma^3 r^3} \exp \left[- \frac{r^{2/3}}{t} \right] \quad (3)$$

These two solutions were obtained for cases of isotropic diffusion with no shear-diffusion or convective mixing. In 1959 another approximate solution which accounted for shear-diffusion was presented by Raimondi *et al.* (1959). By assuming that the ratio of the hydrodynamic dispersion represented by $D(r)$ and the convective velocity $v(r)$, is small, Raimondi obtained an asymptotic solution of the form

$$C = \frac{M}{2} \operatorname{erfc} \left[\frac{0.5r^2 - Q' t}{\sqrt{\frac{4\alpha r^3}{3} + \frac{D_m}{Q'} r^4}} \right] \quad (4)$$

where Q' and α are constants. Brigham and Smith (1965) amplified on the Raimondi solution and obtained the approximate equation for tracer injection in a five-spot pattern flow in the form

$$C = \frac{M}{2} \operatorname{erfc} \left[\frac{Q' \left[t + \frac{t_1}{2} \right] - \frac{r^2}{2}}{2\sqrt{\alpha \left[\frac{r^3}{3} \right]}} \right] - \operatorname{erfc} \left[\frac{Q' \left[t - \frac{t_1}{2} \right] - \frac{r^2}{2}}{2\sqrt{\alpha \left[\frac{r^3}{3} \right]}} \right] \quad (5)$$

where t_1 is the tracer slug injection time while t is the tracer-free water injection time.

Drawing a close analogy between the radial flow and the linear flow systems, along the lines suggested by Brigham and Smith (1965), Antunez (1984) was able to present an approximate analytical solution to the R-D-C-R system of differential equation. This he did by decoupling the reaction system from the diffusion-convection system using the method of characteristics. The solutions of the decoupled system when multiplied together yielded the approximate analytical solution in the form

$$C = \frac{C_0}{2} \exp \left[-\frac{k_r x}{v_x} \left[1 + \frac{a(1 - S_w)}{S_w} \right] \right] \operatorname{erfc} \left[\frac{x - \frac{v_x t S_w}{S_w + a(1 - S_w)}}{2\sqrt{\left[\frac{Kt S_w}{S_w + a(1 - S_w)} \right]}} \right] \quad (6)$$

It is clear from the above analyses that modeling of single-well tracer tests analytically have consistently been based on solutions largely derived from an empirical analogy between the radial flow and the linear flow systems. While such analogy might hold well in some very special cases, it is certainly not always the case as will subsequently be seen in this report.

3. THEORETICAL BASIS OF THE SINGLE-WELL TRACER TEST

The specifics of operating a single-well tracer test involves:

1. Injecting a slug of primary tracer into the reservoir with a carrier fluid,
2. The injected tracer is then displaced deeper into the reservoir by continuing to inject tracer-free carrier fluid.

During the process of injection, the tracer (primary tracer) partitions between the immobile and the mobile fluid saturations, maintaining a dynamic equilibrium between the partitioned species. At the same time, some of the primary tracer which partitioned in the mobile fluid phase saturation undergoes an irreversible chemical reaction with the mobile phase fluid, forming another tracer (the secondary tracer). The secondary tracer is normally unreactive with the immobile phase saturation and its partitionability with this fluid phase is zero (or nearly zero).

More often than not, the reaction rate involved in the formation of the secondary tracer is slow. As a result, an appreciable amount of the secondary tracer is not formed during the tracer injection period. It is therefore always necessary to:

1. Stop injection and shut in the well to allow more time for reaction so that the secondary tracer concentration can be built up to a level that can easily be detected by conventional chemical analysis technique.
2. Open the well to flow so that the concentration profiles of the primary and secondary tracers are monitored for characterization.

The characterization of tracer production profiles enables us to calculate the lag in the arrival times of tracers at the wellbore, and this provides the means of evaluating reservoir *in-situ* fluid saturations.

In consideration of the fluid dynamics of the above described system, it is clear that a limited portion of the reservoir around the test well, can be covered by the test. This limitation implies two things:

1. The fluid saturation obtainable from the test will be a volumetric average saturation of the pore volume covered. It is, however, important to note that this average saturation is more representative of the reservoir saturation than any other obtainable from either well logging or core analysis. (Fluid saturations obtained from well logging and core analysis are based on much smaller reservoir volumes than is normally encountered in single-well tracer tests. Furthermore, these conventional techniques also suffer from severe operational handicaps if the hole is cased.)
2. The hydrodynamics of single-well tracer flow is best described in radial flow geometry. Therefore, the simplest set of differential equations to describe tracer flow phenomena in a single-well test must be expressed in radial coordinates. If the perforated interval of the test well is large, equations must be expressed in cylindrical coordinates.

In describing the above process mathematically, certain simplifying assumptions must be made. For a tracer test designed to evaluate the immobile phase fluid saturation, we can make the following assumptions:

1. Fluid saturations of the mobile and immobile phases are incompressible.
2. The reservoir is homogeneous and isotropic.
3. The primary tracer undergoes an irreversible first order reaction in the mobile fluid phase only.

Using these assumptions, Tomich *et al.* (1973) derived a general equation of the form

$$\nabla \cdot (S_w D \cdot \nabla C_i) - \nabla \cdot (S_w v_w C_i) - R_i(C_i, \bar{C}_i) = \frac{\partial}{\partial t} (S_w C_i + S_0 \bar{C}_i) \quad (7)$$

where

- C_i = concentration of tracer i in the mobile fluid phase.
- \bar{C}_i = concentrations of tracer i in the immobile fluid phase.
- R_i = rate of reaction of tracer i .
- D = Hydrodynamic dispersion tensor in the porous medium.

If we consider the case of radial, adiabatic core (steady-state flow of the mobile phase W), the saturation S_w can be considered constant in Eq. 7 thus simplifying to

$$\frac{1}{r} \frac{\partial}{\partial r} \left[r D(r) \frac{\partial C_i}{\partial r} \right] - \frac{1}{r} \frac{\partial}{\partial r} (r v_w C_i) - \frac{R_i(C_i, \bar{C}_i)}{S_w} = \frac{\partial}{\partial t} \left[\frac{S_w C_i + S_0 \bar{C}_i}{S_w} \right] \quad (8)$$

For a steady-state flow of phase W , the velocity v_w can be based on a radial average defined from pure material balance consideration as

$$v_w = \left[\frac{5 \cdot 615 q}{2\pi h r \phi S_w} \right] \quad (9)$$

From Eq. 9 it can be seen that the product $r v_w$ is a constant provided that the volumetric rate q remains constant as would be the case for a steady-state flow system. Let

$$r v_w = \alpha = \text{constant} \quad (10)$$

Also if we consider that the source/sink term $R_i(C_i, \bar{C}_i)$ is due to the formation of the secondary tracer as a result of an irreversible first order reaction between the mobile-phase saturation and the primary tracer dissolved therein, $R(C_i, \bar{C}_i)$ can be expressed as

$$R(C_i, \bar{C}_i) = k_r (S_w C_i + S_0 \bar{C}_i) \quad (11)$$

where k_r is the reaction rate constant. Using Eqs. 9, 10 and 11 in Eq. 8 yields

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_i}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_i}{\partial r} - k_r \left[C_i + \frac{S_0}{S_w} \bar{C}_i \right] = \left[1 + \frac{S_0}{S_w} \frac{\partial g(C_i)}{\partial C_i} \right] \frac{\partial C_i}{\partial t} \quad (12)$$

In Eq. 12 we have assumed a general equilibrium relationship of the form

$$\bar{C}_i = g(C_i) \quad (13)$$

between the tracer concentration \bar{C}_i partitioned in the immobile fluid phase saturation and the concentration C_i partitioned in the mobile fluid phase.

Even though the assumption of a linear equilibrium relation simplifies the problem considerably the same problem could also be solved with equal mathematical ease had we assumed a linear nonequilibrium relation between \bar{C}_i and C_i (See Appendix G).

Two primary factors are evident in Eq. 12. These are the solute partition factor and the diffusion-convection factor. For the purpose of analysis we can rewrite Eq. 12 in the form

$$\alpha \left[\frac{\partial f_i}{\partial C_i} \right] \frac{1}{r} \frac{\partial C_i}{\partial r} + k_r \left[C_i + \frac{S_0}{S_w} g(C_i) \right] + N(C_i) \frac{\partial C_i}{\partial t} = 0 \quad (14)$$

where the diffusion-convection factor is implicit in a flux term f_i defined as

$$f_i = C_i - \frac{rD(r)}{\alpha} \frac{\partial C_i}{\partial r} \quad (15)$$

and the solute partition factor is contained in the term $N(C_i)$ defined as:

$$N(C_i) = \left[1 + \frac{S_0}{S_w} \frac{\partial g_i(C_i)}{\partial C_i} \right] \quad (16)$$

If we define a new coordinate system x as

$$x = \left[\frac{r^2}{2\alpha} \right] \quad (17)$$

so that

$$\frac{dx}{dr} = \left[\frac{r}{\alpha} \right] \quad (18)$$

Then Eq. 14 simplifies to

$$\left[\frac{\partial f_i}{\partial C_i} \right] \frac{\partial C_i}{\partial x} + N(C_i) \frac{\partial C_i}{\partial t} + k_r \left[C_i + \frac{S_0 g_i(C_i)}{S_w} \right] = 0 \quad (19)$$

It is easily seen from Eq. 19 that the characteristic velocity of any concentration front within the medium is given as:

$$\left[\frac{dx}{dt} \right]_{C_i} = \frac{\left[\frac{\partial f}{\partial C_i} \right]}{N(C_i)} \quad (20a)$$

or

$$\left[\frac{dx}{dt} \right]_{C_i} = \frac{\left[\frac{\partial f_i}{\partial C_i} \right]}{\left[1 + \frac{S_0}{S_w} \frac{\partial g(C_i)}{\partial C_i} \right]} \quad (20b)$$

For any equilibrium relation, $g(C_i)$, $\partial g(C_i)/\partial C_i$ is always positive. Therefore for any given diffusion-convection factor $(\partial f_i / \partial C_i)$, the solute partition factor $N(C_i)$ is greater than 1.0, and therefore acts to retard the velocity of flow of the partitioning species to values lower than the propagation velocity of the pure, mobile aqueous phase for which $N(C_i) = 1.0$.

Another important effect of partitioning is due to the nature of the equilibrium function $g(C_i)$. The most general form of the equilibrium function is offered by the Langmuir equilibrium isotherm where $g(C_i)$ is given in terms of the two constants K_1 and K_2 as

$$g(C_i) = \left[\frac{K_1 C_i}{1 + K_2 C_i} \right] = \bar{C}_1 \quad (21)$$

Three distinct types of (\bar{C}_i, C_i) equilibrium profiles are possible depending on whether

$$K_2 \quad 0 \quad (22)$$

1. For $K = 0$, we have the well known linear isotherm of Freundlich. In this case $N(C_i)$ is unity, implying that the tracer front propagates with a velocity which is independent of tracer concentration for any fixed value of $(\partial f_i / \partial C_i)$.
2. For $K_2 > 0$, the equilibrium relation function is convex as shown in Fig. 3.1. $N(C_i)$ is therefore a decreasing function of C_i . This gives rise to a situation where the tracer concentration profile is self-sharpening thus limiting any tendency of the propagation front to diffuse.
3. In this case of $K_2 < 0$, the equilibrium curve is concave and therefore $N(C_i)$ is an increasing function of C_i . This implies that the propagation front is severely retarded and diffusion will therefore enhance front propagation.

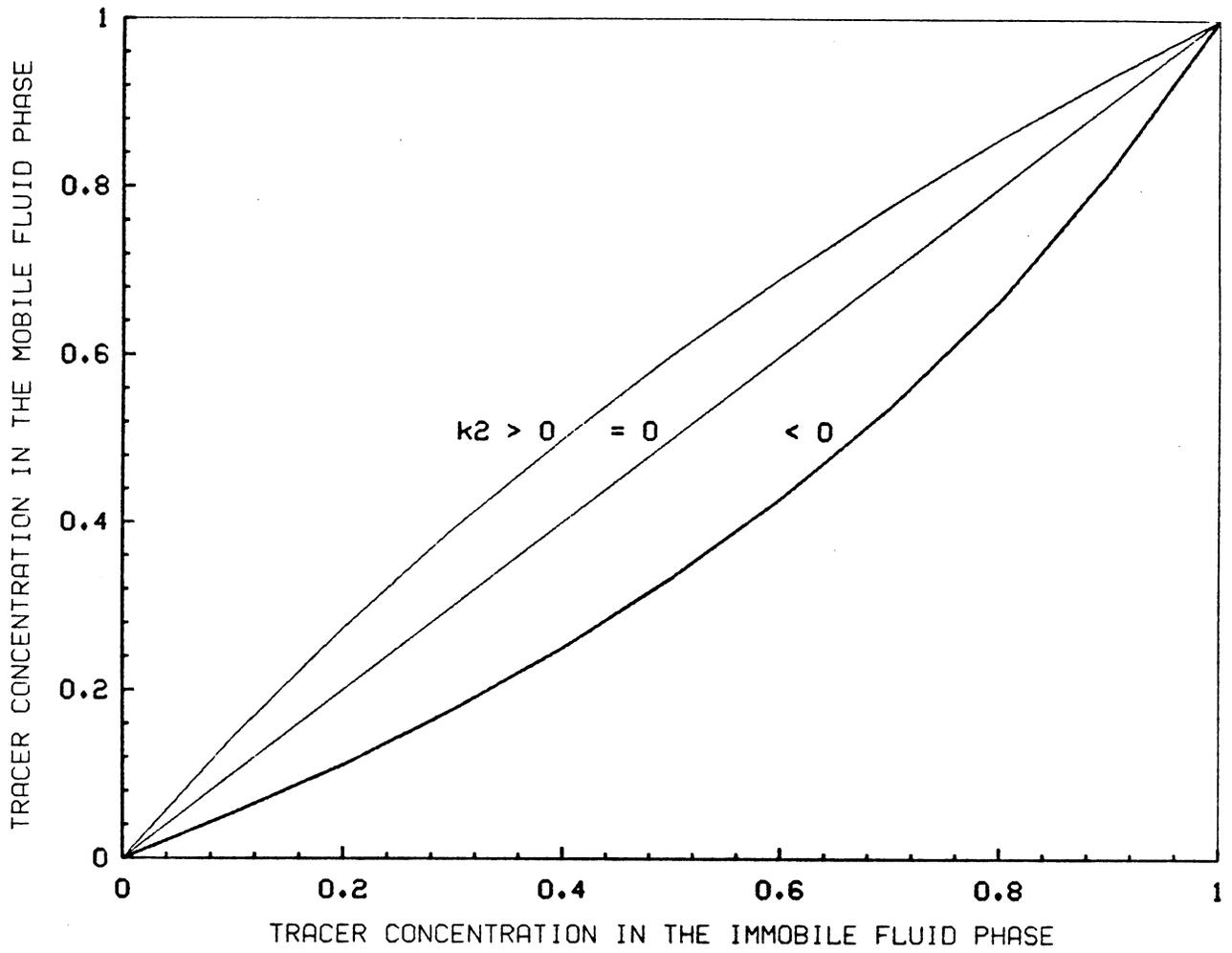


Fig. 3.1 Simulated Equilibrium Isotherm.

While Cases 2 and 3 described above seem rather interesting, they give rise to nonlinear R-D-C-R type second order differential equations which may not be amenable to any exact analytical solutions. In the rest of this report therefore we shall only consider the case of linear equilibrium relation where $K_2 = 0$ and therefore $g_i(C_i)$ is given as:

$$\bar{C}_i = g_i(C_i) = K_1 C_i \quad (23)$$

Using Eqs. 23 in Eq. 12 and setting $i = 1$ for tracer species partitioned in all fluid phases (the Primary Tracer), we have

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_1}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_1}{\partial r} - k_r \left[1 + \frac{K_1 S_0}{S_w} \right] C_1 = \left[1 + \frac{K_1 S_0}{S_w} \right] \frac{\partial C_1}{\partial t} \quad (24)$$

Equation 24 describes the primary tracer concentration profile in the radial domain.

The secondary tracer formed as a result of an irreversible first order reaction between the mobile fluid phase and the primary tracer only exists in the mobile fluid phase. Its partition coefficient with respect to the immobile fluid saturation is zero. For the secondary tracer therefore, we have the following relations:

$$\frac{\partial g(C_i)}{\partial C_i} = 0 \quad (25a)$$

$$k_{r_i} \left[1 + \frac{K_1 S_0}{S_w} \right] C_i = -k_r \left[1 + \frac{K_1 S_0}{S_w} \right] C_1 \quad (25b)$$

and

$$i = 2 \quad (25c)$$

using Eqs. 25 in Eq. 12 yields

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_2}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_2}{\partial r} + k_r \left[1 + \frac{K_1 S_0}{S_w} \right] C_1 = \frac{\partial C_2}{\partial t} \quad (26)$$

Note that in Eq. 26, the solute partition coefficient is absent in the accumulation term, and therefore the secondary tracer is not subjected to any chromatographic delay as it propagates through the reservoir.

Equations 24 and 26 are the basic equations describing the hydrodynamics of the primary and the secondary tracers respectively. These equations must be solved subject to appropriate initial and boundary conditions consistent with the various stages of operation of a single-well tracer test as described earlier.

4. ANALYTICAL SOLUTIONS TO SINGLE-WELL TRACER TEST EQUATIONS

4.1. PRIMARY TRACER

4.1.1. Tracer-Injection Period

The basic equation for the flow of primary tracer during tracer injection period is given as Eq. 24.

$$\frac{1}{r} \frac{\partial}{\partial r} \left[r D(r) \frac{\partial C_1}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_1}{\partial r} - k_r \left[1 + \frac{K_1 S_0}{S_w} \right] C_1 = \left[1 + \frac{K_1 S_0}{S_w} \right] \frac{\partial C_1}{\partial t} \quad (24)$$

The associated initial and boundary conditions are as follows:

$$C_1(r, t = 0) = 0 \quad (27a)$$

$$C_1(r \rightarrow \infty, t) = 0 \quad (27b)$$

$$C_1(r = r_w, t) = C_0 \quad (27c)$$

The boundary conditions expressed in Eq. 27 are only good for a system subjected to a continuous injection of the primary tracer of concentration C_0 at a wellbore of radius r_w . If we know the solution to Eqs. 24 and 27, we can easily obtain the corresponding solution to the slug injection system by using superposition in time.

If we define a dimensionless radial distance r_D as

$$r_D = \frac{r}{r_w} \quad (28a)$$

and

$$\Phi = r_w^2 \left[1 + \frac{K_1 S_0}{S_w} \right] \quad (28b)$$

Equation 24 can be expressed as

$$\frac{1}{r_D} \frac{\partial}{\partial r_D} \left[r_D D(r_D) \frac{\partial C_1}{\partial r_D} \right] - \frac{\alpha}{r_D} \frac{\partial C_1}{\partial r_D} - \Phi k_r C_1 = \Phi \frac{\partial C_1}{\partial t} \quad (29)$$

On expanding Eq. 29, we have

$$\frac{\partial^2 C_1}{\partial r_D^2} + \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \frac{\partial C_1}{\partial r_D} - \frac{\Phi k_r C_1}{D} = \frac{\Phi}{D} \frac{\partial C_1}{\partial t} \quad (30a)$$

where

$$D' = \frac{d}{dr_D} [D(r_D)] \quad (30b)$$

The associated initial and boundary conditions are

$$C_1(r_D, t = 0) = 0 \quad (31a)$$

$$C_1(r_D \rightarrow \infty, t) = 0 \quad (31b)$$

$$C_1(r_D = 1, t) = C_0 \quad (31c)$$

Equation 30 is a linear second differential order equation with variable coefficients and can be transformed to a Sturm-Louisville equation by using a Cole-type (Cole, 1951) transformation of the form

$$C_1(r, t) = \phi_1 e^{-\frac{1}{2} \int_1^r \left[\frac{D'}{D} + \frac{D - \alpha}{D\xi} \right] d\xi} \quad (32)$$

to obtain

$$\frac{\partial^2 \phi_1}{\partial r_D^2} - \left[U_1(r_D, D) + \frac{k_r \Phi}{D} \right] \phi_1 = \frac{\Phi}{D} \frac{\partial \phi_1}{\partial t} \quad (33)$$

where

$$U_1(r_D, D) = \frac{1}{4} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]^2 + \frac{1}{2} \frac{d}{dr_D} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \quad (34)$$

From Eq. 33 it can easily be observed that the nature of the function $U_1(r_D, D)$ will largely determine the form of solution one can expect. Even though $U_1(r_D, D)$ is r -dependent and therefore not constant, still, we can say quite generally that there are two fundamentally different types of solutions obtainable from Eq. 33. For example, if $U_1(r_D, D)$ were strictly positive, then only exponential solution are admissible. On the other hand, a negative $U_1(r_D, D)$ may give rise to periodic solutions. Thus the function $U_1(r_D, D)$ or $D(r_D)$ needs be specified before an exact solution to Eq. 33 can be formulated.

It must be mentioned however that in cases where $U_1(r_D, D)$ can not be specified, an approximate solution can be obtained by transforming Eq. 33 into the Riccati differential equation. Such approximate solutions are based on the KWB (Krammer, Wenzel and Brillouin) assumptions normally valid for large values of $U_1(r_D, D)$ (Lanczos, 1961; Lakin *et al.*, 1970).

The function $U_1(r_D, D)$ is completely specified if the hydrodynamic dispersion function $D(r_D)$ is known. It is generally believed that $D(r_D)$ is a function of the absolute value of the convection velocity field $|v_w|$, and can be represented by an expression of the form (Raimondi, 1959; Brigham *et al.*, 1961).

$$D(r_D) = D_m + D_0|v_w| \quad (35)$$

In Eq. 35, the term D_m is the molecular diffusion constant while D_0 is the dispersive mixing constant. Using Eq. 10 in Eq. 35 we can express $D(r_D)$ as

$$D(r_D) = D_m + \frac{\alpha D_0}{r_D} \quad (36)$$

For all practical purposes, the molecular diffusion constant D_m is relatively very small compared with the dispersive mixing term (Brigham and Smith, 1961). The hydrodynamic dispersion function $D(r_D)$ can therefore be approximated as:

$$D(r_D) \approx \frac{\alpha D_0}{r_D} \quad (37)$$

Using Eq. 37 in Eq. 33 yields

$$\frac{\partial^2 \phi_1}{\partial r_D^2} - \left[\frac{1}{4D_0^2} + \frac{\Phi k_r}{\alpha D_0} r_D \right] \phi_1 = \frac{\Phi r_D}{\alpha D_0} \frac{\partial \phi_1}{\partial t} \quad (38)$$

In the Laplace space we have

$$\frac{d^2 \bar{\phi}_1}{dr_D^2} - \left[\frac{1}{4D_0^2} + \frac{\Phi}{\alpha D_0} (k_r + \lambda) r_D \right] \bar{\phi}_1 = 0 \quad (39)$$

A general solution to the homogeneous Sturm-Louisville Eq. 39 can be found in the form (Appendix A):

$$\bar{\phi}_1(\xi, \lambda) = \beta_1 A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] + \beta_2 B_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] \quad (40)$$

where

$$\xi(r_D, \lambda) = \frac{1}{4D_0^2} + \frac{\Phi(k_r + \lambda)}{\alpha D_0} r_D \quad (41a)$$

λ is the Laplace parameter. $Ai(x)$ and $Bi(x)$ are the Airy integrals defined as (Luke, 1962):

$$Ai(x) = \frac{1}{\pi} \int_0^{\infty} \cos \left[\frac{r^3}{3} + xt \right] dt \quad (41b)$$

$$Bi(x) = \frac{1}{\pi} \int_0^{\infty} e^{-\left[\frac{r^3}{3} - xt \right]} dt + \frac{1}{\pi} \int_0^{\infty} \sin \left[\frac{r^3}{3} + xt \right] dt \quad (41c)$$

The associated boundary conditions are

$$\bar{\Phi}_1(\xi \rightarrow \infty, \lambda) = 0 \quad (42a)$$

$$\bar{\Phi}_1[\xi(r_D = 1), \lambda] = \frac{C_0}{\lambda} \quad (42b)$$

Using Eq. 42 on Eq. 40 yields a solution in the form

$$\bar{\Phi}_1(\xi, \lambda) = \frac{C_0}{\lambda} \frac{Ai \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{Ai \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right]} \quad (43)$$

In terms of the original variable C_1 , we use the inverse transform of Eq. 32 to obtain

$$\bar{C}_1(\xi, \lambda) = \frac{C_0 \exp \left[\frac{r_D - 1}{2D_0} \right]}{\lambda} \frac{Ai \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{Ai \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right]} \quad (44)$$

The Airy function $Ai(x)$ can also be expressed in terms of the Bessel function of second kind of fractional order $K_{1/3}(z)$ as (Abramowitz *et al.*, 1972):

$$Ai(x) = \frac{1}{\pi} \sqrt{\frac{x}{3}} K_{1/3} \left[\frac{2}{3} x^{3/2} \right] \quad (45)$$

Using Eqs. 45 in 44 yields

$$\bar{C}_1(\xi, \lambda) = \frac{C_0 \exp \left[\frac{r_D - 1}{2D_0} \right]}{\lambda} \sqrt{\frac{\xi(r_D)}{\xi(r_D = 1)}} \left[\frac{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{3/2} \right]}{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{3/2}(r_D = 1) \right]} \right] \quad (46)$$

Equation 46 describes the concentration profile for a situation where the primary tracer is continuously injected into the reservoir such that a tracer concentration of value C_0 is always maintained at the wellbore. Equation 46 therefore constitutes the fundamental solution with the other phases of single-well tracer test equations that can be built.

4.1.2. Tracer-Free Water Injection Period

If the tracer was injected at time t and then followed by the injection of tracer-free water at time t_1 , then the primary tracer concentration profile at time t is obtained by superposition in time using Eq. 46 as the fundamental equation. The solution then is given as:

$$\begin{aligned} \bar{C}_1(\xi, \lambda) = C_0 \exp \left[\frac{r_D - 1}{2D_0} \right] & \left\{ \frac{1}{\lambda} \sqrt{\frac{\xi(r_D, \lambda)}{\xi(r_D = 1, \lambda)}} \left[\frac{K_{1/3} \left[\frac{2/3 \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{2/3}(r_D, \lambda)}{\xi^{2/3}(r_D = 1, \lambda)} \right]}{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{2/3}(r_D = 1, \lambda)} \right]} \right] \right. \\ & \left. - \frac{1}{\lambda_1} \sqrt{\frac{\xi(r_D, \lambda_1)}{\xi(r_D = 1, \lambda_1)}} \left[\frac{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda_1)} \right] \xi^{2/3}(r_D = 1, \lambda_1)}{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda_1)} \right] \xi^{2/3}(r_D = 1, \lambda_1)} \right]} \right] \right] \right\} \quad (47) \end{aligned}$$

where λ is the Laplace parameter corresponding to injection time t , while λ_1 corresponds to time t_1 . Equation 47 is the equation that describes the transport of the primary tracer through the reservoir during the injection period, in Laplace space.

4.1.3. Asymptotic Solution Valid for Large Values of $x = [\alpha D_0 / \Phi(k_r + \lambda)]^{2/3} \xi$

The basic solution function for the R-D-C-R system of differential equation is given by Eq. 44. If we set

$$x = \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \quad (48)$$

Then Eq. 44 can be written as

$$\bar{C}(r_D, \lambda) = \frac{C_0 \exp \left[\frac{r_D - 1}{2D_0} \right]}{\lambda} \frac{Ai(x)}{Ai(x_1)} \quad (49)$$

For large values of $Ai(x_1) \rightarrow 0$, therefore Eq. 49 becomes singular and cannot be evaluated.

If we expand the Airy function $Ai(x)$ asymptotically for large values of x we have (Abramowitz and Stegun, 1972),

$$Ai(x) \approx \frac{1}{\sqrt{4\pi x^{1/2}}} \exp\left[-\frac{2}{3} x^{3/2}\right] \quad (50)$$

Using this in Eq. 49 we have

$$\bar{C}(r_D, \lambda) = \frac{C_0 \exp\left[\frac{r_D - 1}{2D_0}\right] \left[\frac{x_1}{x}\right]^{1/4} \exp\left[-\frac{2}{3} (x^{3/2} - x_1^{3/2})\right]}{\lambda} \quad (51)$$

Expressed in terms of ξ we have

$$\bar{C}(r_D, \lambda) = \frac{C_0 \exp\left[\frac{r_D - 1}{2D_0}\right] \left[\frac{\xi(r_D = 1)}{\xi(r_D)}\right]^{1/4} \exp\left[-\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \left[\xi^{3/2}(r_D) - \xi^{3/2}(r_D = 1)\right]\right]}{\lambda} \quad (52)$$

Equation 52 is equivalent to Eq. 46 for large values of x . This same solution could also have been obtained by going through the Riccati formulation and using the *KWB* assumptions as earlier discussed for large values of $U_1(r_D, D)$.

4.2. SECONDARY TRACER

4.2.1. Tracer Injection Period

During the tracer injection period, the secondary tracer is formed as a result of an irreversible first order reaction involving the injected primary tracer and the carrier mobile fluid phase. Thus the secondary tracer is subjected to the same conditions of diffusion and convection as the primary tracer. However, because the secondary tracer flows with the carrier, mobile fluid phase, it is not subjected to the kind of flow retardation which the primary tracer suffers. Also, the source term of the R-D-C-R system of differential equations is a positive reaction term. Considering the above, the secondary tracer flow equation can be written as

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_2}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_2}{\partial r} + k_r \left[1 + \frac{K_1 S_0}{S_w} \right] C_1 = \frac{\partial C_2}{\partial t} \quad (53)$$

The initial and boundary conditions can simply be put as:

$$C_2(r, t = 0) = 0 \quad (54a)$$

$$C_2(r \rightarrow \infty, t) = 0 \quad (54b)$$

$$C_2(r = r_w, t) = 0 \quad (54c)$$

The imports of Eq. 53 are quite obvious since the secondary tracer is formed *in-situ* from a primary tracer that is being continuously pushed into the reservoir by a stream of tracer-free water. There can be no secondary tracer at the wellbore or the outer boundary which is infinitely located.

Proceeding as for the primary tracer, we can define the dimensionless radial distance r_D and Φ as in Eq. 28 so that Eq. 53 can be written as

$$\frac{1}{r_D} \frac{\partial}{\partial r_D} \left[r_D D(r_D) \frac{\partial C_2}{\partial r_D} \right] - \frac{\alpha}{r_D} \frac{\partial C_2}{\partial r_D} + k_r \Phi C_1 = r_w^2 \frac{\partial C_2}{\partial t} \quad (55)$$

which on expansion yields

$$\frac{\partial^2 C_2}{\partial r_D^2} + \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \frac{\partial C_2}{\partial r_D} + \frac{k_r \Phi}{D} C_1 = \frac{r_w^2}{D} \frac{\partial C_2}{\partial t} \quad (56)$$

Using the transformation given in Eqs. 32, Eq. 56 becomes

$$\frac{\partial^2 \phi_2}{\partial r_D^2} - U_2(r_D, D) \phi_2 + \frac{k_r \Phi}{D} \phi_1 = \frac{r_w^2}{D} \frac{\partial \phi_2}{\partial t} \quad (57)$$

where

$$U_2(r_D, D) = \frac{1}{4} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]^2 + \frac{1}{2} \frac{d}{dr_D} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]$$

In the Laplace space, Eq. 57 becomes

$$\frac{\partial^2 \bar{\phi}_2}{\partial r_D^2} - \left[U_2(r_D, D) + \frac{r_w^2 \lambda}{D} \right] \bar{\phi}_2 = - \frac{k_r \Phi \bar{\phi}_1}{D} \quad (58a)$$

or

$$\frac{\partial^2 \bar{\phi}_2}{\partial r_D^2} - W(r_D, \lambda) \bar{\phi}_2 = - \frac{k_r \Phi \bar{\phi}_1}{D} \quad (58b)$$

where

$$W(r_D, \lambda) = \left[\frac{1}{4} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]^2 + \frac{1}{2} \frac{d}{dr_D} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] + \frac{r_w^2 \lambda}{D} \right] \quad (58c)$$

If as before we take

$$D(r_D) \approx \frac{\alpha D_0}{r_D} \quad (37)$$

Then, Eqs. 58 simplifies to

$$\frac{\partial^2 \bar{\Phi}_2}{\partial r_D^2} - \left[\frac{1}{4D_0^2} + \frac{r_w^2 \lambda}{\alpha D_0} r_D \right] \bar{\Phi}_2 = - \frac{\Phi k_r r_D \bar{\Phi}_1}{\alpha D_0} \quad (59)$$

The associated boundary conditions are

$$\bar{\Phi}_2(r_D \rightarrow \infty, \lambda) = 0 \quad (60a)$$

$$\bar{\Phi}_2(r_D = 1, \lambda) = 0 \quad (60b)$$

Equation 59 is an inhomogeneous version of Eq. 39 and can be solved by using the method of undetermined coefficient (staff, 1983) to obtain a general solution of the form (Appendix B).

$$\bar{\Phi}_2(\eta, \lambda) = \beta_3 A_i \left[\left[\frac{\alpha D_0}{\lambda r_w^2} \right] \eta \right] - \frac{\Phi k_r}{\lambda [\Phi k_r + \lambda (\Phi - r_w^2)]} \left[\frac{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D, \lambda) \right]}{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1, \lambda) \right]} \right] \quad (61a)$$

where

$$\xi = \frac{1}{4D_0^2} + \frac{\Phi(k_r + \lambda)}{\alpha D_0} r_D$$

$$\eta = \frac{1}{4D_0^2} + \frac{\lambda r_w^2}{\alpha D_0} r_D \quad (61b)$$

subject, of course, to the boundary conditions given in Eq. 60. Application of the boundary conditions to Eq. 61 yields a solution of the form:

$$\bar{\Phi}_2(r_D, \lambda) = \frac{\Phi k_r}{\lambda [\Phi k_r + \lambda (\Phi - r_w^2)]} \left[\frac{A_i \left[\left[\frac{\alpha D_0}{r_w^2 \lambda} \right]^{2/3} \eta(r_D, \lambda) \right]}{A_i \left[\left[\frac{\alpha D_0}{r_w^2 \lambda} \right]^{2/3} \eta(r_D = 1, \lambda) \right]} - \frac{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D, \lambda) \right]}{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1, \lambda) \right]} \right] \quad (62)$$

Equation 62 can be converted to the concentration functions $\bar{C}_2(r_D, \lambda)$ through using Eq. 32 to obtain

$$\bar{C}_2(r_D, \lambda) = \frac{\Phi k_r \exp\left[\frac{r_D - 1}{2D_0}\right]}{\lambda[\Phi k_r + \lambda(\Phi - r_w^2)]} \left[\frac{Ai\left[\left[\frac{\alpha D_0}{r_w^2 \lambda}\right]^{2/3} \eta(r_D, \lambda)\right]}{Ai\left[\left[\frac{\alpha D_0}{r_w^2 \lambda}\right]^{2/3} \eta(r_D = 1, \lambda)\right]} - \frac{Ai\left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)}\right]^{2/3} \xi(r_D, \lambda)\right]}{Ai\left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)}\right]^{2/3} \xi(r_D = 1, \lambda)\right]} \right] \quad (63)$$

Equation 63 represents the concentration profile of the formed secondary tracer when the primary tracer is continuously injected.

4.2.2. Tracer Free Water Injections Period

When the primary tracer is injected for a time t_1 and then followed by a tracer-free water injection for a total injection period of time t , a solution can be obtained by superposition in time using Eq. 63 as the basic solution. Proceeding as we did for the primary tracer we obtain a solution of the form.

$$\bar{C}_2(r_D, \lambda) = \frac{\Phi k_r \exp\left[\frac{r_D - 1}{2D_0}\right]}{\lambda[\Phi k_r + \lambda(\Phi - r_w^2)]} [\chi(r_D, \lambda) - \chi(r_D, \lambda_1)] \quad (64a)$$

where

$$\chi(r_D, \lambda) = \left[\frac{Ai\left[\left[\frac{\alpha D_0}{r_w^2 \lambda}\right]^{2/3} \eta(r_D, \lambda)\right]}{Ai\left[\left[\frac{\alpha D_0}{r_w^2 \lambda}\right]^{2/3} \eta(r_D = 1, \lambda)\right]} - \frac{Ai\left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)}\right]^{2/3} \xi(r_D, \lambda)\right]}{Ai\left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)}\right]^{2/3} \xi(r_D = 1, \lambda)\right]} \right] \quad (64b)$$

Equation 64 describes the movement of the secondary tracer through the porous medium during the injection period.

4.3. SHUT-IN PERIOD

4.3.1. Primary Tracer

The irreversible first order reaction which gives rise to the formation of the secondary tracer is normally very slow. Therefore, in order that an appreciable amount of secondary tracer be formed during a single-well tracer test run, the injection of tracer-free water bank to push the primary tracer should be stopped, and the well shut-in to allow for additional formation of the secondary tracer prior to production. During the shut-in period, therefore, shear diffusion $D_0|v_w|$ is zero since $|v_w| = 0$. Tracer motions could then be attributed solely to molecular diffusion. It follows then that the hydrodynamic dispersion function $D(r_D)$ given as

$$D(r_D) = D_m + D_0|v_w| \quad (35)$$

must be approximated by the molecular diffusion term only so that

$$D(r_D) \approx D_m \quad (65)$$

Thus the two important characteristics of the primary tracer flow during the shut-in period are:

$$|v_w| = |\alpha| = 0 \quad (66a)$$

$$D(r_D) = D_m \quad (66b)$$

Otherwise, the basic equation describing the primary tracer flow remains the same. Using Eq. 66 in the basic Eq. 30 for the primary tracer yields the equation for the primary tracer during the shut-in period as

$$\frac{\partial^2 C_{1s}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial C_{1s}}{\partial r} - \frac{\Phi k_r}{D_m} C_{1s} = \frac{\Phi}{D_m} \frac{\partial C_{1s}}{\partial t} \quad (67)$$

The associated initial and boundary conditions are

$$C_{1s}(r_D, t = 0) = C_1(r_D, t_{inj}) \quad (68a)$$

$$C_{1s}(r_D \rightarrow \infty, t) = 0 \quad (68b)$$

$$C_{1s}(r_D = 1, t) = 0 \quad (68c)$$

The initial condition (Eq. 68a) states that at the time of shut-in, the primary tracer in the system is equal to that available prior to the shut-in period. The boundary conditions (Eqs. 68b and 68c) are obvious.

We can seek the solution Eqs. 67 and 68 in the form (Carslaw and Jaeger, 1959; 1.14; Arsenin, 1968):

$$C_{1s}(r_D, t) = \Psi_{1p}(r_D, t) + \Psi_{2p}(r_D, t) \quad (69)$$

such that $C_{1s}(r_D, t)$ satisfies the boundary condition at $r_D = 1$, i.e.,

$$C_{1s}(r_D, t) = 0 \quad r_D = 1 \quad (70)$$

while $\Psi_{1p}(r_D, t)$ satisfies equation

$$\frac{\partial^2 \Psi_{1p}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial \Psi_{1p}}{\partial r_D} - \frac{\Phi k_r}{D_m} \Psi_{1p} = \frac{\Phi}{D_m} \frac{\partial \Psi_{1p}}{\partial t} \quad (71)$$

subject to

$$\Psi_{1p}(r_D \rightarrow \infty, t) = 0 \quad (72a)$$

$$\Psi_{1p}(r_D, t = 0) = C_1(r_D, t_{inj}) \quad (72b)$$

and $\Psi_{2p}(r_D, t)$ satisfies the equations

$$\frac{\partial^2 \Psi_{2p}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial \Psi_{2p}}{\partial r_D} - \frac{\Phi k_r}{D_m} \Psi_{2p} = \frac{\Phi}{D_m} \frac{\partial \Psi_{2p}}{\partial t} \quad (73)$$

subject to

$$\Psi_{2p}(r_D, \rightarrow \infty, t) = 0 \quad (74a)$$

$$\Psi_{2p}(r_D, t = 0) = 0 \quad (74b)$$

Equations 71 and 72 can be treated as a Cauchy's problem (Arsenin, 1968), and therefore, the solution can be written as

$$\Psi_{1p}(r_D, t) = \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_1(r_D', t) C_1(r_D') dr_D' \quad (75)$$

where $G_1(r_D', t)$ is the Green's function satisfying Eq. 71 and the one-sided boundary condition represented by Eq. 72. In the Laplace space, Eqs. 71, 72, 73, 74 can be rendered as follows:

$$\frac{d^2 \bar{\Psi}_{1p}}{dr_D^2} + \frac{1}{r_D} \frac{d \bar{\Psi}_{1p}}{dr_D} - \frac{\Phi}{D_m} (k_r + \lambda) \bar{\Psi}_{1p} = - \frac{\Phi C_1(r_D, t_{inj})}{D_m} \quad (76)$$

subject to

$$\bar{\Psi}_{1p}(r_D \rightarrow \infty, \lambda) = 0 \quad (77)$$

and

$$\frac{d^2 \bar{\Psi}_{2p}}{dr_D^2} + \frac{1}{r_D} \frac{d \bar{\Psi}_{2p}}{dr_D} - \frac{\Phi}{D_m} (k_r + \lambda) \bar{\Psi}_{2p} = 0 \quad (78)$$

subject to

$$\bar{\Psi}_{2p}(r_D \rightarrow \infty, \lambda) = 0 \quad (79)$$

To obtain a solution to Eqs. 76 and 77 we need to construct the appropriate Green's function $G_1(r_D, \lambda)$ of Eq. 75 in the Laplace space as follows. The fundamental, independent solutions to Eq. 76 are in the form (Bowman, 1983) of:

$$I_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \quad \text{and} \quad K_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]$$

Using these two basic and independent solutions to Eq. 76, we can construct the appropriate Green's function (Courant and Hilbert, 1953), (Appendix C) as:

$$G_1(r_D, r_D', \lambda) = \begin{cases} K_0 \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] I_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] & ; r_D \leq r_D' \\ K_0 \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] I_0 \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] & ; r_D > r_D' \end{cases} \quad (80)$$

Also it can easily be shown that the solution $\bar{\Psi}_{2p}(r_D, \lambda)$ to Eqs. 78 and 79 can be expressed as

$$\bar{\Psi}_{2p}(r_D, \lambda) = A_1 K_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \quad (81)$$

Using Eqs. 75 and 80 in Eq. 69, we obtain the complete solution $\bar{C}_{1s}(r_D, \lambda)$ as

$$\bar{C}_{1s}(r_D, \lambda) = A_1 K_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] + \frac{\Phi}{D_m} \int_{r_D'=1}^{\infty} G_1(r_D', r_D, \lambda) C_1(r_D') dr_D' \quad (82)$$

subject to

$$\bar{C}_{1s}(r_D = 1, \lambda) = 0 \quad (83)$$

Using this boundary condition, the constant A_1 can be evaluated so that a complete solution is obtained in the form

$$\begin{aligned} \bar{C}_{1s}(r_D, \lambda) = & \frac{\left[\frac{\Phi}{D_m} \right]}{K_0 \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]} \left\{ I_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_0 \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \right. \\ & \left. - I_0 \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \right\} \\ & \cdot \int_{r_D'=1}^{\infty} K_0 \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] C_1(r_D') r_D' dr_D' ; \quad r_D \leq r_D' \end{aligned} \quad (84a)$$

and

$$\bar{C}_{1s}(r_D, \lambda) = \frac{\left[\frac{\Phi}{D_m} \right] K_0 \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]}{K_0 \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]} \int_{r_D=1}^{\infty} \left\{ I_0 \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_0 \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \right. \\ \left. - I_0 \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_0 \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \right\} C_1(r_D') r_D' dr ; \quad r_D > r_D' \quad (84b)$$

In the very special case when there is no molecules diffusion the solution to the shut-in equation reduces to a simple form as:

$$C_{1s}(r_D, \lambda) = \frac{C_1(r_D)}{k_r + \lambda} \quad (85)$$

Equation 85 could also be used for such cases where the values of $[\Phi(k_r + \lambda)/D_m]$ would make Eq. 84 singular. Therefore for programming purposes, Eqs. 85 and 84 are used together.

4.3.2. Secondary Tracer

The secondary tracer is subjected to same conditions as the primary tracer during the shut-in period viz:

$$|v_w| = |\alpha| = 0 \quad (86a)$$

$$D(r_D) = D_m \quad (86b)$$

Using the above equations in Eq. 56 the equation of secondary tracer flow during shut-in becomes

$$\frac{\partial^2 C_{2s}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial C_{2s}}{\partial r_D} + \frac{k_r \Phi C_{1s}}{D_m} = \frac{r_w^2}{D_m} \frac{\partial C_{2s}}{\partial t} \quad (87)$$

The associated initial and boundary conditions are:

$$C_{2s}(r_D, t = 0) = C_2(r_D, t_{inj}) \quad (88a)$$

$$C_{2s}(r_D \rightarrow \infty, t) = 0 \quad (88b)$$

$$C_{2s}(r_D = 1, t) = 0 \quad (88c)$$

In the Laplace space, Eqs. 87 and 88 become

$$\frac{\partial^2 \bar{C}_{2s}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial \bar{C}_{2s}}{\partial r_D} + \left[\frac{r_w^2 \lambda}{D_m} \right] \bar{C}_{2s} = - \frac{\Phi}{D_m} \left[k_r C_{1s} + \frac{r_w^2}{\Phi} C_2(r_D) \right] \quad (89)$$

Subject to the boundary conditions

$$\bar{C}_{2s}(r_D \rightarrow \infty, \lambda) = 0 \quad (90a)$$

$$\bar{C}_{2s}(r_D = 1, \lambda) = 0 \quad (90b)$$

The set of equations (Eqs. 89 and 90) are similar to what we had for the primary tracer dynamics during shut in, and hence a solution of the form

$$\bar{C}_{2s}(r_D, \lambda) = \bar{\Psi}_{1s}(r_D, \lambda) + \bar{\Psi}_{2s}(r_D, \lambda) \quad (91)$$

can be found such that $\bar{C}_{2s}(r_D, \lambda)$ satisfy the inner boundary conditions (Eq. 90b) while $\bar{\Psi}_{1s}(r_D, \lambda)$ is a solution of the Cauchy's problem given as:

$$\frac{d^2 \bar{\Psi}_{1s}}{dr_D^2} + \frac{1}{r_D} \frac{d \bar{\Psi}_{1s}}{dr_D} + \left[\frac{r_w^2 \lambda}{D_m} \right] \bar{\Psi}_{1s} = - \frac{\Phi}{D_m} \left[k_r C_{1s} + \frac{r_w^2}{\Phi} C_2(r_D) \right] \quad (92a)$$

subject to

$$\bar{\Psi}_{1s}(r_D \rightarrow \infty, \lambda) = 0 \quad (92b)$$

and $\bar{\Psi}_{2s}(r_D, \lambda)$ is a solution of the homogeneous equation

$$\frac{d^2 \bar{\Psi}_{2s}}{dr_D^2} + \frac{1}{r_D} \frac{d \bar{\Psi}_{2s}}{dr_D} + \left[\frac{r_w^2 \lambda}{D_m} \right] \bar{\Psi}_{2s} = 0 \quad (93a)$$

subject to

$$\bar{\Psi}_{2s}(r_D \rightarrow \infty, \lambda) = 0 \quad (93b)$$

Following a similar procedure as in the primary tracer during shut-in, it can be shown (Appendix D) that

$$\bar{\Psi}_{1s}(r_D, \lambda) = \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_2(r_D', \lambda) \left[k_r C_{1s}(r_D') + \frac{r_w^2}{\Phi} C_2(r_D') \right] dr_D' \quad (94)$$

where the one-sided Green's function $G_2(r_D, \lambda)$ is given as

$$G_2(r_D, r_D', \lambda) = \begin{cases} K_0 \left[r_D' \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] I_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] r_D' ; r_D \leq r_D' \\ K_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] I_0 \left[r_D' \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] r_D' ; r_D > r_D' \end{cases} \quad (95)$$

and

$$\bar{\Psi}_{2s}(r_D, \lambda) = A_2 K_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] \quad (96)$$

Using Eqs. 95 and 96 in Eq. 91 yields a general solution of the form

$$\bar{C}_{2s}(r_D, \lambda) = A_2 K_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] + \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_2(r_D', \lambda) \left[k_r C_{1s}(r_D') + \frac{r_w^2}{\Phi} C_2(r_D') \right] dr_D' \quad (97)$$

Subject to the inner boundary conditions

$$\bar{C}_{2s}(r_D = 1, \lambda) = 0 \quad (90b)$$

Using Eq. 90b on Eq. 97 the constant A_2 can be evaluated so that a solution to Eqs. 87 and 88 can be written as:

$$\begin{aligned} \bar{C}_{2s}(r_D, \lambda) = & \frac{\left[\frac{\Phi}{D_m} \right]}{K_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right]} \left[I_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] K_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right] - I_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right] K_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] \right] \\ & \cdot \int_{r_D=1}^{\infty} K_0 \left[r_D' \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] \left[k_r C_{1s}(r_D') + \frac{r_w^2}{\Phi} C_2(r_D') \right] r_D' dr_D' ; r_D \leq r_D' \end{aligned} \quad (98a)$$

and

$$\begin{aligned} \bar{C}_{2s}(r_D, \lambda) = & \frac{\left[\frac{\Phi}{D_m} \right] K_0 \left[r_D \sqrt{\frac{r_w^2 \lambda}{D_m}} \right]}{K_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right]} \int_{r_D=1}^{\infty} \left[k_r C_{1s}(r_D') + \frac{r_w^2}{\Phi} C_1(r_D') \right] \\ & \cdot \left[I_0 \left[r_D' \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] K_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right] - I_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right] K_0 \left[r_D' \sqrt{\frac{r_w^2 \lambda}{D_m}} \right] \right] r_D' dr_D' \\ & r_D > r_D' \end{aligned} \quad (98b)$$

In the very special case where the molecular diffusion equals to zero, the solution to the secondary tracer flow during the shut-in period reduces to

$$C_{2s}(r_D, \lambda) = \left[C_2(r_D, \lambda) + \frac{k\Phi}{\lambda r_w^2} \cdot C_{1s}(r_D, \lambda) \right] \frac{1}{\lambda} \quad (92)$$

Equation 99 is also applicable for such values of $(\lambda r_w^2/D_m)$ that make Eq. 98 singular.

4.4. TRACER PRODUCTION PERIOD

4.4.1. Primary Tracer

The hydrodynamics of tracer flow during the production period is basically the same as during the injection period though the flow velocity is reversed in the latter.

The primary tracer flow equation can therefore be written as:

$$\frac{1}{r_D} \frac{\partial}{\partial r_D} \left[r_D D(r_D) \frac{\partial C_{1p}}{\partial r_D} \right] + \frac{\alpha}{r_D} \frac{\partial C_{1p}}{\partial r_D} - \Phi k_r C_{1p} = \Phi \frac{\partial C_{1p}}{\partial t} \quad (100)$$

where C_{1p} is primary tracer concentration during the production period while Φ and r_D retain their usual definitions as

$$r_D = \frac{r}{r_w} \quad (28a)$$

and

$$\Phi = r_w^2 \left[1 + \frac{S_0 K_1}{S_w} \right] \quad (28b)$$

respectively.

To construct an inner-boundary condition to Eq. 100, we can take the simplest route by setting the effluent concentration equal to the *in-situ* concentration. Thus the associated initial and boundary conditions to Eq. 100 are:

$$C_{1p}(r_D, t = 0) = C_{1s}(r_D, t_{sh}) \quad (101a)$$

$$C_{1p}(r_D \rightarrow \infty, t) = 0 \quad (101b)$$

$$C_{1p}(r_D = 1, t) = f_{1p}(r_D = 1, t) \quad (101c)$$

Equation 101a stipulates that the *in-situ* tracer concentration at the initial time of production be equal to the tracer concentration at the end of shut-in period as would be expected. Equation 101b says that the tracer concentration level at an infinitely located position in the system be zero, while Eq. 101c is a statement of the equality of the effluent concentration and the *in-situ* concentration at the wellbore.

The effluent concentration $f_{1p}(r_D = 1, t)$ is defined as in Eq. 15 to be:

$$f_{1p}(r_D = 1, t) = \left[C_{1p} - \frac{D(r_D)}{\alpha} \frac{\partial C_{1p}}{\partial r} \right]_{r_D=1} \quad (102)$$

Using Eq. 102 in Eq. 101c and simplifying yields:

$$\left[\frac{\partial C_{1p}}{\partial r_D} \right]_{r_D=1} = 0 \quad (103)$$

Using basically the same analytical approach that was used during the injection period, we can expand Eq. 100 to the form

$$\frac{\partial^2 C_{1p}}{\partial r_D^2} + \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right] \frac{\partial C_{1p}}{\partial r_D} - \frac{\Phi k_r}{D} C_{1p} = \frac{\Phi}{D} \frac{\partial C_{1p}}{\partial t} \quad (104)$$

Using a transform of type

$$C_{1p}(r_D, t) = \phi_{1p}(r_D, t) \exp - \left[\frac{1}{2} \int_{r_D=1}^{r_D} \left[\frac{D'}{D} + \frac{D + \alpha}{D\xi} \right] d\xi \right] \quad (105)$$

on Eq. 104, we have

$$\frac{\partial^2 \phi_{1p}}{\partial r_D^2} - \left[U_{1p}(r_D, D) + \frac{k_r \Phi}{D} r_D \right] \phi_{1p} = \frac{\Phi}{D} \frac{\partial \phi_{1p}}{\partial t} \quad (106a)$$

where

$$U_{1p}(r_D, D) = \frac{1}{4} \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right]^2 + \frac{1}{2} \frac{d}{dr_D} \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right] \quad (106b)$$

subject to the following initial and boundary conditions:

$$\phi_{1p}(r_D, t=0) = \hat{C}_{1s}(r_D, t_{sh}) \quad (107a)$$

$$\left[\frac{\partial \phi_{1p}}{\partial r_D} - \frac{1}{2} \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right] \phi_{1p} \right]_{r_D=1} = 0 \quad (107b)$$

$$\phi_{1p}(r_D \rightarrow \infty, t) = 0 \quad (107c)$$

where

$$\hat{C}_{1s}(r_D, t_{sh}) = C_{1s}(r_D, t_{sh}) \exp \left[\frac{1}{2} \int_1^{r_D} \left[\frac{D'}{D} + \frac{D + \alpha}{D\xi} \right] d\xi \right] \quad (107d)$$

Substituting the appropriate functions for $D(r_D)$

$$D(r_D) \approx \frac{\alpha D_0}{r_D} \quad (37)$$

Equations 106 and 107 become

$$\frac{\partial^2 \phi_{1p}}{\partial r_D^2} - \left[\frac{1}{4D_0^2} + \frac{\Phi k_r}{\alpha D_0} r_D \right] \phi_{1p} = \frac{\Phi r_D}{\alpha D_0} \frac{\partial \phi_{1p}}{\partial t} \quad (108)$$

subject to

$$\phi_{1p}(r_D, t = 0) = \hat{C}_{1s}(r_D) \quad (109a)$$

$$\phi_{1p}(r_D \rightarrow \infty, t) = 0 \quad (109b)$$

$$\left[\frac{\partial \phi_{1p}}{\partial r_D} - \frac{\phi_{1p}}{\alpha D_0} \right]_{r_D=1} = 0 \quad (109c)$$

Equations 108 and 109 can be solved in Laplace space to obtain a solution of the form (Appendix E):

$$\begin{aligned} \bar{C}_{1p}(\xi, \lambda) &= \frac{\pi \Phi}{\alpha D_0} \beta^{1/3} \left[\frac{\beta^{2/3} [A'_i(x)_{x_1} B_i(x) - A_i(x) B'_i(x)_{x_1}] - \gamma [A_i(x_1) B_i(x) - A_i(x) B_i(x_1)]}{\beta^{2/3} A'_i(x)_{x_1} - \gamma A_i(x_1)} \right] \\ &\cdot \int_{r_D=1}^{\infty} A_i(x') C_{1s}(r'_D) \exp \left[\frac{r'_D - r_D}{\alpha D_0} \right] r'_D dr'_D ; \quad x(r_D) \leq x'(r'_D) \end{aligned} \quad (110a)$$

and

$$\begin{aligned} \bar{C}_{1p}(\xi, \lambda) &= \frac{\pi \Phi}{\alpha D_0} \beta^{1/3} A_i(x) \int_{r_D=1}^{\infty} \left[\frac{\beta^{2/3} [A'_i(x)_{x_1} B_i(x') - A_i(x') B'_i(x)_{x_1}] - \gamma [A_i(x_1) B_i(x') - A_i(x') - A_i(x') B_i(x_1)]}{\beta^{2/3} A'_i(x)_{x_1} - \gamma A_i(x_1)} \right] \\ &\cdot C_{1s}(r'_D) \exp \left[\frac{r'_D - r_D}{\alpha D_0} \right] r'_D dr'_D ; \quad x(r_D) > x'(r'_D) \end{aligned} \quad (110b)$$

The effluent concentration is given as

$$\bar{C}_p[\xi(r_D = 1), \lambda] = - \frac{\Phi \beta}{\alpha D_0} \int_{r_D=1}^{\infty} \frac{A_i(x') C_{1s}(r'_D) \exp \left[\frac{r'_D - 1}{\alpha D_0} \right] r'_D dr'_D}{\beta^{2/3} A'_i(x)_{x_1} - \gamma A_i(x_1)} \quad (111)$$

4.4.2. Secondary Tracer

The secondary tracer flow equation during the production period can be written as

$$\frac{1}{r_D} \frac{\partial}{\partial r_D} \left[r_D D(r_D) \frac{\partial C_{2p}}{\partial r_D} \right] + \frac{\alpha}{r_D} \frac{\partial C_{2p}}{\partial r_D} + \Phi k_r C_{1p} = r_w^2 \frac{\partial C_{2p}}{\partial t} \quad (112)$$

The associated initial and boundary conditions are

$$C_{2p}(r_D, t = 0) = C_{2s}(r_D) \quad (113a)$$

$$C_{2p}(r_D \rightarrow \infty, t) = 0 \quad (113b)$$

$$f_{2p}(\lambda) = C_{2p}(r_D = 1, \lambda) \quad (113c)$$

Using the same procedures as were used for the primary tracer, Eqs. 112 and 113 can be written in the Laplace space as (Appendix F):

$$\frac{d^2 \bar{\Phi}_{2p}}{dr_D^2} - \left[\frac{1}{4D_0^2} + \frac{r_w^2 \lambda}{\alpha D_0} r_D \right] \bar{\Phi}_{2p} = -\frac{r_D}{\alpha D_0} [r_w^2 \hat{C}_{2s}(r_D) + \Phi k_r \hat{C}_{1p}(r_D)] \quad (114a)$$

where

$$\hat{C}_{2s}(r_D) = C_{2s} \exp \left[\frac{r_D - 1}{\alpha D_0} \right] \quad (114b)$$

subject to

$$\bar{\Phi}_{2p}(r_D \rightarrow \infty, \lambda) = 0 \quad (115a)$$

$$\frac{d\bar{\Phi}_{2p}}{dr_D} - \delta \bar{\Phi}_{2p} = 0 \quad (115b)$$

where

$$\delta = \frac{0.5}{D_0} \left[\frac{\alpha D_0}{\lambda r_w^2} \right] \quad (115c)$$

Equations 114 and 115 can be solved in the Laplace space to obtain

$$\bar{C}_{2p}(\xi, x) = \left[\frac{\sigma^{2/3} [A_i'(z)_{z_1} B_i(z) - A_i(z) B_i'(z)_{z_1}] - \delta [A_i(z_1) B_i(z) - A_i(z) B_i(z_1)]}{\sigma^{2/3} A_i'(z)_{z_1} - \gamma A_i(z_1)} \right. \\ \left. \cdot \frac{\pi \sigma^{1/3}}{\alpha D_0} \int_{r_D=1}^{\infty} A_i(z') \exp \left[\frac{r_D' - r_D}{2D_0} \right] [r_w^2 C_{2s}(r_D') + \Phi k_r C_{1p}(r_D')] r_D' dr_D' ; z(r_D) \leq z'(r_D) \right] \quad (116a)$$

$$\bar{C}_{1p}(\xi, \lambda) = \frac{\pi \sigma^{1/3}}{\alpha D_0} A_i(z) \int_{r_D=1}^{\infty} \exp \left[\frac{r_D' - r_D}{2D_0} \right] [r_w^2 C_{2s}(r_D') + \Phi k_r C_{1p}(r_D')] r_D' \\ \left[\frac{\sigma^{2/3} [A_i'(z) B_i(z') - A_i(z') B_i'(z)_{z_1}] - \sigma [A_i(z)_{z_1} B_i(z') - B_i(z_1) A_i(z')] }{\sigma^{2/3} A_i'(z)_{z_1} - \delta A_i(z_1)} \right] dr_D'; z(r_D) > z'(r_D) \quad (116b)$$

where

$$z = \sigma^{2/3} \eta \quad (117a)$$

$$\eta(r_D) = \frac{1}{4D_0^2} + \frac{r_w^2 \lambda}{\alpha D_0} r_D \quad (117b)$$

and

$$\sigma = \left[\frac{\alpha D_0}{\lambda r_w^2} \right] \quad (117c)$$

The effluent concentration is obtained at the wellbore where $x(r_D) = x(r_D = 1)$ as:

$$\bar{\Phi}[\xi(r_D = 1), \lambda] = \frac{-\sigma}{\alpha D_0} \int_{r_D=1}^{\infty} \frac{A_i(\sigma^{2/3} \eta') [r_w^2 C_{2s}(r_D') + \Phi k_r C_{1p}(r_D')] r_D' dr_D'}{\sigma^{2/3} A_i'([\sigma^{2/3} \eta(r_D = 1)]) - \delta A_i([\sigma^{2/3} \eta(r_D = 1)])} \quad (118)$$

5. DISCUSSION AND RESULTS

Diffusion models in radial coordinates under conditions of shear mixing and reaction, here referred to as the *radial-diffusion-convection-reaction* (or R-D-C-R) systems of differential equations, are the appropriate models for single-well tracer tests for residual oil saturation evaluation. Similar models without reaction have been used in other areas of studies such as miscible flood or tracer test in patterned flow (Brigham and Smith, 1965). Whether applied to tracer tests or other studies, past usages of the R-D-C-R system of differential equations always end up with approximate analytical solutions. In the particular case of single-well tracer tests, there are approximate solutions for the tracer injection phase (Antunez, 1984), but no known successful attempt has been made to obtain an analytical solution, be it exact or approximate, to the tracer production phase of the single-well tracer test model. Previous workers have had to lean rather heavily on intuitive reasoning (Antunez, 1984) or the use of numerical simulation (Tomich, 1973; Chase, 1971) models, to work out what one can call an "engineering solution." The exact analytical solution demonstrated in the report is therefore the first known solution in the literature.

5.1. TRACER INJECTION PERIOD

One of the important achievements of this work is the development of exact analytical solutions to the R-D-C-R systems of differential equations from which analytical expressions to all phases of operation for a single-well tracer test can be obtained.

In this section of our report, therefore, we will describe the characteristics of our exact solution and compare this to known approximation solution of the Antunez-Brigham-Raimondi models.

Throughout this report, we have found it very convenient to develop our analytical solutions in Laplace space. Because of the nature of these solutions it was not considered prudent to attempt an inversion to real time space. Instead a numerical inversion procedure using the Stehfest inversion algorithm (Stehfest, 1970) was used. The numerical inversion was found to be most stable for the system of equations developed when $N = 16$ iterations.

Using Eq. 46, the exact analytical solution to the R-D-C-R system of differential equations and the Stehfest algorithm, tracer concentration profiles were generated for various times of injection in the range 1.0 to 9.0 days as shown in Fig. 5.1. As should be expected, the traces penetrates the reservoir deeper and deeper as injection continues but the rate of penetration decreases a the time of injection increases. This tends to confirm in a qualitative way, our earlier assumption that

$$v_w(r) = \frac{\alpha}{r_D} \quad (10)$$

which suggests that flow velocity decreases with increasing radius. It must be mentioned that Eq. 10 is based on material balance consideration and therefore r_D must be the average dimensionless radius of penetration.

Analytical solution represented by Eq. 46 for the tracer injection phase provides a valuable opportunity to examine the correctness of some of the known approximate solutions available in the literature.

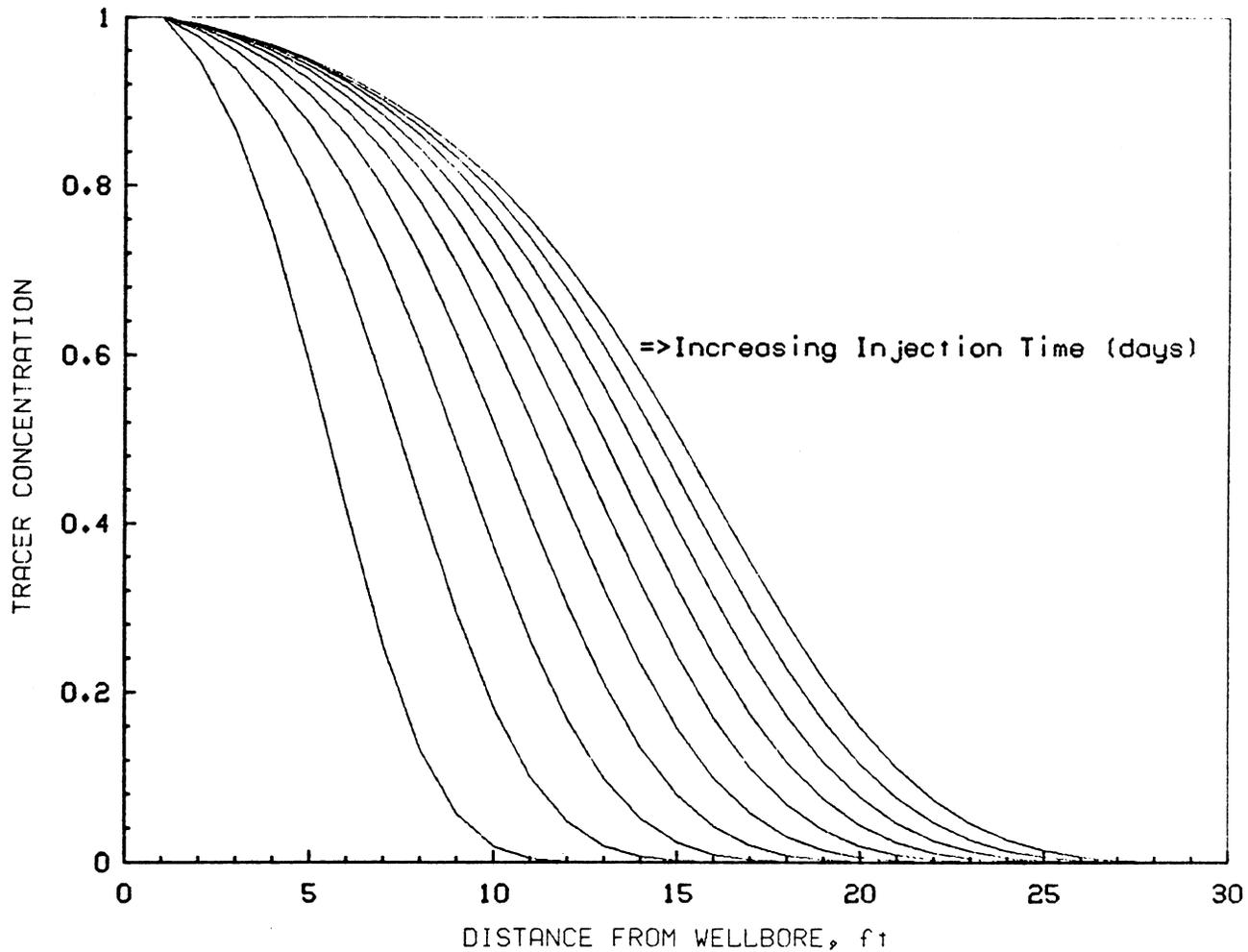


Fig. 5.1 Primary Tracer Concentration Profiles
(Continuous Tracer Injection Model).

5.1.1. Comparison of Injection Phase Solutions

Equation 46 is a solution to the R-D-C-R system of differential equation. The closest approximate solutions to similar problems in the literature do not take account of reaction. Therefore in order to establish a basis for comparing these approximate solution to our exact solution, Eq. 46 must be evaluated with a reaction rate constant of zero ($k_r = 0$). Under such conditions, we can validly compare our exact solutions with the approximate solutions of Antunez (1980), Brigham and Smith (1965).

The work of Antunez was based largely on the earlier work of Brigham and Smith even though the former is not presented in radial geometry. In as much as the techniques of solution are identical, we can present these two approximate solutions in a unified form as:

$$C(r, t) = \frac{C_0}{2} \operatorname{erfc} \left[\frac{r^2 - \bar{r}^2}{2\sqrt{\frac{4}{3} \alpha r^3}} \right] \quad (119a)$$

when \bar{r} is defined as

$$\bar{r} = \sqrt{\frac{qt}{\pi h \phi (S_w + \alpha S_0)}} \quad (119b)$$

The parameter α in Eqs. 119 is the diffusion constant for the flowing system and ϕ is the formation porosity.

Figure 5.2 is a comparison of Eq. 119 with the exact analytical solution when $k_r = 0$. It is clear from this figure that approximate solution is reasonably good for small values of radial distance from wellbore. However, with the approximation solution, the tracers seem to move faster than they should be at trailing edge; and, particularly so, at the leading edge of the tracer concentration profile.

Under normal conditions of operations for a single-well tracer test, a slug injection of tracer is followed with an injection of tracer-free water. The analytical solutions for this latter mode of injection are easily obtained from Eqs. 108 and 46 using linear superposition in time, i.e.,

$$C(r, t) = C(r, t) - C(r, t_1) \quad (120)$$

where

- t = total time of injection
- t_1 = time of tracer-free water injection

Using the above technique, on Eq. 119, the approximate solution for tracer slug injection was obtained and compared with the exact analytical solutions presented as Eq. 47, modified for a system with $k_r = 0$.

Figure 5.3 is a graphical comparison of the exact and approximate solution under conditions described above. As was seen in Fig. 5.2, the tracers remain faster than normal at the edges particularly at the leading edge. This apparent fast motion at the leading edges may be

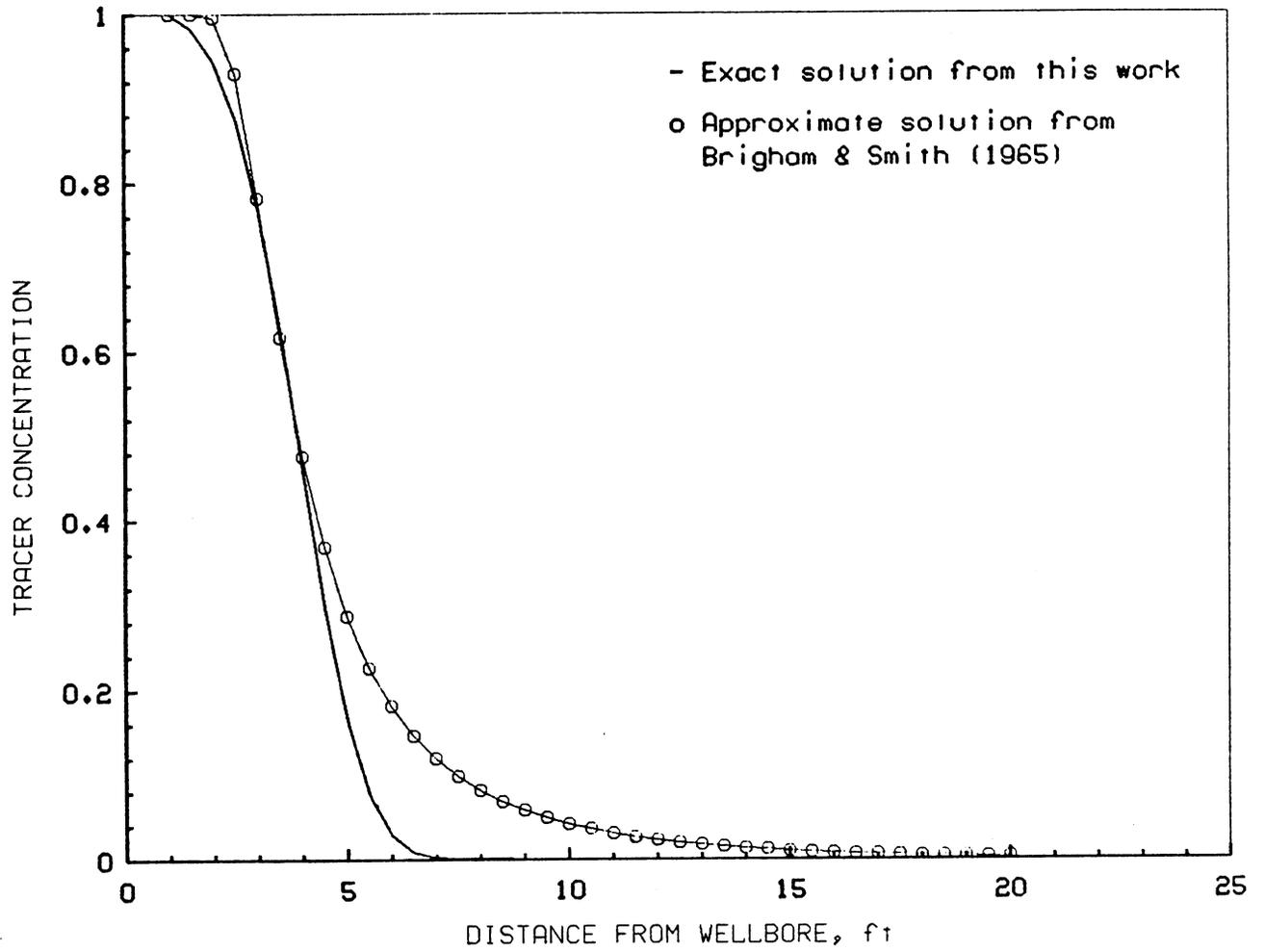


Fig. 5.2 Comparison of Exact and Approximate Solutions (Continuous Tracer Injection Model).

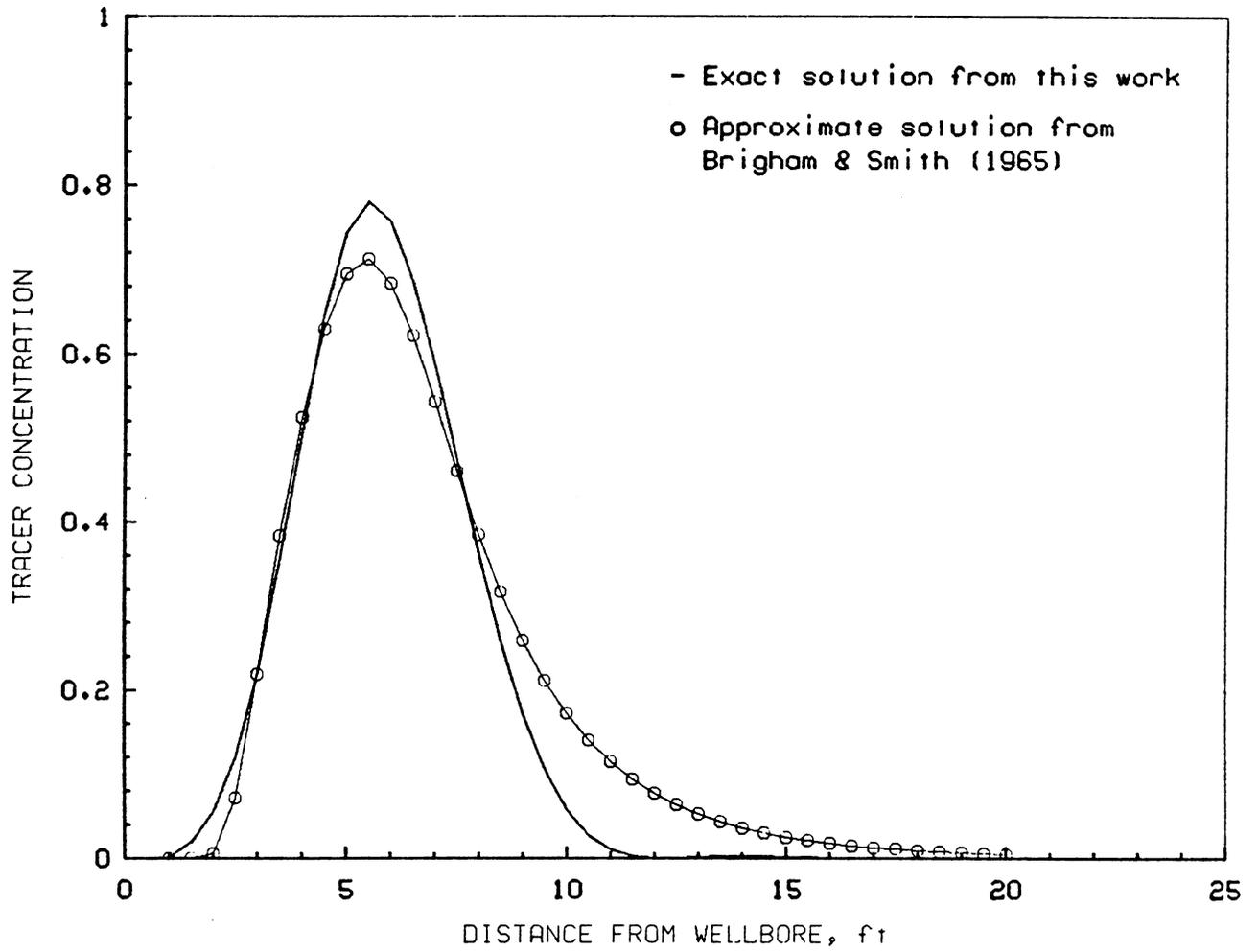


Fig. 5.3 Comparison of Exact and Approximate Solutions (Tracer Slug Injection Model).

due to excessive spreading in the forward direction. Since the α term is largely associated with spreading and it derives from the diffusion constant $D(r)$, the diffusion term $D(r)$ must have been underrated in the models that lead to the approximate solution under consideration. This is not surprising in that the approximate model was in fact based on the assumption that $\alpha(\partial^2 C/\partial r^2)$ term is relatively small.

An important fact about the approximate solution which is of interest is the fact that the point of maximum tracer concentration for both exact and approximate solutions are the same. This may suggest that the approximate solution may still give good test results for single-well tracer tests even when the predicted concentration values are not correctly predicted. This arises because analyses of single-well tracer test data are based on points of maximum concentration rather than the absolute concentration values.

Figures 5.4 and 5.5 show the concentration profiles at various injection times for the primary and the secondary tracers, respectively. These graphs are based on the exact analytical solutions for the secondary and the primary tracers under conditions of a slug injection of the primary tracer as presented in Eq. 64 and 47, respectively.

5.2. SHUT-IN PERIOD

During the shut-in period, the shear-mixing effect is absent, leaving the molecular diffusion and the chemical reaction effects. In the earlier referenced work of Antunez (1983), it was convenient to assume a negligible molecular diffusion term so that simple mathematical relations shown in Eqs. 85 and 99 can be used to describe tracer dynamics during the shut-in term.

In this study we have solved the tracer equation for a system where an effective molecular diffusion do exist. For cases where the molecular diffusion term becomes rather too small, the alternative solutions presented in Eqs. 85 and 99 are used for calculating the tracer concentration profiles.

Equations 84, 85, 91 and 99 are the exact solutions for the primary and secondary tracer equations during the shut-in period. Figure 5.6 is a composite graph showing the profiles of the primary and the secondary tracer before and after the shut-in period. A very interesting aspect of tracer dynamics during this period is emphasized in Fig. 5.6. During the shut-in period, tracers are only subjected to uniform molecular diffusion since the convection velocity is zero. The primary tracer, in particular, is also subjected to an irreversible first order reaction, forming new species of secondary tracers. The consequence of these superimposed simultaneous actions is that the primary tracer concentration decreases uniformly along its entire profile. The maximum decrease being at the point of maximum concentration as would be expected from reaction kinetics point of view. Most importantly, the point of maximum concentration for the primary tracer remains unchanged throughout the shut-in period. The secondary tracer on the other hand slowly builds up its concentration during the shut-in period. However, because, newly formed species of secondary tracers are only subjected to very slow brownian motions, they remain practically at the locality of formation. This localized buildup of secondary tracer causes the point of maximum concentration of the secondary tracer prior to shut-in to change continuously during the shut-in period as can be seen in Fig. 5.6. This phenomena also gives rise to the possibility that the points of maximum concentration of the secondary tracer can be shifted to coincide with that of the primary tracer by prolonging the shut-in period.

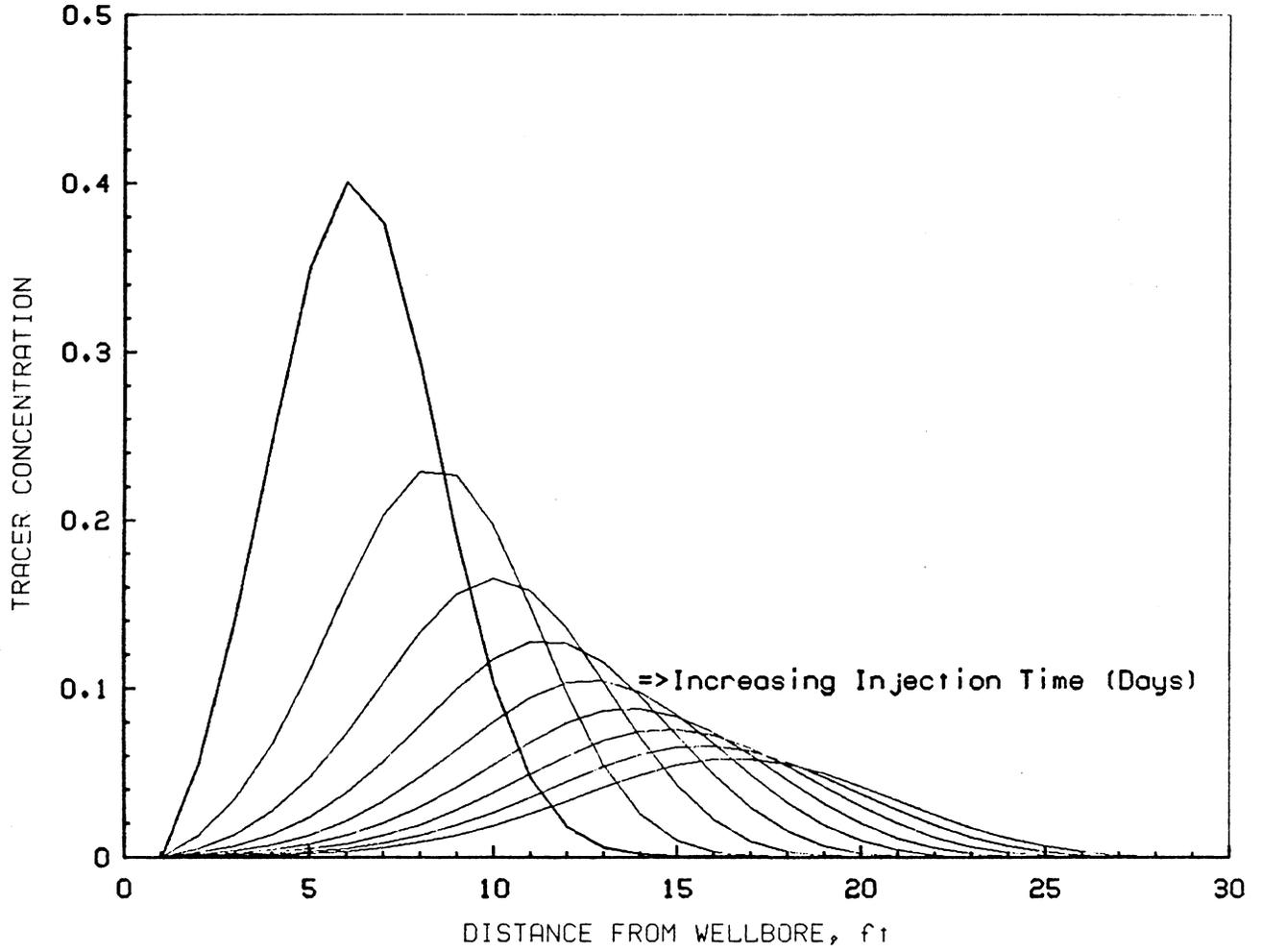


Fig. 5.4 Primary Tracer Concentration Profiles (Tracer Slug Injection Model).

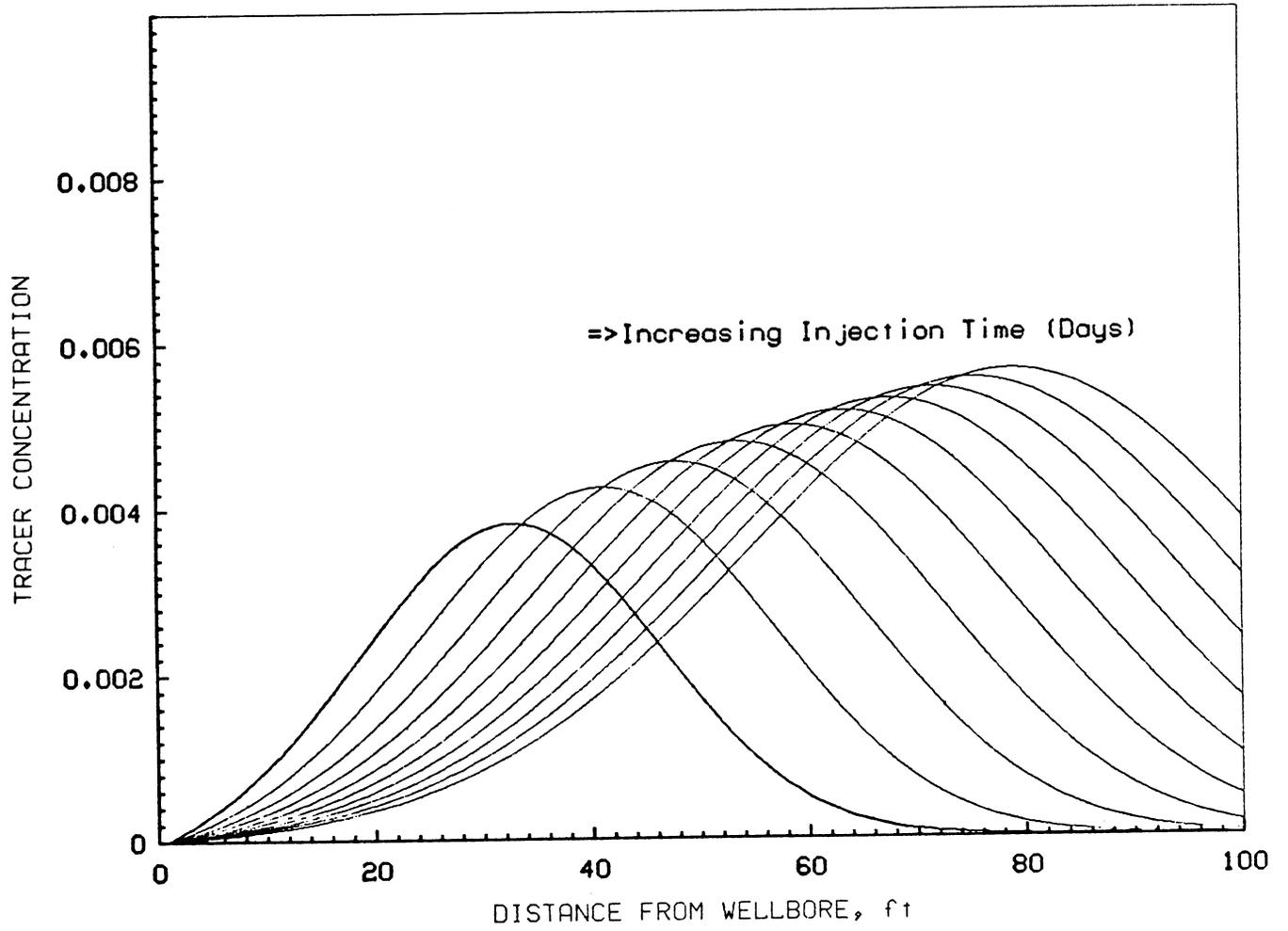


Fig. 5.5 Secondary Tracer Concentration Profiles
(Tracer Slug Injection Model).

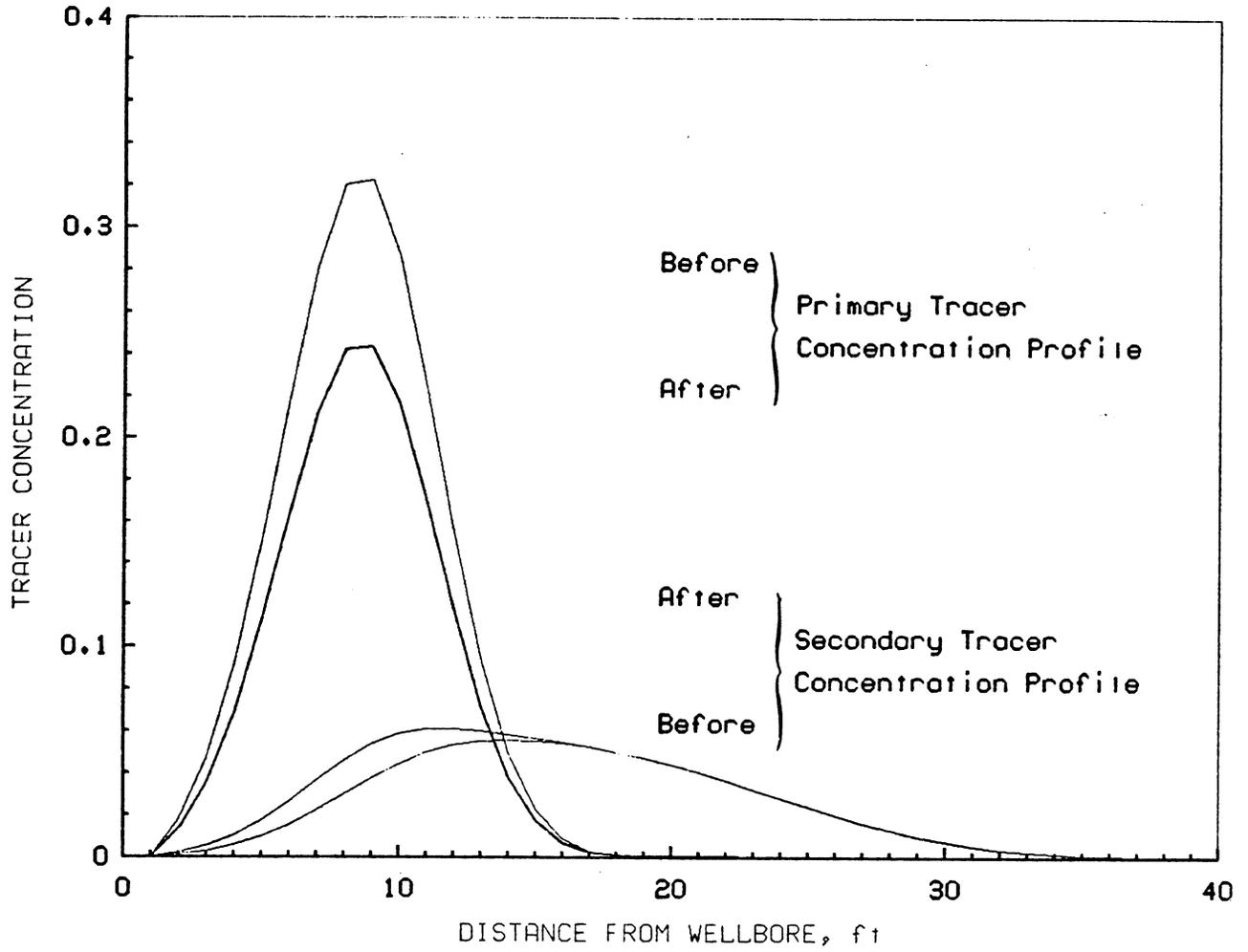


Fig. 5.6 Primary and Secondary Tracer Concentration Profiles Before and After Shut-in.

5.3. TRACER PRODUCTION PHASE

After the shut-in period, the well is opened up to flow so that the tracer species which have migrated deep into the reservoir are reversed out to be produced at the wellbore. To be able to solve the R-D-C-R system of differential equation for this flow period it was necessary to design an appropriate boundary condition(s) at the wellbore. The most attractive condition that initially came to mind was the Danckwerts (1953) or Parulekar *et al.*, (1984) boundary condition. This, basically, is a material balance equation at the wellbore, viz.

$$qf + \Phi \frac{\partial C}{\partial t} = 0 \quad (121)$$

where f is the effluent concentration defined in Eq. 15 or Eq. 102. The alternative procedure was to specify that the effluent concentration be the same as the *in-situ* concentration at the wellbore, i.e.,

$$f = C(r_D = 1, t) \quad (122)$$

The latter was eventually used as the inner boundary condition largely because the Stehfest numerical inversion routine gave a more stable result than with the former. The mathematics of using either of these boundary conditions are identical.

Using the inner boundary condition (Eq. 122), the tracer production equation was solved to obtain the solution expressed in Eq. 110. This equation describes primary tracer distribution in the reservoir for all the values of time. A similar solution using precisely the same method was obtained for the secondary tracer as shown in Eq. 116.

For purposes of data analyses, the most important piece of information needed from a single-well tracer test is the production concentration profiles of the various tracer species at the wellbore. Analytical relations for these concentration profiles for the primary and the secondary tracers are easily derivable from Eqs. 110 and 116 respectively by setting $r_D = 1.0$. Such relations are contained in Eq. 111 for the primary tracer and Eq. 118 for the secondary tracer.

Figure 5.7 is a graphical presentation of Eq. 110 for *in-situ* tracer distribution after production times of 0.0, 0.4, 0.8 and 2.0 days. As can be observed in this graph, the peak concentration in the reservoir at any given time falls to lower values as production continues. As a result of this, the highest concentration produced at the wellbore is always less than the peak tracer concentration in the reservoir just before production was initiated. This decrease is due largely to chemical reaction, which continuously converts the primary tracer to the secondary tracer, and to a lesser extent, to shear-mixing and diffusion as tracer flows back to the wellbore. In this particular experiment, our peak concentration breakthrough to the wellbore at about 1.6 days. After this time, the wellbore production concentrations gradually falls as shown in Fig. 5.8.

The behavior of the secondary tracer during production is somewhat different. Because new species of secondary tracers are formed as tracer production proceeds the *in-situ* concentration of the secondary tracer increases sharply initially. Also, because some of the secondary tracer is being produced at the wellbore, the effect of tracer depletion coupled with shear-mixing and diffusion tends to push down the peak concentration of the secondary tracer. These opposing effects of depletion, shear mixing and chemical reaction tend to slow down the growth of the secondary tracer concentration in the reservoir. The *in-situ* concentration of the

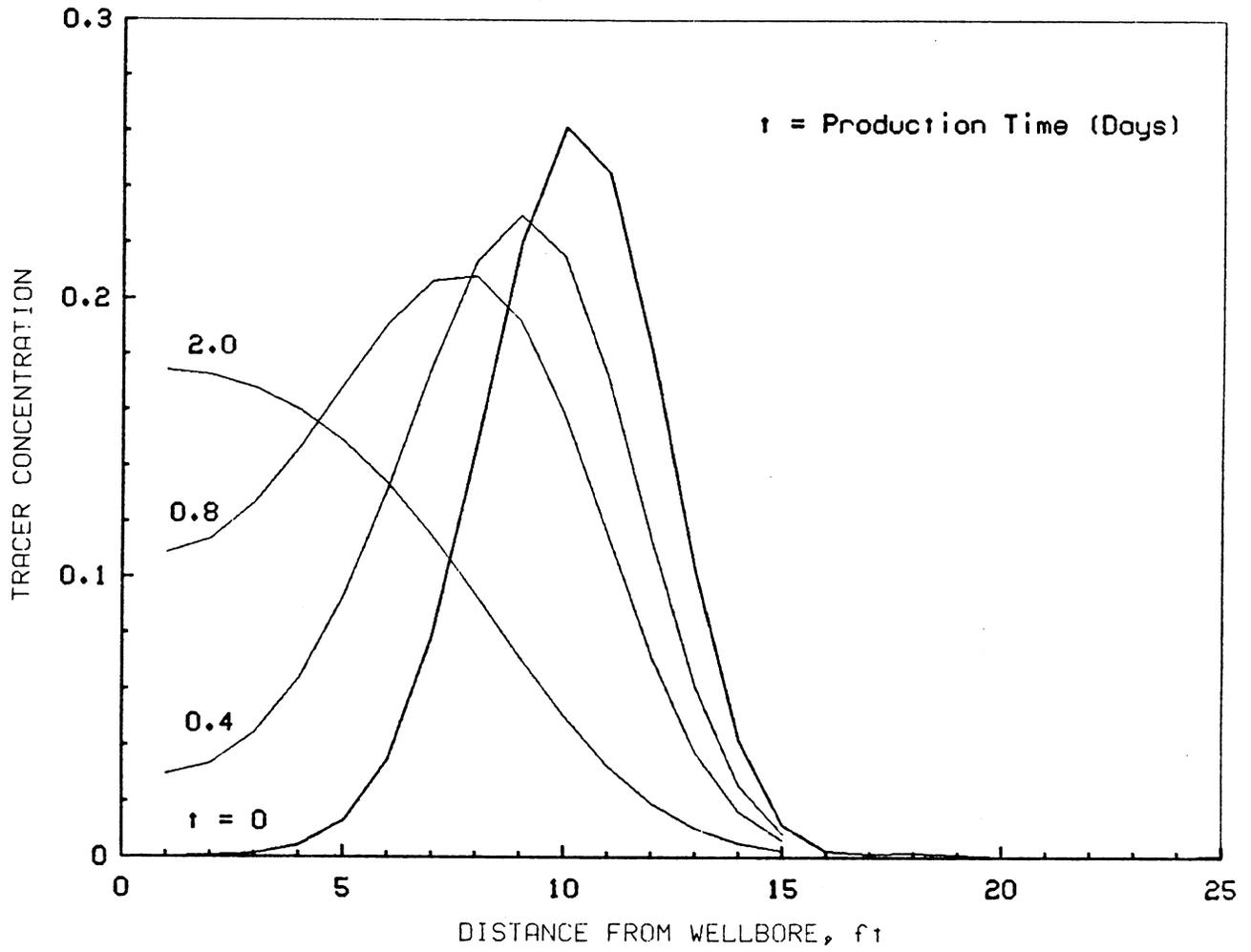


Fig. 5.7 Primary Tracer Concentration Profiles (Production Period).

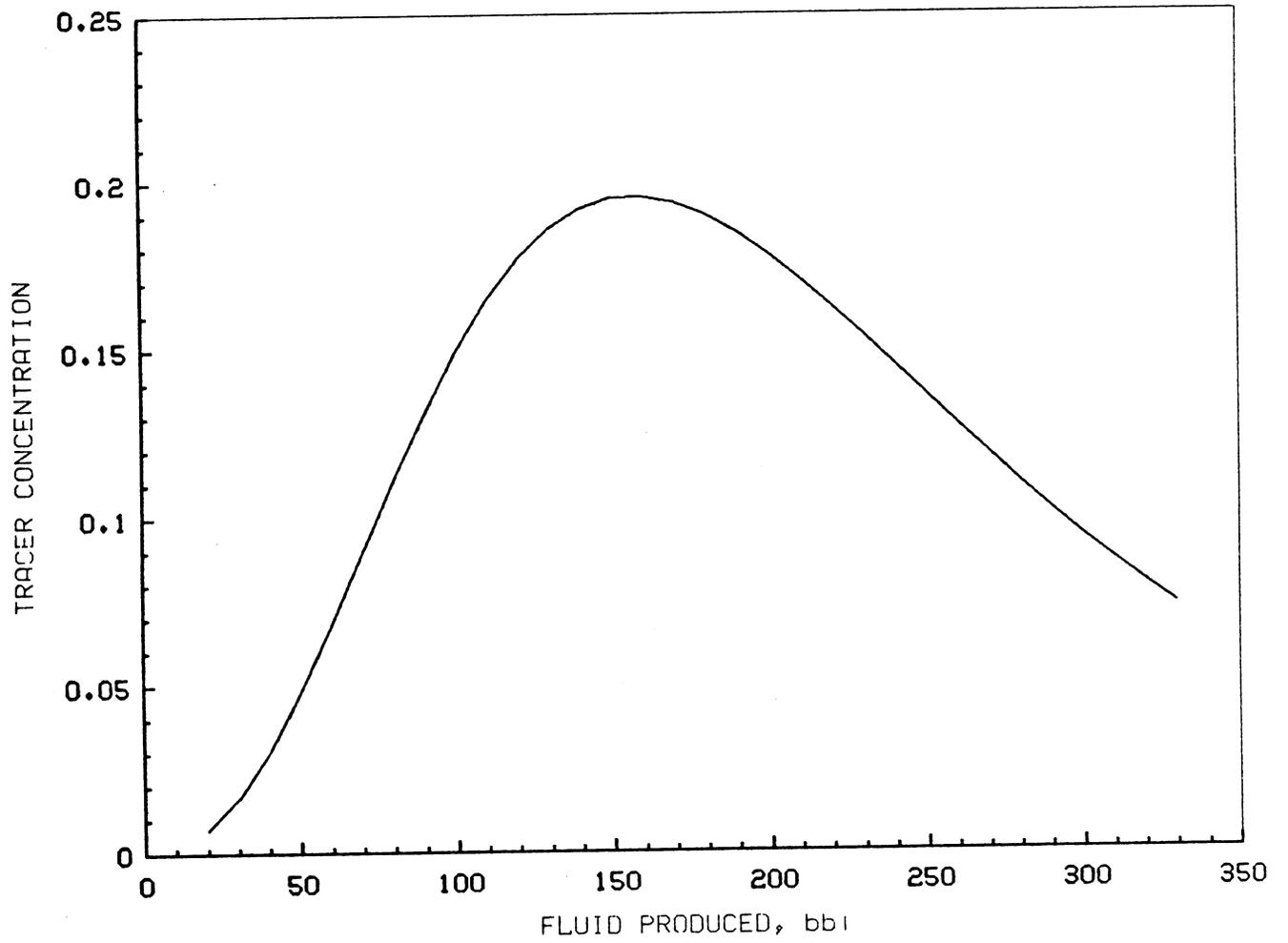


Fig. 5.8 Produced Primary Tracer Concentration Profile.

secondary tracer is, however, maintained at higher values than it was prior to initiating production. This remains so until the peak tracer concentration breakthrough to the wellbore. Beyond this time, the secondary tracer concentration at the wellbore and in the reservoir fall gradually to zero as production continues. Figure 5.9 is a graphical representation of secondary tracer production concentration variation with time. Figure 5.10 is the corresponding wellbore concentration history.

5.4. CORRELATION OF TRACER PEAK CONCENTRATION

In single-well tracer test, tracer production curves are usually characterized by evaluating the arrival times of the produced tracer peak concentrations. These times of arrival (or their variants) are then correlated to evaluate the required reservoir *in-situ* fluid saturation.

The times of arrival of the peak concentrations for the primary and the secondary tracers are known to be influenced by various test parameters (Antunez, 1983) such as:

- Fluid injection and production rates q_i, q_p
- Tracer slug injection time t_s
- Tracer free water injection time t_1
- Total shut-in time t_{sh}
- Convective mixing constant D_0
- Formation adsorption constant K
- Formation *in-situ* mobile fluid saturations S_w and possibly
- Formation porosity ϕ .

In mathematical terms the above can also be presented as

$$t_{bt} = f(q_i, q_p, t_s, t_1, t_{sh}, D_0, K, S_w)$$

where t_{bt} is the arrival time of peak tracer concentration. In tracer test correlation, t_{bt} can be interpreted as the ratio of the arrival times of peak concentrations of the primary tracer to that of the secondary tracer as will be assumed in this analysis. Any attempt to investigate the individual effects of the above listed variables on t_{bt} will be expensive and time-consuming. An alternative approach which was tried by Antunez (1983) is to reduce the number of variables involved by designing tracer tests such that similar variables such as q_i and q_p , t_s , t_1 and t_{sh} are related in a prespecified manner. For this approach to be meaningful in terms of yielding a unique result, the governing solution equation must be uniquely expressible in terms of these predesigned variable groups only. This, however, may unfortunately not always be possible, particularly in cases such as this work where time is the variable of interest, and solution equations are only available in the Laplace space.

Figure 5.12 and 5.13 show the concentration production profiles for produced primary and secondary tracers; obtained for adsorption constants of 2.5 and 5.0, respectively. All other variables being the same for the two runs. In these experiments, the production rates of fluid are equal to the injection rates. As is evident in these graphs, the peak concentrations of the primary and the secondary tracer species move faster towards the wellbore for larger values of adsorption constants while the primary tracer species is largely unaffected. There may be other important factors which combine to generate the production characteristics shown in these graphs.

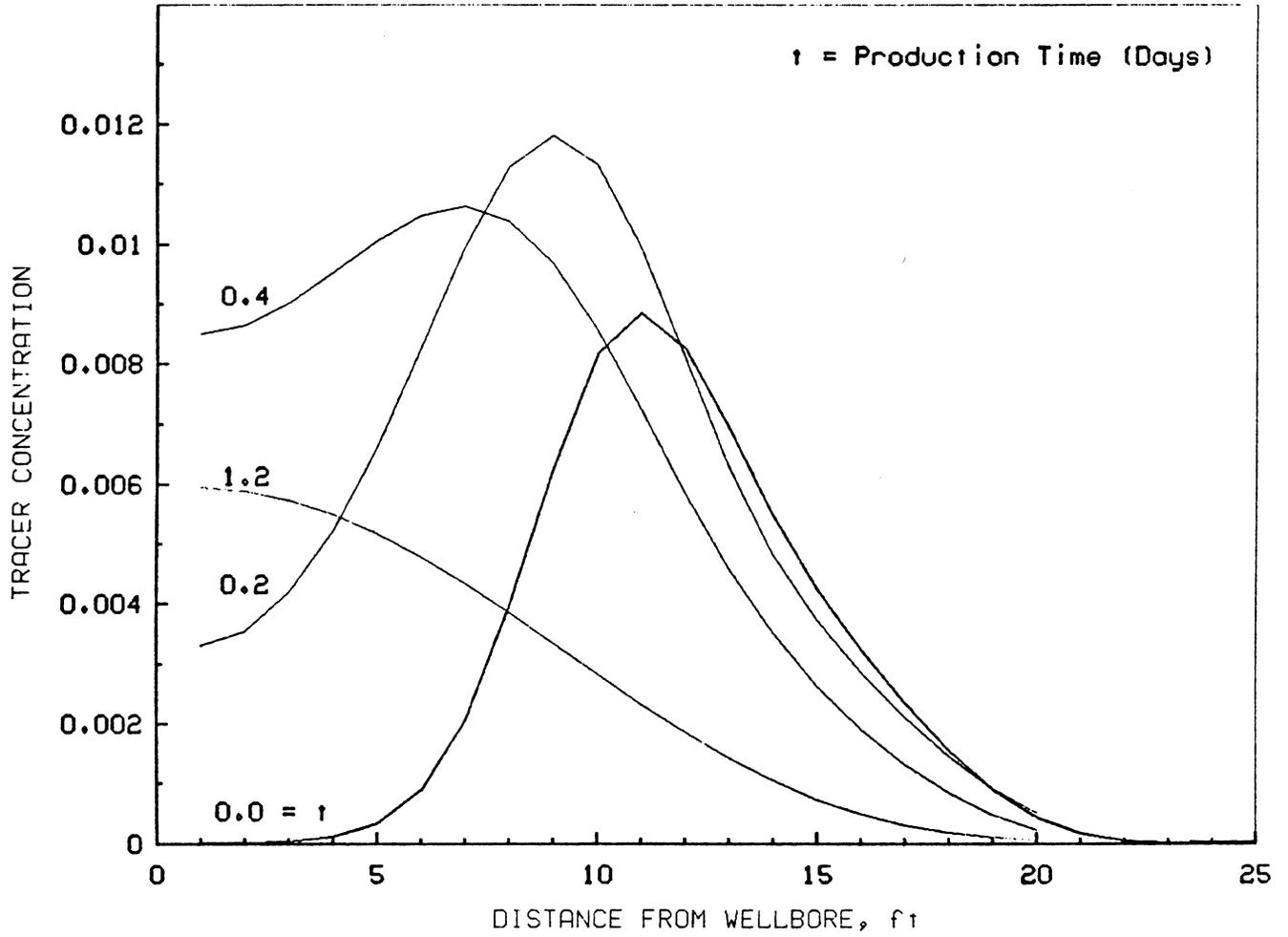


Fig. 5.9 Secondary Tracer Concentration Profiles (Production Period).

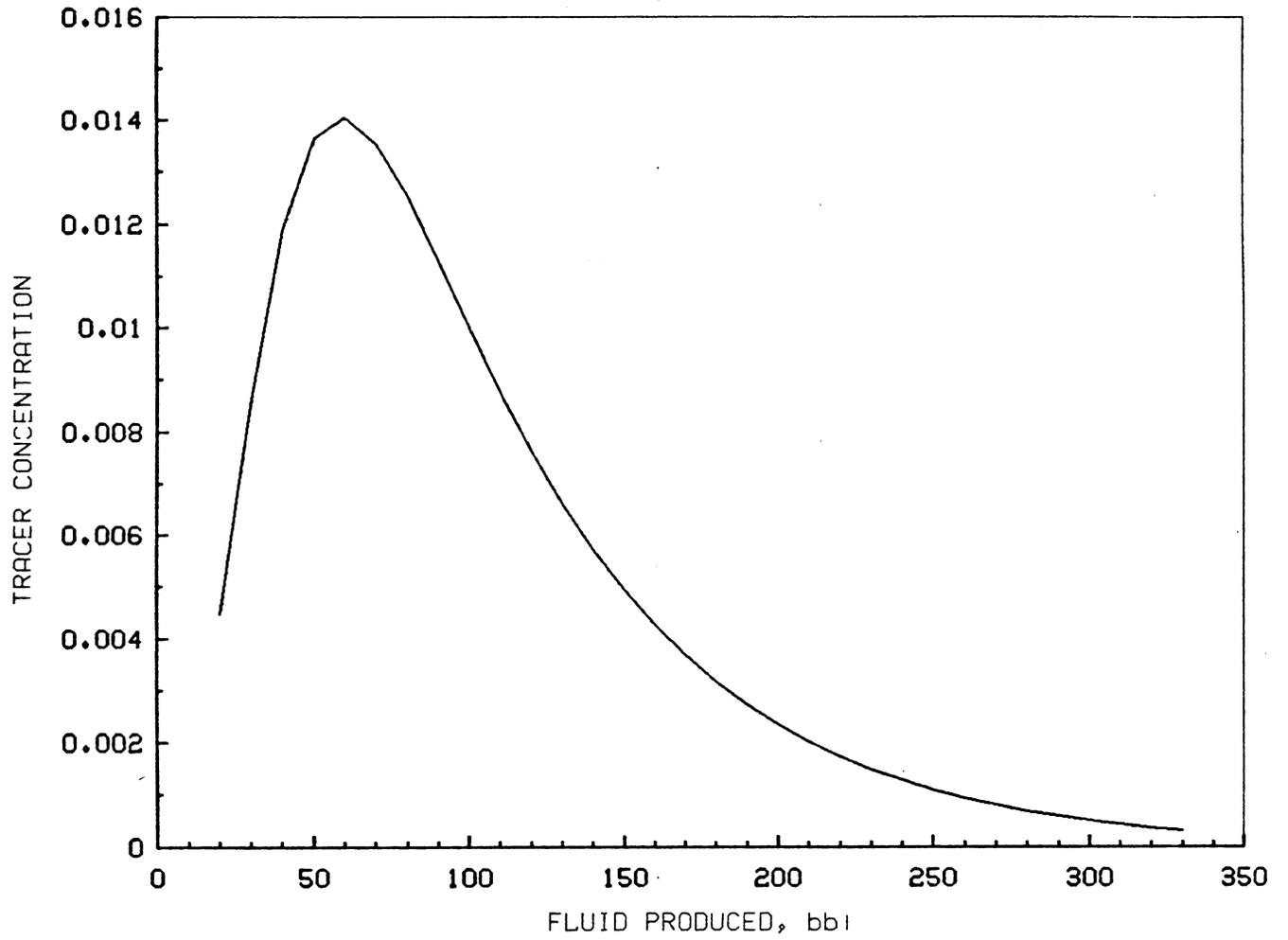


Fig. 5.10 Produced Secondary Tracer Concentration Profile.

Fluid Injection Rate (Barrels/Day) = 100.0
Tracer Slug Injection Time (Days) = 1.0
Pure Water Injection Time (Days) = 2.0
Total Injection Time (Days) = 3.0
Total Shut-in Time (Days) = 2.0
Convective Mixing Constant = 0.6
Formation Thickness (Feet) = 50.0
Formation Porosity = 0.25
Formation Water Saturation = 0.75
Formation Adsorption Constant = 5.0

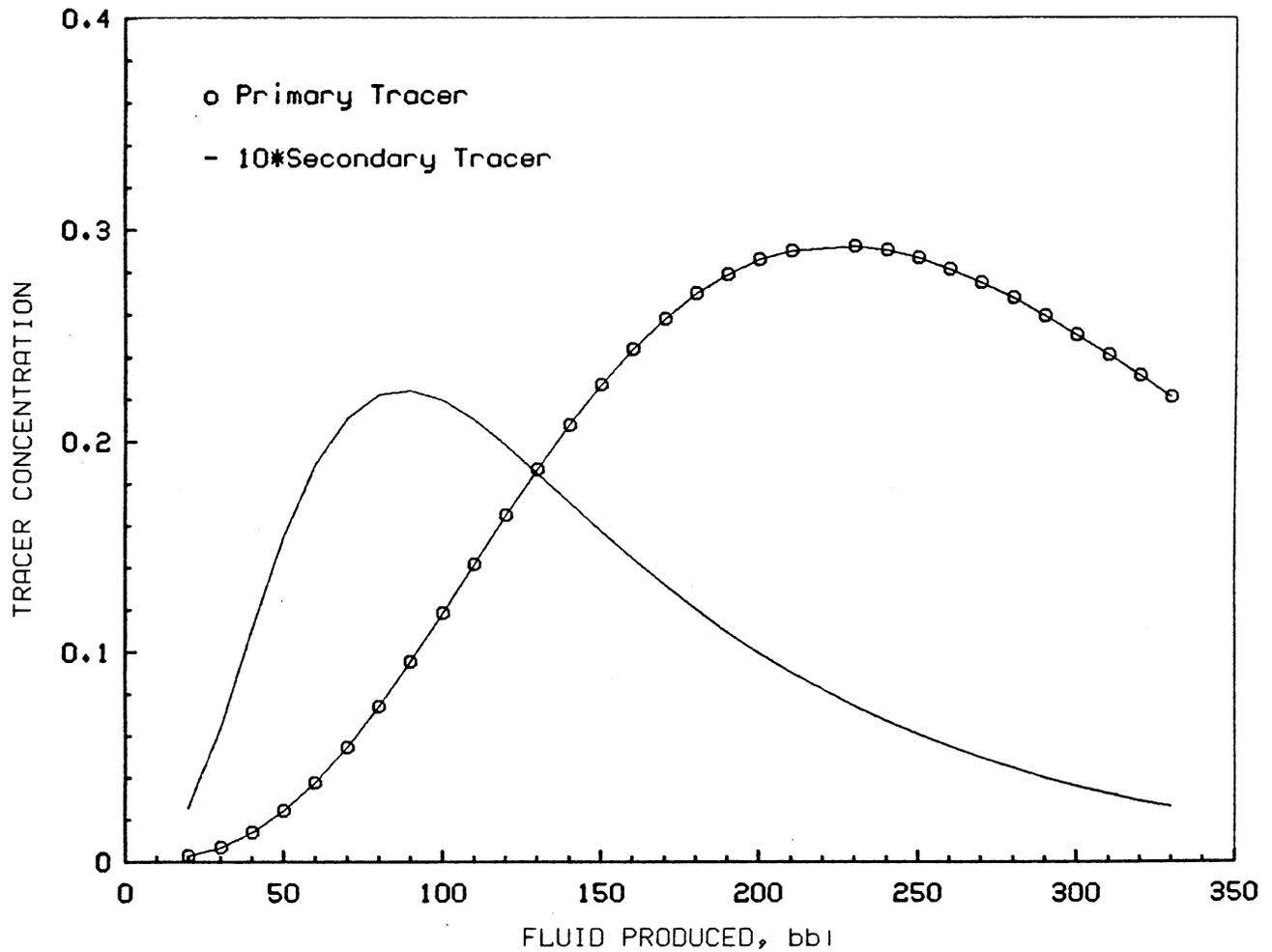


Fig. 5.11 Concentration Profiles of Produced Tracers.

Fluid Injection Rate (Barrels/Day) = 100.0
Tracer Slug Injection Time (Days) = 1.0
Pure Water Injection Time (Days) = 2.0
Total Injection Time (Days) = 3.0
Total Shut-in Time (Days) = 2.0
Convective Mixing Constant = 0.6
Formation Thickness (Feet) = 50.0
Formation Porosity = 0.25
Formation Water Saturation = 0.75
Formation Adsorption Constant = 2.5

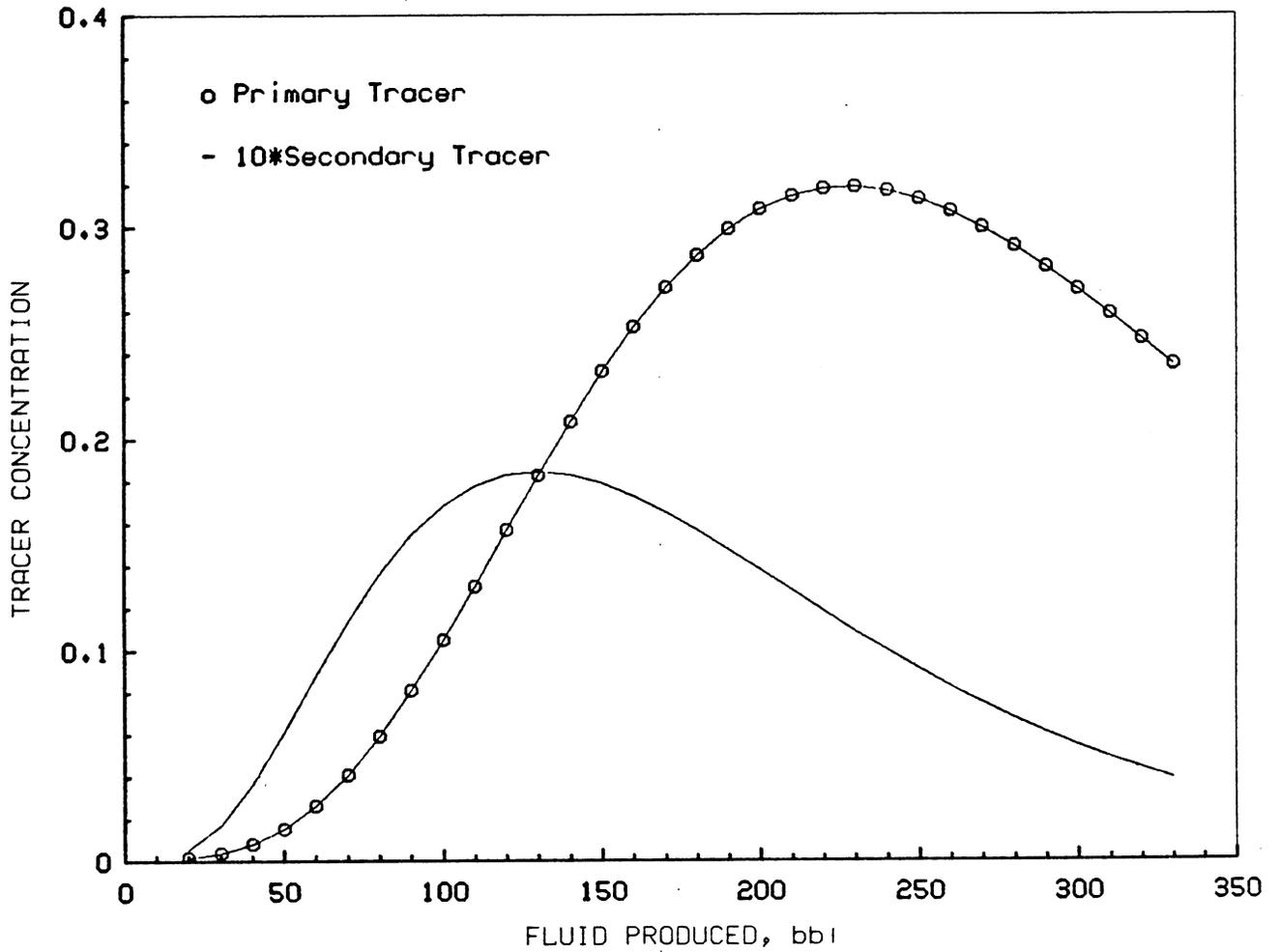


Fig. 5.12 Concentration Profiles of Produced Tracers.

Fluid Injection Rate (Barrels/Day) = 100.0
Tracer Slug Injection Time (Days) = 0.5
Pure Water Injection Time (Days) = 1.5
Total Injection Time (Days) = 2.0
Total Shut-in Time (Days) = 2.0
Convective Mixing Constant = 0.6
Formation Thickness (Feet) = 50.0
Formation Porosity = 0.25
Formation Water Saturation = 0.75
Formation Adsorption Constant = 5.0

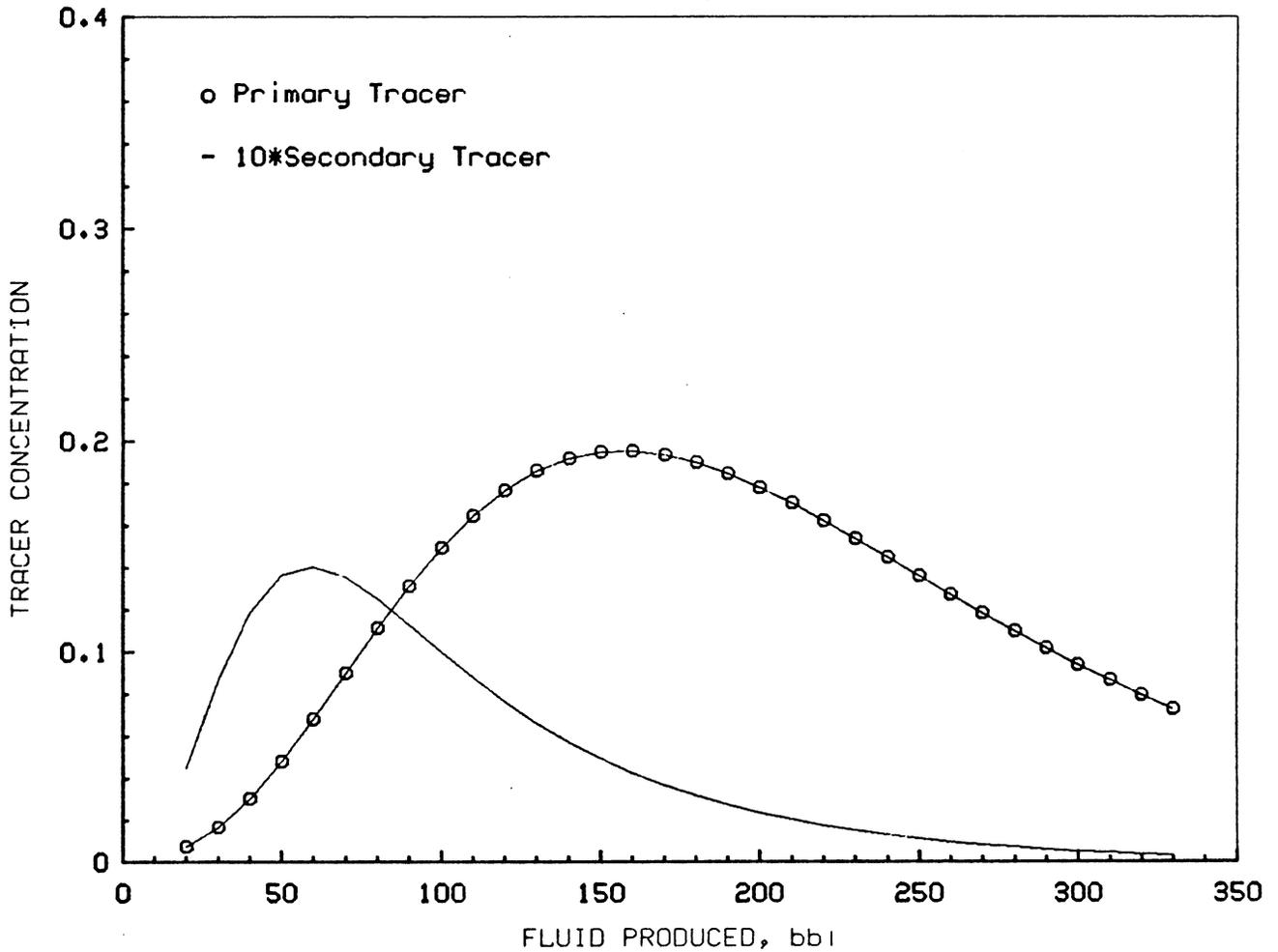


Fig. 5.13 Concentration Profiles of Produced Tracers.

Figures 5.11 and 5.13 are another set of production concentration profiles for the primary and secondary tracers. In this case, the rate of fluid injection or production are the same but the duration of tracer slug injections and tracer-free water injections are different. This means that fluid input in Fig. 5.11 is larger than in Fig. 5.13. As could be expected, the tracers move deeper into the formations at greater fluid input as shown in Fig. 5.11 compared to Fig. 5.13. This difference in fluid penetration into the formation is of a reflected when the tracers are produced; the rates for both experiments being the same at 100

Another interesting case is shown in Figs. 5.12 and 5.14. Here, the rate of injection/production are different at 100 B/D and 75 B/D, respectively, as in the last example. However, in this case, the ratio of the total volume of fluid injected to the volume of tracer slug injected are the same. A very casual observation seems to suggest that the production profiles for both figures look qualitatively the same. Figure 5.14 seems to show that both the primary and the secondary tracer peak concentrations breakthrough faster than in Fig. 5.12. However, if the fluid produced is converted to time, it is easily verified that the peak tracer concentrations for each for the primary and secondary tracers for each of these two experiments breakthrough at the same times of 1.3 and 2.3 days, respectively. This clearly shows that these two experiments are the same, and therefore, the ratio of the volumes of tracer slug injected to that of total fluid injected could be a reasonable parameter group to note in tracer test data correlations.

An efficient approach which could be used in data correlation is along the lines of casting variables into parameter groups. Such parameter groups which would reduce the number of variables involved in correlation to about two or three. However, for this parameter to be useful, they should be usable in the solution equations with a view to casting the equation into parametric form. The effects of the parameter groups could then be investigated in a broad general sense to cover the range of practical interests without creating any form of variable redundancy or lack of uniqueness in solutions.

The above approach is suggested as a continuation of this work.

Fluid Injection Rate (Barrels/Day) = 75.0
Tracer Slug Injection Time (Days) = 1.0
Pure Water Injection Time (Days) = 2.0
Total Injection Time (Days) = 3.0
Total Shut-in Time (Days) = 2.0
Convective Mixing Constant = 0.6
Formation Thickness (Feet) = 50.0
Formation Porosity = 0.25
Formation Water Saturation = 0.75
Formation Adsorption Constant = 2.5

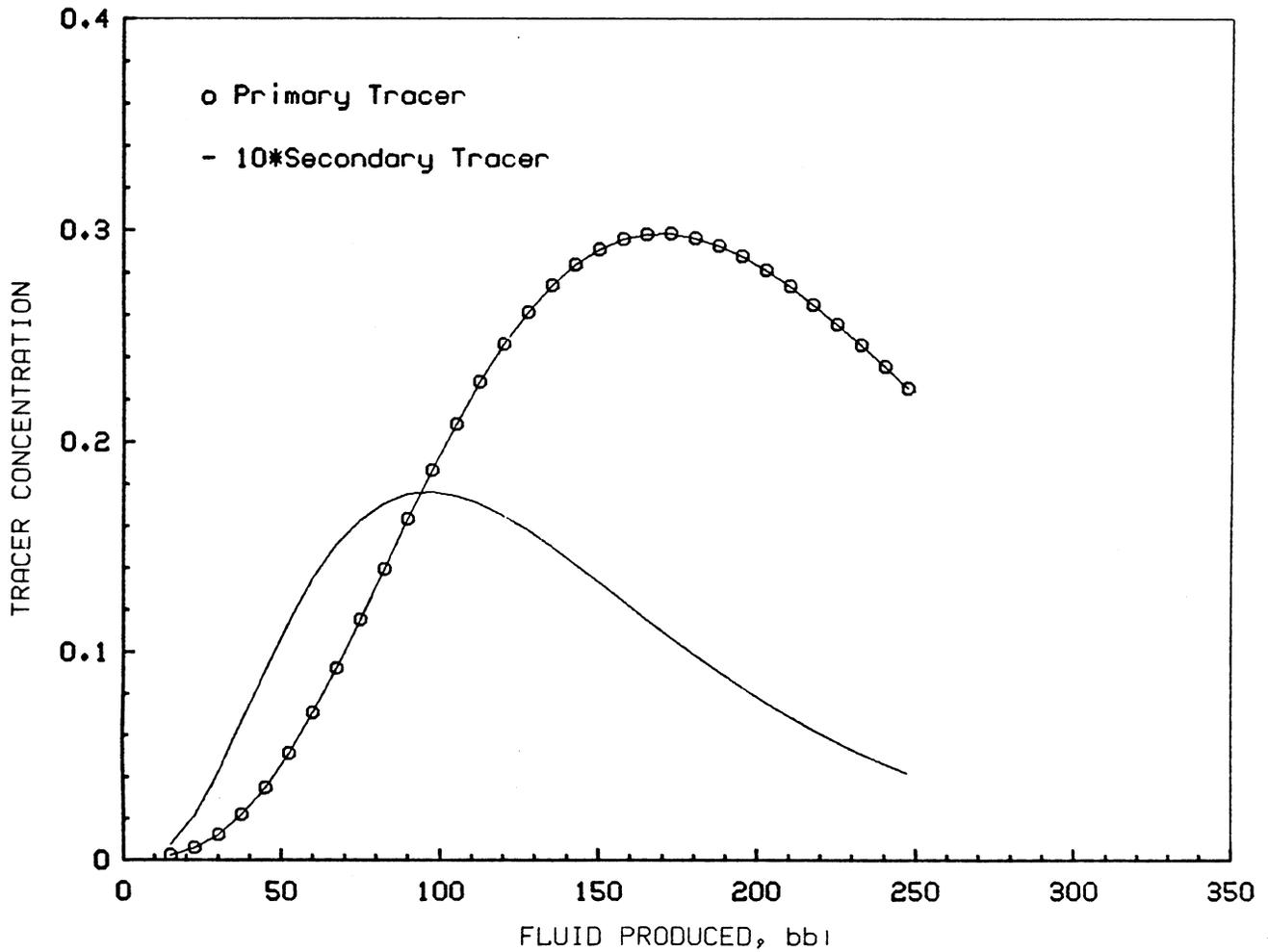


Fig. 5.14 Concentration Profiles of Produced Tracers.

6. CONCLUSIONS

1. One major conclusion derivable from this work is that the radial flow, diffusion, convection, reaction (R-D-C-R) equation which describes the single-well tracer flow test can be solved analytically.
2. Such equations describing the dynamics of the primary and the secondary tracers during injection, shut-in and production periods were solved for exact analytical solutions in Laplace space.
3. The exact analytical solutions in Laplace space are in form of the Airy functions which behave like the exponential functions. Because of these characteristics, the range of arguments usable in these equations needs to be evaluated carefully before computation. For example, the solutions are singular for very small values of time or very large values of distance.
4. A judicious combination of the parameters constituting the arguments used in the equation can afford a wide variation of values of these parameters for the purpose of peak concentration correlation.
5. It is also shown whether an equilibrium adsorption isotherm or a nonequilibrium isotherm is used in building the flow model, the mathematical difficulties in obtaining an exact analytical solutions for either model are substantially the same. However, since a nonequilibrium model will require the specification of the dynamic adsorption and desorption constants, which may not be practicable, the equilibrium model is deemed adequate for this kind of study.

7. RECOMMENDATIONS

The main thrust of this work is to obtain analytical solutions to the different equations describing the single-well tracer test. The solution thus obtained can now be used to construct a set of correlation curves for the purpose of tracer test interpretation. To achieve this, it is suggested that the solutions be fashioned into a parametric form of not more than three parameter group variables. This will ease the correlation work considerably.

If the above correlation work can successfully be completed for this model, then one can consider an extension to the more general, but certainly more difficult cases involving one or more of the following effects, drift, solution dilution, nonunity mobility, formation stratification, multi-phase flow.

8. NOMENCLATURE

$A_i(x)$	= Airy function
$B_i(x)$	= Airy function
C	= Concentration
C_1	= Primary tracer concentration
C_2	= Secondary tracer concentration
C_i	= Concentration of tracer i in the mobile fluid phase ($i = 1, 2$).
\bar{C}_i	= Concentration of tracer i in the immobile fluid phase ($i = 1$).
C_{is}	= Tracer i concentration during shut-in period
\hat{C}_{is}	= Tracer i concentration at the end of shut-in period
C_{ip}	= Tracer i concentration during production period
$D(r_D)$	= Hydrodynamic dispersion function
D_m	= Molecular dispersion constant
D_0	= Dispersive mixing constant
$f(C_i)$	= Concentration flux
$g(C_i)$	= Equilibrium function
h	= Formation thickness
i	= Concentration component number
K_1	= Equilibrium adsorption constant
K_2	= Equilibrium desorption constant
$K_{1/3}(x)$	= Modified Bessel function of second kind of order 1/3.
k_r	= Reaction constant
L	= Linear differential operator as defined in text
M	= Linear differential operator as defined in text
$N(C_i)$	= Chromatographic delay factor
P	= Diffusion velocity of Joseph & Sendner
$P(r_D)$	= Some function of r_D as defined in text
q	= Fluid injection/production rate
$R(C_i, \bar{C}_i)$	= Generalized reaction function
r	= Radial distance
r_w	= Wellbore radius
r_D	= Dimensionless wellbore radius
S_i	= Saturation of component i ($i = o, w$)
$S(r_D)$	= Some function of r_D as defined in text
t	= total time of injection
t_1	= Time of tracer-free water injection
U	= Linear differential operator as defined in text
V	= Linear differential operator as defined in text
v_w	= Fluid velocity in formation

$W(X, Y)$	= Wronskian of X and Y
x	= Transformed distance variable
X	= Transformed distance variable
α	= Constant defined in text
ξ	= Transformed distance variable as in text
ζ	= Transformed distance variable as in text
η	= Transformed distance variable as in text
λ	= Laplace transform parameter
γ	= Energy dissipation function of Ozmidov
ν	= Constant defined in text
Φ	= Constant defined in text
Ψ_{is}	= Transformed function of C_i during shut-in period
Ψ_{ip}	= Transformed function of C_i during production period
$\bar{\Psi}_{ip}$	= Laplace transform of Ψ_{ip}
$\bar{\Psi}_{is}$	= Laplace transform of Ψ_{is} .

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APPENDIX A ANALYTICAL SOLUTION TO THE PRIMARY TRACER EQUATION

The general equation and the associated boundary conditions for the primary tracer is

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_1}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_1}{\partial r} - k_r \left[1 + \frac{K_1 S_o}{S_w} \right] C_1 = \left[1 + \frac{K_1 S_o}{S_w} \right] \frac{\partial C_1}{\partial t} \quad (\text{A.1})$$

and

$$C_1(r, t) = 0 \quad \text{at} \quad t = 0 \quad (\text{A.2a})$$

$$C_1(r, t) = 0 \quad \text{at} \quad r \rightarrow \infty \quad (\text{A.2b})$$

$$C_1(r, t) = C_0 \quad \text{at} \quad r = r_w \quad (\text{A.2c})$$

Equations A.1 and A.2 have been transformed and reduced to the Sturm-Louville equation in Laplace space of the form (See Eq. 39)

$$\frac{d^2 \bar{\Phi}_1}{dr_D^2} - \left[\frac{1}{4D_o^2} + \frac{\Phi(k_r + \lambda)}{\alpha D_o} r_D \right] \bar{\Phi}_1 = 0 \quad (\text{A.3})$$

The associated boundary conditions are as follows:

$$\bar{\Phi}_1 (r_D \rightarrow \infty, \lambda) = 0 \quad (\text{A.4a})$$

$$\bar{\Phi}_1 (r_{D=1}, \lambda) = \frac{C_0}{\lambda} \quad (\text{A.4b})$$

A closer look at Eq. A.3 reveals that we can construct a comparison equation in the form of the Airy equation (Lakin *et al.*, 1970). For if we define a new independent variable $\xi(r_D)$ in terms of r_D as:

$$\xi (r_D) = \frac{1}{4D_o^2} + \frac{\Phi(k_r + \lambda)r_D}{\alpha D_o} \quad (\text{A.5})$$

The Eq. A.3 reduces to

$$\frac{d^2 \bar{\Phi}_1}{d\xi^2} - \left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^2 \xi \bar{\Phi}_1 = 0 \quad (\text{A.6})$$

Equation A.6 is an Airy equation with a general solution of the form (Jeffrey, 1972; Miller, 1963).

$$\bar{\Phi}_1 (\xi, \lambda) = \beta_1 A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] + \beta_2 B_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] \quad (\text{A.7})$$

where $A_i(x)$ and $B_i(x)$ are the Airy integrals defined as

$$A_i(x) = \frac{1}{\pi} \int_0^{\infty} \cos \left[\frac{t^3}{3} + xt \right] dt \quad (\text{A.8a})$$

$$B_i(x) = \frac{1}{\pi} \int_0^{\infty} e^{-\left[\frac{t^3}{3} - xt \right]} dt + \frac{1}{\pi} \int_0^{\infty} \sin \left[\frac{t^3}{3} + xt \right] dt \quad (\text{A.8b})$$

The boundary conditions associated with Eq. A.7 are:

$$\bar{\Phi}_1(\xi \rightarrow \infty, \lambda) = 0 \quad (\text{A.9a})$$

$$\bar{\Phi}_1[\xi(r_{D=1}), \lambda] = \frac{C_0}{\lambda} \quad (\text{A.9b})$$

As can be seen from Abramowitz, *et al.*, (1972), $A_i(x)$ behaves as the exponential function with negative argument, $\exp(-x)$; while $B_i(x)$ behaves as $\exp(+x)$. In consideration of the boundary condition (Eq. A.4a) therefore, the constant β_2 in Eq. A.7 must be set to zero. The other constant β_1 in Eq. A.7 can be determined using the remaining boundary condition to obtain

$$\beta_1 = \frac{C_0}{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right] \lambda} \quad (\text{A.10})$$

In view of (A.10), the exact analytical solution to our problem can written as:

$$\bar{\Phi}_1(\xi, \lambda) = \frac{C_0}{\lambda} \left\{ \frac{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{A_i \left[\left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_{D=1}) \right]} \right\} \quad (\text{A.11})$$

The Airy function $A_i(x)$ can also be expressed in terms of the modified Bessel function of fractional order $K_{1/3}(x)$ (Abramowitz & Stegun 1972):

$$A_i(x) = \frac{1}{\pi} \sqrt{\frac{x}{3}} K_{1/3} \left[\frac{2}{3} x^{3/2} \right] \quad (\text{A.12})$$

so that Eqs. A.11 can be expressed as

$$\bar{\Phi}_1(\xi, \lambda) = \frac{C_0}{\lambda} \frac{\frac{\sqrt{\xi(r_D)}}{\sqrt{\xi(r_{D=1})}} K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{3/2} \right]}{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{3/2}(r_{D=1}) \right]} \quad (\text{A.13})$$

where

$$\xi(r_D) = \frac{1}{4D_0^2} + \frac{\Phi(k_r + \lambda)}{\alpha D_0} r_D$$

The solution function $\bar{\phi}_1(\xi, \lambda)$ can be converted back to the $C_1(\xi, \lambda)$ function by using Eq. 32 and noting that

$$\left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] = - \left[\frac{1}{D_0} \right] \quad (\text{A.14})$$

to obtain

$$\bar{C}_1(\xi, \lambda) = \frac{C_o \exp\left[\frac{r_D - 1}{2D_0}\right]}{\lambda} \sqrt{\frac{\xi(r_D)}{\xi(r_D=1)}} \left\{ \frac{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{3/2} \right]}{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right] \xi^{3/2} (r_D = 1) \right]} \right\} \quad (\text{A.15})$$

Equation A.15 is the exact analytical solution to the radial flow of tracer in a porous medium under constant and continuous tracer injection in Laplace space.

APPENDIX B ANALYTICAL SOLUTION TO THE SECONDARY TRACER EQUATION

The general equation and the associated initial and boundary conditions for the secondary tracer is give as

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_2}{\partial r} \right] - \frac{\alpha}{r} \frac{\partial C_2}{\partial r} + k_r \left[\frac{C_1 S_w + S_o \bar{C}}{S_w} \right] = \frac{\partial C_2}{\partial t} \quad (\text{B.1})$$

$$C_2(r, t) = 0 \times @ t = 0 \quad (\text{B.2a})$$

$$C_2(r, t) = 0 \times @ r \rightarrow \infty \quad (\text{B.2b})$$

$$C_2(r, t) = 0 \times @ r = r_w \quad (\text{B.2c})$$

Using the definitions, transformations and simplifications already described for the primary tracer equation, Eqs. B.1 and B.2 can be written as:

$$\frac{\partial^2 \phi_2}{\partial r_D^2} - \left[\frac{1}{4} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]^2 + \frac{1}{2} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \right] \phi_2 + \frac{\Phi k_r \phi_1}{D} = \frac{r_w^2}{D} \frac{\partial \phi_2}{\partial t} \quad (\text{B.3})$$

and

$$\phi_2(r_D, t = 0) = 0 \quad (\text{B.4a})$$

$$\phi_2(r_D \rightarrow \infty, t) = 0 \quad (\text{B.4b})$$

$$\phi_2(r_D = 1, t) = 0 \quad (\text{B.4c})$$

Expressing Eq. B.3 in the Laplace space yields

$$\frac{d^2 \bar{\phi}_2}{dr_D^2} - \left[\frac{1}{4} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]^2 + \frac{1}{2} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] + \frac{r_w^2 \lambda}{D} \right] \bar{\phi}_2 = \frac{-\Phi k_r \bar{\phi}_1}{D} \quad (\text{B.5a})$$

or

$$\frac{d^2 \bar{\phi}_2}{dr_D^2} - W(r_D, \lambda) \bar{\phi}_2 = -\frac{\Phi k_r \bar{\phi}_1}{D} \quad (\text{B.5b})$$

where

$$W(r_D, \lambda) = \left[\frac{1}{4} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right]^2 + \frac{1}{2} \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] + \frac{r_w^2 \lambda}{D} \right] \quad (\text{B.5c})$$

Since

$$D(r_D) = \frac{\alpha D_o}{r_D} \quad (37)$$

so that

$$\left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] = -\frac{1}{D_o} \quad (\text{B.5d})$$

the functions $W (r_D, \lambda)$ reduces to

$$W(r_D, \lambda) = \left[\frac{1}{4D_o^2} + \frac{r_w^2 \lambda}{\alpha D_o} r_D \right] \quad (\text{B.6})$$

and Eq. B.5 simplifies to

$$\frac{d^2 \bar{\phi}_2}{dr_D^2} - \left[\frac{1}{4D_o^2} + \frac{r_w^2 \lambda}{\alpha D_o} r_D \right] \bar{\phi}_2 = - \frac{\Phi k_r r_D \bar{\phi}_1}{\alpha D_o} \quad (\text{B.7})$$

As before we can define a new independent variable $\eta(r_D)$ as :

$$\eta(r_D) = \frac{1}{4D_o^2} + \frac{r_w^2 \lambda}{\alpha D_o} r_D \quad (\text{B.8})$$

So that Eq. B.7 reduces to

$$\frac{d^2 \bar{\phi}_2}{d\eta^2} - \left[\frac{\alpha D_o}{r_w^2 \lambda} \right]^2 \eta \bar{\phi}_2 = - \left[\frac{\alpha D_o}{r_w^2 \lambda} \right]^2 \frac{\Phi k_r r_D \bar{\phi}_1}{\alpha D_o} \quad (\text{B.9})$$

The associated boundary conditions are

$$\bar{\phi}_2(\eta \rightarrow \infty, \lambda) = 0 \quad (\text{B.10a})$$

$$\bar{\phi}_2[\eta(r_d = 1), \lambda] = 0 \quad (\text{B.10b})$$

Equation B.9 is an inhomogeneous equation with a solution composed of a homogeneous and particular components, viz

$$\bar{\phi}_2(\eta, \lambda) = \bar{\phi}_{2h}(\eta, \lambda) + \bar{\phi}_{2p}(\eta, \lambda) \quad (\text{B.11})$$

From our knowledge of the expression for the primary tracer concentration profile $\bar{\phi}_1(\xi, \lambda)$, we can assume a particular solution to Eq. B.9 of the form

$$\bar{\phi}_{2p}(\eta, \lambda) = \beta_o A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] \quad (\text{B.12})$$

Since this solution must satisfy the governing equation (Eq. B.9) to be admissible, a substitution of Eq. B.12 into the governing equation (Eq. B.9) provides a means of evaluating the constant β_o . Differentiating Eq. B.12 twice yields

$$\frac{d^2 \bar{\phi}_{2p}}{d\eta^2} = \beta_o \left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^2 \xi \left[\frac{d\xi}{d\eta} \right]^2 A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]$$

or

$$\frac{d^2 \bar{\Phi}_{2p}}{d\eta^2} = \beta_o \left[\frac{\alpha D_o}{\lambda r_w^2} \right]^2 \xi A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] \quad (\text{B.13})$$

Using this in Eq. B.9 yields

$$\beta_o \left[\frac{\alpha D_o}{\lambda r_w^2} \right]^2 (\xi - \eta) A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right] = - \left[\frac{\alpha D_o}{\lambda r_w^2} \right]^2 \frac{\Phi k_r r_D \bar{\Phi}_1}{\alpha D_o} \quad (\text{B.14})$$

but

$$\bar{\Phi}_1(\xi, \lambda) = \frac{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{\lambda A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right]}$$

Therefore

$$\beta_o = \frac{-\Phi k_r}{\lambda \left[\Phi k_r + \lambda (\Phi - r_w^2) \right] A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right]} \quad (\text{B.15})$$

Using Eq. B.15 in B.12 we have

$$\bar{\Phi}_{2p}(\eta, \lambda) = \frac{-\Phi k_r}{\lambda \left[\Phi k_r + \lambda (\Phi - r_w^2) \right]} \frac{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right]} \quad (\text{B.16})$$

Solving the homogeneous part of Eq. B.9 together with the outer boundary condition, Eq. B.10a, we have

$$\bar{\Phi}_{2h}(\eta, \lambda) = \beta_3 A_i \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right]^{2/3} \eta \right] \quad (\text{B.17})$$

Using Eqs. B.17 and B.16 in Eq. B.11 yields

$$\bar{\Phi}_2(\eta, \lambda) = \beta_3 A_i \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right]^{2/3} \eta \right] + \frac{-\Phi k_r}{\lambda \left[\Phi k_r + \lambda (\Phi - r_w^2) \right]} \left\{ \frac{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi(r_D = 1) \right]} \right\} \quad (\text{B.18})$$

Applying the inner boundary condition, Eq. B.10b, we can evaluate the constant β_3 as

$$\beta_3 = \frac{\Phi k_r}{\lambda \left[\Phi k_r + \lambda(\Phi - r_w^2) \right] A_i \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right]^{2/3} \eta (r_D=1) \right]} \quad (\text{B.19})$$

Using β_3 in Eq. B.18 finally yields:

$$\bar{\Phi}_2(\eta, \lambda) = \frac{\Phi k_r}{\lambda \left[\Phi k_r + \lambda(\Phi - r_w^2) \right]} \left\{ \frac{A_i \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right]^{2/3} \eta \right]}{A_i \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right]^{2/3} \eta (r_D = 1) \right]} - \frac{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \right]}{A_i \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right]^{2/3} \xi (r_D = 1) \right]} \right\} \quad (\text{B.20})$$

Expressing the $A_i(x)$ functions in terms of $K_{1/3}(x)$ we have

$$\bar{\Phi}_2(\eta, \lambda) = \frac{\Phi k_r}{\lambda \left[\Phi k_r + \lambda(\Phi - r_w^2) \right]} \left\{ \sqrt{\frac{\eta(r_D)}{\eta(r_D=1)}} \cdot \frac{K_{1/3} \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right] \eta^{3/2} \right]}{K_{1/3} \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right] \eta^{3/2}(r_D = 1) \right]} - \sqrt{\frac{\xi(r_D)}{\xi(r_D = 1)}} \cdot \frac{K_{1/3} \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right] \xi^{3/2} \right]}{K_{1/3} \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right] \xi^{3/2}(r_D = 1) \right]} \right\} \quad (\text{B.21})$$

The solution $\bar{\Phi}_2(\eta, \lambda)$ can be converted to the $\bar{C}_2(\eta, \lambda)$ function by using Eq. 32 to obtain

$$\bar{C}_2(\eta, \lambda) = \frac{\Phi k_r \exp \left[\frac{r_D - 1}{2D_o} \right]}{\lambda \left[\Phi k_r + \lambda(\Phi - r_w^2) \right]} \left\{ \sqrt{\frac{\eta(r_D)}{\eta(r_D = 1)}} \cdot \frac{K_{1/3} \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right] \eta^{3/2} \right]}{K_{1/3} \left[\left[\frac{\alpha D_o}{\lambda r_w^2} \right] \eta^{3/2}(r_D = 1) \right]} - \sqrt{\frac{\xi(r_D)}{\xi(r_D = 1)}} \cdot \frac{K_{1/3} \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right] \xi^{3/2} \right]}{K_{1/3} \left[\left[\frac{\alpha D_o}{\Phi(k_r + \lambda)} \right] \xi^{3/2}(r_D = 1) \right]} \right\} \quad (\text{B.22})$$

Equation B.22 is the exact solution to the secondary tracer equation derivable from a continuous injection of the primary tracer in Laplace space.

**APPENDIX C
PRIMARY TRACER CONCENTRATION PROFILE
DURING THE SHUT-IN PERIOD**

During the shut-in period, fluid flow velocity within the medium is zero. The hydrodynamic dispersion function $D(r_D)$ can therefore be modified such that

$$D(r_D) \approx D_m \quad (65)$$

Using the above simplifications in the original equation for the flow of primary tracer, we have an equation for the shut-in period in the form:

$$\frac{\partial^2 C_{1s}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial C_{1s}}{\partial r_D} - \frac{\Phi k_r}{D_m} C_{1s} = \frac{\Phi}{D_m} \frac{\partial C_{1s}}{\partial t} \quad (C.1)$$

$$C_{1s}(r_D, t = 0) = C_1(r_D) \quad (C.2a)$$

$$C_{1s}(r_D \rightarrow \infty, t) = 0 \quad (C.2b)$$

$$C_{1s}(r_D = 1, t) = 0 \quad (C.2c)$$

Converting Eq. C.1 into the Laplace space yields

$$\frac{d^2 \bar{C}_{1s}}{dr_D^2} + \frac{1}{r_D} \frac{d\bar{C}_{1s}}{dr_D} - \frac{\Phi}{D_m} (k_r + \lambda) \bar{C}_{1s} = - \frac{\Phi \bar{C}_1(r_D)}{D_m} \quad (C.3)$$

The associated boundary conditions are

$$\bar{C}_{1s}(r_D \rightarrow \infty, \lambda) = 0 \quad (C.4a)$$

$$\bar{C}_{1s}(r_D = 1, \lambda) = 0 \quad (C.4b)$$

Equation C.3 is a linear, inhomogeneous differential equation. Therefore, if we define a linear operator L as

$$L = \frac{d^2}{dr_D^2} + \frac{1}{r_D} \frac{d}{dr_D} - \frac{\Phi}{D_m} (k_r + \lambda) \quad (C.5)$$

Equation C.3 can be written as

$$L \left[\bar{C}_{1s}(r_D, \lambda) \right] = - \frac{\Phi}{D_m} \bar{C}_1(r_D) \quad (C.6)$$

The complete solution to Eq. C.6 subject to the boundary condition (Eq. C.4) can be written as (Carslaw and Jaeger 1958, Arsenin 1968)

$$\bar{C}_{1s}(r_D, \lambda) = \bar{\Psi}_{1p}(r_D, \lambda) + \bar{\Psi}_{2p}(r_D, \lambda) \quad (C.7)$$

where $\bar{\Psi}_{1p}(r_D, \lambda)$ satisfies the following set of equations:

$$L \left[\bar{\Psi}_{1p}(r_D, \lambda) \right] = \frac{-\Phi \bar{C}_1(r_D)}{D_m} \quad (C.8)$$

subject to the boundary conditions

$$\bar{\Psi}_{1p}(r_D \rightarrow \infty, \lambda) = 0 \quad (C.9a)$$

$$\bar{\Psi}_{1p}(r_D = 1, \lambda) = \text{finite} \quad (C.9b)$$

and $\bar{\Psi}_{2p}(r_D, \lambda)$ is a solution of the homogeneous equation

$$L \left[\bar{\Psi}_{2p}(r_D, \lambda) \right] = 0 \quad (C.10)$$

subject to the boundary conditions

$$\bar{\Psi}_{2p}(r_D \rightarrow \infty, \lambda) = 0 \quad (C.11a)$$

$$\bar{\Psi}_{2p}(r_D = 1, \lambda) = \text{finite} \quad (C.11b)$$

In view of the fact that neither $\bar{\Psi}_{1p}(r_D, \lambda)$ nor $\bar{\Psi}_{2p}(r_D, \lambda)$ need to satisfy the inner-boundary condition (Eq. C.4b) exactly, the complete solution given by Eq. C.7 must be made to satisfy this boundary condition exactly.

Equation C.8 basically is a Cauchy problem (Arsenin, 1968) with a general solution which can be written in terms of the Green's function $G_1(r_D, r'_D, \lambda)$ of the linear equation $L = 0$; viz.

$$\bar{\Psi}_{1p}(r_D, \lambda) = \frac{\Phi}{D_m} \int_{r'_D=1}^{\infty} G_1(r_D, r'_D, \lambda) \bar{C}_1(r'_D) dr'_D \quad (C.12)$$

CONSTRUCTION OF THE GREEN'S FUNCTION $G_1(r_D, r'_D, \lambda)$

We can construct the Green's function for the linear equations $L(\bar{\Psi}_{1p})$ under the prescribed boundary conditions defined by Eqs. C.9 by considering any solutions $\bar{\Psi}_{1p}(r_D, \lambda)$ of the differential equation $L(\bar{\Psi}_{1p}) = 0$ which satisfies the boundary condition at $r_D \rightarrow \infty$. As can easily be verified (Bowman 1958, Watson, 1952) such solution can be written as

$$\bar{\Psi}_{1p_1}(r_D, \lambda) = A_1 K_0 \left[r_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] \quad (C.13)$$

The other independent solution of the equation $L \left[\bar{\Psi}_{1p}(r_D, \lambda) \right] = 0$ is

$$\bar{\Psi}_{1p_2}(r_D, \lambda) = A_2 I_o \left[r'_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] \quad (C.14)$$

The solution (Eq. C.13) do not satisfy the outer boundary at $r_D \rightarrow \infty$ but satisfies the finiteness of $\bar{C}_{1s}(r_D, \lambda)$ as $r_D \rightarrow 1$. These two solution curves are distinct and independent and form the basis on which the systems fundamental solution is based. It can be shown that if the constants A_1 and A_2 of Eqs. C.14 and C.13 are very carefully chosen, we can construct the desired Green's function as (Courant and Hilbert 1953)

$$G_1(r_D, r'_D, \lambda) = \begin{cases} \frac{K_o \left[r_D \sqrt{\frac{\Phi}{D_m}} (k_r + \lambda) \right] \cdot I_o \left[r'_D \sqrt{\frac{\Phi}{D_m}} (k_r + \lambda) \right]}{W \left[K_o(x), I_o(x) \right]_x \frac{dx}{dr}} & ; r_D > r'_D \\ I_o \left[r_D \sqrt{\frac{\Phi}{D_m}} (k_r + \lambda) \right] \cdot K_o \left[r'_D \sqrt{\frac{\Phi}{D_m}} (k_r + \lambda) \right]}{W \left[K_o(x), I_o(x) \right]_x \frac{dx}{dr}} & ; r_D \leq r'_D \end{cases} \quad (C.15a)$$

In Eq. C.10, x is defined as

$$x = r_D \sqrt{\frac{\Phi}{D_m}} (k_r + \lambda) \quad (C.15b)$$

and $W[K_o(x), I_o(x)]$ is the Wronskian of the Bessel functions $K_o(x)$ and $I_o(x)$ and is defined as:

$$W \left[K_o(x), I_o(x) \right] = K_o(x) \frac{d}{dx} \left[I_o(x) \right] - I_o(x) \frac{d}{dx} \left[K_o(x) \right] \quad (C.16a)$$

$$= \frac{1}{x} \quad (C.16b)$$

Using Eqs. C.16 in Eq. C.14 yields

$$G_1(r_D, r'_D, \lambda) = \begin{cases} K_o \left[r_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] I_o \left[r'_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] r'_D; & r_D > r'_D \\ K_o \left[r'_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] I_o \left[r_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] r'_D; & r_D \leq r'_D \end{cases} \quad (C.17)$$

Equation C.17 can be recognized as the instantaneous cylindrical surface source located at $r_D = r_D$ at $t = 0$ in an infinite medium (Carslaw and Jaeger, 1958).

In addition to the above, we need to obtain a complementary solution for the set of Eqs. C.10 and C.11. It is easily verified that the appropriate solution for these equations is

$$\bar{\Psi}_{2p}(r_D, \lambda) = A_1 K_o \left[r_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] \quad (C.18)$$

Using Eqs. C.12 and C.18 in Eq. C.7, we can therefore write the general solution to the system of Eqs. C.3 and C.4

$$\bar{C}_{1s}(r_D, \lambda) = A_1 K_o \left[r_D \sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right] + \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_1(r_D, r'_D, \lambda) \bar{C}_1(r'_D) dr'_D \quad (C.19)$$

The general solution (Eq. C.19) must now be made to satisfy the inner boundary condition

$$\bar{C}_{1s}(r_D, \lambda) = 0 \quad \text{at} \quad r_D = 1 \quad (C.20)$$

Using Eq. C.20 on Eq. C.19, we can evaluate the constant A_1 as

$$A_1 = \frac{-\frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_1(r'_D, 1, \lambda) \bar{C}_1(r'_D) dr'_D}{K_o \left[\sqrt{\frac{\Phi(k_r + \lambda)}{D_m}} \right]} \quad (C.21)$$

Thus

$$\begin{aligned} \bar{C}_{1s}(r_D, \lambda) &= \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} \bar{C}_1(r'_D) G_1(r_D, r'_D, \lambda) dr'_D \\ &- \frac{K_o \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]}{K_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]} \cdot \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} \bar{C}_1(r'_D) G_1(r'_D, 1, \lambda) dr'_D \end{aligned} \quad (C.22)$$

where $G_1(r_D, r_D, \lambda)$ is given by Eq. C.17 and $G(r'_D, 1, \lambda)$ is given as

$$G_1(r'_D, 1, \lambda) = r'_D K_o \left[r'_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \cdot I_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] ; r_D \leq r'_D \quad (C.23)$$

Simplifying Eq. C.22 yields

$$\bar{C}_{1s}(r_D, \lambda) = \frac{\left[\frac{\Phi}{D_m} \right]}{K_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]} \int_{r_D'=1}^{\infty} \bar{C}_1(r_D') K_o \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]$$

$$\left[I_o \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] - I_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_o \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \right] r_D' dr_D' ;$$

$r_D \leq r_D'$ (C.24)

Equation C.24 is valid for $r_D \leq r_D'$. For a solution in the range $r_D > r_D'$, we simply interchange r_D and r_D' in Eq. C.24 to obtain

$$\bar{C}_{1s}(r_D, \lambda) = \frac{\left[\frac{\Phi}{D_m} \right]}{K_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]} \int_{r_D'=1}^{\infty} \bar{C}_1(r_D') K_o \left[r_D \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right]$$

$$\left[I_o \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] - I_o \left[\sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] K_o \left[r_D' \sqrt{\frac{\Phi}{D_m} (k_r + \lambda)} \right] \right] r_D' dr_D' ;$$

$r_D > r_D'$ (C.25)

APPENDIX D SECONDARY TRACER CONCENTRATION PROFILE DURING THE SHUT-IN PERIOD

As earlier discussed in Appendix C for the primary tracer concentration profile during shut-in, the hydrodynamic dispersion function $D(r_D)$ degenerates to the molecular diffusion D_m and the equation describing the secondary tracer behavior can be written as:

$$\frac{\partial^2 C_{2s}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial C_{2s}}{\partial r_D} + \frac{\Phi k_r}{D_m} C_{1s} = \frac{r_w^2}{D_m} \frac{\partial C_{2s}}{\partial t} \quad (\text{D.1})$$

The associated initial and boundary conditions are

$$C_{2s}(r_D, t = 0) = C_2(r_D) \quad (\text{D.2a})$$

$$C_{2s}(r_D \rightarrow \infty, t) = 0 \quad (\text{D.2b})$$

$$C_{2s}(r_D = 1, t) = 0 \quad (\text{D.2c})$$

Converting Eqs. D.1 and D.2 into Laplace space yields:

$$\frac{d^2 \bar{C}_{2s}}{dr_D^2} + \frac{1}{r_D} \frac{d\bar{C}_{2s}}{dr_D} - \frac{r_w^2 \lambda}{D_m} \bar{C}_{2s} = -\frac{\Phi}{D_m} \left[k_r \bar{C}_{1s}(r_D) + \frac{r_w^2}{\Phi} C_2(r_D) \right] \quad (\text{D.3})$$

The associated boundary conditions are

$$\bar{C}_{2s}(r_D \rightarrow \infty, \lambda) = 0 \quad (\text{D.4a})$$

$$\bar{C}_{2s}(r_D = 1, \lambda) = 0 \quad (\text{D.4b})$$

Equations D.3 and D.4 are similar to Eqs. C.3 and C.4 of Appendix C. Therefore the solution to Eqs. D.3 and D.4 can immediately be written down by straight analogy with the known solution to Eqs. C.3 and C.4. Thus

$$\bar{C}_{2s}(r_D, \lambda) = \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_2(r_D, r'_D, \lambda) \left[k_r \bar{C}_{1s}(r'_D) + \frac{r_w^2}{\Phi} C_2(r'_D) \right] dr'_D \quad (\text{D.5})$$

where in this case, $G_2(r_D, r'_D, \lambda)$ is the one-sided Green's function for the system, and defined as

$$G_2(r_D, r'_D, \lambda) = \begin{cases} K_0 \left[r'_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] I_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] r'_D; & r_D \leq r'_D \\ K_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] I_0 \left[r'_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] r'_D; & r_D > r'_D \end{cases} \quad (\text{D.6})$$

In addition to Eq. D.5, a complementary solution to the homogeneous part of the differential equation must be generated. Such solution which is consistent with the boundary condition at infinity is

$$K_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right]$$

Thus the complete general solution to Eq. D.3 is

$$\bar{C}_{2s}(r_D, \lambda) = A_2 K_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] + \frac{\Phi}{D_m} \int_{r_D=1}^{\infty} G_2(r_D, r'_D, \lambda) \left[k_r \bar{C}_{1s}(r'_D) + \frac{r_w^2}{\Phi} C_2(r'_D) \right] dr'_D \quad (D.7)$$

Proceeding as in Appendix C, we can evaluate the constant A_2 and hence obtain a solution for $\bar{C}_{2s}(r_D, \lambda)$ in the form

$$\bar{C}_{2s}(r_D, \lambda) = \frac{\left[\frac{\Phi}{D_m} \right]}{K_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right]} \int_{r_D=1}^{\infty} \left[k_r \bar{C}_{1s}(r'_D) + \frac{r_w^2}{\Phi} C_2(r'_D) \right] K_0 \left[r'_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] \left[I_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] K_0 \left[\sqrt{\frac{\lambda r_w^2}{D_m}} \right] - I_0 \left[\sqrt{\frac{\lambda r_w^2}{D_m}} \right] K_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] \right] r'_D dr'_D; r_D \leq r'_D \quad (D.8)$$

and

$$\bar{C}_{2s}(r_D, \lambda) = \frac{\left[\frac{\Phi}{D_m} \right]}{K_0 \left[\sqrt{\frac{r_w^2 \lambda}{D_m}} \right]} \int_{r_D=1}^{\infty} \left[k_r \bar{C}_{1s}(r'_D) + \frac{r_w^2}{\Phi} C_2(r'_D) \right] K_0 \left[r_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] \left[I_0 \left[r'_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] K_0 \left[\sqrt{\frac{\lambda r_w^2}{D_m}} \right] - I_0 \left[\sqrt{\frac{\lambda r_w^2}{D_m}} \right] K_0 \left[r'_D \sqrt{\frac{\lambda r_w^2}{D_m}} \right] \right] r'_D dr'_D; r_D > r'_D \quad (D.9)$$

**APPENDIX E
PRIMARY TRACER CONCENTRATION PROFILE
DURING THE PRODUCTION PERIOD**

The equation governing primary tracer dynamics during the production period is the same as during injection though the flow velocity is reversed. Thus

$$\frac{1}{r_D} \frac{\partial}{\partial r_D} \left[r_D D(r_D) \frac{\partial C_{1p}}{\partial r_D} \right] + \frac{\alpha}{r_D} \frac{\partial C_{1p}}{\partial r_D} - \Phi k_r C_{1p} = \Phi \frac{\partial C_{1p}}{\partial t} \quad (\text{E.1})$$

The associated initial and boundary conditions are

$$C_{1p}(r_D, t = 0) = C_{1s}(r_D) \quad (\text{E.2a})$$

$$C_{1p}(r_D \rightarrow \infty, t) = 0 \quad (\text{E.2b})$$

$$f_{1p} = C_{1p}(r_D = 1, t) \quad (\text{E.2c})$$

In Eq. E.2c, the term f_{1p} represents the effluent concentration at the wellbore, and is defined as

$$f_{1p} = \left[C_{1p} - D_0 \frac{\partial C_{1p}}{\partial r_D} \right]_{r_D=1} \quad (\text{E.3})$$

Making appropriate transformations and substitutions as were used in Appendix A, Eqs. E.1 through E.3 become

$$\frac{\partial^2 \phi_{1p}}{\partial r_D^2} - \left[\frac{1}{4D_0^2} + \frac{\Phi k_r r_D}{\alpha D_0} \right] \phi_{1p} = \frac{\Phi r_D}{\alpha D_0} \frac{\partial \phi_{1p}}{\partial t} \quad (\text{E.4})$$

$$\phi_{1p}(r_D, t = 0) = C_{1s}(r_D) \cdot \exp \left[\frac{r_D - 1}{\alpha D_0} \right] = \hat{C}_{1s} \quad (\text{E.5a})$$

$$\phi_{1p}(r_D \rightarrow \infty, t) = 0 \quad (\text{E.5b})$$

$$\left[\frac{\partial \phi_{1p}}{\partial r_D} - \frac{\phi_{1p}}{\alpha D_0} \right]_{r_D=1} = 0 \quad (\text{E.5c})$$

Converting Eqs. E.4 and E.5 into the Laplace space we have

$$\frac{d^2 \bar{\phi}_{1p}}{dr_D^2} - \left[\frac{1}{4D_0^2} + \frac{\Phi}{\alpha D_0} (k_r + \lambda) r_D \right] \bar{\phi}_{1p} = - \frac{\Phi r_D \hat{C}_{1s}}{\alpha D_0} \quad (\text{E.6})$$

$$\bar{\phi}_{1p}(r_D \rightarrow \infty, \lambda) = 0 \quad (\text{E.7a})$$

$$\left[\frac{d\bar{\phi}_{1p}}{dr_D} - \frac{\bar{\phi}_{1p}}{\alpha D_0} \right]_{r_D=1} = 0 \quad (\text{E.7b})$$

Defining a new independent variable $\xi(r_D)$ as:

$$\xi(r_D) = \frac{1}{4D_0^2} + \frac{\Phi}{\alpha D_0} (k_r + \lambda)r_D \quad (\text{E.8})$$

Equations E.7 and E.6 become

$$\frac{d^2 \bar{\phi}_{1p}}{d\xi^2} - \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^2 \xi \bar{\phi}_{1p} = - \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^2 \frac{\Phi r_D \hat{C}_{1s}(r_D)}{\alpha D_0} \quad (\text{E.9a})$$

or

$$\frac{d^2 \bar{\phi}_{1p}}{d\xi^2} - \beta^2 \xi \bar{\phi}_{1p} = - \beta^2 \frac{\Phi r_D \hat{C}_{1s}(r_D)}{\alpha D_0} \quad (\text{E.9b})$$

where

$$\beta = \frac{\alpha D_0}{\Phi(k_r + \lambda)} \quad (\text{E.9c})$$

subject to the boundary conditions:

$$\bar{\phi}_{1p}(r_D \rightarrow \infty, \lambda) = 0 \quad (\text{E.10a})$$

$$\frac{d\bar{\phi}_{1p}}{d\xi} - \gamma \bar{\phi}_{1p} = 0 \quad (\text{E.10b})$$

where

$$\gamma = \left[\frac{\beta}{2D_0} \right] \quad (\text{E.10c})$$

Equations E.9 is a nonhomogeneous, linear, second order, differential equation of the Airy type. To this, we must construct a solution subject to the boundary conditions Eqs. E.10.

We can define linear operators L and U defined as

$$L = \frac{d^2}{d\xi^2} - \beta^2 \xi \quad (\text{E.11a})$$

$$U = \frac{d}{d\xi} - \gamma \quad (\text{E.11b})$$

Using Eq. E.11 on Eqs. E.9 and E.10 we have

$$L [\bar{\phi}_{1p}(\xi, \lambda)] = - p(r_D) \quad (\text{E.12a})$$

where

$$p(r_D) = \frac{\beta^2 \Phi r_D \hat{C}_{1s}(r_D)}{\alpha D_0} \quad (\text{E.12b})$$

subject to

$$\bar{\Phi}_{1p}(\xi \rightarrow 0, \lambda) = 0 \quad (\text{E.13a})$$

and

$$U [\bar{\Phi}_{1p}(\xi, \lambda)]_{r_D=1} = 0 \quad (\text{E.13b})$$

Using the method of variation of parameters (Jeffreys and Jeffrey, 1972) on Eq. E.12, we can define a general solution of the form:

$$\bar{\Phi}_{1p}(\xi, \lambda) = v_1(\xi)A_i(\beta^{2/3}\xi) + v_2(\xi)B_i(\beta^{2/3}\xi) \quad (\text{E.14})$$

In Eqs. E.14, $A_i(\beta^{2/3}\xi)$ and $B_i(\beta^{2/3}\xi)$ are the two independent solutions of the homogeneous Airy equations:

$$L[\bar{\Phi}_{1p}(\xi, \lambda)]_h = 0 \quad (\text{E.15})$$

while $v_i(\xi)$, $i = 1, 2$; are undetermined coefficients to be chosen such that

$$v_1'(\xi)A_i(\beta^{2/3}\xi) + v_2'(\xi)B_i(\beta^{2/3}\xi) = 0 \quad (\text{E.16a})$$

$$v_i'(\xi) = \frac{d}{d\xi} [v_i(\xi)] \quad (\text{E.16b})$$

Differentiating Eq. E.14 once w.r.t. ξ , we have

$$\bar{\Phi}_{1p}'(\xi, \lambda) = v_1'(\xi)A_i(x) + v_2'(\xi)B_i(x) + [v_1(\xi)A_i'(x) + v_2(\xi)B_i'(x)] \quad (\text{E.17a})$$

where

$$x = \left[\frac{\alpha D_0}{\Phi(k_r + \lambda)} \right]^{2/3} \xi \quad (\text{E.17b})$$

Using Eq. E.16 in E.17 we have

$$\bar{\Phi}_{1p}'(\xi, \lambda) = [v_1(\xi)A_i'(x) + v_2(\xi)B_i'(x)] \quad (\text{E.18})$$

Differentiating Eq. E.18 once again yields

$$\bar{\Phi}_{1p}''(\xi, \lambda) = v_1'(\xi)A_i'(x) + v_2'(\xi)B_i'(x) + [v_1(\xi)A_i''(x) + v_2(\xi)B_i''(x)] \quad (\text{E.19})$$

Using Eqs. E.19 and E.18 in E.12 yields

$$L [\bar{\Phi}_{1p}(\xi, \lambda)] = v_1(\xi)L [A_i(x)] + v_2(\xi)L [B_i(x)] + [v_1'(\xi)A_i'(x) + v_2'(\xi)B_i'(x)] = -p(r_D) \quad (\text{E.20})$$

Since $A_i(x)$ and $B_i(x)$ are independent solutions of the homogeneous equations given by Eq. E.15 it then follows that

$$L [A_i(x)] = 0 = L [B_i(x)] \quad (\text{E.21})$$

Therefore, Eq. E.20 reduces to

$$v_1'(\xi)A_i'(x) + v_2'(\xi)B_i'(x) = -p(r_D) \quad (\text{E.22})$$

Equations E.14 is therefore only a valid solution to the problem posed when the restrictions expressed by Eqs. E.22 and E.16 hold on $v_1(\xi)$ and $v_2(\xi)$, viz

$$v_1'(\xi)A_i(x) + v_2'(\xi)B_i(x) = 0 \quad (\text{E.16})$$

$$v_1'(\xi)A_i'(x) + v_2'(\xi)B_i'(x) = -p(r_D) \quad (\text{E.22})$$

The simultaneous equations (E.16) and (E.22) in $v_1'(\xi)$ and $v_2'(\xi)$ can easily be solved using Cramer's rule to obtain

$$v_1'(\xi) = \frac{B_i(x)p(r_D)}{W[A_i(x), B_i(x)]_\xi} \quad (\text{E.23a})$$

and

$$v_2'(\xi) = -\frac{A_i(x)p(r_D)}{W[A_i(x), B_i(x)]_\xi} \quad (\text{E.23b})$$

where $W[A_i(x), B_i(x)]_\xi$ is the Wronskian of $A_i(x)$ and $B_i(x)$ with differentiations w.r.t. ξ . From Eqs. E.23, $v_1(\xi)$ and $v_2(\xi)$ can be obtained by integration as:

$$v_1(\xi) = \int_{a_0}^{\xi} \frac{B_i(x')p(r_D)}{W[A_i(x), B_i(x)]} d\xi' + C_1 \quad (\text{E.24a})$$

and

$$v_2(\xi) = -\int_{a_0}^{\xi} \frac{A_i(x')p(r_D)}{W[A_i(x), B_i(x)]} d\xi' + C_2 \quad (\text{E.24b})$$

C_1 and C_2 are constants of integration. The Wronskian $W[A_i(x), B_i(x)]_\xi$ of $A_i(x)$ and $B_i(x)$ is here defined as

$$[A_i(x)B_i'(x)_\xi - A_i'(x)_\xi B_i(x)] = \frac{1}{\pi} \quad (\text{E.25})$$

When this is expressed in terms of x rather than ξ , Eq. E.25 becomes

$$[A_i(\beta^{2/3}\xi) B_i'(\beta^{2/3}\xi)_x - A_i'(\beta^{2/3}\xi)_x B_i(\beta^{2/3}\xi)] \frac{dx}{d\xi} = \frac{\left[\frac{dx}{d\xi} \right]}{\pi} \quad (\text{E.26})$$

or

$$W[A_i(x), B_i(x)]_\xi = \frac{dx}{\pi \frac{d\xi}{dx}} \quad (\text{E.27})$$

Using Eq. E.26 in E.24 gives

$$v_1(\xi) = \frac{\pi}{\frac{dx}{d\xi}} \int_{a_0}^{\xi} B_i(\beta^{2/3}\xi') p(r_D) d\xi' + C_1 \quad (\text{E.28a})$$

$$v_2(\xi) = -\frac{\pi}{\frac{dx}{d\xi}} \int_{a_0}^{\xi} A_i(\beta^{2/3}\xi') p(r_D) d\xi' + C_2 \quad (\text{E.28b})$$

Expressing Eqs. E.28 in terms of r_D and recalling that

$$x = \beta^{2/3} \xi$$

$$\xi = \frac{1}{4D_0^2} + \frac{\Phi(k_r + \lambda)}{\alpha D_0} r_D$$

we have

$$v_1[\xi(r_D)] = \frac{\pi}{\beta^{5/3}} \int_{a_0}^{r_D} B_i[\beta^{2/3} \xi(r_D)] p(r_D) dr_D + C_1 \quad (\text{E.29a})$$

$$v_2[\xi(r_D)] = \frac{-\pi}{\beta^{5/3}} \int_{a_0}^{r_D} A_i[\beta^{2/3} \xi(r_D)] p(r_D) dr_D + C_2 \quad (\text{E.29b})$$

Using Eqs. E.29 in E.14, we have

$$\begin{aligned} \bar{\Phi}_{1p}(\xi, \lambda) = & C_1 A_i(\beta^{2/3}\xi) + C_2 B_i(\beta^{2/3}\xi) + \frac{\pi}{\beta^{5/3}} \int_{a_0}^{r_D} [A_i(\beta^{2/3}\xi) B_i(\beta^{2/3}\xi) \\ & - B_i(\beta^{2/3}\xi) A_i(\beta^{2/3}\xi)] p(r_D) dr_D \end{aligned} \quad (\text{E.30})$$

Equation E.30 can be written in a more compact form as

$$\bar{\Phi}_{1p}(\xi, \lambda) = C_1 A_i(x) + C_2 B_i(x) + \frac{\pi}{\beta^{5/3}} \int_{a_0}^{r_D} H(x, x') p(r_D) dr_D \quad (\text{E.31})$$

where $H(x, x')$ is a one-sided Green's function for the system under consideration and is defined as

$$H(x, x') = \begin{vmatrix} A(x) & B(x) \\ A(x') & B(x') \end{vmatrix}$$

Since $H(x, x')$ is the one-sided Green's function for the equation

$$L [\bar{\Phi}_{1p}(\xi, \lambda)] = -p(r_D) \quad (\text{E.12a})$$

and $p(r_D)$ is continuously distributed within the interval $(1, \infty)$, we naturally expect that a function $f(\xi, \lambda)$ given as

$$f(\xi, \lambda) = \int_{a_0}^{r_D} H(x, x') p(r'_D) dr'_D \quad (\text{E.32a})$$

should behave like

$$f(\xi, \lambda) = \int_1^{r_D} H(x, x') p(r'_D) dr'_D \quad (\text{E.32b})$$

as $r_D \rightarrow 1$ while as $r_D \rightarrow \infty$, it should behave like

$$f(\xi, \lambda) = - \int_{r_D}^{\infty} H(x, x') p(r'_D) dr'_D \quad (\text{E.32c})$$

In view of Eqs. E.32, we can define a modified Green's function $g(x, x')$ (Miller, 1963; Arsenin, 1968) such that

$$f(\xi, \lambda) = \int_{r_D=1}^{\infty} g(x, x') p(r'_D) dr'_D \quad (\text{E.33})$$

where

$$g(x, x') = \begin{cases} H(x, x') ; & x > x' \\ -H(x, x') = H(x', x) ; & x \leq x' \end{cases} \quad (\text{E.34})$$

Then Eq. E.31 becomes

$$\bar{\Phi}_{1p}(\xi, \lambda) = C_1 A_i(x) + C_2 B_i(x) + \frac{\pi}{\beta^{5/3}} \int_{r_D=1}^{\infty} g(x, x') p(r'_D) dr'_D \quad (\text{E.35})$$

Applying the boundary condition as $r_D \rightarrow \infty$ we can further reduce Eq. E.35 to

$$\bar{\Phi}_{1p}(\xi, \lambda) = C_1 A_i(x) + \frac{\pi}{\beta^{5/3}} \int_{r_D=1}^{\infty} g(x, x') p(r'_D) dr'_D \quad (\text{E.36})$$

Subject to the inner boundary condition given as

$$U [\bar{\Phi}_{1p}(\xi, \lambda)] = 0 \quad \text{at} \quad r_D = 1 \quad (\text{E.13b})$$

Using Eq. E.13b we can evaluate the constant C_1 as

$$C_1 = \frac{-\pi}{\beta^{5/3}} \left[\frac{\int_{r_D=1}^{\infty} U [g(x, x')]_{r_D=1} \cdot p(r'_D) dr'_D}{U [A_i(x)]_{r_D=1}} \right] \quad (\text{E.37})$$

In Eq. E.37, it must be noted that the linear operator U only operates on x and not on x' in any given situation. Using Eq. E.37, Eq. E.36 can be written in the form:

$$\bar{\Phi}_{1p}(\xi, \lambda) = \frac{-\pi}{\beta^{5/3}} \int_{r_D=1}^{\infty} \left[\frac{A_i(x)U[g(x, x')]_{r_D=1} - g(x, x')U[A_i(x)]_{r_D=1}}{U[A_i(x)]_{r_D=1}} \right] \cdot p(r'_D) dr'_D \quad (\text{E.38})$$

where

$$U [A_i(x)] = \frac{d}{d\xi} [A_i(x)] - \gamma A_i(x) \quad (\text{E.39})$$

and

$$U[g(x, x')] = \begin{cases} \begin{vmatrix} U[A_i(x)] & U[B_i(x)] \\ A_i(x') & B_i(x') \end{vmatrix} & ; \quad x > x' \\ - \begin{vmatrix} U[A_i(x)] & U[B_i(x)] \\ A_i(x') & B_i(x') \end{vmatrix} & ; \quad x \leq x' \end{cases} \quad (\text{E.40})$$

Alternatively, Eq. E.38 can be written in the form:

$$\bar{\Phi}_{1p}(\xi, \lambda) = \frac{\pi}{\beta^{5/3}} \int_{r_D=1}^{\infty} G(x, x') p(r'_D) dr'_D \quad (\text{E.41})$$

where $G(x, x')$ is the system's Green's function definable as

$$G(x, x') = \frac{-1}{U [A_i(x)]_{r_D=1}} \begin{vmatrix} A_i(x) & U [A_i(x)]_{r_D=1} \\ g(x, x') & U [g(x, x')]_{r_D=1} \end{vmatrix} \quad (\text{E.42})$$

$G(x, x')$ can be expanded and expressed in terms of $A_i(x)$ and $B_i(x)$ in the form

$$G(x, x') = A_i(x') \left[\frac{[A'(x_1)B(x) - A(x)B'(x_1)] - \gamma[A(x_1)B(x) - A(x)B(x_1)]}{A'(x_1) - \gamma A(x_1)} \right] \quad (\text{E.43})$$

where

$$A'_i(x) = \frac{d}{d\xi} [A_i(\beta^{2/3} \xi)] = \beta^{2/3} \frac{d}{dx} [A_i(x)] \quad (\text{E.44a})$$

and

$$[A_i(x)]_{r_D=1} = A_i(x_1) \quad (\text{E.44b})$$

Using Eqs. E.44 in E.43 yields

$$G(x, x') = A_i(x') \left[\frac{\beta^{2/3} [A'_i(x_1)_x B_i(x) - A_i(x) B'_i(x_1)_x] - \gamma [A_i(x_1) B_i(x) - A_i(x) B(x_1)]}{\beta^{2/3} A'_i(x_1)_x - \gamma A_i(x_1)} \right] \quad (\text{E.45})$$

using Eq. E.45 in Eq. E.41 we have

$$\bar{\Phi}_{1p}(\xi, \lambda) = \frac{\pi}{\beta^{5/3}} \int_{r_D=1}^{\infty} \left[\frac{\beta^{2/3} [A'_i(x_1)_x B_i(x) - A_i(x) B'_i(x_1)_x] - \gamma [A_i(x_1) B_i(x) - A_i(x) B(x_1)]}{\beta^{2/3} A'_i(x_1)_x - \gamma A_i(x_1)} \right] \cdot A_i(x') p(r'_D) dr'_D ; \quad x \leq x' \quad (\text{E.46})$$

But

$$p(r_D) = \frac{\beta^2 \Phi r_D C_{1s}(r_D) \exp \left[-\frac{r_D - 1}{2D_o} \right]}{\alpha D_o} \quad (\text{E.47})$$

Therefore

$$\Phi_{1p}(\xi, \lambda) = \frac{\Phi \pi \beta^{1/3}}{\alpha D_o} \int_{r_D=1}^{\infty} \left[\frac{\beta^{2/3} [A'_i(x_1)_x B_i(x) - A_i(x) B'_i(x_1)_x] - \gamma [A_i(x_1) B_i(x) - A_i(x) B(x_1)]}{\beta^{2/3} A'_i(x_1)_x - \gamma A_i(x_1)} \right] \cdot A_i(x') C_{1s}(r'_D) \exp \left[-\frac{r'_D - 1}{2D_o} \right] r'_D dr'_D ; \quad x(r_D) \leq x'(r_D) \quad (\text{E.48})$$

For computational consideration, Eq. E.48 is good within the region $x \leq x'$. The equivalent equation for use within the region $x > x'$ is obtained by interchanging x and x' in Eq. E.48.

Equation E.48 could be converted to the concentration $\bar{C}_{1p}(\xi, \lambda)$ by using appropriate inverse transform of Eq. E.48. Thus

$$\bar{C}_{1p}(\xi, \lambda) = \frac{\pi\Phi}{\alpha D_o} \beta^{1/3} \left[\frac{\beta^{2/3} \left[A_i'(x_1)_x B_i(x) - A_i(x) B_i'(x_1)_x \right] - \gamma \left[A_i(x_1) B_i(x) - A_i(x) B_i(x_1) \right]}{\beta^{2/3} A_i'(x_1)_x - \gamma A_i(x_1)} \right] \int_{r_D=1}^{\infty} A_i(x') C_{1s}(r_D) \exp \left[\frac{r_D' - r_D}{2D_o} \right] r_D' dr_D' ; \quad x_D \leq x'(r_D) \quad (\text{E.49a})$$

and

$$\bar{C}_{1p}(\xi, \lambda) = \frac{\pi\Phi}{\alpha D_o} \beta^{1/3} A_i(x) \int_{r_D=1}^{\infty} \left[\frac{\beta^{2/3} \left[A_i'(x_1)_x B_i(x') - A_i(x') B_i'(x_1)_x \right] - \gamma \left[A_i(x_1) B_i(x') - A_i(x') B_i(x_1) \right]}{\beta^{2/3} A_i'(x_1)_x - \gamma A_i(x_1)} \right] C_{1s}(r_D) \exp \left[\frac{r_D' - r_D}{2D_o} \right] r_D' dr_D' ; \quad x(r_D) > x'(r_D) \quad (\text{E.49b})$$

The concentration at the wellbore is obtained by evaluating Eq. E.49 $x = x(r_D = 1)$ to obtain,

$$\bar{C}_{1p}[\xi(r_D=1), \lambda] = \frac{-\frac{\pi\Phi\beta}{\alpha D_o} \cdot W[A_i(x) B_i(x)]_{x=x_1}}{\beta^{2/3} A_i'(x_1) - \gamma A_i(x_1)} \int_{r_D=1}^{\infty} A_i(x') C_{1s}(r_D) \exp \left[\frac{r_D' - 1}{2D_o} \right] r_D' dr_D' \quad (\text{E.50})$$

Evaluating $W \left[A_i(x), B_i(x) \right]_{x=x_1}$ and simplifying Eq. E.50, we have

$$\bar{C}_{1p}[\xi(r_D = 1), \lambda] = \frac{-\Phi\beta}{\alpha D_o} \int_{r_D=1}^{\infty} \frac{A_i(\beta^{2/3}\xi) C_{1s}(r_D) \exp \left[\frac{r_D' - 1}{2D_o} \right] r_D'}{\beta^{2/3} A_i'(x_1)_x - \gamma A_i(x_1)} dr_D'$$

APPENDIX F
SECONDARY TRACER CONCENTRATION PROFILE DURING THE PRODUCTION PERIOD

The equation governing the secondary tracer flow during the production period is similar to that of the secondary tracer during injection, and is given as:

$$\frac{1}{r_D} \frac{\partial}{\partial r_D} \left[r_D D(r_D) \frac{\partial C_{2p}}{\partial r_D} \right] + \frac{\alpha}{r_D} \frac{\partial C_{2p}}{\partial r_D} + \Phi k_r C_{1p} = r_w^2 \frac{\partial C_{2p}}{\partial t} \quad (\text{F.1})$$

The associated initial and boundary conditions are

$$C_{2p}(r_D, t = 0) = C_{2s}(r_D) \quad (\text{F.2a})$$

$$C_{2p}(r_D \rightarrow \infty, t) = 0 \quad (\text{F.2b})$$

$$f_{2p}(r_D) = C_{2p} \text{ @ } r_D = 1 \quad (\text{F.2c})$$

Here, as in Appendix E, $f_{2p}(r_D)$ is the effluent concentration at the wellbore defined as

$$f_{2p}(r_D) = C_{2p} - \frac{D(r_D)}{\alpha} \frac{\partial C_{2p}}{\partial r_D} \quad (\text{F.3})$$

Using the same arguments as in Appendix B, Eq. F.1 can be written as

$$\frac{\partial^2 \phi_{2p}}{\partial r_D^2} - W(r_D) \phi_{2p} + \frac{\Phi k_C}{D} \hat{C}_{1p} = \frac{r_w^2}{D} \frac{\partial \phi_{2p}}{\partial t} \quad (\text{F.4a})$$

where

$$W(r_D) = \left[\frac{1}{4} \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right]^2 + \frac{1}{2} \frac{d}{dr_D} \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right] \right] \quad (\text{F.4b})$$

$$\hat{C}_{1p}(r_D, t) = C_{1p}(r_D, t) \cdot \exp \left[\frac{1}{2} \int_{r_D=1}^{r_D} \left[\frac{D'}{D} + \frac{D + \alpha}{Dr_D} \right] dr_D \right] \quad (\text{F.4c})$$

since

$$D(r_D) = \frac{\alpha D_o}{r_D} \quad (37)$$

Equation F.4 simplifies to

$$\frac{\partial^2 \phi_{2p}}{\partial r_D^2} - \left[\frac{1}{4D_o^2} \right] \phi_{2p} = \frac{r_w^2 r_D}{\alpha D_o} \frac{\partial \phi_{2p}}{\partial t} - \frac{\Phi k_r}{\alpha D_o} r_D \hat{C}_{1p}(r_D) \quad (\text{F.5})$$

Converting Eq. F.5 into the Laplace space and taking cognizance of the initial condition Eq. F.2b we have

$$\frac{d^2 \bar{\phi}_{2p}}{dr_D^2} - \left[\frac{1}{4D_o^2} + \frac{r_w^2 \lambda}{\alpha D_o} r_D \right] \hat{\phi}_{2p} = - \frac{r_D}{\alpha D_o} \left[r_w^2 \hat{C}_{2s}(r_D) + \Phi k_r \hat{C}_{1p}(r_D) \right] \quad (\text{F.6a})$$

where

$$\hat{C}_{2s} = C_{2s} \exp \left[\frac{r_D - 1}{\alpha D_o} \right] \quad (\text{F.6b})$$

Furthermore, if we define η as

$$\eta(r_D) = \frac{1}{4D_o^2} + \left[\frac{r_w^2 \lambda}{\alpha D_o} \right] r_D \quad (\text{F.8})$$

Then Eq. F.6 becomes

$$\frac{d^2 \bar{\phi}_{2p}}{d\eta^2} - \left[\frac{\alpha D_o}{\lambda r_w^2} \right]^2 \eta \bar{\phi}_{2p} = - \left[\frac{\alpha D_o}{\lambda r_w^2} \right]^2 \frac{r_D}{\alpha D_o} \left[r_w^2 \hat{C}_{2s}(r_D) + \Phi k_r \hat{C}_{1p}(r_D) \right] \quad (\text{F.9})$$

The associated boundary conditions are

$$\bar{\phi}_{2p}(r_D \rightarrow \infty, \lambda) = 0 \quad (\text{F.10a})$$

$$\frac{d\bar{\phi}_{2p}}{d\eta} - \left[\frac{\alpha D_o}{\lambda r_w^2} \right] \frac{\bar{\phi}_{2p}}{2D_o} = 0 \quad @ \quad r_D = 1 \quad (\text{F.10b})$$

The set of Eqs. F.9 and F.10 is not substantially different from the set of Eqs. E.9 and E.10 and therefore the same procedure of solution described in Appendix E can be used to obtain a solution to the set Eqs. F.9 and F.10.

If we define the following variables in the manner of Appendix E,

$$\sigma = \left[\frac{\alpha D_o}{\lambda r_w^2} \right] \quad (\text{F.11a})$$

$$s(r_D) = \frac{\sigma^2 r_D}{\alpha D_o} \left[r_w^2 \hat{C}_{2s}(r_D) + \Phi k_r \hat{C}_{1p}(r_D) \right] \quad (\text{F.11b})$$

and

$$\delta = \frac{\sigma}{2D_o} \quad (\text{F.11c})$$

Equations F.9 and F.10 can be written as

$$\frac{d^2 \bar{\Phi}_{2p}}{d\eta^2} - \sigma^2 \eta \bar{\Phi}_{2p} = -s(r_D) \quad (\text{F.12})$$

$$\bar{\Phi}_{2p} \left[\eta(r_D) \rightarrow \infty, \lambda \right] = 0 \quad (\text{F.13a})$$

$$\frac{d\bar{\Phi}_{2p}}{d\eta} - \delta \bar{\Phi}_{2p} = 0 \quad (\text{F.13b})$$

Defining a linear differential operators **M** and **V** as :

$$\mathbf{M} = \frac{d^2}{d\eta^2} - \sigma^2 \eta \quad (\text{F.14})$$

and

$$\mathbf{V} = \frac{d}{d\eta} - \delta \quad (\text{F.15})$$

Equations F.12 and F.13 become

$$\mathbf{M} \left[\bar{\Phi}_{2p}(\eta, \lambda) \right] = -s(r_D) \quad (\text{F.16})$$

$$\bar{\Phi}_{2p} \left[\eta(r_D) \rightarrow \infty, \lambda \right] = 0 \quad (\text{F.17a})$$

$$\mathbf{V} \left[\bar{\Phi}_{2p}(\eta, \lambda) \right]_{r_{D=1}} = 0 \quad (\text{F.17b})$$

Equation F.16 is directly analogous to Eq. E.12 of Appendix E. Also, the outer boundary condition given by Eq. F.17a is the same as Eq. E.10a of Appendix E while Eq. F.17b for the outer boundary condition is analogous to Eq. E.13b of Appendix E. The above strong analogy between our equations of this appendix and those of Appendix E which has been solved makes it easy to write down the solution to the secondary tracer production profile in line with the earlier solution obtained for the primary tracer production profile. The secondary tracer production concentration profile can therefore be written as:

$$\bar{\Phi}_{2p}(\eta, \lambda) = \frac{\pi}{\sigma^{5/3}} \int_{r_{D=1}}^{\infty} \left[\frac{H(\eta, \eta') \mathbf{V} \left[A_i(\sigma^{2/3} \eta) \right]_{r_{D=1}} - A_i(\sigma^{2/3} \eta) \mathbf{V} \left[H(\eta, \eta') \right]_{r_{D=1}}}{\mathbf{V} \left[A_i(\sigma^{2/3} \eta) \right]_{r_{D=1}}} \right] \cdot s(r'_D) dr'_D \quad (\text{F.18})$$

where

$$\mathbf{V} \left[A_i(\sigma^{2/3}\eta) \right] = \frac{d}{d\eta} \left[A_i(\sigma^{2/3}\eta) \right] - \delta A_i(\sigma^{2/3}\eta) \quad (\text{F.19a})$$

$$H(\eta, \eta') = - \begin{vmatrix} A_i(\sigma^{2/3}\eta) & B_i(\sigma^{2/3}\eta) \\ A_i(\sigma^{2/3}\eta') & B_i(\sigma^{2/3}\eta') \end{vmatrix} \quad (\text{F.19b})$$

$$\mathbf{V} \left[H(\eta, \eta') \right] = - \begin{vmatrix} \mathbf{V} \left[A_i(\sigma^{2/3}\eta) \right] & \mathbf{V} \left[B_i(\sigma^{2/3}\eta) \right] \\ A_i(\sigma^{2/3}\eta') & B_i(\sigma^{2/3}\eta') \end{vmatrix} \quad (\text{F.19c})$$

Substituting for $s(r_D)$ in Eq. F.18 we have

$$\bar{\Phi}_{2p}(\eta, \lambda) = \frac{\pi}{\alpha D_o} \sigma^{1/3} \int_{r_{D=1}}^{\infty} G(\eta, \eta') \left[r_w^2 \hat{C}_{2s}(r'_D) + \Phi k_r \hat{C}_{1p}(r'_D) \right] r'_D dr'_D \quad (\text{F.20})$$

where $G(\eta, \eta')$ is the system's Green's function defined as

$$G(\eta, \eta') = \frac{1}{\mathbf{V} [A_i(\sigma^{2/3}\eta)]_{r_{D=1}}} \begin{vmatrix} H(\eta, \eta') & A_i(\sigma^{2/3}\eta) \\ \mathbf{V} [H(\eta, \eta')]_{r_{D=1}} & \mathbf{V} [A_i(\sigma^{2/3}\eta)]_{r_{D=1}} \end{vmatrix} \quad (\text{F.21})$$

Expanding $G(\eta, \eta')$ in terms of $A_i(Z)$ and $B_i(Z)$ yields

$$G(\eta, \eta') = A_i(Z') \left[\frac{\sigma^{2/3} \left[A'_i(Z_1) B_i(Z) - A_i(Z) B'_i(Z_1) \right] - \delta \left[A_i(Z_1) B_i(Z) - A_i(Z) B_i(Z_1) \right]}{\sigma^{2/3} A'_i(Z_1) - \delta A_i(Z_1)} \right] \quad (\text{F.22a})$$

where

$$Z = \sigma^2 \eta \quad (\text{F.22b})$$

$$Z_1 = \sigma^{2/3} \eta (r_D = 1) \quad (\text{F.22c})$$

Thus Eq. F.20 can be written as:

$$\bar{\Phi}_{2p}(\eta, \lambda) = \frac{\pi}{\alpha D_o} \sigma^{1/3} \int_{r_{D=1}}^{\infty} \left[\frac{\sigma^{2/3} \left[A'_i(Z_1) B_i(Z) - A_i(Z) B'_i(Z_1) \right] - \delta \left[A_i(Z_1) B_i(Z) - A_i(Z) B_i(Z_1) \right]}{\sigma^{2/3} A'_i(Z_1) - \delta A_i(Z_1)} \right] A_i(Z') \left[r_w^2 \hat{C}_{2s}(r'_D) + \Phi k_r \hat{C}_{1p}(r'_D) \right] r'_D dr'_D \quad (\text{F.23})$$

Converting Eq. F.23 back to concentration yields:

$$\bar{C}_{2p}(r_D, \lambda) = \left[\frac{\sigma^{2/3} \left[A_i(Z_1) B_i(Z) - A'_i(Z) B'_i(Z_1) \right] - \delta \left[A_i(Z_1) B_i(Z) - A_i(Z) B_i(Z_1) \right]}{\sigma^{2/3} A'_i(Z_1) - \delta A_i(Z_1)} \right]$$

$$\cdot \frac{\pi \sigma^{1/3}}{\alpha D_o} \int_{r_D=1}^{\infty} \exp \left[\frac{r'_D - r_D}{2D_o} \right] A_i(Z') \left[r_w^2 C_{2s}(r'_D) + \Phi k_r C_{1p}(r'_D) \right] r'_D dr'_D; \quad r_D \leq r'_D \quad (\text{F.24a})$$

The corresponding equation valid in the range $r_D > r'_D$ is obtained by interchanging Z and Z' in Eq. F.24a; thus

$$\bar{C}_{2p}(r_D, \lambda) = \frac{\pi \sigma^{1/3}}{\alpha D_o} A_i(Z) \int_{r_D=1}^{\infty} \exp \left[\frac{r'_D - r_D}{2D_o} \right]$$

$$\cdot \left[\frac{\sigma^{2/3} \left[A'_i(Z_1) B_i(Z') - A_i(Z') B'_i(Z_1) \right] - \delta \left[A_i(Z_1) B_i(Z') - A_i(Z') B_i(Z_1) \right]}{\sigma^{2/3} A'_i(Z_1) - \delta A_i(Z_1)} \right]$$

$$\cdot \left[r_w^2 C_{2s}(r'_D) + \Phi k_r C_{1p}(r'_D) \right] r'_D dr'_D; \quad r_D > r'_D \quad (\text{F.24b})$$

The produced concentration is obtained from Eq. F.24a by setting $Z = Z_1$ to obtain

$$\bar{C}_{2p}(r_D = 1, \lambda) = \frac{\pi \sigma}{\alpha D_o} \cdot \frac{W \left[A_i(Z_1), B_i(Z_1) \right]}{\sigma^{2/3} A'_i(Z_1) - \delta A_i(Z_1)} \int_{r_D=1}^{\infty} A_i(Z') \left[r_w^2 C_{2s}(r'_D) + \Phi k_r C_{1p}(r'_D) \right] r'_D dr'_D \quad (\text{F.25})$$

or

$$\bar{C}_{2p}(r_D=1, \lambda) = - \frac{\sigma}{\alpha D_o} \int_{r_D=1}^{\infty} \frac{A_i(\sigma^{2/3} \eta') \left[r_w^2 C_{2s}(r'_D) + \Phi k_r C_{1p}(r'_D) \right] r'_D dr'_D}{\sigma^{2/3} A'_i[\sigma^{2/3} \eta(r_D = 1)] - \delta A_i[\sigma^{2/3} \eta(r_D = 1)]} \quad (\text{F.26})$$

APPENDIX G NONEQUILIBRIUM MODEL

In our earlier model it was necessary to specify an equilibrium relation between tracer species adsorbed in the immobile fluid phase and those in the mobile fluid phase. This assumption may be true and valid for cases where the rate of adsorption is instantaneous and/or the fluid flow velocity is low. However, in cases where the fluid flow rate is high, and/or the rate of adsorption is finite, a nonequilibrium adsorption isotherm would be more appropriate.

For the nonequilibrium adsorption isotherm, we can, in general, specify that

$$\frac{d\bar{C}_i}{dt} = f(C_i, \bar{C}_i) \quad (G.1)$$

For a system with a finite rate of adsorption, we can formulate a simple first order rate equation of the form

$$f(C_i, \bar{C}_i) = k_1 C_i - k_2 \bar{C}_i \quad (G.2)$$

where k_1 and k_2 are the finite adsorption and desorption rate constants respectively. Thus

$$\frac{d\bar{C}_i}{dt} = k_1 C_i - k_2 \bar{C}_i \quad (G.3)$$

From Eq. 1 of the main text, the hydrodynamics of tracer is described by the equation

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial C_i}{\partial r} \right] - \frac{1}{r} \frac{\partial}{\partial r} (rv_w C_i) - R_i(C_i, \bar{C}_i) = \frac{\partial C_i}{\partial t} + \frac{S_0}{S_w} \frac{\partial \bar{C}_i}{\partial t} \quad (G.4)$$

Expanding Eq. G.4 in terms of r_D and simplifying, we have for species $i = 1$,

$$\frac{\partial^2 C_1}{\partial r_D^2} + \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \frac{\partial C_1}{\partial r_D} - \frac{R_1(C_1, \bar{C}_1)}{D(r_D)} r_w^2 = \frac{r_w^2}{D(r_D)} \left[\frac{\partial C_1}{\partial t} + \frac{S_0}{S_w} \frac{\partial \bar{C}_1}{\partial t} \right] \quad (G.5)$$

where the reaction term can be written as

$$R_1(C_1, \bar{C}_1) = k_r \left[C_1 + \frac{S_0}{S_w} \bar{C}_1 \right] \quad (G.6)$$

The associated initial and boundary conditions can be written

$$C_1(r_D, t) = 0 \quad (\text{G.7a})$$

$$\bar{C}_1(r_D, t = 0) = 0 \quad (\text{G.7b})$$

$$C_1(r_D = 1, t) = C_0 \quad (\text{G.7c})$$

$$C_1(r_D \rightarrow \infty, t) = 0 \quad (\text{G.7d})$$

Considering Eqs. G.3, G.5, and G.7 in the Laplace space we have

$$\frac{\partial^2 C_1^*}{\partial r_D^2} + \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \frac{\partial C_1^*}{\partial r_D} - \frac{r_w^2 k_r}{D(r_D)} \left[C_1^* + \frac{S_0}{S_w} \bar{C}_1^* \right] = \frac{\lambda r_w^2}{D(r_D)} \left[C_1^* + \frac{S_0}{S_w} \bar{C}_1^* \right] \quad (\text{G.8})$$

Equation G.3 becomes

$$\lambda \bar{C}_1^* = k_1 C_1^* - k_2 \bar{C}_1^* \quad (\text{G.9a})$$

or

$$\bar{C}_1^* = \frac{k_1 C_1^*}{\lambda + k_2} \quad (\text{G.9b})$$

where C_i^* is the Laplace transform of C_i as

$$C_i^* = L \left[C_i(r_D, t) \right] = \int_0^{\infty} C_i(r_D, s) e^{-\lambda s} ds \quad (\text{G.10})$$

The associated boundary conditions are

$$C_1(r_D = 1, \lambda) = \frac{C_0}{\lambda} \quad (\text{G.11a})$$

$$C_1(r_D \rightarrow \infty, \lambda) = 0 \quad (\text{G.11b})$$

Eliminating \bar{C}_1^* from Eqs. G.8 and G.9a we have

$$\begin{aligned} \frac{d^2 C_1^*}{dr_D^2} + \left[\frac{D'}{D} + \frac{D - \alpha}{Dr_D} \right] \frac{dC_1^*}{dr_D} - \frac{k_r r_w^2}{D(r_D)} \left[1 + \frac{S_0}{S_w} \left[\frac{k_1}{\lambda + k_2} \right] \right] C_1^* \\ = \frac{\lambda r_w^2}{D(r_D)} \left[1 + \frac{S_0}{S_w} \left[\frac{k_1}{\lambda + k_2} \right] \right] C_1^* \end{aligned} \quad (\text{G.12})$$

Using transformations

$$C_1^*(r_D, \lambda) = \bar{\psi}_1(r_D, \lambda) \exp \left[- \frac{1}{2} \int_{r_D=1}^{r_D} \left[\frac{D'}{D} + \frac{D - \alpha}{D\xi} \right] d\xi \right] \quad (\text{G.13})$$

and

$$D(r_D) \approx \frac{D_0 \alpha}{r_D} \quad (\text{G.14})$$

we have

$$\frac{d^2 \bar{\psi}_1}{dr_D^2} - \left[\frac{1}{4D_0^2} + \frac{\Phi^*}{\alpha D_0} (k_r + \lambda) r_D \right] \bar{\psi}_1 = 0 \quad (\text{G.15a})$$

where

$$\Phi^* = \left[1 + \frac{S_0}{S_w} \left[\frac{k_1}{\lambda + k_2} \right] \right] r_w^2 \quad (\text{G.15b})$$

Equation G.15 is similar to Eq. 39 and hence the solutions are similar. The only difference is that the delay factor Φ^* is now time dependent unlike Φ for the equilibrium model which is time independent.

Thus, an exact analytical solution for the nonequilibrium model can immediately be written by mere analogy with the equilibrium model viz.

$$\bar{C}_1(r_D, \lambda) = \frac{C_0 \exp\left[\frac{r_D - 1}{2D_0}\right]}{\lambda} \sqrt{\frac{\xi(r_D)}{\xi(r_D = 1)}} \left[\frac{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi^*(k_r + \lambda)} \right] \xi^{2/3}(r_D) \right]}{K_{1/3} \left[\frac{2}{3} \left[\frac{\alpha D_0}{\Phi^*(k_r + \lambda)} \right] \xi^{2/3}(r_D = 1) \right]} \right] \quad (\text{G.16a})$$

where

$$\xi(r_D) = \frac{1}{4D_0^2} + \frac{\Phi^*(k_r + \lambda)}{\alpha D_0} r_D \quad (\text{G.16b})$$

Therefore, the nonequilibrium model is not substantially different from the equilibrium model. The nonequilibrium model is, however, only useful to the extent that the adsorption and desorption rate constants k_1 and k_2 can be found with reasonable accuracy.

