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THE THEORY AND SELECTION OF CHEMICALLY REACTIVE TRACERS FOR RESERVOIR THERMAL CAPACITY PRODUCTION

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ABSTRACT

The theory behind how chemically reactive tracers are used to characterize the velocity and temperature distribution in steady flowing systems is reviewed. Ranges of kinetic parameters are established as a function of reservoir temperatures and fluid residence times for selecting appropriate reacting systems. Reactive tracer techniques are applied to characterize the temperature distribution in a laminar-flow heat exchanger. Models are developed to predict reactive tracer behavior in fractured geothermal reservoirs of fixed and increasing size.

INTRODUCTION AND SCOPE

Inlet-outlet tracer measurements are an accepted experimental method for determining internal characteristics of continous flow sytems. Typically, a known amount of material is injected into the inlet with concentrations monitored at the outlet. Chemical reactors, process equipment, biologic systems, and underground reservoirs are examples of flow sytems in which tracers have been utilized successfully.

Unfortunately, in most flow systems of practical interest, inlet-outlet tracer techniques cannot uniquely determine the details of internal convective flow and fluid mixing. This non-uniqueness problem becomes even more severe when other characteristics of the system must be determined, such as internal temperatures, or local porosities and permeabilities. Frequently, a deterministic flow model with adjustable parameters is used to fit experimental tracer data. Thus, some non-uniqueness results in the absence of complete hydrodynamic and geometric information.

The primary focus of the present study is to develop new reactive tracer techniques and methods of data analysis which provide model-independent information about the internal flow and temperature fields of nonisothermal, continuous flow systems. A transient response experiment in which the tracer disperses and partially reacts contains information about both the internal flow and temperature fields of a flow system. Residence time distribution (RTD) theory (Danckwerts, 1953) and its extensions (Nauman and Buffham, 1983) are employed in the analysis of this chemically reactive tracer technique. In this paper, we outline the mathematical development necessary to rigorously describe the behavior of a reacting tracer in a nonisothermal flow system. Simplifications to yield practical models are discussed next, followed by a review of the quantitative criteria used in selecting tracers for geothermal reservoir diagnostics. Results of experiments in a laminar flow heat exchanger are presented to verify the validity of the reactive tracer technique, and to identify practical uncertainties and limitations of the theoretical concepts. Finally, applications to geothermal reservoir analysis are introduced through the use of simplified models of fractured systems undergoing heat extraction.

As this paper only overviews our current work on chemically reactive tracers, interested readers should consult Robinson and Tester (1986) and Robinson, Tester, and Brown (1987) for complete detailed coverage of the subject.

THEORETICAL DEVELOPMENT

When a non-reacting tracer of mass m_p is injected as a pulse into an isothermal steady flow system, the concentration-time response C(t) is measured in the outlet, and the residence time distribution (RTD) f(t) is obtained:

$$f(t) = QC(t)/m_p \qquad (1)$$

For steady state, incompressible fluid flow, f(t)dt = the fraction of fluid in the exit stream with residence times between t and t + dt. If another tracer that undergoes an irreversible, first-order reaction

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*currently with the Los Alamos National Laboratory, Los Alamos, NM 87545 is introduced into the same isothermal system, the dimensionless, steady state, outlet conversion C_0/C_{in} is given exactly by:

$$C_0/C_{in} = \int_0^\infty f(t)\exp(-kt)dt \qquad (2)$$

Equation (2) demonstrates that when an estimate of chemical reactor conversion or performance is desired for a first order reaction, the RTD is quite useful even without a detailed description of the flow field once f(t) is known. However, for reservoir engineering studies utilizing tracers, the internal flow and temperature patterns or other characteristics are often needed, and thus flow modeling is employed. For fractured reservoirs with relatively small deviations from plug flow caused by turbulent or mechanical mixing, a two-or one-dimensional axial dispersion model can be used to describe tracer dispersion. In this case the mathematical expression describing dispersive mixing of a reactive tracer in a convective flow field is:

$$\nabla\cdot(\underset{\approx}{D}\nabla C) - \underset{\sim}{U}\cdot\nabla C - kC = dC/dt \qquad (3)$$

where $\underset{\approx}{D}$ is the dispersion coefficient tensor and $\underset{\sim}{U}$ the flow velocity vector. The term -kC has been introduced to account for the disappearance of tracer by way of a first order chemical reaction whose instantaneous rate is linearly proportional to the local concentration of tracer (C).
For systems with substantial internal flow maldistribution (that is large-scale internal velocity gradients) which cannot be modeled adequately assuming either perfect backmixing (the CSTR) or plug flow with axial dispersion, the situation becomes more difficult. Internal slow-moving (sluggish) or channeling zones must be described using models which treat the overall flow system as a composite of superimposed internal regions of different flow velocity.

Equation (3) is directly coupled to the <u>in situ</u> temperature field within the system because k, the first order rate constant, is a strong function of temperature. Its dependence is commonly expressed in Arrhenius form as:

$$k = A_r\exp\,[-E/RT] \qquad (4)$$

For typical reactions in aqueous geothermal environments ranging from say 50 to 250°C from the injection to the production region, k will vary by several orders of magnitude.

One very important potential application of reactive tracers is to provide a measure of reservoir thermal capacity before actual thermal breakthrough occurs. The concept is actually quite simple incorporating the strong temperature dependence of k given in equation (4). Suppose a slug of tracer is injected into an initially hot reservoir and the overall conversion given by equation (2) is about 50% ($C_0/C_{in} = 0.5$). After some period of heat extraction a second slug of tracer is introduced. The conversion this time should be less than 50% given that a portion of the reservoir has been cooled reducing the value of k and the reaction rate in that region. Consequently, a series of reactive tracer tests will, in theory, map the rate of growth of the cooled region of the reservoir as heat extraction proceeds, and hopefully provide early warning of thermal drawdown.

The theory of generalized reaction times was proposed by Nauman (1977) and Nauman and Buffham (1983) to extend the existing mathematics of RTD theory to handle a greater number of reacting flow systems. By appropriately defining an equivalent reaction time for the more complex case, conventional RTD analysis may be used simply by replacing the residence time with a generalized reaction time, and the RTD with a generalized time distribution. The first such extension of RTD theory was proposed by Orcutt et al. (1962), who demonstrated the usefulness of the contact time in the analysis of a fluid-solid catalytic reactor.

For nonisothermal systems, the relevant generalized time is the thermal time θ proposed by Nauman (1977):

$$\theta = \int_0^t \exp(-E/RT)dt \qquad (5)$$

for which an Arrhenius expression is assumed. The integral is performed over the time-temperature history of a molecule in a nonisothermal system. For a group of reactant molecules traveling through the same nonisothermal path, the integrated first order rate law is

$$C/C_{in} = \exp(-A_r\theta) \qquad (6)$$

Note that the rate law of Eqn. (6) reduces to exp[-kt] in an isothermal system.

Nauman (1977) then defined a thermal time distribution (TTD) $h(\theta)$ as follows: $h(\theta)d\theta$ = the fraction of molecules in the exit stream with thermal times between θ and θ + $d\theta$. For nonisothermal system, Eqn. (2) may be converted by replacing t with θ and f(t) by h (θ) to give:

$$C_0/C_{in} = \int_0^\infty h(\theta)\exp(-A_r\theta)d\theta \quad (7)$$

which is rigorous for a single-phase, irreversible, first-order reaction in a steady state, nonisothermal system.

A system of this type can be described with a bivariate thermal/residence time distribution function $P(t,\theta)$: $P(t,\theta)dtd\theta$ = the fraction of molecules in the exit stream with residence time between t and t + dt and thermal time between θ and $\theta + d\theta$. This normalized function represents an inventory of thermal and residence time properties of molecules in the exit stream. It is at the intersection of f(t) and $h(\theta)$, where the normalization is carried out so that,

$$\int_0^\infty\int_0^\infty P(t,\theta)dtd\theta = 1 \quad (8)$$

The function $P(t,\theta)$ is defined so that it is related to f(t) and to the thermal time distribution $h(\theta)$. Integrating over all thermal times at a given residence time:

$$f(t) = \int_0^\infty P(t,\theta')d\theta' \quad (9)$$

Likewise, integrating over all residence times for a given thermal time:

$$h(\theta) = \int_0^\infty P(t',\theta)dt' \quad (10)$$

If the distribution function approach is to be used, the bivariate distribution function $P(t,\theta)$ must enter into any rigorous description of a nonisothermal flow system. This is true because fluid or reactant molecules exiting with the same residence time need not have experienced the same time-temperature histories. Thus, the outlet chemical concentration of molecules at a given residence time is, in general, a result of superimposed reactant concentrations from different flow and temperature paths which have reacted to different extents.

The physical significance of the RTD f(t), TTD $h(\theta)$, and bivariate distribution $P(t,\theta)$ can each be demonstrated using a simple thought experiment. Picture the injection of a tracer pulse containing a very large number of small droplets of identical size which contain a reactant undergoing a first order reaction. The droplets are immiscible in the reactor fluid, yet follow the same flow paths with the same RTD as the injected fluid. Assume also that the droplets are collected at the outlet and analyzed separately so that the residence time and extent of reaction within each drop are known. This idealized experiment could, in theory, be used to measure the RTD, the TTD, and the bivariate distribution $P(t,\theta)$.

f(t): If the outlet fluid is collected between t and t + dt, the number of droplets in this sample, divided by the total number injected, equals f(t)dt.

$h(\theta)$: The dimensionless concentration in a droplet equals $\exp[-A_r\theta]$. Thus, a thermal time may be obtained for each droplet from a measurement of the extent of reaction. The number of droplets for which the thermal time falls between θ and $\theta + d\theta$, regardless of residence time, divided by the total number of droplets, equals $h(\theta)d\theta$.

$P(t,\theta)$: The number of droplets which exit between t and t + dt and possess thermal times between θ and $\theta + d\theta$, divided by the total number of droplets, equals $P(t,\theta)dtd\theta$.

INTERPRETATION OF EXPERIMENTAL TRACER DATA

Although the theoretical experiment just described facilitates an explanation of the various distribution functions in a nonisothermal reacting flow system, it is obviously too cumbersome an experiment to carry out practically. Thus, we propose a simpler form of the experiment, called the transient reactive tracer experiment, in which a pulse of a miscible tracer is injected into a nonisothermal flow system, and the concentration-time behavior of the reactant or product is monitored at the outlet. The term "transient" refers to the time-dependent nature of the tracer measurement, and not to time-varying operating conditions of the flow system. Only steady state (or quasi-steady state) flow and temperature fields are considered. In addition to the convective, molecular diffusive, and mechanical dispersive mechanisms that influence inert tracer behavior, the reactive tracer also undergoes an irreversible, first order reaction.

The amount of tracer remaining at different residence times will be measured at the outlet. The dispersion of both the reactants and products is governed by the f(t) curve, while the percent reaction at each residence time is controlled by the internal time-temperature histories of the tracer. It can be shown that the outlet conversion (C_0/C_{in}) given rigorously by equation (7) can alternatively be expressed in terms of $P(t,\theta)$ as,

$$C_0/C_{in} = \int_0^\infty\int_0^\infty P(t,\theta)\exp(-A_r\theta)d\theta dt \quad (11)$$

The key to understanding the transient reactive tracer analysis is that the C(t) and f(t) data provide conversion or thermal time information for molecules of different residence time. Since the thermal time, which is the fundamental variable for reaction in nonisothermal systems, is calculated from an integral along the flow path, conversion data is a lumped, macroscopic result which does not provide a microscopic description of the actual time-temperature history. Nonetheless, the experiment will directly detect nonisothermalities which are specifically linked to residence time. For example, if the temperature field encountered by fluid of small residence time t is different than that of the long-residence-time fluid, the transient reactive tracer response will indicate this phenomenon. However, temperature patterns along a flow path cannot be determined from the single transient tracer analysis unless other information about the temperature pattern is available.

In many systems large-scale heterogeneities cause the observed RTD. These would include multifracture reservoirs with channeling or multidimensional flow in specific fractures, where different residence times are associated with specific physical locations within the reservoir. If these internal flow regions possess different temperature fields, then the C(t) response may be interpreted to obtain the extent of nonisothermality. For maldistributed flow fields, a useful simplification of the internal flow and temperature field is to assume that each residence time corresponds to one and only one value of the thermal time. This assumption will hereafter be called the residence time-thermal time correspondence criterion. Under these conditions in our hypothetical droplet experiment, all droplets exiting at a given time t would have the same chemical reaction conversion. This implies that the bivariate distribution function $P(t,\theta)$ is nonzero for only one value of thermal time, expressed using a Dirac delta function δ () as,

$$P(t,\theta) = \delta[\theta - \theta(t)]f(t) \qquad (12)$$

where $\theta(t)$ is the thermal time corresponding to the flow path of residence time t. The steady state outlet conversion given by equation (7) is used in equation (2) to calculate an "isothermal equivalent" $\bar{k}$, which is the rate constant required for the same steady state conversion in an isothermal reservoir having an identical RTD or f(t) curve. The isothermal equivalent response curve $C_p(t)$ to a pulse injection is then determined from:

$$C_p^I(t)/f(t) = \exp(-\bar{k}t) \qquad (13)$$

Correspondence between residence time and thermal time, if it exists, will be observed by comparing $C_p^I(t)$ with the actual $C_p(t)$ data.

The calculated $C_p^I(t)$ curve will exhibit differences in reactant conversion with residence time which are due only to the residence time, while the measured $C_p(t)$ curve may take a different shape depending on the temperature field. There are at least three types of internal flow/temperature fields which could give rise to different reactive tracer behavior, as shown conceptually in Figure 1. The first, labelled uniform reaction environment, results in identical $C_p(t)$ curves for the actual and isothermal equivalent cases. In such a system, all flow paths encounter similar temperature fields, regardless of residence time. Obviously, all isothermal systems are examples of uniform reaction environments, with θ (t) = texp(-E/RT). Nonisothermal systems may also exhibit this behavior if all fluid elements experience the same temperature field, regardless of residence time.

In the temperature-enhanced reaction environment, the extent of reaction at longer residence times is greater than that which can be explained by residence time alone. A temperature effect compounds the normal increase in reactant conversion with residence time. For a system exhibiting this type of reactive tracer behavior, the longer residence time flow paths are, on average, at higher temperatures.

By the same reasoning, the temperature-compensated reaction environment is one in which longer residence times correlate with cooler average temperatures. A single transient reactive tracer experiment, when analyzed using the isothermal equivalent method, provides model-independent information for complex, nonisothermal systems. The analysis just outlined could be used as the starting point in the construction of a descriptive flow and thermal model. Internal flow zones of different volume, flow velocity, and temperature could be established on the basis of an analysis of the inert f(t) and reactive $C_p(t)$ responses.

REACTIVE TRACER SELECTION AND CHARACTERIZATION

In addition to having all the desirable characteristics of inert tracers, reactive tracers kinetic parameters (A_r and E) should be such that the characteristic reaction time τ_r = 1/k for a 1st order reaction is of the same order of magnitude as the mean residence time τ.

Kinetic experiments were performed in a constant-temperature reactor to identify candidate reactive tracers for different geothermal applications. The rates of hydrolysis of six organic esters and three unsubstituted amides were determined in a buffer system consisting of mixtures of sodium bicarbonate and acetic acid in deionized water. The kinetic rate law for the alkaline hydrolysis of ethyl acetate is given by

$$d[EA]/dt = -k_2[OH^-][EA] \qquad (14)$$

In these buffered solutions of pH between 5.6 and 7.3, $[OH^-]$ is constant during an experiment, but its value at elevated temperature is much higher than at 25°C due to the temperature-dependence of the equilibrium constants of the water, bicarbonate, and acetic acid dissociation reactions. A chemical equilibrium model was developed to predict $[OH^-]$ at high temperature for a closed system of known chemical conditions at 25°C.

This model is used to evaluate the autoclave hydrolysis data obtained for ethyl acetate in buffered solutions as summarized in Figure 2. The autoclave data agree with alkaline hydrolysis kinetic parameters obtained at high pH and low temperature (typically 0.01 M NaOH and 30-60°C) by previous investigators and in the present study. However, if we merely assume $[OH^-]=10^{(pH-14)}$, without accounting for temperature, the observed reaction rates are 2-3 orders of magnitude higher than expected. Also, experiments performed at higher pH exhibited the rate behavior predicted by the $[OH^-]$ model.

Similar agreement with published alkaline hydrolysis data was obtained for all but one of the esters (t-butyl acetate). The amides also appear to follow the proper rate versus $[OH^-]$ behavior, but the absolute rates were higher than expected from the extrapolated literature results. Figure 3 shows the results of the autoclave hydrolysis experiments in the form of reaction time ($1/k_2[OH^-]$ versus $1/T$ for geofluid of pH 6. Finally, preliminary rock compatibility studies using crushed granite showed no evidence of catalytic effects, but the esters of higher molecular weight had a slight tendency to adsorb on the rock surface.

VERIFICATION OF REACTIVE TRACER ANALYSIS TECHNIQUES

The reactive tracer techniques introduced earlier were verified experimentally for the case of a vertical, countercurrent, shell and tube heat exchanger with laminar flow. Assuming a parabolic velocity profile, temperature independent thermal physical properties, and negligible axial conduction of heat, the well known Graetz solution is applicable (see Eckert and Drake (1972) for details). Under these conditions the axial and radial temperature profile is given by:

$$T^+ = T^+(x^+,r^+) = \sum_{n=o} C_n R_n(r^+) \exp(-\lambda_n^2 x^+) \qquad (15)$$

when C_n is a numerical constant corresponding to each Eigenvalue λ_n. $R_n(r^+)$ are the radial function for each Eigenvalue λ_n. Equation (15) can be asymptotically approximated by

$$T^+ = T^+(x^+,r^+) = 0.7764 \int_0^{n} \exp(- {}_{\eta}^{3}/3)\, d\, {}_{\eta} \qquad (16)$$

where dimensionless variables are defined as:

$$x^+ = x/(r_0 RePr) \ : \ r^+ = r/r_0$$

$$T^+ = (T-T_w)/)T_0-T_w)$$

Fluid flows up through the inside tube and is heated or cooled from the outside. First, the constant-wall temperature Graetz solution was coupled to the theoretical tracer response assuming the parabolic velocity profile and no molecular diffusion of tracer. Calculated reactive tracer response curves are shown in Figure 4 for cold injection fluid heated from the outside and hot fluid cooled from the outside. The dramatic difference detected by the transient reactive tracer curves demonstrates that the $C_p(t)$ response can be used to evaluate the internal temperature field of this system.

Heat transfer and inert and reactive tracer experiments were performed in a laminar flow heat exchanger (Re = 100) to evaluate the Graetz model and the reactive tracer techniques. The chemical reaction used was the alkaline hydrolysis of ethyl acetate (EA) to ethanol and acetic acid. When $[EA] >> [OH^-]$, the pseudo-first order rate law is

$$d[OH^-]/dt = -k[OH^-], \qquad (17)$$

where $k = \exp(-E/RT)A_{r,2}[EA]$ is the psuedo-first order rate constant. The term $\exp(-E/RT)A_{r,2}$ is the second order rate constant for the reaction, and the apparent A_r under these conditions is $A_{r,2}[EA]$. In this case the reactive tracer is OH^-

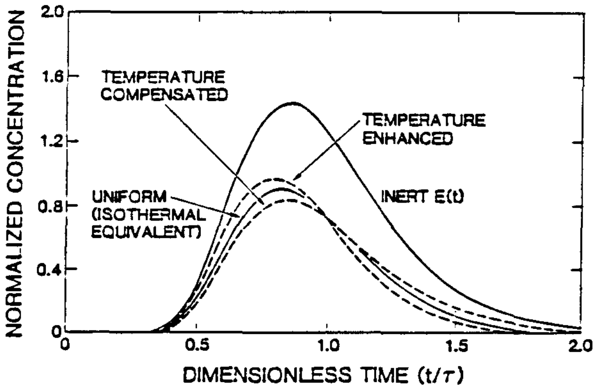

Figure 1. Typical reactive tracer pulse response curves for the three reaction environments.

measured on-line in the outlet stream using a pH electrode. Varying [EA], while always keeping it large compared to $[OH^-]$, is a convenient way to vary A_r or k over a large range. The inverse step or washout tracer technique was employed in these tests. Stock solution (EA dissolved in deionized water) and OH^- in the form of a concentrated solution of NaOH, were injected continuously until a steady state outlet value of C_o/C_{in} was obtained. At $t = 0$, the OH^- stream was shut off, and the transient response to the negative step of $[OH^-]$ was measured at the exit. Non-reactive tracer tests were performed similarly by injecting a stock solution of pure deionized water without EA. Equations governing this mode of tracer injection and resulting "washout" curves were derived from the pulse response equations.

The experimental heat transfer and non-reactive tracer results suggest that a combined forced-free convection flow field existed in the heat exchanger. Calculated heat transfer coefficients for both heating and cooling from the outside were much larger than predicted from the Graetz solution, which considers only forced convection. Also, the non-reactive tracer response for the three nonisothermal flow fields were similar to each other, but dramatically different than an experiment performed in the isothermal tube as shown in Figure 5. The shapes of the nonisothermal response curves indicated more uniform flow and less long-residence-time tailing which is consistent with the model of natural circulation and mixing of fluid near the wall. The possible effects of temperature-induced viscosity variations across the tube radius were also considered and found to be a much less likely explanation for the data.

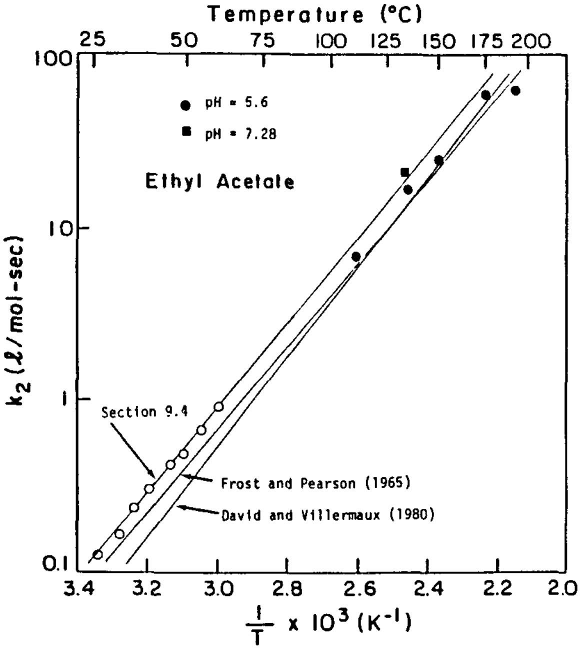

Figure 2. Comparison of ethyl acetate hydrolysis parameters obtained in basic solutions

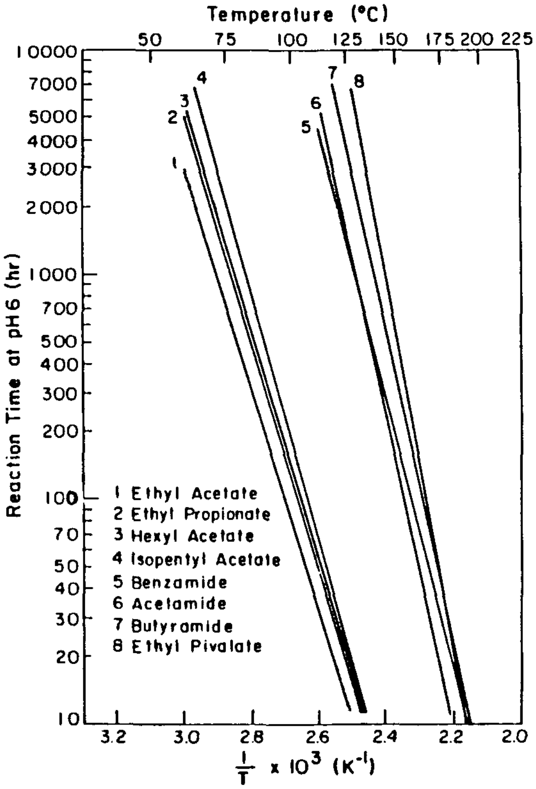

Figure 3. Summary of alkaline hydrolysis kinetic experiments: reaction time versus temperature in a geothermal fluid of pH = 6

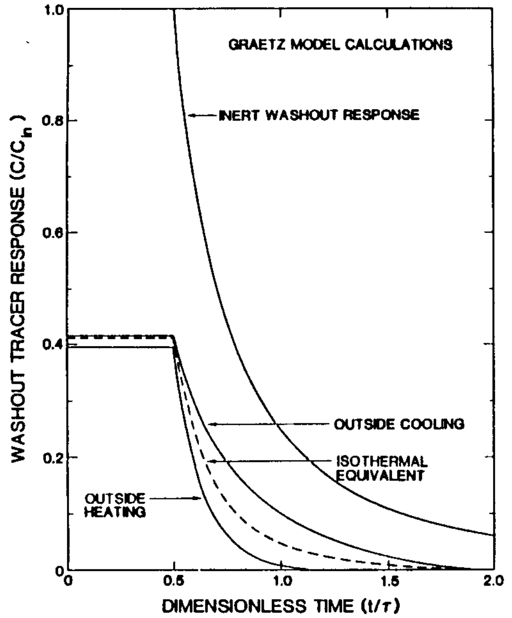

Figure 4. Transient reactive tracer response curves calculated assuming the Graetz solution applies for heating or cooling to a fluid flowing in laminar flow inside a tube

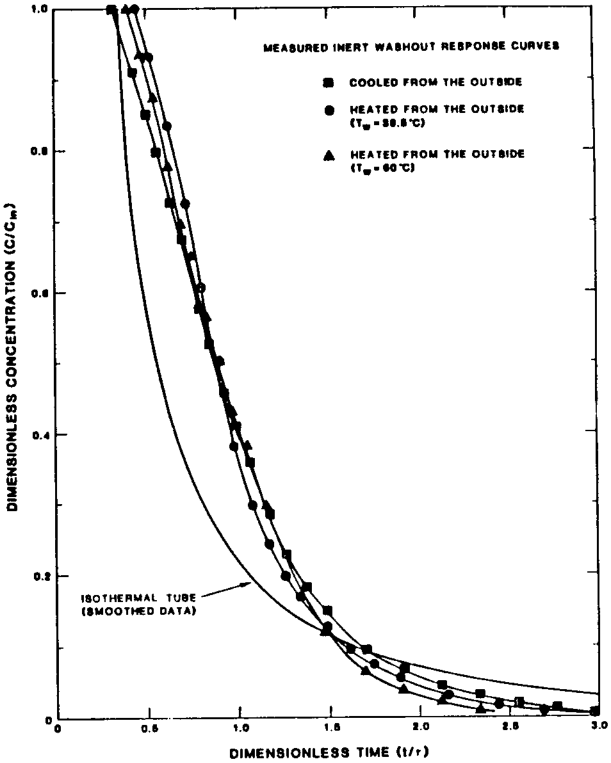

Figure 5. Comparison of measured inert tracer response in a washout experiment for the three thermal situations: isothermal, outside heating, and outside cooling.

APPLICATIONS TO FRACTURED RESERVOIR SIZING

A major challenge facing the development of artificially stimulated hot dry rock (HDR) reservoirs is the prediction of lifetime and thermal capacity early in the production history of the reservoir. (Armstead and Tester, 1987). This is a very difficult task in view of the complex flow systems that seem to typify the prototype HDR systems developed in the US at the Fenton Hill site and in the U.K. at the Rosemanowes site. The RTD's of both systems appear to be composites of superimposed flow from a number of separate/ fracture joint systems (Batchelor, et al., 1986 and Robinson et al., 1987). An additional complication appears as the reservoir undergoes dynamic changes during the heat extraction period. Observations at Fenton Hill and Rosemanowes both indicate a large increase in reservoir volume over relatively short periods of heat removal (30 days to 400 days). It is quite likely that this increase in size will also lead to an increase in thermal lifetime at the same heat extraction rate. (Tester, et al., 1986).

To summarize, HDR reservoir systems created by hydraulic stimulation in low permeability crystalline rock are generally characterized by highly dispersed flow as a result of superimposed, multidimensional flow in interconnected joint sets. Furthermore, this composite fracture system undergoes dynamic changes induced by thermal and/or hydraulic stress effects as a result of pressurized circulation of fluid to extract heat. Our initial modeling approach for reactive tracer analysis has been to simplify the system enough to make it tractable but to retain sufficient complexity to capture the basic physical and chemical phenomena that are occurring.

Rather than try to deal with the composite fracture system in its entirety, we have decided to subdivide the reservoir into separate flow systems as a starting point for analysis. Initially, a multiple set of individual joints with 1-dimensional areal flows and specified geometries was assumed to contribute to the early portion of the RTD near the modal volume while the longer tail of the RTD with extremely large residence times was due to more volumetric-like flow in highly fractured secondary flow paths. A numerical heat transfer model was developed to account for transient effects in the fracture system and to provide estimates for spatial temperature distributions along each fracture. Individual fractures were assumed to be non-interacting thermally but relative flow rates could be altered to simulate reservoir growth and other dynamic changes. The thermal field was simulated for each individual fracture over a given heat extraction period with fracture geometry, thermal physical properties, and a flow rate schedule specified. Then the inert and reactive tracer response was estimated using a numerical finite difference solution to equation (3) written for 1-dimensional flow with a fixed Peclet number ($Pe = UL/D$). For initial trials a value of 50 was used for Pe to represent an appropriate level of dispersion within a single fracture. The thermal simulation was used to specify values of k spatially along the fracture face. Finally the predicted outlet tracer conversions for individual fracture were superimposed to provide a composite result for comparison with field values.

CONCLUSIONS

A rigorous theoretical treatment of the behavior of chemically reacting tracers has been presented to show its potential application to fractured geothermal reservoir analysis. Simplifications were proposed to allow for modeling estimates in the absence of complete fracture geometry, flow field and temperature field specification. The most significant of these was the residence time-thermal time correspondence criterion. Verification of the theoretical techniques developed was established for a laminar flow heat exchanger. A tractable approach for employing reactive tracers in modeling the thermal performance of fractured HDR geothermal systems was presented.

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NOMENCLATURE

A_r- reaction pre-exponential factor (s^{-1})

C- concentration of product or reactant (mol/liter or kg/liter)

C(t)-concentration versus time response of a tracer (kg/liter)

D- dispersion coefficient (m/s)

E- reaction activation energy (kJ/mol)

f(t)-residence time distribution function (s^{-1})

F(t)-cumulative residence time distribution function

$h(\theta)$-thermal time distribution function (s^{-1})

k- 1st order reaction rate constant (s^{-1})

$\bar{k}$- isothermal equivalent reaction rate constant (s^{-1})

k_2- 2nd order reaction rate constant (liter/mol s)

L- fracture length (m)

m_p- mass of tracer injected in a pulse experiment (kg)

r_o- tube radius (m)

R- Universal gas constant = 8.314 J/mol K

Re- Reynolds number

$P(t,\theta)$-bivariate residence time/thermal time distribution function (s^{-2})

Pe- dispersional Peclet number

Pr- Prandtl number

T- Temperature (°C or K)

t - time (s)

u- fluid velocity

GREEK

τ- mean residence time (s)

τ_r- characteristic reaction time = 1/k (s)

η- dummy variable in equation (15)

λ_n- Eigenvalues in Graetz series solution

θ- thermal time (s^{-1})

REFERENCES

Armstead, H.C.H. and J. W. Tester, Heat Mining, E. F. Spon, London (1987).

Batchelor, A.S. et al, "Reservoir Behavior in a Simulated HDR System", 11th Annual Workshop On Geothermal Reservoir Engineering, Stanford University, Stanford, CA (Jan. 21-23, 1986).

David, R. and J. Villermaux, "Comments on: A Mixing Model for a Continuous Flow Stirred Tank Reactor", Ind. Eng. Chem. Fundamentals 19, 326-327 (1980).

Eckert, E.R.G. and R. M. Drake, Analysis of Heat and Mass Transfer, 2nd ed., McGraw Hill, NY (1972).

Frost, A.A. and R. G. Pearson, Kinetics and Mechanism, 2nd ed., J. Wiley and Sons, NY (1965).

Orcutt, J.C., J. F. Davidson, and R. L. Pigford, "Reaction Time Distributions in Fluidized Catalytic Reactors", Chem. Eng. Prog. Symp. Ser., No. 32, 58, 1-15 (1962).

Nauman, E. B., "Non-isothermal reactors: Theory and Application of Residence Time Distributions" Ind. Eng. Chem. Fundamentals 32, 359-367 (1977).

Nauman, E.B. and B. A. Buffham, Mixing in Continuous Flow Systems, J. Wiley and Sons, NY (1983).

Robinson, B. A. and J. W. Tester, "Temperature Field Determination Using Chemically Reactive Tracers: Part 1. Theory and Part 2. Experimental Determination in a Laminar-flow Heat Exchanger". (submitted to Ind. Eng. Chem. Res.) (1986).

Robinson, B. A. and J. W. Tester, "Reservoir Sizing Using Inert and Chemically Reacting Tracers", Soc. Pet. Eng. Journal (Reservoir Engineering) (accepted for publication)(1987).

Tester, J. W., H. D. Murphy, C. O. Grigsy, R. M. Potter, and B. A. Robinson, "Fractured Geothermal Reservoir Growth Induced by Heat Extraction", SPE 15124, presented at the 56th California Regional Meeting of the Society of Petroleum Engineers, Oakland, CA (April 2-4, 1986).