LA-UR- 94 - 3195

Title:

HYDROTHERMAL PROCESSING OF HANFORD TANK WASTES: PROCESS
MODELING AND CONTROL

Author(s):

Robert P. Carrier, ESA-9

Submitted to:

Westinghouse Hanford Company,
DOE Richland Office

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Form No. 836 R5
ST 2629 10/91

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**HYDROTHERMAL PROCESSING OF HANFORD TANK WASTES:
PROCESS MODELING AND CONTROL**

Prepared by
LOS ALAMOS NATIONAL LABORATORY
for the
HANFORD TANK WASTE REMEDIATION SYSTEMS (TWRS) PROGRAM

Compiled by:
Robert P. Currier (ESA-9)
Task Area Coordinator: Modeling and Control

Technical Contributors:

D. Breshears (CST-4)
R. Currier (ESA-9)
C. Patterson (T-12)
L. Le (CST-4)
M. Goemans (CST-4)

EXECUTIVE SUMMARY

In the Los Alamos National Laboratory (LANL) hydrothermal process, waste streams are first pressurized and heated as they pass through a continuous flow tubular reactor vessel. The waste is maintained at reaction temperature of 300-550°C where organic destruction and sludge reformation occur. This report documents LANL activities in process modeling and control undertaken in FY94 to support hydrothermal process development. Key issues discussed include non-ideal flow patterns (e.g. axial dispersion) and their effect on reactor performance, the use and interpretation of inert tracer experiments, and the use of computational fluid mechanics to evaluate novel hydrothermal reactor designs. In addition, the effects of axial dispersion (and simplifications to rate expressions) on the estimated kinetic parameters are explored by non-linear regression to experimental data. Safety-related calculations are reported which estimate the explosion limits of effluent gases and the fate of hydrogen as it passes through the reactor. Development and numerical solution of a generalized one-dimensional mathematical model is also summarized. The difficulties encountered in using commercially available software to correlate the behavior of high temperature, high pressure aqueous electrolyte mixtures are summarized. Finally, details of the control system and experiments conducted to empirically determine the system response are reported.

INTRODUCTION

Hydrothermal processing refers to a waste treatment technique in which an aqueous waste stream is fed through a chemical reactor at elevated temperatures and pressures to effect desired chemical transformations and separations. Transformations such as organic and nitrate destruction as well as sludge reformation have been demonstrated at the pilot scale using simulants of Hanford tank wastes. A typical composition for a tank waste simulant is given in Table 1.¹ At sufficiently

TABLE 1. COMPOSITION OF 3:1 DILUTED 101-SY SIMULANT

Component	Molality (mol/kg)	Molarity (mol/L)	wt%
Na ⁺	3.910	3.526	7.05
NO ₂ ⁻	1.012	0.913	3.65
NO ₃ ⁻	0.837	0.755	4.07
OH ⁻	0.763	0.689	1.02
AlO ₂ ⁻	0.530	0.478	2.45
CO ₃ ²⁻	0.233	0.210	1.10
Cl ⁻	0.099	0.089	0.27
EDTA ⁴⁻	0.056	0.051	1.28
K ⁺	0.037	0.033	0.11
Cr ³⁺	0.035	0.032	0.14
PO ₄ ³⁻	0.030	0.027	0.22
SO ₄ ²⁻	0.018	0.017	0.14
F ⁻	0.007	0.006	0.010
Ca ²⁺	0.003	0.002	0.008
Fe ³⁺	0.002	0.002	0.010
Ni ²⁺	0.001	0.001	0.005
Zn ²⁺	1.38×10 ⁻⁴	1.25×10 ⁻⁴	7.09×10 ⁻⁴
Cs ⁺	4.69×10 ⁻⁵	4.23×10 ⁻⁵	4.89×10 ⁻⁴
Sr ²⁺	3.01×10 ⁻⁶	2.71×10 ⁻⁶	2.08×10 ⁻⁵
H ₂ O	55.5	63.889	78.43

high temperatures and pressures (>450°C, 1 kbar), organics and nitrates can be destroyed in seconds producing primarily simple products such as CO₃²⁻, H₂O, N₂, N₂O and OH⁻. Sludges can be reduced in volume and reformulated as rapid settling oxides amenable to downstream separation. Under these conditions, the waste stream is typically a fluid with densities high enough for reasonable process throughputs to be achieved. However, due to the elevated temperatures, transport properties are essentially gas-like, which facilitates rapid chemical reaction rates. Under hydrothermal conditions, oxidation generally occurs at temperatures lower than those typical of incineration, thus limiting the production of undesirable NO_x and char.

In the Los Alamos National Laboratory (LANL) hydrothermal process, the waste stream is first pressurized and heated as it passes through a continuous flow tubular reactor vessel. The waste is maintained at the desired reaction temperature (300-550°C) for a time sufficient to achieve desired levels of organic and nitrate destruction, or to reformulate sludges. Essentially complete destruction of the organic constituents can be achieved without adding other reagents. If nitrate and/or nitrite destruction is required in addition to organic destruction, a reducing agent can easily be added to the feed stream. Upon leaving the reactor, the effluent is cooled and depressurized to the point where the gaseous, liquid, and solid components can be separated. Solids are possible products since the Hanford tank wastes are high salt content streams. Solids precipitation and even plugging of equipment have been observed. The ability of water to solvate ions and keep them in solution can be improved by operating at higher pressures (i.e. higher fluid densities). The salts and ions also increase the critical temperature of the mixture. Even after 3:1 dilution with water, the 101-SY waste can exist (at certain densities) as both liquid and vapor at temperatures approaching 550°C. Consequently, hydrothermal processing of Hanford simulants is typically carried out in diluted solutions at fairly high densities, so that the heat of reaction is absorbed by the solvent, two fluid phases can be avoided, and the likelihood of reactor plugging is minimized. Operating parameter selection (e.g. T and P) may also be guided by the constraints associated with the materials of construction.

Laboratory equipment and expertise for measuring physical properties and phase behavior for Hanford tank wastes under hydrothermal conditions has been developed at LANL. A number of kinetics experiments on the hydrothermal reaction of organics and nitrate have also been conducted using both bench-scale and small pilot-scale continuous flow tubular reactors. The experiments utilized both the 3:1 diluted simulant for tank 101-SY and simpler mixtures of the principal reactive components (organic, nitrate, nitrite, hydroxide). A complete description of the experimental set-ups, procedures, and analytical techniques for both the physical properties and chemical kinetics experiments can be found elsewhere.² This report focuses on process modeling and control activities conducted in support of experimental programs for hydrothermal processing of Hanford tank wastes. The general topics discussed below include fluid flow, chemical kinetics, reactor modeling, physical properties correlation, and reactor control strategies. The key fluid flow issues include non-ideal flow patterns (e.g. axial dispersion) and their effect on reactor performance, the use and interpretation of inert tracer experiments, and use of computational fluid mechanics in evaluating novel hydrothermal reactor designs. Chemical kinetics activities include exploring the effects of axial dispersion (and simplifications to rate expressions) on the kinetic parameters deduced by non-linear regression to experimental data, safety-related calculations determining the explosion limits of effluent gases, and the fate of hydrogen as it passes through the reactor. The development and numerical solution of a generalized one-dimensional mathematical

model is summarized in the reactor modeling section. The physical properties correlation section describes the difficulties encountered in using commercially available software to describe the behavior of high temperature, high pressure aqueous electrolyte mixtures. Finally, the process control section details the control system and the experiments conducted to determine the system response. The individual sections which follow, together with their associated appendices, provide more detailed discussion of each topic.

FLUID FLOW

Non-Ideal Flow Patterns. For single phase flow in a tube, the ideal flow pattern is the so-called plug (or piston) flow regime. In ideal plug flow, there are no radial variations in composition or temperature and all fluid elements are in the tube for precisely the mean residence time. Thus, the residence time density (RTD) is a Dirac delta function centered about the mean residence time. However, tubular reactors are not necessarily plug flow reactors. Deviations from plug flow result from flow along streamlines (e.g. in non-diffusive laminar regimes) or from dispersion (e.g. due to axial molecular diffusion and/or turbulent eddies). These deviations give rise to different fluid RTDs. Different RTDs result in different levels of conversion, with the differences typically being most dramatic for high levels of conversion and for higher order kinetics. In addition, failure to properly account for deviations from ideal flow patterns when estimating kinetic parameters can result in incorrect values for the intrinsic kinetics, since mixing effects and transport phenomena are superimposed on the parameters. A numerical demonstration of this phenomenon is given below in the Kinetics section.

The axially dispersed plug flow model, which represents plug flow with simultaneous axial dispersion, provides a straightforward means of accounting for slight to moderate deviations from plug flow. Consider the introduction of non-reactive molecules into a tubular reactor of length L . At time $t=0$, the inlet concentration of these molecules is set to C_0 and held at that value. When mass transport by both convection and dispersion are included, a mass balance over a small fluid element perpendicular to the tube axis gives

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} \quad (1)$$

where z is the axial position coordinate (cm), u is the mean flow velocity (cm/sec), C is the concentration of tracer (mol/cm³), and D_m is the mass dispersion coefficient (cm²/sec). Analytic solutions to this equation are shown in Figure 1 for a step change in the inlet concentration.³ Also shown is the response of a continuously stirred (and perfectly mixed) tank reactor (CSTR) and a tubular reactor with laminar flow conditions and no diffusion or dispersion. It is clear that the parameter D_m/uL , which is the inverse Peclet number, governs the response. When $D_m/uL = 0$ a

plug flow response is obtained, while for the case of large amounts of dispersion, the behavior of a CSTR is recovered. Intermediate values of D_m/uL give responses between the two extremes.

In reality, if a narrow pulse of soluble substance is injected into a fluid in laminar flow the pulse spreads due to the combined action of convection and molecular diffusion in both the axial and radial directions. Also, the maximum of the concentration peak travels with the mean flow velocity. With a large enough length-to-diameter aspect ratio, radial diffusion will cause a given particle to sample the various streamlines many times. If no axial diffusion were present, the net result would be that each particle had essentially the same residence time. This time would of course correspond to the mean residence time, as if plug flow existed. Thus a model consisting of plug flow with simultaneous axial dispersion is applicable to laminar flow in large aspect ratio tubes. For a fairly wide range of aspect ratios, Taylor⁴ and Aris⁵ established that using the mean concentration

$$\langle C \rangle = \frac{2}{R^2} \int_0^R r C dr \quad (2)$$

where R is the tube radius, allows the exact convective-diffusion equation

$$\frac{\partial C}{\partial t} = D \left(\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} \right) - 2u \left(\frac{R^2 - r^2}{R^2} \right) \frac{\partial C}{\partial z} \quad (3)$$

to be written in the form of eq. (1), namely,

$$\frac{\partial \langle C \rangle}{\partial t} = D_m \frac{\partial^2 \langle C \rangle}{\partial z^2} - u \frac{\partial \langle C \rangle}{\partial z} \quad (4)$$

where now D_m , is given by the formula

$$D_m = D + \frac{1}{48} \frac{u^2 R^2}{D} \quad (5)$$

In equations (3) and (5), D is the molecular diffusion coefficient. The axially dispersed plug flow form is thus obtained, but now the dispersion coefficient, D_m , is seen to be a sum of ordinary molecular diffusion effects and a second term representing the effects of the fluid velocity. The accuracy and ranges of applicability for the Taylor-Aris results are well established, and semi-empirical correlations for the dispersion coefficient are available for turbulent flow conditions.⁶

The Taylor-Aris formula (Eq. (5)) provides a means of estimating the dispersion coefficient at conditions under which some of the laboratory-scale hydrothermal kinetics experiments were conducted. These experiments involved reaction of EDTA, nitrate, and nitrite under hydrothermal conditions. Dispersion coefficients were estimated using both the molecular diffusion coefficient for water and an estimated value for EDTA. While EDTA is likely to decomposed into smaller, more mobile fragments, these calculations should provide useful estimates of the upper and lower bounds on the amount of dispersion, provided no complicating factors (e.g. multiple phases) are

present. Values for the dispersion coefficient were estimated using eq. (5) and are summarized in Table 2. The calculations suggest the amount of axial dispersion is expected to be moderate (based

TABLE 2. LAMINAR DISPERSION BASED ON TAYLOR-ARIS FORMULA.*

Flow Rate u (cm/sec)	Reynolds No. (based on water)	Dispersion Coefficient D_m	Peclet Number $Pe = (uL/D_m)$	Inverse Peclet Number
5.6	989	13.3 (H ₂ O)	56.8 (H ₂ O)	0.018 (H ₂ O)
		53.8 (EDTA)	14.1 (EDTA)	0.071 (EDTA)
7.8	1377	25.9 (H ₂ O)	40.7 (H ₂ O)	0.025 (H ₂ O)
		104.3 (EDTA)	10.1 (EDTA)	0.099 (EDTA)
10.0	1764	42.5 (H ₂ O)	31.7 (H ₂ O)	0.032 (H ₂ O)
		171.4 (EDTA)	7.88 (EDTA)	0.127 (EDTA)

* Calculation are for T=450°C, P=15,000 psia, a reactor length of L=135 cm, and a reactor diameter of d=0.21 cm, which corresponds to the isothermal portion of one laboratory-scale reactor. The molecular diffusion coefficient for EDTA is taken to be the water value (at the same T & P) times the square root of the ratio of molecular weights. The molecular weight of EDTA is taken to be 292. The values of D for water are taken from Lamb et al. (J. Chem. Phys. 74(12): 6875 (1981)).

on water) to substantial (based on EDTA). Using values for the inverse Peclet number from Table 2, a rough indication of the response expected from a step change in the inlet concentration can be obtained from Figure 1. With the actual reactor, possible precipitation of solids (with entrainment of fluid) may cause more severe axial dispersion than indicated by this analysis. Similarly, if more than one fluid phase is present axial dispersion may be further enhanced. Also, the rheology of the reacting mixture may be non-Newtonian with fundamentally different flow characteristics. Given these complicating factors, a program was initiated to directly measure the extent of axial dispersion using inert tracers.

Use of Inert Tracers. The general procedure for experimentally measuring axial dispersion in a tubular reactor includes an experimental apparatus for inert tracer experiments, a means of introducing a well-characterized change in tracer concentration (e.g. a pulse or step), and a means of interpreting the data and relating it back to an appropriate flow model.

The apparatus constructed for the inert tracer experiments consists of high pressure pumps and tracer injection manifold leading into a heated tube. The apparatus is designed for conducting tracer measurements under actual hydrothermal conditions. Both inlet and exit concentrations of tracer are determined using spectroscopic techniques. Detailed description of the apparatus can be found elsewhere.⁷ At present, the device has been pressure tested, the optical diagnostics have been evaluated, and initial experiments have been conducted. However, not enough data has been obtained to provide reliable estimates of the dispersion coefficients.

An experiment involving an imperfect (i.e. a non-delta function), but known pulse of tracer can be interpreted by considering a system with a volumetric flow rate Q (cm³/sec). Denote the concentration of inert tracer by C (mol/cm³) and the residence time density function by $f(t)$. For an arbitrary input of tracer, the number of particles that enter in the interval $(t', t'+dt')$ and leave in the interval $(t, t+dt)$ is given by the product: $Q C_{in}(t') f(t-t') dt dt'$. This is simply the fraction with a residence time of $(t-t')$. During the interval $(t, t+dt)$, the total outflow is given by $Q C_{out}(t) dt$. This outflow consists of particles which entered at all previous times. Thus a mass balance yields

$$Q C_{out}(t) dt = Q dt \int_{-\infty}^t C_{in}(t') f(t-t') dt' \quad (6)$$

where the integral sums all particles entering at previous times, t' , and which have a residence time of $(t-t')$. For the typical tracer experiment, the system may be considered to be initially "relaxed", that is, $C_{in}(t') = 0$ for all $t' < 0$. Equation 6 then becomes a convolution integral

$$\begin{aligned} C_{out}(t) &= \int_0^t C_{in}(t') f(t-t') dt' \\ &= \int_0^t C_{in}(t-t') f(t') dt' \\ &= C_{in}(t) * f(t) \end{aligned} \quad (7)$$

which, in the Laplace domain ($t \rightarrow s$), becomes

$$\frac{\bar{C}_{out}(s)}{\bar{C}_{in}(s)} = \bar{f}(s) \quad (8)$$

where the overbars denote Laplace transformation. Thus for an arbitrary (but known) input of $C_{in}(t)$, equation 7 shows that the output is mathematically convoluted with that input. Also, the Laplace transform of the RTD is the "transfer function" for the system. This establishes an analogy with the transfer functions encountered in linear circuit and control theories. Numerical de-convolution techniques could be employed to separate the input and output. However, direct use of the procedure with experimentally obtained data has proven to be somewhat inaccurate in determining flow model parameters. This is attributed to scatter and uncertainty in the data, especially in the "tail" of the distribution (i.e. long residence times). More desirable techniques are discussed in Appendix A. Although perhaps not of great practical utility, equation (8) does provide a basis for interpreting imperfect pulse experiments. In addition, it forms the basis for estimating model parameters (e.g. dispersion coefficients) based on the experimental data and for discriminating between various models, as outlined in Appendix A.

Novel Reactor Designs. An exploratory analysis of a novel reactor design was conducted using computational fluid dynamics (CFD) as a tool. The basic reactor configuration mimics that of the

classical stirred-tank reactor. However, rather than utilizing a mechanical stirrer, the feed is jetted into the tank with velocity sufficient to cause extensive mixing in the vessel. This conceptual design offers the possibility of easy solids removal and the use of the heat of reaction to heat the incoming feed stream. Detailed CFD calculations were conducted to examine details of the mixing which results and to aid in determining the feasibility of the design concept.

The preliminary design is for a 10 gallon/minute hydrothermal reactor operating at 15,000 psi. The reactor was designed so that the liberation of heat from the fuel makes the reaction self-sustaining even though the fuel enters the reactor below the temperature needed to initiate the reaction. In these calculations, the incoming fuel is first heated to the reaction temperature of 673°K, corresponding to the activation energy of 240 kJ/g. The fuel liberates enough heat to raise the temperature about 100 K. In the reactor, the reactants circulate so that the incoming fuel will be quickly heated by fuel which has already burned as shown in Figure 2. The reactor is designed with a mean residence time of 25 seconds. The incoming fuel is in a pipe of 2 cm radius inserted into the reactor with a radius of 10 cm and length of 40 cm. Only half of the reactor is shown and the dashed line is the line of symmetry at the center of the reactor. The flow rate in the entrance pipe is about 40 cm/s. The time constant for the fuel is 10 seconds at 673°K so that the residence time is 2.5 the time constant. Thus, fuel is completely mixed before reaching the exit while about $e^{-2.5}=0.92$ of it will be consumed at 673°K. At higher temperatures more complete reaction will occur.

In Figure 2 we see that the recirculation of the heated fuel helps to heat the incoming fuel. Also gravity is in the positive x direction so the fuel enters from the left (top) and leaves from the right (bottom) of the reactor in the direction of gravity. The tendency of the heated fuel to rise promotes extensive mixing before the fuel can exit at the bottom. Indeed this tendency is what promotes the circulation seen in the reactor. In Figure 3 we show the streamlines which make the large recirculating eddy resulting from the convection currents clearly visible. The temperature profile of the reacting fuel is shown in Figure 4 showing a temperature rise of about 100°K with isotherms every 10°K. Note that the fuel recirculates returning to the entrance nozzle at a temperature of 755°K. The amount of fuel remaining can be displayed in mole fraction increments of 0.1. Due to the high temperature, over 98% of the fuel is burned.

The entrance temperature of the fuel was lowered by 50°K so that it enters at 623°K. This is below the ignition temperature. The incoming fuel still reacts because the fuel already heated in the reactor quickly brings it up to ignition temperature as shown in Figure 5. That is, the reactor is self-sustaining due to the recirculation of heated fuel caused by the convection currents. The final temperature of the fuel drops to 700°K but still results in a nearly complete consumption of fuel.

Locating the exit of the reactor sufficiently below the entrance serves to maximize mixing of the incoming fuel with the heated fuel in the reactor. This occurs as long as the fuel liberates heat.

The tendency of the heated fuel to rise causes substantial convection currents so that there is little fuel which can make the short-cut directly from the entrance to the exit without being mixed and heated. There is also no need to place the exit at the top of the reactor and use a baffle to direct the flow to the bottom of the reactor to ensure complete mixing. Finally, placement of the exit at the bottom of the reactor should allow precipitated solids to be removed automatically from the reactor.

CHEMICAL KINETICS

Effects of Axial Dispersion on Kinetic Parameters. In order to assess the impact axial dispersion may have on kinetic parameters, computer codes were assembled to solve the species mass balance equations

$$0 = D_{mi} \frac{\partial^2 C_i}{\partial z^2} - u \frac{\partial C_i}{\partial z} - RR_i \quad i = 1, \dots, N \quad (9)$$

where RR_i is the reaction rate expression for consumption of the i -th specie and where $N < 21$. For boundary conditions, continuity of flux is specified at the inlet while continuity of flux and concentration is specified at the outlet. This gives rise to the standard Danckwerts boundary conditions

$$uC_i(0,t) = uC_{i0} + D_{mi} \left[\frac{\partial C_i}{\partial z} \right]_{z=0} \quad (10)$$

$$\left[\frac{\partial C_i}{\partial z} \right]_{z=L} = 0 \quad (11)$$

The numerical technique employed to solve these boundary value problems involved orthogonal collocation over finite elements, with B-splines as trial functions and automatic mesh generation. Details of the numerical algorithms can be found elsewhere.^{8,9} The computer codes were tested first against differential equations to which the analytical solution is known. This included the axial dispersion model with a simple first order reaction rate. It was then verified that for slightly more complicated kinetic expressions, the numerical solution obtained with large Peclet numbers (e.g. $Pe=5000$) matches the plug flow results which were obtainable in closed analytical form. The differential equation solver was then used in a non-linear least squares routine. The Levenberg-Marquardt algorithm (as implemented in the MINPACK software package¹⁰) was used for the non-linear regressions. It was tested independently of the differential equation solver on sample regression problems to which the solution was known. Given a suitable amount of experimental data, this numerical framework provides a means of estimating parameters in axial dispersion-type flow models, using these model to estimate kinetic parameters in flow experiments, and determining the impact of various assumptions on the estimated parameters, as will now be shown.

For demonstration purposes, results from a series of laboratory-scale experiments are used as test data. These experiments focused on the reaction of EDTA, nitrate, and nitrite under hydrothermal conditions. The EDTA is represented and measured as total organic carbon (TOC), while the nitrate and nitrite are assumed to be present simply as NO_x . These results are a subset of the data obtained under the kinetics portion of the program and are summarized in Table 3.

TABLE 3. DATA USED FOR REGRESSION OF KINETIC PARAMETERS*

Run	Temperature (°K)	Mean Residence Time (sec)	Initial TOC (mmole/l)	Initial NO_x (mmole/l)	TOC Conversion
1	738	22.4	586.1	1621	0.98
2	738	32.7	586.1	1621	0.99
3	718	17.3	596	1648	0.93
4	718	24.2	596	1648	0.94
5	683	13.3	558.7	1743	0.79
6	683	18.5	558.7	1743	0.82
7	683	31.2	558.7	1743	0.92
8	653	14.3	550.7	1661	0.70
9	653	22.9	550.7	1661	0.74
10	653	39.2	550.7	1661	0.81
11	623	17.5	572	1653	0.49
12	623	22.8	572	1653	0.57
13	623	33.6	572	1653	0.60

* Experiments were conducted at $P=15,000$ psia, in a reactor tube of length of $L=135$ cm and diameter of $d=0.21$ cm.

Two forms were considered for the reaction rate term, RR_i . The first assumes that the rate is conversion invariant with respect to the NO_x concentration

$$RR = A \exp(-E/RT) [\text{TOC}]^\alpha [\text{NO}_{x0}]^\beta \quad (12)$$

where $[\text{NO}_{x0}]$ is the initial NO_x concentration. This requires solving one differential equation of the form given by eq. (9), as only the mass balance for TOC is necessary. The second form relaxes the conversion invariant assumption

$$RR = A \exp(-E/RT) [\text{TOC}]^\alpha [\text{NO}_x]^\beta \quad (13)$$

and requires mass balances for both TOC and NO_x . This gives rise to two differential equations which must be solved simultaneously.

These kinetic expressions were substituted into eq. (9) and solved first for the case of plug flow (i.e. large Pe). The parameters A , E , α , and β were determined by regression to the TOC conversion data in given Table 3. The calculations were repeated using TOC and NO_x dispersion coefficients estimated by the method described above in the Fluid Flow section. In making these estimates, the molecular weight of EDTA was taken to be 292 while that of NO_x was taken to be 62. The results of the calculations to determine the parameters A , E , α , and β are summarized in Table 4 (next page). It can be seen that each model gives about the same quality fit to the data. A comparison of calculated and observed conversion is shown in Figure 11 for the axial dispersion case. Comparison plots from the other case are virtually identical. The negative value for β

TABLE 4. REGRESSED KINETIC PARAMETERS

CASE	A	E	α	β	S-O-S
PF with conversion invariant approximation for NO _x	5.714×10^8	1.408×10^5	2.627	-2.547	0.0047
AD with conversion invariant approximation for NO _x	4.168×10^9	1.697×10^5	2.931	-3.548	0.0043
PF with no conversion invariant approximations	3.547×10^9	1.396×10^5	2.982	-2.609	0.0054
AD with no conversion invariant approximations	5.579×10^{10}	1.691×10^5	3.419	-3.652	0.0051

(PF denotes plug flow conditions, AD denotes axial dispersion, S-O-S denotes the final sum of squared errors between calculated and observed TOC conversions)

suggests that addition of NO_x decreases the TOC destruction rate. This may be due to the fact that only a subset of the data is being used and that regression is being made only to observed TOC conversions. Notice that for both the plug flow and axial dispersion calculations, the activation energy is essentially the same regardless of whether or not the conversion invariant approximation is made. Furthermore, notice that either with or without the conversion invariant approximation, the introduction of dispersion results in an increase in α of approximately 0.5 while the absolute value of β is increased by roughly 1.0. With the introduction of dispersion, there is also approximately a 17% increase in the apparent activation energy. Since the models have different overall orders, it is difficult to directly compare rate constants in a meaningful way. However, the net rates of TOC removal, i.e. the apparent reaction rates, can be compared. This has been done for the conversion invariant case using the plug flow and axial dispersion models, and is shown in Figure 12. The apparent reaction rate is higher in the presence of dispersion. This is in agreement with the general fact that a wider residence time distribution corresponds to lower conversion. In Figure 12, large differences in the predicted TOC removal rate are apparent, even though each expression gives essentially the same predictions (i.e. fit to data) when used in the appropriate governing differential equation. These calculations underscore the importance of independently determining the extent of dispersion (e.g. via a tracer study) in flow models which are to be used to estimate kinetic parameters.

Explosion Limits of H₂/N₂O Mixtures. Laboratory experiments indicate that effluent gases from hydrothermal processing of simulated Hanford tank waste can contain significant fractions of H₂ and N₂O. This is of some concern, since H₂-N₂O mixtures are known to explode under certain conditions. We have thus investigated the potential for explosion in two effluent gas mixtures, whose composition is given in Table 5.

Table 5: Effluent Gas Composition (T = 300 K)

	Mixture 1 (Torr)	Mixture 2 (Torr)
H ₂	966.0	1683.8
N ₂ O	409.0	654.8
N ₂	498.0	5369.5
H ₂ O	31.1	31.1
He	750.0	0.0
Total (Torr)	2654.1	7739.2
Total (Atm)	3.5	10.3

Mixture 1 is representative of the LANL experiments in laboratory-scale reactors, Mixture 2 is typical of the pilot-scale experiments. Mixture 2 contains 355 Torr CH₄ and ~22 Torr C₂H₆ as well.

Calculations of reaction rates in these mixtures were performed using the Chemkin computer software package.¹¹ The mechanism (chemical reactions and rate constants) used in the computations is given in the Appendix B. It consists of the "complete" NASP mechanism¹² for the H₂-O₂ system (reactions B-1 through B-29) plus those reactions known or believed to be important in the H₂-N₂O system (reactions B-30 to B-40). Calculations using this mechanism give quite good agreement with reported rate measurements in H₂-N₂O-He mixtures at 540 and 600 °C and reasonably good agreement with measurements in flames.^{13,14} The CH₄ and C₂H₆ in Mixture 2 were ignored in the calculation; possible effects of their inclusion are discussed below.

The reaction between H₂ and N₂O is believed to proceed via the radical straight-chain mechanism comprising the reactions (equation numbers are those found in Appendix B)

Under thermal conditions, the chain is initiated by the dissociation of N₂O,

followed by

and reaction (B-1), resulting in two H atoms for each O atom produced by reaction (B-34). Again, under thermal conditions, the chain comprising reactions (B-30) and (B-1) is terminated by the reaction

The overall reaction,

is approximately 78 kcal/mole exothermic at 298 K, the rate constant for reaction (B-34) increases with temperature (activation energy ~60 kcal/mole), so that even with no radical chain branching, the reactions above can lead to *thermal* explosion, i.e., the reaction rate increases *solely* due to the reaction exothermicity. This is in contrast to the $\text{H}_2\text{-O}_2$ system, where a radical chain-branching mechanism also contributes to the rate increase.

Reaction can also be initiated by a perturbation such as a spark, the most likely result being dissociation of some fraction of the N_2O , reaction (B-34). Again, reactions (B-3) and (B-1) rapidly convert the O atoms to H atoms. Depending on the temperature and relative concentrations of H atoms and N_2O , recombination of H atoms,

can be the initial primary path for H atom removal. However, since reactions (B-16 to B-20) are second order in H atoms, while reaction (B-30) is first order, reaction (B-30) will dominate during the later stages of H atom decay. Further, since reactions (B-16 to B-20) are 104 kcal/mole exothermic at 298 K, the mixture will heat during the recombination-dominated stage, and thus be at a higher temperature when reaction (B-30) does become dominant.

Chemkin calculations were performed to simulate two cases leading to possible explosion. Case A is for thermal reaction alone, while in Case B an initial O atom concentration equal to 10 percent of the initial N_2O concentration was added to simulate the effect of a spark. In both cases the volume was held constant. The calculated time-dependent temperature increase for Mixture 1 initially at 700 K is shown for the two cases in Figure 8, where the time scale for Case B has been multiplied by 2×10^8 . We assume a rapid increase in temperature results in explosion. Thus Case A would lead to explosion in ~500 s, while the time for Case B is ~5 μs . The Chemkin calculations include no heterogeneous reactions, and it is probable that on a 500 s time-scale, removal of H atoms at the walls would terminate the chain more rapidly than would reaction (B-35), and thus explosion might well not occur. Case B would definite lead to explosion. The final temperature for Case B exceeds that for Case A by ~100 K, reflecting the initial heating due to H atom recombination.

Figure 9 shows the calculated ignition delay time for each case in each mixture as a function of initial temperature in the range 400-1500 K. Ignition delay time is defined somewhat arbitrarily here as the time required for a temperature increase of 400 K. For thermal reaction (Case A), Mixture 2 is slightly more stable than Mixture 1, although the difference is slight. In either case, the results suggest that thermal explosion is highly improbable for initial temperatures less than ~600 K.

The values in Figure 8 for simulated spark initiation (Case B) exhibit some interesting features. First, Mixture 2 clearly is more stable than Mixture 1 at all temperatures. The

bimolecular rate constant for H atom recombination, reactions (B-16 to B-20), is proportional to total concentration [M], and since the total pressure of Mixture 2 is three times that of Mixture 1, while the N₂O partial pressure is only ~30 percent higher, a greater fraction of H atoms will recombine before reaction (B-30) becomes dominant. Second, as temperature decreases, the values for each mixture exhibit an abrupt increase (at 400-500 K for Mixture 1; at 700-900 K for Mixture 2). Apparently, at this point, essentially all the H atoms have decayed by recombination, reactions (B-16 to B-20), but in so doing have heated the mixture sufficiently for it to react thermally. The values in Figure 8 suggest that spark-initiated explosion will be improbable for initial temperatures below ~400 K for Mixture 1 and ~600 K for Mixture 2.

Consideration of the effects of CH₄ and C₂H₆ in Mixture 2 would require, at the very least, addition of the following reactions (R, R' = CH₃ and/or C₂H₅):

In this reaction sequence R and R' play the same role as does H in the mechanism described above. The sequence will significantly increase the potential for explosion only if the rate constant for reaction (B-44) significantly exceeds that for reaction (B-30). To date, a search for experimental data for this rate constant has been unsuccessful, so that a quantitative assessment of the effects of RH has not been made. The results of this study suggest that the potential for explosion, both thermal and spark-initiated, can be minimized by high dilution of reaction products at high total pressure.

Fate of Hydrogen. The potential explosion hazard from H₂-N₂O production in hydrothermal processing of tank waste obviously disappears if H₂ production is insignificant. Figure 10 shows laboratory data for the number of moles of H₂ produced per mole of total organic carbon (TOC) destroyed in hydrothermal processing of tank-waste simulant. The data are shown as a function of temperature, parametric in average residence time at reaction temperature and pressure. The trends in the data are clearly apparent: At each residence time, H₂ production drops significantly with increasing temperature, reaching insignificant values at temperatures greater than ~470 °C. Since reaction temperatures in this range are also desirable for efficient destruction of total organic carbon (TOC), no safety hazard is expected due to H₂ production under normal reactor operating conditions.

GENERALIZED 1-DIMENSIONAL REACTOR MODEL

If one is interested in conversions in the range of 99% or higher, the deviations from plug flow (if present) are important and should be accounted for in the reactor model. Destruction of organic wastes in a single-pass hydrothermal reactor calls for organic conversions in this range. Furthermore, for both the Hanford simulants and other potential (non-Hanford) waste streams, a variety of processing conditions and flow rates are likely to be encountered. Some of these may tax the applicability of the existing plug flow models. For example, a given stream may have slow chemical kinetics. Laminar flow rates may then be required to achieve mean residence times appropriate for the desired conversions. This may result in significant deviations from plug flow. Additional factors, which are summarized below, may also contribute to deviations from ideal plug flow. Consequently, a more general model has been formulated which can account for such deviations. This model keeps computational times to a minimum and allows the flow model to be utilized in a least squares regression routine to determine kinetic parameters, which requires that it be solved a large number of times.

Development of the general 1-dimensional (1-D) model proceeds as follows. First, process and operating characteristics are reviewed. Special emphasis is placed on those factors which may cause deviations from ideal plug flow. The physical ideas and approximations inherent in the proposed model are then outlined. Connections are made to the classic axial dispersion and plug flow models. The basic forms of the relevant mass and energy balances are presented. It is outlined how model parameters can be estimated from inert tracer studies. A brief description of the numerical methods used to solve the model is given and calculations are performed to highlight the model's flexibility.

Process Characteristics. As noted above, the Taylor-Aris analysis provides a basis for estimating whether or not significant deviations from plug flow can be expected. When applied to the LANL laboratory-scale hydrothermal reactors, their criteria suggest that deviations should be expected. However, there are a number of complicating factors present when processing Hanford tank wastes. The first concerns the fact that the hydrothermal reactors are often not isothermal. The classic results pertain to isothermal conditions. The effect of a large axial thermal gradient on the residence time distribution is not clear. For the dispersion of heat, the effect can be significant. For example, Taylor derived an expression for the axial dispersion for mass in turbulent flow.¹⁵ When his analysis is applied to the analogous problem of axial dispersion of heat, there is both experimental data and analysis indicating that, in the presence of large radial heat fluxes, values of

the turbulent heat dispersion coefficient predicted by Taylor's analysis are an order of magnitude too low.¹⁶

Several other factors may cause significant deviations from plug flow in the hydrothermal reactors. These are denoted pictorially in Figure 11. In Figure 11(a), the possibility of species adsorption on the tube walls is considered. It has been postulated that a number of the key reactions occur at the walls. If so, this may involve significant lifetimes on the wall which would contribute to a wider distribution of residence times. In Figure 11(b), the effects of precipitating solids are denoted. If the mean flow velocity is high enough, a state of homogeneous flow results wherein the solids are uniformly distributed in the tube. However, past estimates indicate that under the present operating conditions mean flow velocities are not that high.² Thus, either heterogeneous or saltation flow is suspected when salts precipitate. In the heterogeneous flow case, a density gradient exists from top to bottom in the tube. This causes a change in the velocity profile. The net effects of this change on the residence time distribution are unclear. In saltation flow, the solids move along the tube bottom as "dunes" which may grow large enough to cause periodic plugging. The solids entrain fluid which is expected to result in a fairly wide distribution of residence times. In Figure 11(c), the role of reactor geometry in creating localized "stagnant" regions is shown. Use of both a bent tube and tubes of differing diameter have been proposed for future reactor designs. These reactor configurations can also contribute to a spread in residence times. Thus, there are a number of additional factors which may contribute to deviations from plug flow. Assessing the extent of dispersion in the hydrothermal reactors actually involves more than just a straightforward application of the isothermal Taylor-Aris criteria.

Generalized 1-D Model. In light of large radial heat fluxes, possible wall adsorption, entrainment of fluid by solids, and stagnant regions, a truly rigorous model would involve a 3-dimensional computational fluid dynamics calculation, with finite chemistry and a precipitation model. This would limit use in real time calculations, such as data regression. Thus as an alternative, a 1-D model is proposed which at least qualitatively accounts for these phenomena. The basic physical assumption is that the process stream can be separated into two zones. The first zone is mobile and is subject to axially dispersed plug flow (i.e. plug flow with simultaneous axial dispersion). The second zone is considered to be "stationary". Mass transfer is allowed between the two zones. The mass transport rate between zones is assumed to be proportional to the concentration difference between zones. The physical situation is shown schematically in Figure 12. Although not strictly correct, it is assumed that this stationary zone is distributed uniformly over the length of the reactor. This allows the model to remain one-dimensional. Note that in the limit of decreasing stationary zone volume, the classic axial dispersion model results. Also, if the amount of dispersion then goes to zero, the ideal plug flow model is recovered. With proper values for the

volume fraction of stationary zone and mass transfer coefficient, a range of residence time distributions should be implicitly represented by this generalized model. As a historical note, models of this general form were first proposed decades ago to describe chromatography.¹⁷

The development of the mathematical form for this physical model involves material and heat balances over the shell of thickness Δz . The material balances will be presented and discussed first. For mobile phase, zone 1, a material balance performed over Δz gives

$$\frac{\partial C_1}{\partial t} = D_m \frac{\partial^2 C_1}{\partial z^2} - u \frac{\partial C_1}{\partial z} - \beta k_m (C_1 - C_2) + \sum_{\text{"1"}} R_1 \quad (14)$$

while for zone 2 one finds

$$\frac{\partial C_2}{\partial t} = k_m (C_1 - C_2) + \sum_{\text{"2"}} R_2 \quad (15)$$

The notation for these and subsequent equations is described in Table 6. Terms on the right-hand-

TABLE 6: NOTATION FOR GENERALIZED MODEL

Symbol	Meaning	Subscripts
α	volume fraction of mobile zone (-)	i --> inside of tube
β	volume stationary zone/volume mobile zone (-)	o --> outside of tube
C	concentration of key reacting specie (or inert tracer) (mol/cm ³)	w --> wall
Q	volumetric flow rate through tube (cm ³ /sec)	a --> ambient
A	cross sectional area of inside of tube (cm ²)	I --> insulation
A_w	cross sectional area of tube wall (cm ²)	c --> cylindrical enclosure around tube
r	tube radius (cm)	f --> fluid
u	mean flow velocity ($Q/A\alpha$) in mobile zone (cm/sec)	1 --> mobile zone
z	axial variable (cm)	2 --> stationary zone
L	length of tube (cm)	in --> "feed" conditions
D_m	mass dispersion coefficient in mobile zone (cm ² /sec)	s --> surroundings
D_H	heat dispersion coefficient (J/(cm sec °K))	
k_m	mass transfer coefficient between zones (1/sec)	
h	internal fluid-wall convective heat transfer coefficient (J/(cm ² sec °K))	
h_{FB}	fluidized bed-wall convective heat transfer coefficient (J/(cm ² sec °K))	
c_p	heat capacity (J/(g °K))	
k_T	thermal conductivity of tube material (J/(cm sec °K))	
ρ	density (g/cm ³)	
T	temperature (°K)	
t	time (sec); the Laplace domain analog of t is s (1/sec)	
R_n	reaction rate (e.g. $-k[C]$) in zone "n" (mol/(cm ³ sec))	
ΔH_n	heat of reaction for a reaction in zone "n" (J/mol)	

side of eq. (1) correspond to material transport by dispersion, convection, interzone exchange, and consumption by reactions occurring in zone "1". In eq. (15), the terms account for interzone exchange and consumption by reactions occurring in zone "2". A given reaction may of course occur in both zones. For boundary conditions, standard Danckwerts conditions are assumed:

$$uC_1(0,t) = uC_{in} + D_m \left[\frac{\partial C_1}{\partial z} \right]_{z=0} \quad (16)$$

and

$$\left[\frac{\partial C_1}{\partial z} \right]_{z=L} = 0 \quad (17)$$

In order to demonstrate how the parameters in the model can be estimated using data taken from inert tracer experiments, the transfer function will now be obtained. For an imperfect (but known) pulse of inert tracer, $C_{in}(0,t)$, the relevant equations become

$$\frac{\partial C_1}{\partial t} = D_m \frac{\partial^2 C_1}{\partial z^2} - u \frac{\partial C_1}{\partial z} - \beta k_m (C_1 - C_2) \quad (18)$$

and

$$\frac{\partial C_2}{\partial t} = k_m (C_1 - C_2) \quad (19)$$

If the system is initially relaxed when the pulse is introduced, the boundary conditions are $C_1(z,0) = C_2(z,0) = 0$ for all z (20)

and

$$C_1(0,t) = C_{in}(0,t) \quad (21)$$

In addition, the response must remain bounded. Laplace transformation (denoted by overbars) of eqs. (18-21) gives

$$\frac{\bar{C}_1(L,s)}{\bar{C}_{in}(0,s)} = \exp \left\{ \frac{Lu}{2D_m} \left(1 - \left(1 + \frac{4sD_m}{u^2} \left(1 + \frac{\beta k_m}{s + k_m} \right) \right)^{1/2} \right) \right\} \quad (22)$$

as the transfer function. As expected, in eq. (22) the limit $\beta \rightarrow 0$ gives the transfer function for the canonical axial dispersion model. General characteristics of eq. (22) have been explored in the context of fluid "hold-up" in packed tubular reactors.¹⁸ For small k_m , a response qualitatively similar to the axial dispersion model is obtained but with a long, slowly decaying tail. For large k_m , the response more closely resembles the canonical axial dispersion model. Thus, the model is capable of representing a range of residence time distributions.

As shown in Appendix A, the left-hand-side of equation (22) can be formed from the experimental tracer data and used in a Laplace domain least squares fitting routine to estimate the parameters D_m , k_m , and β . However, our hydrothermal systems pose special difficulties for tracer experiments. For example, if precipitation of solids is an important contributor to dispersion, the tracer test should be conducted under actual operating conditions. While candidate tracers might include D_2O , Rn, and Ar, detection in the presence of the solids may be difficult. If tracer experiments cannot be conducted under actual operating conditions, an alternative is suggested. It consists of first cleanly determining the chemical kinetic parameters by conducting experiments in a

reacting mixture at concentrations just below where precipitation occurs. Inert tracer experiments could provide D_m , k_m , and β under these conditions. These flow parameters are then used to determine the kinetic parameters (with no solids). These kinetic parameters are in turn used to compare the model with conversion data taken under actual operating conditions (which may involve solids) in order to determine the set of D_m , k_m , and β values appropriate to actual operating conditions.

An energy balance strictly analogous to the mass transfer case could easily be formulated. However, this would introduce a heat transfer coefficient between the two zones. Unfortunately, unlike the mass transfer case, there is no independent means of estimating this interzone transfer coefficient. Thus, an approximation is suggested. It will be assumed that within any fluid element of thickness Δz , there are no spatial (interzone) variations in temperature. Furthermore, it is assumed that convective heat transfer between the fluid and wall is proportional to $h(T_f - T_w)$, where h is well-described by the standard empirical correlations for flow in tubes. In analogy with the mass balance, axial dispersion of heat is allowed. An energy balance over the element Δz then gives

$$\rho_f c_{pf} \frac{\partial T_f}{\partial t} = \alpha D_H \frac{\partial^2 T_f}{\partial z^2} - \alpha u \rho_f c_{pf} \frac{\partial T_f}{\partial z} + \alpha \sum_{i=1} (-\Delta H_1) R_1 + (1-\alpha) \sum_{i=2} (-\Delta H_2) R_2 + H_s \quad (23)$$

where the term H_s (J/cm³sec) accounts for heat transfer between the fluid and its surroundings. In addition to the trivial isothermal option (no heat balance required), several options are envisioned for the H_s term:

- (a) adiabatic
- (b) specified outside tube wall temperature
- (c) sand-bath (specified bed temperature)
- (d) specified heat generation in the tube wall
- (e) radiative transport to/from coaxial cylindrical cavity

The first of these is self explanatory ($H_s = 0$). Case (b) may be used for what is commonly referred to as the "reactor" section. It may also prove useful when the exterior tube wall is maintained at specified temperatures by radiative heaters. Case (c) is intended for the fluidized bed reactors and includes heat transfer resistances on both the inside and outside of the tube, as well as through the tube wall. Case (d) is intended for the electrically heated tube. Case (e) is an alternative means of treating the radiative transfer case, wherein radiative transfer terms appear explicitly. The form of H_s corresponding to each case is given in Appendix C. These options should provide the flexibility needed to use the model for both the laboratory and pilot scale reactors at LANL.

In addition to specifying an initial temperature profile, boundary conditions analogous to the mass transfer Danckwerts equations are suggested:

$$u\rho_f c_{pf} T_f(0,t) = u\rho_f c_{pf} T_{in}(0,t) + D_H \left[\frac{\partial T_f}{\partial z} \right]_{z=0} \quad (24)$$

and

$$\left[\frac{\partial T_f}{\partial z} \right]_{z=L} = 0 \quad (25)$$

Again these correspond to continuity of flux at the inlet and continuity of both flux and temperature at the exit. Computational results are usually not overly sensitive to details at the boundaries unless an inordinate amount of dispersion takes place. If an inordinate amount of dispersion is present, serious consideration should be given to alternative models which may more realistically represent the dispersion characteristics.

The generalized 1-D model was formulated for systems with fluid hold-up and deviations from idealized plug flow. Under appropriate conditions, the model reduces to the axial dispersion model and ultimately to the ideal plug flow model. With the options outlined for heat transfer with the surroundings (Appendix C), the model should apply to the currently used hydrothermal reactor configurations.

Numerical Demonstration. The steady state (i.e. time independent) version of the model gives rise to differential algebraic equations (DAEs). In general, this system of non-linear equations requires numerical techniques slightly different than those used above to solve the canonical axial dispersion model. A code package for solving DAEs has been obtained but has not yet been implemented. At steady state, note that for a single reactive species consumed isothermally by a simple first or second order reaction, the algebraic equation can be solved for C_2 and the result substituted into the mass balance for zone 1. This gives just one differential equation which can be solved using the orthogonal collocation technique employed above. Figure 13 shows the effects of β on calculated conversions, for a fixed k_m , and a single second order reaction. (Variations due to changing k_m at fixed β are discussed elsewhere.¹⁸) It can be seen that for a fixed value of the mobile phase Peclet number, a increase in the amount of hold-up (i.e. β) serves to increase the conversion. In order to demonstrate how these changes can impact reactor design and performance, consider the following scenario. Suppose β equals 0.30 and the target conversion is 0.99. The Peclet number which gives the desired conversion is approximately 9. If β is 0.0, then the desired conversion cannot be reached unless Pe is 30 or more. Upon correcting for the fact that the Peclet numbers depend on the mobile phase volume fraction (see Table 6), one finds that these differences in Peclet numbers correspond to reactor lengths which differ by more than a factor of two. Thus, the β parameter provides a degree of flexibility beyond the dispersion coefficient. This additional flexibility may prove useful in systems with substantial fluid hold-up.

PHYSICAL PROPERTIES CORRELATION

Accurate representation of physical properties is often the primary link-to-reality during process simulation. Correlation and prediction of phase behavior in high salt content hydrothermal solutions poses special challenges. High temperatures and relatively low densities are typically encountered above the critical point of water. Under these conditions, the magnitude of the solvent (water) dielectric constant drops dramatically. This results in less dielectric shielding in solution and thus water acts as a relatively poor solvent when compared to ambient conditions. As an example, consider the solubility of sodium carbonate in sodium hydroxide-water mixtures. This is a system of interest to hydrothermal processing of Hanford tank wastes since the solutions contain significant amounts of hydroxide (Table 1), while carbonate is produced by reaction of organics. At low to moderate temperatures, the amount of sodium carbonate soluble in the water-hydroxide mixture decreases with increasing sodium hydroxide concentration. Apparently, adding NaOH increases the activity of the sodium ions. The equilibrium of the sodium carbonate precipitation reaction is then shifted to favor formation of the solid sodium carbonate. However, at elevated temperatures ($>300^{\circ}\text{C}$), the carbonate solubility is retrograde, i.e. the amount of carbonate in the mixture increases with addition of sodium hydroxide. The poor solvent character of water under these conditions may encourage formation of sodium and hydroxide ion pairs in solution. These ion pairs, which are polar, may then provide dielectric shielding between the sodium and carbonate ions. Thus addition of NaOH has the effect of improving the solvent, which can now be thought of as a mixture of water and the Na-OH ion pairs. An initial evaluation of selected commercial software packages was conducted to determine their applicability under hydrothermal conditions. Although approximate in nature, these codes could serve as an interim means of correlating phase behavior while more robust thermodynamic models are developed.

The first package examined was the Environmental Simulation Program (ESP) from OLI Systems, Inc. This code makes use of techniques due to Helgeson for the standard state properties of species in water, the NIST steam tables for the water properties, and a proprietary combination of Bromley, Zemaitis, and Meissner correlations for the excess properties. While data regression capabilities are provided, the package has a substantial data base of parameters and is primarily intended to be used for predictive purposes. This being the case, the program was used to predict the solubility limits of sodium carbonate in concentrated NaOH-H₂O solutions. Details of the calculations can be found in Appendix D. Within the ranges of the data base (150°C for carbonate and 350°C for NaOH), the predictions are quite good. However for the ternary mixture, the code fails to show the retrograde solubility behavior using the supplied set of parameters. Regression of

new interaction parameters will be required to determine the accuracy of ESP's predictions under hydrothermal conditions.

An attempt was also made to correlate the high temperature solubility data using the Aspen Plus program from Aspen Technology, Inc. Electrolyte thermodynamics models in Aspen Plus generally require data on the system of interest and provide a basis for data correlation (and modest extrapolation). An input file was prepared using carbonate solubility data taken at LANL and Aspen's recommended activity coefficient model (electrolyte NRTL). An expression was supplied for the dielectric constant of water under hydrothermal conditions. Executing the data regression package led to a reasonable fit to the data. However, error messages appeared from the steam tables indicating that water properties were requested for a temperature above the critical. The code then assumed the critical temperature when calculating physical properties (e.g. a molar volume). Since the code does allow the user to modify the physical property calculation routes and models, this option was explored as a means of avoiding such calls to the steam tables and to have the code utilize a user supplied correlation for the necessary physical properties. However, it appears that reliance on the steam tables is hard-wired (this observation has been verified with Aspen customer support). Thus the same error messages were encountered. One option does remain to effectively utilize this code. It consists of using the mixed solvent electrolyte option, which still requires one solvent be water. One could introduce a very small amount of water while the second solvent's properties are all user supplied. The properties of supercritical water would then be entered for the second solvent, which is given a name other than water. In this way errors introduced by the calls to the steam tables (for what the code thinks is the water fraction of the solvent) will be small and the essential properties of supercritical water will be utilized. An approach such as this is recommended for future calculations using Aspen Plus.

PROCESS CONTROL

Operating hydrothermal processing units at pressures greater than 15,000 psia and at fluid temperatures exceeding 350°C requires a well-controlled process. We have addressed process control issues to meet the desired rate of organic destruction while maintaining a safe and controlled working environment. For the pilot scale units, the data acquisition and control systems are physically separated from the process, except for the necessary sensors and control devices. The computerized feedback control systems are designed for remote operation of the unit and include start-up and shut-down capabilities. The systems also include automatic shut-down procedures should significant process upsets occur, e.g. an over-pressurization. Limits or bounds on the acceptable temperature and pressure are set according to materials design specifications and

ASME code. A more complete description of the pressure and temperature control system used on the pilot scale facilities is given below.

For several hydrothermal processing units operating in parallel, it is envisioned that each subunit will have its own computerized feedback control loop. Sensors will monitor temperature, pressure, flow rates, and radiation levels. Should a off-normal condition occur in one of the reactor subunits, it will automatically be isolated and shut-down in a controlled manner. A degree of centralization will exist where a "master" computer/control system will monitor the subunits and provide a focal point for information exchange with other elements of the process, such as down stream separation and filtration units.

Pressure Control. Due to surging associated with the high pressure feed pumps, fairly severe pressure fluctuations were observed in the 2 gal/hr pilot scale reactor. In order to reduce these high-frequency fluctuations, 0.010-in ID stainless-steel tubing was installed in conjunction with two pulsation dampeners at the pump outlet. This tubing is intended to act analogously to a low-pass RC filter which filters out undesirable high-frequency noise components. The pulsation dampeners mimic capacitors while the small diameter tubing functions as a resistor. The performance of the RC filter improves with an increase in the resistance or in the capacitance (see Appendix E for details). Figures 14 and 15 show how the pressure fluctuations decrease inside the reactor using the capillary tubing as a filter. Fluctuations also decrease with an increase in the capillary length. A longer capillary would mean more resistance to the fluid flow. Thus this simple low-pass "filter" improved system performance by "smoothing out" pressure fluctuations.

Initially, on the 2 gal/hr pilot scale unit, a linear air-to-close pneumatic Badger-Meter control valve was placed at the reactor outlet for pressure control. Flow was supplied by a Hydro-Pac pump consisting of a hydraulically-driven, single-headed intensifier and a series of check valves. The pilot-scale reactor typically operates at flow rates between one and three gallons per hour. The pressure drop across the valve (ΔP) can be determined from

$$\Delta P = g_s * [Q / C_v * f(x)]^2$$

where Q is the fluid flow rate, C_v is the valve coefficient, $f(l)$ is the flow characteristic, x is the valve stem position, and g_s is the specific gravity of fluid. The pressure drop across the control valve is affected by the flow rate and also depends on the valve stem position.

At high pressures and pressure drops, check valve failure was observed. This led to undesirable flow fluctuations. Consequently, the pressure and temperature control responses were adversely affected. Wear of the control valve stem and seat is unavoidable and must be expected when using a pressure let-down valve. To avoid problems associated with wear on the control valve, the desired reactor pressure was maintained by generating a large pressure drop across small-diameter tubing. The cost of replacing these tubes is negligible compared to that of the

control valves. Thus we have replaced the pressure let-down valves with another section of 0.010-in ID stainless-steel tubing. Pressures were maintained near the desired set points using capillary tubing as a pressure let-down device.

Temperature Control. Temperatures are controlled using a proportional-integral-derivative (PID) feedback controller. The fluid temperature, measured at the end of preheater section, is controlled by supplying the power to the preheater section. Step response data (with water flowing through the reactor at 1.5 gallon per hour and 15,000 psia) demonstrated that the process is well-represented by a first-order model with time delay (see Process Control Appendix for details).

Through trial-and-error, the controller settings were "fine-tuned" to get a response more sluggish than that from the standard Cohen-Coon parameters. As seen in Figure 16, there is a stable yet sluggish closed-loop response for a change in temperature set point from 350°C to 400°C. It takes 30 minutes for a fifty-degree change in the fluid temperature. There is an overshoot of less than 2°C (or 4%). This sluggish response is favorable for two reasons: (1) maintaining equipment integrity and a controlled working environment and (2) obtaining conservative controller settings that should also apply to more exothermic reactions. The control system is designed to prevent a temperature overshoot which could lead to tubing rupture. Conservative controller settings also reduce the magnitude of the temperature overshoot and prevent severe responses when highly exothermic reactions occur.

REFERENCES

1. Hohl, T. M., Westinghouse-Hanford Company Report WHC-SD-WM-TI-549, May 1993.
2. Oldenberg, R. et al., "Evaluation of IPM Selection Criteria for Hydrothermal Processing", Report submitted to the IPM Selection Panel for Organic Destruction Technologies (June 9, 1994).
3. M. Smith, Chemical Engineering Kinetics, 2nd Ed., McGraw-Hill, New York (1970).
4. G.I. Taylor, Proc. Roy. Soc. A219: 186 (1953).
5. R. Aris, Proc. Roy. Soc. A235: 67 (1956).
6. C.Y. Wen and L.T. Fan, Models for Flow Systems and Chemical Reactors, Marcel Dekker, New York (1975).
7. Anderson, G. et al., Final (LANL) Report on Physical Properties for Hydrothermal Processing of Hanford Tank Wastes (1994).
8. U. Ascher, J. Christiansen, and R.D. Russell, Math. Computation 33(146): 659 (1979).
9. U. Ascher, J. Christiansen, and R.D. Russell, ACM Trans. Math. Software 7(2): 209 (1981).
10. B.S. Garbow, K.E. Hillstom, J.J. More, Argonne National Laboratory, MINPACK Project, (1980).
11. Kee, R. et. al., Sandia National Laboratories Report SAND89-8009B UC-706, April 1992.
12. "Hypersonic Combustion Kinetics:" Status Report of the Rate Constant Committee, NASP High Speed Propulsion Technology Team, December 1989; and updates thereto.
13. Baldwin et al., J. Chem. Soc., Faraday Trans. I 71, 1265 (1975).
14. Balakhnine et al., Combust. Flame 28, 165 (1977).
15. G.I. Taylor, Proc. Roy. Soc. A223: 446 (1954).
16. L.V. Beckman, et al., AIChE J. 36(4): 598 (1990).
17. L. Lapidus and N.R. Amundson, J. Phys. Chem. 56: 984 (1952).
18. M.L. Michelsen, Chem. Eng. J. 4: 171 (1972).

Figure 1. System Response to Step Change in Input. Ratio of outlet-to-inlet concentration for a step increase in inlet concentration occurring at time zero. The response is plotted as a function of time, θ , divided by the mean residence time. The response is shown for different values of the inverse Peclet number, D_L/uL , where D_L is the dispersion coefficient, u is the mean flow velocity, and L is the reactor length. Also shown for comparison purposes is the laminar segregated (no diffusion or dispersion) flow response.

Figure 2. Velocity Vectors in Tank Reactor. Fuel injection point is at left ($x=0$) while the reactor exit is at the right. The dashed line ($y=0$) corresponds to the reactor mid-line. The size of the individual vectors is in proportion to the magnitude of the velocity.

Figure 3. Plot of Stream Function. The stream function clearly shows the recirculating pattern induced by the convection currents.

Figure 4. Spatial Distribution of Temperatures. The cooler temperatures (673°K) are at the reactor entrance. Maximum values occur in the reactor due to the heat of reaction.

Figure 5. Spatial Distribution of Temperatures. The cooler inlet temperatures (623°K) are again at the reactor entrance. The maximum values (700°K) are somewhat lower than those seen in Figure 4.

Figure 6. Calculated vs. Observed Conversion.
Results obtained by nonlinear regression using the axial dispersion model (adm).

Figure 7. TOC Removal Rates With and Without Dispersion.

"pf" denotes plug flow while "ad" refers to the axial dispersion model.

Figure 8. Calculated temperature increase versus time in Mixture 1 for Case A (thermal reaction; curve 1A) and Case B (spark-initiated reaction; curve 1B). The time scale for curve 1B has been multiplied by 2×10^8 .

Figure 9. Ignition Delay Times.

Figure 10. Hydrogen (H_2) gas production in laboratory experiments on hydrothermal processing of tank-waste simulant. The number of moles of H_2 produced per mole of total organic carbon (TOC) destroyed is plotted versus reaction temperature, parametric in average residence time at reaction temperature and pressure. The legend gives the average and standard deviation of the residence times for each data series. The data points at the two highest temperatures correspond to absolute quantities of H_2 below the analytical detection limit.

Figure 11. Schematic of Factors Contributing to Dispersion.

Figure 12. Physical Model for 1-D Flow with "Hold-Up".

Figure 13. Effects of Fluid Hold-Up (β) on Conversion.
 For this calculation, $k_m=1.0e5$, $L/u=35$, $k=8.0e4$, and $C_0=5.0e-4$.
 The second order reaction term was taken to be of the form $k(C_i)^2$.

Figure 14. Pump and Reactor Pressure. The reduction in pressure fluctuations resulting from insertion of the capillary tubing is clearly visible.

Figure 15. Pump and Reactor Pressure. The reduction in pressure fluctuations resulting from insertion of the capillary tubing is clearly visible.

Figure 16. Closed-Loop Temperature Response.

APPENDIX A. INTERPRETATION OF TRACER DATA.

Several techniques for characterizing the experimentally obtained RTD and determining model parameters are described in this appendix. Included are the method of moments, time domain fitting, and Laplace domain fitting. A few others are mentioned only briefly.

Method of Moments. Before discussing the method, some general relationships are presented. The n -th central moment, μ_n , is defined by

$$\mu_n \equiv \int_0^{\infty} t^n f(t) dt \quad (\text{A-1})$$

Recall that the RTD is related to the washout function, $W(t)$, and the residence time distribution, $F(t)$ through

$$f(t) = \frac{dF}{dt} = - \frac{dW}{dt} \quad (\text{A-2})$$

Also recall that while $f(t)$ is obtained experimentally from a pulse input, $W(t)$ is obtained from a step decrease in tracer concentration and $F(t)$ is obtained from a step increase. Equation A-2 can be used to obtain a useful alternative to A-1, namely,

$$\mu_n = n \int_0^{\infty} t^{n-1} W(t) dt \quad (\text{A-3})$$

Another relationship of interest is the cumulant generating function. The cumulants, $\{\kappa_i\}$, are related to the moments in a straightforward manner and have the nice property that they are strictly additive for independent systems in series. The cumulants are defined by

$$\kappa_n \equiv (-1)^n \lim_{s \rightarrow 0} \frac{d^n}{ds^n} \ln \bar{f}(s) \quad (\text{A-4})$$

It turns out that the first cumulant is the mean of $f(t)$ and the second is the variance. Equation A-4 also provides a basis for relating parameters of a given model to characteristics of the RTD. For a particular model, Laplace transformation of the governing differential equation gives the transfer function. Subsequent substitution into A-4 yields equations relating parameters of the model to the mean and variance of the RTD. Parameter values can then be estimated from these relationships.

For imperfect inputs, e.g. a less-than-perfect delta function pulse, the method of moments relies on the additive property of cumulants. Determining the mean and variance at the inlet and exit measuring points allows one to obtain the mean and variance of the system RTD by a simple difference. Of course, the tracer injection point should be close to the first measurement point so as to avoid the "small difference of large numbers" problem.

Direct calculation of the mean and variance via equation A-1 has difficulties in the tail region of the RTD. Note that at large times, the inherent errors in measurement are magnified by the t^n factor. The results are also quite sensitive to where the calculation is truncated. Measurement of the washout function, together with equation A-3, alleviates this problem

somewhat. In fact, for direct calculation of moments the experimental measurement is almost always $W(t)$ rather than $f(t)$. [As a general precaution, $W(t)$ and $F(t)$ probably should be measured anyway to check for effects the tracer may have on the dynamics (e.g. through a change in density)]. With $W(t)$ and equation A-3, the higher order moments are still notoriously inaccurate and are rarely even reported. In general, estimation of n model parameters will require accurate values for the first n moments.

Time Domain Fitting. This approach involves solving the model equations in real time subject to the inlet condition $C(t)=C_{in}(t)$, where $C_{in}(t)$ is the concentration measured at the inlet point. Values for C_{out} are obtained from the model and compared to the C_{out} determined by the exit point measurements. The parameters in the model are adjusted to give a best fit (in a least squares sense) to the experimentally determined C_{out} . As with the moments approach, parameter values are often sensitive to errors in measuring the tail and thus to truncation. In practice, experimental data are sometimes extrapolated to large times using an analytic functional approximation, such as an exponential. "Weighted" least squares can be used to effectively de-emphasize the effects of the tail on the calculated parameter values. For example, given a weighting function $w_o(t)$, minimizing

$$\int_0^{\infty} \left[C_{out}(t) - \int_0^t C_{in}(t - \tau) f(\tau, P) d\tau \right]^2 w_o(t) dt$$

with respect to the vector of model parameters, P , provides the best-fit model parameters. Of course, weighting functions other than exponentials can be utilized.

A modified method of moments can also be formulated in this spirit. For example, by differentiating equation 8 in the main text n -times with respect to s and then equating s to a positive real number, k , modified moments of the form

$$M_{n,k} \equiv \int_0^{\infty} C_{in}(t) t^n \exp(-kt) dt$$

are obtained. Note that the t^n factor is now counteracted by the $\exp(-kt)$ term and the exponential is essentially the weighting function, $w_o(t)$. It turns out that these $M_{n,k}$'s can also be related directly to derivatives of the system transfer function, thus providing a means of parameter estimation. The number of relationships required for parameter estimation can be obtained by choosing different values of k (it is not necessary to calculate higher order $M_{n,k}$'s). These modified time domain fitting approaches have proven to be fairly accurate.

Laplace Domain Fitting. This approach estimates parameters in the Laplace domain. As with the time domain example given above, it seeks to exploit a property of integral transformations whose kernel is a decaying exponential. Large values of t get mapped into small values of s through Laplace transformation. Thus it is hoped that the difficulties encountered in the time domain at large t will not have the same negative impact if appropriately chosen methods of

analysis are performed in the Laplace domain. The method consists of forming the left-hand-side of equation 8 from the data while the right-hand-side is formed from the Laplace transform of the model differential equation. As an example, the experimentally determined transfer function can be found from

$$\bar{f}(s) \equiv \frac{\bar{C}_{out}(s)}{\bar{C}_{in}(s)} = \frac{\int_0^{\infty} C_{out}(t) \exp(-st) dt}{\int_0^{\infty} C_{in}(t) \exp(-st) dt} \quad (A-5)$$

where C_{in} and C_{out} are experimentally measured concentrations. Again note that the large time values of C are "damped" by the exponential term. In practice, the integrals on the right-hand side must be evaluated using the experimental data for a range of s -values. The literature does provide some guidance in selecting s ranges for a given mean residence time. For determination of n model parameters, only n values of s are actually required. However, better results are obtained if a larger number are used along with a least squares comparison to the model's transfer function. As an example of how the left-hand-side of A-5 is obtained, consider the axial dispersion model

$$\tau \frac{\partial C}{\partial t} + \frac{\partial C}{\partial z} - \frac{1}{Pe} \frac{\partial^2 C}{\partial z^2} = 0 \quad (A-6)$$

where τ is the mean residence time, z the dimensionless axial position (position/reactor length), and Pe is the Peclet number (mean flow velocity times reactor length/dispersion coefficient). The Laplace transform of equation A-6 gives

$$\bar{f}(s) = \frac{\bar{C}_{z=1}}{\bar{C}_{z=0}} = \exp \left\{ \frac{Pe}{2} \left(1 - \left(1 + \frac{4s\tau}{Pe} \right)^{1/2} \right) \right\} \quad (A-7)$$

which can be rearranged to read

$$\left(\ln \left(\frac{1}{\bar{f}(s)} \right) \right)^{-1} = \tau s \left(\ln \left(\frac{1}{\bar{f}(s)} \right) \right)^{-2} - \frac{1}{Pe} \quad (A-8)$$

Thus, using the experimentally determined values for the right-hand side of equation A-5 in a plot of $(-\ln \bar{f}(s))^{-1}$ versus $s(-\ln \bar{f}(s))^{-2}$ yields a line of slope τ and intercept $-1/Pe$. In this special case, only linear regression is required to find the parameter values. For more complicated models, non-linear least squares fitting in the s -domain will be required.

Other Methods. Methods analogous to the Laplace domain approach, but based on the Fourier transform, are available as are methods employing orthogonal function representations of the RTD. At this juncture no clear advantage is seen in these methods over the weighted time domain fitting and Laplace domain approaches.

APPENDIX B. CHEMKIN CALCULATIONS

CHEMKIN INTERPRETER OUTPUT: CHEMKIN-II Version 2.5 Dec. 1990
DOUBLE PRECISION

ELEMENTS CONSIDERED	ATOMIC WEIGHT
1. H	1.00797
2. O	15.9994
3. AR	39.9480
4. N	14.0067

SPECIES CONSIDERED	C		MOLECULAR WEIGHT	TEMPERATURE		ELEMENT COUNT			
	P	H		LOW	HIGH	H	O	AR	N
	A	R							
1. H	G	0	1.00797	300.0	5000.0	1	0	0	0
2. O	G	0	15.99940	300.0	5000.0	0	1	0	0
3. AR	G	0	39.94800	300.0	5000.0	0	0	1	0
4. OH	G	0	17.00737	300.0	5000.0	1	1	0	0
5. H2	G	0	2.01594	300.0	5000.0	2	0	0	0
6. O2	G	0	31.99880	300.0	5000.0	0	2	0	0
7. H2O	G	0	18.01534	300.0	5000.0	2	1	0	0
8. HO2	G	0	33.00677	300.0	5000.0	1	2	0	0
9. H2O2	G	0	34.01474	300.0	5000.0	2	2	0	0
10. N2	G	0	28.01340	300.0	5000.0	0	0	0	2
11. N2O	G	0	44.01280	300.0	5000.0	0	1	0	2
12. NO	G	0	30.00610	300.0	5000.0	0	1	0	1
13. HNO	G	0	31.01407	300.0	5000.0	1	1	0	1
14. NH	G	0	15.01467	300.0	5000.0	1	0	0	1

REACTIONS CONSIDERED	(k = A T**b exp(-E/RT))		
	A	b	E
B 1. OH+H2=H2O+H	2.14E+08	1.5	3449.0
B 2. H+O2=OH+O	9.75E+13	.0	14851.0
B 3. H2+O=OH+H	3.87E+04	2.7	6259.0
B 4. H+HO2=H2+O2	4.27E+13	.0	1411.0
B 5. H+HO2=OH+OH	1.69E+14	.0	874.0
B 6. O+HO2=O2+OH	3.30E+13	.0	.0
B 7. OH+HO2=H2O+O2	1.02E+13	.0	-827.0
B 8. H+O2+M=HO2+M	1.00E+20	-1.5	.0
H2O	Enhanced by	0.000E-01	
H2	Enhanced by	0.000E-01	
AR	Enhanced by	0.000E-01	
B 9. H+O2+H2O=HO2+H2O	1.60E+22	-2.0	.0
B 10. H+O2+H2=HO2+H2	2.00E+18	-.8	.0
B 11. H+O2+AR=HO2+AR	1.20E+18	-.9	.0

B 12.	H+OH+M=H2O+M		1.30E+22	-2.0	.0
	H2O	Enhanced by	0.000E-01		
		Enhanced by	0.000E-01		
		Enhanced by	0.000E-01		
B 13.	H+C → H2O+H2O		6.50E+22	-2.0	.0
B 14.	H+C → H2O+H2		3.20E+22	-2.0	.0
B 15.	H+O → H2O+AR		8.00E+21	-2.0	.0
B 16.	H+H → H2+M		5.40E+18	-1.3	.0
	H2O	Enhanced by	0.000E-01		
	H2	Enhanced by	0.000E-01		
	AR	Enhanced by	0.000E-01		
	H	Enhanced by	0.000E-01		
B 17.	H+H+H2O=H2+H2O		5.08E+20	-1.6	.0
B 18.	H+H+H2=H2+H2		1.00E+17	-.6	.0
B 19.	H+H+AR=H2+AR		7.00E+17	-1.0	.0
B 20.	H+H+H=H2+H		3.20E+15	.0	.0
B 21.	H+O+M=OH+M		6.20E+16	-.6	.0
	H2O	Enhanced by	5.000E+00		
B 22.	O+O+M=O2+M		1.00E+17	-1.0	.0
	H2O	Enhanced by	1.860E+01		
	H2	Enhanced by	2.860E+00		
B 23.	OH+OH=O+H2O		1.88E+06	1.9	-1331.0
B 24.	OH+OH+M=H2O2+M		4.73E+11	1.0	-6370.0
	H2O	Enhanced by	1.625E+01		
	H2	Enhanced by	2.500E+00		
B 25.	H2O2+OH=H2O+HO2		7.00E+12	.0	1435.0
B 26.	H2O2+O=HO2+OH		2.80E+13	.0	6398.0
B 27.	H2O2+H=HO2+H2		1.70E+12	.0	3775.0
B 28.	H2O2+H=H2O+OH		1.00E+13	.0	3577.0
B 29.	HO2+HO2=H2O2+O2		2.00E+12	.0	.0
B 30.	H+N2O=OH+N2		2.53E+10	.0	4550.0
	Declared duplicate reaction...				
B 31.	H+N2O=OH+N2		2.23E+14	.0	16750.0
	Declared duplicate reaction...				
B 32.	O+N2O=N2+O2		1.00E+14	.0	28017.0
B 33.	O+N2O=NO+NO		6.92E+13	.0	26626.0
B 34.	N2O(+M)=N2+O(+M)		1.48E+11	.0	58821.0
	Low pressure limit: 0.26200E+16 0.00000E+00 0.55442E+05				
	TROE centering: 0.10000E+01 0.30000E+03 0.37900E+03				
	0.24710E+04				
	AR	Enhanced by	1.000E-01		
B 35.	H+N2O=NH+NO		1.42E+14	.0	25295.0
B 36.	NH+N2O=HNO+N2		2.00E+12	.0	5961.0
B 37.	H+HNO=H2+NO		1.26E+13	.0	3974.0
B 38.	OH+HNO=H2O+NO		1.26E+12	.5	1987.0
B 39.	O+HNO=OH+NO		5.01E+11	.5	1987.0
B 40.	H+NO+M=HNO+M		2.70E+15	.0	-596.0
	H2O	Enhanced by	6.000E+00		
	H2	Enhanced by	2.000E+00		
	N2O	Enhanced by	2.000E+00		

NOTE: A units mole-cm-sec-K, E units cal/mole

APPENDIX C. HEAT TRANSFER TERMS

Specific forms for the term H_s are given in this appendix for steady state heat transfer.

Case (a). For an adiabatic reactor

$$H_s = 0 \quad (C-1)$$

Case (b). For a specified outside wall temperature, $T_{wo}(z)$, the driving force for heat transfer is the quantity $(T_{wo}(z) - T_f(z))$. The wall-to-fluid resistance and conduction through the wall can be treated as resistances in series. Thus,

$$H_s = \frac{(T_{wo}(z) - T_f(z))}{A \left(\frac{1}{2\pi r_i h} + \frac{\ln(r_o/r_i)}{2\pi k_T} \right)} \quad (C-2)$$

Case (c). For a specified fluidized bed temperature, T_{FB} , the driving force for heat transfer is the quantity $(T_{FB} - T_f(z))$. The wall-to-fluid resistance, conduction through the wall, and outside wall-to-fluidized bed resistance can be treated as resistances in series. Thus,

$$H_s = \frac{(T_{FB} - T_f(z))}{A \left(\frac{1}{2\pi r_i h} + \frac{\ln(r_o/r_i)}{2\pi k_T} + \frac{1}{2\pi r_o h_{FB}} \right)} \quad (C-3)$$

Correlations are available for fluid-to-tube wall heat transfer coefficients in fluidized beds (i.e. for h_{FB}).

Case (d). For direct electrical heating of the tube, heat generation is actually concentrated at the outer surface of the tube. At the expense of obscuring the role played by conduction through the wall, the calculations can be kept 1-dimensional. If it is assumed that heat generation is uniform within the tube and that using a single wall temperature T_w is sufficient:

$$H_s = \frac{2\pi r_i h}{A} (T_w(z) - T_f(z)) \quad (C-4)$$

The variable T_w must now be expressed in terms of known quantities. An additional equation which does this is obtained from a heat balance over the tube:

$$0 = k_T A_w \frac{\partial^2 T_w}{\partial z^2} + 2\pi r_i h (T_w - T_f) + \frac{2\pi k_I}{\ln(r_i/r_o)} (T_a - T_w) + Q_g \quad (C-5)$$

where Q_g is the rate of heat generation per unit length in the tube (J/cm sec). The terms in C-5 correspond to axial conduction in the tube, heat transfer with the fluid, heat transfer with the

ambient surroundings (though the insulation), and heat generation. For boundary conditions on C-5, assume the thermal gradients are known at the inlet and exit:

$$\left[\frac{\partial T_w}{\partial z} \right]_{z=0} = B_1 \quad \text{and} \quad \left[\frac{\partial T_w}{\partial z} \right]_{z=L} = B_2 \quad (C-6)$$

The values of B_1 and B_2 can either set to zero or estimated based on typical thermocouple readings. Note that at steady state, equations C-5 and C-6 can be solved analytically for T_w and the result substituted into C-4. Other approaches are possible and are under consideration. For example, a wall conduction "factor" could also be employed.

Case (e). If the thermocouples used to control power input into the radiative heaters actually touch the tube wall, then use of the specified wall temperature option (case (b)) should suffice. However, for situations with large heats of reaction it may be desirable to explicitly include radiative transfer. This will generally require an additional equation. For this case we have

$$H_s = \frac{(T_{wo}(z) - T_f(z))}{A \left(\frac{1}{2\pi r_i h} + \frac{\ln(r_o/r_i)}{2\pi k_T} \right)} \quad (C-7)$$

where now, an additional equation is required to express T_{wo} in terms of known quantities. The required equation can be developed by equating heat transfer rates per unit length at the exterior surface of the tube. This rate, q , is related to the fluid temperature through

$$q = \frac{(T_{wo}(z) - T_f(z))}{\left(\frac{1}{2\pi r_i h} + \frac{\ln(r_o/r_i)}{2\pi k_T} \right)}$$

This must also equal the transfer rate per unit length by radiation. Thus

$$\frac{(T_{wo} - T_f)}{\left(\frac{1}{2\pi r_i h} + \frac{\ln(r_o/r_i)}{2\pi k_T} \right)} = 2\pi r_c \sigma F_{cw} (\epsilon_c T_c^4 - \epsilon_{wo} T_{wo}^4) \quad (C-8)$$

provides the additional equation. In C-8, σ is the Stefan-Boltzmann constant ($J/cm \text{ sec } ^\circ K^4$), ϵ denotes the emissivity, "c" denotes the cavity housing the radiative heaters, and F_{cw} is the radiative "view factor" between coaxial cylinders, the formula for which is known.

APPENDIX D. CORRELATING ELECTROLYTE PROPERTIES

The OLI database presently covers Na_2CO_3 precipitation up to temperatures of 200°C . This could be extended using a more extensive data base. As a first step, the solubility limits of the binary system Na_2CO_3 in H_2O were determined. For various temperatures, the amounts of Na_2CO_3 predicted are shown in Table D-1 along with the corresponding experimental values.¹ The agreement on both the precipitated phase and amount of Na_2CO_3 present at saturation is generally favorable.

Table D-1. Predictions of OLI Electrolyte Package (On a basis of 1 kg H_2O).

T ($^\circ\text{C}$)	P (psia)	Sat. Soln. g Na_2CO_3	Predicted Precipitate	Observed Precipitate	Calc. g-mol Na_2CO_3	Expt. g-mol Na_2CO_3
75	4.64	443.24	$\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$	4.18	4.28
100	12.22	436.69	$\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$	4.12	4.22
120	24.26	429.26	Na_2CO_3	Na_2CO_3	4.05	4.03
140	44.39	387.13	Na_2CO_3	Na_2CO_3	3.65	3.71
160	77.47	360.44	Na_2CO_3	Na_2CO_3	3.40	3.44
180	127.45	329.30	Na_2CO_3	Na_2CO_3	3.11	3.16
200	201.39	303.33	Na_2CO_3	Na_2CO_3	2.86	2.89

The binary system NaOH -water was examined next. Again, the low temperature comparisons were favorable. Since high temperature vapor pressure data is available for this system, comparisons were also made in the range of 300 - 350°C . Figure D-1 shows a comparison of the OLI predictions (solid lines) to available high temperature data. The squares are data from Dibrov et al.² while the triangles from Korobkov and Galinker,³ and the circles from Urusova.⁴ Rather than simply using an empirical correlation, e.g. a polynomial, to predict vapor pressure the OLI code performs the phase equilibrium calculations. Thus, the agreement seen in Figure D-1 suggests that the OLI formalism for electrolyte thermodynamics is capable of favorably correlating properties at reasonably high temperatures.

The solubility of Na_2CO_3 in NaOH - H_2O solutions was then examined. Data has been reported⁵ for this ternary system for temperatures at and above 150°C . It was reported that a small amount of water vapor was present during the experiments. Unfortunately, the precise amount was not determined. This uncertainty affects the results since for non-volatile salts, the presence of

Figure D-1. Vapor pressure of the NaOH-water system at high temperatures.

water vapor decreases the amount of liquid water. Consequently, this increases the effective salt concentration. However, if the amount of vapor is in fact small, a comparison of predicted and experimental solubility can be made by assuming the system is at the bubble point pressure. Thus, the OLI code was used to determine both the bubble point pressure and the solubility limit of Na_2CO_3 at 150°C . The results of the calculations and comparison to data are shown in Figure D-2. As a larger vapor phase fraction forms, the amount of Na_2CO_3 predicted at saturation is decreased somewhat. In general, the predictions compare favorably with the data using the bubble point pressure.

At higher temperatures, this ternary system shows rather interesting behavior. The amount

Figure D-2. Predicted (solid-line) and observed Na_2CO_3 solubility.

of Na_2CO_3 present at saturation actually increases with increasing NaOH concentration. This trend is shown in Figure D-3, using data reported by Borovaya and Ravich.⁵ Preliminary data taken at LANL in the range of 425-450°C shows the same qualitative trends seen in Figure D-3. Extrapolations based on the OLI code at higher temperatures yields results which continue to

Figure D-3. Na_2CO_3 solubility in NaOH- H_2O solutions.

qualitatively follow the trend seen in Figure D-2, although the curves do "flatten-out" as the temperature rises. It will likely prove necessary to regress new values for the interaction parameters directly from higher temperature data in order for the OLI package to be accurate at hydrothermal processing temperatures. A data regression capability is provided to accomplish this and discussions have been conducted with OLI on implementing such a program.

It appears that the standard OLI package may still find direct application in predicting solubility limits at lower temperatures (e.g. in cool-down heat exchangers). However, additional data sets and data regression will be necessary in order to correlate and predict solubility limits at reactor temperatures, i.e. those in the range 300-500°C.

Appendix D: References

1. F. Linke, "Solubilities of Inorganic and Metal-Organic Compounds" Am. Chem. Soc., 4th Ed., Vol. 2 (1965).
2. Dibrov et al., Zh. Prikl. Khim. 37:1920 (1964).
3. Korobkov and Galinker, Zh. Prikl. Khim. 29:1479 (1956).
4. Urusova, Russ. J. Inorgan. Chem. 19(3):450 (1974).
5. Borovaya and Ravich, Russ. J. Inorgan. Chem. 13(12):1720 (1968).

APPENDIX E. PROCESS CONTROL

Low-pass RC filter. The purpose of a low-pass RC filter is to remove undesirable high-frequency components, like noise. It consists of a voltage source with a resistor and capacitor connected in series. The voltage-in is supplied by the voltage source (V_s), and the voltage-out is drawn across the capacitor (V_C). The impedance of a conductor is the ratio between the peak values of the voltage and the current. The impedances of the resistor and the capacitor are R and $1/\omega C$, respectively. Here, R is the resistance, ω is the signal frequency, and C is the capacitance. For conductors connected in series, the equivalent impedance (Z_{eq}) is the sum of the individual impedances. In this case Z_{eq} is equal to $(1+\omega RC)/\omega C$. The loop current is equated as the ratio between the source voltage and the equivalent impedance. The voltage across the capacitor is proportional to the integral of the current.

To demonstrate how such a filter operates, let V_s equal $V_p \sin(\omega t)$, so that the current is $[V_p \omega C / (1 + \omega RC)] \sin(\omega t)$ and voltage across the capacitor is $[-V_p / (1 + \omega RC)] \cos(\omega t)$. The peak values of the inlet voltage ($V_{p,in}$) and the outlet voltage ($V_{p,out}$) are V_p and $V_p / (1 + \omega RC)$, respectively. The ratio between $V_{p,out}$ and $V_{p,in}$ is $1/(1 + \omega RC)$. As ω increases toward infinity, this ratio approaches zero. This ratio also decreases with an increase in the value of R or C . Thus, the high-frequency components are filtered out. The performance of the low-pass RC filter thus improves with an increase in either the resistance or capacitance.

First-order model with time delay. In the Laplace domain the process transfer function, $G_p(s)$, for a first-order model with time delay is described by

$$G_p(s) = K_p \exp[(-\theta s) / (\tau_p s + 1)] \quad (E-1)$$

where K_p is the process gain, θ is the time delay due to transportation lag, and τ_p is the process time constant. K_p is the ratio between the change in process variable and the change in manipulated variable. For temperature control, the process variable is the fluid temperature (measured at the end of the preheater section) while the manipulated variable is the digital-to-analog voltage signal sent from the GPIB to the dc power supply box. The supply box then sends a dc voltage to the preheater. Heat is generated through resistive heating in the wall of the Inconel tubing. Both process and manipulated variables are expressed in percentage. The temperature span is 600°C and the voltage signal span is 6.2V .

A step test was performed by making a step change in the manipulated variable value. The graphical approach was employed to determine the process time constant and time delay. A straight line was drawn tangent to the inflection point of the step response curve. The time delay θ is the value of time at the intersection between the tangent line and the initial steady-state value. The quantity $\theta + \tau_p$ is the value of time at the intersection between the tangent line and the final

steady-state value. Figure E-1 shows a step response curve for an open-loop experiment with water at 1.5 gallon per hour and 15,000 psia. The manipulated variable was changed from 40% to 45%. The following first-order parameters were deduced from the response

Process gain: $K_p = 2.9$

Process time: $\tau_p = 154$ sec

Time delay: $\theta = 43$ sec

The controller parameters were initially calculated using the empirical relations developed by Cohen and Coon. Strictly speaking, these relations would apply to a first-order process with a time delay giving a closed-loop response, with a quarter decay ratio. The decay ratio is the ratio between magnitudes of two successive peaks of a damped, oscillatory response. The feedback controller settings ultimately used to control the 2 gal/hr pilot plant reactor were:

	Cohen-Coon controller settings	Actual controller settings
Controller gain: K_c	1.7	0.1
Integral time: τ_i	94 sec	90 sec
Derivative time: τ_d	14 sec	30 sec

Figure E-1. Results and analysis of Step Response.