PNL-10108
UC-721

Organic Destruction Technology Development Task Annual Report - FY 1993

Hydrothermal Processing of Hanford Tank Waste

R. J. Orth
A. J. Schmidt
A. H. Zacher
M. R. Elmore
T. R. Hart
J. C. Poshusta
G. G. Neuenschwander
E. O. Jones
S. R. Gano

September 1993

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

Summary

Low-temperature hydrothermal processing (HTP) is a thermal-chemical autogenous processing method that can be used to destroy organics and ferrocyanide in Hanford tank waste at temperatures from 250°C to 400°C. In turn, this system can help eliminate safety hazards and meet downstream processing and disposal requirements. With HTP, organics react with oxidants, such as nitrite and nitrate, already present in the waste. Ferrocyanides and free cyanide will hydrolyze at similar temperatures and may also react with nitrates or other oxidants in the waste. No air or oxygen or additional chemicals need to be added to the autogenous HTP system. However, enhanced kinetics may be realized by air addition, and, if desired, chemical reductants can be added to the system to facilitate complete nitrate/nitrite destruction. Tank waste can be processed in a plug-flow, tubular reactor, or a continuous-stirred tank reactor system designed to accommodate the temperature, pressure, gas generation, and heat release associated with decomposition of the reactive species.

The work described in this annual report was conducted in FY 1993 for the Organic Destruction Technology Development Task of Hanford's Tank Waste Remediation System (TWRS). This task is part of an overall program to develop organic destruction technologies originally funded by TWRS to meet tank safety and waste form disposal criteria and condition the feed for further pretreatment. The work has since been transferred to the Initial Pretreatment Module (IPM) project. The primary focus of this task has been to evaluate and develop low-temperature hydrothermal processing (HTP). During FY 1993 the project completed seven experimental test plans, a 30-hr pilot-scale continuous run, over 200 hr of continuous bench-scale HTP testing, and 20 batch HTP tests; two contracts were established with commercial vendors, and a commercial laboratory reactor was procured and installed in a glovebox for HTP testing with actual Hanford tank waste. The HTP program at Pacific Northwest Laboratory is integrated with a complementary high-temperature HTP program at Los Alamos National Laboratory.

During FY 1993, PNL established the destruction efficiency of low-temperature HTP for organics with tank simulant based on Tank 241-SY-101 using batch, continuous bench-scale, and pilot-scale test systems. To provide a basis for testing and comparing organic destruction technologies, PNL completed evaluations on target organic and ferrocyanide destruction requirements, waste simulant compositions, and analytical methods for measuring destruction.

The results of experiments performed in a 1-L continuous flow tubular reactor showed that at 365°C, 3000 psig, and a 7-min residence time, the total organic carbon (TOC) in the simulant could be reduced by 80%. This level of organic destruction is sufficient to meet the IPM organic destruction criterion (i.e., reduction of the TOC level to less than 1556 ppm TOC in a tank waste at 5 M sodium). If required, higher levels of TOC reduction can be achieved by increasing the residence time and/or increasing the reactor temperature.

In addition to evaluating HTP, Zimpro Environmental, Inc. (Zimpro), under a subcontract, evaluated the feasibility of using wet air oxidation (WAO), a process similar to HTP but requiring the addition of air or oxygen. WAO has been used commercially for 30 years to destroy a wide variety of organics, and Zimpro has constructed over 200 commercial systems, including modular 20-gpm units similar to the type of HTP system envisioned for IPM. In FY 1993, Zimpro performed a series

of WAO batch autoclave tests with tank simulant and completed a preliminary materials-of-construction corrosion study. The test results demonstrated the required organic destruction level at less than 300°C and 2000 psig for most of the tested simulants.

Contents

Figures

Tables

1.0 Introduction

At the U.S. Department of Energy's Hanford Site, the underground storage tanks considered to be highest priority with respect to safety are flammable gas (H_2) generating tanks, organic tanks, and ferrocyanide tanks. The problems associated with these types of tanks could be lessened dramatically if the organic material (and/or ferrocyanide) could be destroyed or removed. This report discusses work conducted by Pacific Northwest Laboratory (PNL)[a] in FY 1993 to evaluate and develop organic destruction technologies that may be incorporated into the Initial Pretreatment Module (IPM) to meet tank safety and waste form disposal and condition the feed for further pretreatment. The work is part of the Organic Destruction Technology Development Task, which originally was funded by the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project being led by Westinghouse Hanford Company (WHC). This work has since been transferred to the IPM project.

Two types of related hydrothermal processes for organic destruction are emphasis here: low-temperature hydrothermal processing (HTP) and commercially available wet air oxidation (WAO). Other destruction technologies evaluated included: corona discharge, heat and digest, and electrochemical oxidation techniques. Work is continuing on HTP and WAO, and further results will be addressed in the FY 1994 annual report.

Low-temperature HTP is a thermal-chemical autogenous processing method that can be used to accelerate the naturally occurring reactions in the tank waste in a controlled manner. In turn, the safety hazards are eliminated and downstream feed process specification requirements can be met. With HTP, organics react with oxidants such as nitrite and nitrate already present in the waste. Ferrocyanides and free cyanide will hydrolyze at similar temperatures and may also react with nitrates or other oxidants present in the waste. For autogenous HTP, air or oxygen does not need to be added to the system; however, enhanced kinetics may be realized by air addition. Chemical reductants can also be used to destroy nitrates. Processing of the tank waste with HTP can be done in a plug-flow, tubular reactor system designed to accommodate the temperature, pressure, gas generation, and heat release associated with decomposition of the reactive species.

Wet air oxidation is a thermal-chemical process in which air or oxygen is added to tank waste in a heated, pressurized reactor to oxidize organic compounds and nitrite. The technology is commercially available for wastewater treatment applications, and was tested in this study to determine the viability of treating simulated Hanford tank waste in WAO systems.

Five experimental activities conducted during FY 1993 are described within this report: batch HTP testing with simulants (Section 3.0), batch WAO testing with simulants (Section 4.0), batch HTP testing with actual tank waste (Section 5.0), continuous bench-scale HTP testing with simulants (Section 6.0), and pilot-scale HTP testing with simulants (Section 7.0). For each of these activities,

---

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

the objectives, test approach, results, status, and direction of future investigations are discussed. Conclusions and Recommendations are provided in Section 2.0.

2.0 Conclusions and Recommendations

This section gives conclusions and recommendations based on the five experimental activities covered here.

2.1 Conclusions

During FY 1993, more than 200 hr of continuous HTP processing with tank waste simulant were conducted at PNL. Additionally, about 20 batch autoclave reactor tests were completed. The results of these tests showed that HTP can reduce the total organic carbon (TOC) in a simulant tank waste by 80% at 365°C and a residence time of 7 min in a tubular reactor system. This level of organic destruction is sufficient to meet the IPM organic destruction criterion (i.e., reduction of the TOC level to less than 1556 ppm TOC in a tank waste at 5 M sodium). The simulant represents Hanford's Tank 241-SY-101 (101-SY) waste.

Most of PNL's runs have been conducted with 3X diluted 101-SY simulant containing EDTA as the source of organic. Some organics, such as acetate, are much more difficult to destroy than EDTA. For 70% to 90% acetate destruction, HTP must operate at temperatures greater than 350°C. Before recommending higher operating temperatures, it must be determined if significant concentrations of acetate exist in the tanks, or if acetate will be produced as a degradation product from HTP treatment of more complex organic species. At this time, there is considerable uncertainty regarding which organic species exist in the tank waste at significant concentrations and which particular organic species will affect grout or other downstream processes.

2.1.1 Batch HTP Testing with Simulant

Batch testing can give preliminary information on the likelihood of successful organic destruction at a set of conditions (temperature, pressure, and residence time) at about 25% the cost of a continuous run. Results from batch testing with a 3X EDTA simulant indicate that little organic destruction occurs at temperatures below 250°C at residence times less than 5 hr. Batch testing results also showed that the extent of organic destruction is relatively insensitive to pressure; that is, at a constant temperature and residence time, organic destruction was relatively constant for runs conducted at 2000 psi and at 4000 psi.

2.1.2 Batch HTP Testing with Tank Waste

No mechanism has been established to independently supply IPM with large quantities of actual tank waste for testing. Therefore, small samples from waste characterization will be used to confirm results from testing waste simulants.

2.1.3 Batch WAO Testing with Simulant

Preliminary results indicate that WAO can be used to achieve the required level of organic destruction at conditions significantly less severe than HTP. Based on the results of batch testing, it appears that a WAO system operating at 300°C and a 60-min residence time could potentially meet the needs of IPM. A number of systems deployed in industry with concentrated brines are operating at these conditions.

2.1.4 Continuous Bench-Scale HTP Testing with Simulant

Continuous bench-scale testing has been conducted to specifically obtain data on the efficiency and kinetics of the HTP process. With low-temperature HTP, nitrite and organic carbon are being destroyed to an appreciable extent, whereas nitrate appears to be fairly unreactive. On the average, 0.78 mole of nitrite is consumed for each mole of EDTA destroyed.

A kinetic model has been developed through the analysis of the results of the bench-scale work. For the model, which is first order with respect to EDTA and nitrite, an activation energy of 24.7 Kcal/mole EDTA carbon was determined. Evaluation of the analytical results from the bench-scale testing indicated that very good closure was achieved for carbon and nitrogen material balances. In both cases, material balance closures were between 97% and 103%.

Based on more than 200 hr of testing, it appears that in the temperature range 350°C to 375°C, approximately 2 to 4 L of noncondensible offgas are produced per liter of feed (3X diluted with EDTA). For a 20-gpm HTP system, this would amount to a noncondensible offgas generation rate of less than 11 scfm.

The composition of the offgas from low-temperature HTP processing of 101-SY simulant containing EDTA was 30% to 55% N_2O, 30% to 50% H_2, 10% to 20% N_2. Ammonia was also produced, with more than 99% of it remaining in the liquid product. Typical ammonia concentrations measured in the liquid product were about 1000 to 2000 ppm. The offgas compositions were similar for 101-SY simulant containing formate and acetate as the source of organic; however, the concentration of ammonia in the liquid product when processing acetate ranged from 100 to 300 ppm. No ammonia was detected when processing formate.

2.1.5 Pilot-Scale HTP Testing with Simulant

Low-temperature HTP has successfully been demonstrated on a pilot-scale system (10 to 15 L/hr) at 330°C. Because the pilot-scale system was designed for another project, typical HTP operating temperatures (350°C to 375°C) could not be achieved.

The EDTA destruction obtained in the pilot-scale system, with respect to temperature and residence time, was consistent with the kinetic model developed from the bench-scale testing. This result would indicate that the kinetic model is valid for a least a tenfold scaleup.

A plug that formed in one of the pilot-scale system reactors was successfully removed by switching to a water feed and lowering the reactor temperature. Apparently this change allowed the solids, presumably sodium carbonate, to go back into solution.

2.1.6 Operability and Materials

Under certain operating conditions, the solubility limit of sodium carbonate will be exceeded. In turn, the sodium carbonate will precipitate onto the reactor walls and accumulate to the extent that the reactor will become partially or completely plugged. Accumulation of sodium carbonate and other materials in the reactor may be exacerbated by the very low fluid velocities through the reactor. Most of PNL's runs are conducted at a pressure of approximately 3000 psig. Staff at LANL, who are developing a similar HTP process that operates at higher temperature and pressures, believe that sodium carbonate can be kept in solution by operating HTP systems at pressures between 10,000 and 15,000 psig. PNL found that increasing the hydroxide concentration in a 3X diluted simulant to 1 molar through the addition of potassium hydroxide (KOH) has been effective in minimizing/eliminating reactor plugging.

No visible signs of corrosion were observed in the 1-L 304 stainless steel reactor after 84 cycles, including more than 200 hr of HTP testing. Results from an internal fluorescent penetrant examination indicated no evidence of flaws, cracks, pitting, porosity, or general corrosion.

2.2 Recommendations

The recommendations below are based on the testing results and activities.

2.2.1 Batch HTP Testing with Simulant

Batch testing with simulant should be conducted under identical conditions to batch testing conducted with the actual waste to establish the simulant as a valid representation of the actual waste and its processing characteristics.

Results from FY 1993 have shown that batch testing is useful for evaluating relative reaction rates of the destruction of various organic species. It is recommended that this testing be expanded to evaluate inorganic compositions with other organics such as oxalate, citrate, tributyl phosphate, and N-paraffin hydrocarbon. There is considerable uncertainty regarding the speciation and relative concentrations of organic constituents in the actual tank waste, and new species are likely to be identified as a result of ongoing tank waste characterization efforts. Consequently, concomitant testing to evaluate and determine conditions at which HTP can effectively destroy these new species will be needed.

2.2.2 Batch HTP Testing with Tank Waste

Equipment procurement delays and staff availability limitations in FY 1993 prevented the completion of some of the planned batch HTP testing with tank waste. It is critical that this work be continued in FY 1994 to ensure that test results with simulants are applicable to actual tank waste. Comprehensive analysis should be performed on HTP treated and untreated tank waste to determine if solids are being produced. Additionally, the concentrations of transuranics, cesium, and strontium in the supernatant and the concentrations of these species associated with the solid phase should be determined.

2.2.3 Continuous Bench-Scale HTP Testing with Simulant

The design, fabrication, and installation of a new bench-scale test system should be pursued. The current system was designed to meet the needs of another ongoing project, and its availability is limited. A new system would be designed for operation at higher temperatures and pressures and to achieve higher velocities. More uniform heating would be provided through the use of heat transfer fluids as opposed to resistance heating.

During FY 1993, a kinetic model was developed based on the destruction of EDTA in 101-SY tank simulant. Additional testing should be conducted to develop similar kinetic models with other organics expected to be present in the tank waste.

Two activities initiated in FY 1993 that should be continued are 1) testing with high-velocity, high-pressure, small-diameter, coiled tubular reactors and 2) long-term testing with the existing continuous-stirred tank reactor (CSTR). Coiled tubular reactors provide an inexpensive approach to evaluating HTP at more severe conditions. Use of a CSTR is expected to minimize plugging, and would also provide a full-scale HTP system a greater margin of safety with respect to handling nonhomogeneous feed (i.e., a CSTR would effectively dilute a large spike of organics in the feed, thereby minimizing the probability of a runaway exothermic reaction).

2.2.4 Pilot-Scale HTP Testing with Simulant

PNL does not recommend conducting another HTP run in the existing pilot-scale system. Without a major reconfiguration of the system, the pilot plant cannot be operated at target HTP conditions. However, before constructing a new pilot plant, the identification of effective, low-maintenance equipment is needed for safe and reliable operation. Two particular components of the HTP system are critical to the long-term reliability of the process; these are the high-pressure slurry pump and the pressure letdown system. Candidate pumps and pressure letdown systems must be identified, procured, and evaluated through long-term testing.

In addition to performing testing on pumps and pressure letdown systems, an engineering evaluation should be conducted to examine equipment and designs for reactors, feed preheaters, and effluent cooldown devices. Factors that should be investigated include size, reliability, mean time between failures, safety, efficiency, availability, and cost.

2.2.5 Operability and Materials

Testing should be continued to identify fail-safe operating conditions at which plugging can be prevented while achieving adequate TOC conversion. Investigations should be directed at determining stable operating conditions at which recovery from process upsets will be possible. Testing should be done to determine the effects of feed dilution; base addition, temperature, pressure, and feed rate excursions; and the ability to stop and restart the system.

A pressure control device that operates reliably at pressures between 3000 and 6000 psig for a 0.5 to 2.5 L/hr stream has not been found. The search for new devices should continue, and new materials be examined for construction of the valve seats.

3.0 Batch HTP Testing with Simulants

3.1 Objectives

The primary objectives of the batch experiments are to develop and demonstrate the low-temperature HTP system through testing with a tank waste simulant and to develop and examine the analytical strategies and methods used to evaluate the process. Experience and results gained from the batch experiments are being used in the development and implementation of the continuous HTP testing. The batch testing has created an initial base of information from which temperature effects, pressure effects, solids formation, and other phenomena can be examined.

3.2 Test Approach

Batch testing was performed using a simulant representing Tank 241-SY-101 (SY1-SIM-93A) developed for organic destruction experimentation. (The simulant composition is given in Table 6.1 in Section 6.0). In addition, variants containing both formate and acetate instead of EDTA were used. Tests were performed at temperatures ranging from 150°C to 350°C and pressures ranging from 1000 to 4000 psig. The completed test matrix and TOC results are outlined in Table 3.1.

For each batch test, a weighed quantity of tank waste simulant, approximately 300 mL, was placed in the 1-L batch autoclave reactor, which was then purged and pressure tested at 1000 psig with an inert gas. Next the autoclave reactor was vented to approximately 100 psig and heated to the designated temperature. The heating cycle took from 40 to 100 min, depending on the target conditions. Approximately every 30 min, while the autoclave reactor was at the designated operating temperature, gas samples were taken and analyzed by gas chromatograph. At the conclusion of the run, liquid samples were taken, sent for analysis, and archived. In addition, at the conclusion of each run, the autoclave reactor was cooled by the introduction of water through the integral cooling coils. Upon cooling, the autoclave reactor was depressurized, and the liquid and gas contents were measured and analyzed. Profiles of cooling and heating periods were generated in later batch runs, which demonstrated that the cooldown time to inert temperatures (150°C to 200°C) was relatively fast. The relatively steep profile added confidence to the reported process times for most batch runs. Figure 3.1 illustrates a temperature profile from a typical batch run (Run 17).

3.3 Equipment

A 1-L batch autoclave reactor, manufactured by Autoclave Engineers, was used for the experiments (Figure 3.2). The autoclave reactor consists of standard heating, cooling, and stirring apparatus but also is equipped with a stainless steel liner used to contain the simulant and facilitate cleanup between runs. The system is equipped with both liquid and gas sampling ports that can be operated remotely during tests, and the entire autoclave reactor is situated behind a 1/4-in. steel

Table 3.1. Batch Experiment Results

Run No.	Simulant	Op. Temp (°C)	Time at hold (min)	Op. Pressure psi	TOC Dest. (%)
Run 1	EDTA	150	305	160	--
Run 2	EDTA	250	310	650	--
Run 3	EDTA	350	125	2200	96.3
Run 4	EDTA	150	335	2020	0.9
Run 5	EDTA	150	330	4290	0.4
Run 6	EDTA	350	170	2170	98.2
Run 7(a)	EDTA	350	170	4070	98.6
Run 10(a)	Acetate	350	60	2200	18
Run 12(b)	EDTA	250	360	3660	--
Run 13	Acetate	300	60	3120	0
Run 14	Acetate	350	60	3120	--
Run 15	Acetate	350	60	2850	15
Run 16	Formate	350	60	3340	98
Run 17	EDTA	350	60	3280	94
Run 18	EDTA	350	60	2940	95
Run 19	EDTA	350	15	3320	78
Run 20	Acetate	400	60	4720	99.7

(a) Missing run numbers result from subsequent reevaluations of the test plan. Run numbers 8, 9, and 11 were specified in the test plan, but were not executed.

(b) Test performed with nickel catalyst.

barricade with all controls and monitoring devices located outside of the barricade. Further information on the setup and operation can be found in the Standard Operating Procedures (SOP) for the batch autoclave reactor (SOP-CPDL-1-90-1-Rev2).

3.4 Results and Discussion

Batch testing has produced data on operable temperature ranges; pressure effects; catalyst effects; solids formation; batch temperature effects (on EDTA); batch residence time effects (on acetate); and relative amounts of destruction among acetate, EDTA, and formate. The TOC destruction results for all batch experiments were shown in Table 3.1.

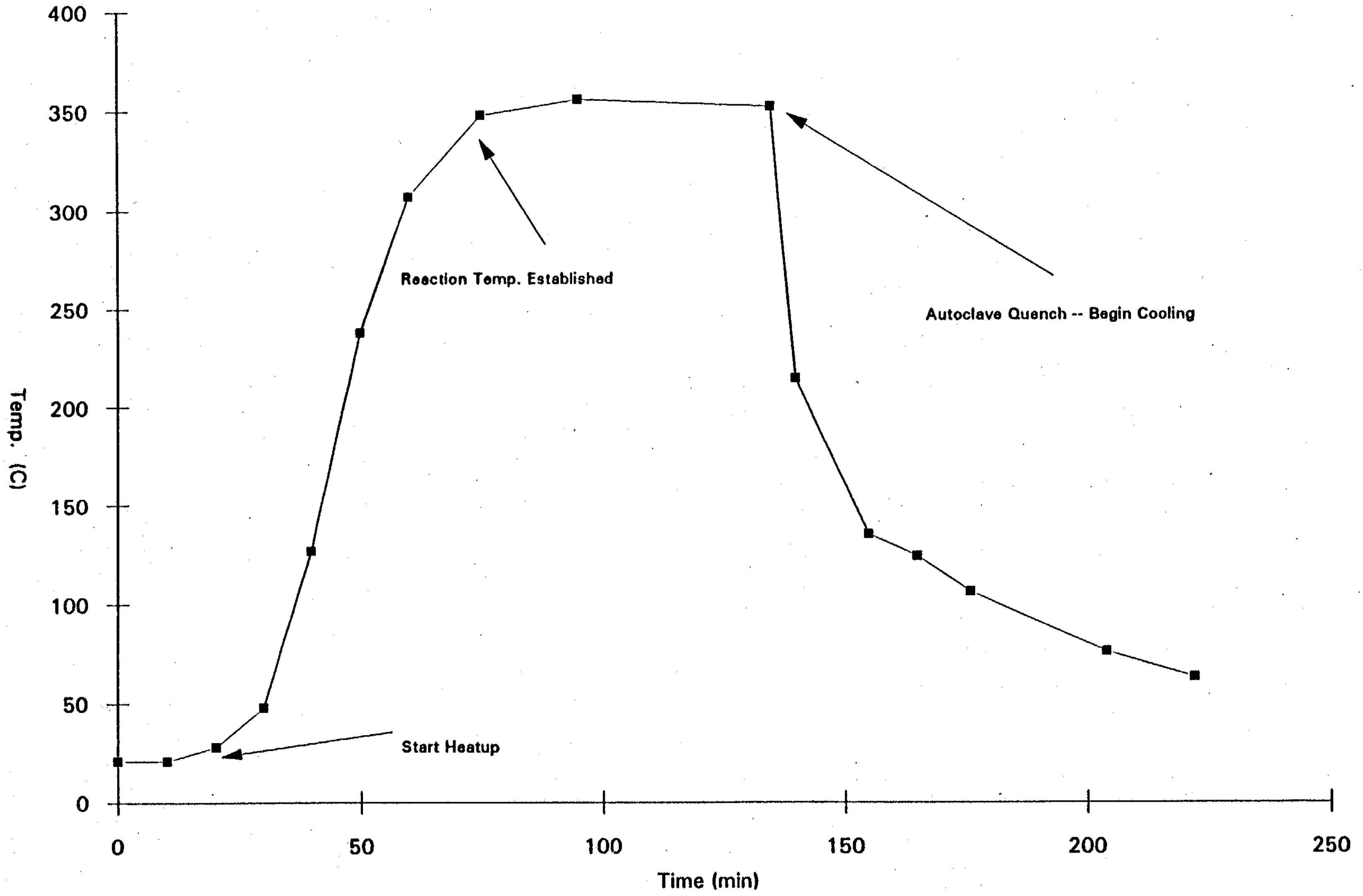

Figure 3.1: Temperature Profile for Batch Autoclave Run 17

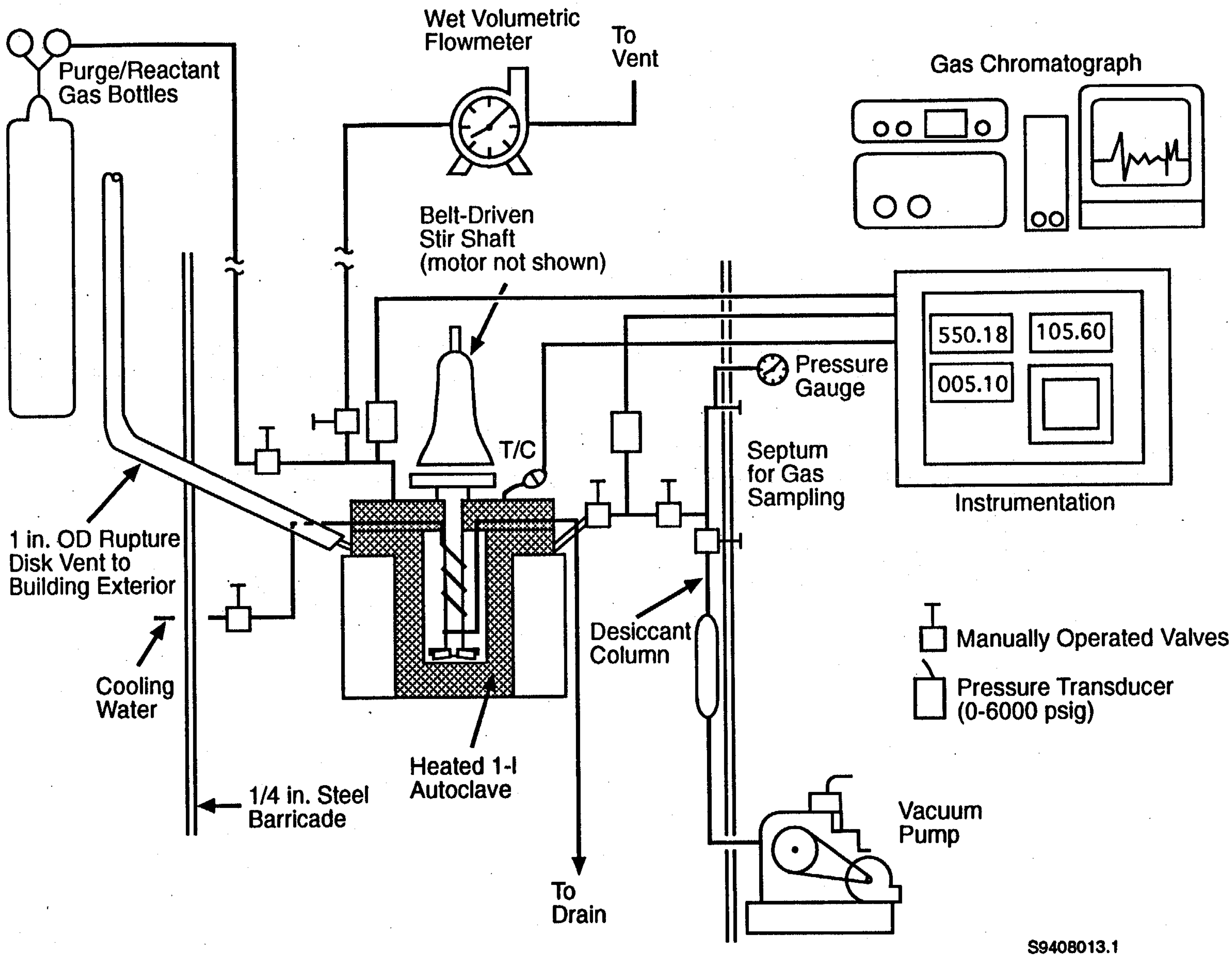

Figure 3.2. Schematic Diagram of the Batch Autoclave Reactor System

Range finding experiments (1 through 3) indicated that organic destruction progressed at unacceptably slow rates at 150°C and 250°C. However, at 350°C, TOC was reduced more than 98%. This information provided the necessary indications to pursue organic destructions in the 300°C to 400°C range and affected the target temperature for further batch and continuous work.

A set of four runs (4 through 7) was performed to determine pressure effects on organic destruction. Runs 4 and 5 at 150°C, which were performed at 2000 psi and 4300 psi, respectively, indicated minimal TOC reduction (less than 1%) at both pressures, with no noticeable difference in pressure effects. In addition, Runs 6 and 7 at 350°C, which were performed at 2200 psi and 4000 psi, respectively, yielded excellent TOC reduction (greater than 98%) yet minimal difference in pressure effects. However, both sets of experiments were performed at the outermost fringes of the %TOC reduction scale. Pressure effect behavior may have been unnoticeable because the ranges measured were so close to the beginning and end points. However, later pressure effect testing with the continuous bench-scale system corroborated the observations made with the batch system and, indeed, there was little effect on TOC reduction by pressure (see Section 5). Thus, it was concluded that the operational pressures for further operations, both batch and otherwise, should be selected by other criteria than the concern for effects of pressure on destruction efficiency.

A cursory test (Run 12) was conducted to investigate catalyst effectiveness in the HTP scenario. The catalyst, while providing slightly better organic destruction at 250°C (estimated through relative ammonia product formation), degraded severely within the autoclave reactor. The catalyst may have been preferentially oxidized over the organics by the nitrate/nitrite in the autoclave reactor or affected by unusually high pH of the simulant. Further catalyst testing was discontinued, as the catalyst was not considered integral to achieving organic destruction goals with HTP.

It should be noted that Runs 1 through 7 and Run 12 were performed while the TOC analytical methods for these samples were first being developed and refined. Thus, some of the early data are suspect and, in some cases, unavailable. Samples from Runs 3 through 5 were reanalyzed using a later generation TOC procedure; other indicators, such as gas product production, COD, and ion concentrations were also used to supplement qualitative assessments.

Special analysis of some of the early experiments was performed to determine the nature of solids formation in this system. Solids were sampled from the crystals formed on the inside of the autoclave reactor following Runs 6 and 7 and analyzed by X-ray diffraction (XRD). The semi-quantitative results are shown in Table 3.2. While some of the compounds are only tentatively identified, it is clear that the major solids of interest formed are $NaNO_3$ and $NaCO_3 \cdot H_2O$. Sodium carbonate precipitation, if due to extensive carbonate production, is in clear agreement with proposed reactions suggested earlier. Thus, maximizing the solubility of carbonate within the reaction mixture may be of critical importance and, hence, may be the criterion with which to select the operating pressures. It must be noted, however, that XRD can only analyze solids in crystalline form. Amorphous solids, such as $Al_2(OH)_3$, cannot be identified by this test.

A sequence of experiments was performed at 350°C using EDTA as the primary organic constituent. The batch tests were made over a series of process times varying from 15 min to 3 hr. In Figure 3.3, %TOC reduction is plotted versus process time. The overlaid curve follows a first-order reaction in a batch experiment; however, the plot does not seem to follow precisely. Most likely, the

Table 3.2. X-ray Diffraction Results

	Run #	
Compound	503-6	503-7
$NaNO_3$	15	65
$NaCO_3 \cdot H_2O$	55	30
$Na_2S_2O_3$	5	-
$Ca_2Al_3CrO_{10} \cdot 12H_2O$	15[a]	-
$NaAl_3(SO_4)_2(OH)_6$	10	-
$Al(OH)_3$	-	<5
$Ca_5(CrO_4)_3O_{0.5}$	-	<5[a]
$Na_6CO_3(SO_4)_2$	-	<5[a]

(a) Indicates best available identification.

EDTA oxidation reaction may be complemented by a slow zeroth order reaction that takes an intermediate carbon species to complete oxidation as carbonate. However, the mechanism is as yet unknown. This analysis demonstrates the difficulty in kinetically interpreting data from a batch system with unknown or partially understood characteristics. Uncertainty in knowing the extent to which the reaction progresses during heatup and cooldown periods complicates the interpretation and comparison of the data. This is consistent with a previous finding that the batch autoclave reactor system is useful for evaluating relative reaction rates but is of limited use in determining absolute reaction rates. As a result, detailed kinetic evaluations were made based on results from continuous bench-scale testing (see Section 6.0).

The destruction efficiencies of the three organic species (EDTA, formate, and acetate) were compared to examine susceptibility to HTP. Three experiments were performed at 350°C with a process time of 1 hr using each of the three simulants. The analysis showed the average % TOC reductions for the simulants to be 98% for formate, 94.5% for EDTA, and 16.5% for acetate. Additional testing was performed to evaluate the rates of destruction for acetate at different temperatures. A residence time of 1 hr and temperatures ranging from 300°C to 400°C were used. Results plotted in Figure 3.4 show that, essentially, no acetate is destroyed below 300°C in a 1-hr batch process time, and it decomposed completely after 1 hr at 400°C. These results highlight the importance of tight process control, as the window for efficient destruction of acetate is narrow. While it is accepted that the critical point of the 3:1 simulant dilution (with water) can be as high as 500°C, the steep destruction curve is possibly due in part to critical water effects. The predicted curve shown in Figure 3.4 may be more accurately depicted by two separate effect curves joined around the critical transition temperature of water. However, the mechanistic chemistry must be more clearly understood.

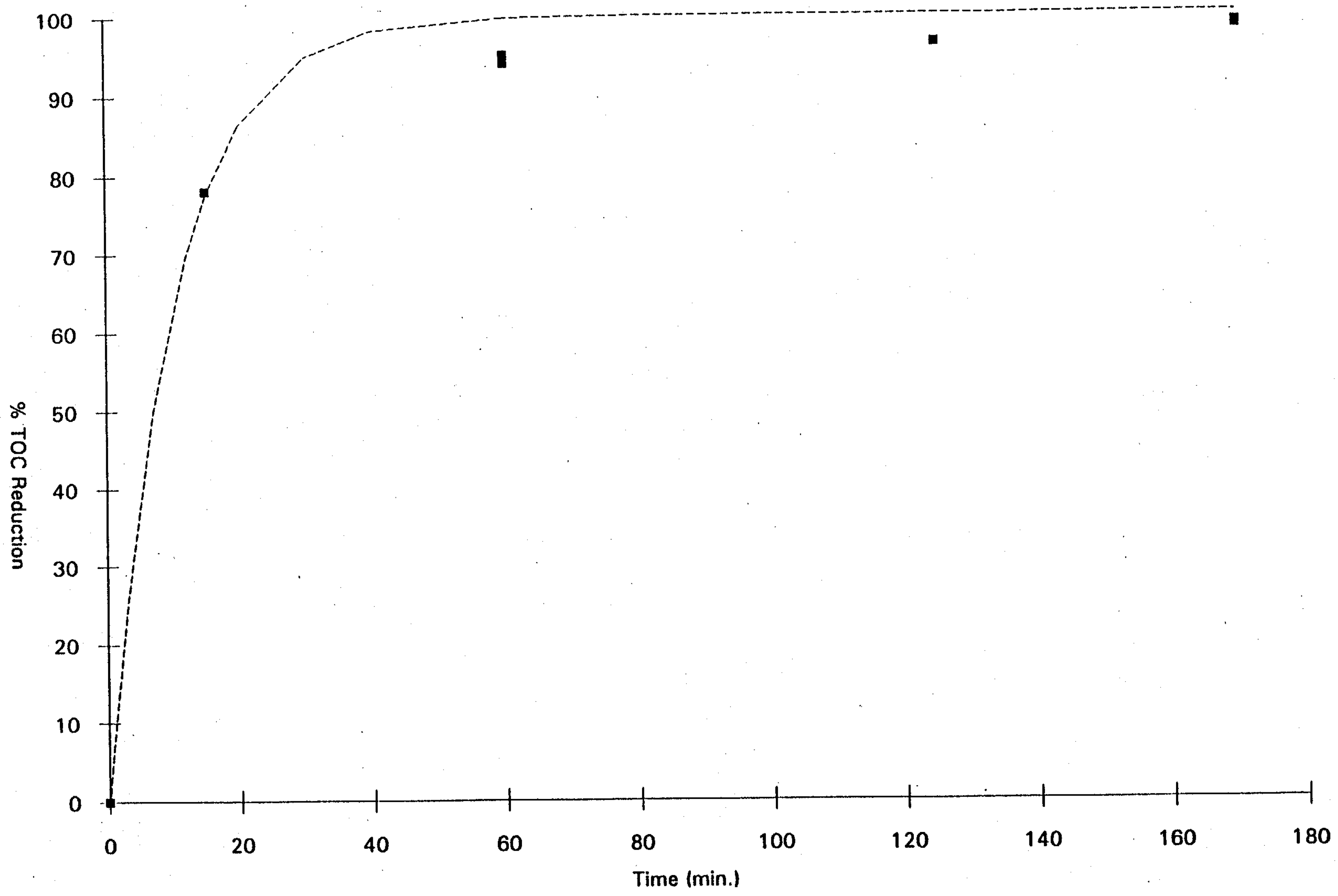

Figure 3.3. TOC Reduction vs. Time for EDTA-based Simulant at 350°C

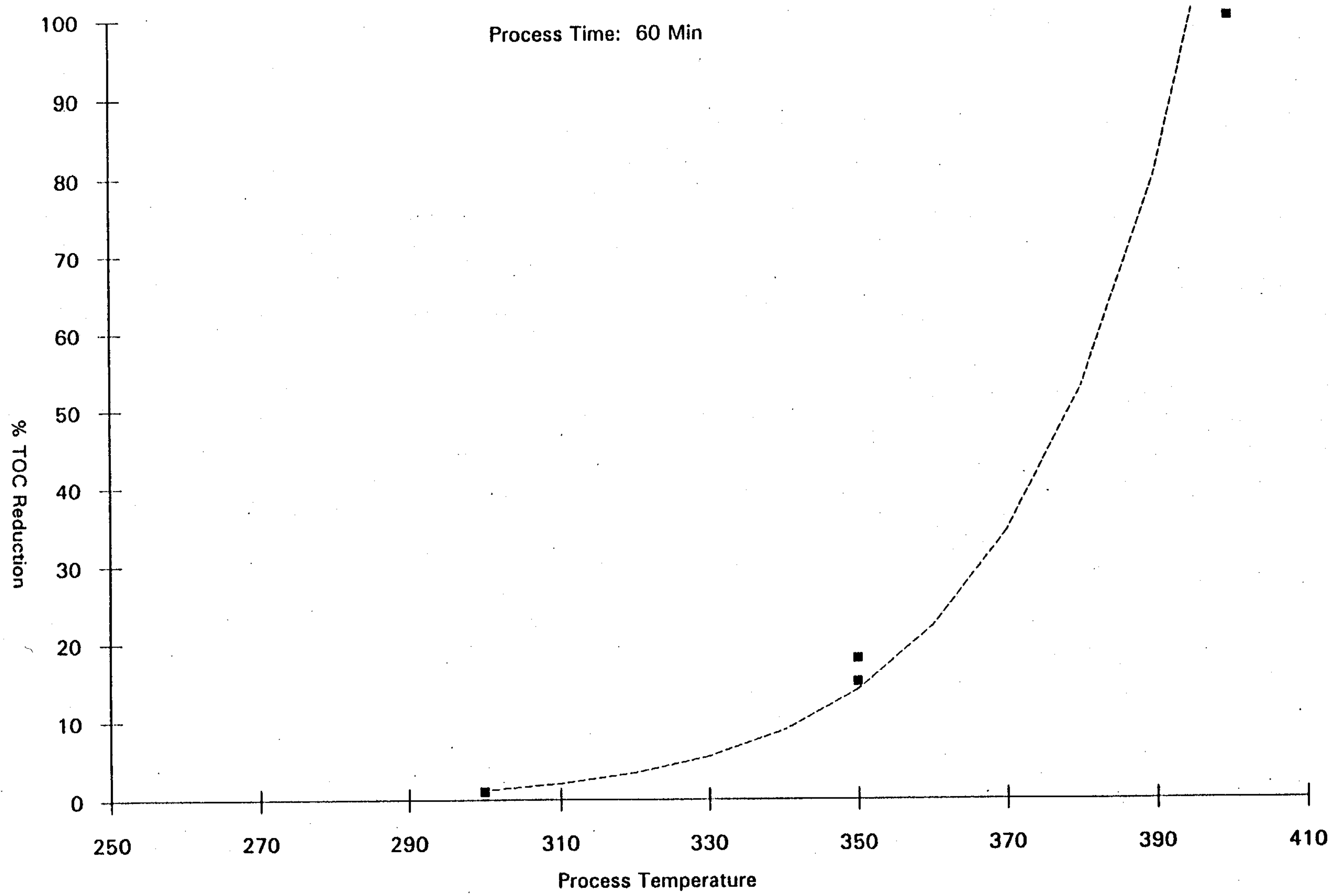

Figure 3.4. TOC Reduction vs. Temperature for Acetate-based Simulant at 60-Min Residence Time

3.5 Directions of Future Testing

Plans for future testing include using the batch autoclave reactor to fully simulate and characterize the conditions and results of batch testing with actual tank waste. The primary goal of this testing would be to identify and possibly reconcile any discrepancies between the simulant batch tests and the batch tests with actual waste. This information would indicate the validity of the using the simulant in the continuous and pilot-scale tests. Substantiating the simulant as representative of the actual waste and its processing characteristics would greatly benefit the interpretation of the data generated from other bench-scale tests.

Batch testing has been shown to be useful for evaluating relative reaction rates of the destruction of various organic species. It is planned to expand this testing to evaluate other organics such as citrate, tributyl phosphate, and N-paraffin hydrocarbon. There is considerable uncertainty regarding the speciation and relative concentrations of organic constituents in the actual tank waste, and new species are likely to be identified as a result of ongoing tank waste characterization efforts. Consequently, there will be an ongoing need to perform testing to evaluate and determine conditions at which HTP can effectively destroy these newly identified species.

Additionally, batch testing will most likely be used to verify and expand the WAO results generated by Zimpro Environmental, Inc. (Zimpro) (see Section 4.0). Tests involving WAO may provide a means to achieve target organic destruction levels at lower temperatures and pressures than those required for the auto-oxidation process presently being tested.

4.0 Wet Air Oxidation Testing with Simulants

4.1 Objective

Under a subcontract, Zimpro Environmental, Inc., evaluated WAO for its potential to decompose organics and ferrocyanides in tank waste. WAO is a thermal-chemical process in which air or oxygen is added to waste material in a heated, pressurized reactor to oxidize species such as organic and ferrocyanide constituents. The technology is commercially available for aqueous waste treatment applications and has been used for 30 years to destroy a wide variety of organics. Zimpro has constructed more than 200 commercial systems, including 20-gpm units similar to the HTP units being considered for the IPM.

Zimpro performed a series of batch wet oxidation tests to evaluate the process chemistry and determine operating conditions for optimum destruction, and also performed a preliminary evaluation of materials of construction. Preliminary results from this testing are reported here. A detailed report will be issued by Zimpro during the first quarter of FY 1994.

4.2 Test Approach

During FY 1993, 37 batch tests (18 tests in duplicate plus one additional test) were conducted in 500-mL and 750-mL autoclave reactors with five simulant compositions (variations of SY1-SIM-93A). Each simulant composition was evaluated at three operating temperatures between 250°C and 325°C. Most of this testing involved the addition of air to the autoclave reactors; however, one set of tests was performed without air addition to compare against PNL's autogenous HTP test results.

For the batch WAO tests, measured quantities of simulant were placed in autoclave reactors at ambient temperatures. Next, the autoclave reactors were sealed and charged to predetermined pressures with air or an inert gas. After charging, the autoclave reactors were placed in a heat-jacketed rocker assembly, which was heated to the desired test temperature and controlled at that temperature for a period of 1 hr. At the end of the holding period, the autoclave reactors were cooled and depressurized. The volume of the generated noncondensible offgas was measured and recorded. Concentrations of the following species in the offgas were determined: O_2, N_2, H_2, CO, CO_2, N_2O, NO_x, and CH_4. The liquid feed and treated simulant were analyzed for chemical oxygen demand (COD), TOC, metals, total suspended solids (TSS), total solids (TS), pH, NH_3, NO_2, and NO_3.

In conjunction with the batch testing, Zimpro conducted materials evaluation/corrosion studies at the conditions expected in a WAO system. For this testing, Zimpro evaluated commercially available coupons fabricated from a varity of corrosion-resistant materials. Before exposure, the coupons were cleaned, weighed, and examined for manufacturing defects. The coupons were exposed to the five variants of simulant material. During the corrosion testing, the test vessel was charged with fresh simulant every 24 hr. An excess of oxygen was maintained in the cover gas at all times. After exposure, the coupons were reweighed and examined visually and microscopically for evidence of corrosion.

4.3 Results and Discussion

For this task the goal was to reduce the TOC to less than 1556 ppm when the simulant is concentrated/diluted to 5 M sodium. Test results showed that this reduction could be achieved at 300°C for the simulant containing EDTA and formate. At 260°C, the ferrocyanide-containing simulant was treated to the extent that the ferrocyanide was below detection.

The preliminary corrosion evaluation indicated that 316L, 304L, or Inconel 600 would be acceptable materials of construction. However, long-term materials of construction evaluations are recommended prior to the construction of a full-scale system.

4.4 Directions of Future Testing

Based on the outcome of Zimpro's batch testing and IPM's programmatic needs, PNL and Zimpro have the option of exercising the second phase of the subcontract, pilot-scale testing. If initiated, Zimpro will perform 200 hr of continuous processing at a feed rate in the range of 2 to 6 L/min (0.5 to 1.5 gpm) in accordance with an approved test plan. Two simulant compositions will be tested with the pilot-scale system. The objectives of the pilot-scale testing are to demonstrate the feasibility of processing simulant tank waste on a large scale; to support considerations on design of a large-scale treatment process; to obtain kinetic data; to obtain sufficient processing data to develop a heat and material balance; and to obtain a measure of plant corrosion behavior.

5.0 Batch HTP Testing with Actual Tank Waste Samples

5.1 Objectives

The objective of this testing is to investigate the organic destruction capability of HTP on samples of actual organic-bearing tank waste. Incomplete characterization of organic species in the tank wastes may lead to differences in simulant formulations compared with actual tank waste speciations. These differences may then produce different reactions during HTP tests. The tests using actual organic tank waste and specified processing conditions will be compared with results of simulant tests.

The autoclave reactor systems have been procured and delivered. One system is being installed in a glovebox; the other will be used for comparison batch testing identified in the FY 1994 work plan. Operability testing was successfully completed for the system being moved to the glovebox. Some minor problems identified on the "nonradioactive" system (bad pressure gauge, faulty tachometer pickup, etc.) have been corrected. The next step will be to complete installation of the radioactive system in the glovebox. Once installation and leak checking are completed, the first "run" with the system is planned to be done with a simulated waste (same as used in earlier batch and continuous simulant tests) to help establish a baseline for later comparisons, and as a safety considerations before testing with the radioactive tank waste (FY 1994).

5.2 Test Approach

Batch autoclave reactor tests will be conducted initially using samples of a 101-SY core sample. Testing will be performed in a glovebox. Batch tests will be conducted at temperatures ranging from ~150°C to 400°C in a commercially available stirred batch autoclave reactor with an inert gas overpressure. Samples of the waste will be analyzed before and after the tests to determine organic destruction.

A series of four batch autoclave batch reactor tests will be performed and compared with similar nonradioactive simulant tests. For each test, approximately 30 mL of dilute (3:1) 101-SY waste will be placed into the autoclave reactor at ambient conditions. The autoclave reactor will then be sealed and purged with an inert gas, such as nitrogen or argon, to sweep out air and then pressurized to ~1000 psig to test for leaks. After leak testing, the autoclave reactor will be vented to ~500 psig or less overpressure. The autoclave reactor will be heated to the desired test temperature and held at that temperature for the selected duration of each test. It is expected that the pressure in the autoclave reactor will range from ~1000 to 4000 psig, depending on the initial inert gas overpressure, operating temperature, and gas generation from organic destruction. It is also expected that the runs will be terminated after 1 to 5 hr at the operating temperature.

At the end of each run, the autoclave reactor will be cooled to ambient temperature and disassembled. The remaining waste contents will be sampled and analyzed. Organic destruction will be measured by comparing before and after results of TOC analyses of the waste samples. Other analyses or analytical techniques for better determining organic destruction may be identified and recommended by the ongoing simulant testing efforts. Other potential analyses include OH, NH_3, NO_2, and NO_3.

5.3 Test Apparatus/Facility Description

The glovebox to be used for testing is a typical design for radioactive work. The reactor system (Microclave, 50-mL batch stirred autoclave from Autoclave Engineers, Inc.) and associated equipment are presently being set up.

Stirring will be accomplished with an internal agitator magnetically coupled to a drive motor. Wetted parts of the autoclave reactor are fabricated from Hastelloy C-276, a suitably corrosion-resistant alloy compatible with the waste type. The autoclave reactor is surrounded by an electrical heater capable of sustaining it at the desired temperature for the duration of the test. The heater is controlled by a thermocouple inserted along the outer wall of the autoclave reactor, and fluid temperature is monitored by a thermocouple in a thermowell submerged in the fluid. Autoclave reactor pressure is read from a pressure gauge mounted on the autoclave reactor frame inside the glovebox.

5.4 Test Documentation

The following documents have been required in preparation for the radioactive batch tests.

- Test Plan - Written and approved by program management, line management, building management, and lab safety. Prior to lab safety approval an "unresolved safety question" (USQ) was raised regarding the performance of this type of work in a glovebox. Analysis of the concern showed that a USQ by definition did not exist. Following lab safety review and approval of the USQ determination, the test plan was approved.

- Radiation Control Protocol - Prepared and submitted to radiation protection organization. The protocol provides specific information on the radiological hazards associated with the radioactive materials and the manner in which they are to be handled. From the information in the protocol and the test plan, the radiation protection organization prepares the Radiation Work Procedure (RWP) for this activity. An approved RWP has been prepared and posted for this work.

A significant concern would exist if the effluent material from the HTP testing were to be considered a waste. No disposal pathway exists for these materials, yet once the tests are completed a 90-day satellite accumulation limit supposedly begins. However, there is sufficient interest in saving the materials for other types of follow-on testing that the waste disposal is not an issue for now. The implications of this waste disposal issue must be kept in mind and considered for future testing, especially for possible larger-scale testing.

5.5 Work Completed

A sample of the 101-SY waste material was submitted to the analytical labs for TOC analysis using the "hot persulfate" method. Along with this sample, several other simulant samples (one simulant feed and several HTP product samples) were also submitted for TOC analyses. This direct comparison of simulant and actual waste using the same analytical method, equipment, and operator were expected to provide more complete information regarding comparison of simulant and actual waste analyses. The analyses were completed, and for each of the simulant samples the TOC analyses were lower than previous analyses of the same samples performed by another lab using a Dohrmann Carbon Analyzer that relies on either sodium or potassium persulfate and UV at ambient temperatures to oxidize the organic carbon. The results of these analyses are shown in Table 5.1. The reasons for the difference between labs using the same method are not yet understood but are being investigated.

Table 5.1. Total Organic Carbon Analyses of 101-SY Tank Waste and Waste Simulant Feed and Products Performed by Two Separate Analytical Laboratories

Sample ID	TOC Analyses Hot Persulfate Method (μg/g)[a]	TOC Analyses Dohrmann Persulfate/ UV Method/(μg/g)
101-SY Composite	14200[b]	not analyzed
Simulant Feed	3490	4811
Simulant Prod 1[c]	1500	1770
Simulant Prod 2[c]	1320	1838
Simulant Prod 3[c]	1240	2530[d]

(a) Based on the average of duplicate aliquots.

(b) TOC is much higher for actual waste sample than simulant feed because simulant feed was prepared to simulate a "3:1 dilution." For HTP testing, the actual waste will be appropriately diluted to similar concentrations.

(c) Intermediate product samples taken from the reactor at progressively longer retention times.

(d) Suspect analysis. Other samples of series around this sample have lower TOC values (about 1700 μg/g).

5.6 Directions of Future Work

Continuing and future efforts will be to complete installation of the batch autoclave reactor system in the glovebox, and conduct tests with simulated 101-SY and the available sample of 101-SY waste. Testing with other organic-bearing tank wastes is also being considered, and will depend on availability of the materials. Interest in additional analytical work (such as speciation of Al, Cs, Sr, TRU, etc.) is increasing and may be performed on feed and product samples from these tests.

6.0 Bench-Scale HTP Testing with Simulant Tank Waste

6.1 Objective

The objective of the bench-scale continuous testing is to develop and demonstrate a low-temperature HTP system for destruction of organic constituents in the tank waste. Batch autoclave reactor testing with simulants (Section 3.0) has been conducted to investigate the effects of temperature on destruction efficiencies and phase behavior. The results from the batch testing have been used to assist in the selection of operating conditions for the bench-scale continuous testing.

The bench-scale continuous testing has been conducted specifically to obtain data on the efficiency and kinetics of the HTP process for the destruction of organics in tank waste simulants. The information obtained from this testing is being used to support the selection of the most feasible organic destruction method for treatment of tank waste within the IPM concept.

6.2 Test Approach

Continuous bench-scale tests have been conducted with 101-SY simulant in a 1-L tubular reactor. To date, a total of 29 tests, most lasting approximately 6 to 8 hr, have been conducted. The operating ranges covered were approximately 0.5 to 2 L/hr (residence times 2 to 20 min); 300°C to 380°C temperature range; and approximately 2000 to 4500 psig.

During the testing, liquid and gas samples were collected at specific time intervals to monitor the composition of reaction products and to determine the organic destruction efficiency. Factors that have been evaluated during the continuous bench-scale testing include reaction kinetics for various operating conditions, pumping and fluid flow characteristics in the tubular reactor, salt formation, corrosion, gas/sludge separation, and heat and material requirements. From previous experience, it has been determined that the bench-scale tubular reactor system approached ideal plug flow in most cases and, therefore, could be used to determine reaction kinetics for larger reactor systems.

6.3 Equipment

The PNL continuous reactor system (CRS) used for the tests includes a 1-L 304 stainless steel tubular reactor, a feeding system, a product recovery system, and a data acquisition and control system (Figure 6.1). The dimensions of the 1-L reactor are 1 in. ID, 2 in. OD, and 72 in. length. In this configuration, the reactor is capable of operation at pressures up to 6000 psig and temperatures up to 450°C. Heat is supplied to the tubular reactor with a 6 kW, clamshell-style, three-zone furnace. The heating rate in each zone can be independently controlled. Feed is injected into the reactor with a high-pressure Milton Roy pump capable of pumping 0.5 to 3 L/hr at pressures from 1000 to 4500 psig.

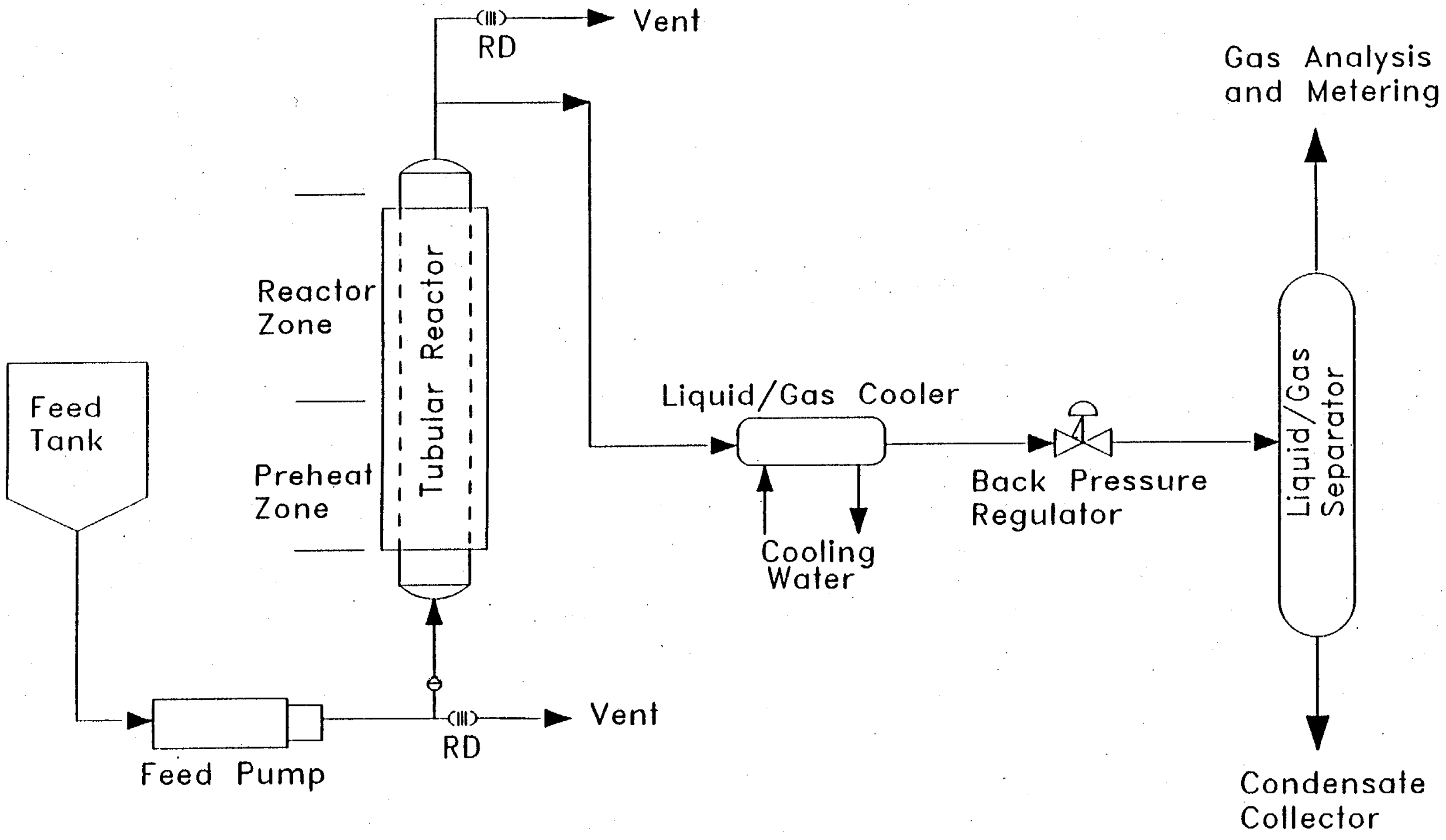

Figure 6.1. Schematic Diagram of the Bench-Scale Continuous Reactor System

The residence time of the feed in the reactor can be controlled by varying the pump feed rate as well as by adjusting the effective reaction volume of the tubular reactor. The effective volume can be decreased with the addition of inert stainless steel packing or by shutting down one or two of the heating zones on the lower portion of the reactor. In runs conducted without packing, it was more difficult to estimate the actual average temperature of the solution because there were wider variations in the reactor wall and internal temperatures than in the packed reactor case. This is due in part to the very low velocities in the unpacked reactor. Thus, the majority of the runs were conducted with packing in the reactor. With the turndown range of the pump, the option of using or not using inert packing, and by manipulation of the heating zones, the reactor can be operated at residence times between 2 and 20 min.

The reactor and the majority of the ancillary equipment under pressure are contained inside a 0.25-in. steel barricade. Temperature, pressure, feed rate indicators, controllers, and alarms are located outside the barricade.

All but one of the tests have been conducted in the tubular reactor system (i.e., plug-flow conditions). In the other test, a continuous-stirred tank reactor (CSTR) with a working volume of approximately 0.9 L was used.

6.4 Results and Discussion

The following sections discuss the degree of organic destruction using the bench-scale reactor system described above. The experimental results to date will be presented, followed by a discussion of proposed chemical reactions and a kinetic analysis of the data. Preliminary results of these runs were summarized previously (Schmidt et al. 1993). The results presented here may vary slightly from the preliminary values because temperatures and residence times have been more rigorously calculated, and more precise selection of steady-state operations for obtaining data were used in the present case. In addition, since the time of the previous report, additional tests have been conducted and more analyses have been obtained.

6.4.1 Experimental Results

Based on the results of the batch testing, continuous testing has been conducted at temperatures between approximately 300°C and 380°C, and primarily at 3000 psig. The majority of the testing has been conducted in a plug-flow reactor system, using the 72-in.-long, 1-in.-ID upflow tubular reactor that was described above. One of the plug-flow tests was conducted in a 0.2-in.-ID coiled tubing reactor. The total tubing length of this reactor is 60 ft. Thus, compared with the 72-in.-long, 1-in.-ID reactor, much higher linear velocities are achievable, and longer residence times can be achieved at similar linear velocities. However, in the run conducted, using the coiled reactor, large temperature gradients were observed (i.e., due to uneven heating of the coiled reactor). This limited the usefulness of the data from a kinetic development viewpoint. Additionally, one continuous test was conducted using a CSTR system.

During FY 1993, most of the tests were conducted using 101-SY simulant (which contains EDTA as the only organic source). The formulation of this simulant (SY1-SIM-93A), which is based on analyses of "Window E" core samples taken from Tank 101-SY during December 1991, is given in Table 6.1 (Hohl 1993). The EDTA that has been added to the simulant amounts to a TOC value of 1.53 wt%. In most of the tests, the 101-SY simulant has been diluted with 3 parts of water, on a volumetric basis, because water at this ratio is expected to be added to the waste to facilitate tank waste retrieval.

Table 6.1. 101-SY Simulant Formulation SY1-SIM-93A (Undiluted)

Component	Wt%
Na_4EDTA	4.83
Na_3P0_4 - 12 H_2O	2.56
$NaNO_2$	15.72
$NaNO_3$	13.02
Na_2CO_3	5.55
Na_2SO_4	0.59
NaCl	1.30
NaF	0.07
$Ca(NO_3)_2$ - $4H_2O$	0.14
KNO_3	0.84
$ZnCl_2$	$4.2x10^{-3}$
$CsNO_3$	$2.1x10^{-3}$
$Sr(NO_3)_2$	$1.2x10^{-4}$
NaOH	5.86
$Cr(NO_3)_3$ - $9H_2O$	3.15
$Fe(NO_3)_3$ - $9H_2O$	0.20
$Ni(NO_3)_3$ - $6H_2O$	0.07
$NaAlO_2$ - 0.21NaOH - $1.33H_2O$	13.70
H_2O	32.40
Total	~100.00

During each run, two, and sometimes three, different operating conditions were evaluated at steady state. Primarily, the effects of operating temperature, operating pressure, residence time in the reactor, and feed dilution have been investigated. Parameters affecting plugging in the reactor and the destruction of organics other than EDTA have also been investigated. The specific test conditions are summarized in Table 6.2. Unless mentioned otherwise, the test results discussed below pertain to runs in which EDTA was used as the organic carbon source.

Table 6.2. Continuous Test Run Summary[(a)]

Feed Dilution (water:101-SY simulant, v:v)	Operating Temperature (°C)	Operating Pressure (psig)	Calculated Residence Time at Temperature in Reactor (minutes)
Residence Time/Temperature Effects			
3:1	301	2950	3.7
3:1	301	2950	5.5
3:1	305	2950	7.0
3:1	302	2910	9.0
3:1	319	2870	10.8
3:1	320	2830	11.5
3:1	325	2940	3.8
3:1	326	2900	6.9
3:1[(b)]	333	2900	9.0
3:1	350	2950	3.3
3:1	351	2960	4.6
3:1	342	2970	5.2
3:1[(b)]	347	2910	7.8
3:1[(b)]	354	3170	8.3
3:1	353	2900	8.4
3:1	345	2990	9.8
3:1	368	2930	2.0
3:1	365	2960	3.0
3:1	363	2920	3.1
3:1	360	2900	6.1
3:1[(b)]	361	3260	7.7
3:1[(b)]	365	2910	8.6
3:1[(b)]	359	3000	19.5
3:1	372	3050	5.5
Pressure Effects			
3:1	305	1510	7.9
3:1	351	2490	6.1
3:1	351	2800	5.9
3:1[(c)]	353	4070	2.5
Dilution Effects			
4:1	300	2950	4.3
4:1	302	2890	10.9
4:1	350	2920	2.5
4:1	350	2890	5.3
4:1	365	2900	3.2

Table 6.2. (contd)

Feed Dilution (water:101-SY simulant, v:v)	Operating Temperature (°C)	Operating Pressure (psig)	Calculated Residence Time at Temperature in Reactor (minutes)
Dilution/Solids Effects			
6:1	378	2980	2.4
6:1[(d)]	368	3140	5.0
KOH Effects[(e)]			
3:1	377	2970	2.4
3:1	380	2950	3.0
3:1[(f)]	362-375	3050	3.0-2.4
Continuous Stirred Tank Reactor			
3:1	376	2950	13.0
3:1	381	2980	26.5
Acetate as Carbon Source			
3:1	326	3010	3.3
3:1	323	2940	8.1
3:1	357	2940	3.9
3:1	380	2950	3.2
3:1	379	2950	4.2
Formate as Carbon Source			
3:1	362	3060	2.9
3:1[(g)]	360	3160	3.5

(a) EDTA as organic carbon source, packed 1-in.-I.D. reactor used except where indicated otherwise.

(b) Unpacked 1-in.-I.D. reactor used.

(c) Coiled 0.15-in.-I.D. reactor used.

(d) Supernatant only.

(e) KOH added to feed, making net [OH$^-$] = 1.2M.

(f) Test conducted with and without KOH added to feed for increasing temperatures.

(g) KOH added to feed, making net [OH$^-$] = 1.6M.

6.4.1.1 Effects of Operation Pressure

As in the batch runs, operating pressure had little or no effect on total organic destruction. The results are summarized in Table 6.3. In this table, the destruction of EDTA carbon and the TOC are given. In hydrothermal processing, the EDTA can break down into intermediate organic compounds as it decomposes to carbonate (i.e., see Reactions 1 and 2 in Section 6.4.2). In the analysis, TOC (i.e., EDTA + other organics) is measured, and oxalate carbon only is measured. Thus, if it assumed that EDTA and oxalate are the only, or at least major, organic carbon sources present, the amount of EDTA that is destroyed can be calculated.

Table 6.3. Pressure Effects on Organic Destruction[(a)]

Feed Dilution (water: 101-SY simulant, v:v)	Operating Temperature (°C)	Operating Pressure (psig)	Calculated Residence Time at Temperature in Reactor (minutes)	Total EDTA Carbon Destruction (%)	Total Organic Carbon Destruction (%)
3:1	305	1510	7.9	28.8	25.4
3:1	305	2950	7.0	26.8	24.2
3:1	351	2490	6.1	76.9	68.0
3:1	351	2800	5.9	75.6	67.4
3:1	350	2950	3.3	56.5	49.1
3:1[(b)]	353	4070	2.5	60.3	54.7

(a) EDTA as carbon source, packed 1-in.-I.D. reactor used except where indicated otherwise.

(b) Coiled 0.15-in.-I.D. reactor used.

Although operating pressure appears to have little or no effect on the amount of organic (EDTA) destroyed, it may play an important role in preventing reaction products from precipitating from solution. In some of the higher conversion runs (i.e., runs conducted at higher temperature, 365°C to 375°C), sodium carbonate has been observed to precipitate from solution, posing potential processing problems. Higher operating pressures may help prevent this precipitation from occurring or at least minimize it. The prevention of solids formation is the main focus of current and future work, and will be discussed further here and in Section 6.5.

6.4.1.2 Effects of Operating Temperature and Residence Time

Figures 6.2 through 6.6 depict the results of investigating operating temperature and residence time. The effect of both residence time and temperature on total organic destruction is given in Figure 6.2. As would be expected, organic destruction is greater with increasing residence time and temperature.

In Figure 6.3, the TOC, as well as oxalate carbon remaining in the product, is plotted against residence time at 365°C. For these test conditions, it can be seen that the oxalate carbon remains fairly constant at lower conversions, and at the longer residence times, oxalate concentrations decrease significantly.

In Figure 6.4, the oxalate carbon and TOC remaining in the product is shown as a function of temperature. It can be seen that the oxalate concentration increases significantly from approximately 300°C to 325°C, then levels out at intermediate conversions (approximately 350°C), and finally decreases at higher conversion (approximately 365°C).

In Figure 6.5, the effect of residence time (at approximately 365°C) on total organic destruction and nitrate and nitrite consumption is given. From these data it appears that nitrite and organic carbon are being destroyed to an appreciable extent, whereas the nitrate level remains fairly constant. This suggests that primarily nitrite, rather than nitrate, is reacting to destroy the organic carbon.

The effect of temperature on TOC and nitrate and nitrite consumption is given in Figure 6.6. The results are similar to those observed in Figure 6.5. The nitrite and TOC decrease significantly with temperature, whereas the nitrate consumption is minimal.

6.4.1.3 Mitigation of Solids Formation in Reactor

As noted previously, at high conversions and high operating temperatures, partial plugging occurred in the reactor. The most recent testing has focused on determining the cause of the plugging problem and on how to operate while preventing plugging. In previous tests, where plugging occurred, the plug material was removed from the reactor after completion of the run. Analysis of plug material via XRD showed in all cases that the solids were made up primarily of sodium carbonate (i.e., >90 wt%). As the EDTA is destroyed, more carbonate is formed from the breakdown of the EDTA, apparently reaching a point at higher conversions where the solubility of sodium carbonate solubility is exceeded. Feed adjustment, including hydroxide addition, is being evaluated to alleviate solids formation and plugging.

The 6:1 dilution runs listed in Table 6.2 were conducted primarily to 1) determine whether the plugging problem could be alleviated by dilution of the feed (i.e., dilution of the sodium carbonate), and 2) to determine whether the solids that entered with the feed contributed to the plugging (i.e., supernatant only run). As can be seen in Table 6.4, in both runs, high conversions were achieved; however, in both runs, gradual plugging of the reactor took place. Thus, although the greater dilution probably allowed for a higher conversion (i.e., allowed more sodium carbonate to remain in solution), it did not totally alleviate the plugging problem.

It had been noted that Na_2CO_3 as well as $Al(OH)_3$ may contribute to plugging problems (S. A. Bryan and L. R. Pederson, PNL). Thus, runs were conducted in which potassium hydroxide (KOH) was added to the 101-SY simulant. Potassium hydroxide was added 1) to complex potassium with the carbonate formed when EDTA is destroyed to form the more soluble potassium carbonate rather than sodium carbonate, and 2) to increase the OH^- concentration, potentially preventing $Al(OH)_4^-$ from precipitating as $Al(OH)_3$. Enough KOH was added so that the feed contained approximately 1.2 $\underline{M}$ OH^- rather than approximately 0.68 $\underline{M}$ OH^- as in the original 3:1 water:101-SY simulant feed. Concentrated KOH was added so that the water:101-SY simulant ratio remained at approximately 3:1 (v:v).

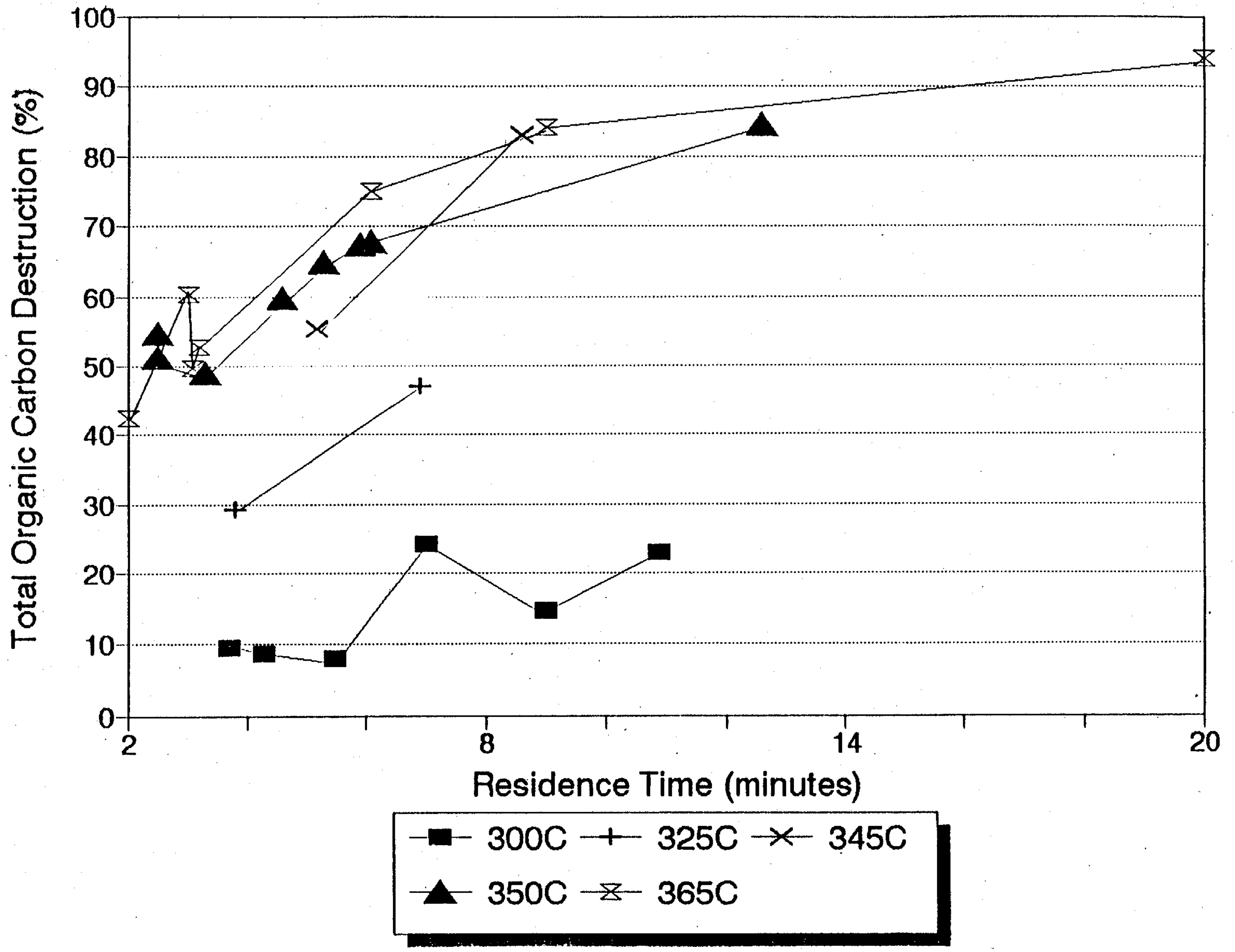

Figure 6.2. TOC vs. Residence Time for Temperatures Between 300°C and 368°C (EDTA as the organic carbon source)

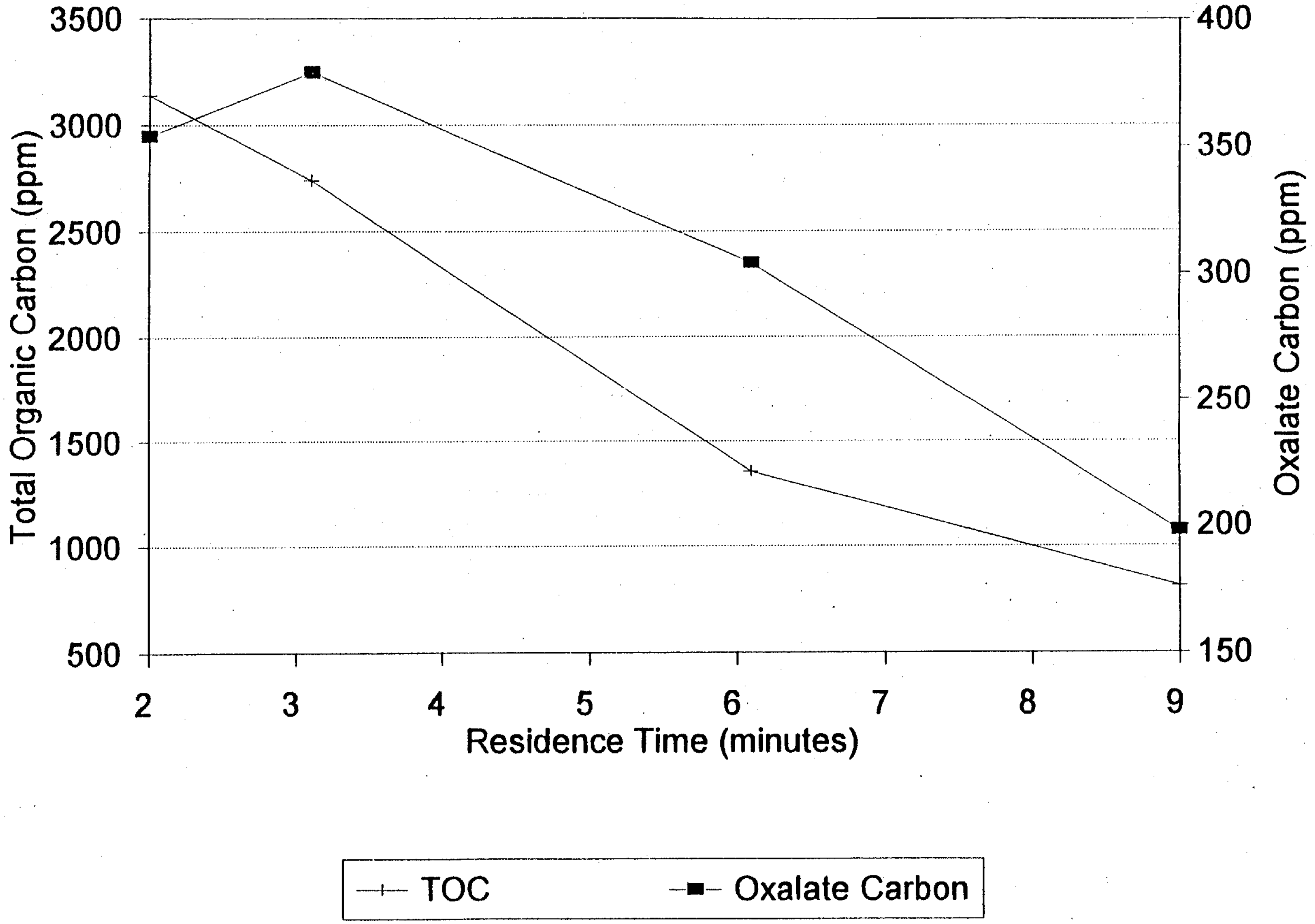

Figure 6.3. TOC and Oxalate vs. Residence Time (approximately 365°C, 3000 psig, EDTA as the organic carbon source)

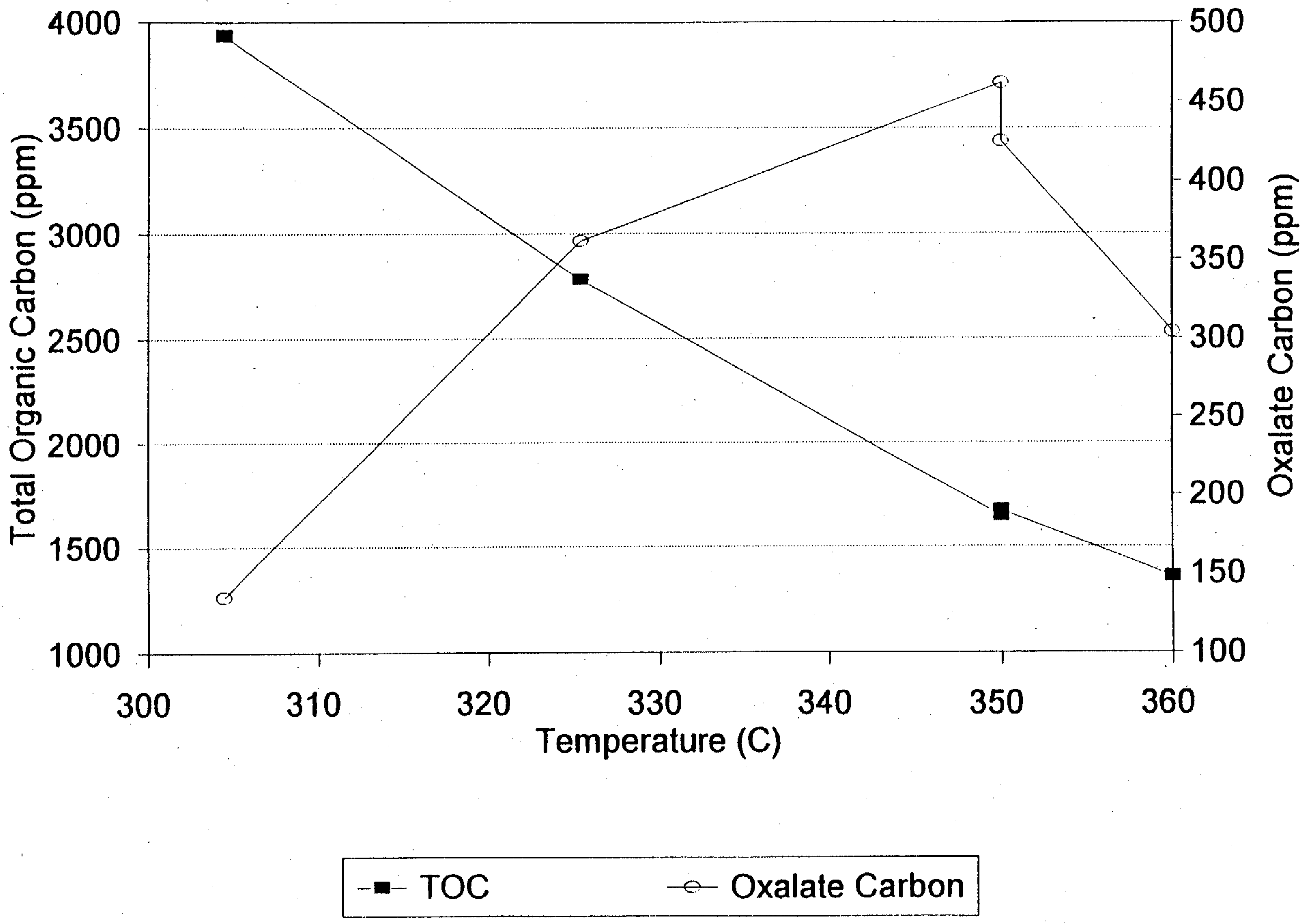

Figure 6.4. TOC and Oxalate vs. Temperature (residence time approximately 6-7 min, EDTA as the organic carbon source)

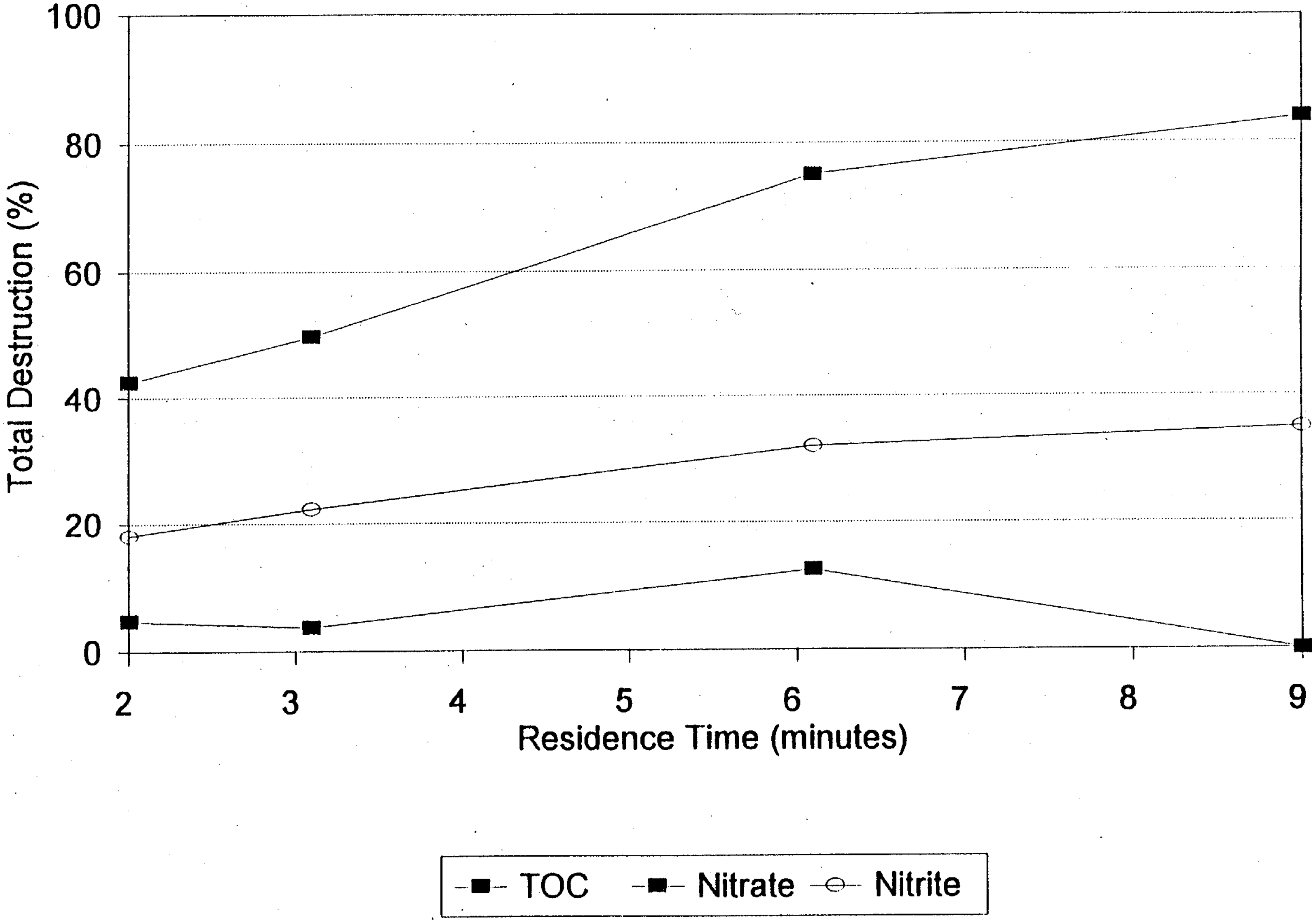

Figure 6.5. TOC, NO_2, and NO_3 vs. Residence Time (approximately 365°C, 3000 psig, EDTA as the organic carbon source)

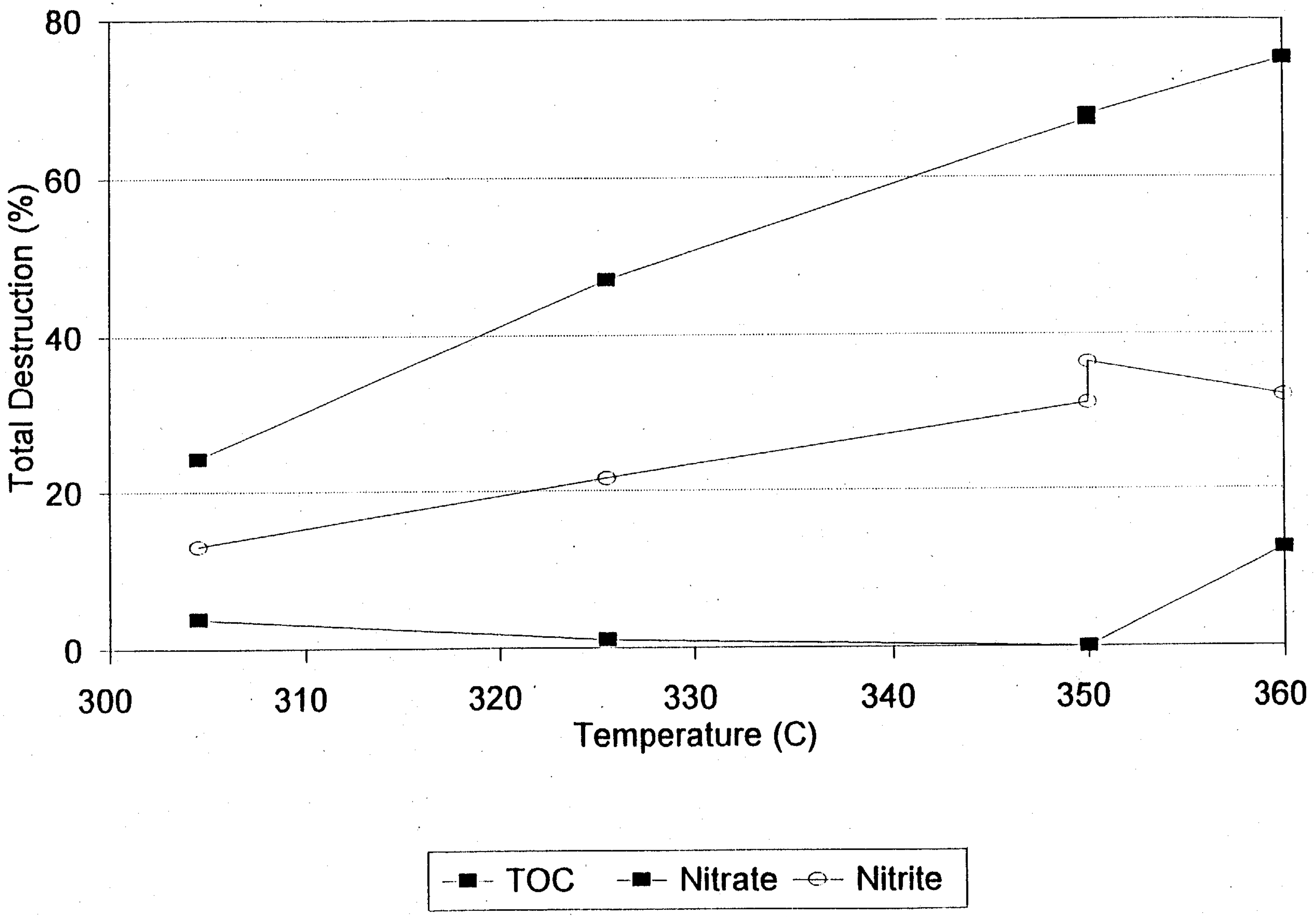

Figure 6.6. Temperature vs. TOC, NO_2, and NO_3 (residence time approximately 6-7 min, EDTA as the organic carbon source)

Table 6.4. Feed Dilution Effects on Organic Destruction[a]

Feed Dilution (water: 101-SY simulant, v:v)	Operating Temperature (°C)	Operating Pressure (psig)	Calculated Residence Time at Temperature in Reactor (minutes)	Total Organic Carbon Destruction (%)
3:1	300.5	2950	3.7	9.6 (12.2)[b]
3:1	300.5	2950	5.5	8.1 (10.4)[b]
4:1	300.0	2950	4.3	8.7 (11.5)[b]
3:1	302.0	2910	9.1	20.9 (23.9)[b]
4:1	302.0	2890	10.9	23.0 (28.0)[b]
3:1[c]	353	4070	2.5	54.7 (60.3)[b]
4:1	350	2920	2.5	51.1 (58.8)[b]
3:1	350	2800	5.9	64.7 (75.7)[b]
4:1	350	2890	5.3	65.1 (72.4)[b]
3:1	363	2920	3.1	49.7 (56.6)[b]
3:1	365	2960	3.0	60.5 (66.3)[b]
4:1	365	2900	3.2	52.7 (57.6)[b]
3:1	360	2900	6.1	75.7 (80.7)[b]
6:1[d]	368	3140	5.0	87.3 (88.8)[b]
3:1[e]	380	2970	3.0	81.9 (91.2)[b]
3:1[e]	377	2970	2.4	75.4 (82.9)[b]
6:1	378	2980	2.4	87.7 (90.7)[b]

(a) EDTA as organic carbon source.
(b) EDTA destruction (TOC = EDTA carbon + oxalate carbon).
(c) Coiled 0.2-in.-I.D. reactor used.
(d) Supernatant only.
(e) KOH added to feed, making $[OH^-] = 1.2M$.

The initial "KOH effects" run listed in Table 6.2 was operated for approximately 6 hr at 377°C without any signs of plugging within the reactor. After 6 hr of operation, the flow rate was changed from 1200 mL/hr to approximately 900 mL/hr (i.e., the second "KOH effects" run listed in Table 6.2). At this point, it was noted that minimal solids were exiting in the product liquid stream. In previous runs this was an indication that a plug was forming or the fluid velocity was not sufficient to carry the solids out of the reactor. After approximately 2 hr of operation no pressure drop was observed in the reactor. To ensure that the absence of solids in the product was not due to plugging in the reactor at high conversions, the reactor was maintained at approximately 3000 psig and 340°C overnight. The following morning, flow to the reactor was initiated, and no resistance to flow was noted, suggesting that a plug had not formed the previous day. The destruction levels for all of the "KOH effects" runs are given in Table 6.5.

The third "KOH effects" run listed in Table 6.2 was initiated using feed without the addition of KOH. After approximately 1 hr of operation, a slight pressure buildup in the reactor was observed, and minimal solids were coming over in the liquid product, indicating that a plug was forming in the reactor. After approximately 3 hr of operation, the pressure buildup in the reactor still existed, and was slowly climbing. At this time KOH was added to the feed, and within approximately 0.5 hr the plug was cleared, and solids were observed coming over in the liquid product. The reactor temperature was then gradually increased to approximately 400°C at an operating pressure of 3200 psig to determine whether plugging would occur at extreme conditions. At this temperature and pressure, the contents of the reactor should most certainly be in the gas phase. A gradual pressure buildup in the reactor was noted as the temperature approached 400°C. The reactor was cooled to approximately 340°C and left overnight as in the previous run. The next morning, flow to the reactor, using the KOH/101-SY simulant was initiated, and no indication of a plug in the reactor was noted. From these runs, it was concluded that the addition of KOH is beneficial in preventing and removing plugs in the reactor.

It should be noted here that due to limitations of the current tubular reactor system, the flow rates used in all of the runs conducted thus far translate to Reynolds numbers of approximately 700 or lower. At higher Reynolds numbers, and higher flow rates (i.e., >2000) solids buildup in the reactor may be minimized. We are currently looking into acquiring a system that is capable achieving such Reynolds numbers. This is discussed further in Section 6.5.

Table 6.5. KOH Effects on Organic Destruction[a]

Total $[OH^-]$ (M)	Operating Temperature (°C)	Operating Pressure (psig)	Calculated Residence Time at Temperature in Reactor (minutes)	Total Organic Carbon Destruction (%)
1.2[b]	377	2970	2.4	75.4 (82.9)[c]
1.2[b]	380	2950	3.0	81.9 (91.2)[c]
1.2[b]	337	2860	720 (overnight)	>93 (>97)[c]
0.68	362-375	3050	3.0-2.4	79-81
1.2[b]	375	3050	2.4	68
1.2[b]	380-410	2900-3400	approx. 2.4-2.0	95.5[d]
1.2[b]	337	3010	840 (overnight)	—

(a) All approximately 3:1 (v:v) dilutions of 101-SY simulant. EDTA as organic carbon source.
(b) KOH added to increase $[OH^-]$ from 0.68M to 1.2M.
(c) EDTA destruction (TOC = EDTA carbon + oxalate carbon).
(d) Not a steady-state value; temperature and pressure were continually increased in an attempt to form a plug at extreme conditions.

A run was recently conducted in a CSTR to determine whether operation in such a system could be conducted without solids plugging of the reactor. It was envisioned that the vigorous stirring in such a system might prevent plugging from the solids that are formed in the reactor. This test was conducted for approximately 8 hr without any indication of plugging in the reactor system. At the end of the test, we intended to cool the reactor, and look within the reactor the next day to determine whether a significant amount of solids had deposited on the reactor walls. However, after the system was shut down, a leak occurred at the top of the reactor. Due to this leak, approximately 50% of the liquid solution was released as vapor. When the reactor was opened the following day, a significant amount of solids deposition on the reactor walls was observed. It is believed that the solids deposition was a result of vaporization of the solution caused by the leak in the reactor.

6.4.1.4 Effect of Organic Carbon Source

The effects of organic carbon source on TOC destruction are presented in Table 6.6. To date, continuous plug-flow runs using EDTA, acetate, and formate as the organic sources have been conducted. For the acetate runs conducted at approximately 325°C and residence times of approximately 3 and 8 min, no measurable TOC reduction was observed. In addition, at the higher temperatures tested (i.e., 357°C to 380°C), only minimal acetate destruction was achieved. In contrast, at approximately 360°C and 3-min residence times, formate and EDTA destructions are significant and comparable to one another. It should also be noted that in the formate run, gradual plugging in the reactor was observed, and upon addition of KOH to the feed, the plug within the reactor was removed.

Table 6.6. Organic Carbon Source: Effect on Organic Destruction[(a)]

Organic Carbon Source	Operating Temperature (°C)	Operating Pressure (psig)	Calculated Residence Time at Temperature in Reactor (minutes)	Total Organic Carbon Destruction (%)
EDTA	325	2940	3.8	29.3 (33.2)[(b)]
Acetate	326	3010	3.3	0
EDTA	326	2900	6.9	47.1 (54.0)[(b)]
Acetate	323	2940	8.1	0
EDTA	363	2920	3.1	49.7 (56.5)[(b)]
Formate	362	3060	2.9	60.0
Acetate	357	2940	3.9	6.4
EDTA[(c)]	380	2950	3.0	81.9 (91.2)[(b)]
Acetate	380	2950	3.2	7.4

(a) All approximately 3:1 (v:v) dilutions of 101-SY simulant.

(b) EDTA destruction (TOC = EDTA carbon + oxalate carbon).

(c) KOH added to feed, making net [OH^-] = 1.2M.

The major gas products from the continuous plug-flow reactor runs using EDTA as the organic carbon source have been H_2, N_2O, N_2, and NH_3. The majority of the NH_3 remains in the liquids as it exits the reactor system; the other gases are vented in the off-gas system. H_2 typically ranges from 27 to 53 mole%; N_2O typically ranges from 33 to 56 mole%; and N_2 ranges from 9 to 17 mole% in the off-gas product. With increasing TOC conversions, the N_2O/H_2 mole ratio typically increases. The NH_3 concentration in the liquid product increases with increasing conversion. At high conversions (e.g., >75% TOC conversion), the NH_3 concentration is in the range of 2000 to 3000 ppm in the liquid product. The volume ratios of off-gas produced per feed (3:1 water:simulant dilution) introduced into the system are typically between 2:1 and 4:1. Higher gas production corresponds with higher TOC conversion. A typical off-gas composition is given in Section 6.4.3.

For the continuous runs conducted with acetate and formate as the organic carbon sources, H_2, N_2O, and N_2 were again the major components in the off-gas. In the two continuous formate runs, the gas composition was approximately 36 mole% H_2, 57 mole% N_2O, and 7 mole% N_2. During this run, no NH_3 was detected in the liquid product stream. In the continuous acetate runs, the gas composition ranged from 6 to 22 mole% H_2; 50 to 60 mole% N_2O; and 26 to 50 mole% N_2. The NH_3 in the liquid product stream ranged from 74 to 313 ppm.

6.4.2 Proposed Chemistry and Reaction Kinetics for EDTA Destruction

Based on preliminary continuous runs (Schmidt et al. 1993), the following chemical reactions were proposed for the destruction of EDTA:

Reaction 1. $C_{10}O_8N_2H_{12}^{-4} + 6NO_2^- \longrightarrow 5C_2O_4^{-2} + 2NH_3 + 3N_2 + 3H_2$

Reaction 2. $5C_2O_4^{-2} + 10OH^- \longrightarrow 10CO_3^{-2} + 5H_2$

In the reaction sequence given by Reactions 1 and 2, oxalate is formed by the reaction between nitrite and EDTA, and then oxalate further decomposes to carbonate. In the experiments conducted in FY 1993, it has been observed that an average 0.78 mole of nitrite is consumed for every mole of EDTA carbon that is destroyed. This is in fairly good agreement with, although consistently higher than, that predicted by Reaction 1. This observation indicates that although the majority of the nitrite is being consumed in the EDTA destruction process, small amounts of nitrite are also being consumed in other reactions.

In the bench-scale continuous runs, it was observed that nitrate levels change minimally, if at all, during the destruction process in the presence of comparable amounts of nitrite. This suggests that nitrate is playing a minor role, if any, in the destruction of organic carbon.

In the continuous tests the major gas products have been NH_3, N_2, H_2, and N_2O. N_2O is the only gas product generated in the bench-scale tests that is not predicted by Reactions 1 and 2. In addition, the NO_2^- consumption is consistently higher and the H_2 production is consistently lower than that predicted by the reactions given above. One possible reaction that is thermodynamically favored and would account for some N_2O gas generation, additional nitrite destruction, and H_2 consumption is:

Reaction 3: $2NO_2^- + 2H_2 \longrightarrow N_2O + 2OH^- + H_2O$

The production of carbonate has also been observed in the continuous runs. In some of the higher-temperature, long-residence-time runs conducted at 3000 psig (i.e., high organic destruction), solids formed within the reactor, in some cases resulting in partial plugging of the reactor. Analyses confirmed that these solids were primarily sodium carbonate. This suggests that at high destruction levels (>90%) and high operating temperatures (>365°C), the solubility limit of sodium carbonate is exceeded. Furthermore, the accumulation of carbonate may be exacerbated by the very low fluid velocities through the reactor. This issue is addressed further in Section 6.5.

The results observed experimentally suggest that the reactions proposed previously (Bryan and Pederson 1992) are potentially applicable for describing a global reaction mechanism for this system, although other side reactions are most likely also taking place. Because the hydroxide analytical technique is still under development and minimal hydroxide results have been obtained, the kinetic analysis that follows will focus on Reaction 1.

If it is assumed that the continuous tubular reactor system operates as a plug-flow reactor, the following general equation can be written for the destruction of EDTA:

$$n_{EDTA}\Delta t|_z - n_{EDTA}\Delta t|_{z+\Delta z} - r_{EDTA}\Delta t\pi R^2\Delta z = 0 \tag{1}$$

where n_{EDTA} = mass flow rate of EDTA carbon
z = longitudinal location within the reactor
r_{EDTA} = reaction rate expression for the destruction of EDTA carbon
t = time
R = radius of reactor

In Equation (1), steady-state operation is assumed. Equation (1) can be rearranged to give:

$$(1/\pi R^2)dn_{EDTA}/dz = -r_{EDTA} \tag{2}$$

Equation (2) can also be written in terms of EDTA carbon concentration:

$$(1/\pi R^2)d(C_{EDTA}V)/dz = -r_{EDTA} \tag{3}$$

where C_{EDTA} = EDTA carbon concentration
V = volumetric flow rate

Since in this system the fluid in the reactor remains in the liquid phase, and if it is assumed that the liquid is at constant temperature in the reactor (i.e., constant density), the total volumetric flow rate (V) can be assumed to remain constant. Furthermore, the volumetric flow rate can be divided by the differential volume element in the reactor ($\pi R^2 dz$) to yield the following expression in terms of residence time (τ):

$$dC_{EDTA}/d\tau = -r_{EDTA} \tag{4}$$

From the experimental results, it appears that nitrite is consumed preferentially over nitrate. As mentioned previously, for all of the data obtained thus far, the molar ratio of nitrite consumed to EDTA carbon destroyed is 0.78 compared with 0.6 as predicted by Reaction 3. Thus, although nitrite is most likely consumed somewhat in other reactions, as a first approximation, for obtaining a global reaction rate expression, it will be assumed that the majority of the nitrite is consumed via Reaction 3. Also, first-order dependence on EDTA carbon and nitrite will be assumed. By making these assumptions, Equation (4) can be written as:

$$dC_{EDTA}/d\tau = -kC_{EDTA}C_{Nitrite} \tag{5}$$

where C_{EDTA} = mass concentration of EDTA carbon
$C_{Nitrite}$ = mass concentration of nitrite
k = second order reaction rate constant

Upon integration, Equation (5) yields:

$$\begin{aligned}&(1/(C_{(nitrite,i}-2.3*C_{EDTA,i})) * (\ln(1/C_{EDTA}*(C_{nitrite,i} - 2.3*(C_{EDTA,i} - C_{EDTA}))) \\ &\qquad - \ln(C_{nitrite,i}/C_{EDTA,i})) = k\tau\end{aligned} \tag{6}$$

In Equation (6), the constant, 2.3, is the mass ratio of nitrite consumed to EDTA carbon destroyed as written in Reaction 3. For the kinetic analysis, the specific units for the variables given in Equation (6) are defined as follows:

$C_{nitrite,i}$ = initial nitrite concentration (ppm)
$C_{EDTA,i}$ = initial EDTA carbon concentration (ppm)
C_{EDTA} = final EDTA carbon concentration (ppm)
k = second-order reaction rate constant (minutes^{-1} ppm^{-1})
τ = residence time (minutes)

The rate constants that were calculated using Equation (6) and experimental data are presented in Figure 6.7 as an Arrhenius plot:

where A = pre-exponential factor (min^{-1} ppm^{-1})
E_a = apparent activation energy (kcal/mole)
R_g = gas constant (kcal/mole °K)

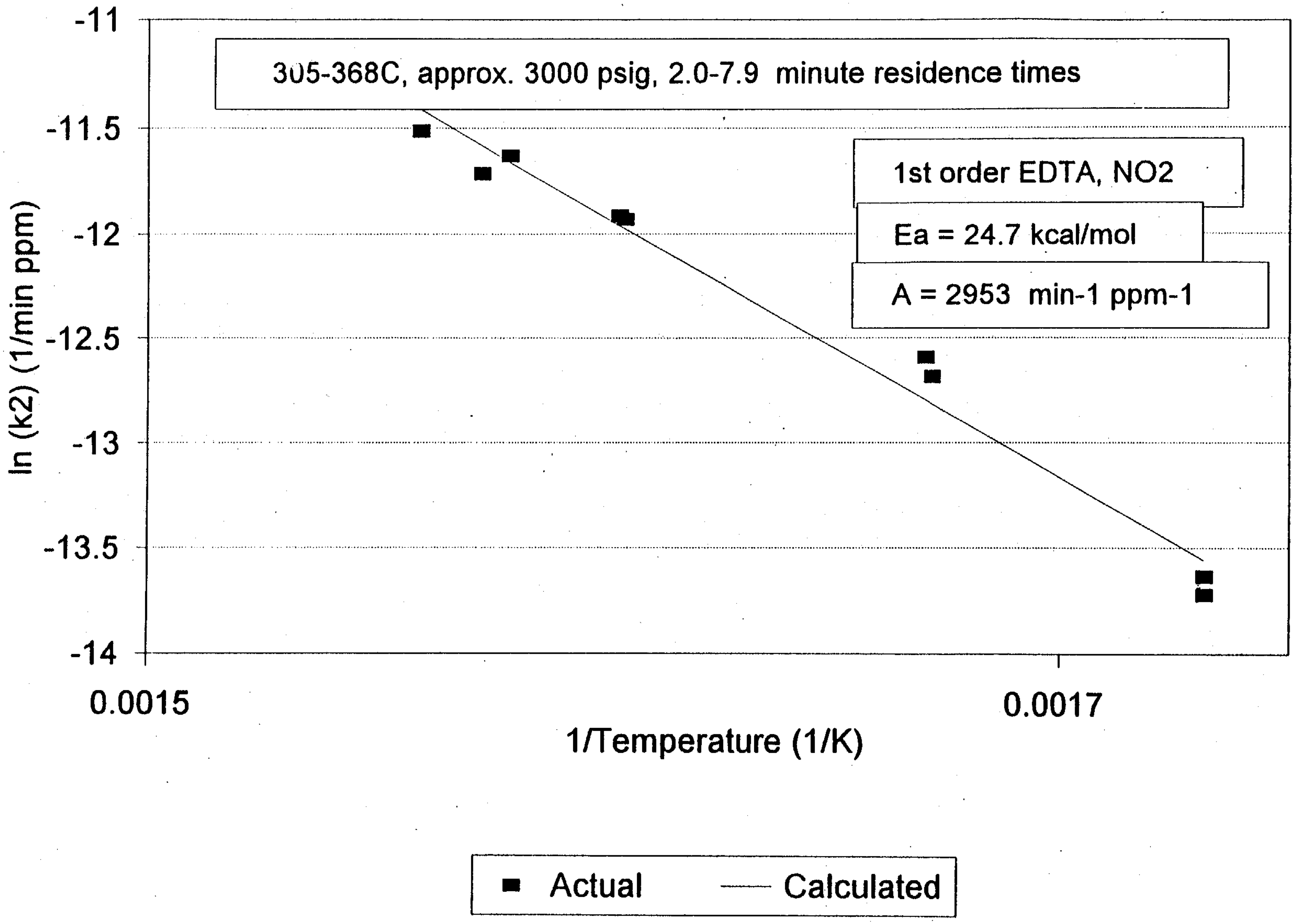

Figure 6.7. Arrhenius Plot (3/1 dilution of 101-SY simulant)

As would be expected, a linear relationship between lnk and 1/T is obtained. From the slope of the "calculated" line (i.e., slope = $-E_a/RT$), an apparent activation energy of 24.7 kcal/mole is obtained; from the intercept, a pre-exponential factor value of 2952 min^{-1} ppm^{-1} is obtained. These updated values are slightly different from previously published preliminary values, i.e., $E_a = 22.1$ kcal/mole and A = 343 min^{-1} ppm^{-1} (Schmidt et al. 1993) because temperatures and residence times have been more rigorously calculated, and more precise selection of steady-state operations for obtaining data were used in the present case. The rate constant values predicted using either set of values and Equation (7) for the temperature range tested (i.e., approximately 300°C to 365°C) agree to within 15% of one another.

In Figure 6.8, the predicted curves for 325°C, 350°C, and 365°C are plotted along with actual data. The predicted curves were obtained by using the updated calculated apparent activation energy and pre-exponential factor to obtain the rate constant, and then by inserting the calculated rate constant into Equation (6). Given values for fraction EDTA carbon destroyed were then inserted into the expression, and a required residence time was calculated. As can be seen, there is good agreement between the actual data and the predicted lines.

This type of plot can be used to estimate the residence time that is required to achieve a given EDTA carbon destruction. For example, to achieve 90% destruction of EDTA carbon, approximately an 8-min residence time is required at 365°C, whereas at 350°C a 12-min residence time is required, and at 300°C, a 25-min residence time is required. In general, the TOC (EDTA+oxalate) conversion is 3% to 8% lower than the EDTA conversion. An empirical kinetic expression for TOC destruction has recently been developed and is presented in Section 6.4.3.

6.4.3 Engineering Support Data

HTP organic destruction data have been provided to British Nuclear Fuels Limited (BNFL) in support of their design efforts for IPM. Along with the data and results discussed in the previous sections, the following data and observations were also provided.

BNFL requested that the predictive kinetic information pertaining to EDTA destruction be presented as residence time versus operating temperature for different conversions. In addition, an empirical kinetic expression for TOC destruction (i.e., EDTA+oxalate carbon) was developed from runs in which EDTA was used as the organic carbon source, and these data were plotted in a similar manner. The expression assumes first-order dependencies on $[NO_2^-]$ and [TOC] as was the case for EDTA destruction. Although Reactions 1 and 2 in Section 6.4.2 suggest a possible dependence of TOC destruction on $[OH^-]$ as well as $[NO_2^-]$, the TOC conversions predicted by this kinetic expression agreed fairly well with the run data (i.e., the error between predicted and actual values was typically ± 18%). The predictive curves are given in Figures 6.9 and 6.10 for EDTA destruction, and Figures 6.11 and 6.12 for TOC (i.e., EDTA+oxalate) destruction.

In addition to the major gas components that were identified for the continuous runs (i.e., H_2, N_2O, N_2), BNFL requested that the off-gas stream be analyzed for other gasses such as CO, CO_2, NO, and NO_2 so that they could determine what type of off-gas treatment system would be required. The quantities of these gases were relatively small and thus had not been detected using the gas

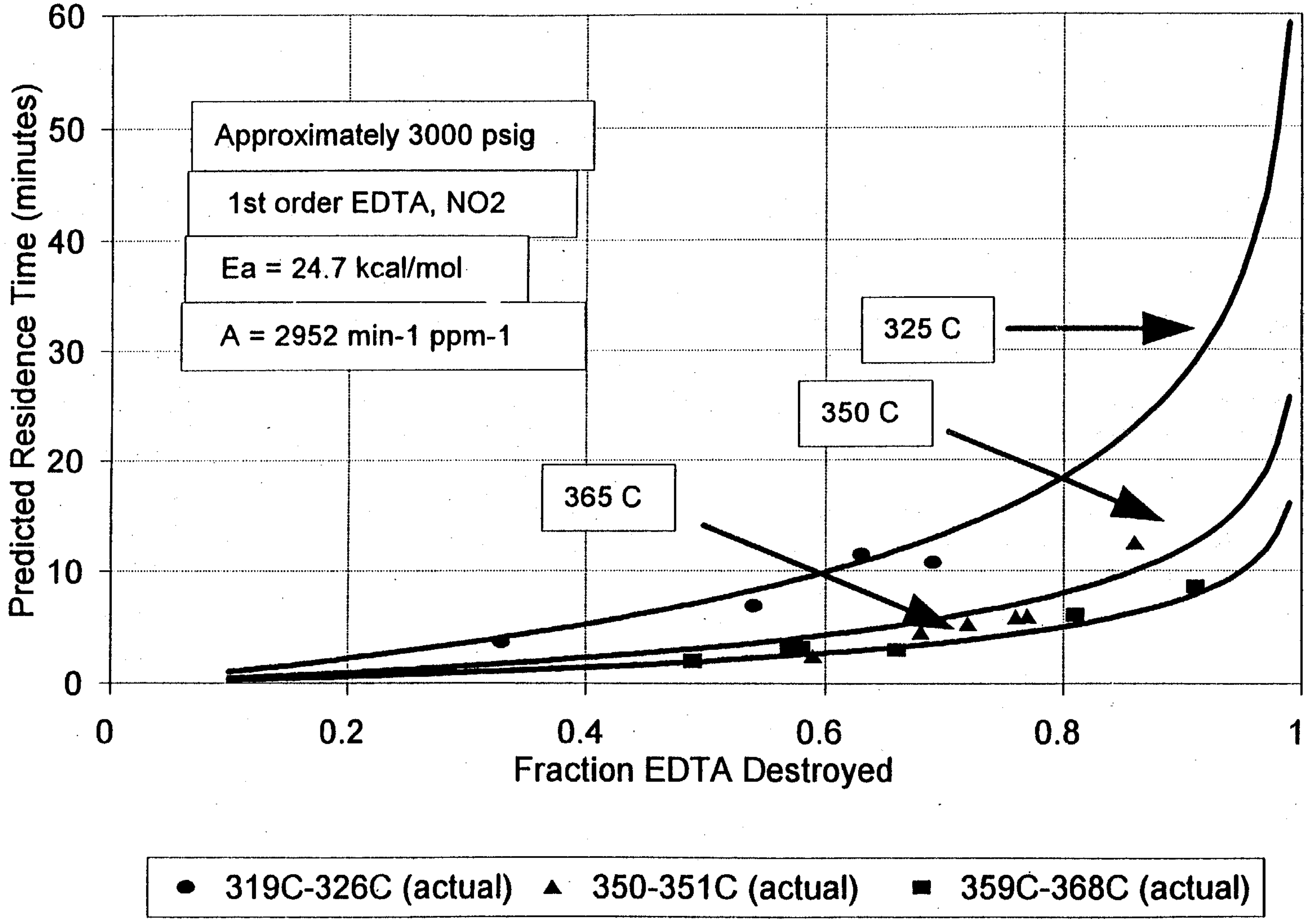

Figure 6.8. Predicted Residence Time vs. EDTA Destroyed (3/1 dilution of 101-SY simulant)

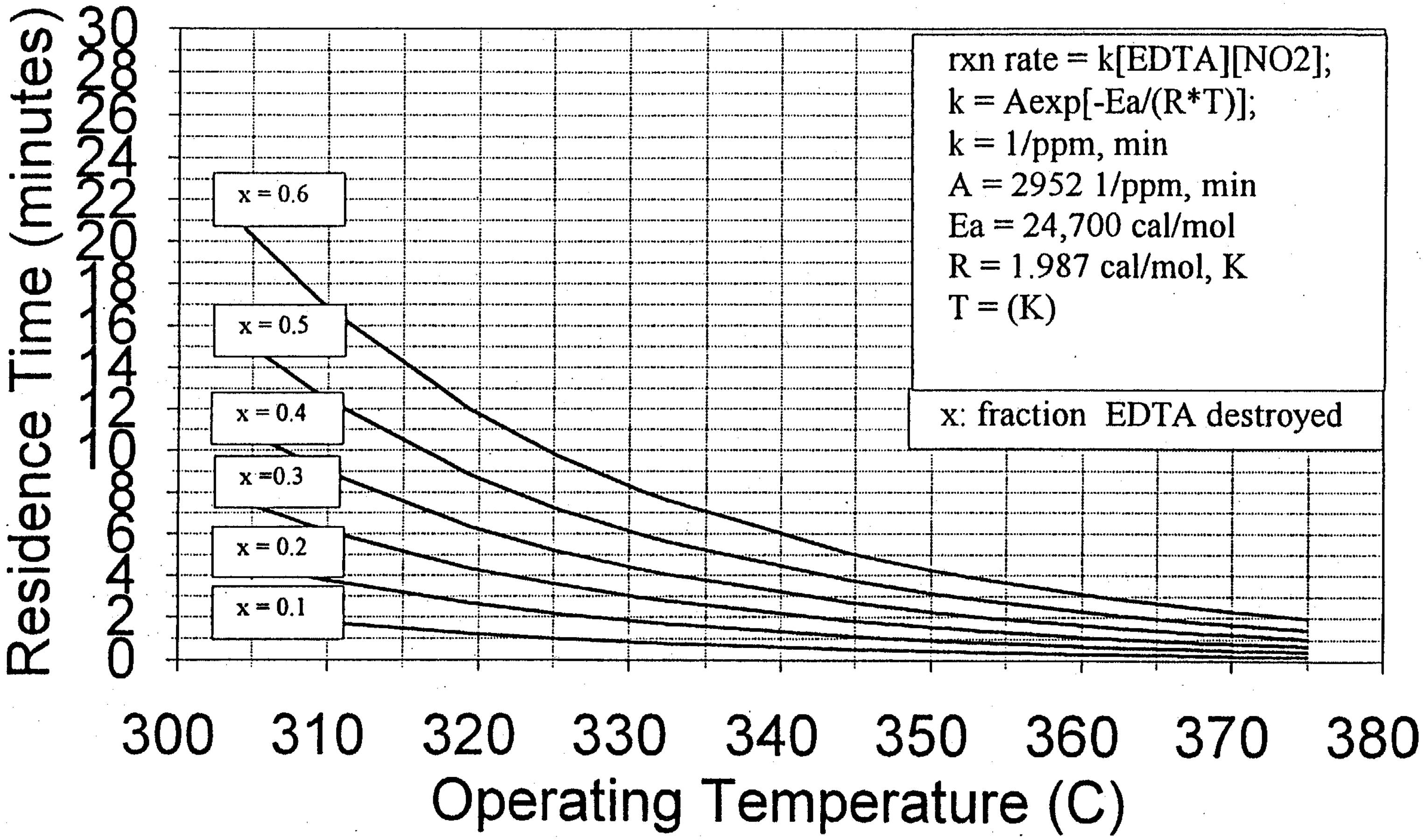

Figure 6.9. Predicted Residence Time vs. Operating Temperature, x_{EDTA} = 0.1-0.6 (3/1 dilution of 101-SY simulant)

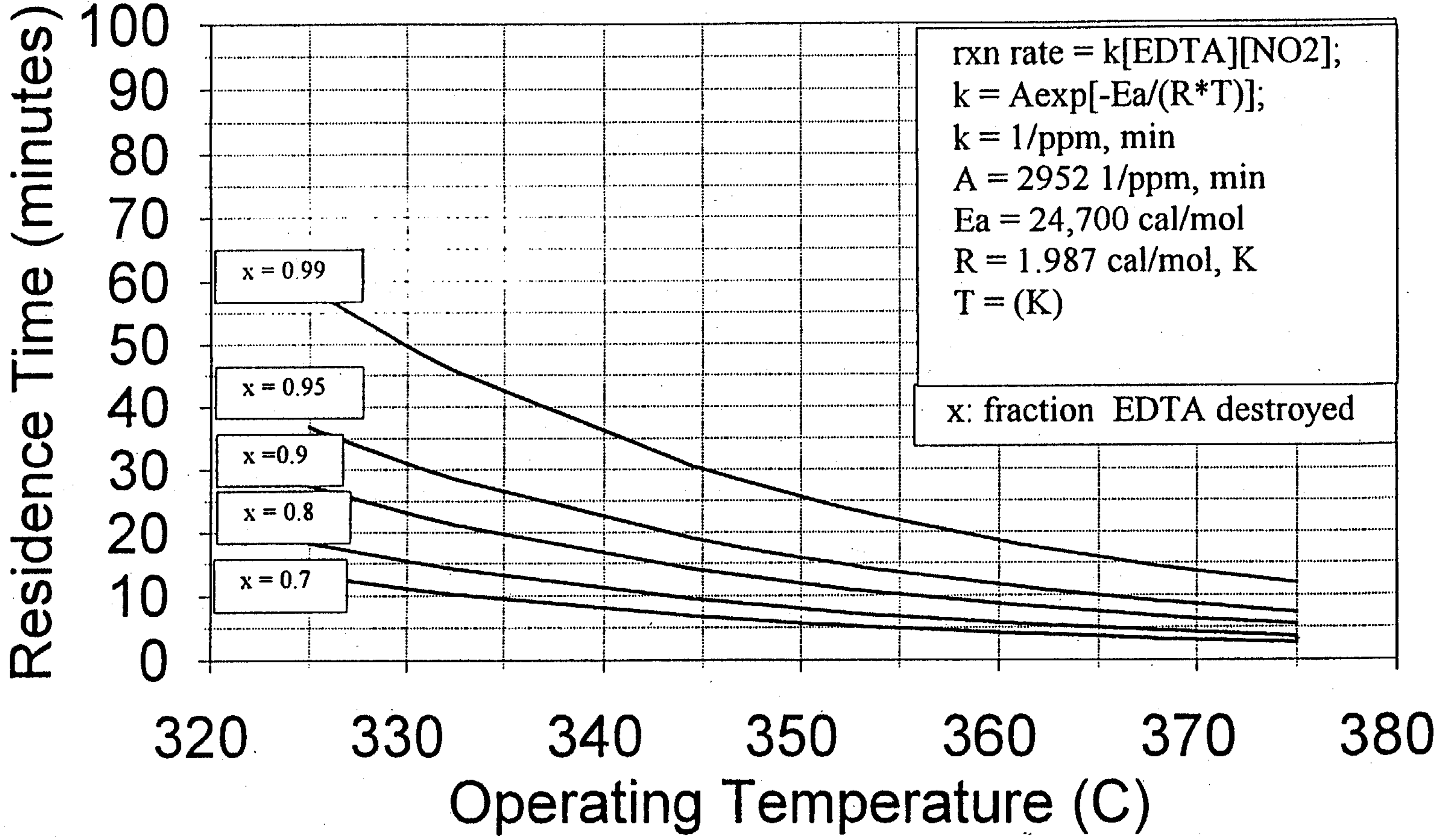

Figure 6.10. Predicted Residence Time vs. Operating Temperature, x_{EDTA} = 0.7-0.99 (3/1 dilution of 101-SY simulant)

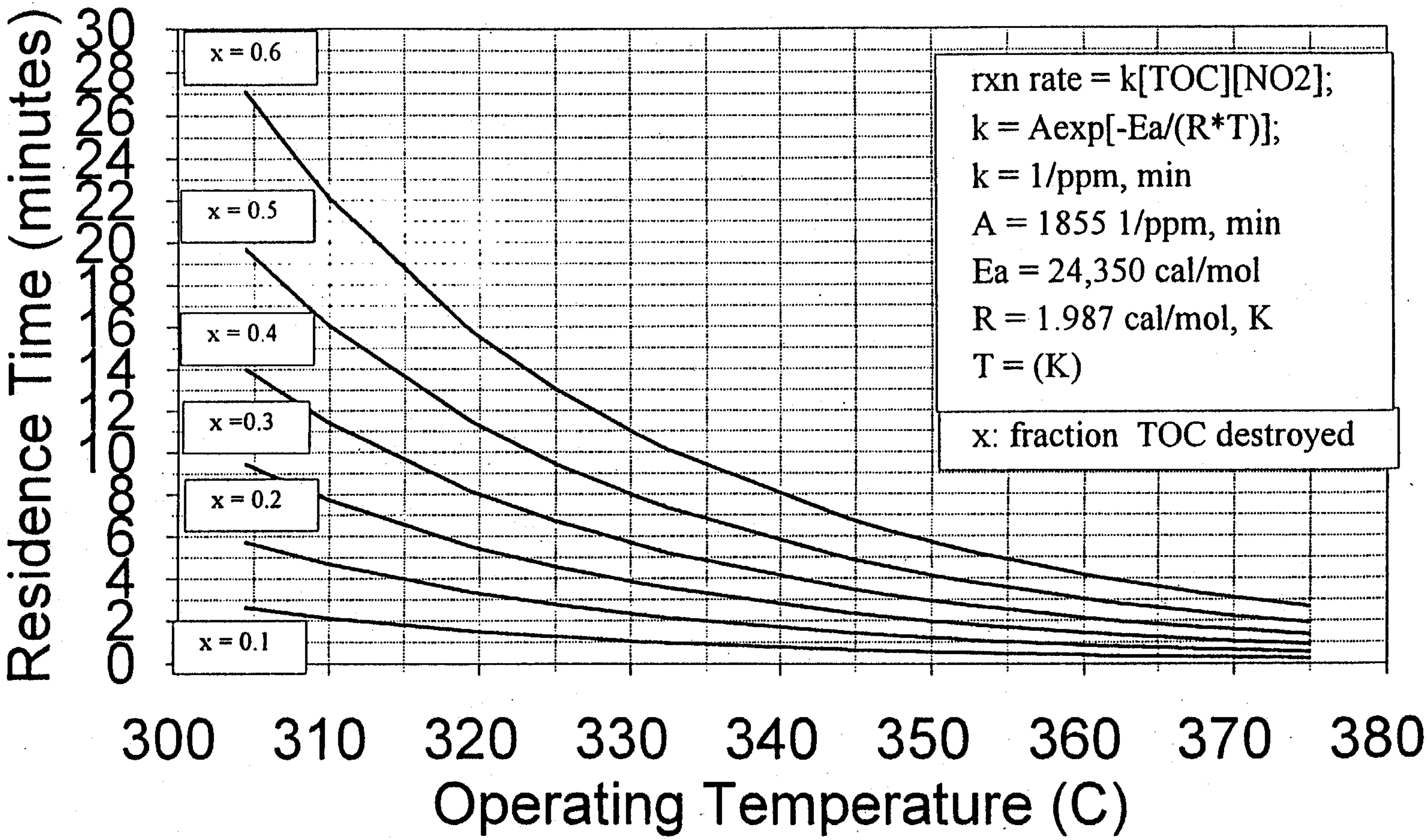

Figure 6.11. Predicted Residence Time vs. Operating Temperature, x_{TOC} = 0.1-0.6 (3/1 dilution of 101-SY simulant)

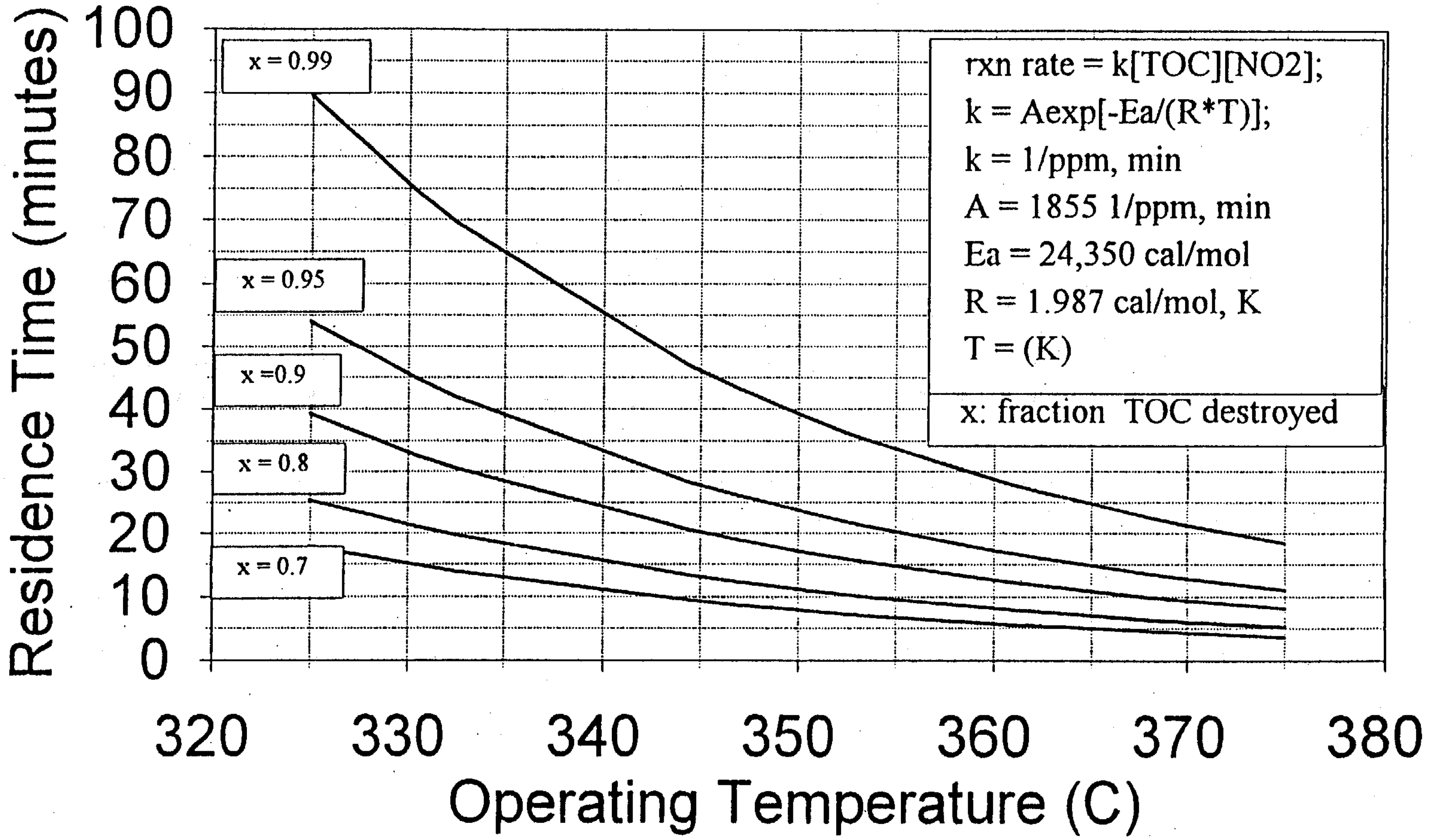

Figure 6.12. Predicted Residence Time vs. Operating Temperature, x_{TOC} = 0.7-0.99 (3/1 dilution of 101-SY simulant)

chromatograph that had been used in previous runs. Thus, in one of the later runs, dragger tubes were used to analyze for NO and NO_2. In addition, the NH_3 concentration in the off-gas was determined from dragger tube analysis. Also in this run, off-gas samples were submitted for analysis via a quantitative mass spectrophotometric gas analyzer. The results of these gas analyses are given in Table 6.7. The major gas components (i.e., H_2, N_2, and N_2O) and the percentages of these gases were the same as those determined via gas chromatography.

Data pertaining to the metals distribution among the solid and liquid phases of the feed and product streams was also supplied to BNFL. These data are presented in Table 6.8. Some caution regarding these data is that, in earlier studies, a white precipitate [most likely $Al(OH)_3$] has been observed in the liquid product as the product ages. The analyses of the samples given in Table 6.8 were conducted approximately 2 weeks after the completion of the run. In filtering tests conducted on the product and feed from this run immediately after the run, it was observed that the product and feed streams contained less than 1 wt% solids. In Table 6.8, the wt% solids were determined by balancing chromium, zinc, and nickel with what is calculated for the feed since an appreciable amount of these three elements exist primarily in the solid phase. As can be seen from Table 6.8, the wt%

Table 6.7. Complete Off-Gas Analyses(a)

Gas Component	Condition 1(b) (mole %)	Condition(c) (mole %)
H_2	32.6 ± 0.2	32.7 ± 0.2
He	0.129 ± 0.005	0.04 ± 0.005
CH_4	0.033 ± 0.003	0.05 ± 0.003
N_2	13.6 ± 0.2	17.5 ± 0.2
CO	0.69 ± 0.07	0.82 ± 0.07
O_2	1.77 ± 0.02	1.87 ± 0.02
Ar	0.074 ± 0.007	0.068 ± 0.007
CO_2	<0.05	0.1 ± 0.1
C_2H_6	0.14 ± 0.02	0.17 ± 0.02
C_xH_y	trace	trace
N_2O	50.9 ± 0.2	46.7 ± 0.2
NO_x	<0.05	<0.05
NO(d)	20 ppm ± 5 ppm	15 ppm ± 5 ppm
NO_2(d)	<2.5 ppm	<2.5 ppm
NH_3(d)	0.25 ± 0.02	>0.3 ± 0.02

(a) Feed = 3:1 (v:v) dilution of 101-SY simulant with EDTA as organic source; KOH added to increase [OH-] from 0.68M to 1.2M. Analyses conducted via quantitative mass spectrometric gas analyzer unless indicated otherwise.

(b) Condition 1: 377°C, 2972 psig, 2.4-min residence time, TOC destruction = 75.4%, EDTA destruction = 82.9%.

(c) Condition 2: 380°C, 2950 psig, 3.0-min residence time, TOC destruction = 81.9%, EDTA destruction = 91.2%.

(d) Analyses conducted via dragger tube measurement.

Table 6.8. Liquid/Solid Metals Distribution[(a)]

Metal Component	Metal Distribution (% metal in liquid; % metal in solid) Feed[(b)]	Condition 1[(c)]	Condition 2[(d)]	Condition 3[(e)]
Al	102.5; 10.4	39.3; 62.4	35.7; 70.8	32.4; 119.2
Ca	148.3; 18.1	17.3; 15.9	43.4; 15.4	21.1; 16.6
Cr	1.8; 113.5	3.8; 77.2	4.4; 87.2	9.3; 99.6
Fe	4.3; 131.9	20.0; 129.0	73.3; 125.3	0.0; 74.2
K	99.7; 0.0	100.8; 0.0	101.4; 0.0	99.4; 0.0
Na	101.8;2.9	103.9; 1.8	98.6;2.0	93.9; 2.6
Ni	59.8; 51.2	54.9; 68.8	27.4; 65.8	0.0; 74.2
Zn	0.0; 73.9	0.0; 90.3	0.0; 125.2	14.4; 115.1

(a) Feed = 3:1 (v:v) dilution of 101-SY simulant with EDTA as organic source. Metals distribution calculated by determining total solids/liquid ratio using analysis of Ni, Cr, and Zn in liquid and solid, and doing a material balance for these three metals.

(b) Calculated total solids = 1.2 wt%.

(c) Condition 1: 368°C, 2926 psig, 2.0-min residence time, TOC destruction = 41.8%, EDTA destruction = 42.8%. Calculated total solids = 2.8 wt%.

(d) Condition 2: 363°C, 2915 psig, 3.1-min residence time, TOC destruction = 49.7%, EDTA destruction = 56.6%. Calculated total solids = 3.2 wt%.

(e) Condition 3: 360°C, 2902 psig, 6.1-min residence time, TOC destruction = 75.1%, EDTA destruction = 80.7%. Calculated total solids = 5.0 wt%.

solids in the liquid product ranges from 2.8 wt% to 5.0 wt%. In addition, as the wt% solids increase, the wt% aluminum in the solid phase increases accordingly . It is suspected that the majority of the aluminum fell out of solution from the time the run was conducted to the time the analyses were conducted. As can be seen, the overall material balance is very good for some of the metals and not for others (e.g., calcium in particular). These data can give at least a qualitative idea of the relative distributions of metals in the liquid and solid phases. For example, most of the chromium, zinc, and iron exist as a solid in the feed and product streams, while most of the potassium and sodium exist in the liquid phase in both the feed and product streams. In addition, as the TOC conversion increases, the amount of aluminum in the solids increases. However, as mentioned above, it appears that aluminum precipitation takes place over a long period of time. It should be emphasized that these are the metals distributions at ambient conditions, and that the metals distribution in the reactor could be quite different (e.g., at 350°C and 3000 psig). Additional samples from selected runs have been submitted to determine solid to liquid ratios, metals content of the solid, and metals content of the liquid. These samples are to be analyzed for cesium and strontium as well as the metals reported above.

Carbonate and OH^- analyses were also supplied to BNFL for runs in which these analyses were conducted. The carbonate results are given in Table 6.9, and the OH^- analyses are given in Table 6.10. As can be seen, a very good carbon balance is obtained using the organic carbon+ inorganic (i.e., carbonate) carbon analyses for the feed and liquid product streams.

Table 6.9. Carbonate (TIC) Analysis and Total Carbon Balance[(a)]

Run Conditions	TIC and TOC Analyses (ppm TIC; ppm TOC) Feed	Liquid Product	Total Carbon Material Balance[(b)]
304.5°C, 2953 psig, 7-min residence time	3323.5; 5199.0	3720.3; 3938.7	89.9
304.5°C, 1508 psig, 7.9-min residence time	3323.5; 5199.0	4472.3; 3876.0	98.0
325.5°C, 2899 psig, 6.9-min residence time	2615.5; 5258.5	5429.1; 2780.7	104.3
325°C, 2937 psig, 3.8-min residence time	2615.5; 5258.5	4219.5; 3716.8	100.8

(a) Feed = 3:1 (v:v) dilution of SY-101 simulant with EDTA as organic source. Carbonate is assumed to be the source for the TIC (total inorganic organic carbon). TOC = total organic carbon.

(b) Material Balance = $[(TIC+TOC)_{liquid\ product}/(TIC+TOC)_{feed}]x100$

Table 6.10. Hydroxide Analysis[(a)]

Run Conditions	OH^- Consumption (mMole/g solution)	Total Organic Carbon converted to Carbonate (mMole/g solution)	OH^- consumption/ Carbonate Formed (mMole/mMole)
300.5°C, 2947 psig, 3.7-min residence time	0.0	0.045	0.0
300.5°C, 2947 psig, 5.5-min residence time	0.005	0.038	0.131
302°C, 2910 psig, 9.0-min residence time	0.02	0.064	0.312
350°C, 2947 psig, 3.3-min residence time	0.10	0.214	0.473
351°C, 2956 psig, 4.6-min residence time	0.10	0.257	0.40

(a) Feed = 3:1 (v:v) dilution of 101-SY simulant with EDTA as organic source. Carbonate is assumed to be the source for the TIC.

For the OH^- analyses, the liquid + solid solution is first treated with $BaCl_2$ to precipitate out the carbonate so that it will not interfere with the OH^- titration. The original solids + $BaCO_3$ precipitate are then filtered and removed from solution. The resulting supernatant is then titrated to pH=7 to determine the total OH^- + $Al(OH)_4^-$ concentration. As this titration takes place, $Al(OH)_4^-$ precipitates as $Al(OH)_3$ which also releases an OH^- upon precipitation. Thus, after this titration, $K_2C_2O_4$ is added to solution to convert $Al(OH)_3$ to soluble $Al(C_2O_4)_3^{3-}$, releasing 3 moles of OH^- for every mole $Al(C_2O_4)_3^{3-}$ formed. This solution is then titrated to pH=7 to determine the $Al(OH)_3$ concentration. By knowing this and the total $Al(OH)_4^-$ + OH^- concentrations from the first titration, the free OH^- concentration can be calculated. As can be seen, these analyses are very complicated. At this time, the precision of the OH^- analyses is being evaluated, and the method is still being refined; therefore, caution should be exercised when using the reported OH^- results.

In Table 6.10, OH^- consumption, TOC converted to carbonate and the ratio of the two are given for several conditions. According to Reaction 2, the molar ratio of OH^- consumed to carbonate formed should be 1:1. Table 6.10 shows that as TOC conversion to carbonate increases, the ratio of OH^- to carbonate formed approaches closer to unity. However, all of the molar ratios given in Table 6.10 are below 1, indicating that 1) the oxalate is being consumed via other reactions; 2) OH^- is being produced via other reactions (e.g., Reaction 3); and/or 3) the OH^- analysis is consistently overestimating the OH^- concentration. Feed solutions were analyzed for the runs given in Table 6.10, and the OH^- concentration that was determined analytically agreed very well (i.e., ± 10%) with what would be predicted from the simulant recipe. Thus, unless other considerations such as aluminum precipitation play a role in analysis of these products, the OH^- analyses given in Table 6.10 should be reasonably accurate. Samples from other runs have also been submitted for OH^- analyses, and the feed and predicted OH^- concentrations were not in agreement with one another. Thus, as mentioned above, further development of the method is continuing.

A nitrogen material balance was also conducted using NO_2^-, NO_3^-, and EDTA as the feed nitrogen sources, and NO_2^-, NO_3^-, unreacted EDTA, NH_3, N_2O, and N_2 as the product nitrogen sources. For the 41 test conditions in which complete data were available, the nitrogen balance (i.e., [product nitrogen/feed nitrogen]x100) was 100.3 ± 4.8%. NO_2^- and NO_3^- were the main sources of nitrogen, accounting for approximately 94% of the nitrogen in the feed (i.e., 100% when acetate or formate were the organic carbon sources). In the product streams, these two components accounted for between 70% (i.e., at high TOC destructions) and 94% (i.e., at low TOC destructions) of the nitrogen.

In addition to chemical and kinetic aspects of the hydrothermal destruction of organics, mechanical and equipment-related information has been supplied to BNFL. No visible signs of corrosion in the 1-in.-I.D. tubular reactor used in the HTP runs during FY 1993 were observed by PNL staff. In August 1993, the tubular reactor was sent to WHC for nondestructive examinations (NDEs) (i.e., white light and fluorescent penetrant examinations). At that time, 84 continuous runs had been conducted in the reactor; 32 were HTP runs. Results from the NDEs indicated no evidence of large internal flaws such as cracks, porosity, or general corrosion.

Until recently, there have been few mechanical problems related to the pump or pressure letdown system. The packing in the pump was recently replaced because the pumping was becoming erratic. The Teflon packing within the pump had last been replaced approximately 18 months earlier. Since the packing and a pump check valve were replaced, the unit has been providing consistent pumping.

The back-pressure regulator that has been used in the 3000 psig and lower runs has operated without any problems to date. Recently a back-pressure regulator was acquired for operation at pressures up to 6000 psi. In the one run conducted to date using this back-pressure regulator, it functioned properly for approximately 6 hr, after which it did not regulate pressure consistently. Upon removal of the regulator, it was observed that the seat within the regulator had been etched. We have been working with the manufacturer of the back-pressure regulator to solve this problem. Two materials that have been recommended are TefZel (duPont) and Kel-F. Fifteen percent carbon fibers will be added to these materials to increase the hardness, thereby making them more resistant to erosion and corrosion. An order has been placed with the manufacturer to obtain seats constructed of these materials.

6.5 Directions of Future Testing

Optimal conditions, with respect to EDTA destruction, can be predicted fairly well from the CRS data and kinetic analysis discussed above. To achieve approximately 90% EDTA destruction, an operating temperature of 365°C and residence time of approximately 8 min are required. In addition, the empirical kinetic expression developed in Section 6.4.3 for TOC destruction is useful in determining the total organic destruction (i.e., EDTA+oxalate carbon) for feeds containing EDTA as the organic carbon source. In general EDTA destruction is 3% to 8% greater than TOC destruction.

As mentioned previously, at high levels of organic destruction and high operating temperatures, solids, mainly as sodium carbonate, form in the reactor. This poses operational problems, potentially causing plugging within the reactor. Partial plugging has been experienced in the bench-scale tests in the 1-in.-diameter reactor system (with packing). In many of these cases, the plug was removed by decreasing the reactor temperature and/or flushing the reactor with water or even dilute HNO_3. In a few cases, and in particular a run using the smaller 0.2-in.-ID coiled reactor, the plug was not identified soon enough, and reduction of temperature and flushing with water was not adequate to remove the plug. As a result, immediate testing plans have and will continue to focus on identifying fail-safe operating conditions at which plugging can be prevented while achieving adequate TOC conversion. These plans include chemical (e.g., KOH addition, dilution) as well as engineering (i.e., alternative reactor designs, operation at higher pressures, operation at higher Reynolds numbers) solutions to the problem.

Most recently, it was observed that KOH can be used to help in the prevention and removal of plugs. While the addition of KOH is not a desirable solution to the problem, this information has aided in further defining chemical parameters that are important in the prevention of plugging.

A run was recently conducted using a CSTR system, and no plugging was observed. While these results were promising, additional testing using the CSTR system is required to verify these initial results, to determine operability of the system over time (i.e., do solids build up over time?), and to compare the "costs and benefits" of operating a CSTR reactor system versus a tubular reactor system.

To date, due to the limitations of the existing tubular reactor system, runs have been conducted at Reynolds numbers of approximately 700 and lower. These laminar flow conditions may contribute significantly to solids deposition and plugging in the reactor. Also, because of the lower limits on flow-rate due to solids settling in the current system, many of the most recent tests have been conducted near 375°C and 3000 psig, and 2- to 3-min residence times so that high conversions could be attained. Although the vapor pressure of the simulant is lower than pure water at given conditions, slightly higher wall temperatures could allow for slight vaporization, and solids deposition. Thus, an improved reactor system design using a hot fluid heating system, capable of turbulent flow, and capable of covering a wide range of temperatures, pressures, and flow rates is currently being considered for FY 1994. This system would also be solely dedicated to this work, as the current system is being shared by a variety of projects.

Additional tests are to be conducted using other organic carbon sources such as citrate, acetate, formate, etc. Data from these runs will be used to develop kinetic expressions similar to that developed for the destruction of EDTA.

6.6 References

Schmidt, A. J., E. O. Jones, and R. J. Orth et al. 1993. "Preliminary Conceptual Design for the Destruction of Organic/Ferrocyanide Constituents in the Hanford Tank Waste with Low-Temperature Hydrothermal Processing." PNL-SA-23181, Pacific Northwest Laboratory, Richland, Washington.

Hohl, T. M. 1993. *Synthetic Waste Formulations for Representing Hanford Tank Wastes.* WHC-SD-WM-TI-549, Rev. 0. Westinghouse Hanford Company, Richland, Washington.

7.0 Pilot-Scale HTP Testing with Simulant

7.1 Objectives

The overall objective of this testing is to operate the Scaled-up Reactor System (SRS) as a pilot plant for the low-temperature HTP system. Continuous tubular reactor testing, Section 6, provided target operating conditions for this investigation. The pilot-scale system was operated with 101-SY simulant to meet three objectives: 1) operation of the pilot-scale system demonstrates the ability to perform this process on a large scale for an extended period of time. The SRS is approximately an order of magnitude scaleup of the bench-scale CRS. 2) the data generated were used to verify reaction chemistry and kinetics developed from the bench-scale system data. 3) the SRS provided data and operational information necessary to scale up the HTP system, specifically, operational conditions and techniques used to prevent precipitation of solids, plugging, and resumption of operation should plugging occur.

7.2 Equipment

The SRS pilot-scale system consists of two 0.98-gal tubular reactors (R1 and R2), feed tanks, feed and mixing pumps, a 0.98-gal preheater vessel (H1), a double-tube heat exchanger, liquid-gas separator tank, and on-line control and data acquisition system. The entire system is mounted on a single 8-ft x 11-ft skid for portability. The reactors and preheater vessel both have the dimensions of 2 in. ID, 3 in. OD, and 72 in. length. Capacity of the test system is approximately 45 L/hr. Design working conditions are 350°C at 3400 psig.

As shown in Figure 7.1, the aqueous organic feedstock is either loaded into or prepared for processing in the feed tanks at the front end of the process. The feed is then pumped through the double pipe heat exchanger in which the process effluent is used to preheat the feed. Final heating is accomplished by passing the feed through the heating tube (H1) similar to the reactor units. After final heating, the feed is passed to the first reactor vessel (R1), and then either may pass through or bypass the second reactor (R2). Both reactors have ceramic external heating units used to keep the feed at the desired temperature. The effluent then passes through the shell side of the double pipe heat exchanger, and another small heat exchanger is used to lower the temperature of the feed with cooling water to protect the separator and the pressure control valve. The third heat exchanger, forced air operated, was not used in this run. The effluent is passed to a gas liquid separator, and the liquid portion is stored in tanks while the gas stream is analyzed and exits the system.

Standard construction materials were used to build the test system to simplify fabrication of a large-scale unit following a successful demonstration of the pilot-scale system. All tubing and connecting hardware are constructed of 304 or 316 stainless steel, providing for a working pressure of 3400 psig at 350°C. The residence time of the feed in the reactor can be controlled by varying the pump feed rate and by adjusting the effective reactor volume.

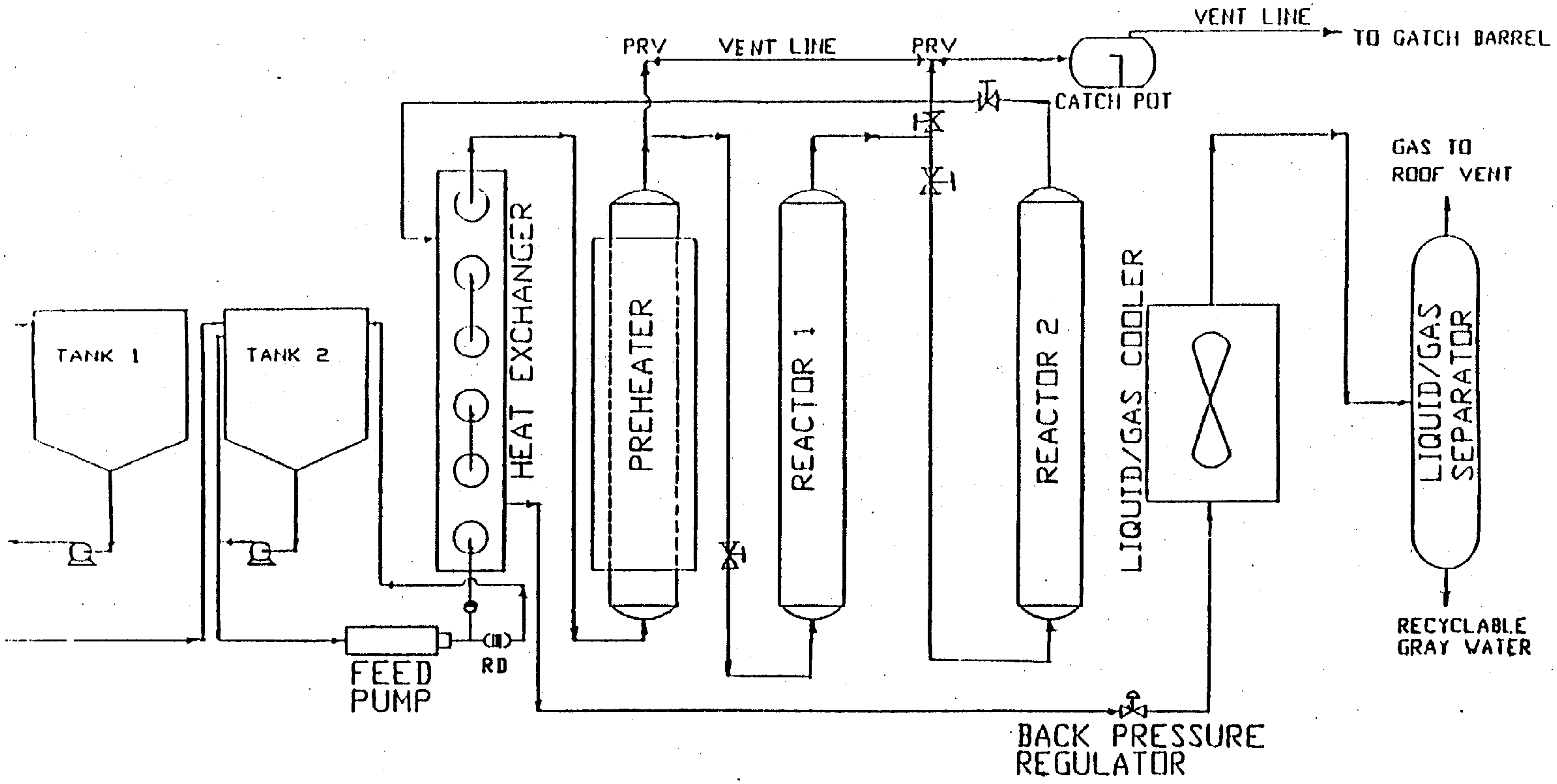

Figure 7.1. Schematic Diagram of the Scaled Up Reactor System

The effective volume can be decreased with the addition of inert stainless steel packing or by valving out R1 or R2. With the turndown range of the pump, the use of inert packing, and by valving out one of the reactors, the pilot plant can be operated at residence times ranging from 5 to 30 min.

7.3 Test Conditions

The pilot-scale testing was performed on a 101-SY tank simulant (SIM-SY1-93A) with tetrasodium ethylenediamine-tetraacetate (Na_4EDTA) as the primary source of organic carbon. The simulant composition was presented in Table 6.1.

The feedstock was prepared 5 days prior to the run to ensure the feed was well mixed. During preparation the simulant was diluted 1:1 with water because it was too viscous for the centrifugal pumps and they overheated. Twenty-four hours after initial preparation, the feed was further diluted to the 3:1 ratio (by volume) with water and continued to be recirculated until the run was completed. Approximately 400 L of feedstock were prepared.

The target run conditions outlined in the test plan were 3000 psig, 350°C, and a 10-min residence time for 24 hr. Actual run conditions were 2900 psig, 335°C, with an average 9-min residence for an 11-hr period at which the pilot plant was operated at a constant feed rate. To achieve these residence times, the heating tube and the reactor vessels were packed with inert stainless steel packing. The void volume of the heating tube and the first reactor was 41%. The second reactor, which contained a different inert packing, had a void volume of 29%.

The wall temperature of all the reactor vessels was not allowed to exceed 375°C to prevent possible precipitation of solids at 2900 psig. This temperature constraint resulted in an overall process temperature 15°C lower than the planned operating temperature of 350°C. Even though the process piping on the pilot plant was simplified prior to the run, heat losses from the tubing connecting the reactor vessels were significant. The temperature profile for the reactors is shown is Figure 7.2.

During the run several attempts were made to try to maintain a process pressure of 3000 psig; however, the backpressure regulator control was cyclic, varying about 150 psi. The regulator control was consistent until the pump speed was reduced from 13-14 L/hr to 11-12 L/hr to increase residence time for a better TOC conversion rate. This change was made about 11 hr into the run. Pressure control varied from very erratic to nonexistent as pressures fell to the vapor pressure of the liquids in the reactors. The reduction in flow, combined with an eroded valve stem seat and a possible system leak, made it impossible to re-establish steady-state operation the first day. Repair of the valve seat was attempted the first day, but in order to replace the seat, the pilot-scale system pump had to be stopped. The 15-min stoppage led to precipitation of sodium carbonate and eventual plugging.

The pilot-scale system run was initially suspended after the first day of operation, but was re-started about 4 hr later after the apparent elimination of the restriction in the reactors. The pressure control system was changed from a hand-loaded back-pressure regulator to a dome-loaded type, and water feed and heatup was resumed. After about 4 hr, temperatures and flow rates had

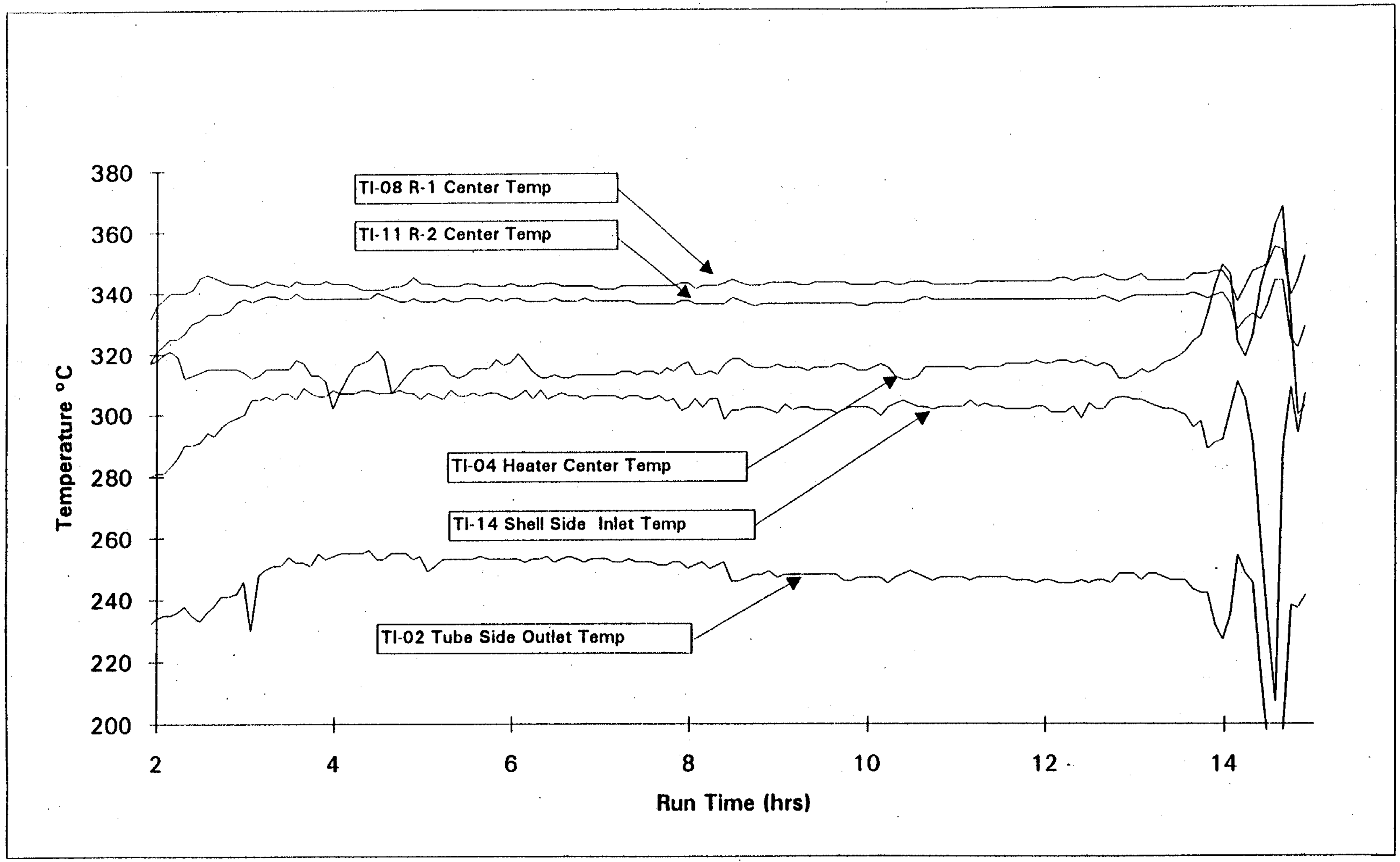

Figure 7.2. SRS504.R1 Temperature

stabilized and simulant was re-introduced to the system. The temperatures were maintained in the same range as the previous day; however, 2 hr after the simulant flow was re-started, plugging again occurred. The system was restricted and unplugged several times by altering temperatures and flow rates. After a several hours of feed rate and pressure fluctuations, it was apparent that steady-state operation would not be re-established due to precipitation of solids remaining in the reactors and a steam leak on top of H1 (heating tube). The pilot-scale system was cooled and flushed with water for shutdown.

7.4 Results and Discussion

Operational and chemical steady state was achieved approximately 6 hr after simulant was introduced into the system. The products remained constant for 4.5 hr until operating conditions were changed and the pressure control problems developed. The operating conditions during steady state were an average reactor temperature of 330°C, 2850 psig, and a 10.4-min (13 L/hr flow rate) residence time. The reactor temperature is an average of all the internally measured temperatures through both R1 and R2, which ranged from 321°C to 349°C. The analytical data are given in Table 7.1.

Table 7.1. SRS Steady-State Analytical Data

	Liquid Effluent						Process Offgas		
Time	COD ppm	pH	NH_3 ppm	TOC ppm	NO_2 ppm	NO_3 ppm	H_2 %	N_2O %	N_2 %
Feed	25000	12.6	–	4810	33700	41200	–	–	–
20:30	10700	12.6	1520	1800	23700	40100	54.7	26.2	19.0
21:00	9740	12.6	1780	1730	23600	39900	50.4	35.9	13.6
21:30	10100	12.8	1580	1730	23900	40800	53.6	27.6	19.7
22:30	9740	12.5	1750	1750	24200	40700	51.9	25.1	23.0
23:00	10300	12.6	1770	1710	23900	40200	49.2	34.1	16.6
23:30	10300	12.6	1740	1670	23800	40700	47.0	38.9	14.0
24:00	9480	12.4	1870	1590	23100	40800	46.2	42.4	11.3
01:00	9740	12.2	2120	1600	22700	39700	49.5	33.6	16.8
Avg.	10000	12.6	1770	1700	23600	40400	50.6	31.9	17.5

Avg. Temperature = 330°C.
Avg. residence time = 10.4 min.
EDTA conversion = 69.8%.
TOC conversion = 64.7%.

The results from the pilot-scale test support the predictive products given in the three reactions shown in Section 6.4.2. When comparing bench-scale system runs at similar conditions and/or conversions, several conversion indicators are the same. Table 7.2 compares the products of three bench-scale system runs and the nitrite destruction with respect to moles of EDTA consumed.

In general, the pilot-scale system results and the bench-scale system results given in Table 7.2 are in good agreement. In the experiments conducted in FY 1993, it has been observed that an average 0.78 mole of nitrite is consumed for every mole of EDTA carbon that is destroyed (see Schmidt et al. 1993 and Section 6.6). The pilot-scale system experimental results were the same with respect to nitrite destruction and quantity of gas and oxalate produced per mole of EDTA consumed. As in the bench-scale system experiments, there were very low levels of nitrate destruction.

The same gas species (H_2, N_2O, and N_2) were produced during the pilot-scale run, although the relative concentrations of H_2 and N_2O were the opposite of what had been typically seen in bench-scale runs. Normally, the concentration of N_2O is greater than H_2 in the majority of the bench-scale system tests. However, there have been instances where the main gas component is H_2 in some of the runs conducted below 330°C. The total liters of gas produced per liter of simulant fed averaged approximately 3.2 L, which agrees favorably with several bench-scale runs that had a 60% to 70% TOC conversion. Figure 7.3 shows the relationship of liters of gas produced and TOC conversion.

The TOC destruction with respect to residence time and temperature is consistent with previous bench-scale system data. Figures 7.4 and 7.5 reflect that the 69% TOC destruction achieved in the pilot-scale system was predictable given the run conditions.

The rate constant for the pilot-scale run was calculated using the integral method for a second-order reaction. The reaction assumed for this system is given by Reaction 1. The development work for the kinetics analysis was given in the Section 6.4.2. Table 7.3 compares the rate constants from two 325°C bench-scale system runs with the constant calculated from the pilot-scale run data. The values are in good agreement with one another.

Table 7.2. CRS/SRS Reaction Chemistry

Run	Moles Gas Produced/ Moles EDTA Consumed	Moles Oxalate Produced/ Moles EDTA Consumed	Moles NO_2 Consumed/ Moles EDTA Consumed
CRS R1 B	0.342	0.035	0.706
CRS R3 A	0.320	0.064	0.730
CRS R4 B	0.332	0.055	0.875
SRS R1	0.383	0.037	0.785

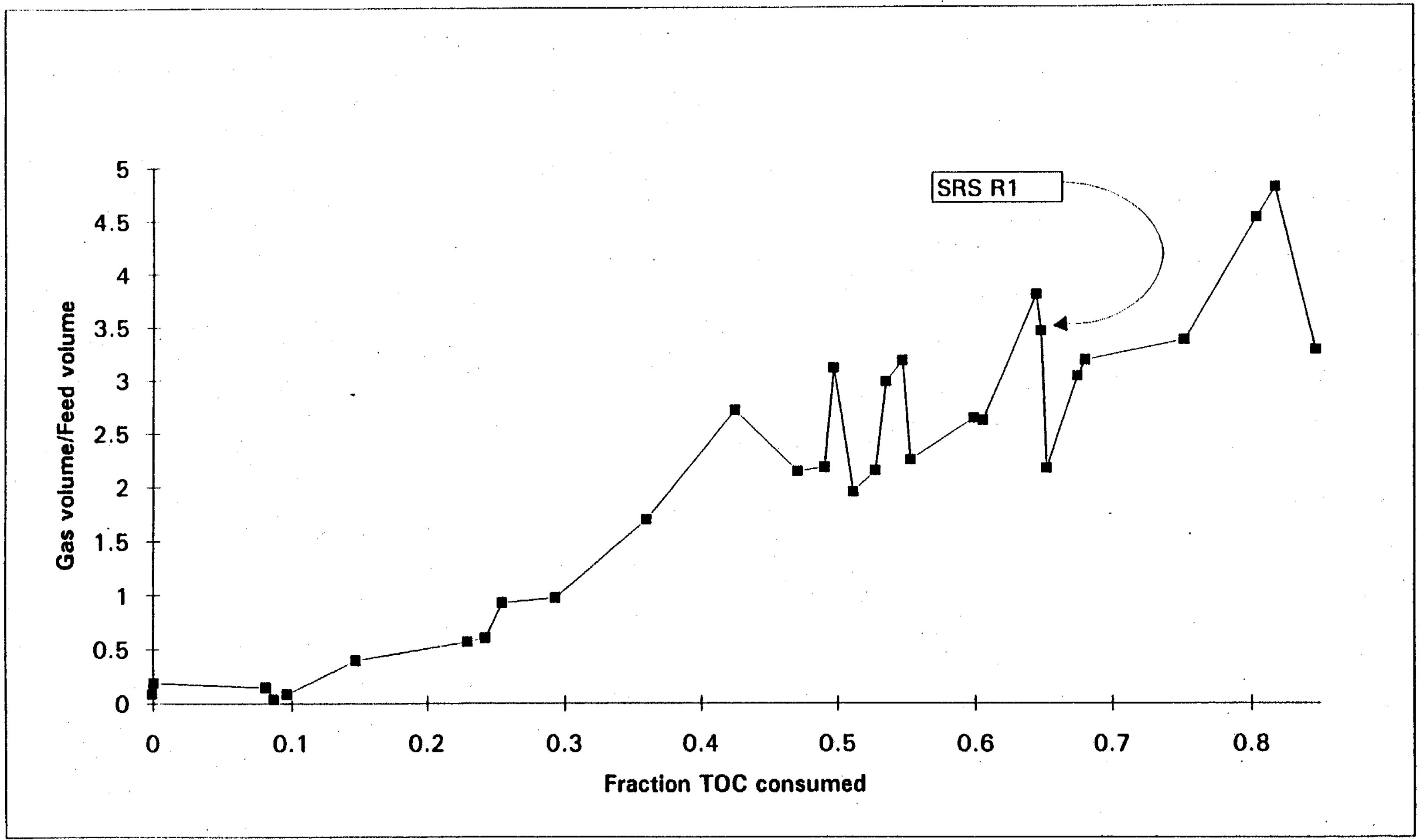

Figure 7.3. Gas Volume/Feed Volume vs. TOC Consumed

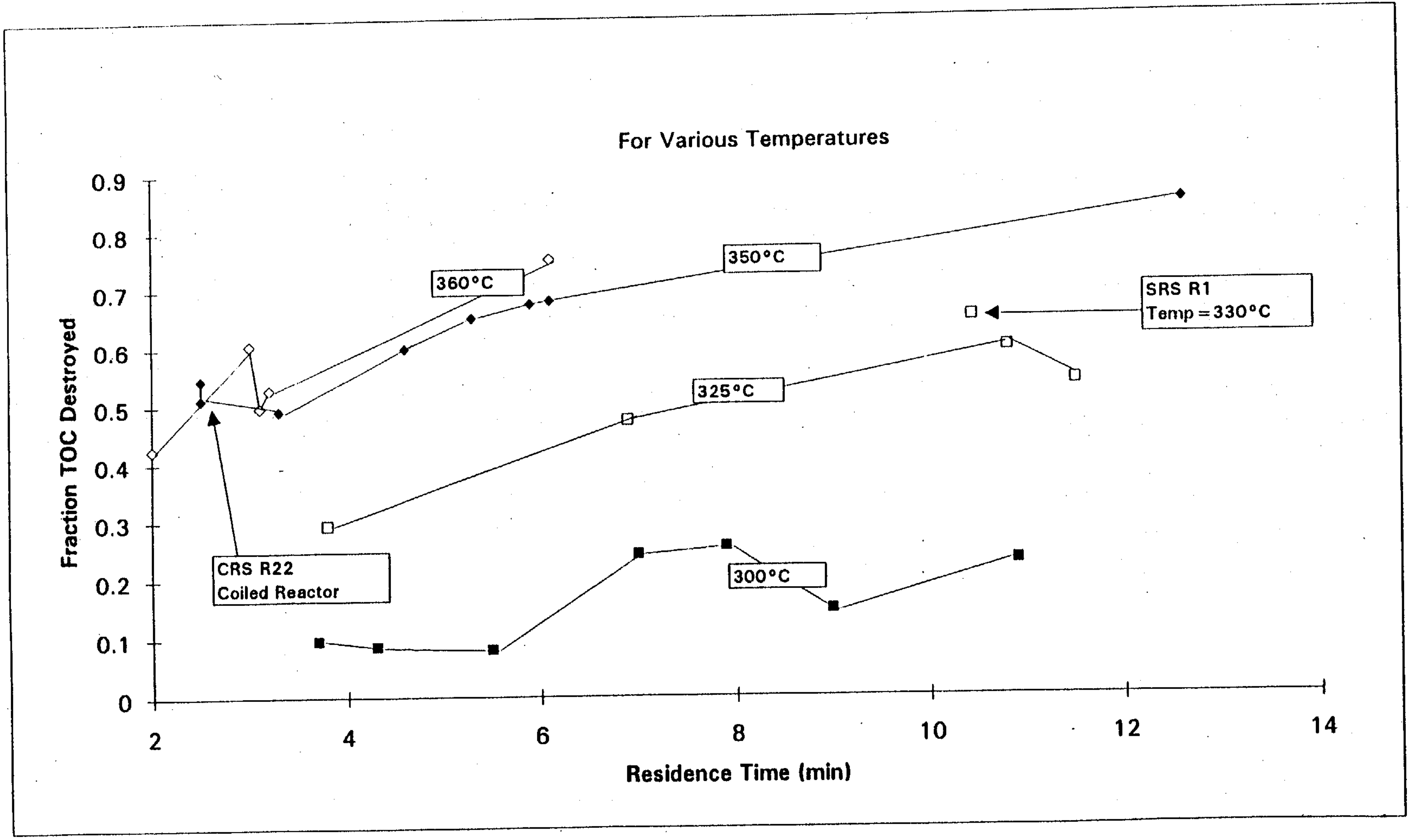

Figure 7.4. TOC Destruction vs. Residence Time

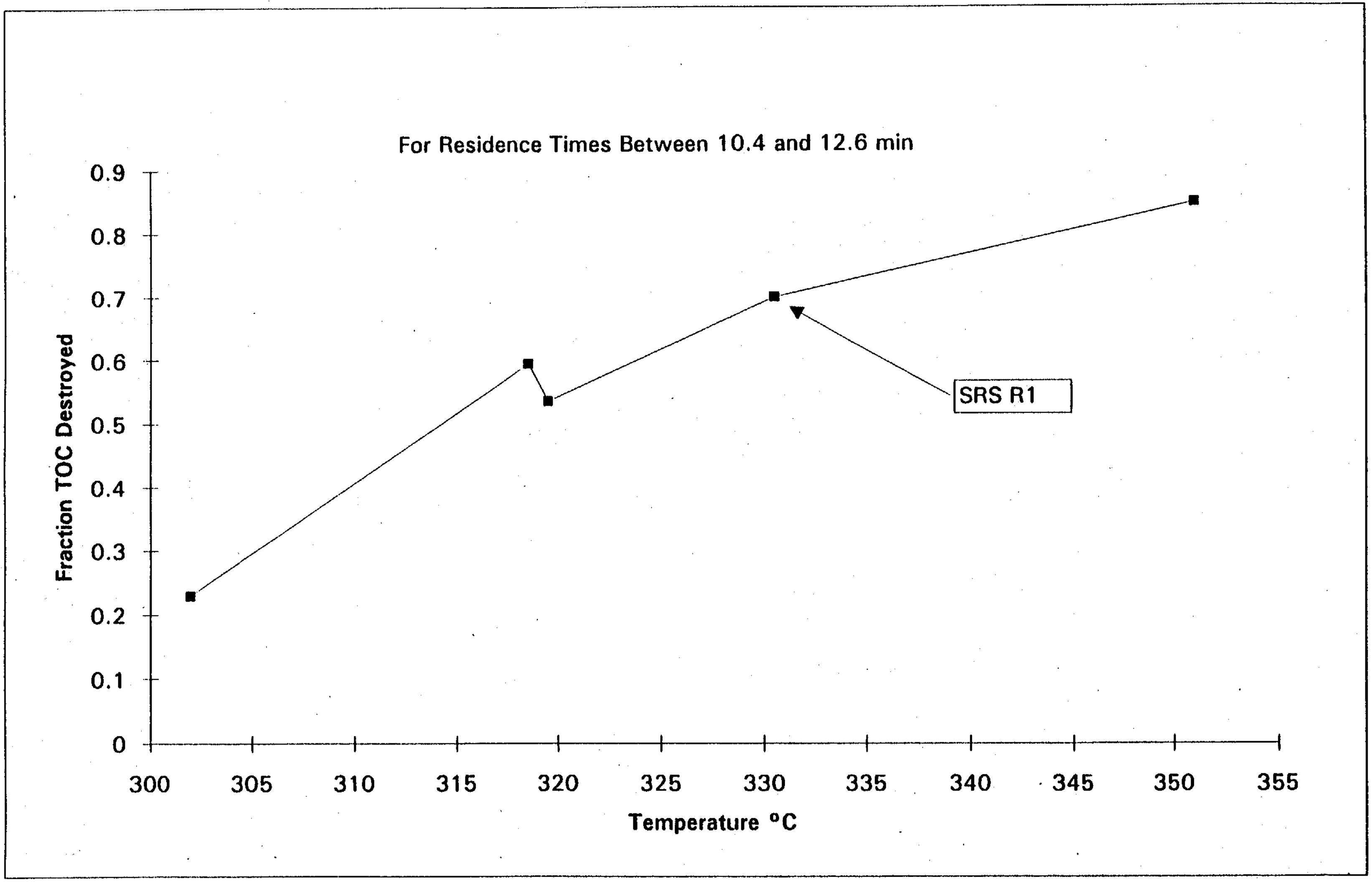

Figure 7.5. Conversion of TOC vs. Temperature

Table 7.3. CRS/SRS Rate Constants

Run	Rate Constant
CRS R3 A	3.4E-06
CRS R3 B	3.1E-06
SRS R1	3.6E-06

An Arrhenius plot was constructed to confirm that the rate constants calculated from bench-scale system temperatures correlate to the pilot-scale system value. Several data points from the bench-scale runs were compared with the pilot-scale run. Table 7.4 contains the tabulated data and Figure 7.6 shows the Arrhenius fit of the pilot-scale system data. As can be seen, the pilot-scale data point is in good agreement with that predicted from the bench-scale data.

Using the kinetic model derived from the bench-scale system data, an expected conversion of EDTA can be predicted given the temperature, residence time, and the initial reactant concentrations in any reactor. The actual conditions of the pilot-scale run for these parameters were as follows: temperature, 331°C; residence time, 10.4 min; initial EDTA conc., 4810 ppm; and initial NO_2 conc., 36,700 ppm.

From the bench-scale system data and the Arrhenius equation, an activation energy, E = 24.7 kcal/mol and pre-exponential factor A = 2950 1/ppm-min, were calculated. A rate constant of 3.3E-06 1/ppm-min was calculated for the 330°C pilot-scale system run. Using this rate constant and solving the integrated rate expression for the final EDTA carbon concentration, the predicted EDTA carbon conversion for the pilot-scale run is 66.9%, which compares to the measured value of 69.8% EDTA carbon conversion.

Table 7.4. Arrhenius Plot Data Points

Run	Temp. (K)	k2 1/ppm-min	1/T	ln(k2)
CRS R2 A	578	1.2E-06	0.00173	-13.65
CRS R2 B	578	1.1E-06	0.00173	-13.68
CRS R3 B	598	3.1E-06	0.00167	-12.69
CRS R3 A	599	3.4E-06	0.00167	-12.59
SRS R1	604	3.6E-06	0.00166	-12.62
CRS R4 B	623	6.6E-06	0.00161	-11.93
CRS R4 A	624	6.7E-06	0.00160	-11.92
CRS R1 B	633	8.9E-06	0.00158	-11.63
CRS R1 A	636	8.2E-06	0.00157	-11.71
CRS R1 C	641	1.0E-05	0.00156	-11.42

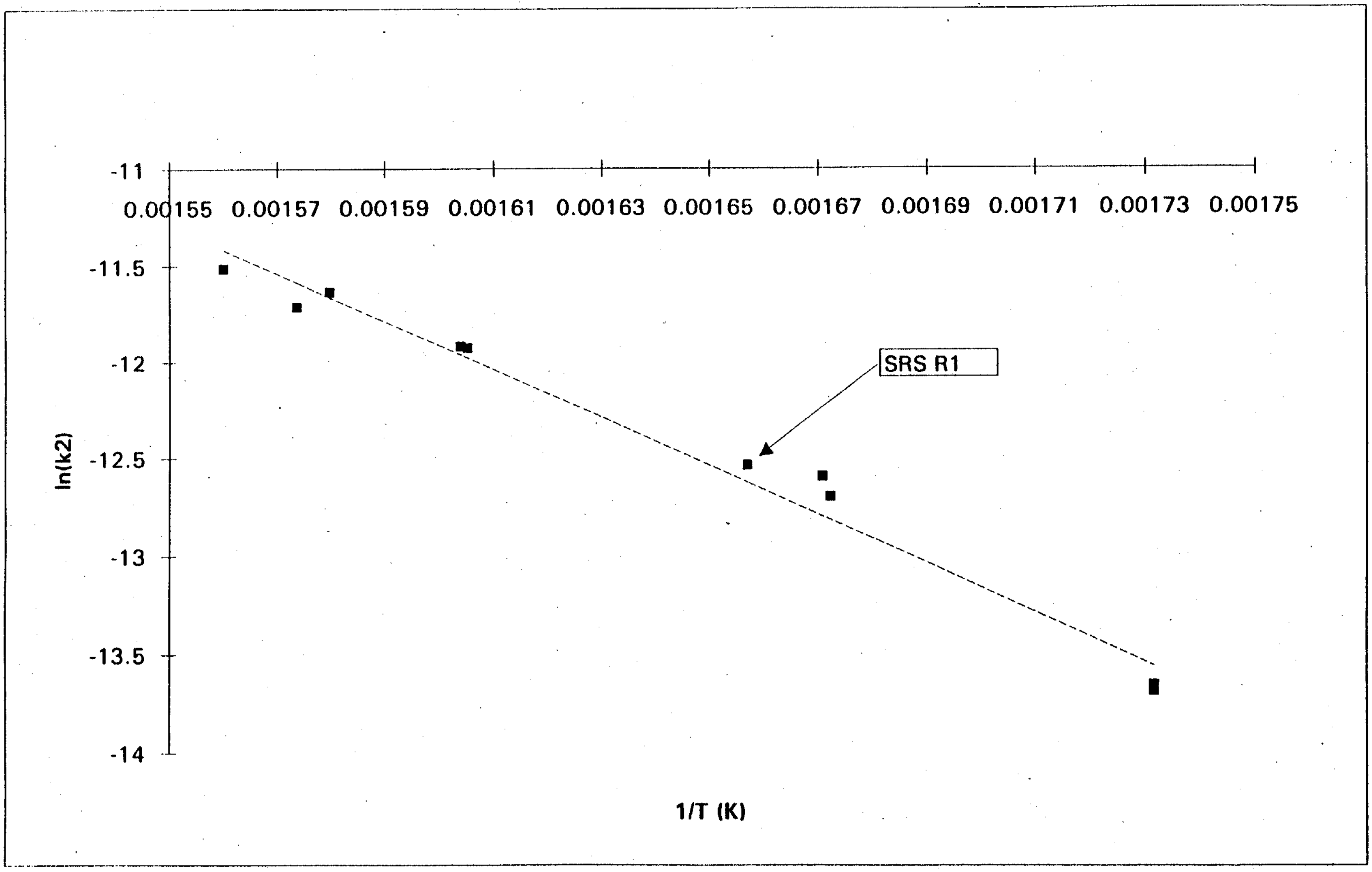

Figure 7.6. Arrhenius Plot

7.5 Conclusions

The kinetic analysis presented here confirms the applicability of bench-scale system data to larger-scale processing of the same simulant under similar process conditions. The reaction rates, conversions, and products are very predictive using the kinetic models developed from the bench-scale test results.

There were several observations made during the pilot-scale test that will be useful for design and operation of a large-scale processing unit. First, when restrictions or plugging occur, lowering the reactor temperatures generally allows the solids to go back into solution and move through the system. Due to the erratic pressure control that started about 11 hr into the run, several opportunities allowed this theory to be tested. When the pressure fluctuated, the flow rates became erratic. This led to partial plugging in R1 and R2 when the reactor temperatures exceeded about 360°C. Temporarily turning off the furnaces and/or increasing the pumping rate reduced the reactor temperatures and eventually unplugged the system. Experience from bench-scale runs has shown that switching to a water feed will also clear a partially restricted reactor.

It is imperative that any reactor system have a reliable constant-flow pumping system and a very stable pressure control device to ensure steady operating conditions. In the event of a restriction, there must be a mechanism to reduce reactor temperatures or to directly introduce water or another flushing medium into the reactor stream. Reactor velocities are most likely an important consideration to keep the solids in solution. However, no substantial data have been obtained to confirm this hypothesis.

7.6 Directions of Future Testing

At this time no plans have been made to conduct another pilot-scale run in the SRS. Current tests with a bench-scale system are being performed to investigate higher reactor temperatures, pressures, and velocities. The SRS pilot-plant cannot be operated at significantly higher temperatures and pressures without a major reconfiguration of the system.

7.7 Reference

Schmidt, A. J., E. O. Jones, and R. J. Orth et al. 1993. "Preliminary Conceptual Design for the Destruction of Organic/Ferrocyanide Constituents in the Hanford Tank Waste with Low-Temperature Hydrothermal Processing." PNL-SA-23181, Pacific Northwest Laboratory, Richland, Washington.

PNL-10108
UC-721

Distribution

No. of Copies

OFFSITE

12 DOE Office of Scientific and Technical Information

ONSITE

3 DOE Richland Operations Office

S. T. Burnum	S7-53
R. L. Higgins	S7-54
P. E. Lamont	S7-53

5 Westinghouse Hanford Company

S. A. Barker	G3-20
W. B. Barton	L4-75
R. A. Kirkbride	L4-75
M. J. Klem	L4-75
R. M. Orme	L4-75

No. of Copies

28 Pacific Northwest Laboratory

C. R. Allen	P7-43
E. G. Baker	P8-38
L. R. Bunnell	P8-44
C. D. Carlson	P7-25
M. R. Elmore	P8-30
L. K. Holton	P7-43
B. M. Johnson	K1-78
E. O. Jones	K3-75
D. E. Kurath	P7-43
J. P. LaFemina	K2-12
R. J. Orth (5)	P8-30
G. J. Sevigny	P7-33
A. J. Schmidt (5)	K3-75
A. H. Zacher	K3-75
Publishing Coordination	
Technical Report Files (5)	