NISTIR 4920

PROCEEDINGS

Workshop on Federal Programs Involving Supercritical Water Oxidation

6-7 July 1992

Editor
Gregory J. Rosasco

U.S. DEPARTMENT OF COMMERCE
Technology Administration
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September 1992

U.S. DEPARTMENT OF COMMERCE
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TECHNOLOGY ADMINISTRATION
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WORKSHOP ON FEDERAL PROGRAMS INVOLVING SUPERCRITICAL WATER OXIDATION

July 6 - 7, 1992

National Institute of Standards and Technology
Gaithersburg, MD

EXECUTIVE SUMMARY

Background

This Workshop on Federal Programs Involving Supercritical Water Oxidation was a follow-on to previous informal meetings held to discuss work in this area. The first was held at the Naval Civil Engineering Laboratory, Port Hueneme, CA in March 1990 and the second at Tyndall Air Force Base, FL in April 1991. As with past meetings, the focus of this Workshop was primarily programmatic not technical. Attendance at these meetings was by invitation, and by and large the list was determined by consultation with the Federal agency participants. To our knowledge all Agencies with a recent involvement in SCWO related technology were contacted. We received correspondence and information from a number of individuals or laboratories who were not able to attend either because of scheduling difficulties or requirements resulting from active contract negotiations. Input relevant to their interests was included in the presentations except in the case of the Environmental Protection Agency. In this regard, Mr. Ron Turner of the Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, OH informs us that an Engineering Bulletin on Supercritical Water Oxidation will be issued soon.

Content of these proceedings

The proceedings include the following:

- List of the attendees, their addresses and phone numbers
- Copies of the speakers' viewgraphs. Some speakers submitted additional material which also is included.
- an SCWO Track Chart which summarizes some of the organizations involved in SCWO technology development and their activities

The last item is derived from a viewgraph originally presented by Mr. Anthony Rodriguez of the Carderock Division of the Naval Surface Warfare Center. We circulated copies of this viewgraph for mark-up and return by the participants. However, the response was somewhat spotty. Therefore, while informative, this SCWO Track Chart is not all-inclusive either with regard to the participants or the nature of the activities in this field.

Panel Discussion of Technical Challenges

The final session in the Workshop was a Panel Discussion titled Technical Challenges in SCWO Implementation. The panel was composed of individuals who had personal familiarity with the design, development, operation, or evaluation of a SCWO reactor system (either direct hands-on experience or experience gained as a contract monitor). The panel did an excellent job in summarizing some of their experiences and concerns and in answering questions from the audience (which participated in the discussion at a very high level).

There was no attempt to arrive at a formal consensus in terms of "technical challenges". However, many participants stressed the importance of a number of topics (in priority order as judged from the amount of discussion and a review of the taped proceedings):

1. materials performance (corrosion)

2. salt separation and reactor plugging

3. scale-up:

    safety

    economics-

        energy costs
        equipment costs
        maintenance costs

    lack of understanding, data, and validated models-

        materials performance
        phases (including kinetics of phase separation)
        chemical kinetics

More detail concerning these topics will be presented below in an assessment of the research needs. However, first we note the absence of concern with respect to the destruction/removal efficiency (DRE) of the SCWO process for the waste materials of interest to the supporting agencies. This reflects the fact that the support for development of SCWO technology to this point has focussed principally on laboratory demonstrations of adequate DRE's for the agency-relevant compounds. (In this context, it was observed by a number of participants that the successful demonstrations for agency-relevant wastes provide useful information which supports the use of this technology for treatment of a wide range of industrial, biological, and pharmacological waste streams.)

Further, we note that it is the view of most of those who have been involved in the development of SCWO that this is a technology "ripe for a successful demonstration project". This explains the fact that the current focus of the funding is on the construction of pilot facilities (two of these are in the 1000 gal/day range). These facilities are seen as test beds critical for technology evaluation. Successful operation was seen as the enabler for an effort to select (or design) optimum technologies and for scale-up to even larger facilities (50,000 gal/day range facilities were discussed). The latter efforts, it was implied (hoped), would include work to enhance our understanding to a level commensurate with design goals, in terms of destruction efficiency, energy usage, reliability, throughput, safety, facility life-cycle, and maintenance. It was acknowledged that a firm basis for identifying and selecting technological alternatives and designing optimized SCWO reactors needs to be developed before this promising chemical process can be successfully deployed. While there are many uncertainties with respect to scale-up, there were consistent reports from many participants that the economics of SCWO-based remediation for a wide-spectrum of waste streams (including common industrial and municipal wastes) are very favorable.

Finally, we observe that a number of participants pointed out that the technical challenges enumerated above persist as major concerns in spite of claims by commercial proponents of the technology that these problems or issues have been "resolved". This observation led to the conclusion that there is a need for better communication among those involved in SCWO technology and that many problems are shared by all interested parties and thus there can be and should be common solutions to these problems.

Research to Address Technical Issues

In the following we summarize in more detail the discussion of the technical issues and the associated research needs which came up during the Workshop and in particular during the Panel session. Materials performance concerns focussed primarily on corrosion of the metals used for construction of these high pressure reactor vessels. There was also some discussion of designs based on corrosion resistant thin liners, e.g. gold, or coatings and designs based on having sacrificial sections in the reactor, which would be made of inexpensive materials replaced on a regular basis, and also of hybrid constructions using metals, elastomers, and ceramic liners. It is accurate to observe that little is known about materials performance in these types of environments. Further, it should be remembered that typical reactor systems provide a very large range of corrosion environments including regions with large chemical, thermal, and phase gradients along with conditions which could lead to stress corrosion cracking and fatigue. High density, high dielectric constant conditions with large ion concentrations are encountered as are conditions in the gas phase with strong oxidative chemistry in progress. Halides and sulfates are common and carbonates are ubiquitous in these systems. The presence of salt layers associated with phase separation and the possibility of surface catalyzed reactions also were considered important. In spite of these complexities, there were strong sentiments that the problems were not insurmountable. There appeared to be universal agreement that systematic studies were required and that microscopic examination and in situ characterization would be invaluable.

In designing large-scale reactors, information will be required about the location of the fluid-fluid and especially the fluid-solid phase boundaries. Crossing a phase boundary causes a phase separation which, in fact, is a vital aspect in the selection of SCWO technology for many of the agency-relevant wastes streams. However, fluid-solid phase boundaries, if encountered in the wrong region of the reactor also can lead to the observed reactor plugging by deposition of solids. Fluid-fluid phase boundaries will lead to the formation of brines which can greatly enhance corrosion as can the formation of salt layers. The kinetics of phase separations affects the carry-over of salts in the effluent stream. Phase behavior is thus intimately connected to the salt separation and reactor plugging issues. It is also important to the chemical behavior of the system. The formation of multiple phases in these inherently multicomponent streams can lead to demixing of reactants and reductions of efficiency. There was some speculation that demixing could lead to potentially dangerous reactant compositions (e.g. hot spots associated with hydrothermal flames and even the possibility of explosive conditions were discussed).

The NIST experts in this area stressed that modelling of phase separation in binary and multicomponent solutions is quite feasible; however, there currently is no modelling effort focussed on the conditions important to SCWO technology. The experts agree that validation by direct observation of phase separation in representative systems is a necessity. Thermophysical property data, enthalpy, density, viscosity, diffusivity, etc., are required for the design of all aspects of preparation of the reactants, the dimensions of reaction sections, and for design of heat recovery and cool down systems. There are few data available for the multicomponent systems of interest to SCWO; however, the prospects of developing a useful model appear good.

We are still lamentably lacking in understanding of the chemistry in a SCWO reactor. By and large, microscopic chemical kinetic models based on radical mechanisms have not been successful in predicting the observed destruction efficiencies. The large range of conditions encountered in typical flow reactor systems raises many important questions with respect to the chemistry. Catalytic effects associated with metal surfaces have been observed; however their contribution to the overall process efficiency is not understood. Conditions for both radical and ionic chemistry are encountered in typical process streams; the importance of each is not known. Stabilization against pyrolysis has been observed, but there is no basis for predicting behavior for the many systems of interest to this technology. It is difficult to specify the important process parameters, concentrations of reactants, temperatures, residence times, and perhaps even pressure, so as to warrant optimal performance in terms of DRE's, energy, and materials performance. In anticipation of this lack of predictive capability, practitioners are forced to design reactors that operate for longer residence times or at more extreme conditions of temperature with the potential for higher cost and higher risk.

All the above topics become increasingly more important as we talk about scale-up to either continuously operating or larger throughput systems. The risks also increase as we push in these directions. There is still a sense within the community that a major failure, either in terms of meeting DRE goals, or economic efficiency goals, and especially in terms of safety would do great harm to the future of this very promising technology. The need to understand the process and the processing system, in terms of materials behavior, phase behavior, or chemical behavior, came up over and over again each time the issues of failure avoidance and wide-scale deployment were raised.

It was clear that SCWO processing holds great promise for waste treatment. As mentioned above, there is substantial confidence in the success of the pilot facilities currently under construction. It is hoped that these successes will provide the basis for the important scientific and engineering studies needed to translate this technology into a reality for safe, efficient hazardous waste treatment.

SCWO TRACK CHART

ORGANIZATION	REQUIREMENT / TASKING	STATUS
CDNSWC Shipboard Waste Processing	Shipboard System Design Destruction of Shipboard Waterwaste	FY 92 1.0 gph Shipboard Wastewater Reactor SCWO Component Test Platform Heat Transer; HP Pump; Air Booster Pump
NCEL Industrial Waste Processing	Destruction of Naval Industrial Site Wastes Waste Characterization, Market & Economic Analyses, Bench Scale Experimental System	FY 93 1.0 gph Hazardous Waste Reactor Salt Separator, Hot Gas Recycle Loop
NASA Space Station Application	Space Station Life Support System Analysis Trade-Off Analysis and Numerical Modeling Zero & Micro Gravity System Design	Conducted Space Station Desgin Tradeoff Analysis Conducted SCWO Waste Destruction Modeling Fabricating Micro Batch Reactor
USAF Funding Organization	Solid Rocket Fuel Destruction	Funded Los Alamos To Conduct Destruction Study & Modeling
DARPA Funding organization	Waste Ordnance Disposal >1000 gpd Pilot Plant Demonstration	Funded FY 92 Contract for Military Ordnance Disposal, and HW: General Atomics & Subcontractors
Los Alamos National Lab. Technology evaluation	Hazardous waste destruction tests Kinetic Experiments	1.0 gph Kinetic Reactor Gas Phase Kinetic Model
Sandia National Lab. Engineering Evaluation and Technology Advancement	Hazardous Waste Processing, Fundamental Kinetic Experiments, Optical Diagnostics Development	1.0 gph Materials Evaluation Reactor Hydrothermal Flame Research
Army Research Office University Research Initiative	Environmental Sciences/Chemical Reactors Chemistry of Water near Critical Point	Massachusettes Inst. of Technology Univ. of Delaware Univ. of Texas, Austin
Univ. of Texas Treatability Studies	Low Temp. Destruction of Industrial Wastes Low Temp. Destruction of Municipal Wastes	Micro Batch Reactors 2 gph Treatability Flow-Through Reactor
MODEC Commercial Development	Site Remediation: Destruction of HW	100 cc/min Kinetic Reactor
Lummus Crest-MODAR Commercial Development	Site Remediation: Destruction of HW	10-Inch Vessel Plug-Flow Reactor Water-Wall Reactor Concept
ECO Waste Tech. Commercial Development	Destruction of HW at Low Temperatures	40 gph Hazardous Waste Reactor
NIST Thermophysical & Thermochemical Properties; Reaction Kinetics; Materials and Corrosion	Treatment of Industrial Wastes, Efficiency studies, Corrosion studies, Optical measurements at SCWO conditions	Developing understanding and engineering models Developing computerized data bases
Office of Industrial Technology **Department of Energy**	Energy recovery from wastes	Funded MODEC, MODAR and Stone Webster

CHEMICAL REACTIONS OF NITROGEN CONTAINING COMPOUNDS IN SUPERCRTICAL WATER

Workshop on Federal Programs involving
Supercritical Water Oxidation

National Institute of Standards and Technology

Gaithersburg, Maryland, July 6, 1992

Steven J. Buelow
Los Alamos National Laboratory
(505) 667-1178

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SCWO RESEARCH AT LOS ALAMOS

- DOE

  Destruction of organics and ferrocynides
  Reduction of nitrates to nitrogen
  Separation of salts
  Oxidation of organics in supercritical CO2
  Destruction of PBX explosives
  (9404, 9501, 9502)

- Air Force

  Destruction of propellants

- Army

  Destruction of scrap explosive material

Los Alamos

LANL PROJECT PERSONNEL

J. H. Atencio	S. J. Buelow	D. A. Counce
P. C. Dell'Orco	B. R. Foy	R. D. McFarland
W. J. Parkinson	J. M. Robinson	P. E. Trujillo
G. K. Anderson	G. T. Baca	G. A. Buntain
W. D. Breshears	G. R. Brewer	R. L. Brewer
R. B. Dyer	K. A. Funk	D. M. Harradine
J. L. Lyman	R. E. McInroy	L. R. Pratt
J. A. Sanchez	T. Spontarelli	D. A. Masten
P.A. Wisnewski	H. K. Eaton	R. T. Reynolds

PROJECT SPONSORS

U.S. Air Force Civil Engineering Support Agency
Department of Energy Office of Technology Development
U.S. Army Civil Engineering Research Laboratory

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COLLABORATORS/SUBCONTRACTS

Jimmie Oxley New Mexico Institute of Mining and Technology
Thermal hazards of energetic materials

Dudley Herschbach Harvard University
Equation of state for SCW mixtures

David Ross SRI International
Chemistry of explosive in subcritical water

Anthony Arrington Furman University
Nitrate Reactions

Earnest Gloyna Univesity of Texas-Austin
Salt solubility

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PROGRAM GOALS

- Efficiency of destruction.
- Products contained in effluent.
- Can process be safely scaled up?
- Is energy recovery possible?

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RESEARCH ACTIVITIES

Kinetics experiments	Process design
Kinetics modeling	Process control
Radionuclide chemistry	Process modeling
Equation of state data	Preprocessing
Equations of state	Safety analysis
Salt solubility data	Corrosion
Optical diagnostics	Chemical analysis

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EXPERIMENTAL METHOD

- Flow reactors: interchangeable metal liners
- Temperatures: 400°C to 600°C
- Pressures: 23 MPa to 35 MPa
- Oxidizer: Hydrogen peroxide or oxygen
- Complete analysis of effluents

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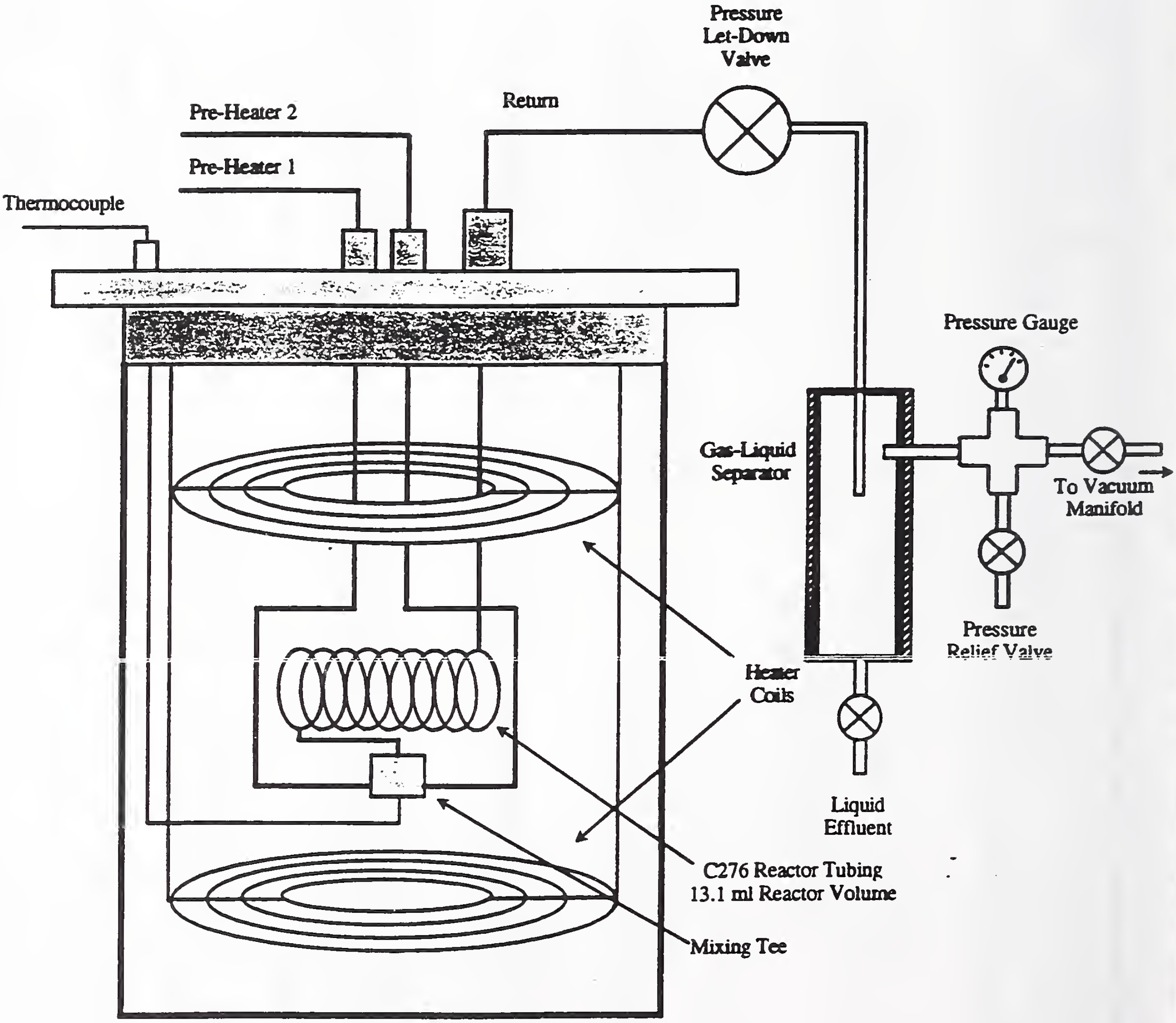
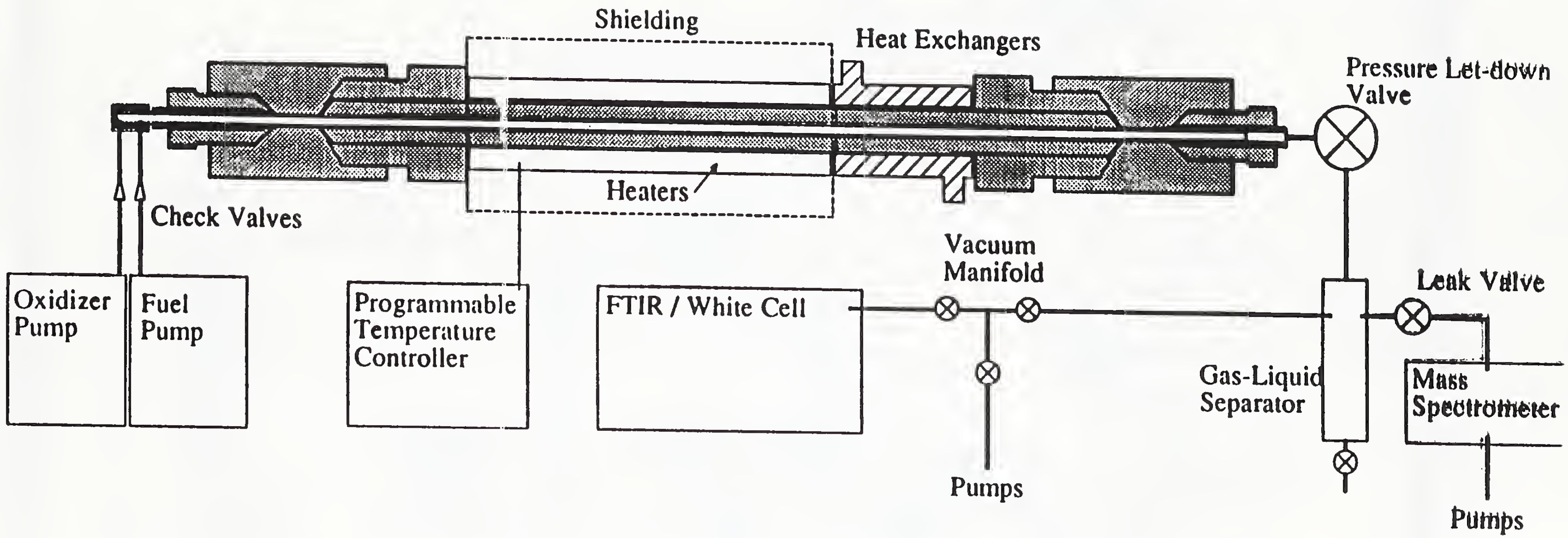
Tubular Flow Reactor



Fluidized Sand Bath



Linear Flow Reactor with Interchangeable Liners

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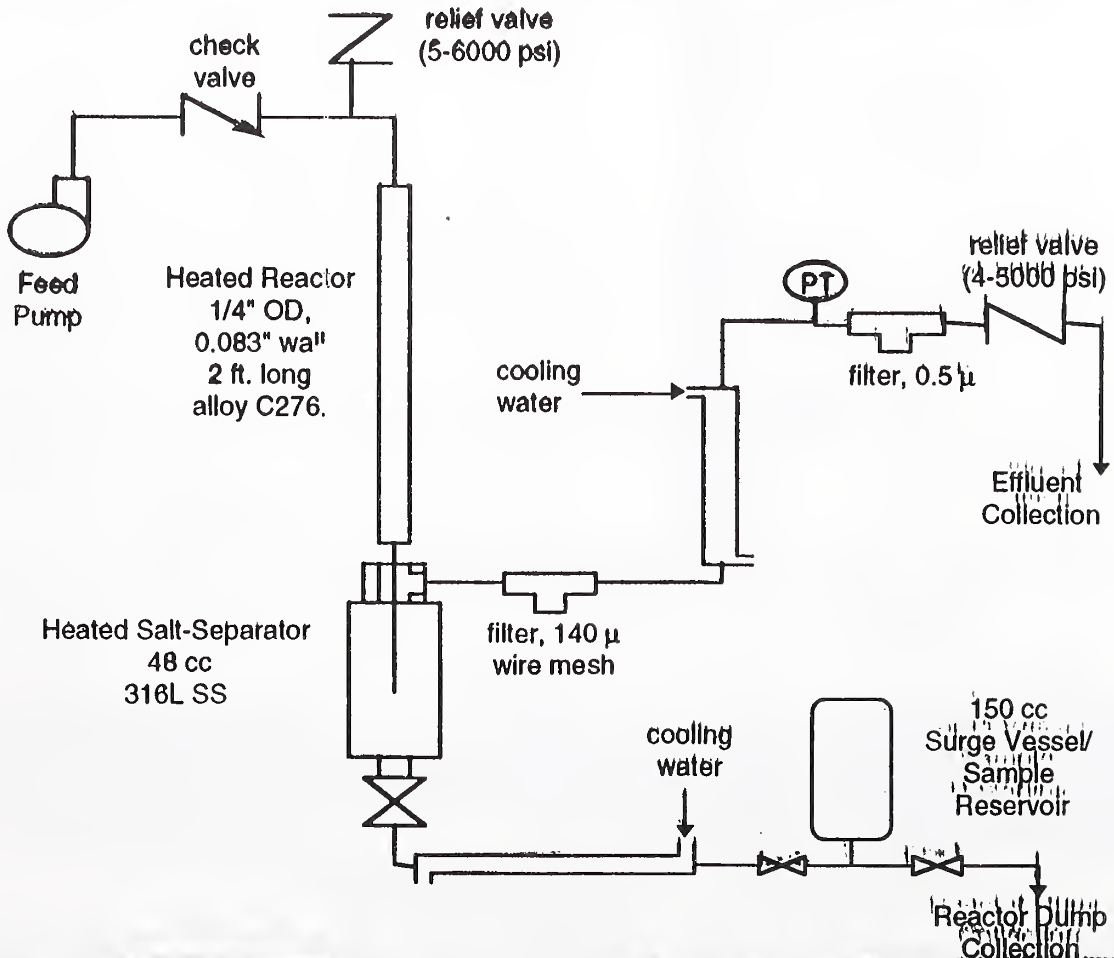
SCWO REACTOR WITH SALT SEPARATOR



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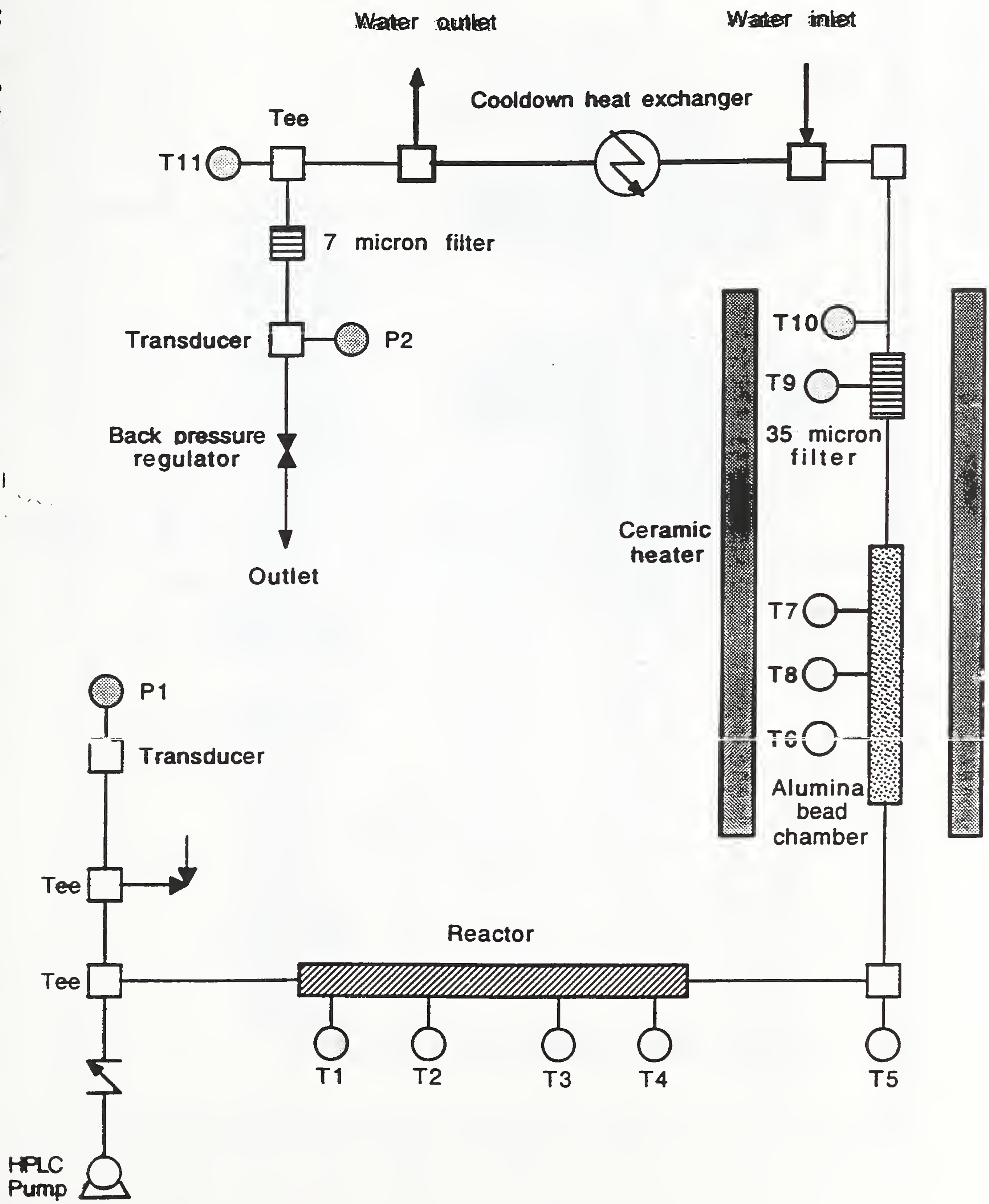
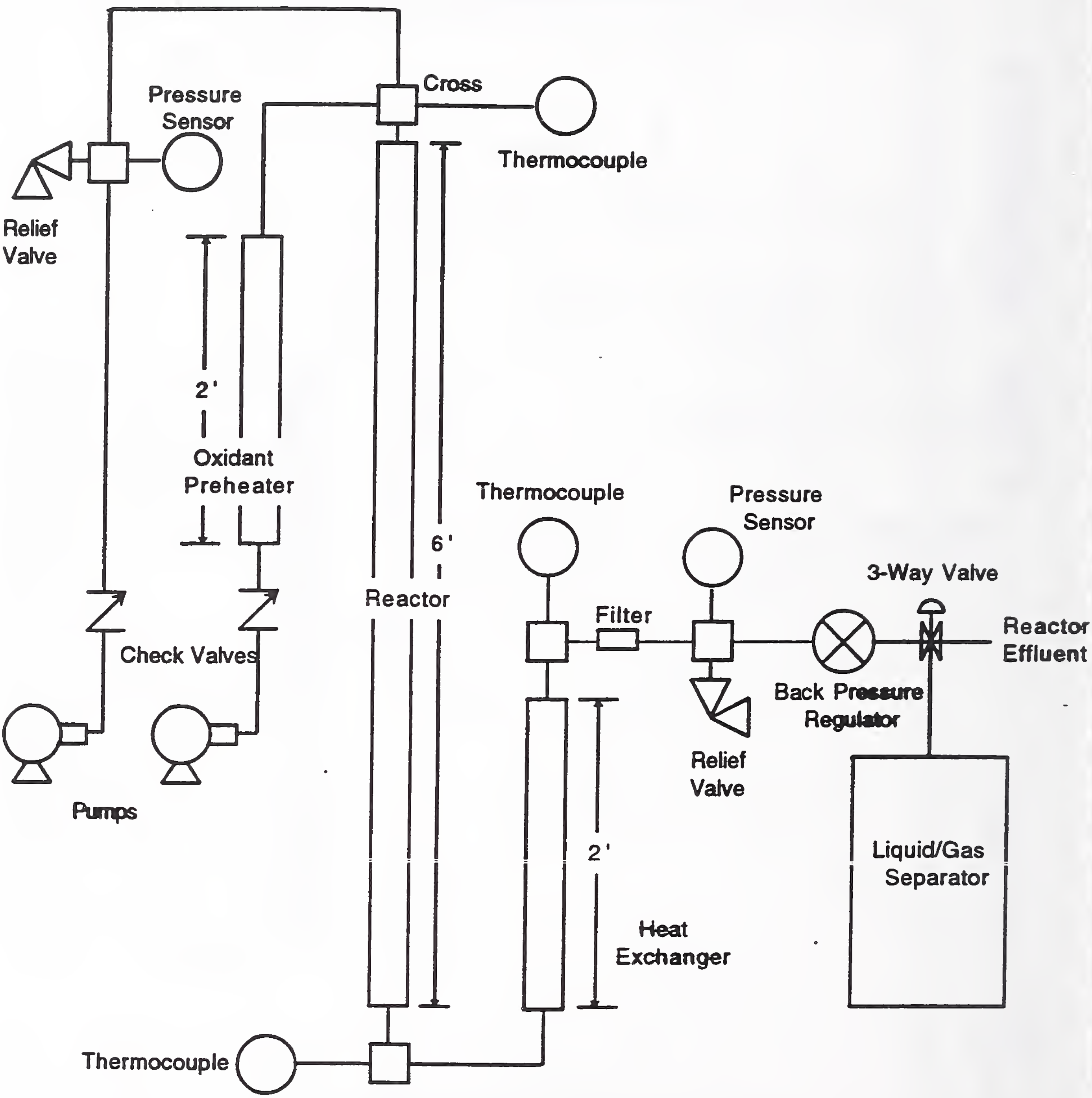
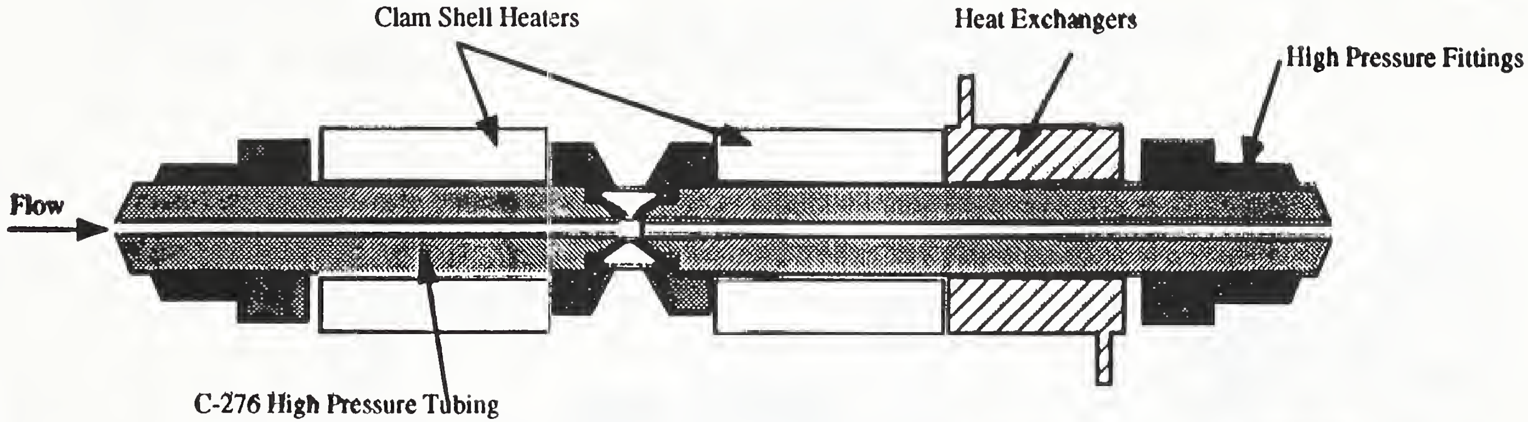
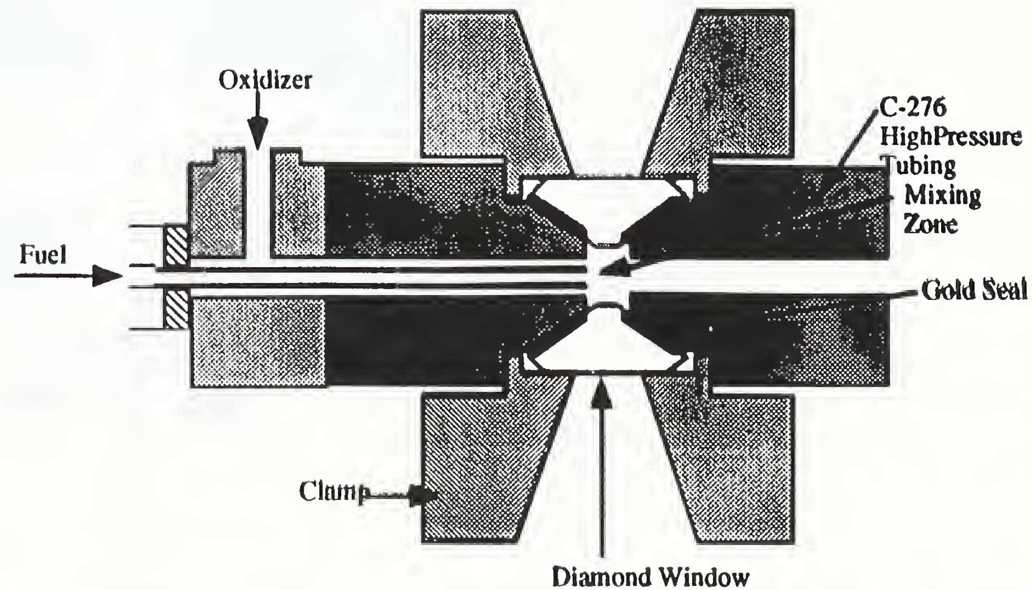
Solubility Reactor





Cold Fuel Injection Reactor





FLOW REACTOR WITH DIAMOND WINDOWS

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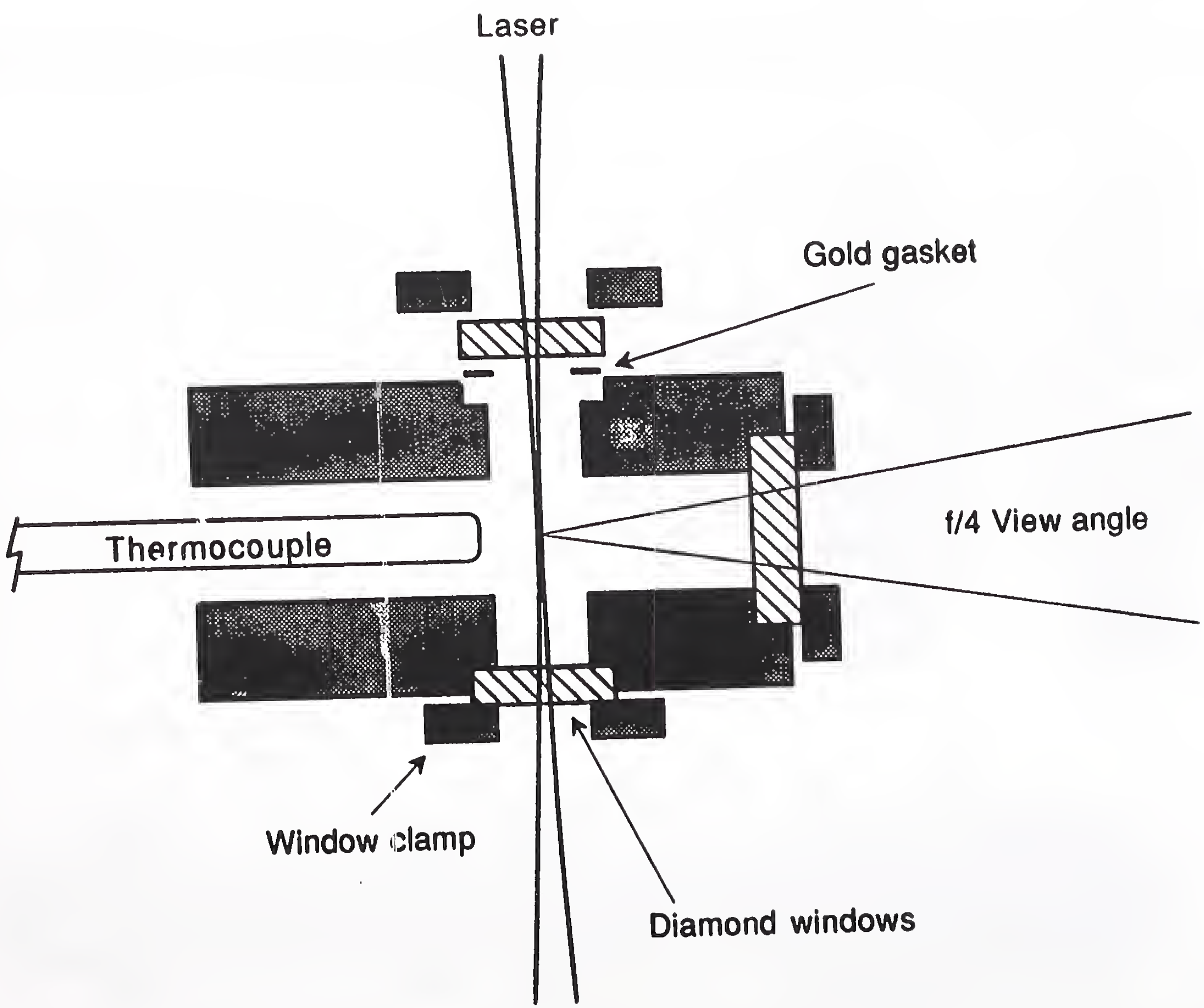


Figure A3. Side view of diamond window cell. Window dimensions are 1 mm thick x 3 or 5 mm diameter. High-pressure seal is made by gold gaskets. Cell material is stainless steel.

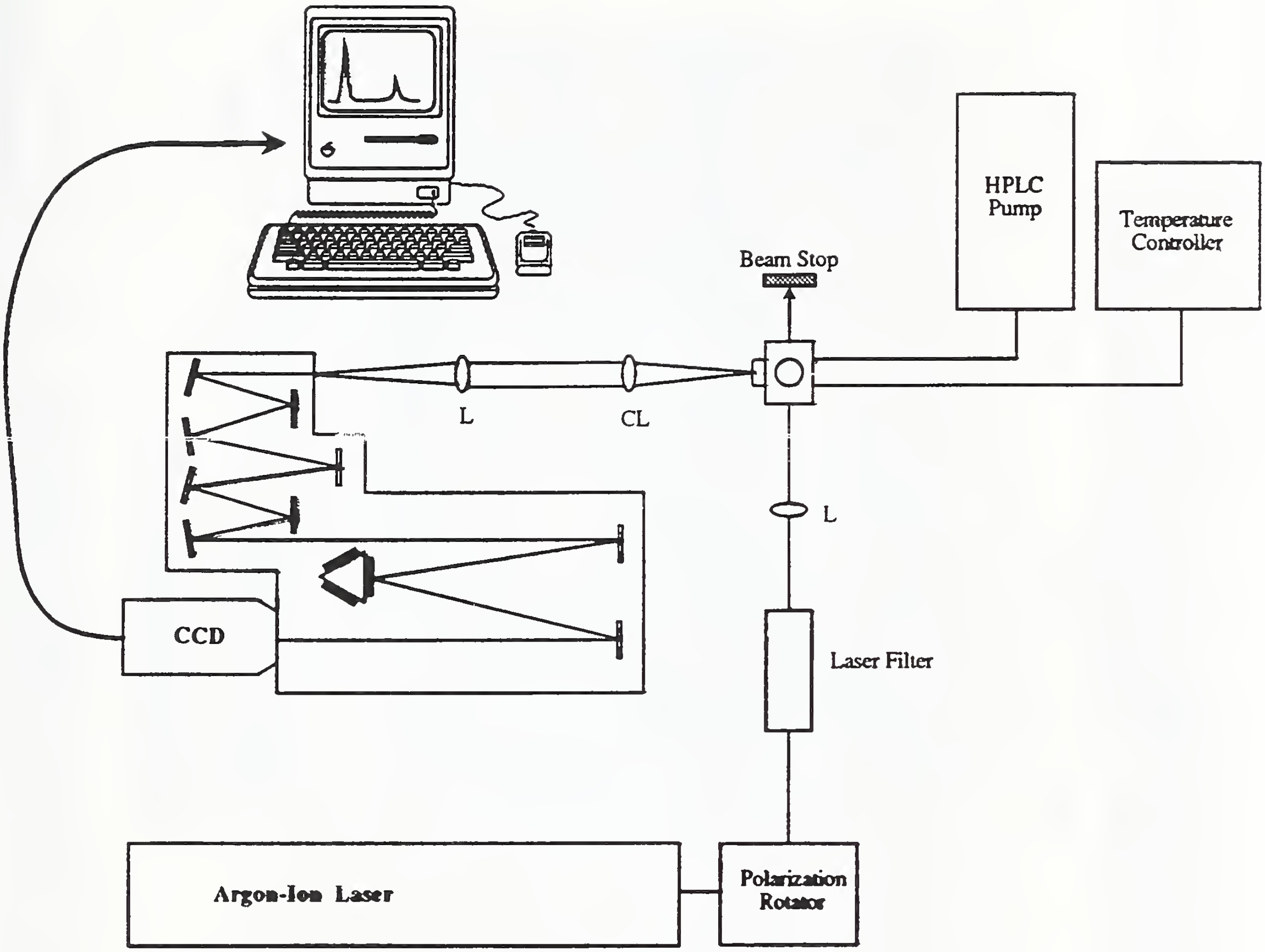
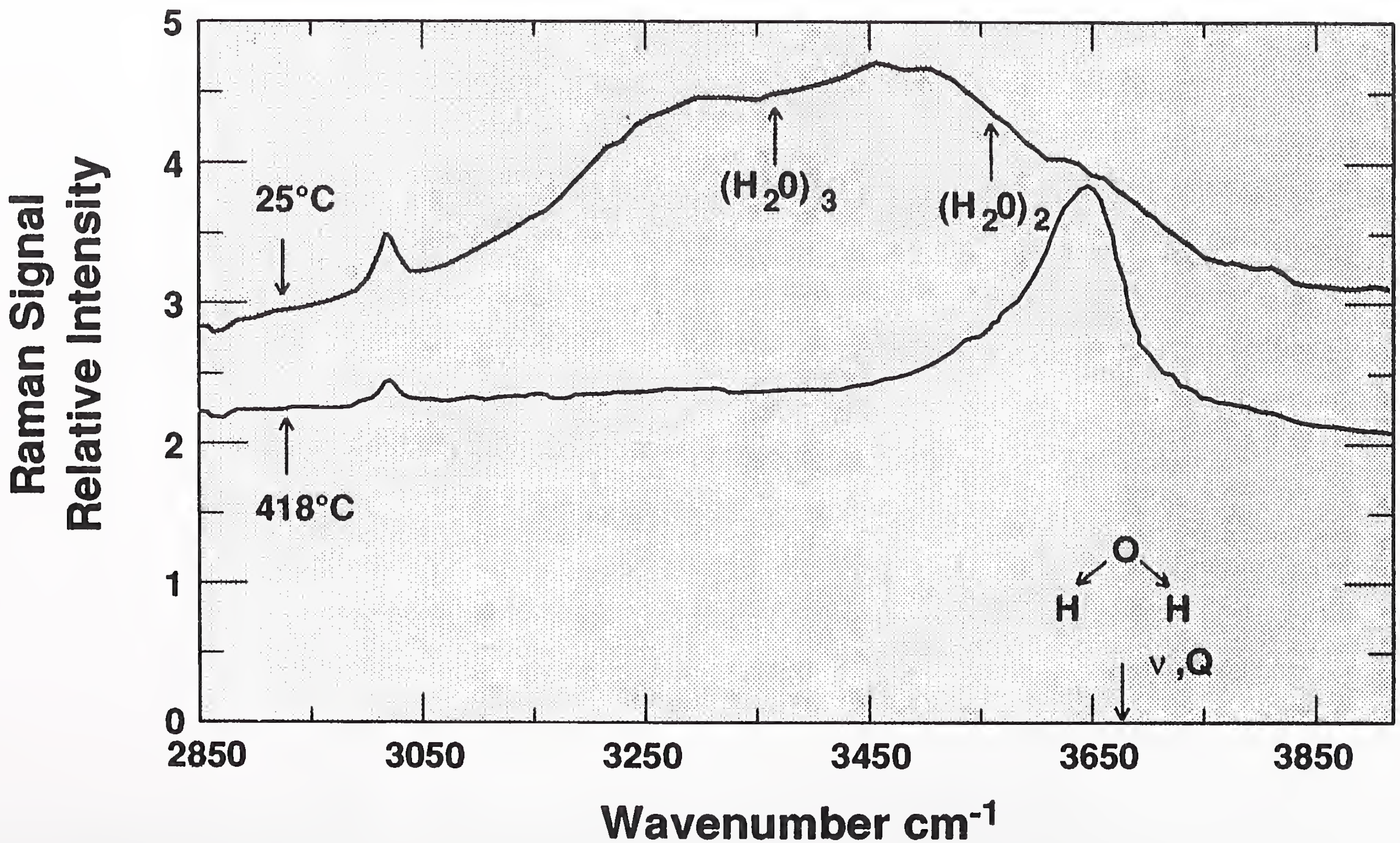


Figure 10. Raman apparatus. Polarization rotator: double romb half-wave retarder; Laser Filter: small monochromator; L: lens; Cl: collection lens; CCD: charge coupled device camera for detection. Data collection using macintosh II computer.

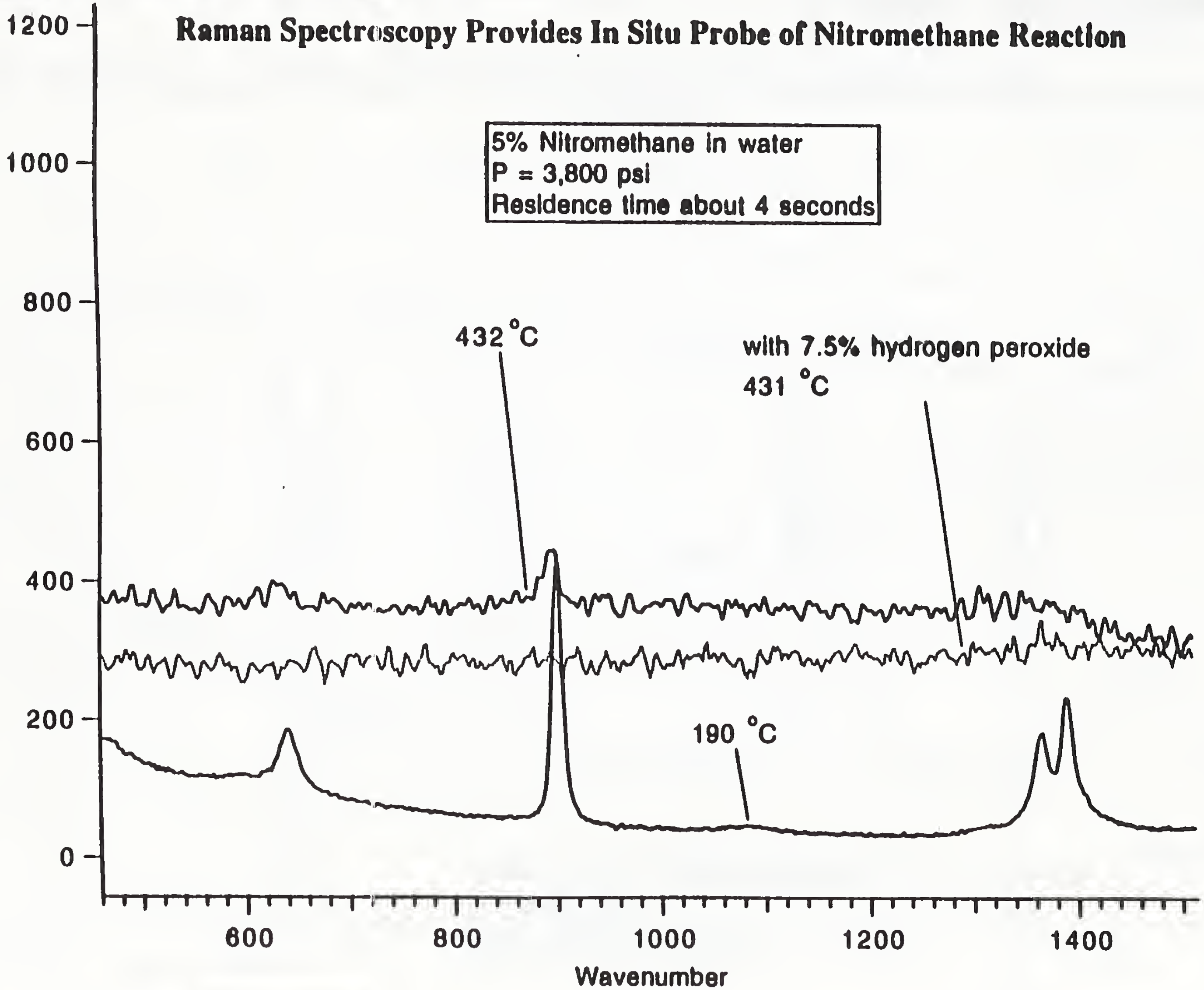
Raman Spectroscopy is a Useful Probe in Supercritical Water Environment



Raman Spectra Nitromethane: 0.93M, 248 atm

Los Alamos

CLS-91-1 021


Raman Spectroscopy Provides In Situ Probe of Nitromethane Reaction
5% Nitromethane in water
P = 3,800 psi
Residence time about 4 seconds
432 °C
with 7.5% hydrogen peroxide
431 °C
190 °C
1200
1000
800
600
400
200
0
600
800
1000
1200
1400
Wavenumber

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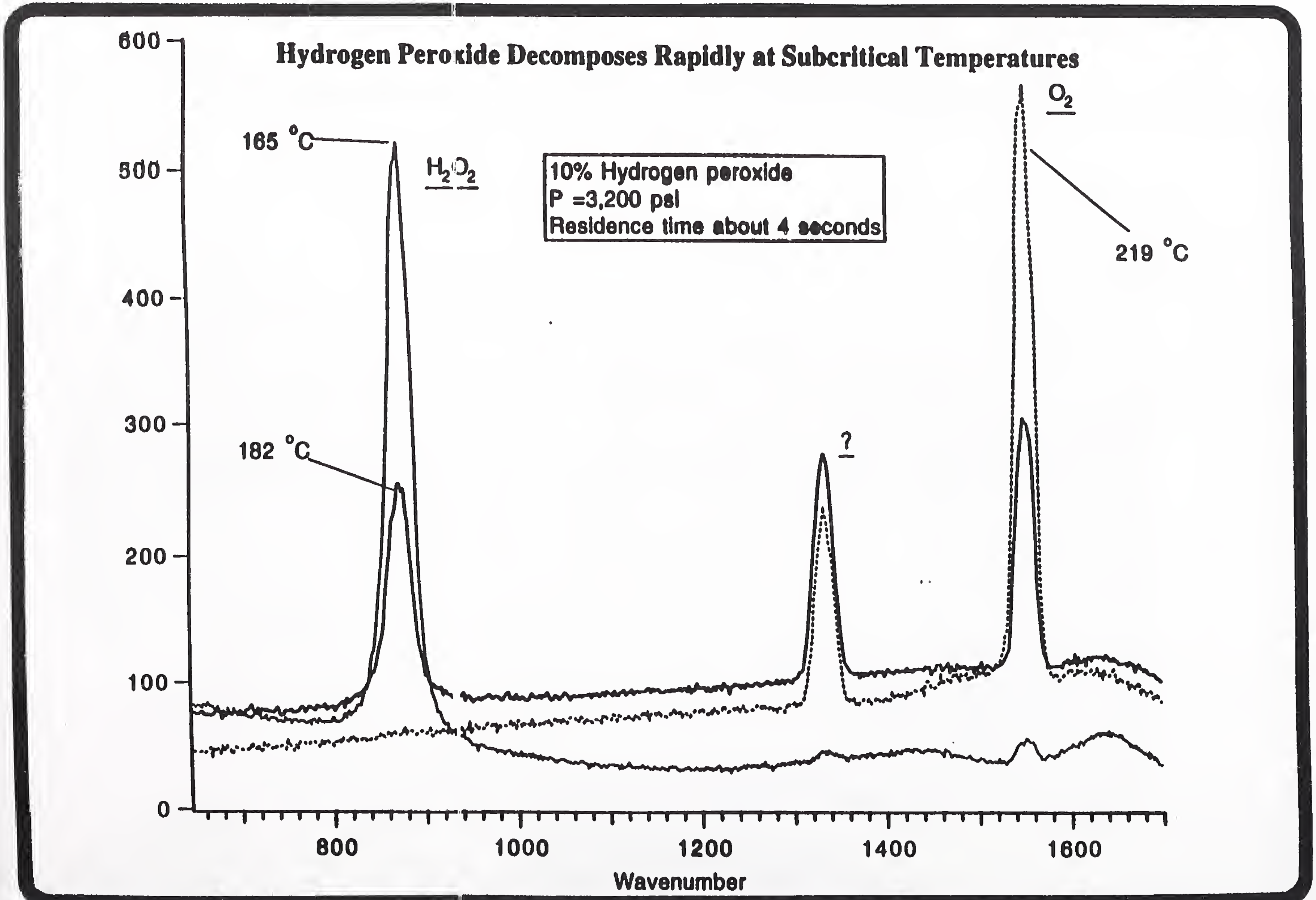

Hydrogen Peroxide Decomposes Rapidly at Subcritical Temperatures
10% Hydrogen peroxide
P =3,200 psi
Residence time about 4 seconds
165 °C
182 °C
219 °C
H_2O_2
?
O_2
600
500
400
300
200
100
0
800
1000
1200
1400
1600
Wavenumber

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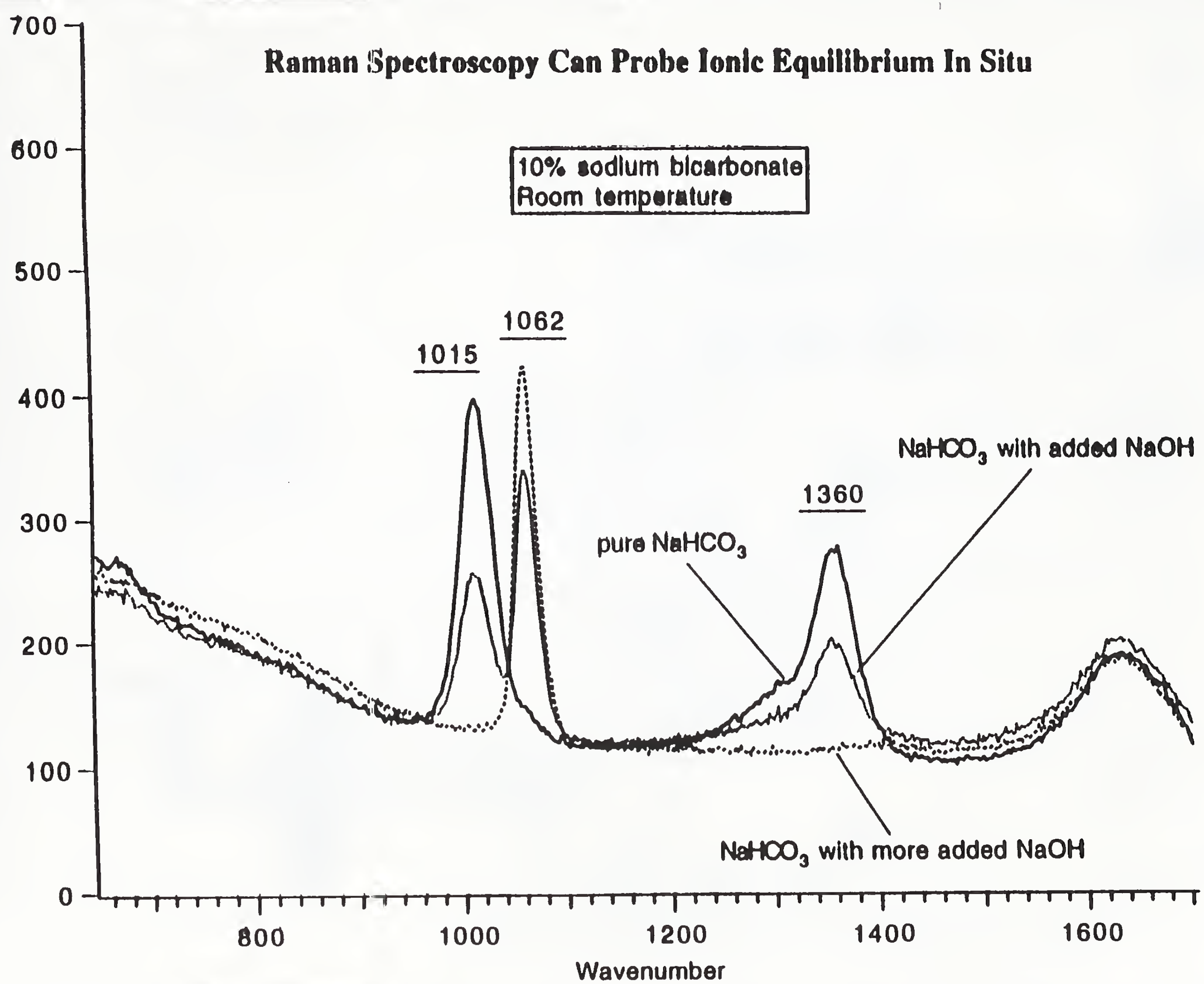
Raman Spectroscopy Can Probe Ionic Equilibrium In Situ



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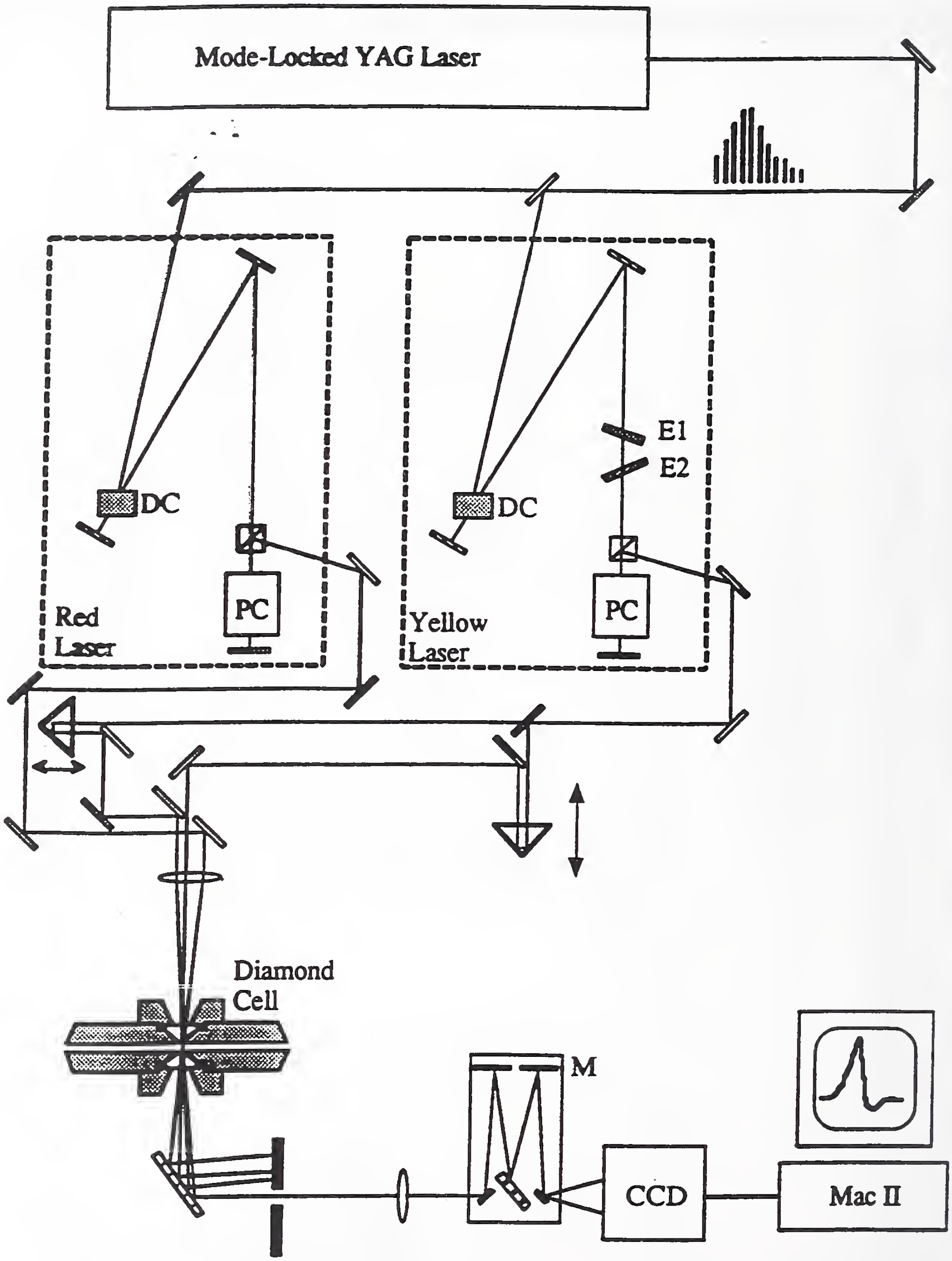
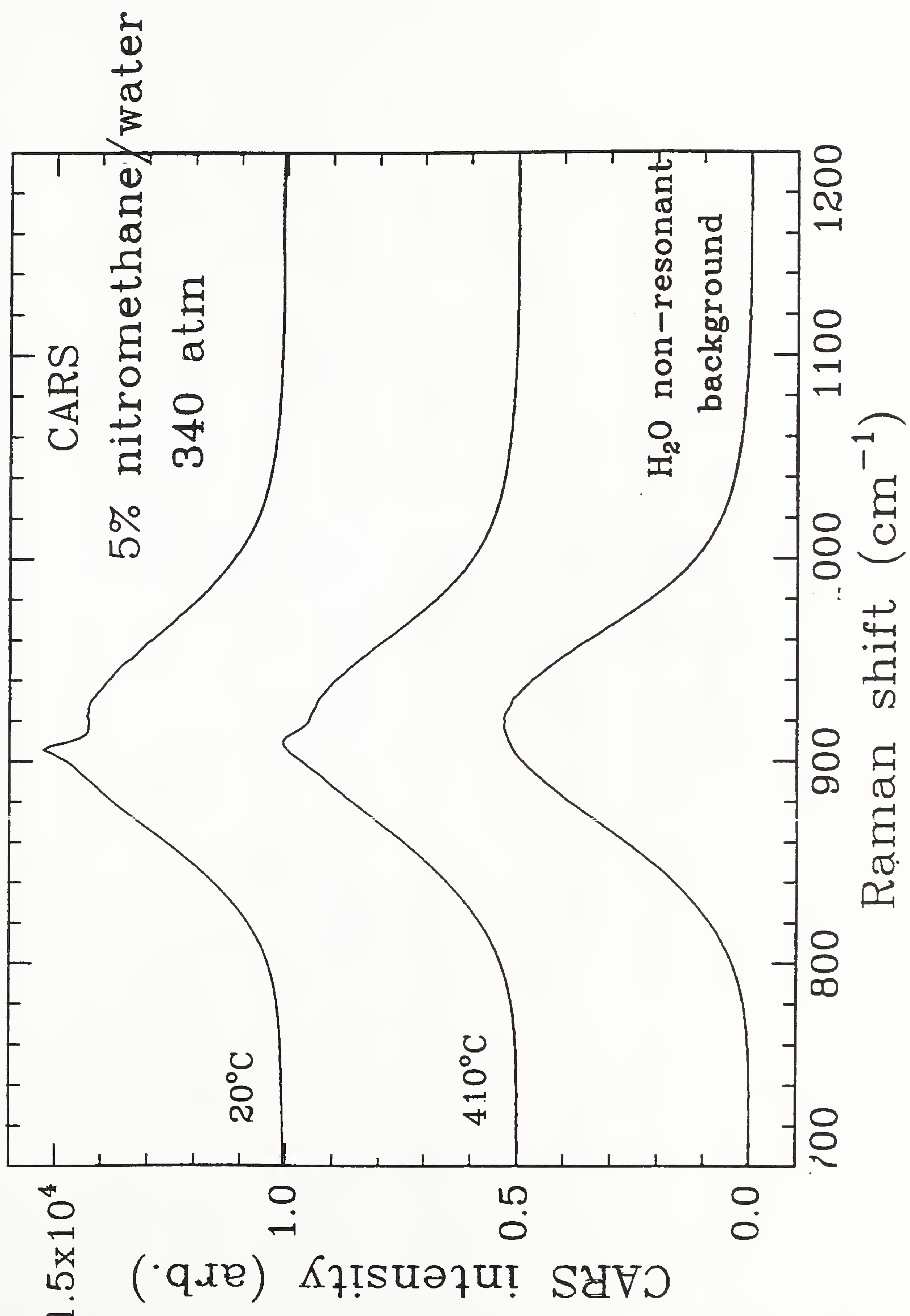
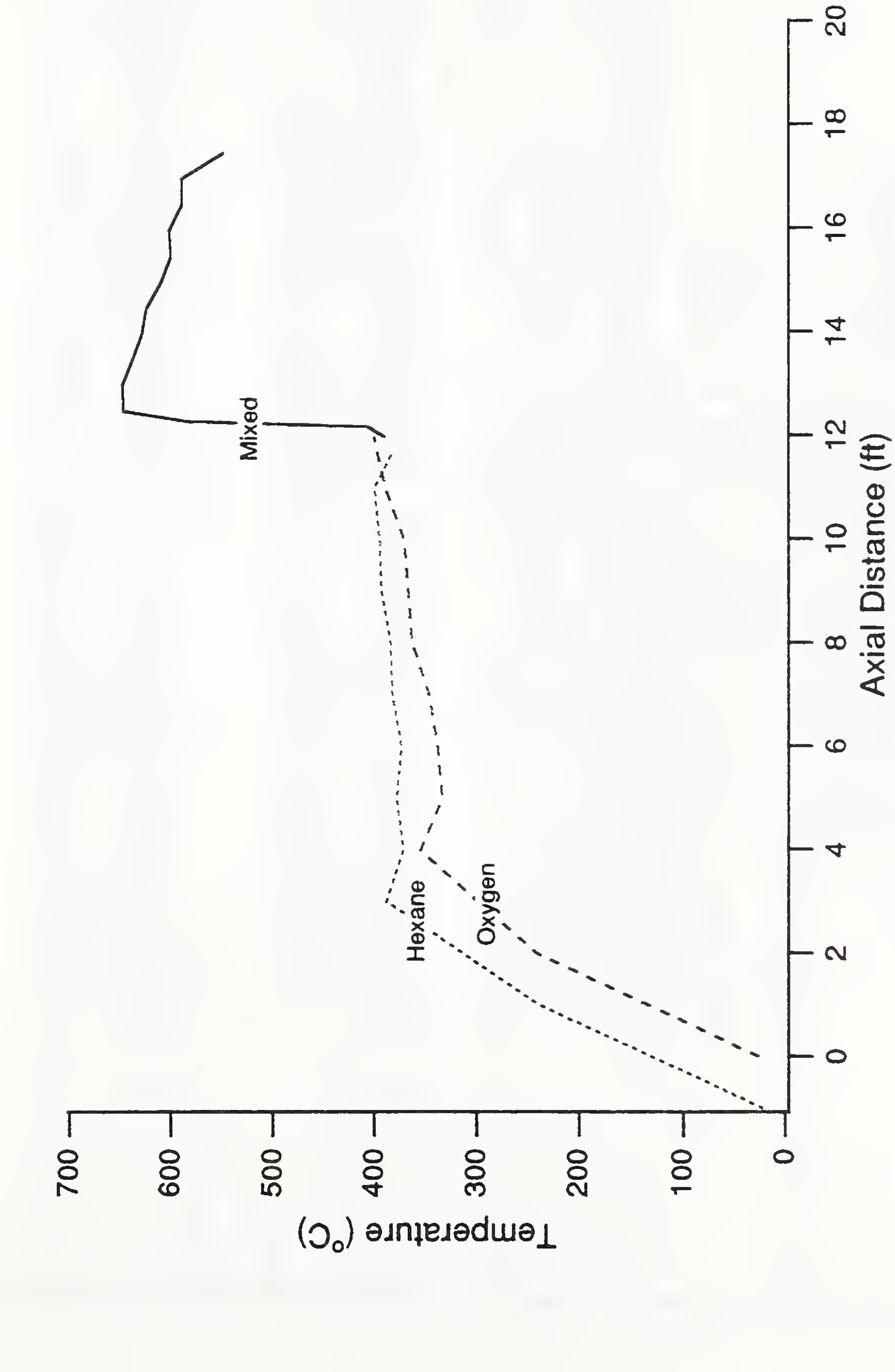


CARS apparatus. DC: dye cell, containing Sulforhodamine 640 for the red laser and Rhodamine 610 for the yellow laser. E1, E2: etalon tuning elements for the yellow laser; these are absent in the broad-band red laser. PC: Pockel's Cell used to fire the dye laser pulse. M: monochromator used to disperse the broad-band CARS beam. CCD: charge-coupled device camera to detect CARS beam. Mac II: computer for data acquisition, display, and analysis.


CARS
5% nitromethane/water
340 atm
20°C
410°C
H_2O non-resonant
background
CARS intensity (arb.)
$1.5x10^4$
1.0
0.5
0.0
Raman shift (cm^{-1})
700
800
900
1000
1100
1200

Temperature Profile SCWO of Hexane



EXPLOSIVES ARE RAPIDLY DESTROYED IN SUPERCRITICAL WATER

- PETN, HMX, RDX, TNT, NQ
  Destroyed below detection limits
  600°C, 11 seconds, 33 MPa

- Products: Carbon dioxide, nitrogen, nitrous oxide, nitrate, nitrite

- Nitrogen product distribution varies with compound, conditions

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SCWO RAPIDLY DESTROYS EXPLOSIVES

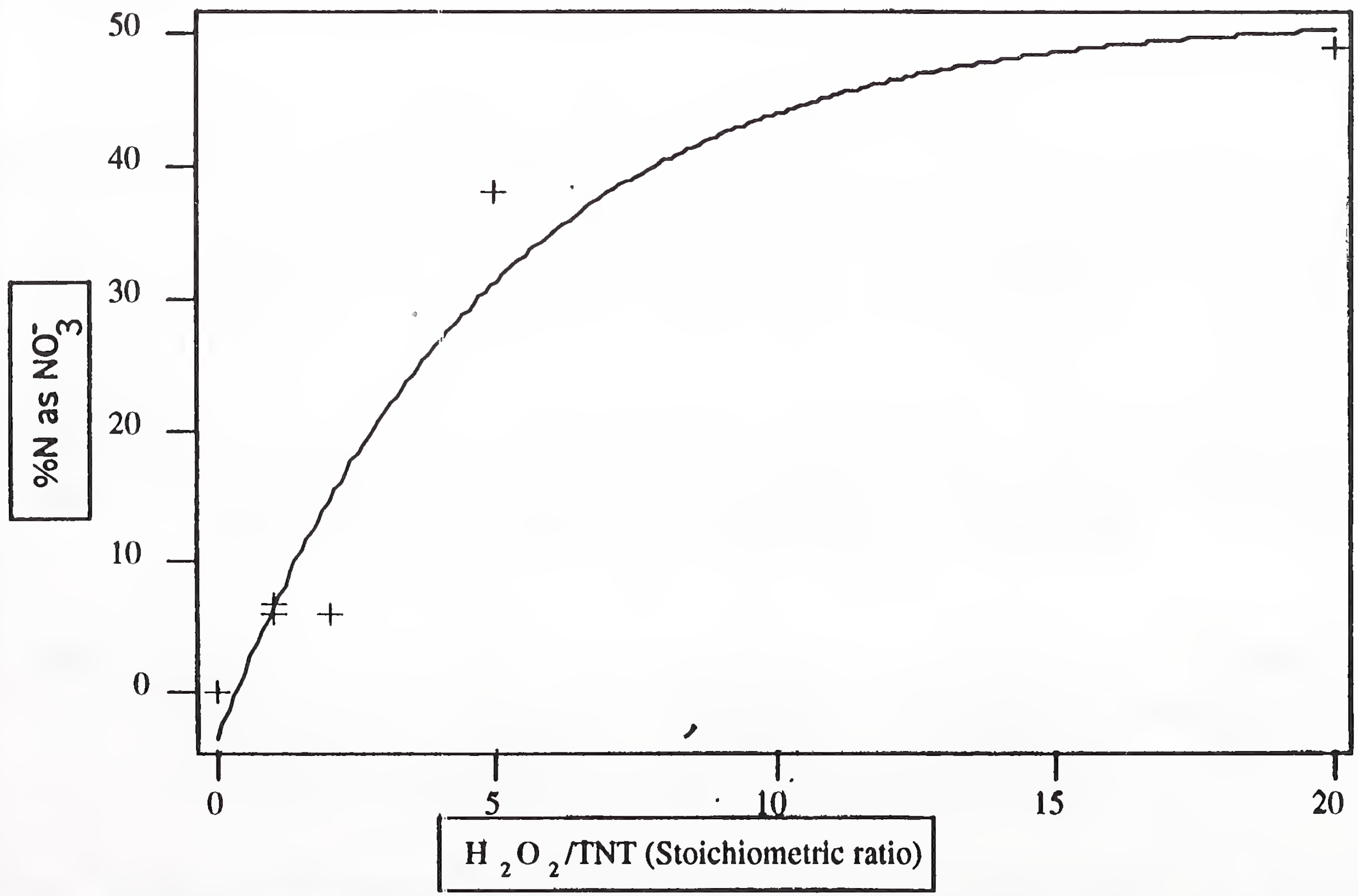
	PETN	HMX	RDX	TNT	NQ
Initial conc. (ppm)	3.8	2.6	35.2	65.5	1700.
Destruction efficiencies	>0.9825	>0.99	>0.9992	>0.9998	>0.9999
NO3- **	0.187	0.124	0.101	0.366	0.0003
NO2- **	0.060	0.053	0.141	0.285	0.0004

** Given as fraction of initial nitrogen.

Operating conditions: 600°C, 340 atm, 7 seconds

TNT DESTRUCTION

NITRATE LEVELS INCREASE WITH OXIDANT CONCENTRATION



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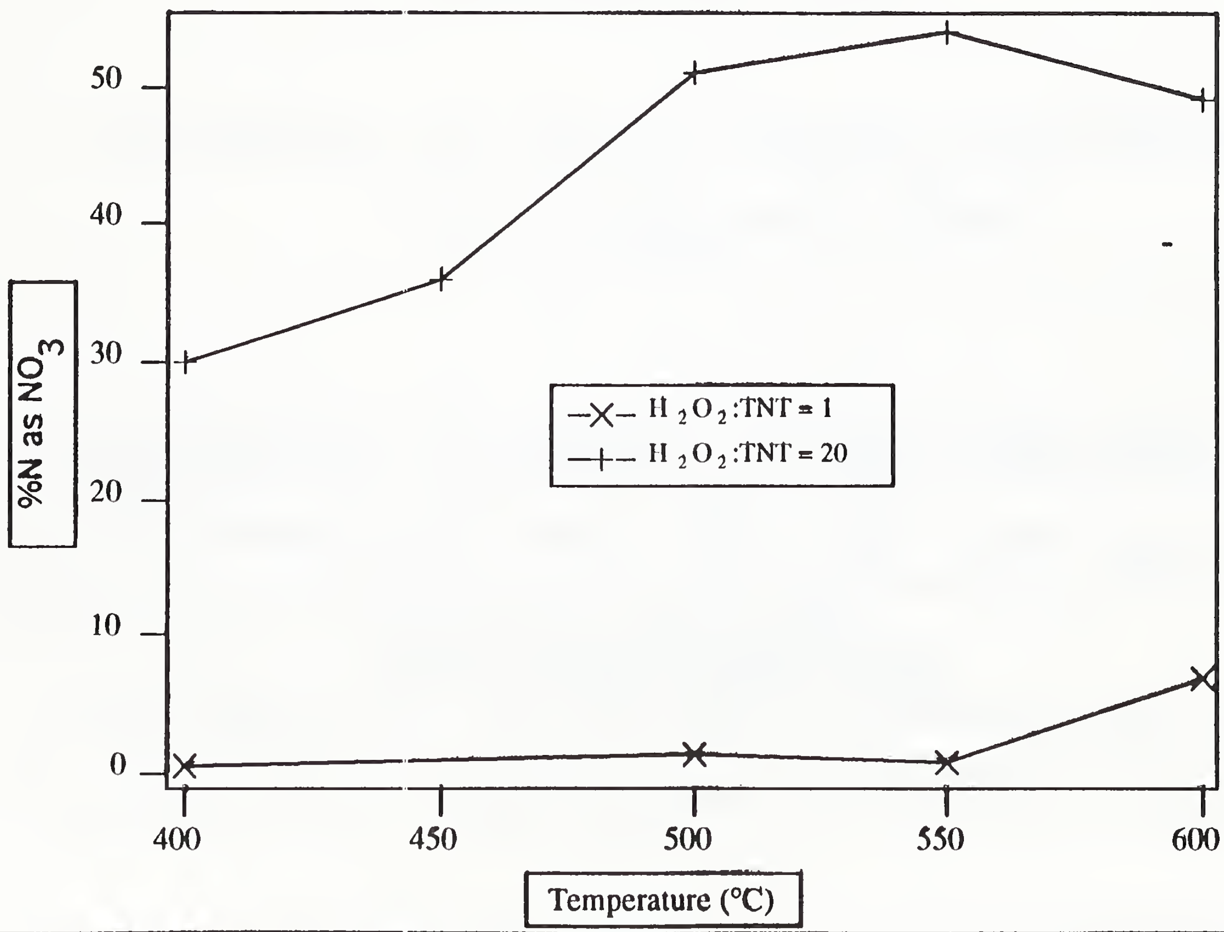
TNT DESTRUCTION

NITRATE LEVELS INCREASE WITH TEMPERATURE



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COMPARISON OF AP SCWO REACTIONS IN C-276 AND GOLD-LINED REACTORS

Destruction Efficiency(%)	400 °C	450 °C	475 °C	500 °C	550 °C	600 °C
C-276 Reactor	0	40	86	99.95	-	-
Gold-Lined Reactor	0	4.5	-	54.0	96.5	99.6

HIGH THROUGHPUT IS NECESSARY TO DECREASE COST

Solubility of many organic explosives
<100 milligrams/liter

- Co-solvents: Organic, carbon dioxide
- Slurries: <100μm particles
- Hydrolysis: Preprocess in alkaline solution

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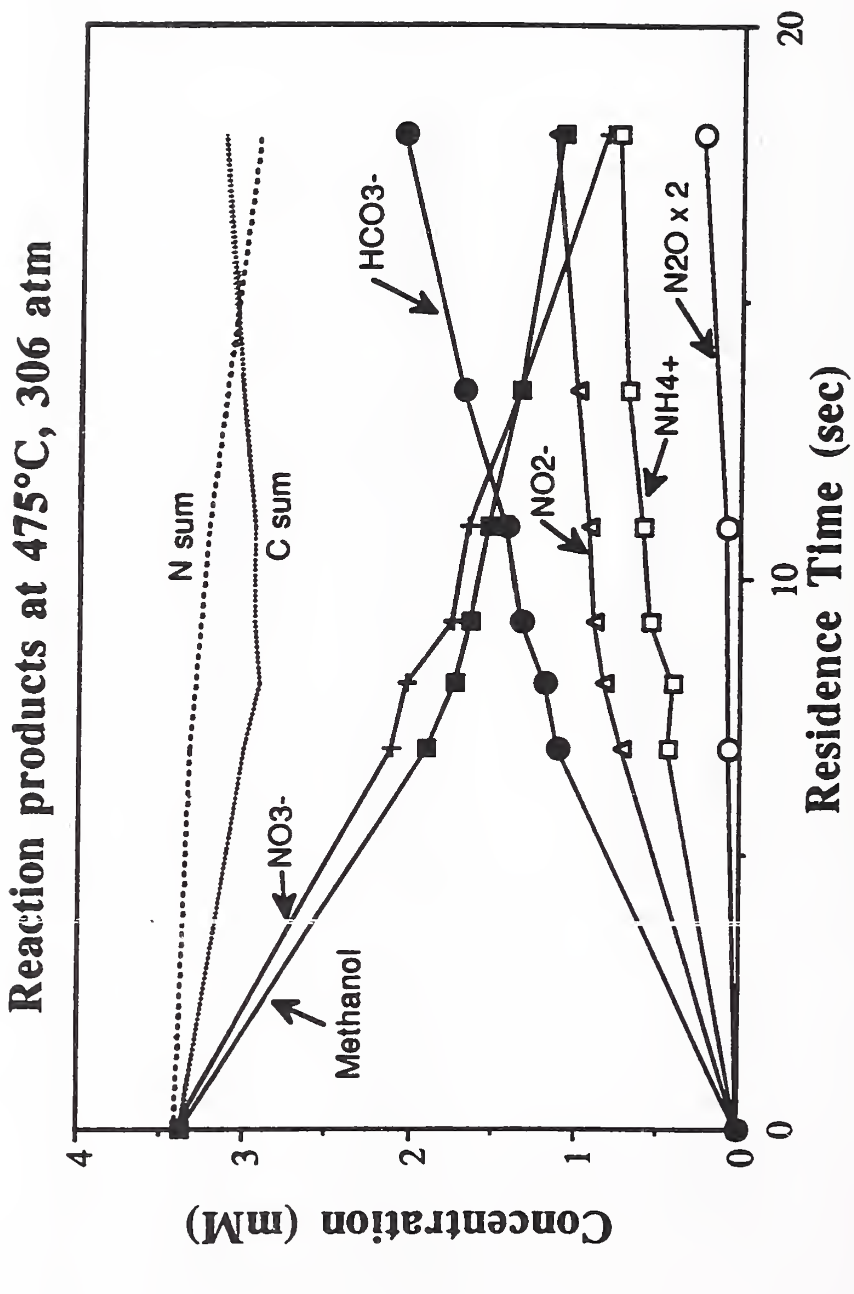
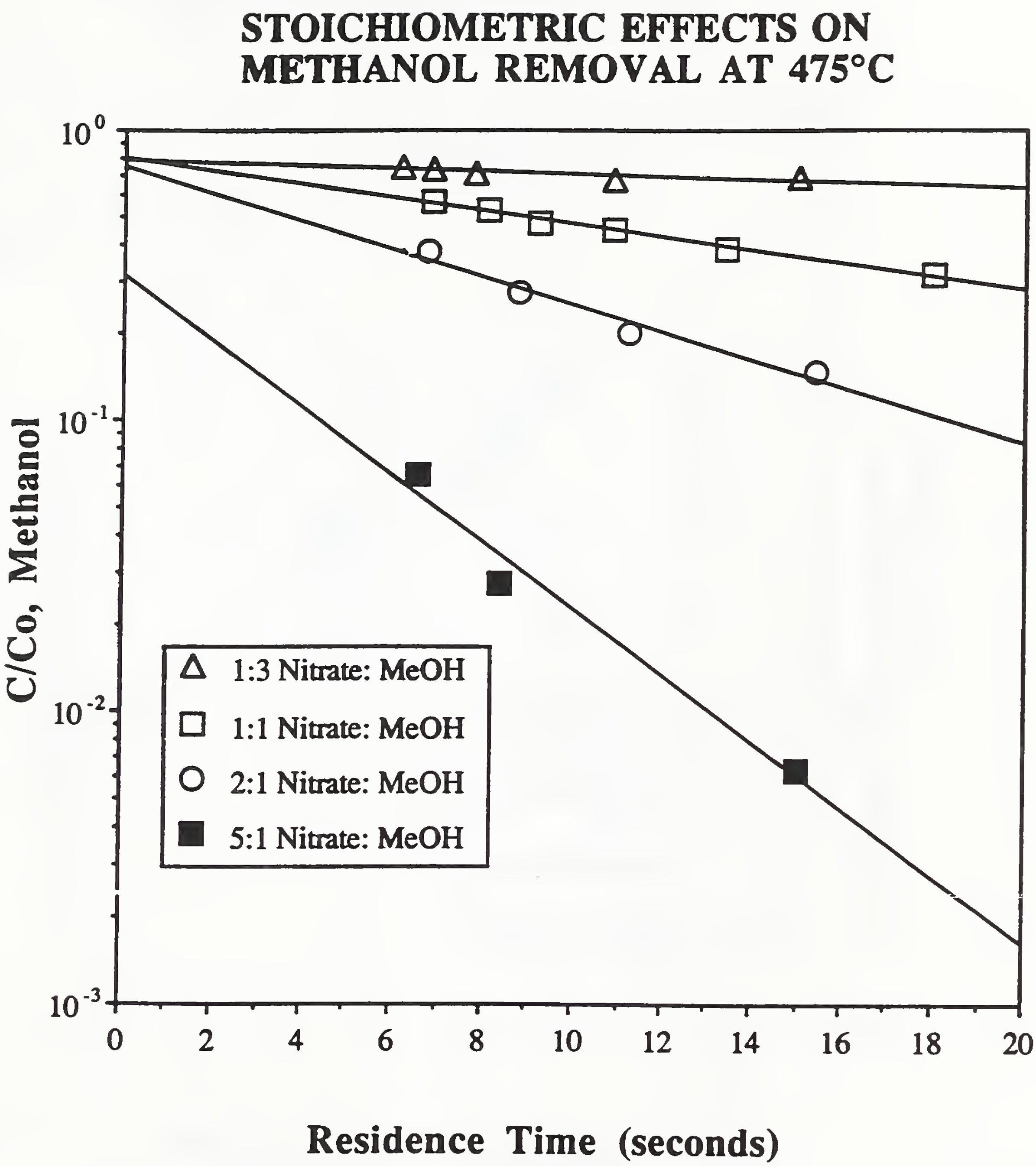
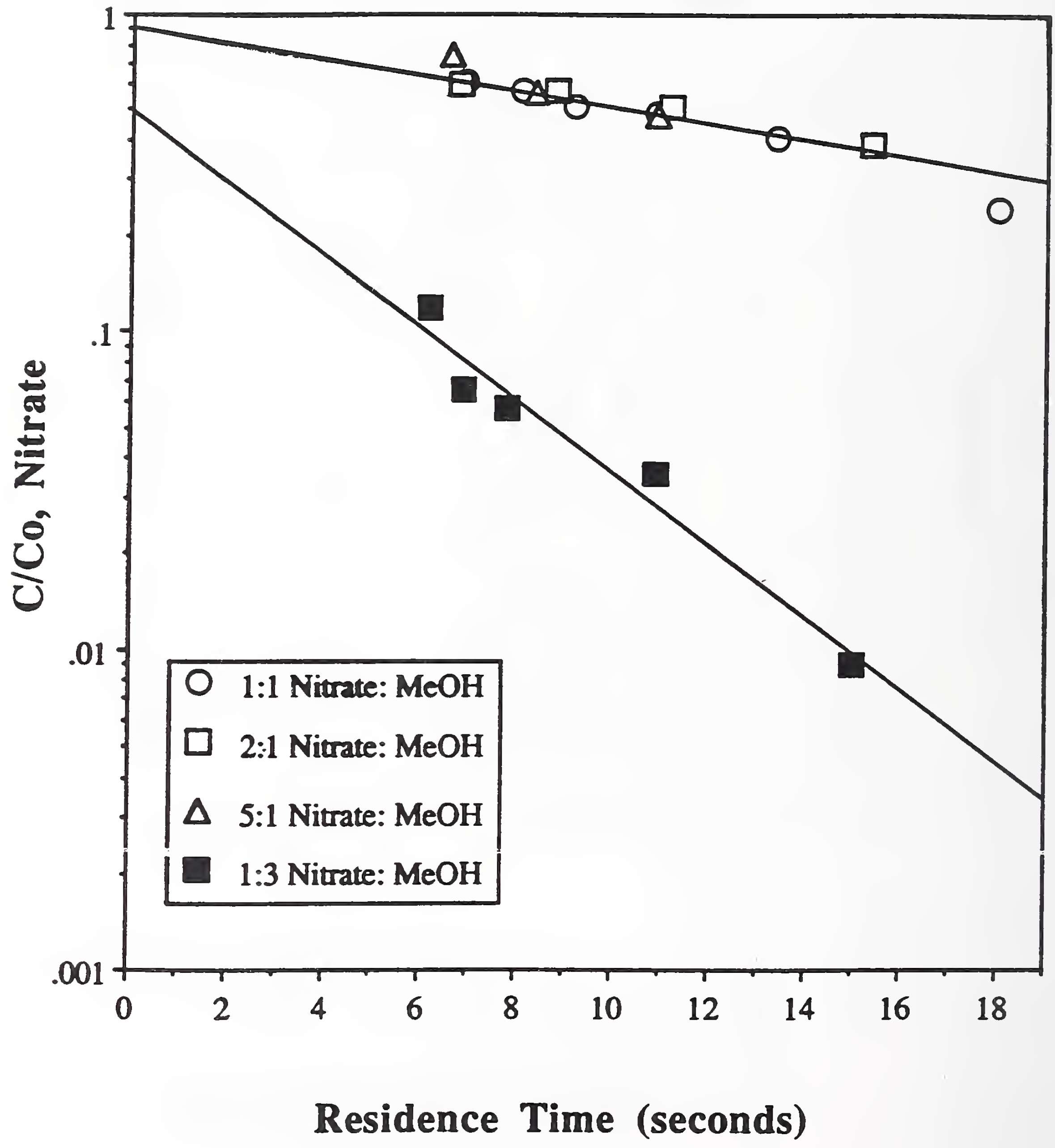


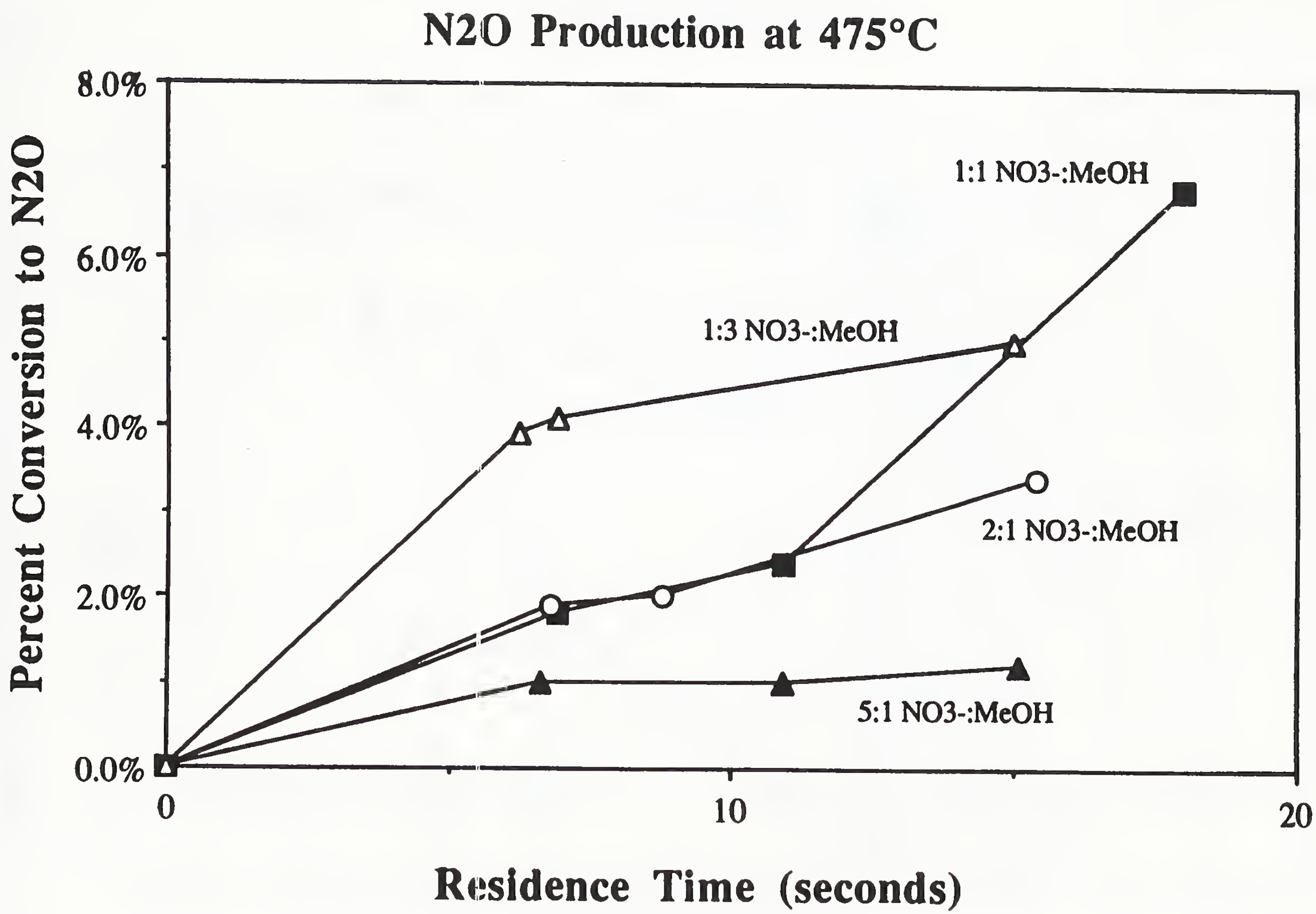
Reaction products at 475°C, 306 atm
Concentration (mM)
Residence Time (sec)
0
1
2
3
4
0
10
20
N sum
C sum
NO3-
Methanol
HCO3-
NO2-
NH4+
N2O x 2



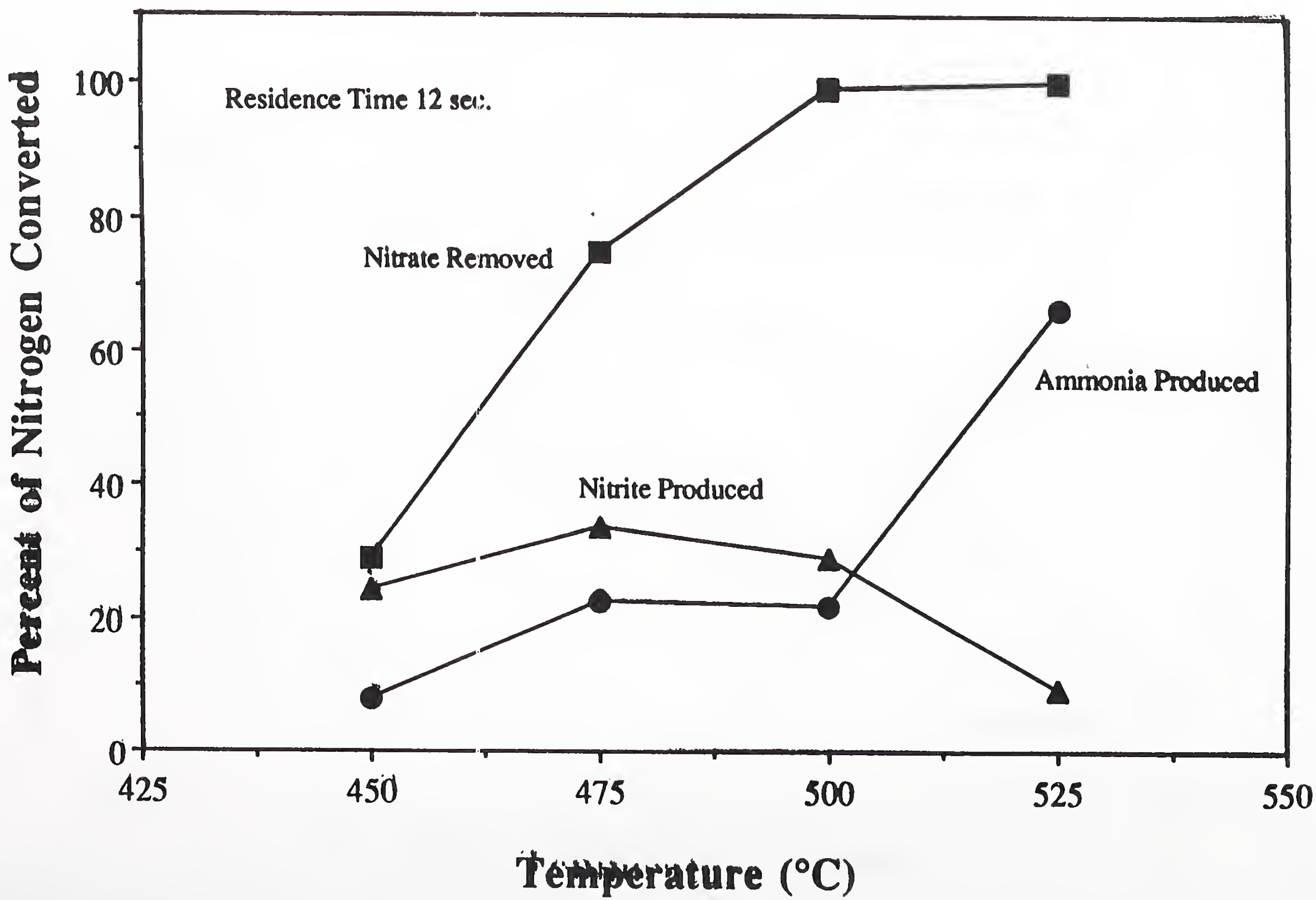
STOICHIOMETRIC EFFECTS ON
METHANOL REMOVAL AT 475°C
C/Co, Methanol
10^{0}
10^{-1}
10^{-2}
10^{-3}
0
2
4
6
8
10
12
14
16
18
20
Residence Time (seconds)
1:3 Nitrate: MeOH
1:1 Nitrate: MeOH
2:1 Nitrate: MeOH
5:1 Nitrate: MeOH

STOICHIOMETRIC EFFECTS ON NITRATE REMOVAL AT 475°C




N2O Production at 475°C
Percent Conversion to N2O
8.0%
6.0%
4.0%
2.0%
0.0%
0
10
20
Residence Time (seconds)
1:1 NO3-:MeOH
1:3 NO3-:MeOH
2:1 NO3-:MeOH
5:1 NO3-:MeOH

Temperature Dependance of Nitrate Reduction to Products



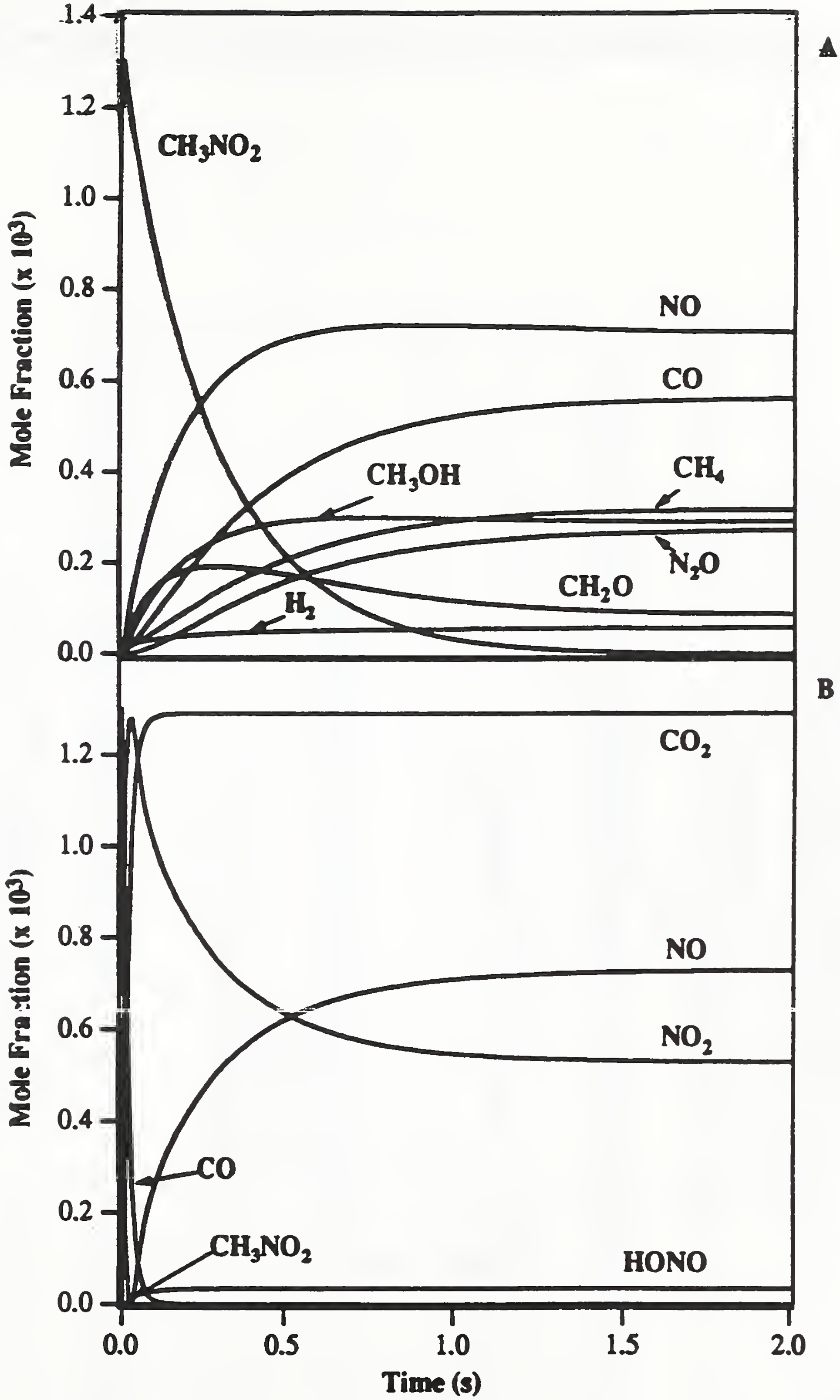
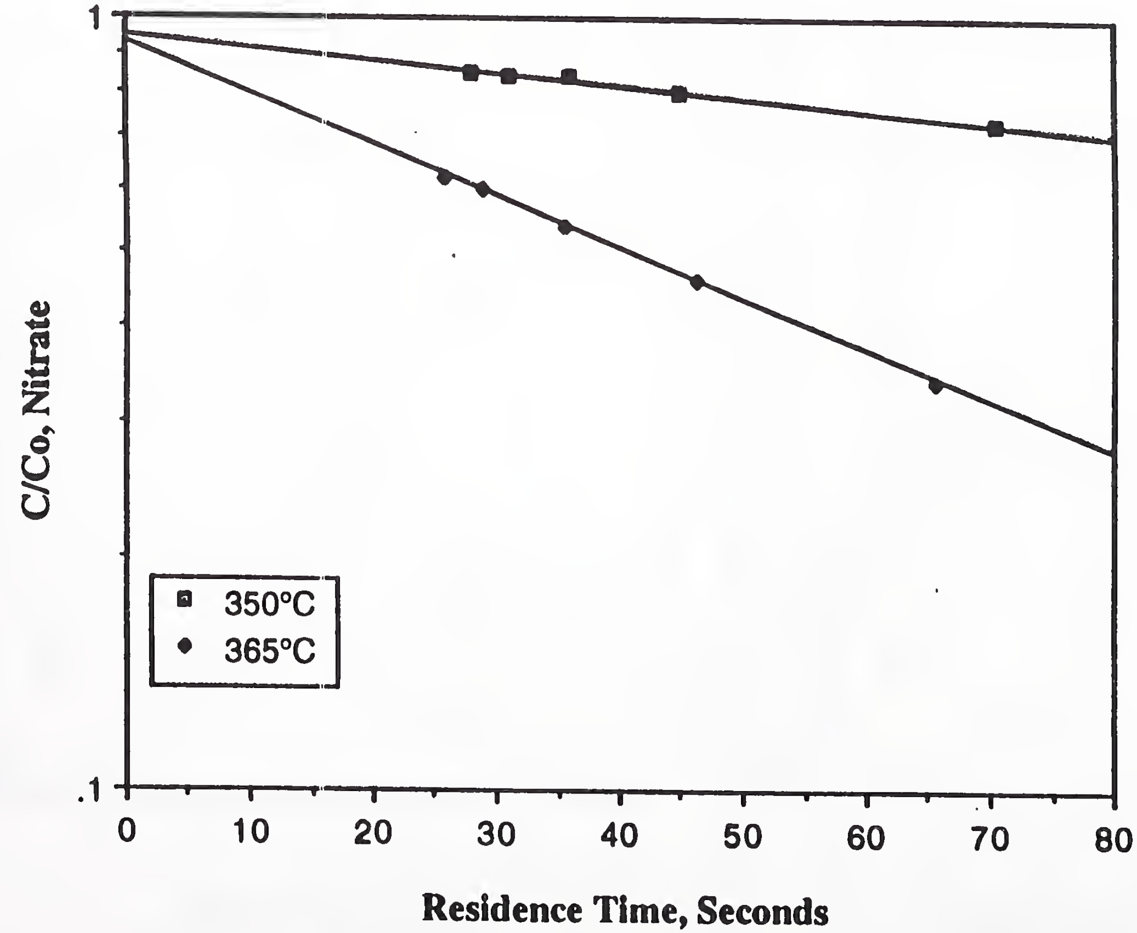


Figure 33 (A) Calculated species profiles for the decomposition of nitromethane in supercritical water at 550 °C, 330 atm and 0.4% v/v nitromethane in water. (B) Same calculation with the addition of H2O2 in a 10:1 molar ratio to nitromethane.

Nitrate/Ammonia Reactions: 1:1 Molar



Los Alamos

Destruction of Ferrocyanide

- 502°C, 4584 psi, 7 seconds, H_2O_2
  - Ferrocyanide/cyanide reduced below detection limits
  - Greater than 99.95% destruction
  - Primary products were ammonia and carbonate
- 502°C, 4584 psi, 7 seconds, $NaNO_3$
  - Ferrocyanide/cyanide reduced below detection limits
  - Greater than 99.95% destruction
  - Primary products were ammonia and carbonate

Los Alamos

Hanford Simulated Waste - Los Alamos

- 400°C, 3600 psi, 60 seconds
  - Near complete separation of Sr from Na, Cs, Cr, Cl^-, NO_3^-
  - No plugging of the reactor

- 500°C, 3600 psi, 51 seconds
  - Greater than 99.5% removal of Al, Na, Sr, NO_3^-, TOC from Effluent
  - Cesium concentration reduced by 96%
  - Intermittent plugging

Los Alamos

Hanford Simulated Waste - Battelle

- 509°C, 4350 psi, 53 seconds

  - Mixture nearly 50 % inorganic salts by weight
    - Aluminum Oxide/Hydroxide 16%
    - Bismuth 3%
    - Iron Oxide/Hydroxide 4.6%
    - Phosphate 8.5%
    - SiO_2 7%
    - Sodium 17.8%
    - Nitrate 27.5 %

  - Sucrose 1:1 Ratio for $CHO+NO_3^- \rightarrow CO_2+N_2O+H_2O$

  - Nitrate level reduced 84%

  - Flocculent solid residue produced

Los Alamos

Supercritical Water Oxidation Research at Sandia

Richard R. Steeper
Nina Bergan French
Sheridan C. Johnston

Sandia National Laboratories

NIST
July 6-7, 1992

Sandia's Supercritical Water Oxidation Program Comprises Three Research Teams

Oxidation Experiments

M. E. Brown
T. T. Bramlette
K. R. Hencken
C. A. LaJeunesse
A. Odeide
S. F. Rice
R. R. Steeper

Materials Studies

C. Kao
B. E. Mills
D. K. Ottesen

Modeling

N. E. Bergan French
P. B. Butler (Univ. of Iowa)
B. Schmitt (Univ. of Iowa)
B. Pitz (LLNL)
C. Westbrook (LLNL)

Sponsors and Research Programs

DOE Office of Basic Energy Sciences

Fundamental studies of diffusion flames in supercritical water-fuel-oxygen mixtures.

U. S. Army Armament Research, Development & Engineering Center

SCWO of colored smoke/dye and pyrotechnic compositions.

Naval Civil Engineering Laboratory

Measurement of destruction efficiencies for Navy industrial hazardous waste materials.

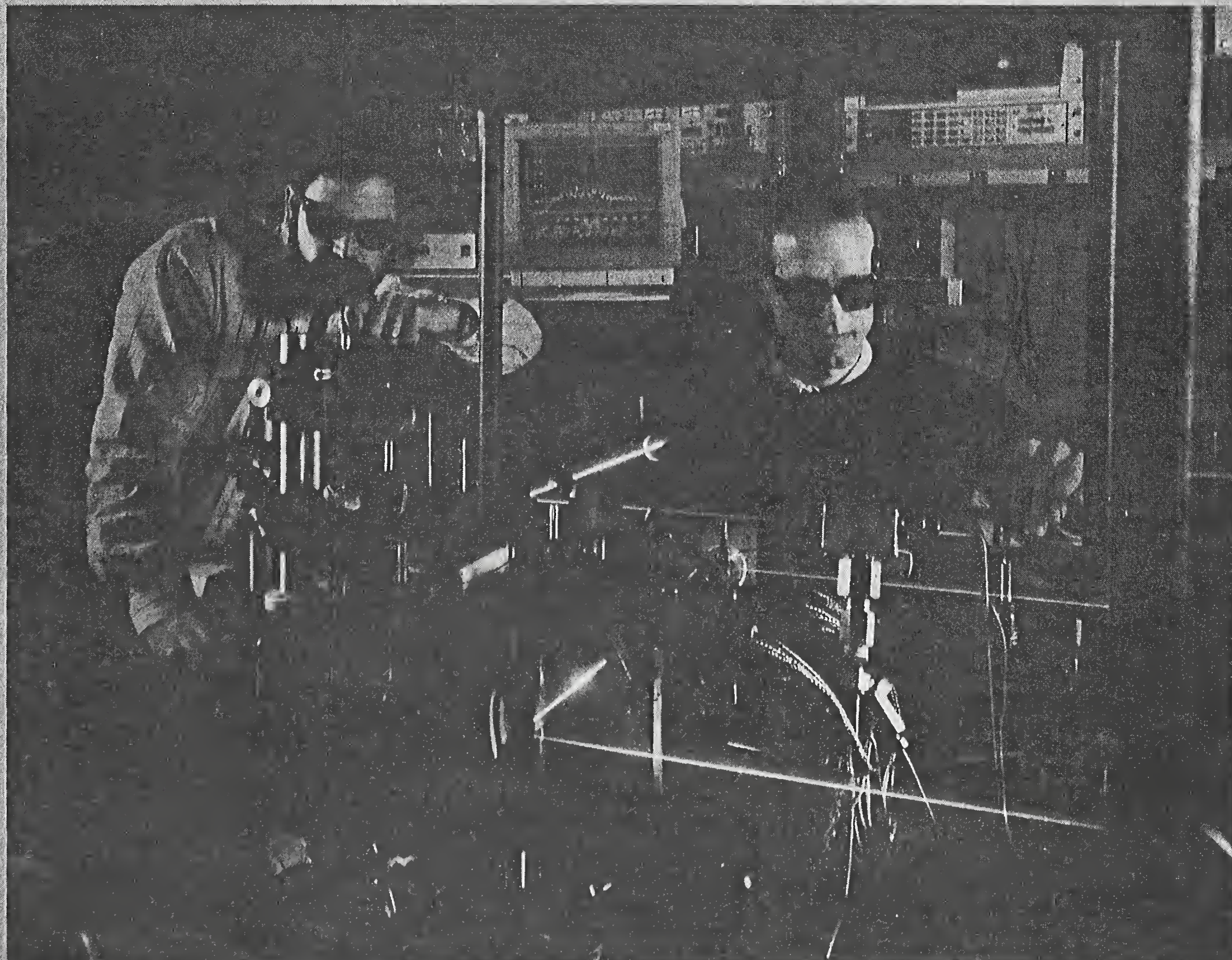
Defense Advanced Research Projects Agency

Chemical kinetics of SCWO: quantum chemistry calculations and in situ optical diagnostics.

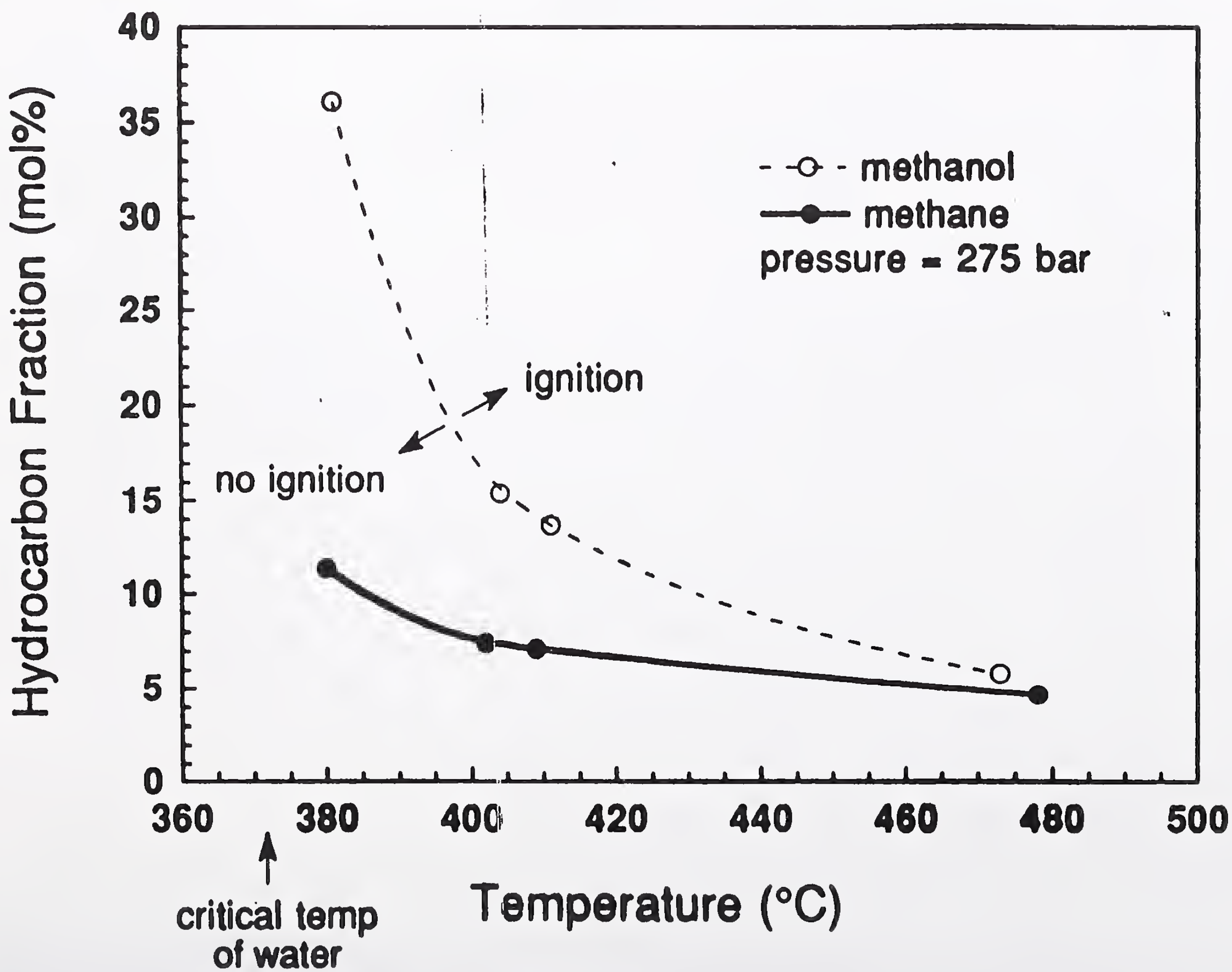
Sandia Internal Funding

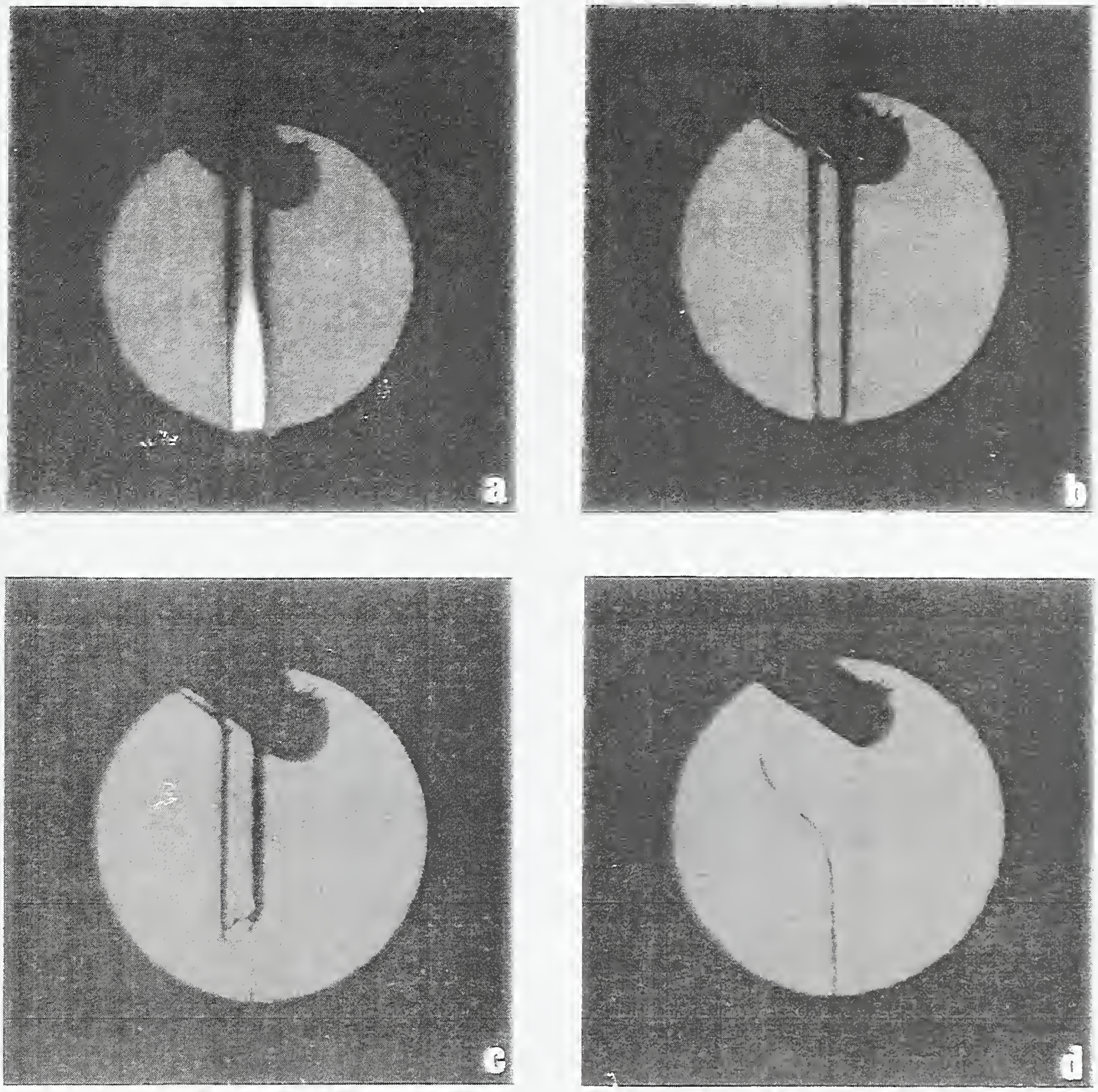
Materials studies, Modeling.

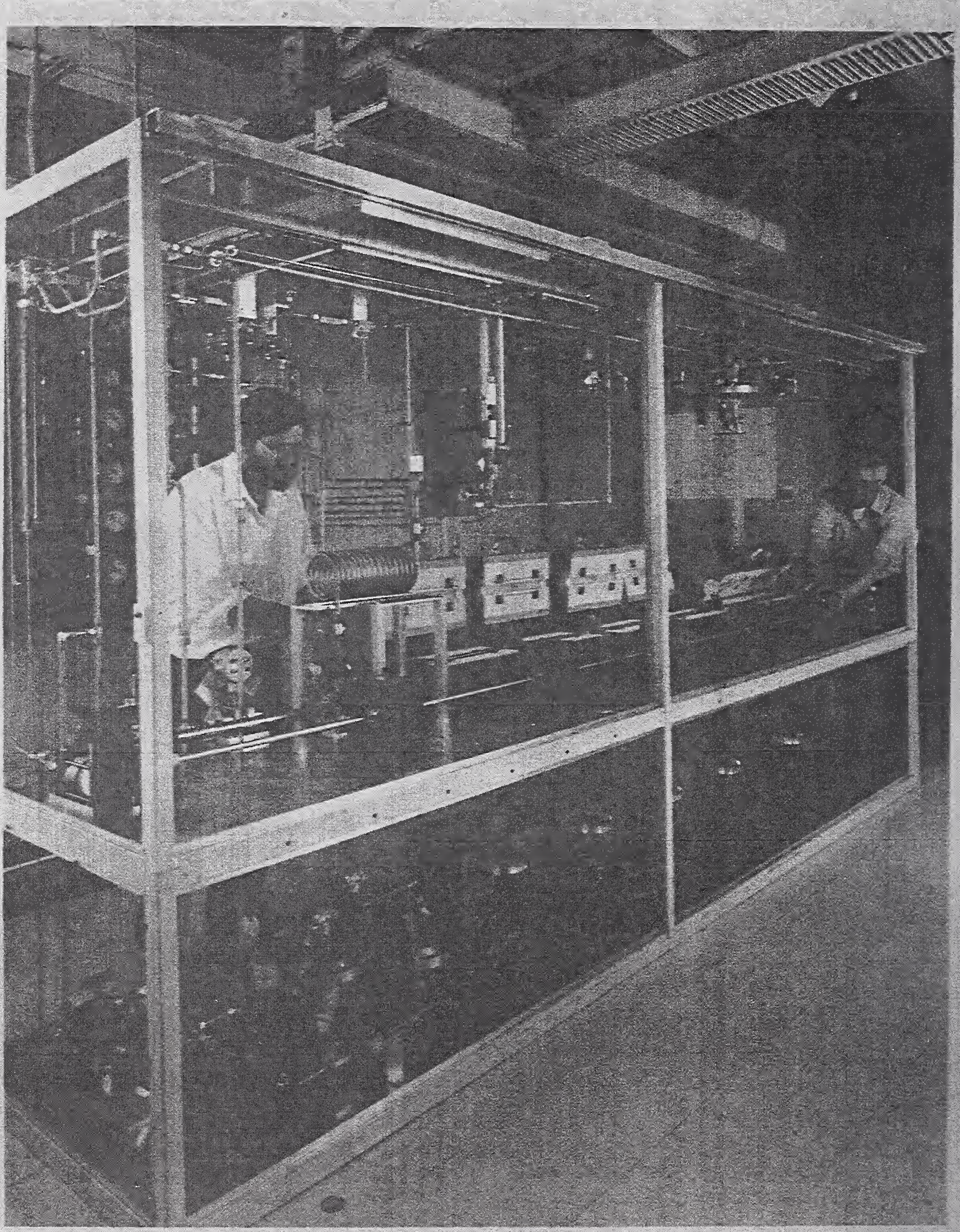
Sandia Hydrothermal Flame Facility

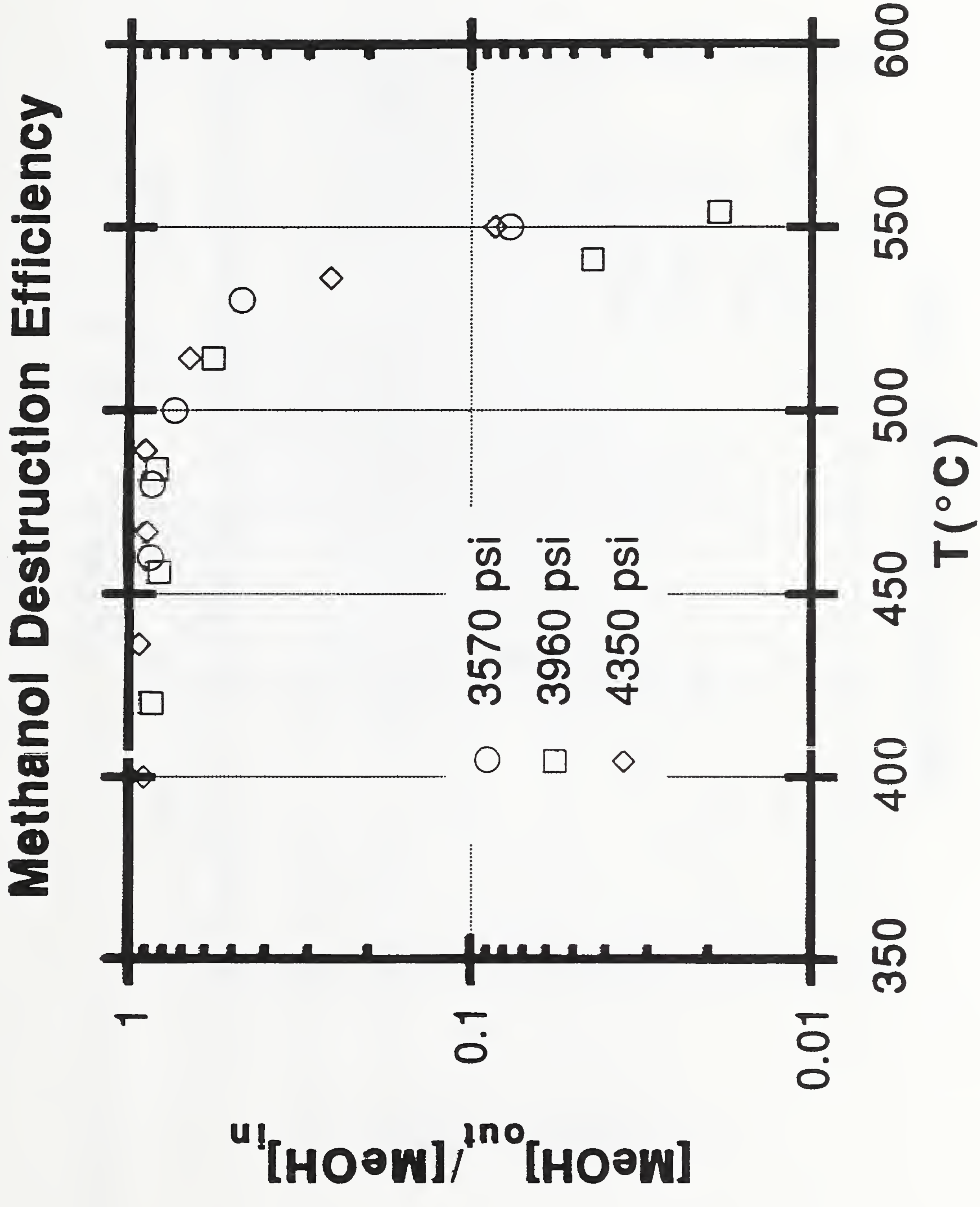


Hydrothermal Flame Minimum Ignition Conditions

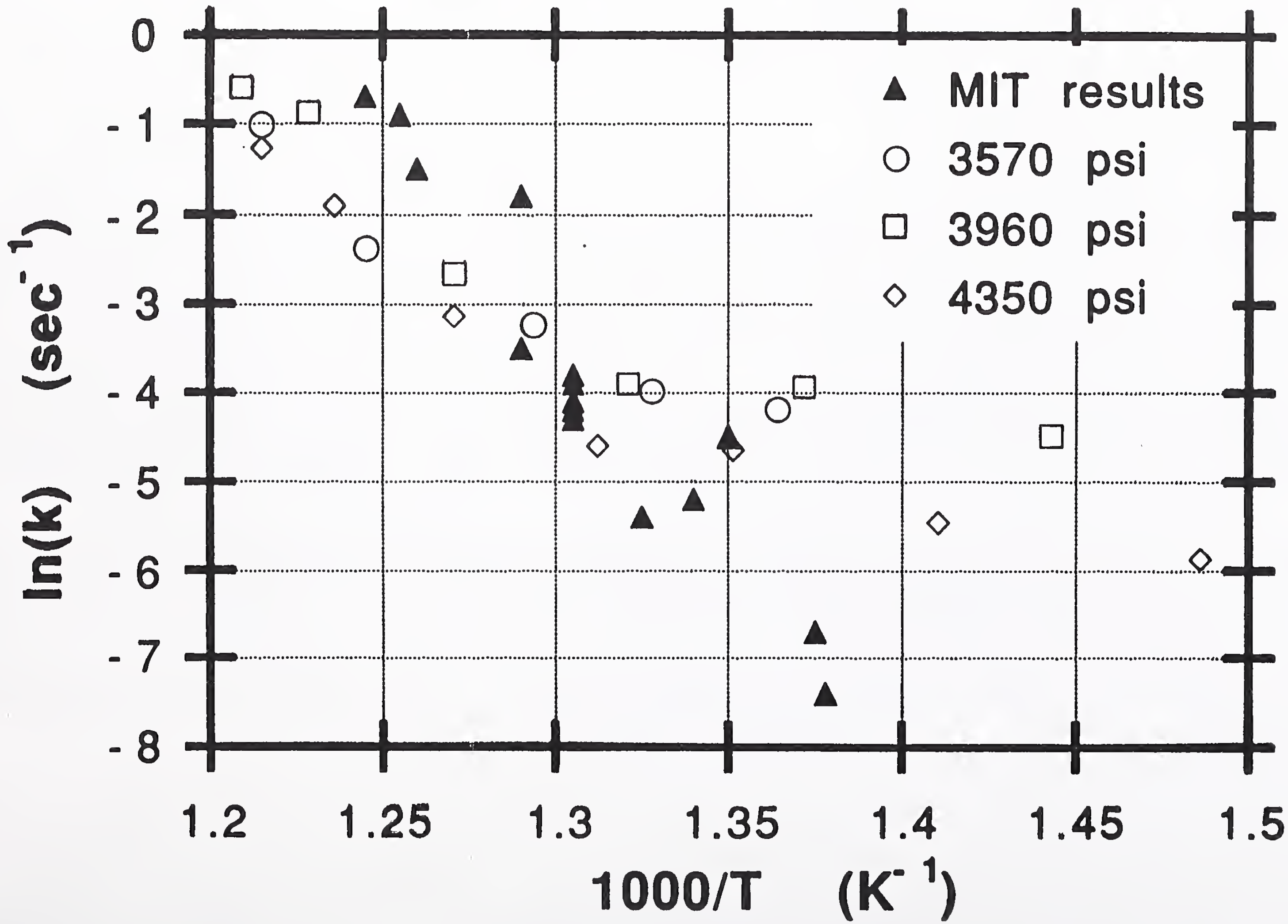



a
b
c
d




Methanol Destruction Efficiency
[MeOH]out/[MeOH]in
1
0.1
0.01
350
400
450
500
550
600
T(°C)
3570 psi
3960 psi
4350 psi

Methanol Reaction Rate

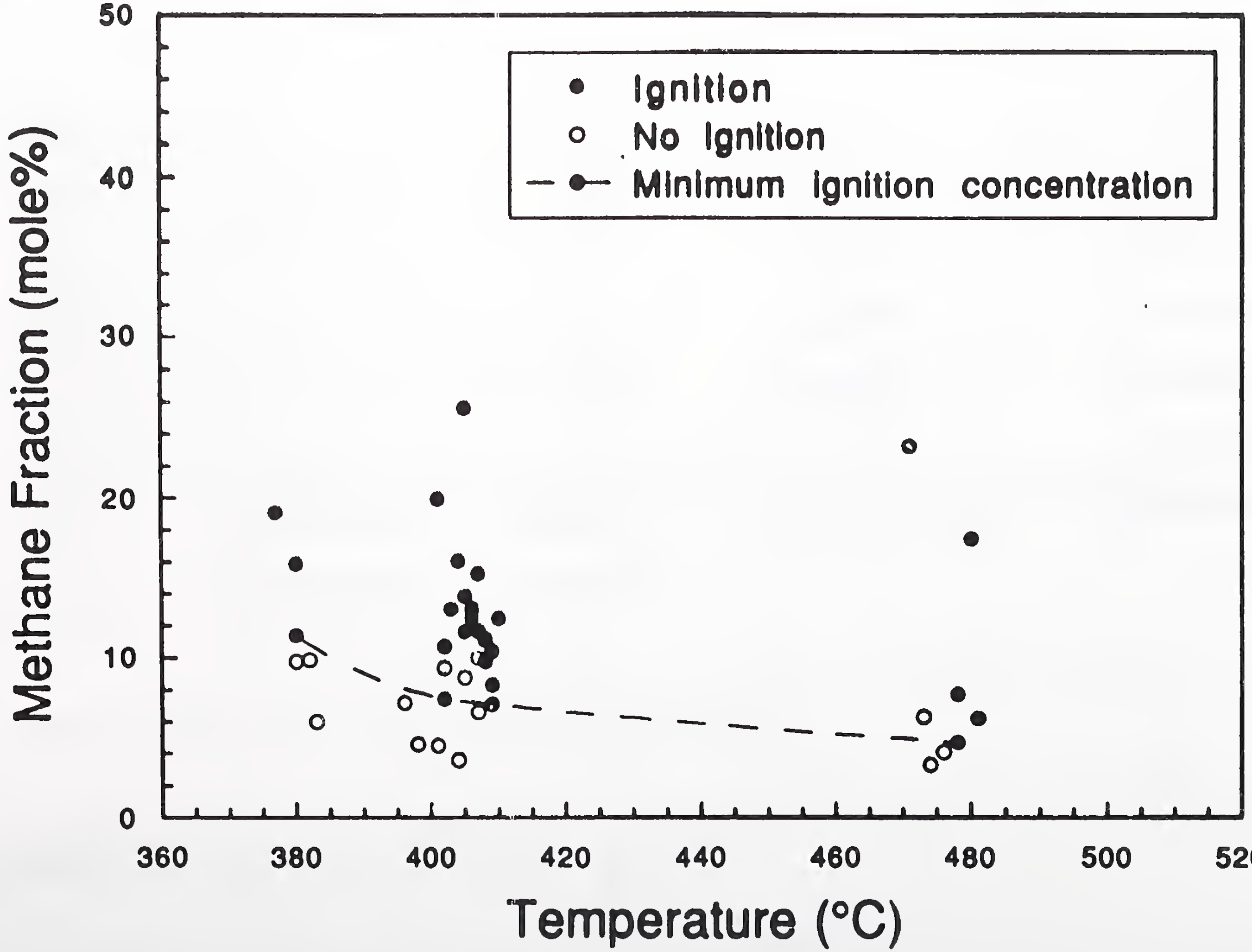


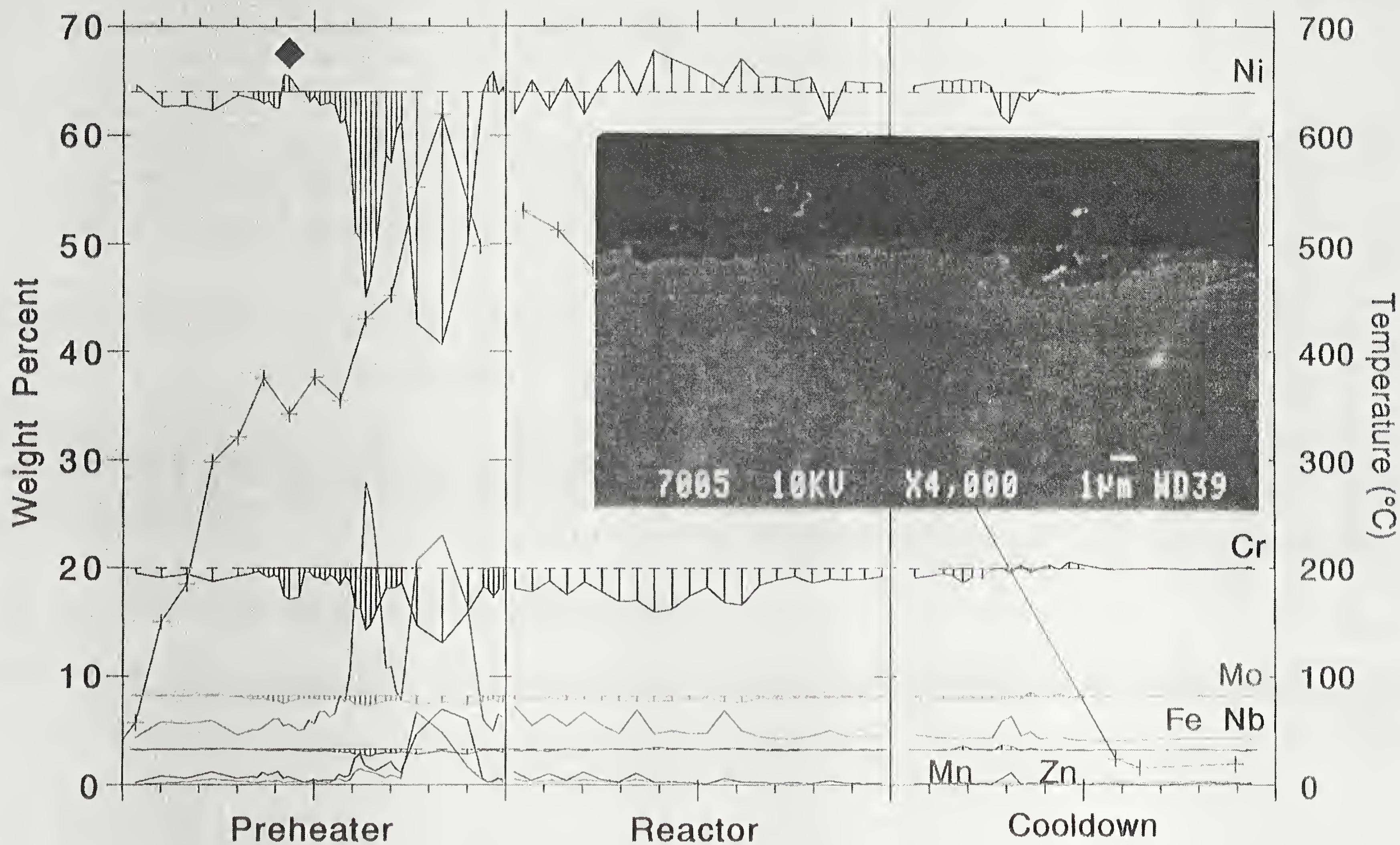
Oxidation of Acid Orange Dye

Input: 2140 ppm TOC (0.5% by weight)

Temp (°C)	Residence Time (sec)	TOC_{OUT} (ppm)	% Destroyed	Appearance
556	7.4	3.35	99.69	colorless
553	7.4	3.39	99.68	colorless
542	7.6	4.51	99.58	colorless
520	8.1	21.4	98.00	pale yellow
506	8.4	180	83.1	brown
484	9.2	247	76.9	brown w/ solids

Methane Minimum Ignition Conditions at 275 Bar





Weight Percent
Temperature (°C)
70
60
50
40
30
20
10
0
700
600
500
400
300
200
100
0
Ni
Cr
Mo
Fe Nb
Mn Zn
7005 10KU X4,000 1µm WD39
Preheater
Reactor
Cooldown

DoE's Quest for Energy Recovery Using SCWO

Dr. Gideon Varga
Department of Energy, Washington DC

DOE - Office of Industrial Technologies (OIT) Goal for Supercritical Water Oxidation:

Develop an aqueous industrial waste oxidation process which

- Conserves energy relative to alternative waste disposal methods
- Produces exportable energy
- Avoids NIMBY

DOE/OIT has viewed SCWO as

- Energy efficient method of destroying organics in aqueous wastes (near-term)
- Method of recovering heating value from wastes (intermediate term)
- Basis of a new power cycle that can generate power from wastes and low grade fuels (long-term)

Current Projects

Contractor:	Stone & Webster/ Modar	Modell Development
Start:	June, 1988	October, 1989
Contract Type:	Competitive Procurement	Grant
Funding:	$2,084k DOE 226k Cost Share	922k DOE 263k Cost Share
Reactor Type:	Shaped Chamber	Linear Chamber

Program Phases

PHASE I	Feasibility Evaluation (Complete)
PHASE II	Proof of Concept
PHASE III	Pilot System Development
PHASE IV	Testing Under Industrial Conditions

Phase I - Feasibility Evaluation Conclusions

- Supercritical preferred over subcritical
- Perceived barriers to commercialization

(1) High capital and operating costs

(2) Continuous operation

(3) Heat and power extraction

Modell Development - Current Activity

- Use existing 30 GPD pipe reactor unit
- Experimental runs completed. Draft report mark up returned
- Evaluate performance of proprietary salt removal technique
- Determine corrosion, wear and deterioration
- Continuous operation demonstrated for 120 hours

Stone & Webster/Modar - Current Activity

- Construct 500 GPD Unit — to 11/92
  Perform Testing — to 4/93

- Demonstrate reactor vessel design approach for minimizing solids deposition

- Determine practicality of on-line filter cleaning

- Demonstrate continuous operation for 168 hours

- Minimize corrosion

- Obtain process data

Whats Next?

- Evaluation of contractor data to determine
  - Energy efficiency relative to waste disposal alternatives
  - Potential for generating exportable energy
  - Capital and operating costs
  - Environmental attractiveness
  - Technology needs
- If warranted
  - Identify/develop heat exchanger (steam) or turbine (electricity)
  - Formulate approach to complete Phases III and IV with limited funding.

Progress on the MODEC & MODAR Supercritical Water Reactors

Mr. Bob Chappell
DoE Idaho Operations

CONFIGURATION (MODEC)

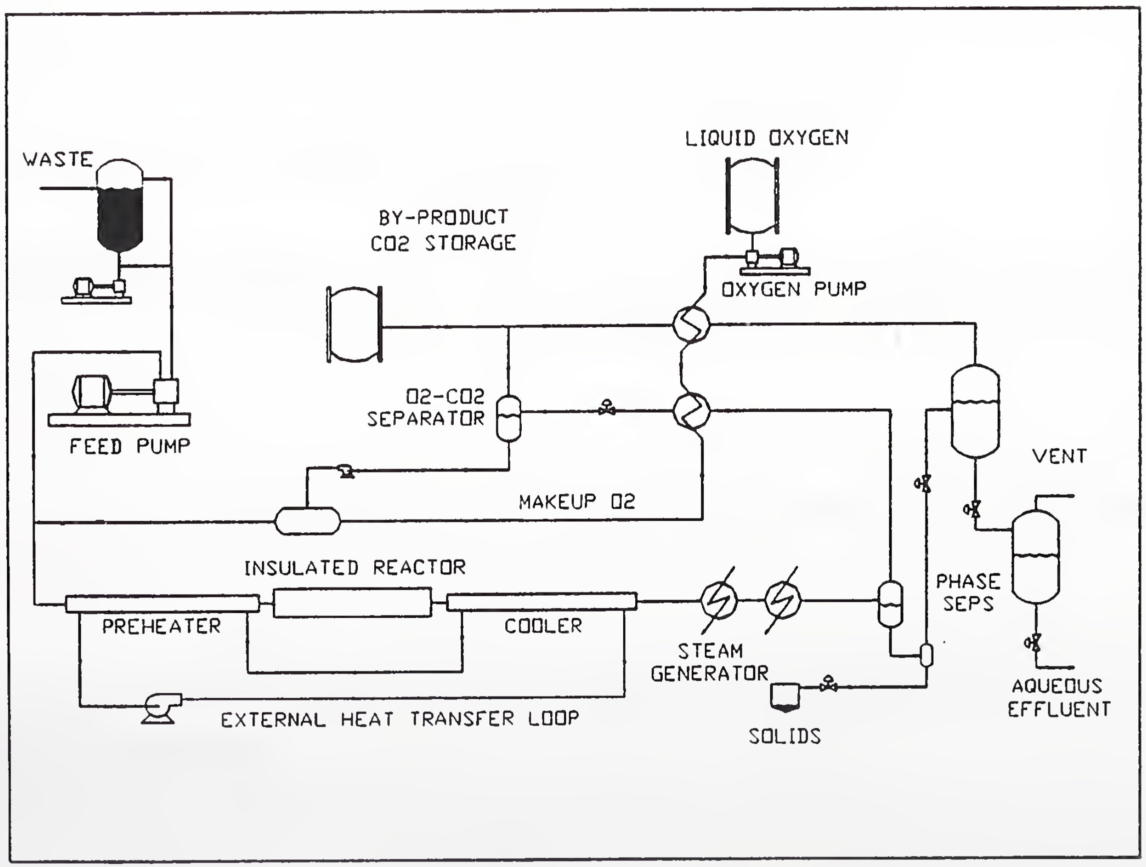
PIPE REACTOR

PREHEATER FOLLOWED BY REACTOR THEN BY COOL-DOWN AND SOLIDS SEPARATION

PRESSURIZE TO 3700 THEN HEAT TO 600 C.

4 TO 6 "9S" DESTRUCTION EFFICIENCY

AVERAGE RESIDENCE TIME 1.5 MIN.



LATEST WORK (MODEC)

THREE TESTS COMPLETED ON SLUDGE FROM PAPER MILL ORGANIC TREATMENT PLANT

- FIRST TEST 50% OPERATING, 50% CLEANING
- SECOND TEST 75% OPERATING, 25% CLEANING
- PROBLEMS ENCOUNTERED WERE RELATED TO UNIT SIZE.
- LARGER UNIT MAY ACHIEVE MUCH HIGHER OPERATING PERCENTAGES.

SOLIDS DEPOSITION PROBLEM SOLVED.

- DEPOSITION PREVENTION
- DEPOSIT REMOVAL

CHLORIDE CORROSION PROBLEM CONTROLLABLE

- UP TO 2,000 PPM CAN BE HANDLED IN CURRENT BENCH SCALE UNIT
- UP TO 20,000 PPM TO BE HANDLED IN NEW UNIT WITH IN SITU NEUTRALIZATION

EFFLUENT DISPOSAL (MODEC)

ALL EFFLUENTS CAPTURED (SYSTEM COMPLETELY ENCLOSED).

CO_2 IS FOOD GRADE (KEY IS IN GAS SEPARATION).

WATER MEETS EPA STANDARDS FOR DISPOSAL INTO STREAMS AND LAKES.

SOLIDS EXCEED THE EPA TCLP TEST BY A FACTOR OF 100 WHICH ALLOWS DISPOSAL IN SANITARY LANDFILLS.

ADVANCED WATER TREATMENT UNDER DEVELOPMENT WHICH WILL MEET GERMAN PHARMACEUTICAL MANUFACTURING ASSOCIATION'S QUALITY STANDARD FOR PROCESS WATER. TREATMENT COSTS INCREASE BY $.01 PER GALLON.

PROJECTED COSTS (MODEC)

CAPITAL COST (ESTIMATED BY APPLIED ENGINEERING, DIVISION OF JACOBS ENGINEERING)

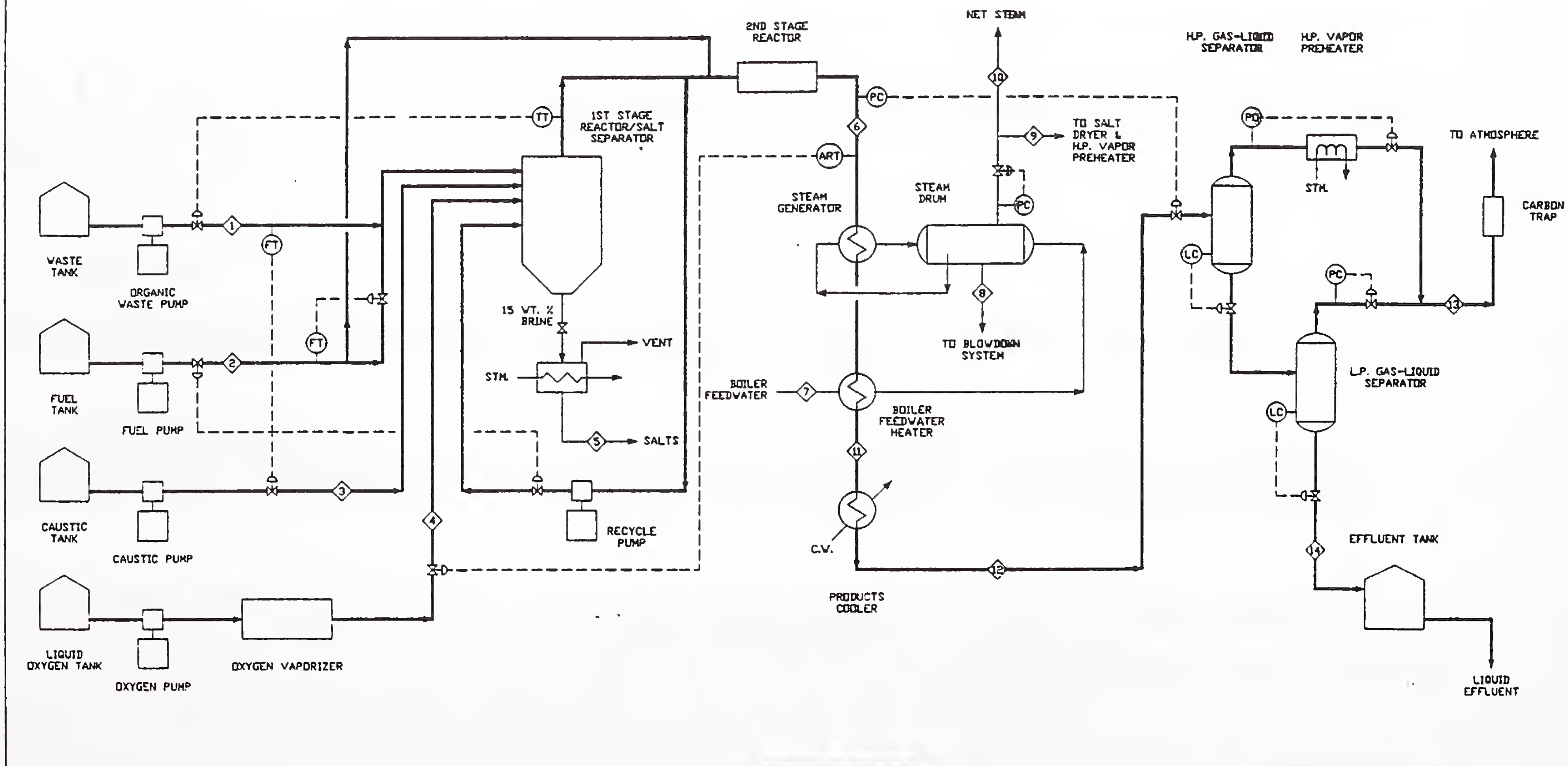
$3,100,000 FOR 5 DRY TON PER DAY SYSTEM

REACTOR IS 10% OF TOTAL CAPITAL COST

OPERATING AND MAINTENANCE COST

$.04 PER GALLON FOR 5 DRY TON PER DAY SYSTEM, 5% BY WEIGHT SOLIDS

CONFIGURATION (MODAR)



STREAM NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14
PRESSURE, PSIA	3700	3700	3700	3700	14.7	3700	240	165	165	165	3700	3700	17	17
TEMPERATURE, °F	60	60	60	60	194	1112	200	366	366	366	302	104	~220	~[illegible]
FLOW, LB/HR	6,960	12	160	2,200	116	8,559	9,401	448	1,206	7,747	8,559	8,559	2,200	[illegible]

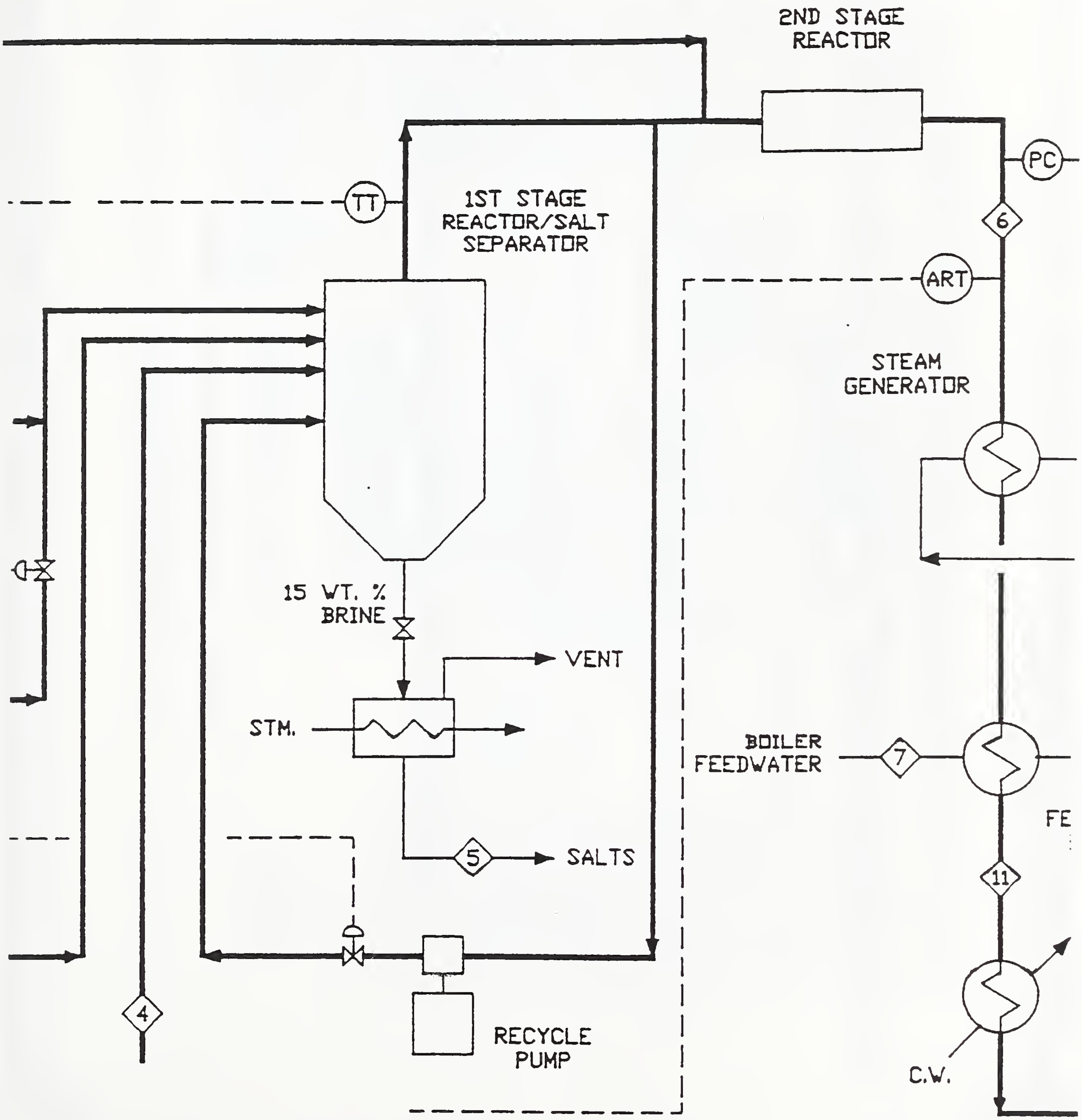
PROCESS FLOW DIAGRAM
WET OXIDATION FOR
HAZARDOUS WASTE DISPOSAL
USING MODAR, INC. TECHNOLOGY
J.O. 18240.04
STONE & WEBSTER ENGINEERING CORPORATION
BOSTON, MASS.
FIGURE 4.2-7

T.A. VIVENZIO

4	3	2 REVISION 1	1 ORIGINAL ISSUE
		JULY 31, 1989	NOV. 18, 1988

FIG4-7

REACTOR DETAIL (MODAR)



Supercritical Water Oxidation for Space Life Support Applications

A Presentation for the Workshop on Federal Programs Invloving Supercritical Water Oxidation

July 6-7, 1992

National Institute of Standards and Technology,

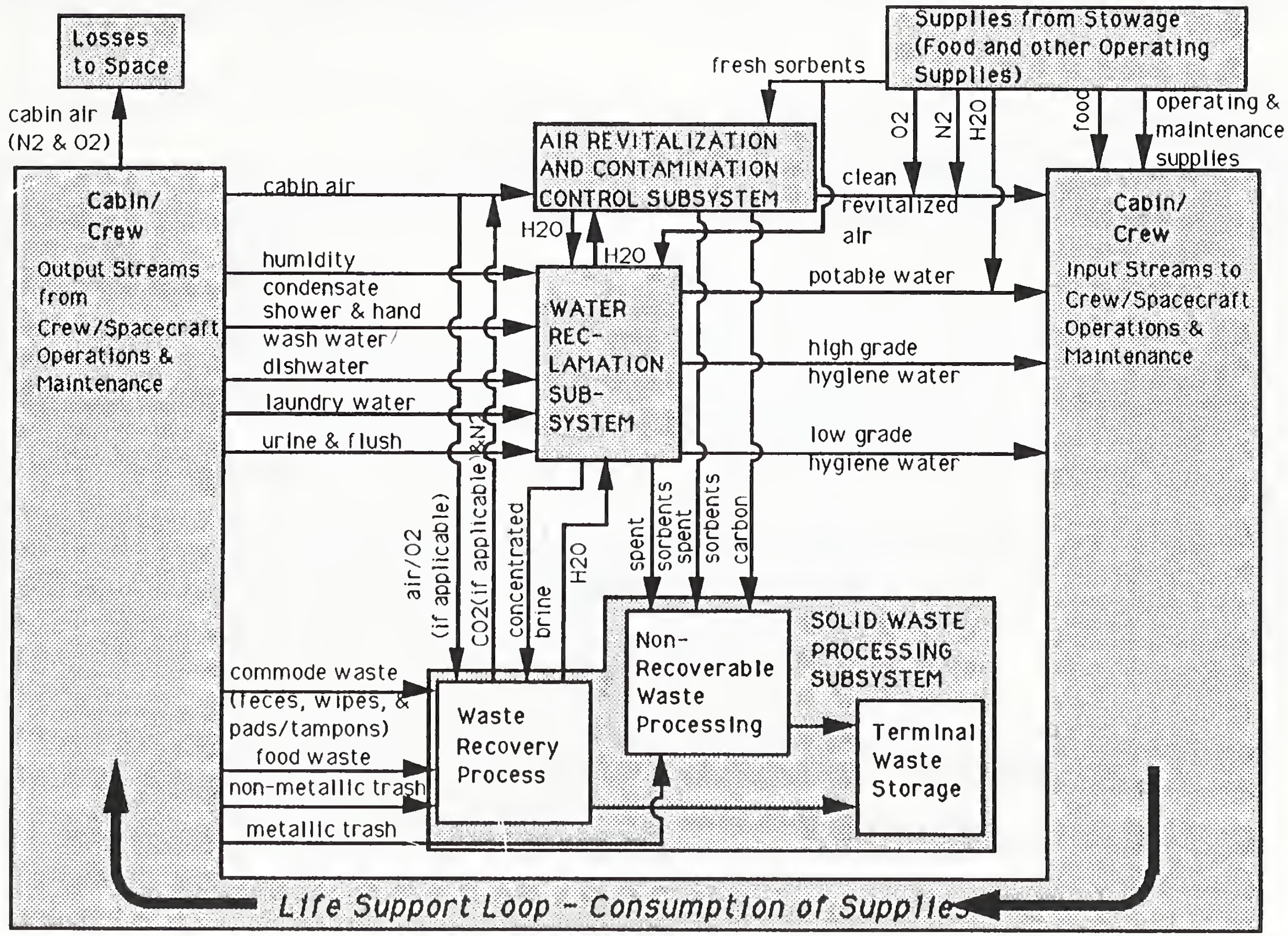
Gaithersburg, MD

T. Mark Hightower

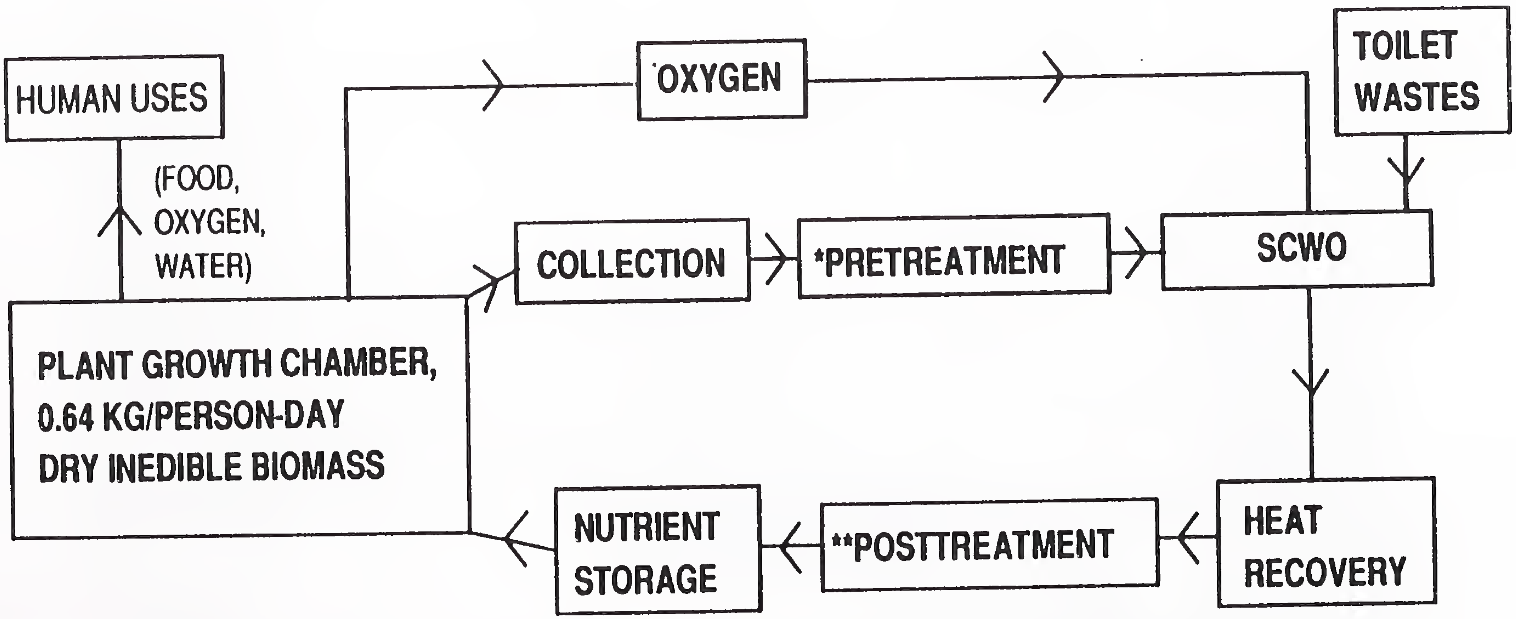
NASA - Ames Research Center

Moffett Field, CA

Physical/Chemical Regenerative Life Support System - Block Flow Diagram



SCHEMATIC FOR PROCESSING INEDIBLE BIOMASS & TOILET WASTES TO RECOVER PLANT NUTRIENTS



* E.G., PARTICLE SIZE REDUCTION, PARTIAL NUTRIENT RECOVERY, GLUCOSE EXTRACTION

** E.G., SALT SEPARATION & NUTRIENT RECOVERY, GAS CLEANUP

Supercritical Water Oxidation (SCWO) - Solid Waste Management for extended duration space habitation

Typical wastes processed

- Feces, concentrated urine and hygiene water brines, food scraps, inedible plant biomass, food packaging, stationary, and wipes

Features of SCWO

- High destruction efficiency (>99.9%) and low residence time (< 5 min) minimize reactor size
- Handles aqueous wastes
- Inorganic salts formed are insoluble in supercritical water and can be separated from the product stream
- Higher thermal efficiency than incineration
- Process does not form harmful NOx and SO2
- Water produced is near potable

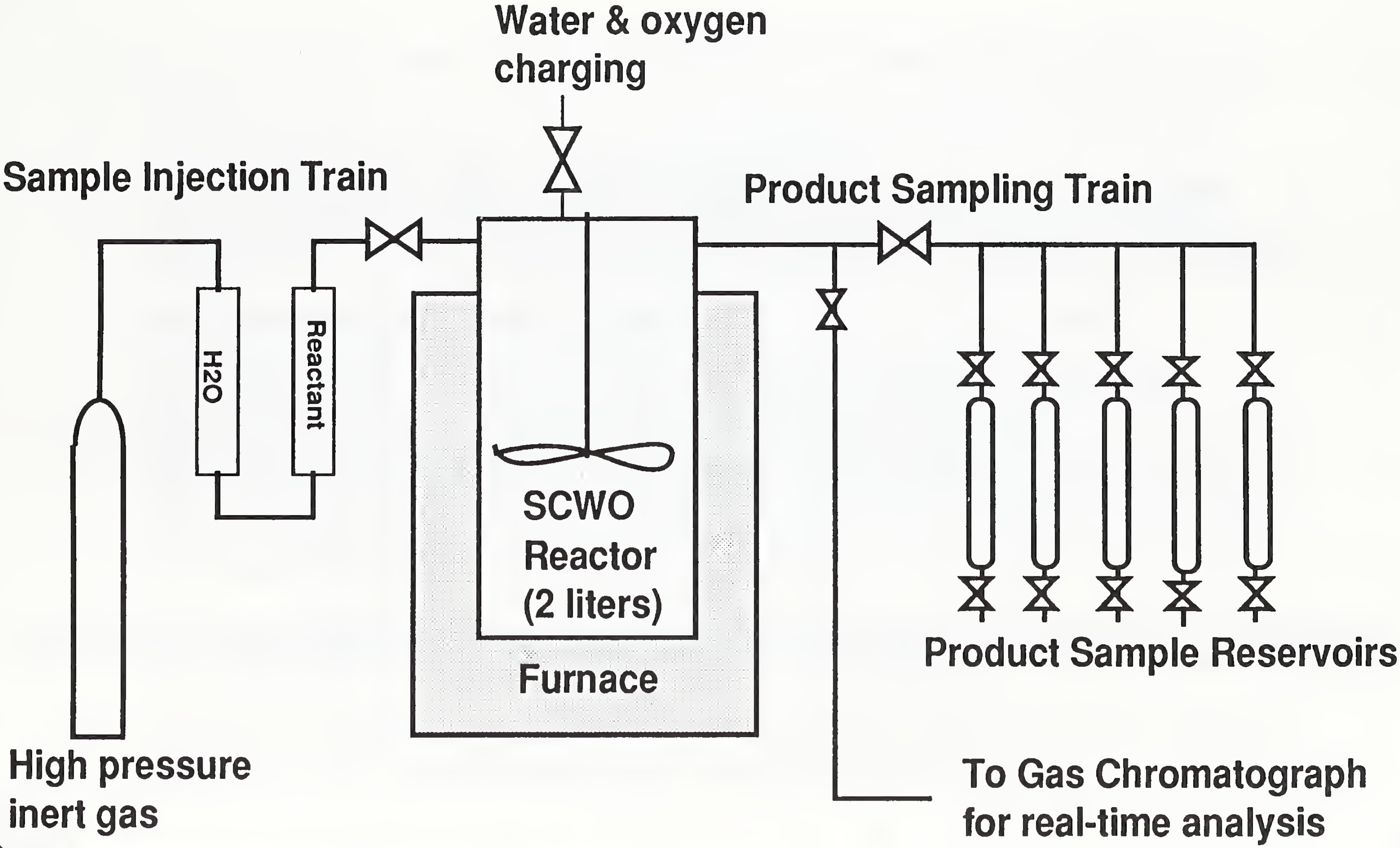
OXIDATIVE PROCESSES ARRANGED IN ORDER OF INCREASING INTENSITY

SCWO

PROCESS	RESIDENCE TIME	ACCEPTS WET WASTES	SPECIAL CONSIDERATIONS
Composting	months	yes	Very high solids effluent
Activated Sludge	weeks	yes	High sludge effluent flow
Sub-critical Wet Oxidation	hours	yes	NH4/organic acids effluent. High pressure process, but not as high as SCWO.
Electrochemical Oxidation	hours	yes	May not handle some solid wastes. May serve best as a polishing process.
Super-critical Water Oxidation (SCWO)	minutes	yes	High pressure process
Incineration (flame combustion)	seconds	yes, but wastes may need to be dried first	High temperature process. NOx, SO2, and particulates in effluent.
Plasma Processing	milli - seconds	no	High temperature process. Energy Intensive

Special thanks to Gary P. Noyes, Ph.D., Life Support Development Laboratory, Lockheed Engineering & Sciences Company, Houston, TX, for help in developing this table. T. Mark Hightower NASA Ames 9/91

Simplified Schematic of the Modified Batch SCWO Reactor



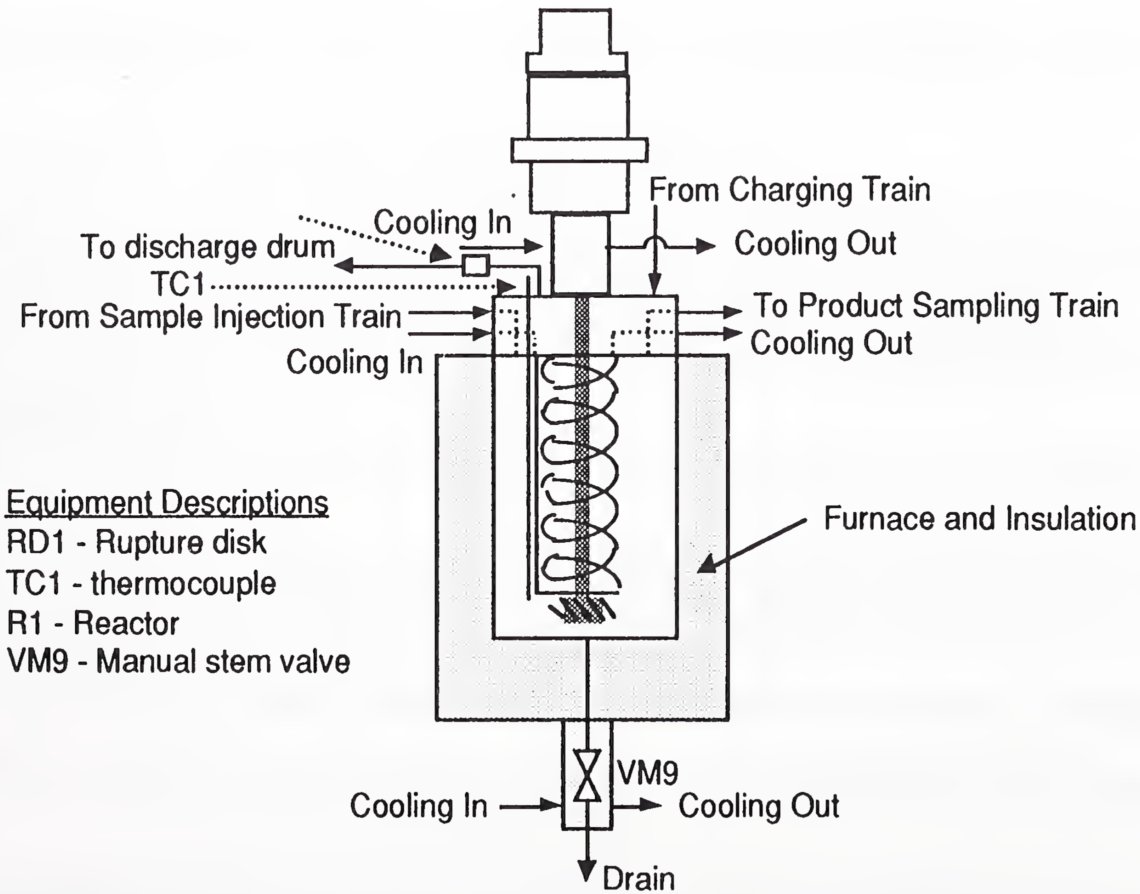
Purpose of Modifications to Ames Batch SCWO Reactor

- Modifications are in progress to allow samples to be quickly injected into the reactor containing water and oxygen preheated to supercritical conditions.
- This provides good temperature control which is essential for obtaining good kinetics data

Simplified Operating Procedure of the Modified Batch SCWO Reactor

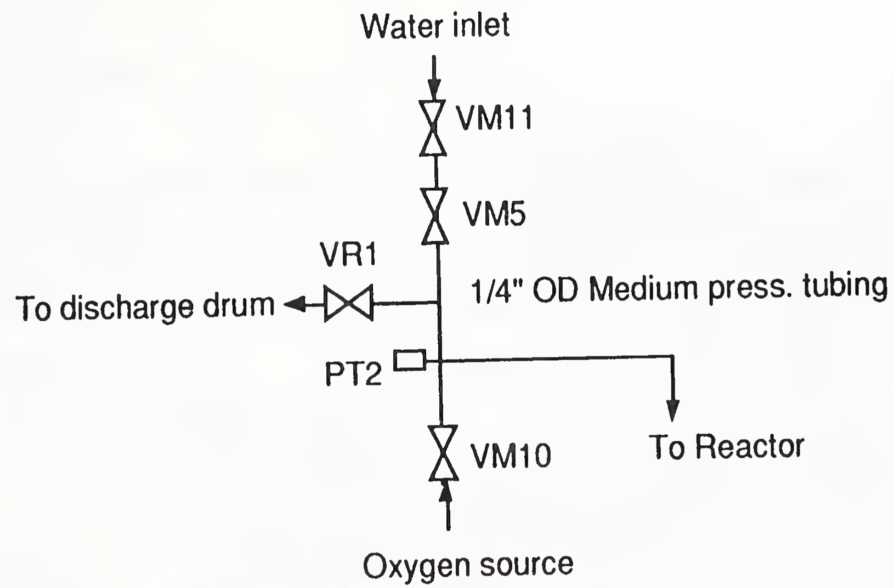
1. Charge water and oxygen to reactor at ambient temperature.
2. Load sample to be oxidized into sample injection train and pressurize with high pressure inert gas.
3. Bring reactor contents up to supercritical temperature and pressure.
4. Inject sample to be oxidized into reactor to start batch reaction run.
5. Take samples from reactor for analysis to assess the extent to which the reaction has proceeded versus time and to determine the products of reaction. (Samples can be retained in reservoirs for later analysis, as well as sent directly to gas chromatograph for real-time analysis.)
6. Automatically actuated valves are used to control the injection and taking of samples in this system.
7. Typical reactions are expected to last anywhere from 1 minute to 10 minutes, depending upon the temperature.

Schematic of Ames Batch SCWO Reactor - Reactor Assembly



Equipment Descriptions
RD1 - Rupture disk
TC1 - thermocouple
R1 - Reactor
VM9 - Manual stem valve

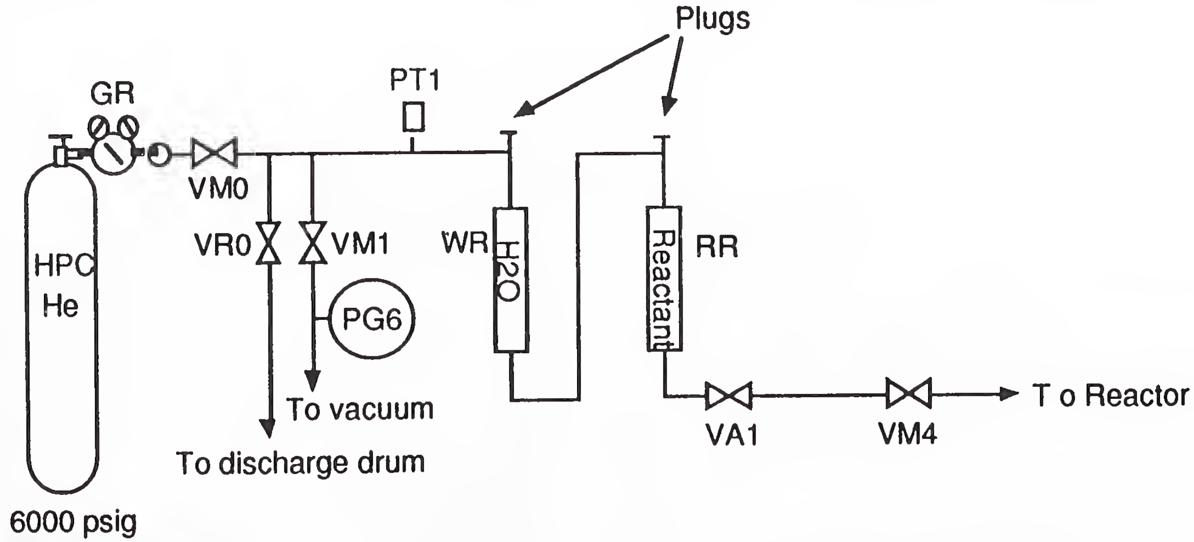
Schematic of Ames Batch SCWO Reactor - Charging Train



<u>Equipment Descriptions</u>

VM5, VM10, VM11 - manual stem valves
VR1 - relief valve
PT2 - Pressure transducer

Schematic of Ames Batch SCWO Reactor - Sample Injection Train



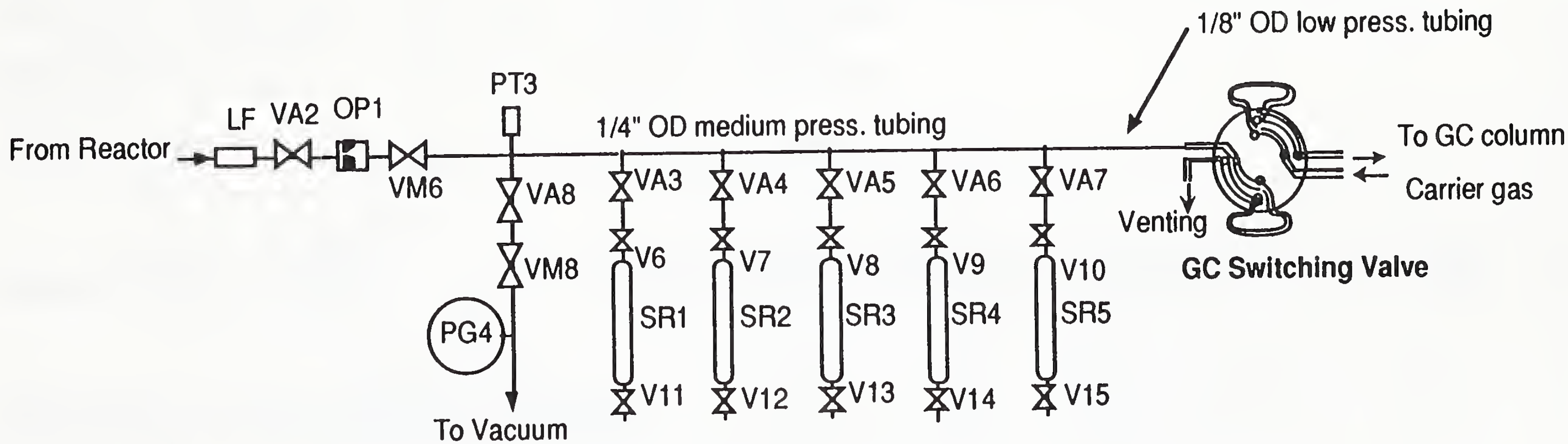
<u>Equipment Descriptions</u>

HPC - high pressure cylinder, helium
GR - Gas regulator
VM0, VM1, VM4 - manual stem valves
VR0 - relief valve
PG6- pressure gauge
PT1 - Pressure Transducer
WR - Water Reservoir
RR - Reactant Reservoir
VA1 - automatic ball valve

<u>Notes</u>

All lines are 1/4" OD medium pressure tubing, except that the WR and RR are 3/8" medium pressure tubing. Medium pressure tubing is rated at 20,000 psi at room temperature.

Schematic of Ames Batch SCWO Reactor - Product Sampling Train



Product Sample Reservoirs

<u>Equipment Descriptions</u>

LF - line Filter, 15, 35, or 65 micron
VA2 - automatic stem valve
OP1 - Orifice Plate, 0.005" diameter
VM6 and VM8 - manual stem valves
PT3 - Pressure Transducer
VA3 to VA8 - automatic ball valves
V6 to V15 - manual stem valves
PG4- pressure gauge
SR1 to SR5 - Product Sample Reservoirs, 9/16" OD medium pressure tubing

<u>Notes</u>

The line from the reactor through and including LF, VA2, OP1, and VM6 will be kept at reactor temperature with heating tape.
Beyond VM6, the system will be kept at 120 degrees C with heating tape.
The GC Switching Valve has its own heater and will be kept at 120 degrees C as well.

Supercritical Oxidation - Basic Kinetics Model

Solid Waste (large molecules) $\xrightarrow[\text{fast reaction}]{\text{Supercritical water}}$ Small molecules

Small molecules + O_2 $\xrightarrow[\text{slow reactions}]{\text{Supercritical water}}$ CO_2 + H_2O + N_2 + Inorganic salts $\downarrow$

<u>Cellulose ($C_6H_{10}O_5$) Oxidation</u>

$C_6H_{10}O_5 + 2\ H_2O \xrightarrow{\text{fast}} CH_3COOH + C_2H_5OH + CH_3OH + CO + O_2$

$CH_3COOH + 2\ O_2 \xrightarrow{\text{slow}} 2\ CO_2 + 2\ H_2O$

$C_2H_5OH + 3\ O_2 \xrightarrow{\text{slow}} 2\ CO_2 + 3\ H_2O$

$CH_3OH + 3/2\ O_2 \xrightarrow{\text{slow}} CO_2 + 2\ H_2O$

$CO + 1/2\ O_2 \xrightarrow{\text{slow}} CO_2 + 2\ H_2O$

SCWO KINETICS DATA & ANALYSIS

The spreadsheet below duplicates the temperature / residence time / destruction efficiency data presented by Modell in Table 8.11.1, page 8.163 in the Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw-Hill, 1989. In addition, the spreadsheet calculates 1000/T, where T is in Kelvin, and ln k, where k is in seconds^(-1). ln k is calculated based upon the assumption of first order kinetics and is a function of residence time and destruction efficiency, according to the equation, ln k = ln((ln(100/(100-%DE)))*(1/(res time*60))), where res time is in minutes. From the 1000/T vs. ln k data, an Arrhenius plot can be prepared from which the first order kinetics hypothesis can be evaluated and first order reaction rate parameters can be derived.

T. M. Hightower 2/8/91

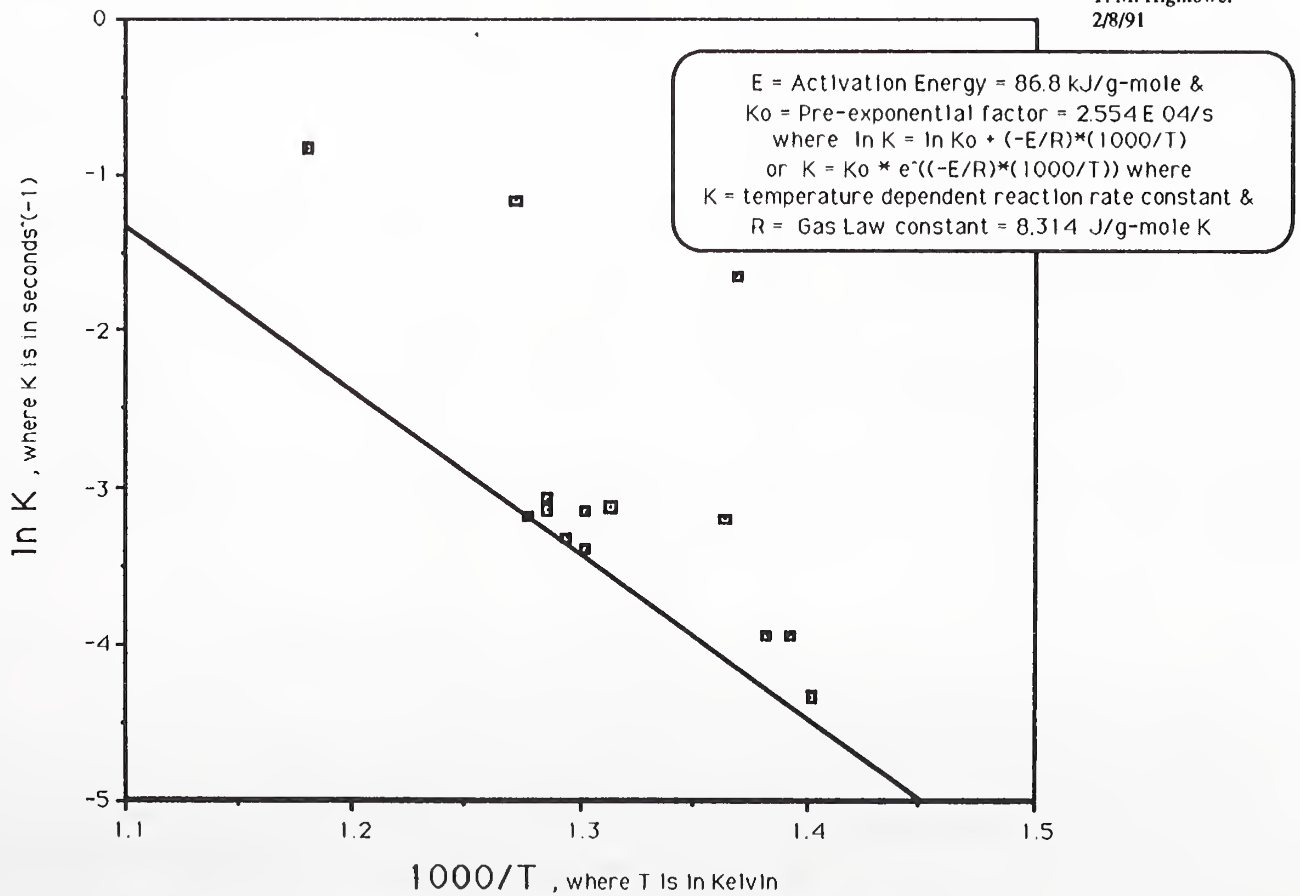
Compound	Temp.,deg C	Res.time, min	DE, %	1000/T	ln(k) **
Aliphatic hydrocarbons					
Cyclohexane	445	7	99.97	1.39246675	-3.94694
Aromatic hydrocarbons					
Biphenyl	450	7	99.97	1.38283897	-3.94694
O-Xylene	495	3.6	99.93	1.30182907	-3.39229
Halogenated aliphatics					
1,1,1-Trichloroethane	495	3.6	99.99	1.30182907	-3.15495
1,2-Ethylene dichloride	495	3.6	99.99	1.30182907	-3.15495
1,2,-Dichloroethane	495	3.6	99.99	1.30182907	-3.15495
1,1,2,2-Tetrachloroethylene	495	3.6	99.99	1.30182907	-3.15495
Hexachlorocyclohexane	495	3.6	99.99	1.30182907	-3.15495
Halogenated aromatics					
o-Chlorotoluene	495	3.6	99.99	1.30182907	-3.15495
Hexachlorocyclopentadiene	488	3.5	99.99	1.31380148	-3.12678
1,2,4-Trichlorobenzene	495	3.6	99.99	1.30182907	-3.15495
4,4-Dichlorobiphenyl	500	4.4	99.993	1.29341008	-3.31763
DDT	505	3.7	99.997	1.28509927	-3.05950
PCB 1234	510	3.7	99.99	1.27689459	-3.18235
PCB 1254	510	3.7	99.99	1.27689459	-3.18235
Oxygenated compounds					
Methyl ethyl ketone	460	3.2	99.96	1.36397736	-3.20029
Methyl ethyl ketone	505	3.7	99.993	1.28509927	-3.14436
Dextrose	440	7	99.6	1.40222954	-4.33161
Organic nitrogen compounds					
2,4-Dinitrotoluene	457	0.5	99.7	1.36958159	-1.64176
2,4-Dinitrotoluene	513	0.5	99.992	1.27202188	-1.15693
2,4-Dinitrotoluene	574	0.5	99.9998	1.1804285	-0.82688

SUPERCRITICAL WATER OXIDATION (SCWO)

GENERALIZED FIRST ORDER REACTION RATE PARAMETER DETERMINATION

The Arrhenius Plot below documents the determination of the Activation Energy and Pre-exponential factor used for the oxidation of organics in supercritical water according to first order kinetics. The data points are based upon the reduction of data from Modell, Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw-Hill, 1989. To be conservative, the best straight line through the data is shifted downward so that predicted reaction rates will be less than or equal to the rates of the data. The three data points which are high are for nitro organic compounds, which explains their higher reactivity.

T. M. Hightower
2/8/91



Comparing Generalized Organics Oxidation Arrhenius Plot to those of Simple Compounds

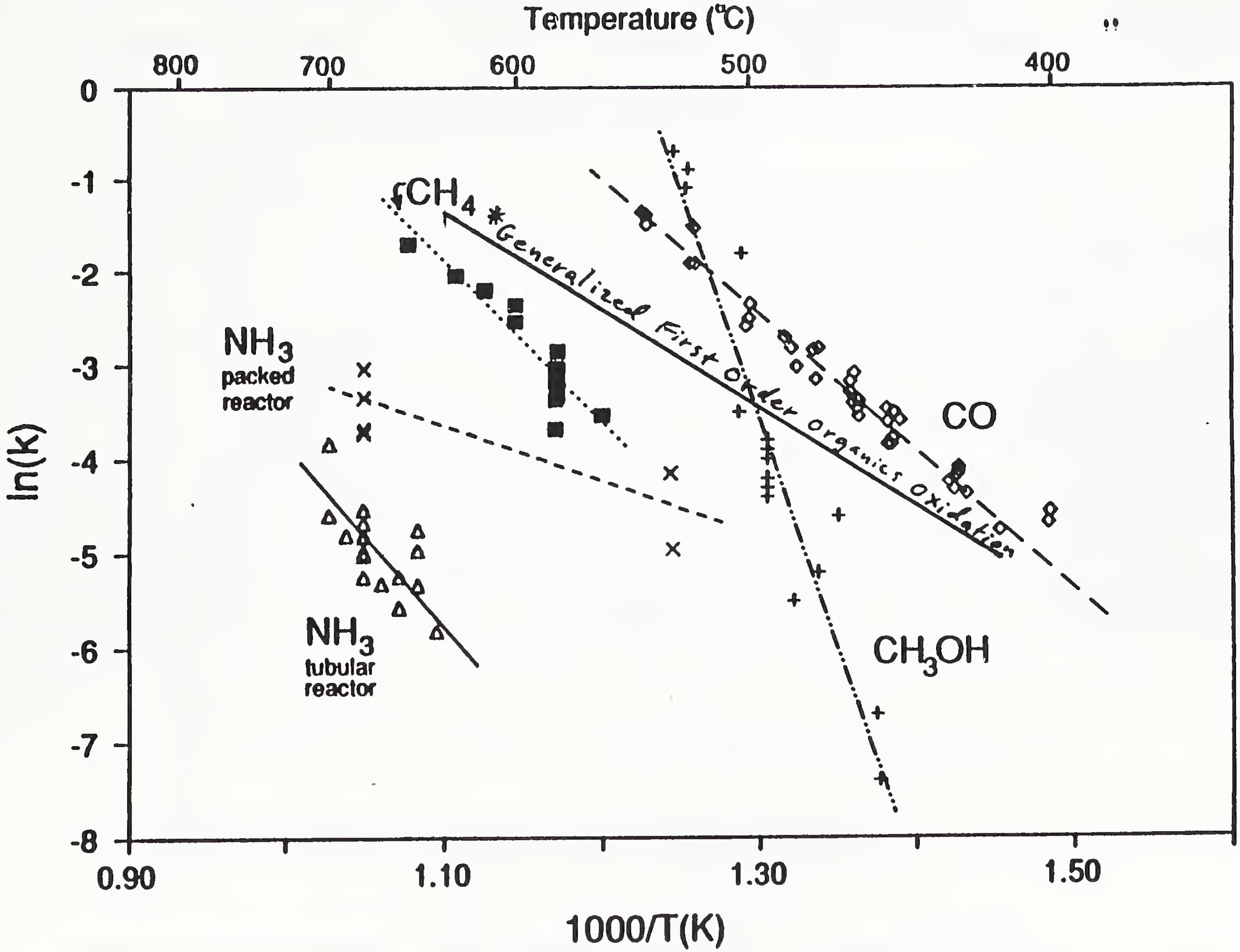
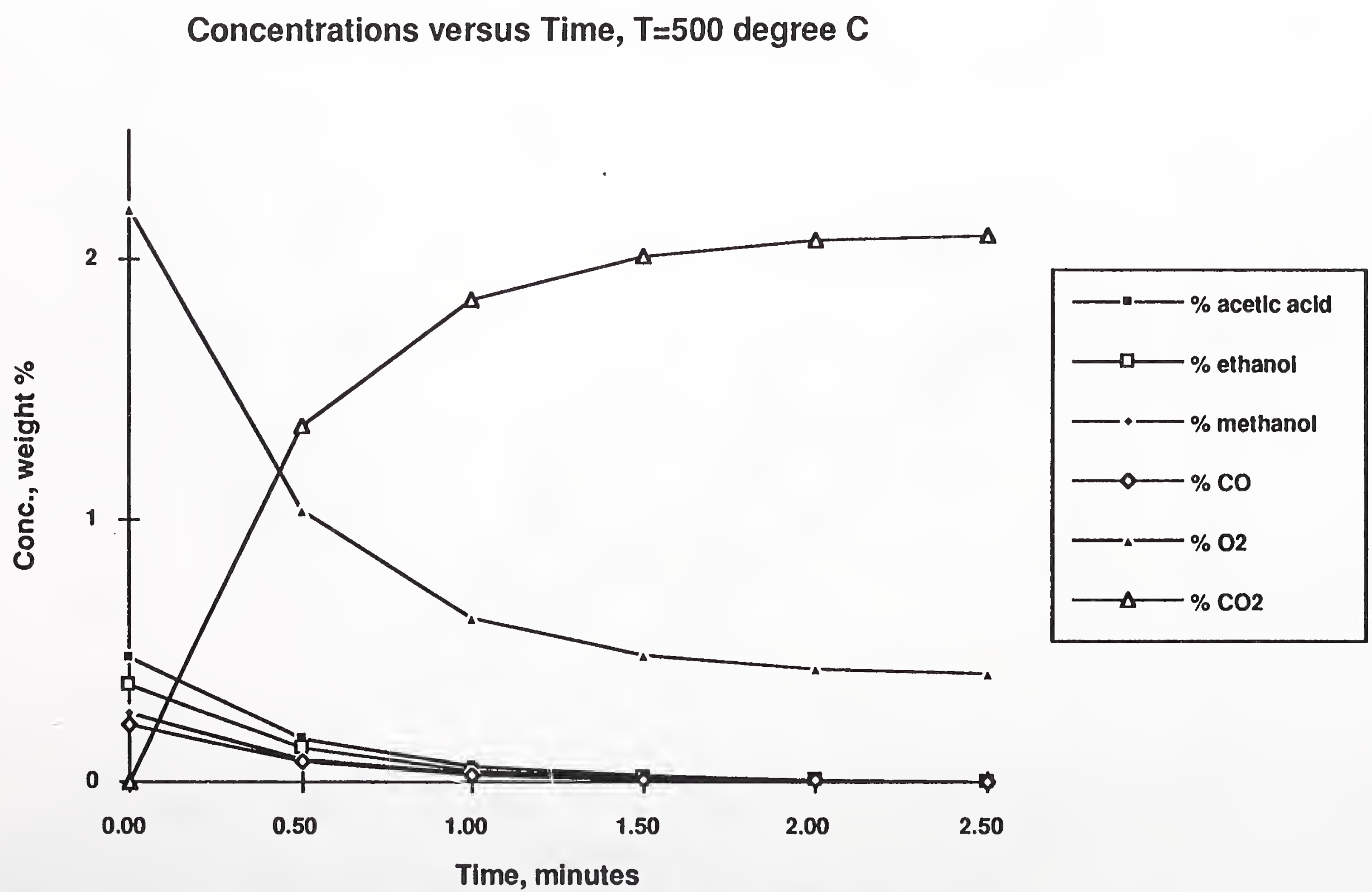


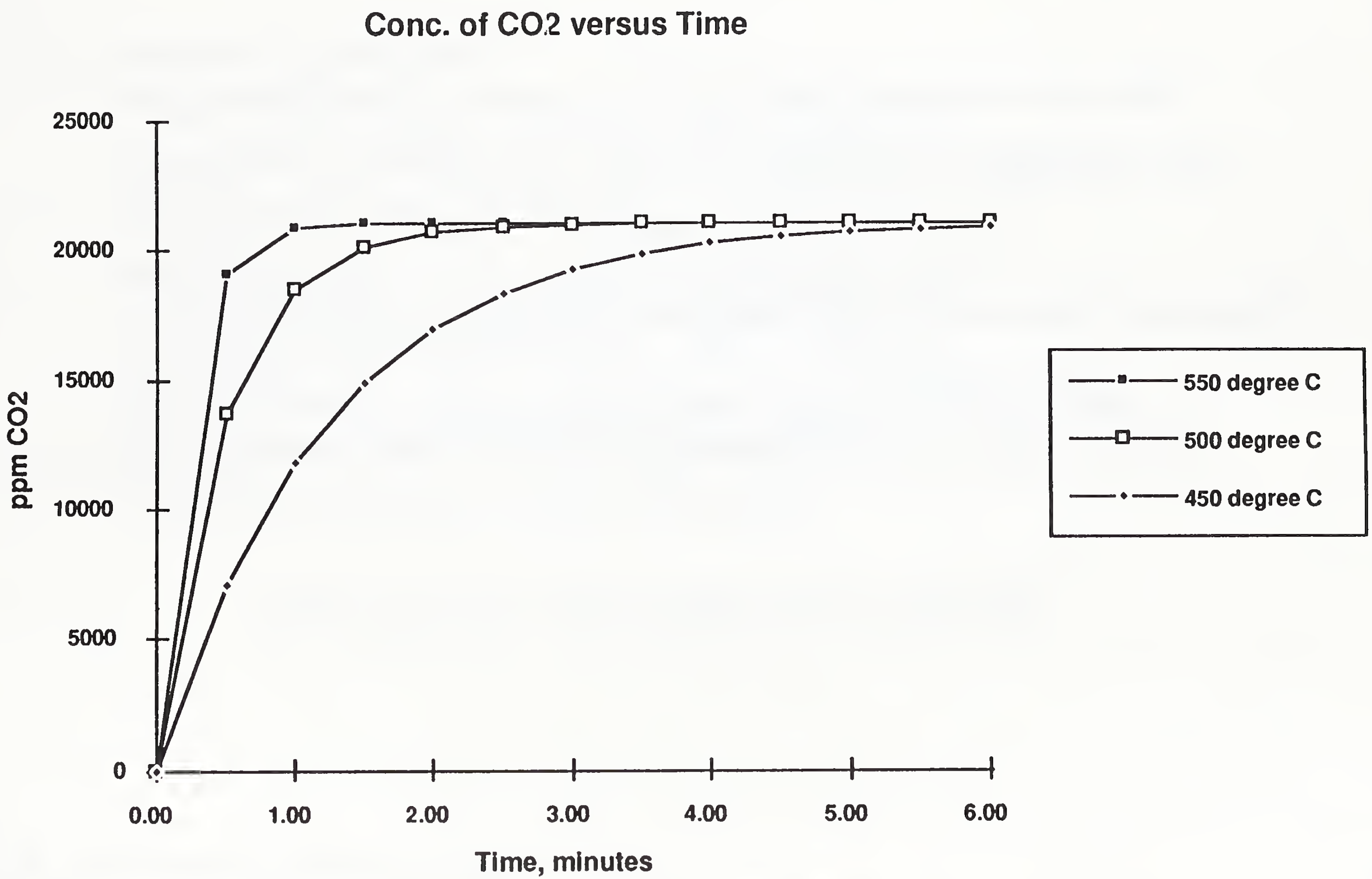
Figure 4. First-order Arrhenius Plot for Oxidation of Model Compounds in Supercritical Water. (J.W. Tester, MIT)

* Generalized organics oxidation Arrhenius plot from data reduction by T.M. Hightower, NASA Ames Research Center, 1991

Modeling results - typical of data to be expected from reactor



Modeling results - typical temperature dependence of reaction



Key SCWO development issues

- Need kinetics data on typical space wastes so that a more rigorous model for the destruction of these wastes can be developed
- Waste feed preparation and handling (i.e. macerating, slurrying, and pumping)
- Salt formation and separation
- Corrosion, including corrosion by-products in effluent water
- Addressing safety concerns especially related to the high pressure of operation

The following figures are from a preliminary draft (April 1992) of a NASA Report entitled "Supercritical Water Oxidation - Process Analysis and Computer Modeling" by T. Mark Hightower. It is planned to publish this report as a NASA Technical Memorandum in the future.

Figure 8 - Spreadsheet model results
SCWO Reactor Residence Time versus Temperature & Destruction Efficiency for Isothermal Plug Flow Reactor with First Order Kinetics
Temperature Range, 700 K - 900 K
Recycle Ratio = 0.0

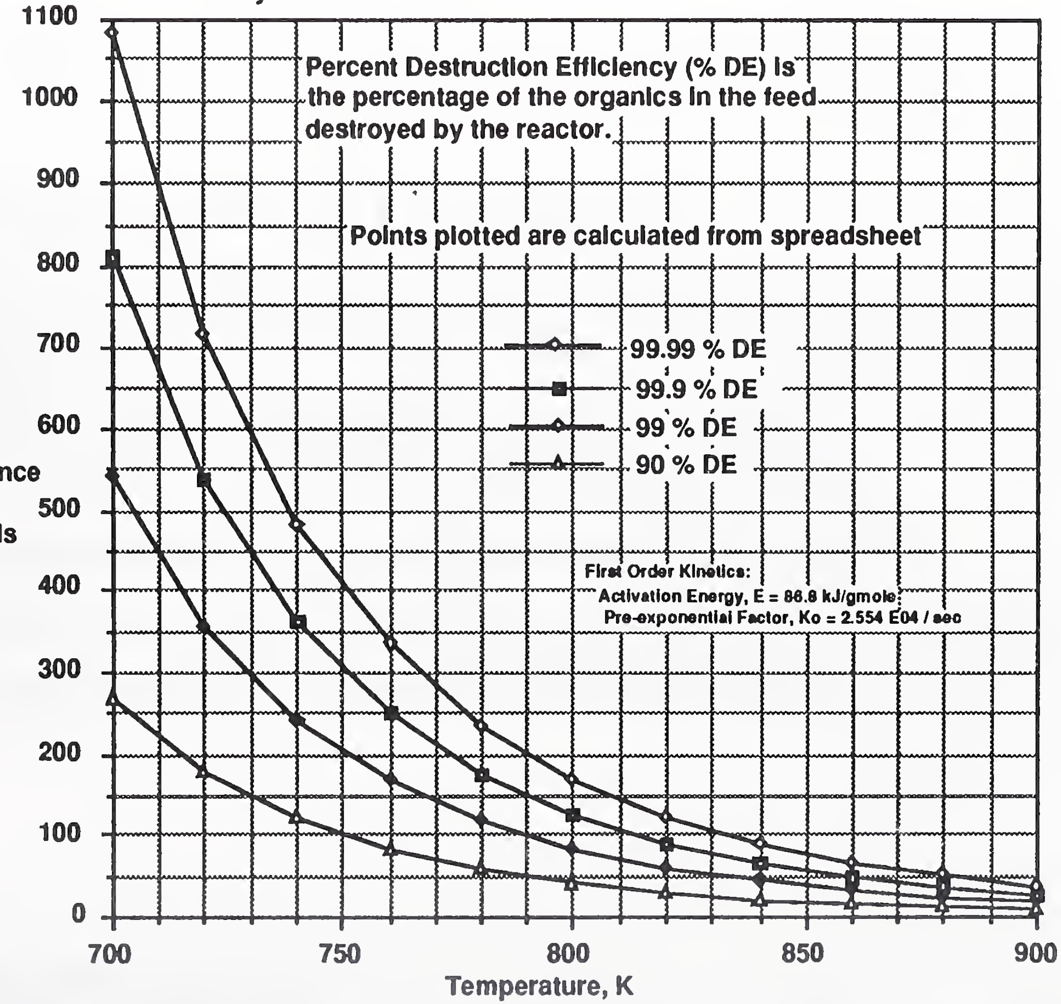


Figure 9 - Spreadsheet model results
SCWO Reactor Residence Time versus Temperature & Destruction Efficiency for Isothermal Plug Flow Reactor with First Order Kinetics
Temperature Range, 900 K - 1100 K
Recycle Ratio = 0.0

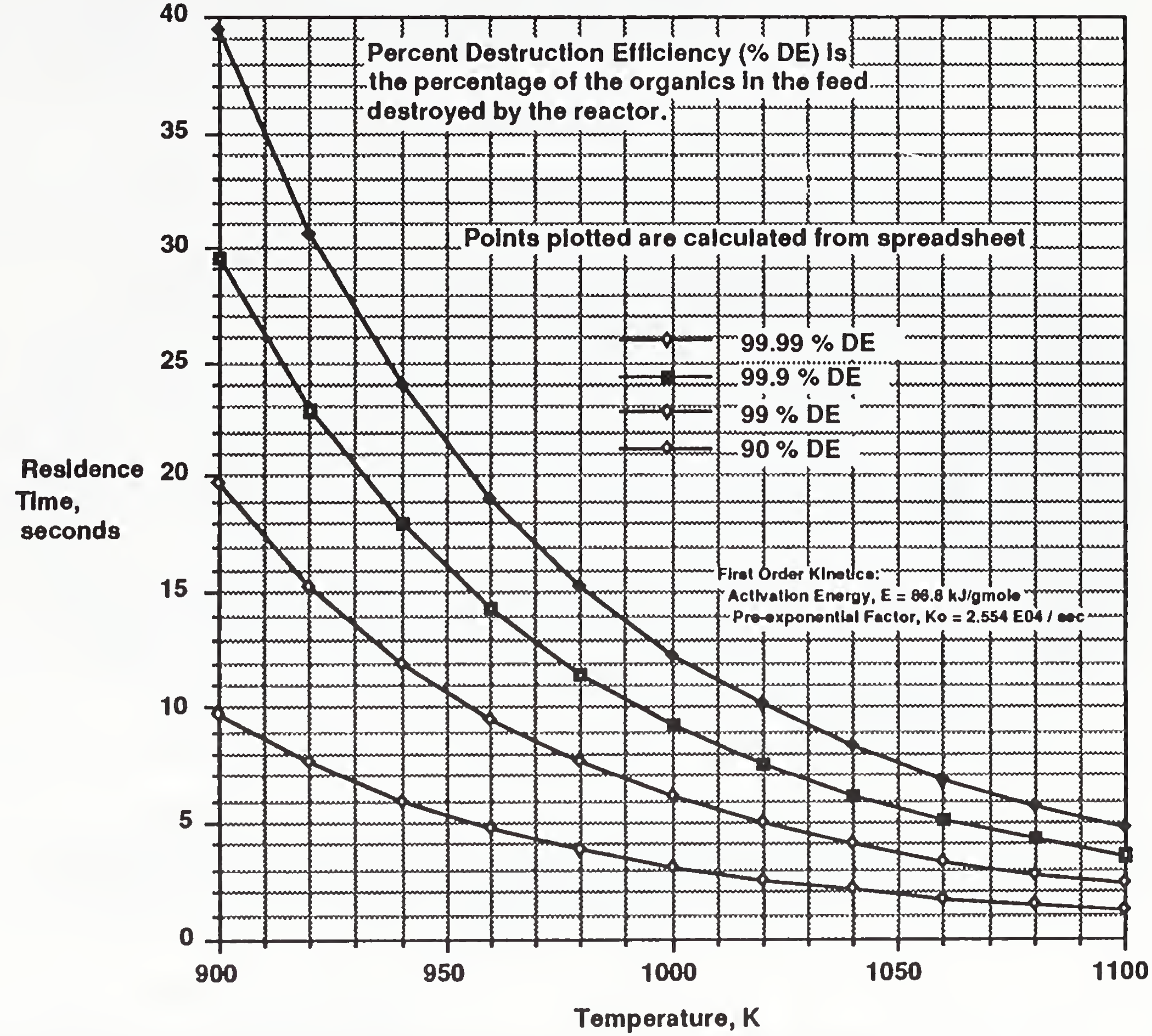
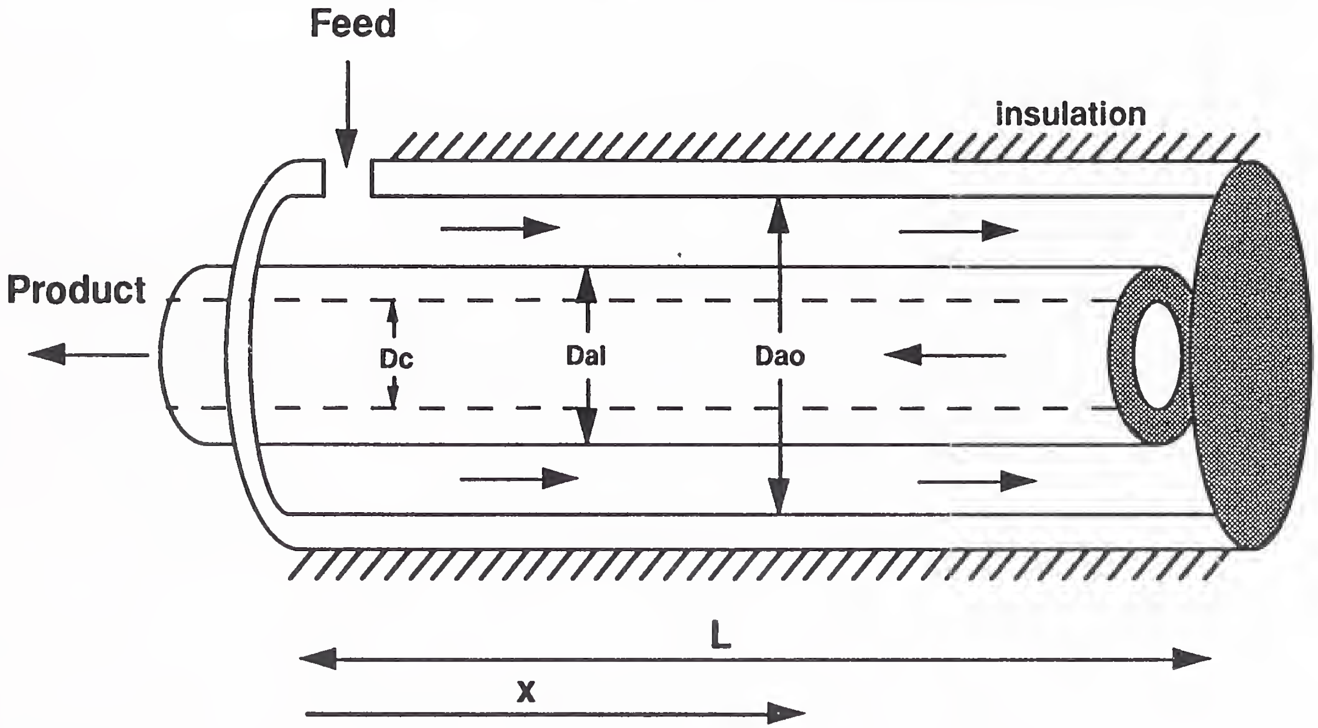
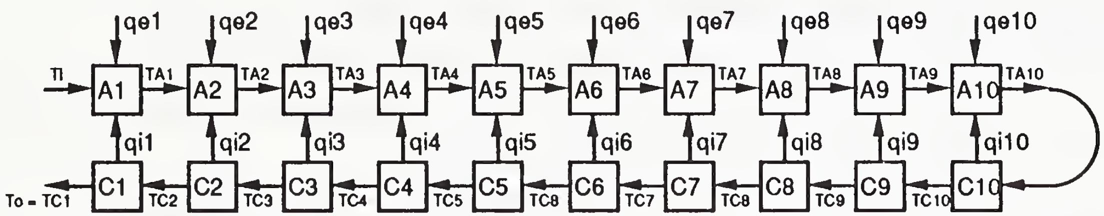


Figure 15
SCWO Concentric Tube Reactor Configuration



Dc = inside diameter of core = 3 cm
Dai = inside diameter of annulus = 3.25 cm
Dao = outside diameter of annulus = 4.5 cm
L = length of reactor, cm
x = distance from reactor inlet for temperature profile reference, cm
U = overall heat transfer coefficient, based on inner area (∏ Dc L), watts/m^2 K

Figure 16 - Modeling Diagram for Concentric Tube Reactor (CTR)



- The Concentric Tube Reactor is divided up into 10 equal sections along its length, each section being modeled as a pair of Continuous Stirred Tank Reactors (CSTR) linked together with a corresponding heat stream.

- Blocks A1 through A10 are linked together by mass flow streams to model the annulus of the CTR.

- Blocks C1 through C10 are linked together by mass flow streams to model the core of the CTR.

- Streams qi1 through qi10 are the heat streams that represent the heat transfer from the core to the annulus.

- Streams qe1 through qe10 represent external heat transfer to the annulus, such as from electrical heaters, or heat losses to the surroundings. If the reactor is well insulated with no external heat input, qe1 through qe10 are all set to zero.

- Each CSTR block in and of itself requires an iterative process to solve for both its material and energy balance.

- All the blocks as a linked system solve together iteratively until a solution is reached. A solution is reached when temperature profiles of the annulus and core are consistent with the internal heat transfer represented by streams qi1 through qi10, that is, such that $qi1 = U \Delta A (TC1-TA1)$, $qi2 = U \Delta A (TC2-TA2)$, etc., where $\Delta A = (1/10) \Pi Dc L$, and Dc is the inside diameter of the core.

Figure 17 - Concentric Tube Reactor Spreadsheet Model Results Temperature Profiles through Annulus and Core of Reactor

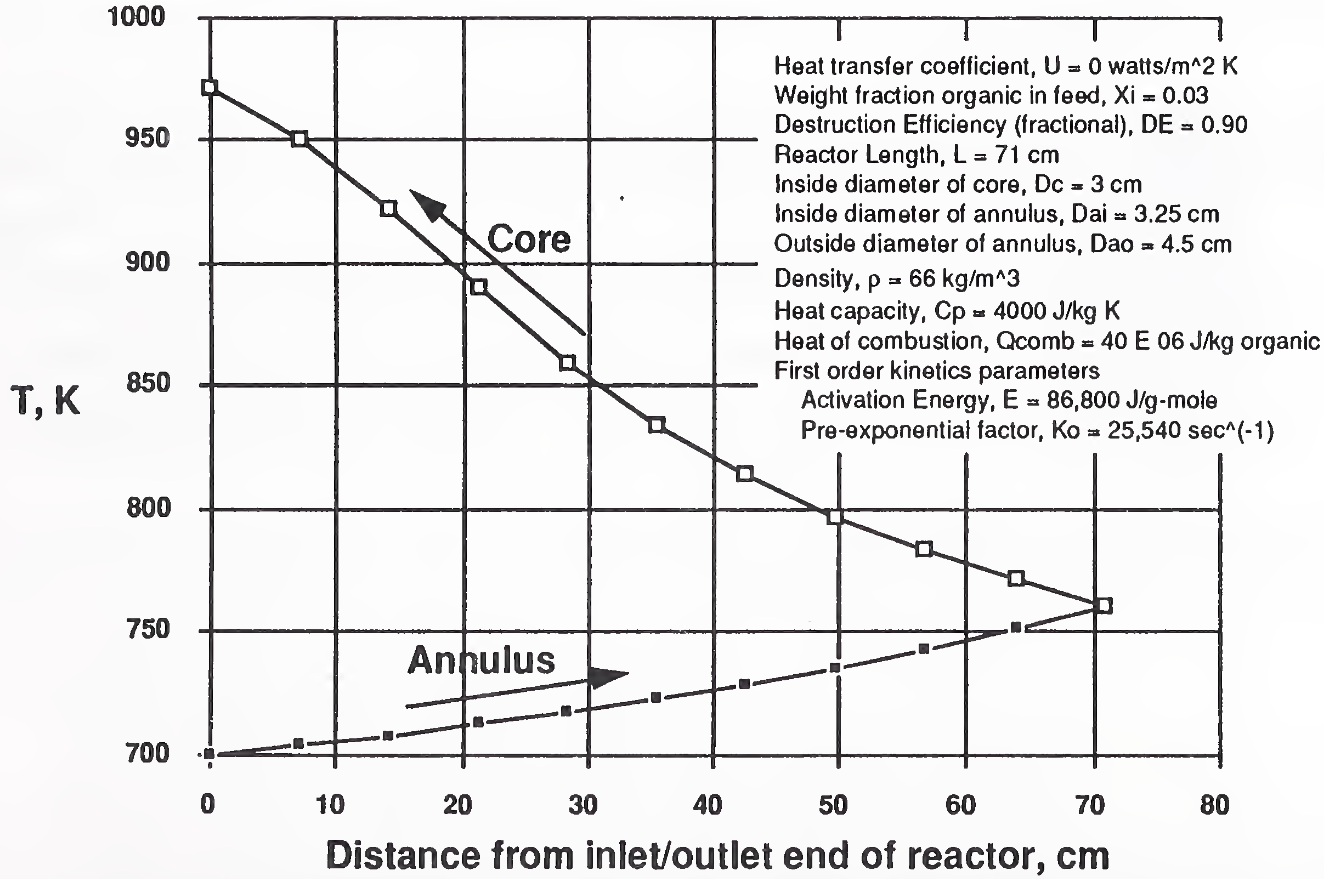


Figure 18 - Concentric Tube Reactor Spreadsheet Model Results Temperature Profiles through Annulus and Core of Reactor

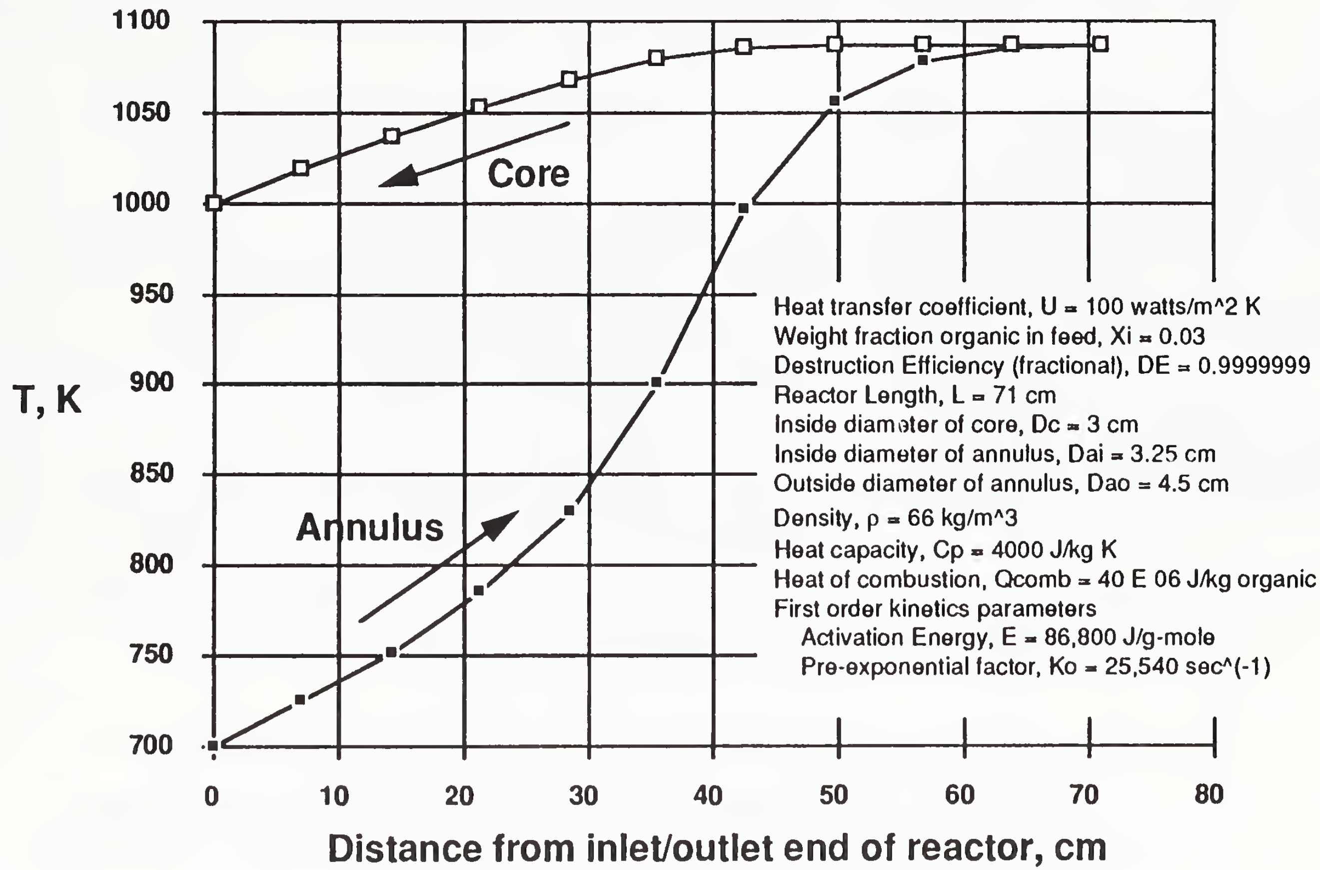
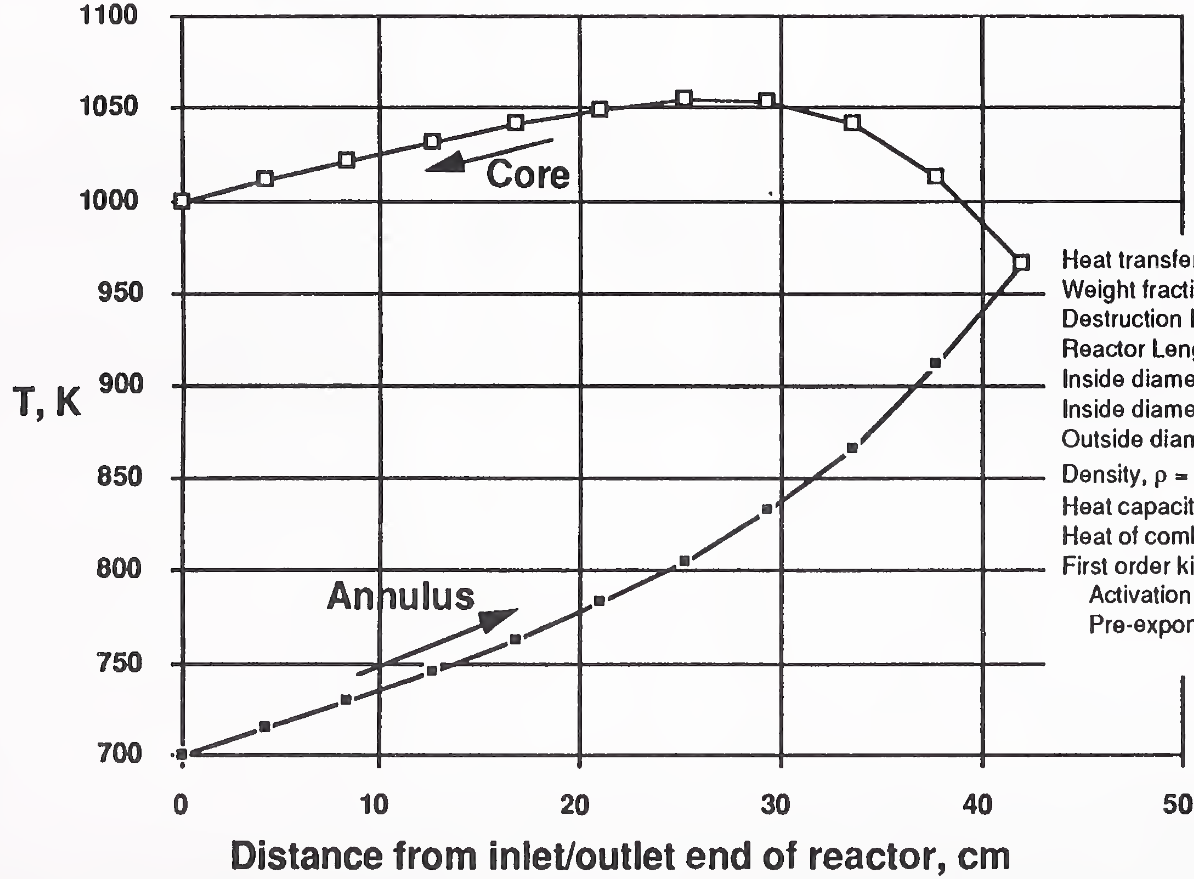


Figure 19 - Concentric Tube Reactor Spreadsheet Model Results Temperature Profiles through Annulus and Core of Reactor



Heat transfer coefficient, U = 100 watts/m^2 K
Weight fraction organic in feed, Xi = 0.03
Destruction Efficiency (fractional), DE = 0.999
Reactor Length, L = 42 cm
Inside diameter of core, Dc = 3 cm
Inside diameter of annulus, Dai = 3.25 cm
Outside diameter of annulus, Dao = 4.5 cm
Density, ρ = 66 kg/m^3
Heat capacity, Cp = 4000 J/kg K
Heat of combustion, Qcomb = 40 E 06 J/kg organic
First order kinetics parameters
Activation Energy, E = 86,800 J/g-mole
Pre-exponential factor, Ko = 25,540 sec^(-1)

Figure 20 - Concentric Tube Reactor Spreadsheet Model Results
Temperature Profiles through Annulus and Core of Reactor

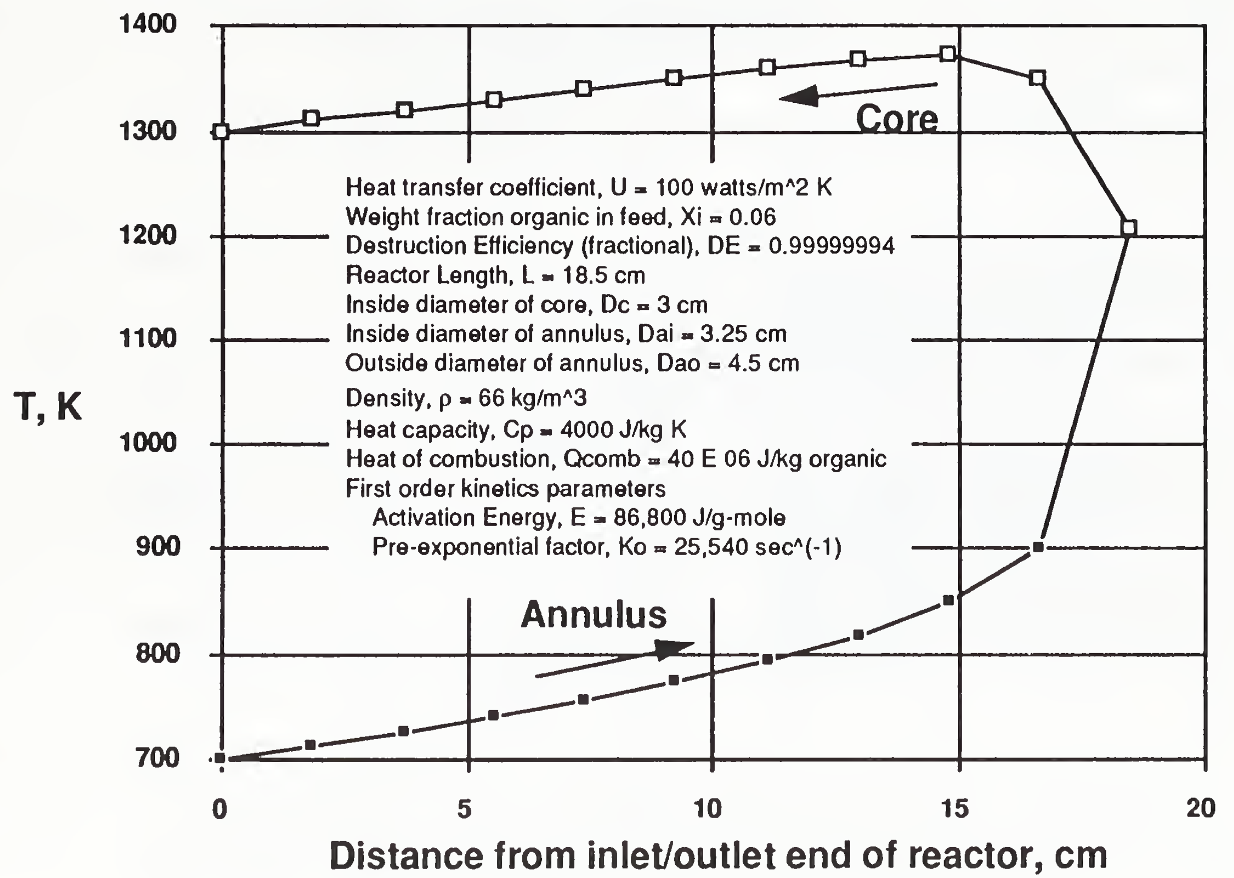


Figure 21 - Concentric Tube Reactor Spreadsheet Model Results Temperature Profiles through Annulus and Core of Reactor

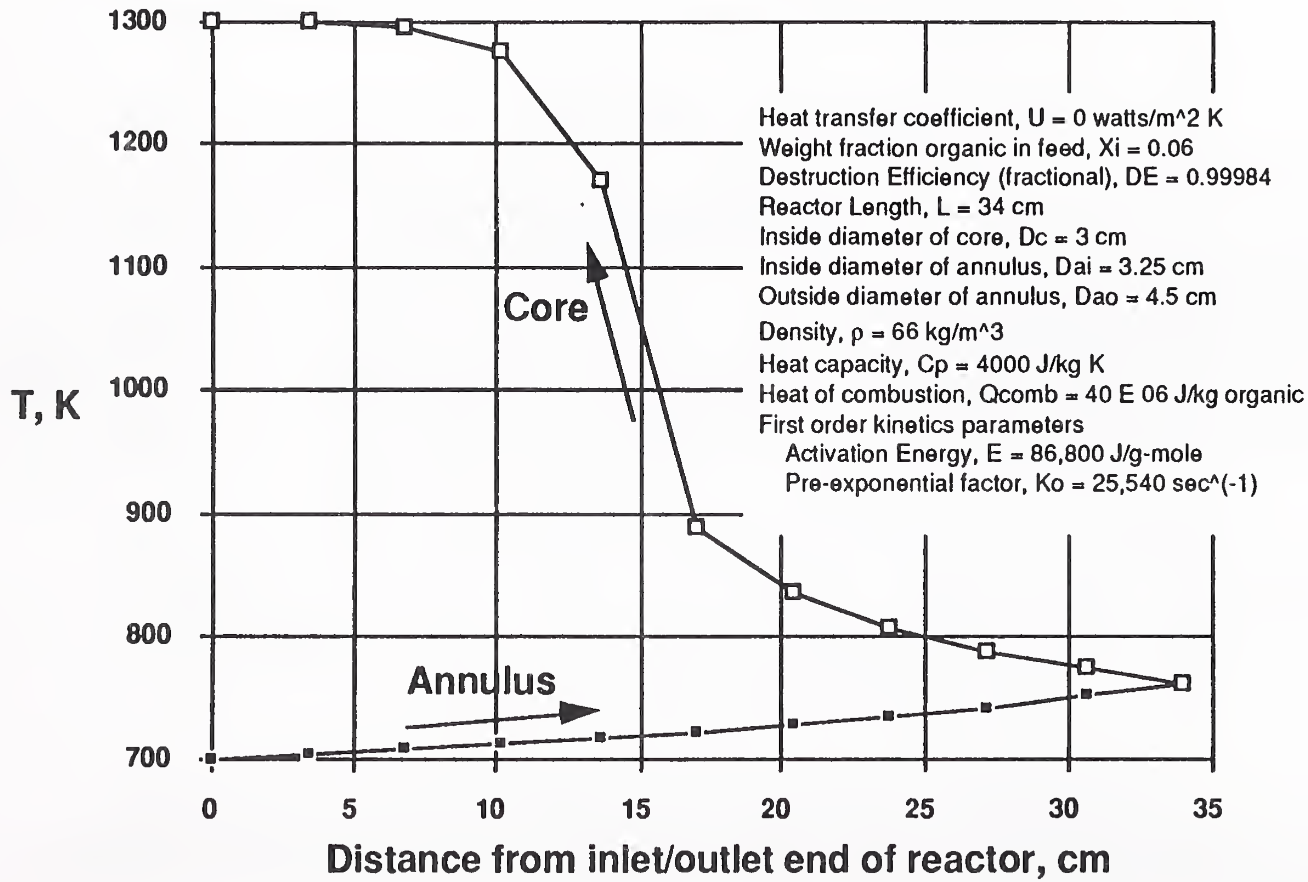


Figure 26 - ASPEN PLUS modeling results
Temperature profiles for counter-current double pipe heat exchanger processing pure water through the critical temperature
Exchanger Length = 4 meters

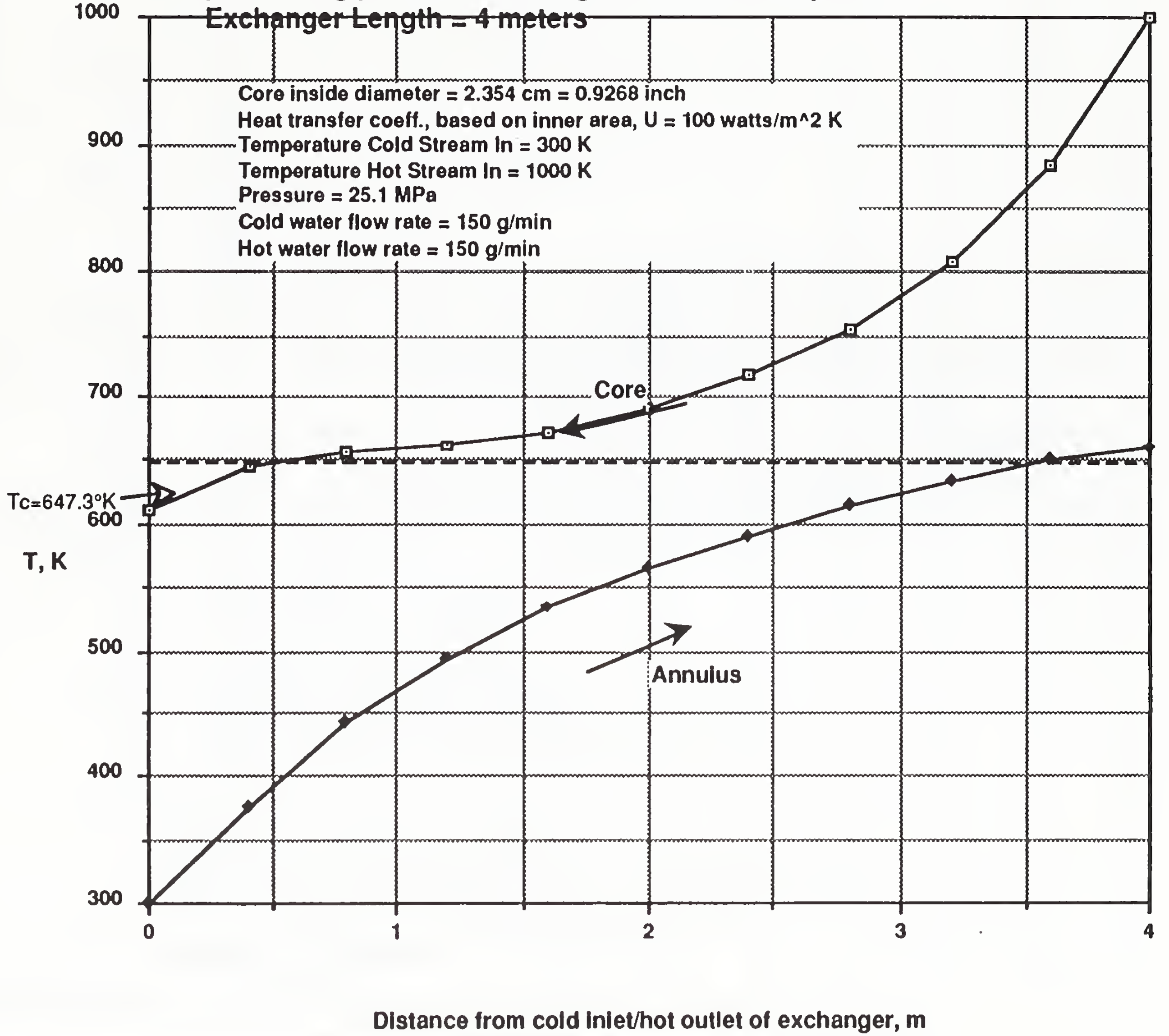


Figure 27 - ASPEN PLUS modeling results
Temperature profiles for counter-current double pipe heat exchanger processing pure water through the critical temperature
Exchanger Length = 20 meters

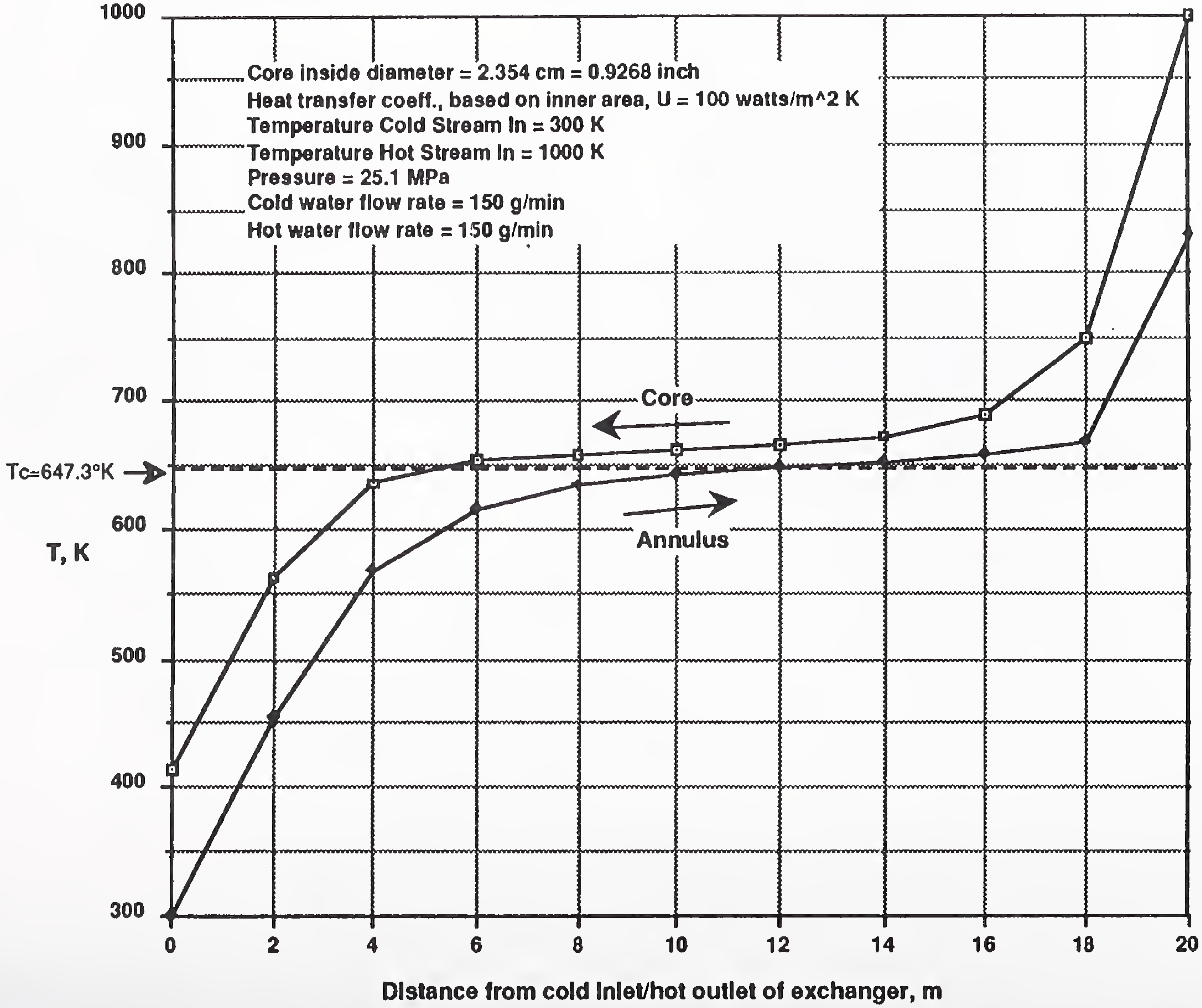


Figure 28 - ASPEN PLUS modeling results
Temperature profiles for counter-current double pipe heat exchanger processing pure water through the critical temperature
Exchanger Length = 100 meters

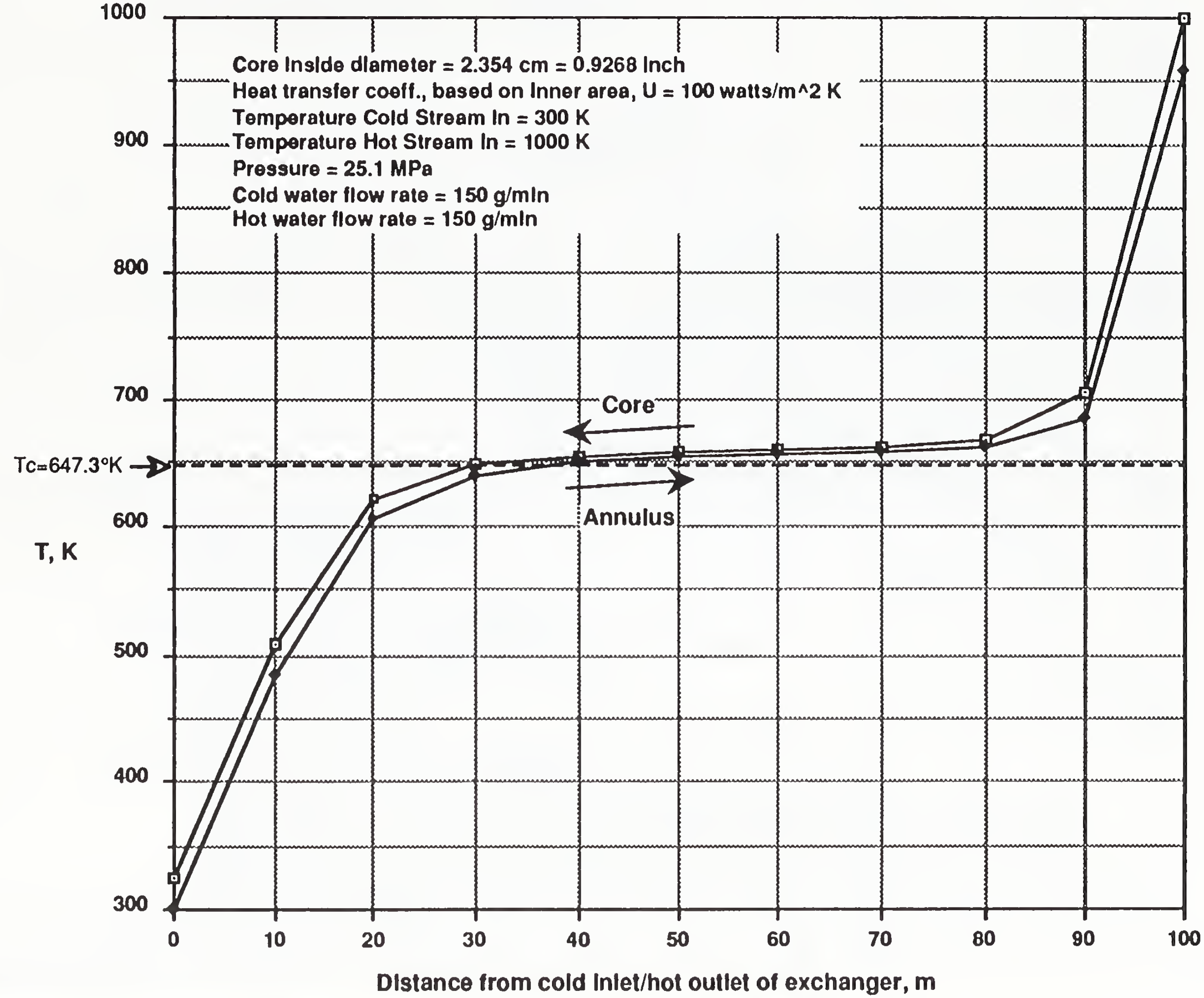


Figure 29 - ASPEN PLUS modeling results compared with idealized linear results obtained from assuming a constant heat capacity of 1 cal/g K. Temperature profiles for counter-current double pipe heat exchanger processing pure water through the critical temperature
Exchanger Length = 4 meters

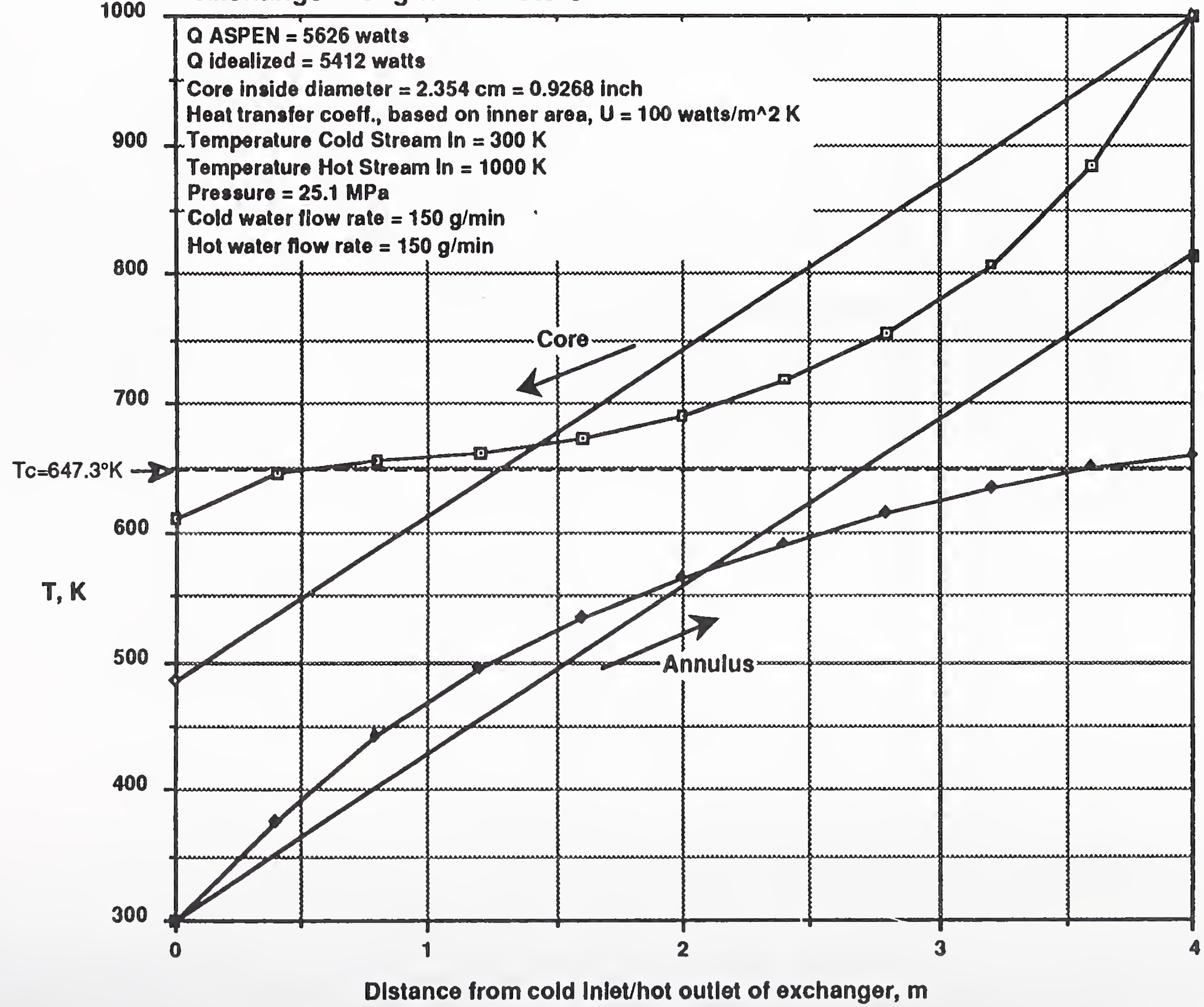


Figure 30 - ASPEN PLUS modeling results compared with idealized linear results obtained from assuming a constant heat capacity of 1 cal/g K. Temperature profiles for counter-current double pipe heat exchanger processing pure water through the critical temperature
Exchanger Length = 20 meters

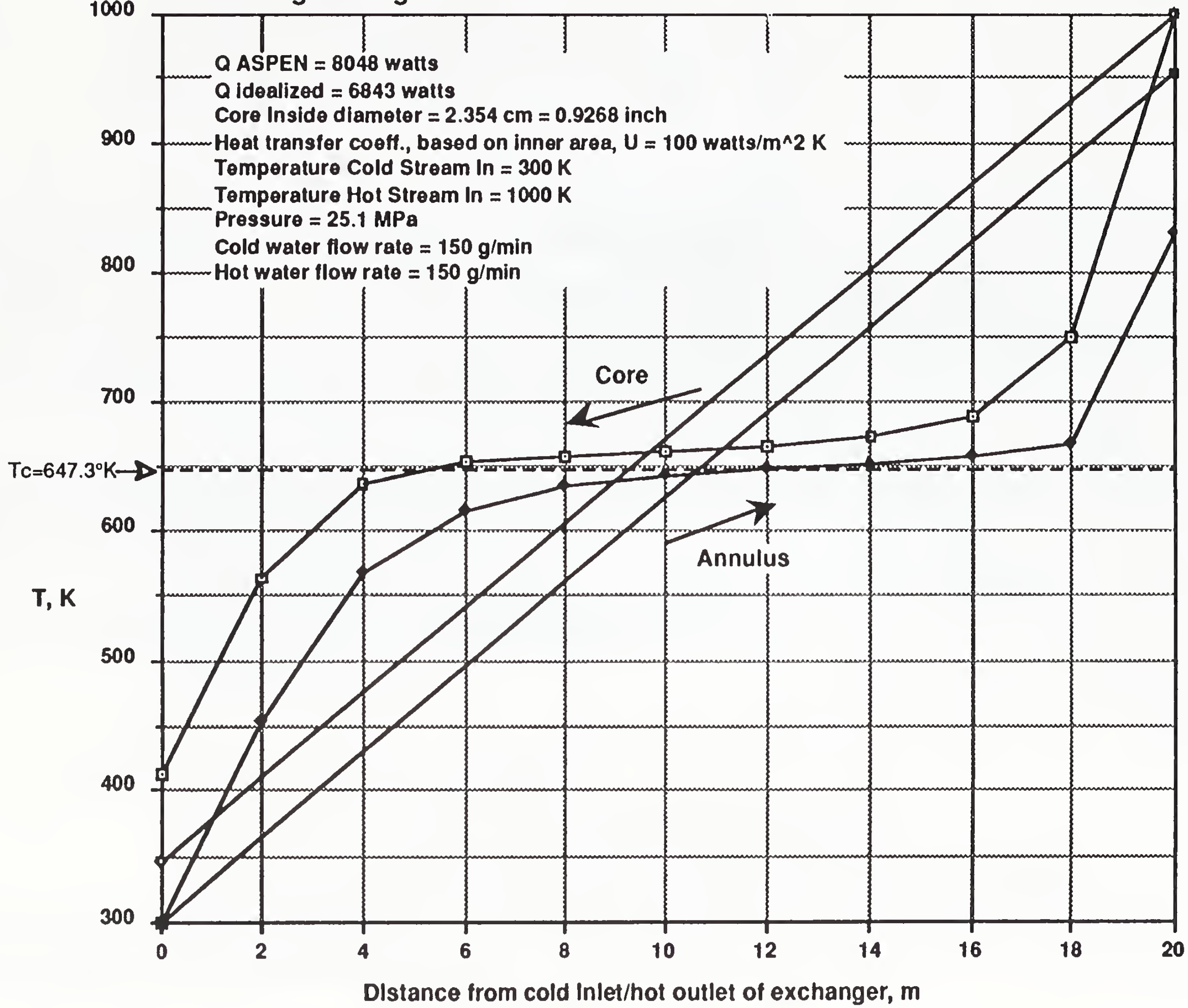
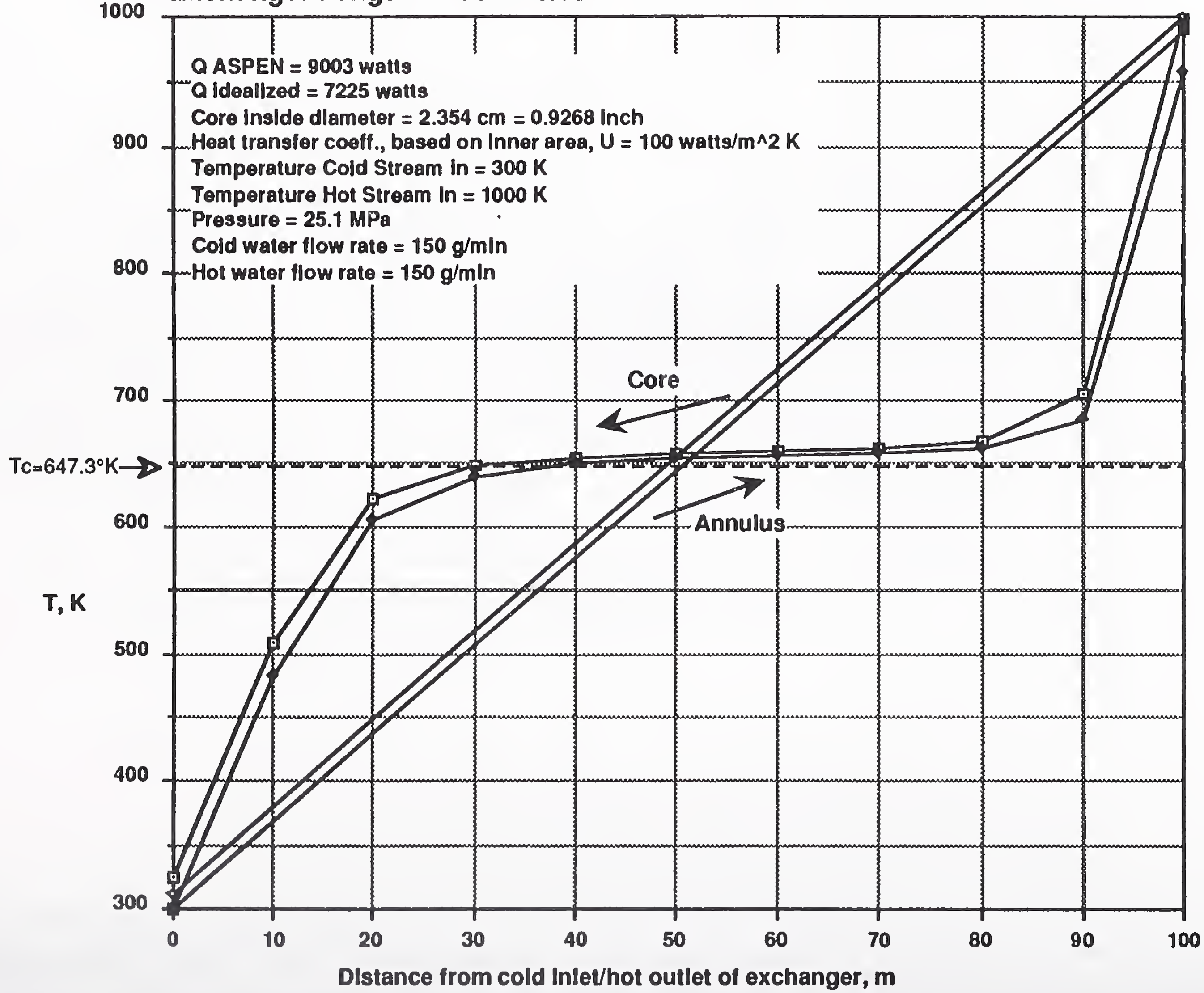
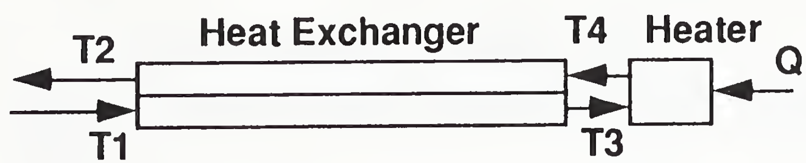


Figure 31 - ASPEN PLUS modeling results compared with idealized linear results obtained from assuming a constant heat capacity of 1 cal/g K. Temperature profiles for counter-current double pipe heat exchanger processing pure water through the critical temperature
Exchanger Length = 100 meters

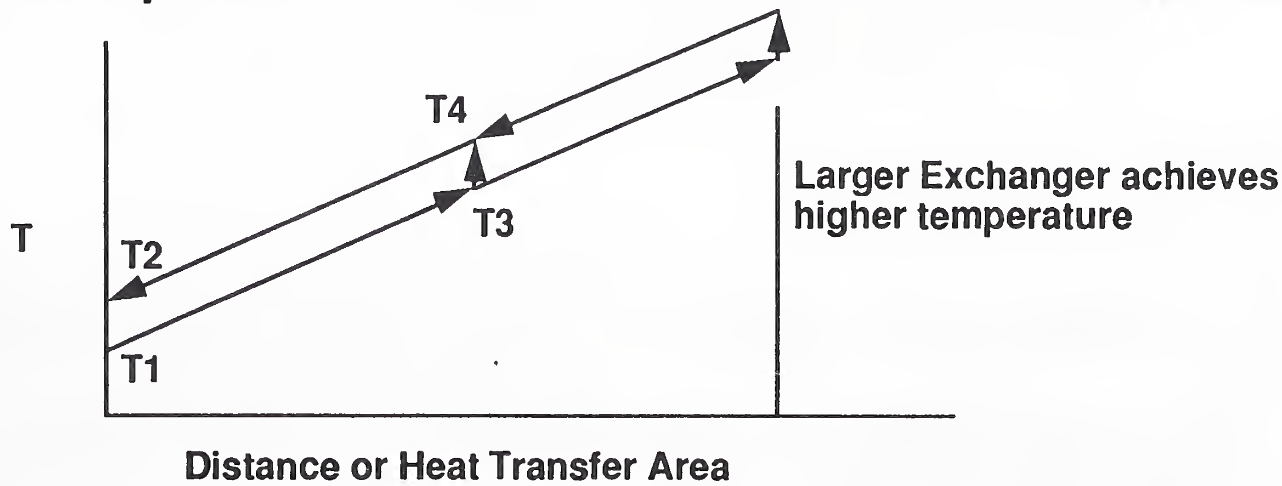


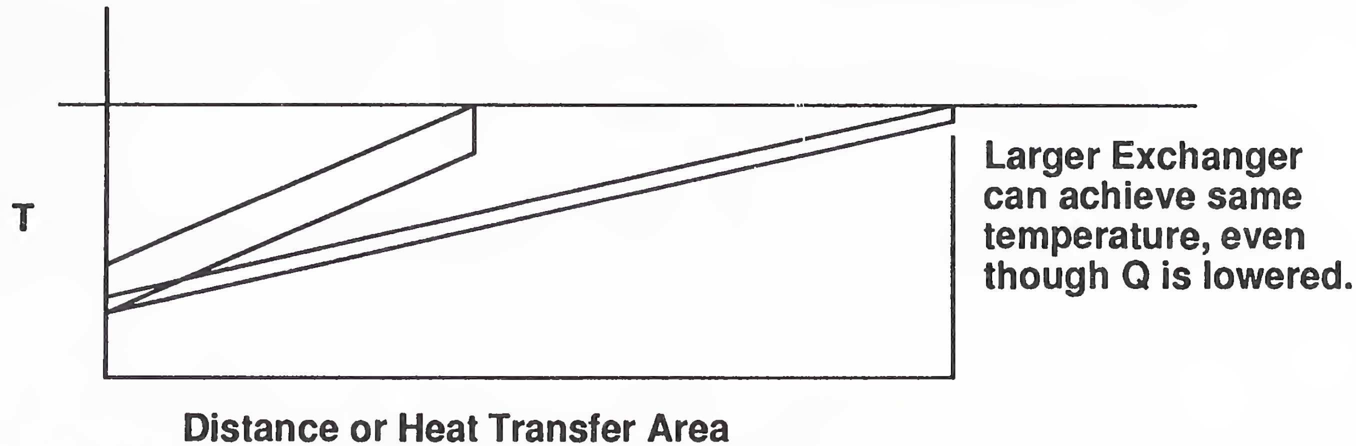
Idealized Concentric Tube Reactor



- To destroy wastes using supercritical water requires that the reactants be brought to a high T and P for a sufficient length of time for the reaction to occur.
- If Q represents the heat of reaction, idealized by assuming that all the heat is liberated in the "Heater" thereby raising the temperature from T3 to T4, then the highest temperature will occur at T4.
- And if there are no heat losses from the system and if physical properties are constant and there are no phase changes, then there is no limit to how high T4 can be, even if Q is very small.
- To make T4 higher, all that is needed is to make the exchanger bigger. This is illustrated on the following page.

Typical Temperature Profiles of Idealized Concentric Tube Reactor





Questions for Consideration

- What is the practical limitation on this approach for a SCWO system? Do the large changes in physical properties of water around the critical point place a limit on this behavior for SCWO?

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Supercritical Water Oxidation of Hazardous Wastes

Richard Kirts
Naval Civil Engineering Laboratory
May 1992

1RKGtm.1

Why Exploratory Development?

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Supercritical Water Oxidation (SCWO)

- DESTROYS Organic Hazardous Wastes
- Produces Few Emissions
- Comparatively Easy to Permit
- Can be Cost Effective

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Navy Need

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- Navy Generates Large Amount of Organic Hazardous Waste
- Disposal Cost is High and is Rising
- Navy Retains Long Term Liability

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Scope Of Work

- Waste Characterization
- Economic Analyses
- Experimental Program

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Waste Characterization

- CY90 NEESA Data Show <u>12K</u> Tons/Yr of Liquid Organic Hazardous Waste

- CY90 NEESA Estimate of Disposal Cost Was <u>$26M</u>

- Navy Industrial Wastes Appear to be Easily Destroyed by SCWO

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SCWO Treatable Wastes

INCLUDED	EXCLUDED
Painting Operations	IWTP Wastewater
Solvent Cleaning	Abrasive Blasting
Fluids Change Out	Electroplating
Chemical Paint Stripping	Asbestos
Ship Offload Stores	Bilge/Tank Cleaning
Pesticides	Battery Shops
•	•
•	•
•	•
11,000 Tons/Yr	44,000 Tons/Yr

Typical Organic Hazardous Waste Disposal Costs* At Norfolk Naval Base

Waste	$/lb	lb/gal	$/Gal
Paint	4.15	10	41.50
Chemical Paint Stripping	2.58	8	20.64
Solvent Degreasing	1.81	8	14.48
Pesticides	4.25	8	34.00
POL (Clean)	1.89	8	15.12
POL (Contaminated)	2.13	8	17.02

* CY-91 Data

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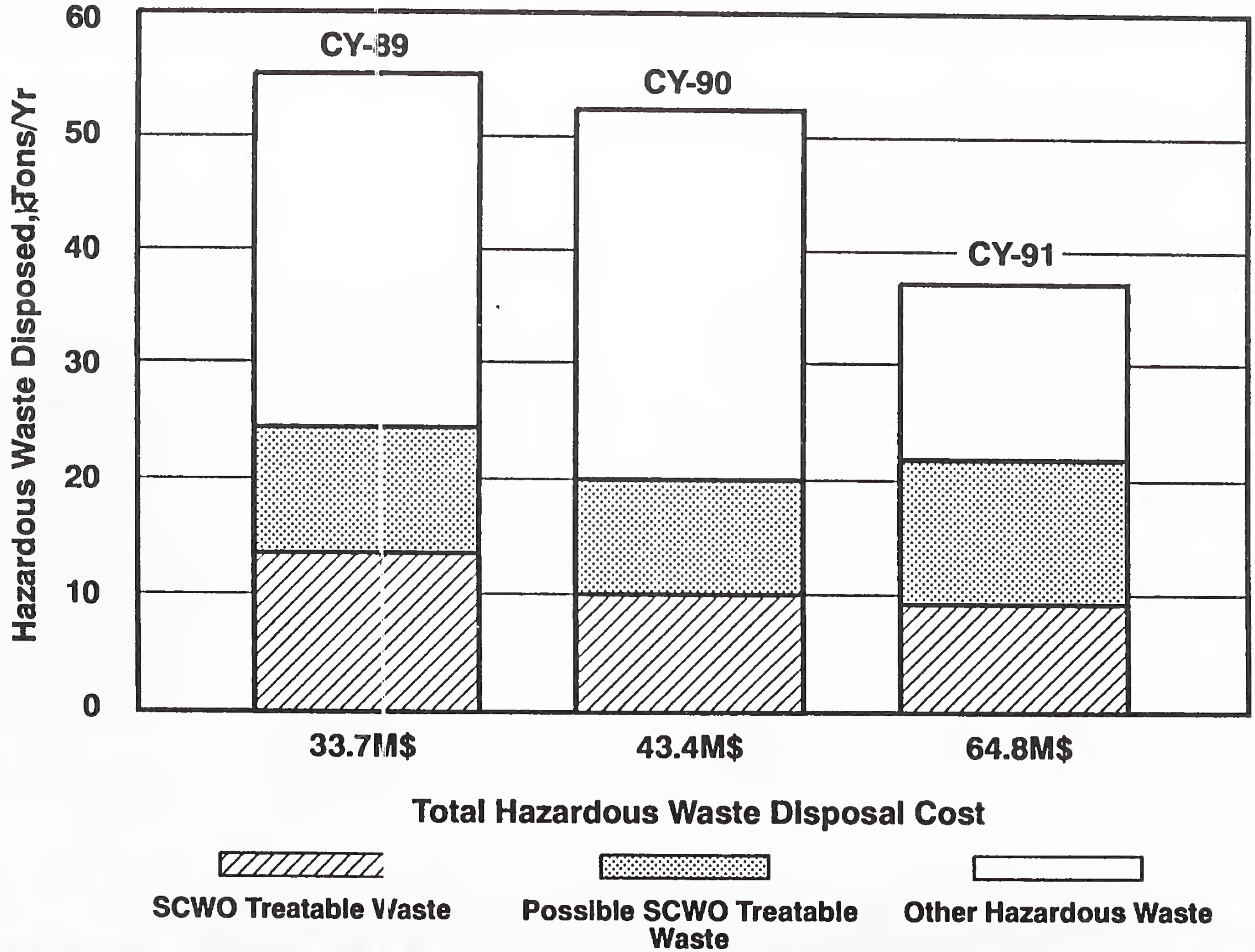

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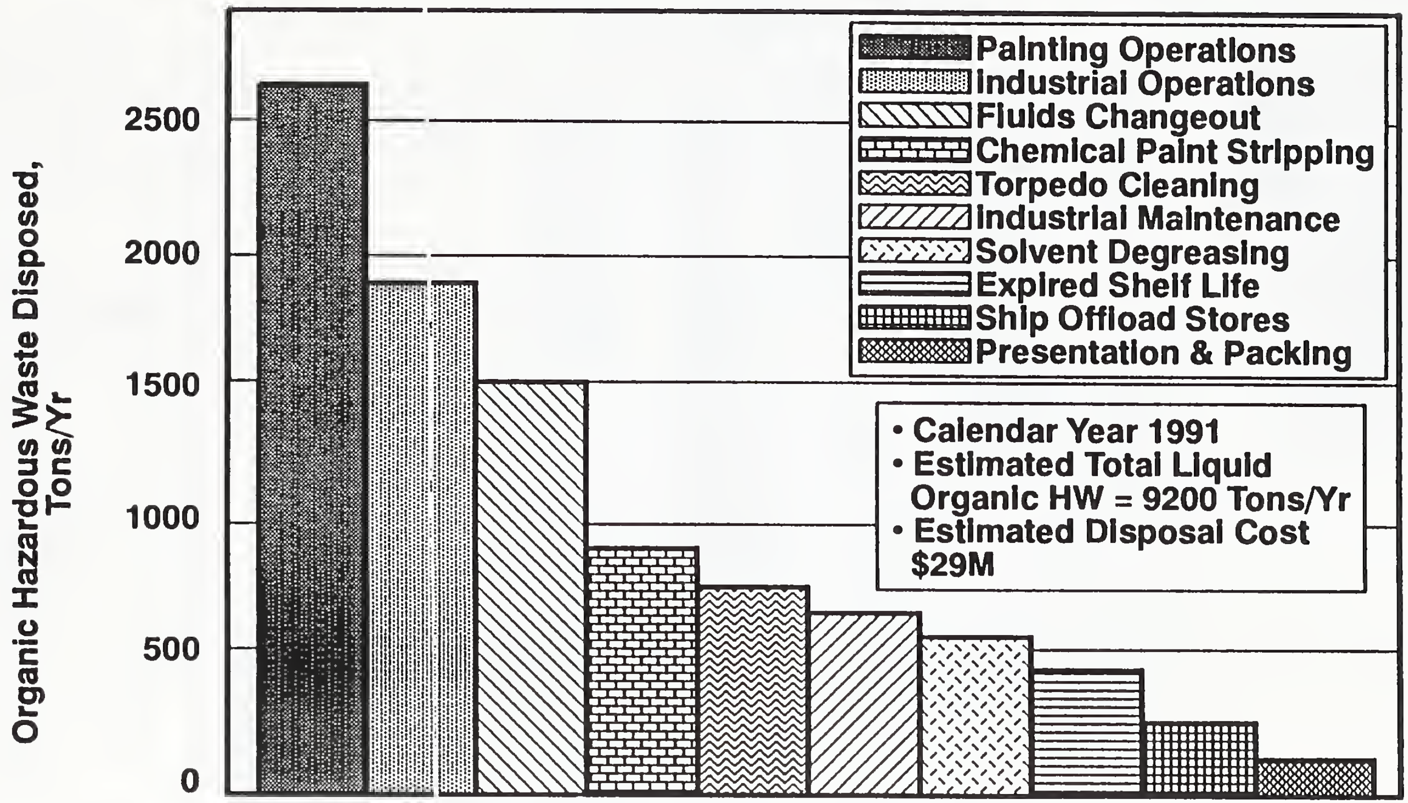

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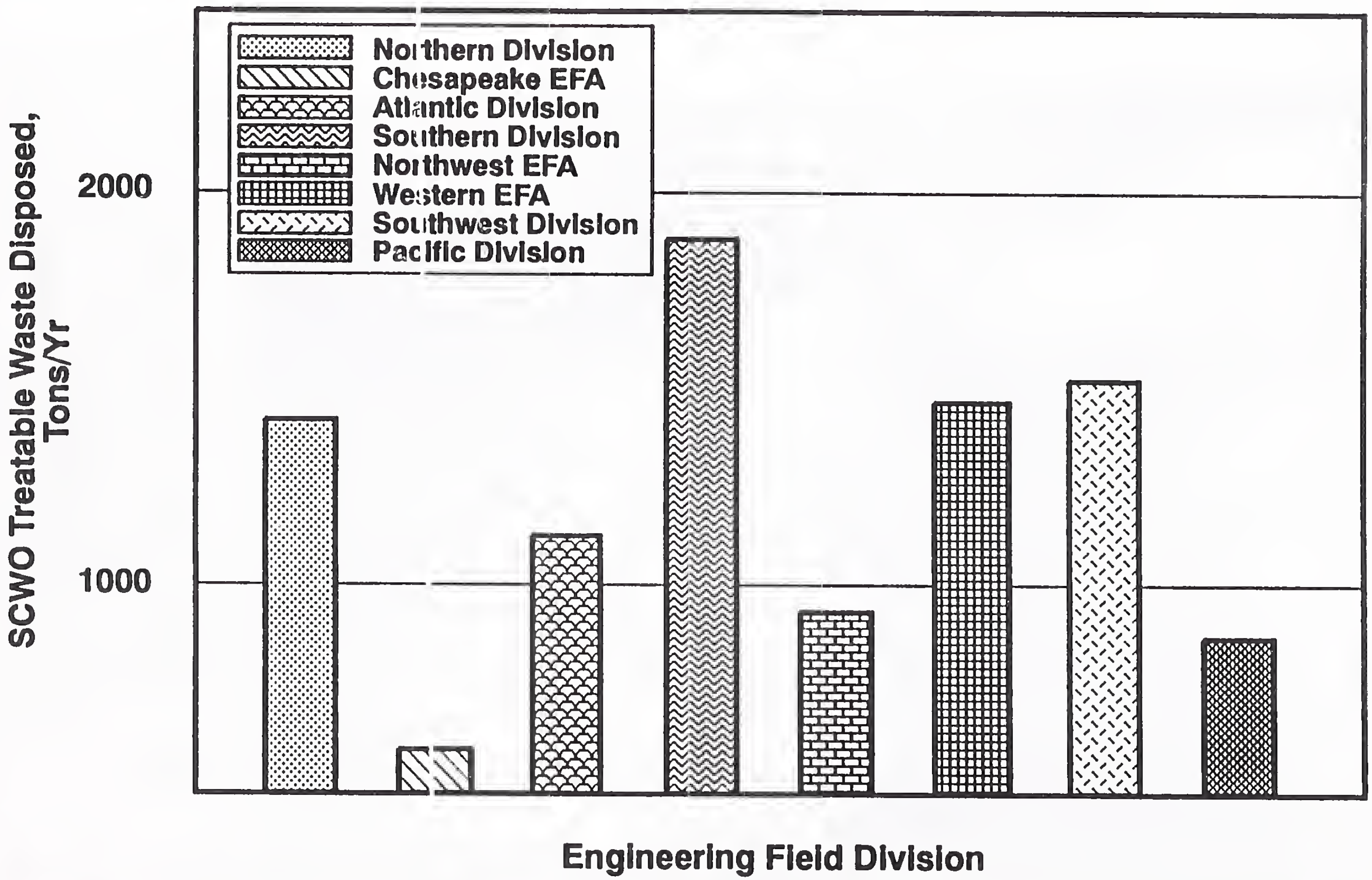
SCWO Treatable Waste Disposed, Tons/Yr
2000
1000
Northern Division
Chesapeake EFA
Atlantic Division
Southern Division
Northwest EFA
Western EFA
Southwest Division
Pacific Division
Engineering Field Division

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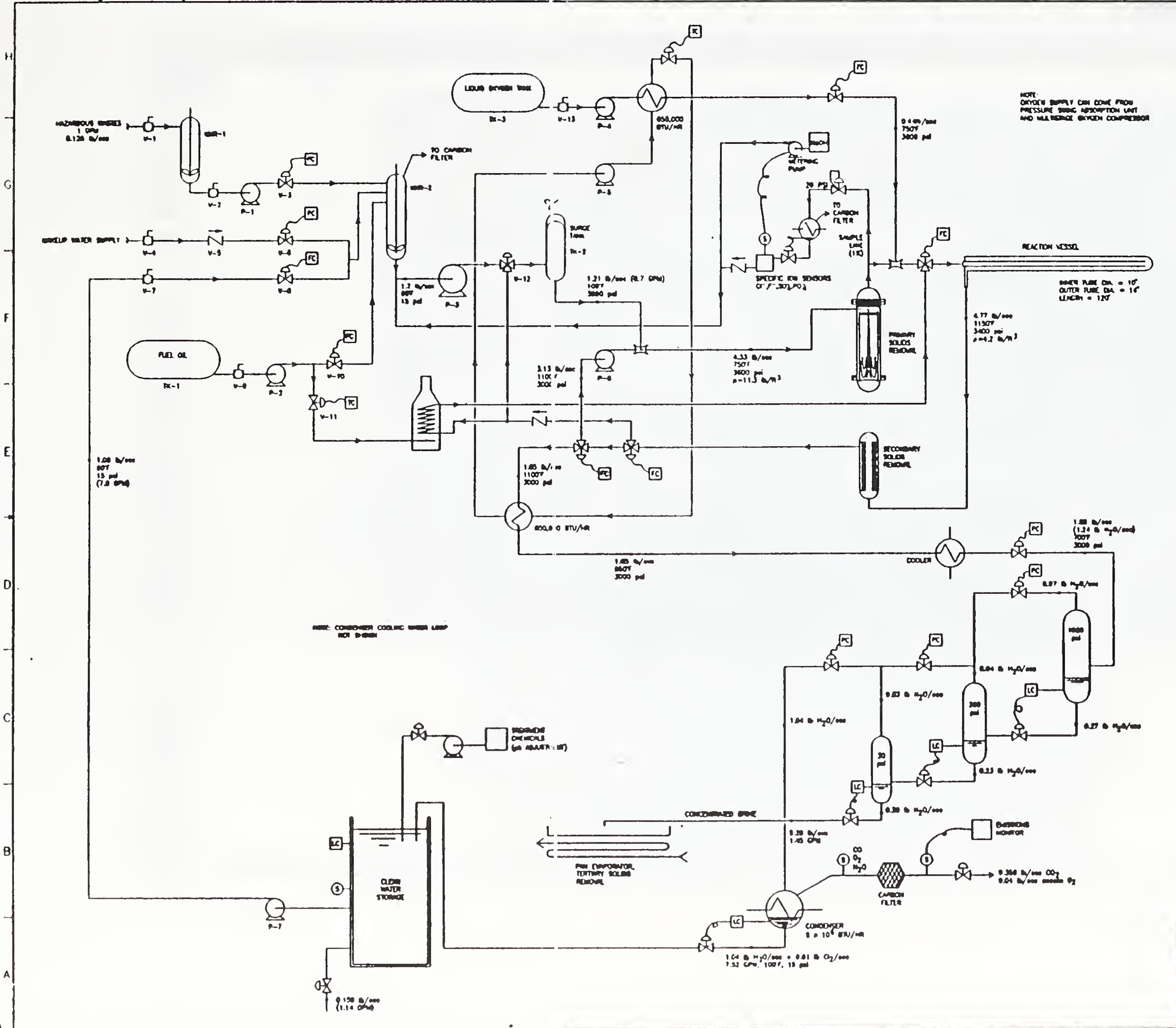

PARTS LIST

I.D. NO.	DESCRIPTION
WMR-1	MIXER, FLUIDS, PROPELLER TYPE, 15 GAL, ELECTRIC DRIVE
WMR-2	MIXER, FLUIDS, PROPELLER TYPE, 100 GAL, ELECTRIC DRIVE
P-1	PUMP, 2 GPM AT 10' OF WATER, PLASTIC DIAPHRAGM
P-2	PUMP, FUEL OIL TRANSFER, 3 GPM AT 15' OF WATER, PLASTIC DIAPHRAGM
P-3	PUMP, HIGH PRESSURE, VARIABLE DISPLACEMENT, SLURRY; 2-10 GPM AT 3800 PSI, 100 MICRON OR LESS, 1 1/2" DIA. SUCTION AND DISCHARGE, ELECTRIC DRIVE, ELECTRICALLY VARIABLE (A) STROKE OR (B) DISPLACEMENT OR (C) SPEED
P-4	PUMP, LIQUID OXYGEN, 27 LB/MIN, 3.7 GPM, 3700 PSI, 7 HP
P-5	
P-6	PUMP, RECIRCULATING, 100 HP
P-7	PUMP, 10 GPM, LOW HEAD
TK-1	TANK, FUEL OIL, 500 GAL
TK-2	TANK, SURGE/PULSATION DAMPER, 5000 PSI RATED WITH P/T RELIEF, BLOW OUT PLUGS, 1 1/2" I/O FITTINGS
TK-3	TANK, LIQUID OXYGEN STORAGE, 25,000 GAL, LOX CAPACITY LENGTH = 34'-0", DIAMETER = 12'-0"
V-1	VALVE, MANUAL BALL/GATE, 1/2", TEFLON/PLASTIC COATED
V-2	VALVE, MANUAL BALL/GATE, 1/2", TEFLON/PLASTIC COATED
V-3	VALVE, ELECTRICALLY OPERATED CONTROL, 1/2" NOM. DIA. COATED
V-4	VALVE, MANUAL BALL/GATE, 1/2", TEFLON/PLASTIC COATED, BRASS OR S.S. ACCEPTABLE
V-5	VALVE, CHECK, SPRING LOADED, 1/2" DIA. BRASS OR S.S.
V-6	VALVE, ELECTRICALLY OPERATED CONTROL, 1/2" NOM. DIA. COATED, BRASS OR S.S. ACCEPTABLE
V-7	VALVE, MANUAL, BALL, 1 1/2" DIA.
V-8	VALVE, ELECTRICALLY OPERATED CONTROL, 1 1/2" DIA.
V-9	VALVE, MANUAL BALL/GATE, 1/2", TEFLON/PLASTIC COATED, BRASS OR S.S. ACCEPTABLE
V-10	VALVE, ELECTRICALLY OPERATED CONTROL, 1/2" NOM. DIA. COATED
V-11	VALVE, ELECTRICALLY OPERATED CONTROL, 1/2" NOM. DIA. COATED
V-12	VALVE, 3-WAY ELECTRICALLY OPERATED CONTROL, 1 1/2" DIA. COATED OR S.S.

SK1733

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SUPERCRITICAL WATER OXIDATION PROCESS
- CONCEPT ONE -

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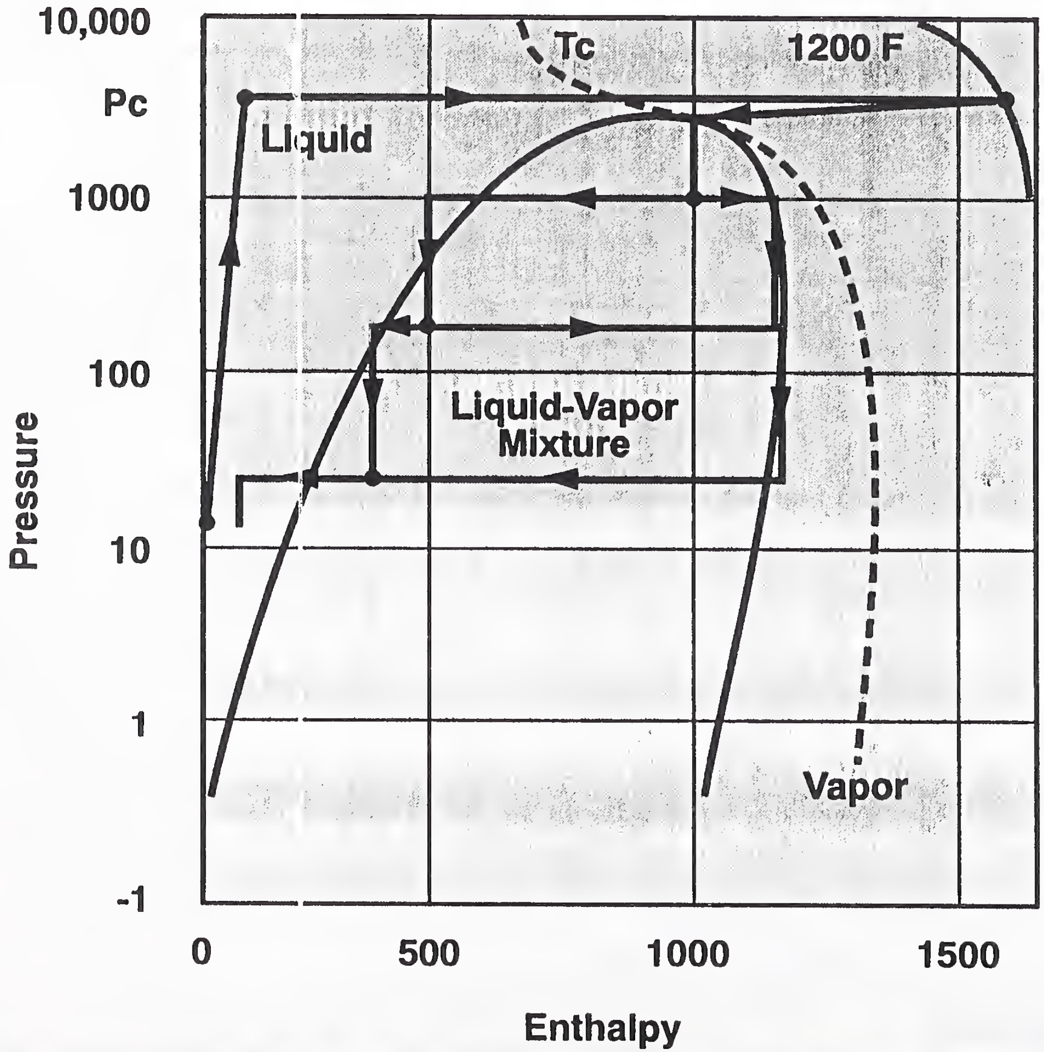

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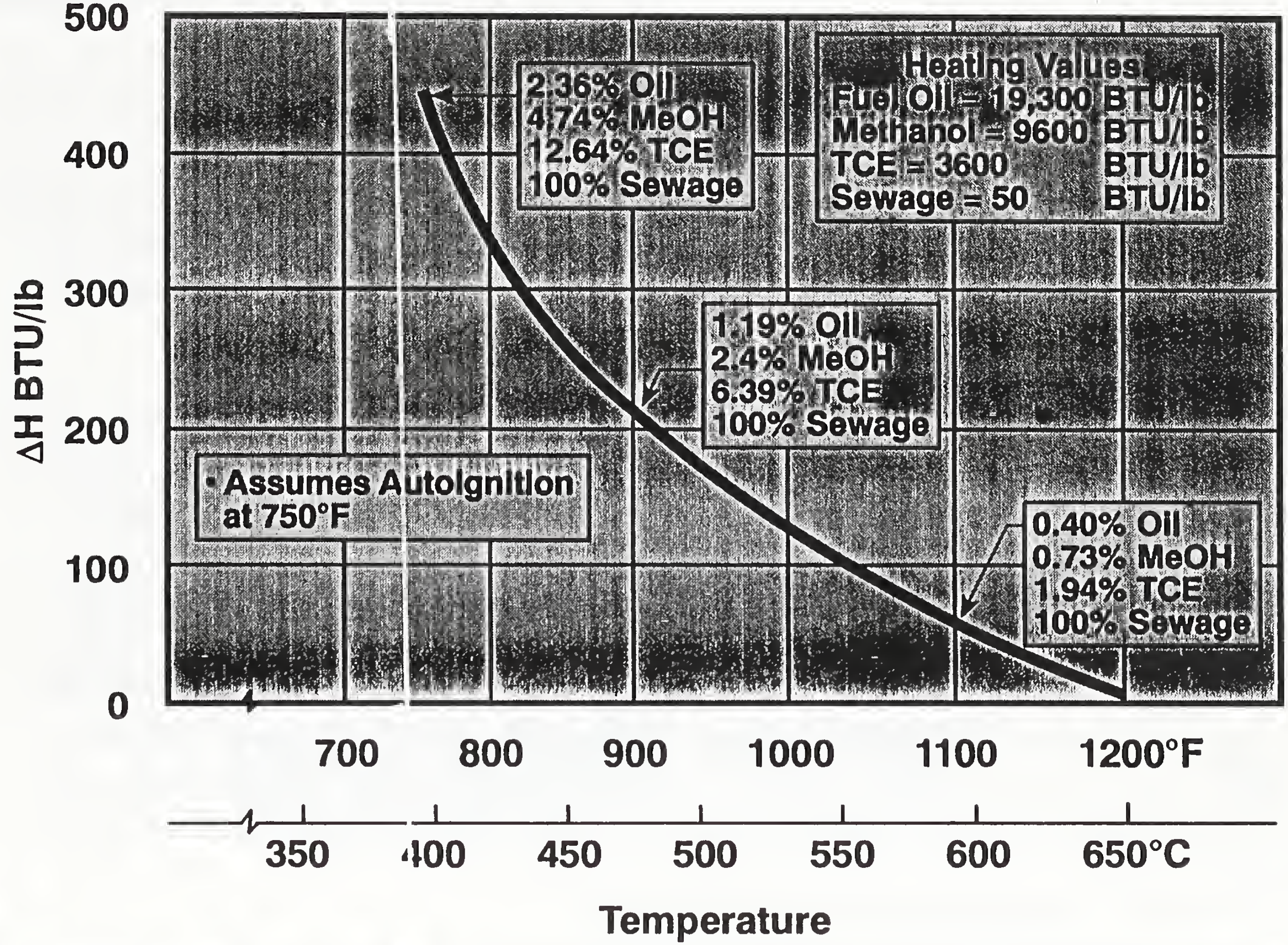

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Economics Update

- Capital Cost = \$7.6M
- Operating Cost = \$1.1M
- Annual Savings = \$2.5M
- Payback Period = 5-10Yr

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Cost Analysis

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Plant Capacity = 830 Tons Organic Waste/Yr
On-Stream Factor = 4,000 Hrs/Yr

CAPITAL COSTS:	
Equipment	$6,180
Design & Installation	1,420
Total Plant	***$7,600***
EXPENSES:	
Oxygen ($80/Ton)	$266
- Fuel Oil	7
- NaOH	80
Electricity ($0.10/kw/hr)	68
Labor (3/Shifts/Day)	232
Maintenance (3% of CapEquip)	177
Cooling Water ($0.10/$10^3$ Gal)	4
Residue disposal ($400/Ton)	93
Plant Overhead (105% DL)	244
Total Annual Expenses	***$1,171***

1RKGtm.13

Cost Analysis (Cont'd)

CREDITS:

Avoided HW Disposal Cost ($10/Gal)	$2,500
Electricity ($0.10/kw/hr)	0 to $200
Carbon Dioxide By-product ($25/ton)	0 to $60
150 psi Stream ($3/$10^3$ lb)	0 to $10

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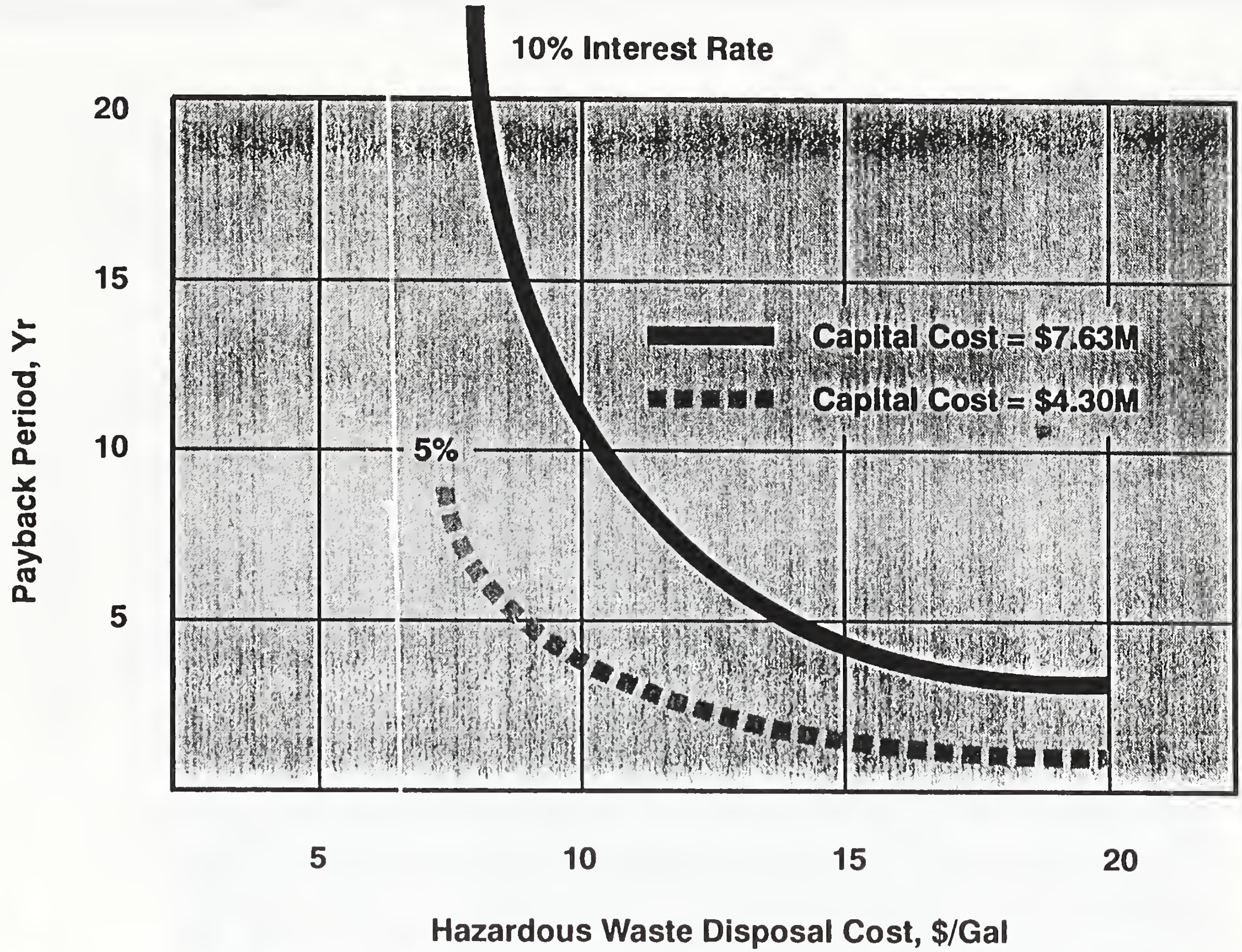

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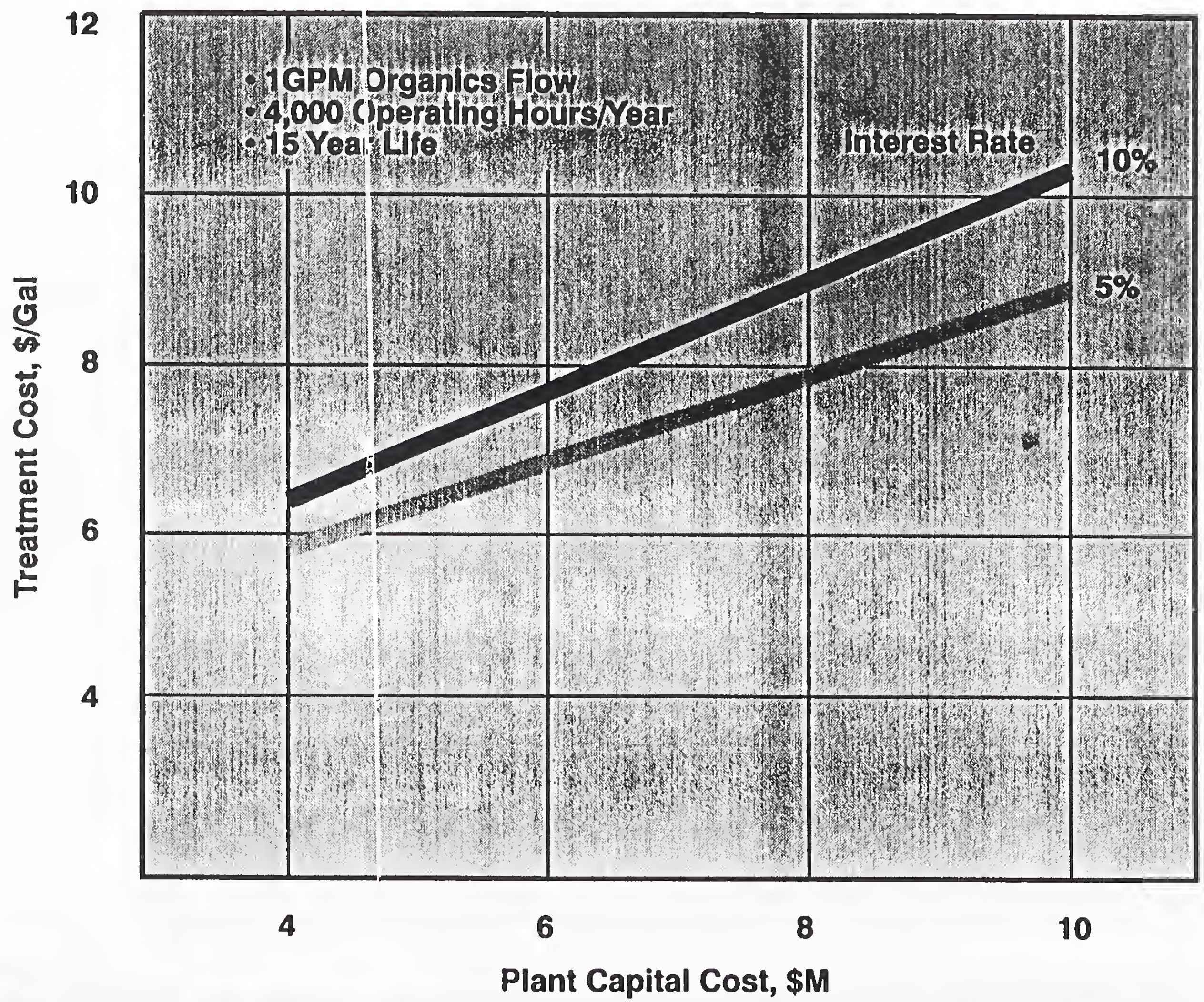

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Economics Update

- Capital Cost can be Reduced to $4.2M Through Better Design

- Design Improvements
  - Replace Cascade P-T Let Down with Turbine
  - Eliminate Heat Exchangers
  - Minimize Use of Control Valves
  - Keep Pipe Sizes Small

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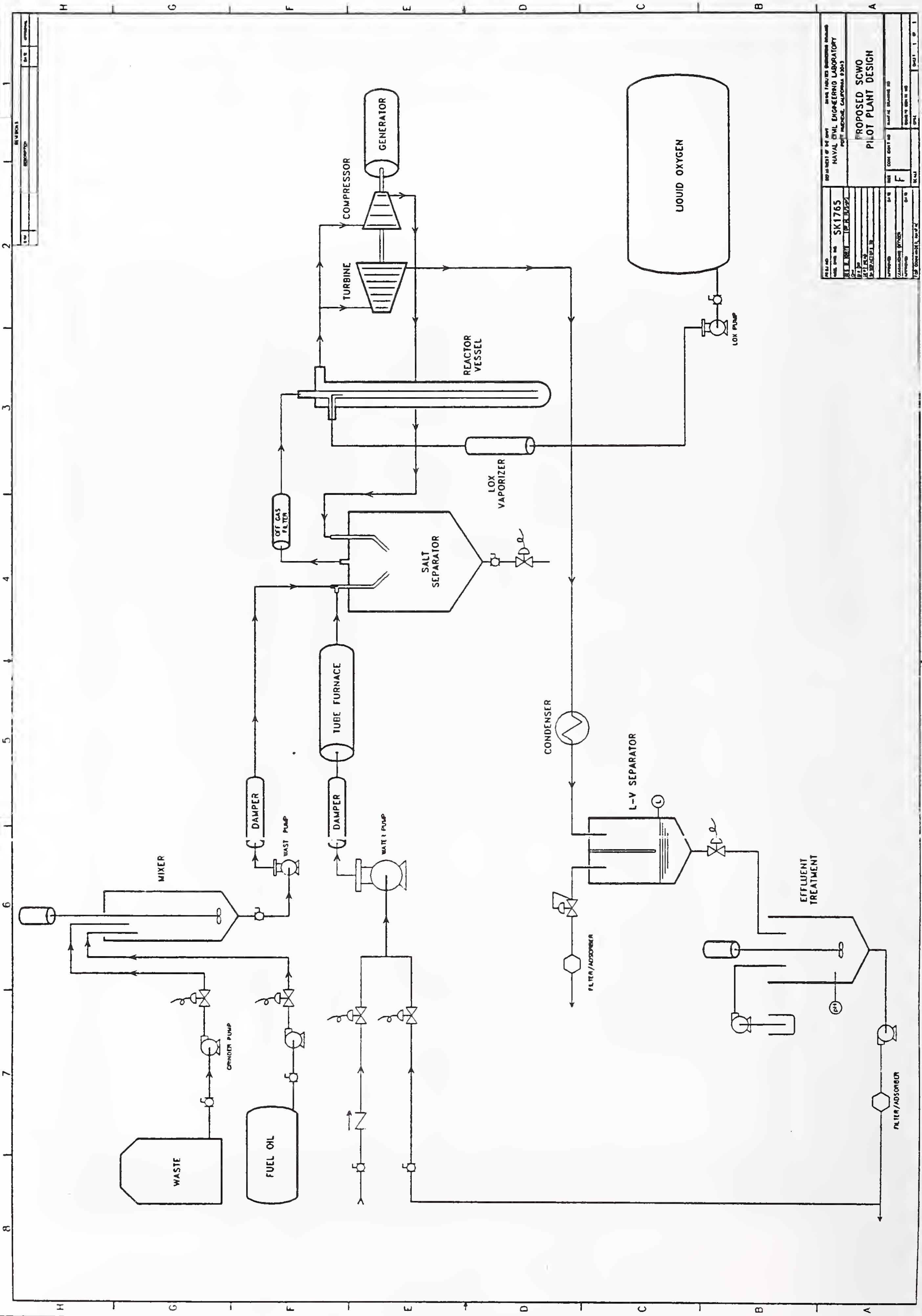
WASTE
FUEL OIL
GRINDER PUMP
MIXER
WASTE PUMP
DAMPER
DAMPER
WATER PUMP
TUBE FURNACE
OFF GAS FILTER
SALT SEPARATOR
REACTOR VESSEL
TURBINE
COMPRESSOR
GENERATOR
LIQUID OXYGEN
LOX PUMP
LOX VAPORIZER
CONDENSER
L-V SEPARATOR
FILTER/ADSORBER
EFFLUENT TREATMENT
FILTER/ADSORBER
NAVAL CIVIL ENGINEERING LABORATORY
PROPOSED SCWO PILOT PLANT DESIGN
SK1765

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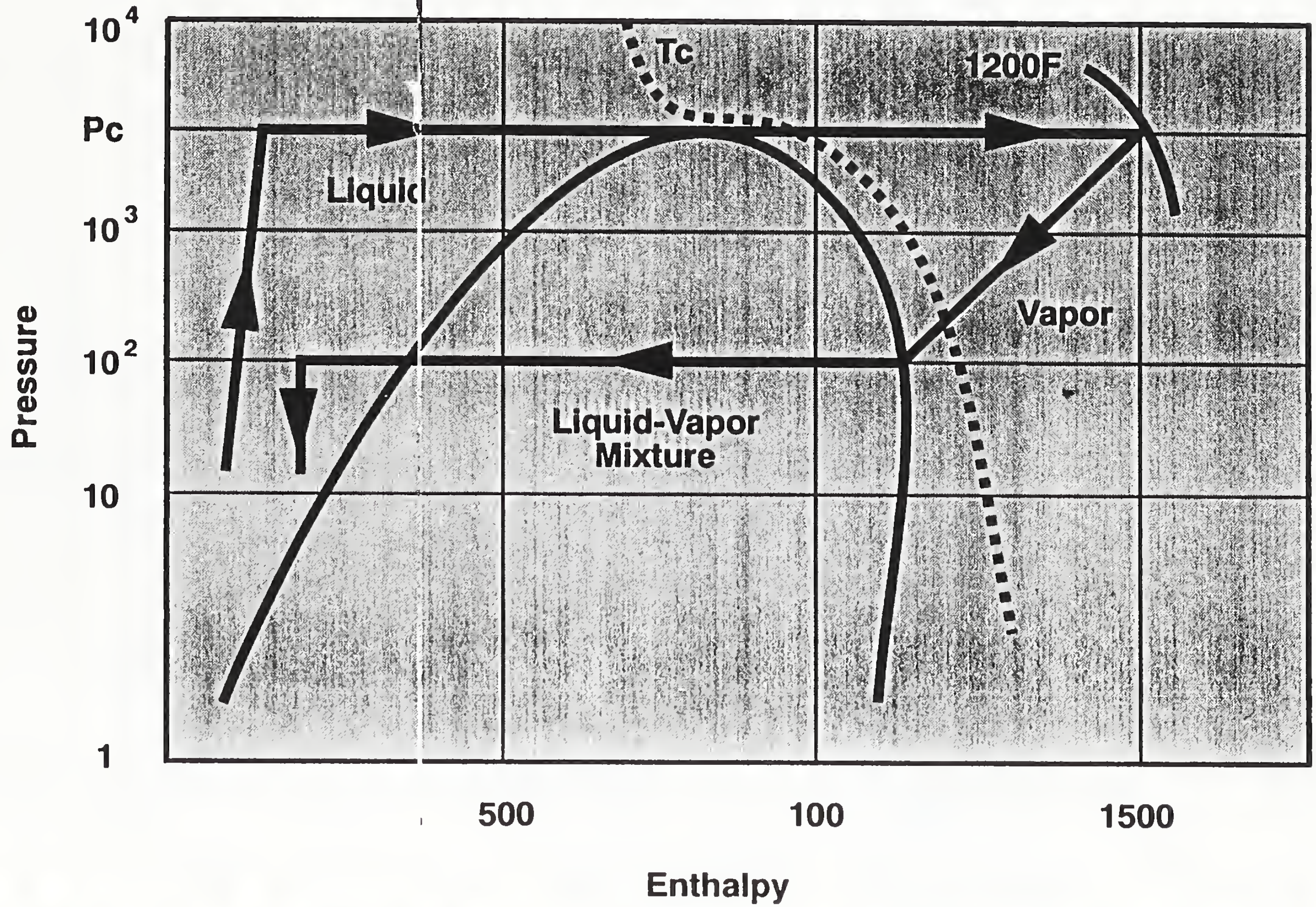

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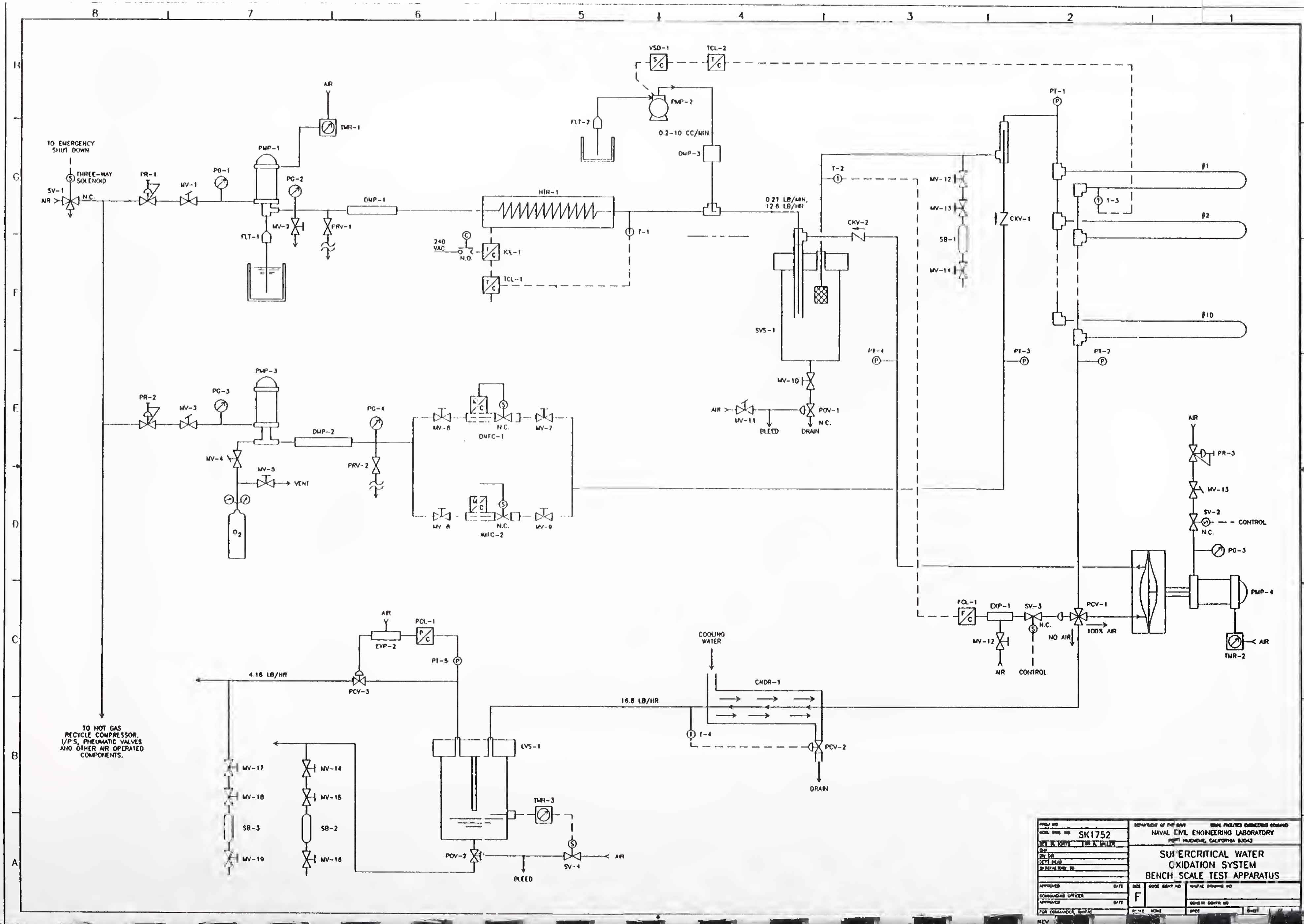
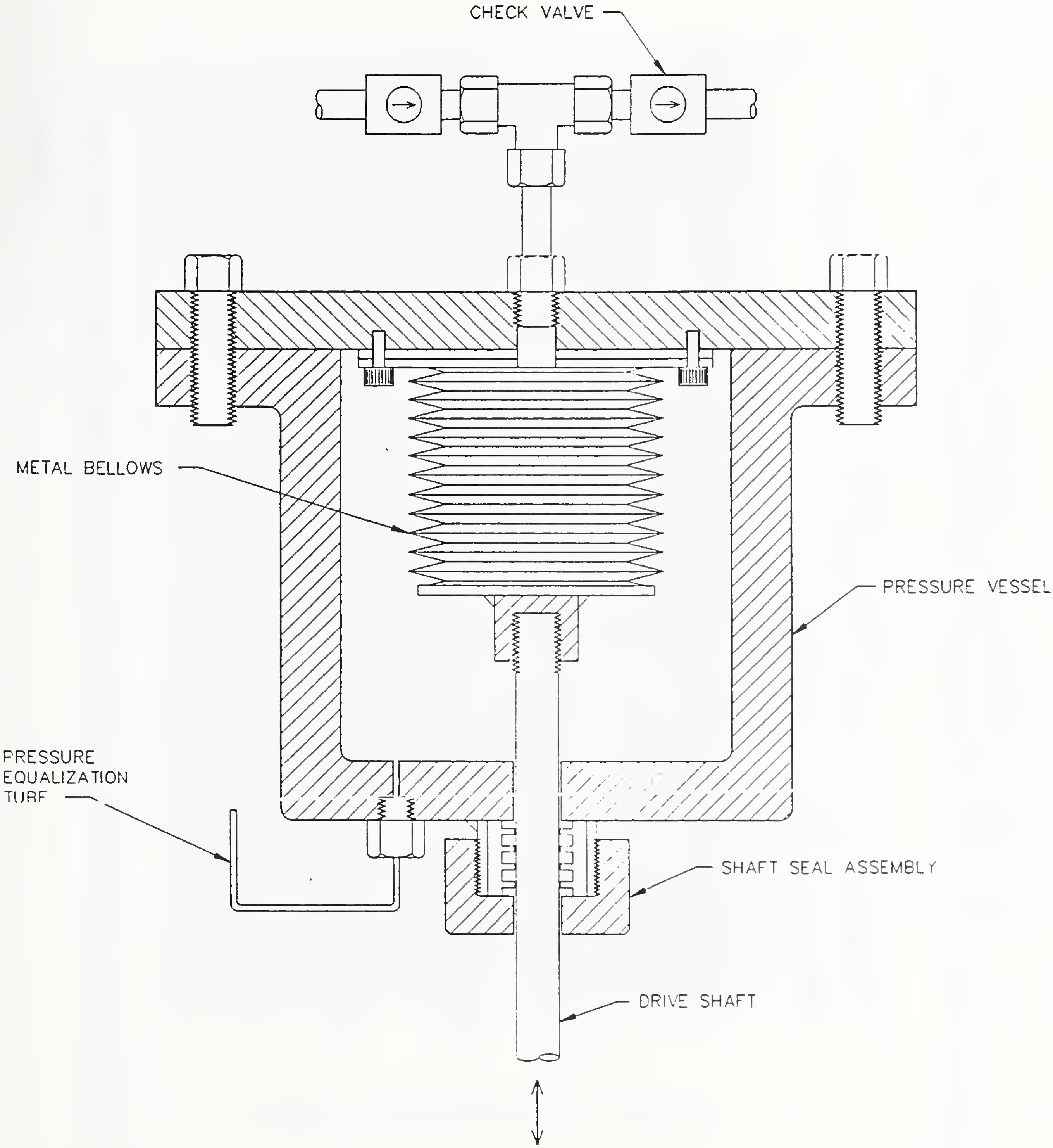


TO EMERGENCY SHUT DOWN
THREE-WAY SOLENOID
SV-1
AIR
N.C.
PR-1
MV-1
PG-1
PMP-1
AIR
TMR-1
PG-2
MV-2
FLT-1
PRV-1
DMP-1
HTR-1
240 VAC
N.O.
ICL-1
TCL-1
T-1
FLT-2
PMP-2
VSD-1
TCL-2
0.2-10 CC/MIN
DMP-3
0.21 LB/MIN, 12.6 LB/HR
T-2
CKV-2
SVS-1
MV-10
AIR
MV-11
BLEED
POV-1
N.C.
DRAIN
PT-4
MV-12
MV-13
SB-1
MV-14
CKV-1
PT-3
PT-1
#1
#2
#10
T-3
PT-2
PR-2
MV-3
PG-3
PMP-3
MV-4
MV-5
VENT
O_2
DMP-2
PG-4
PRV-2
MV-6
DMFC-1
N.C.
MV-7
MV-8
MFC-2
N.C.
MV-9
AIR
PR-3
MV-13
SV-2
CONTROL
N.C.
PG-3
PMP-4
AIR
TMR-2
FCL-1
EXP-1
SV-3
N.C.
PCV-1
100% AIR
NO AIR
MV-12
AIR
CONTROL
TO HOT GAS RECYCLE COMPRESSOR, I/P'S, PNEUMATIC VALVES AND OTHER AIR OPERATED COMPONENTS.
AIR
EXP-2
PCL-1
PT-5
4.18 LB/HR
PCV-3
COOLING WATER
CNDR-1
16.8 LB/HR
T-4
PCV-2
DRAIN
LVS-1
MV-17
MV-18
SB-3
MV-19
MV-14
MV-15
SB-2
MV-16
TMR-3
POV-2
BLEED
SV-4
AIR
SK1752
DEPARTMENT OF THE NAVY
NAVAL FACILITIES ENGINEERING COMMAND
NAVAL CIVIL ENGINEERING LABORATORY
PORT HUENEME, CALIFORNIA 93043
SUPERCRITICAL WATER OXIDATION SYSTEM BENCH SCALE TEST APPARATUS
F

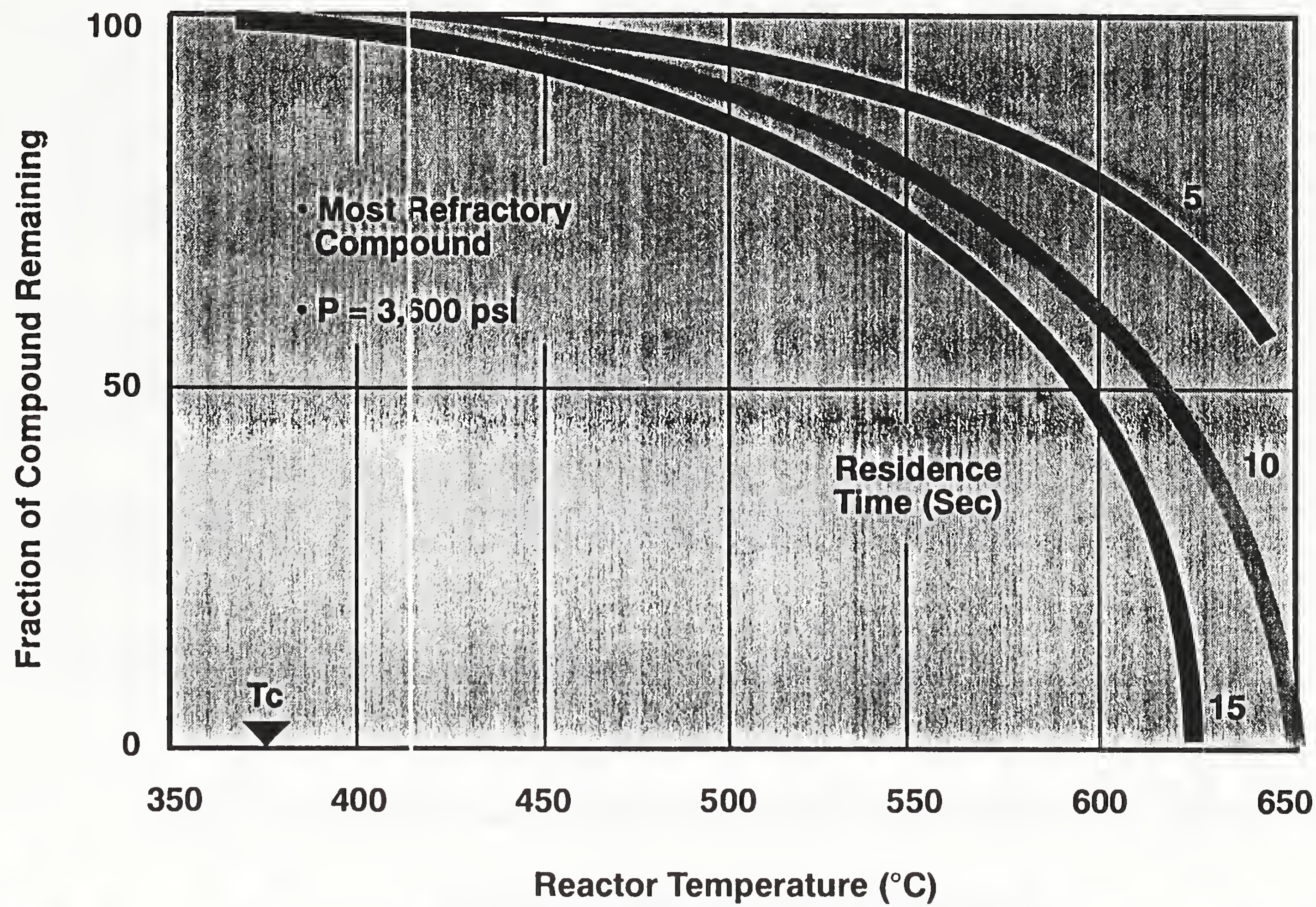


HOT GAS RECIRCULATION COMPRESSOR

SCWO Bench Scale Experiments

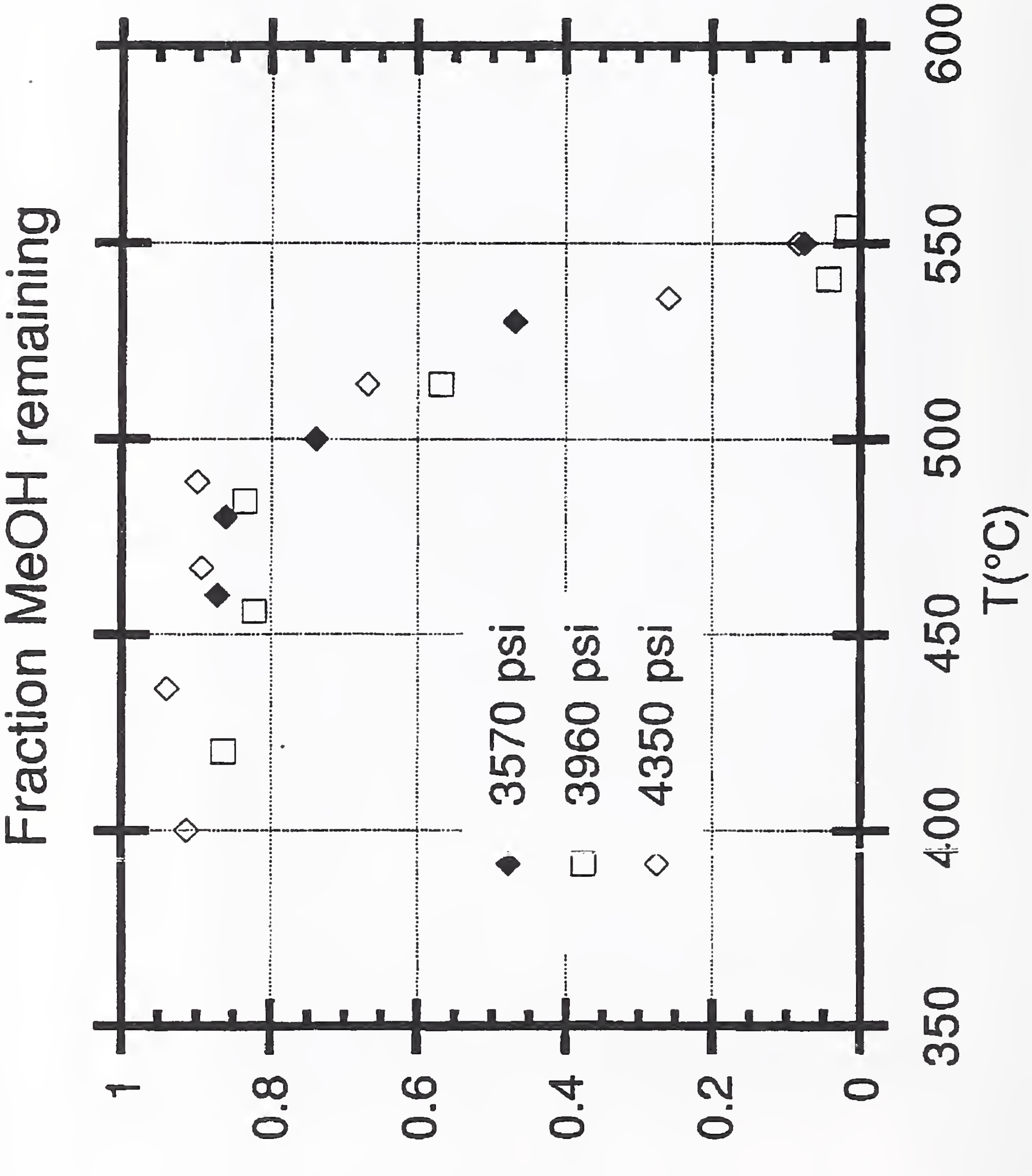
- Destruction of Actual Navy Industrial Hazardous Wastes
- Effectiveness of Exhaust Gas Recirculation
- Salt Separation and Removal
- Control of Acidity
- Process Control
- Materials Performance

1RKGtm.12



Fraction of Compound Remaining
100
50
0
350
400
450
500
550
600
650
Reactor Temperature (°C)
• Most Refractory Compound
• P = 3,600 psi
Tc
Residence Time (Sec)
5
10
15

1RKGtm.16


Fraction MeOH remaining
3570 psi
3960 psi
4350 psi
T(°C)
350
400
450
500
550
600
0
0.2
0.4
0.6
0.8
1

Conclusions

NAVAL CIVIL ENGINEERING LABORATORY

NCEL

- SCWO is a Promising New Technology for Destroying Organic Hazardous Wastes
- Considerable Engineering Development Remains to be Done
- Expensive to Build and Operate
- 2-8 Years to Commercialization

1RKGtm.10

SUPERCRITICAL WATER OXIDATION SYSTEM DEVELOPMENT

Naval Surface Warfare Center
Carderock Division
Annapolis Detachment

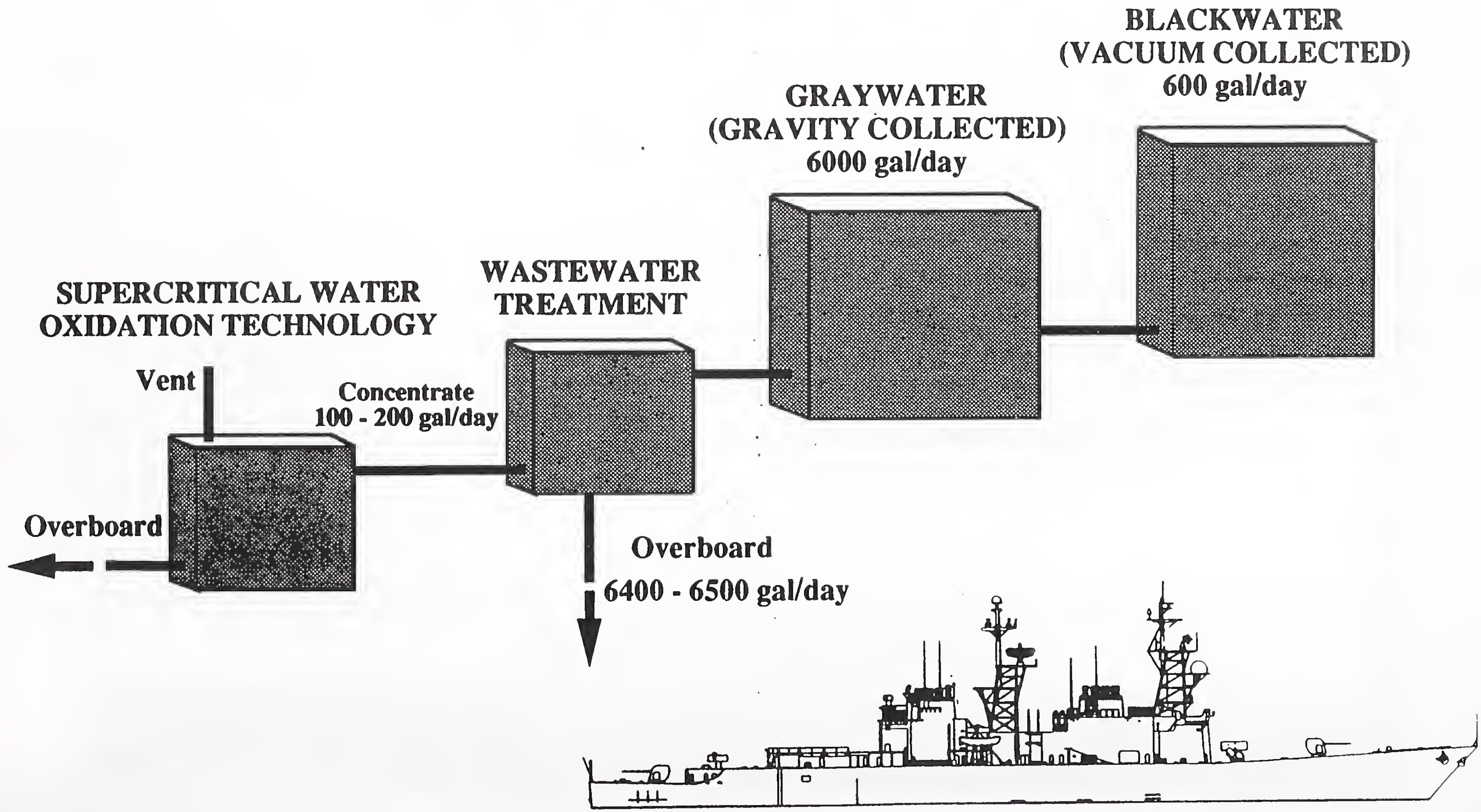
SCWO DEVELOPMENT

TECHNICAL OBJECTIVE

DEVELOP A SHIPBOARD SUPERCRITICAL WATER OXIDATION (SCWO) SYSTEM WHICH IS CAPABLE OF DESTROYING BLACKWATER, CONCENTRATED GRAYWATER, OILY WASTEWATER, & POTENTIALLY OTHER SHIPBOARD WASTESTREAMS.

SCWO DEVELOPMENT

NAVAL SHIP APPLICATION



SCWO DEVELOPMENT

APPROACH

PRELIMINARY ENGINEERING ASSESSMENT & DESIGN

Feasibility Study
BW Treatability Study
PFR Kinetic Study

BENCH-TOP REACTOR & FULL SCALE UNIT DESIGN

Wastewater Kinetic Model
Pretreatment & Concentration
Heat Transfer Model
Preliminary Hazards Analysis
Materials Demonstrations
Scale-Up Factors
Component Testing Platform

Decision Point

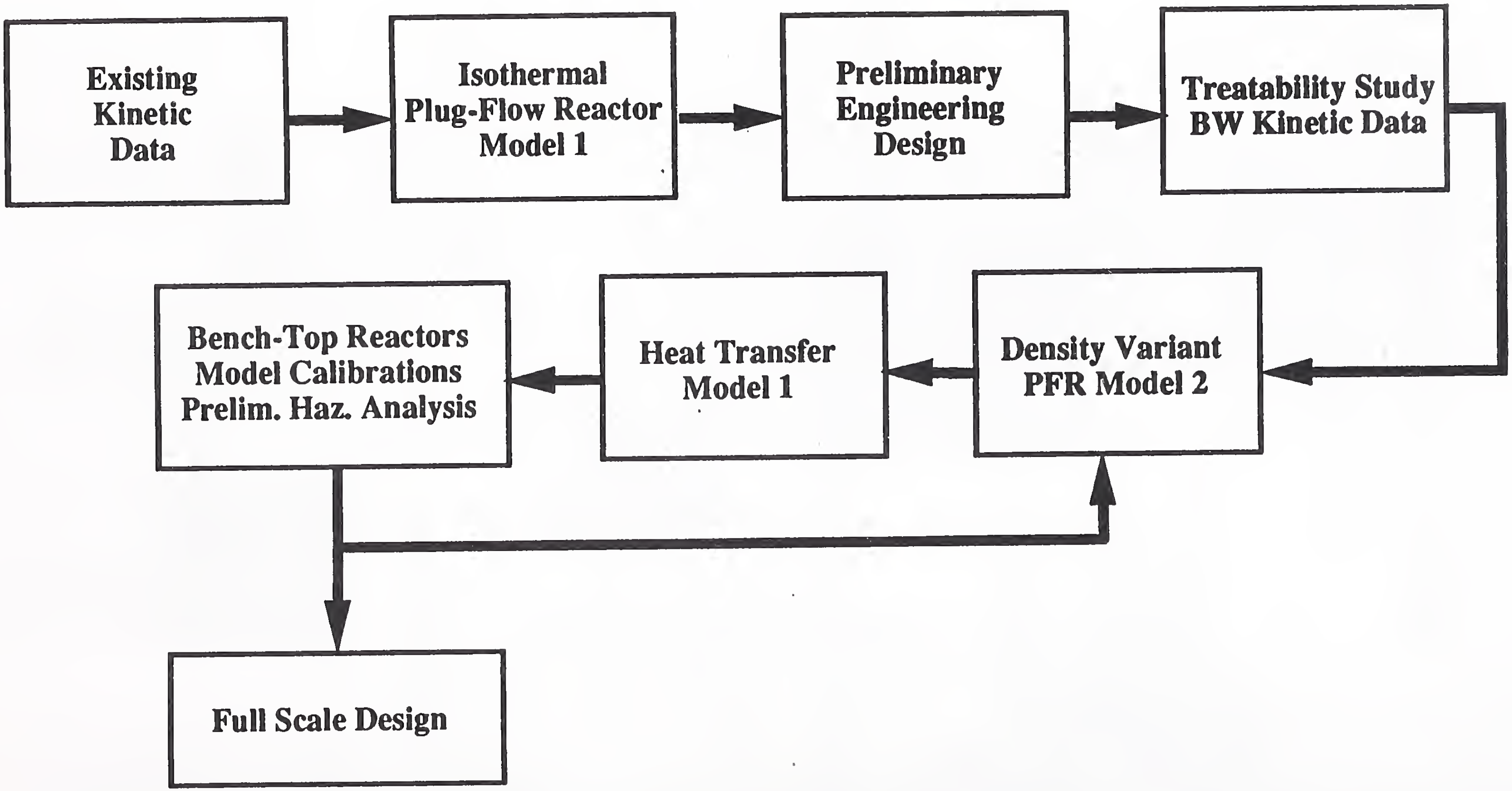
FULL SCALE UNIT DEVELOPMENT

EDM
- High Pressure Pump
- High Pressure Oxidant
- Reactor Materials

Safety Studies
SHIPEVAL
OPEVAL
TECHEVAL
Software Support

SCWO DEVELOPMENT

TECHNICAL APPROACH



SCWO DEVELOPMENT

STATUS

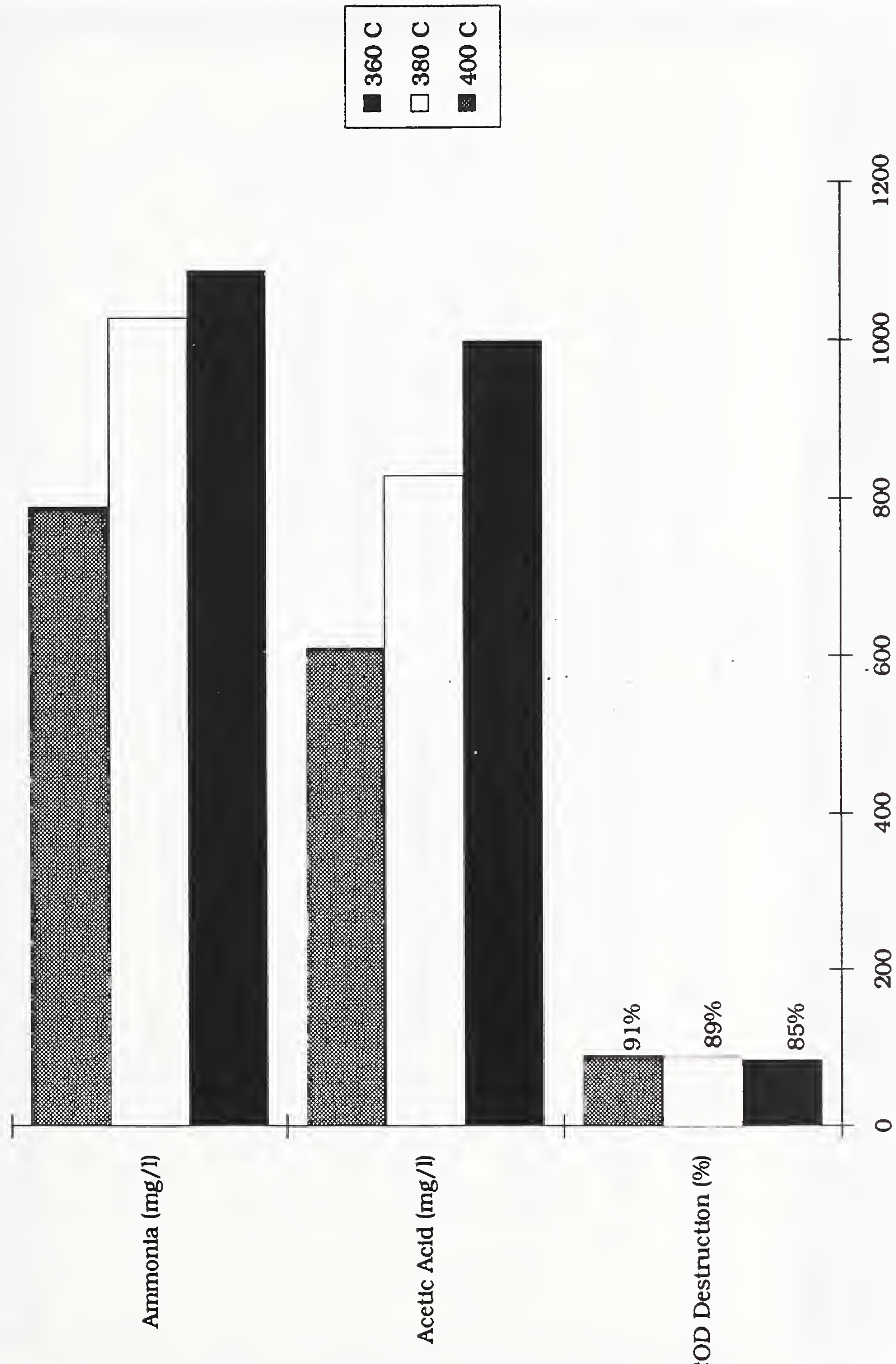
o FEASIBILITY STUDY	Completed FY 91
o PFR MODEL Version 1	Completed FY 91
o BLACKWATER TREATABILITY STUDY	Completed Jan 92
o PRELIMINARY FULL SCALE UNIT DESIGN	Completed Jan 92
o INITIAL MATERIALS SURVEY & SELECTION	Completed Feb 92
o HEAT TRANSFER MODEL Version 1	Completed Mar 92
o BENCH-TOP REACTOR DESIGN & FABRICATION	Initiated Oct 91
o SHIPBOARD MATERIALS STRATEGY	Initiated Oct 91
o PRELIMINARY HAZARDS ANALYSIS STUDY	Initiated Mar 92
o SHIPBOARD EQUIPMENT & DESIGN ANALYSIS	Initiated April 92

SCWO DEVELOPMENT

PROGRESS

BLACKWATER TREATABILITY STUDY

- UNIV OF TEXAS at AUSTIN, CENTER FOR ENERGY STUDIES (SME-91-16 JANUARY 92)
- NAVAL BLACKWATER SUCCESSFULLY OXIDIZED TO CO_2 AND H_2O AT LOW SCWO TEMPERATURES (400 - 450 C)
- RESIDUAL ASH IS STABLE AND LOW IN VOLUME
- NO SIGNIFICANT DIFFERENCE IN OXIDATION KINETICS BETWEEN AIR AND O_2



360 C
380 C
400 C
Ammonia (mg/l)
Acetic Acid (mg/l)
COD Destruction (%)
91%
89%
85%
0
200
400
600
800
1000
1200

SCWO DEVELOPMENT

PROGRESS

- PRELIMINARY FULL-SCALE DESIGN (SME-91-62 JAN 92)

- INITIAL VALUES for PRELIMINARY DESIGN

Feed Rate:	1.0 gal/min	Oxidant Feed Rate:	8 scfm
Pressure:	3700 psi	Oxidant Power Req:	8 hp
Temperature:	<1292 F	Transferred Heat Power:	224 kW
Destruction Eff.	>99%	Pump Power Req:	3 Hp
Oxidant:	Air		
Oxidant Pressure:	4000 psi		

SCWO DEVELOPMENT

PROGRESS

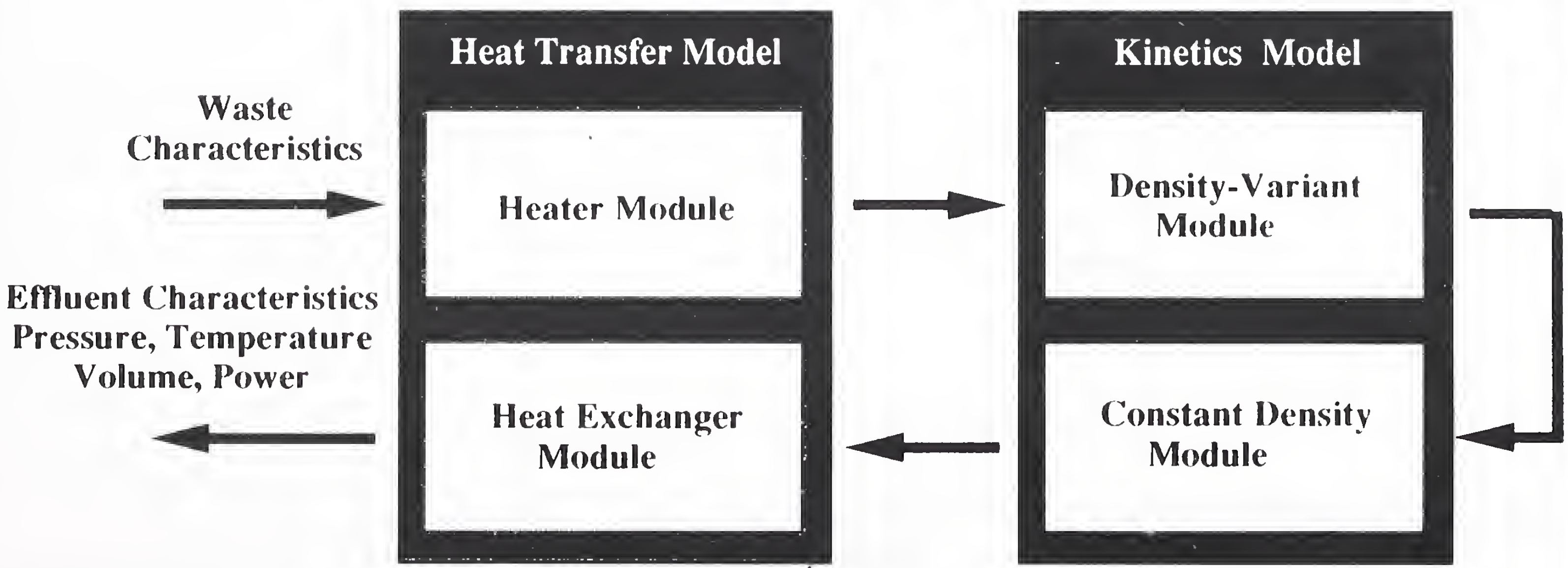
SHIPBOARD MATERIALS STRATEGY

- o MATERIALS STRATEGY SURVEY
  - Survey of Commercial Strategies
    - SS 316 Disposable Reactor
    - Ceramic Liners
  - Existing Bench-Top Units
    - SS 316
    - C-276
    - I-625
  - Univ. Texas at Austin Materials Study
    - No Detectable Corrosion: Ti Grade 9 & 12
    - Uniform Corrosion: C-276, C-22
    - Crevice Corrosion: SS316, SS316L, 2205, 20CB3, I-625, I-825, G-3
- o BENCH-TOP UNIT MATERIALS RECOMMENDATION & SELECTION
  - Non-Corrosive Areas: SS 316
  - SCWO Areas: C-276

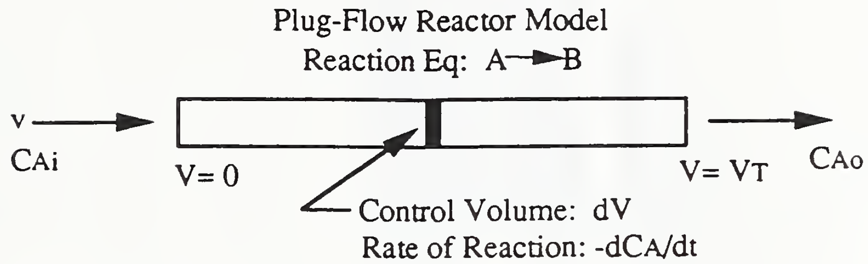
SCWO DEVELOPMENT

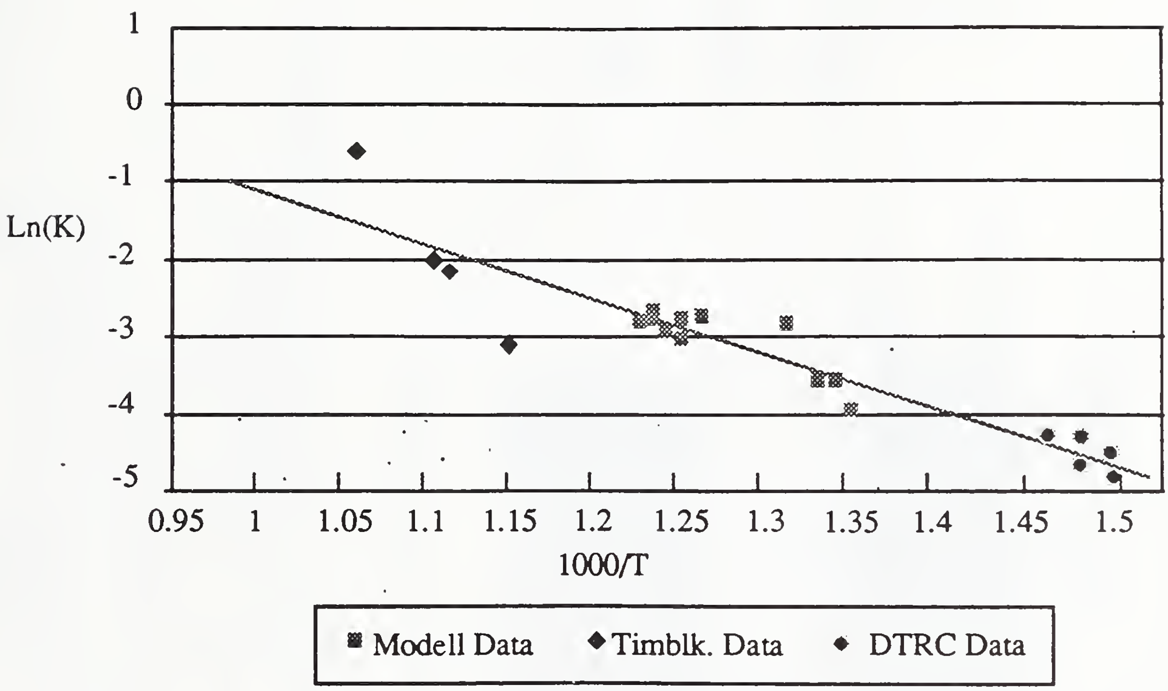
PROGRESS

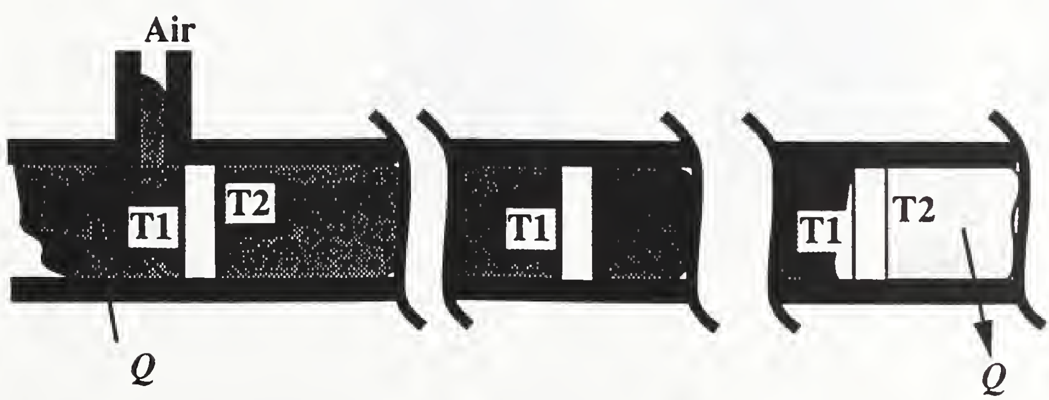
SYSTEM MODELS FOR SCALE-UP



PLUG-FLOW REACTOR MODEL



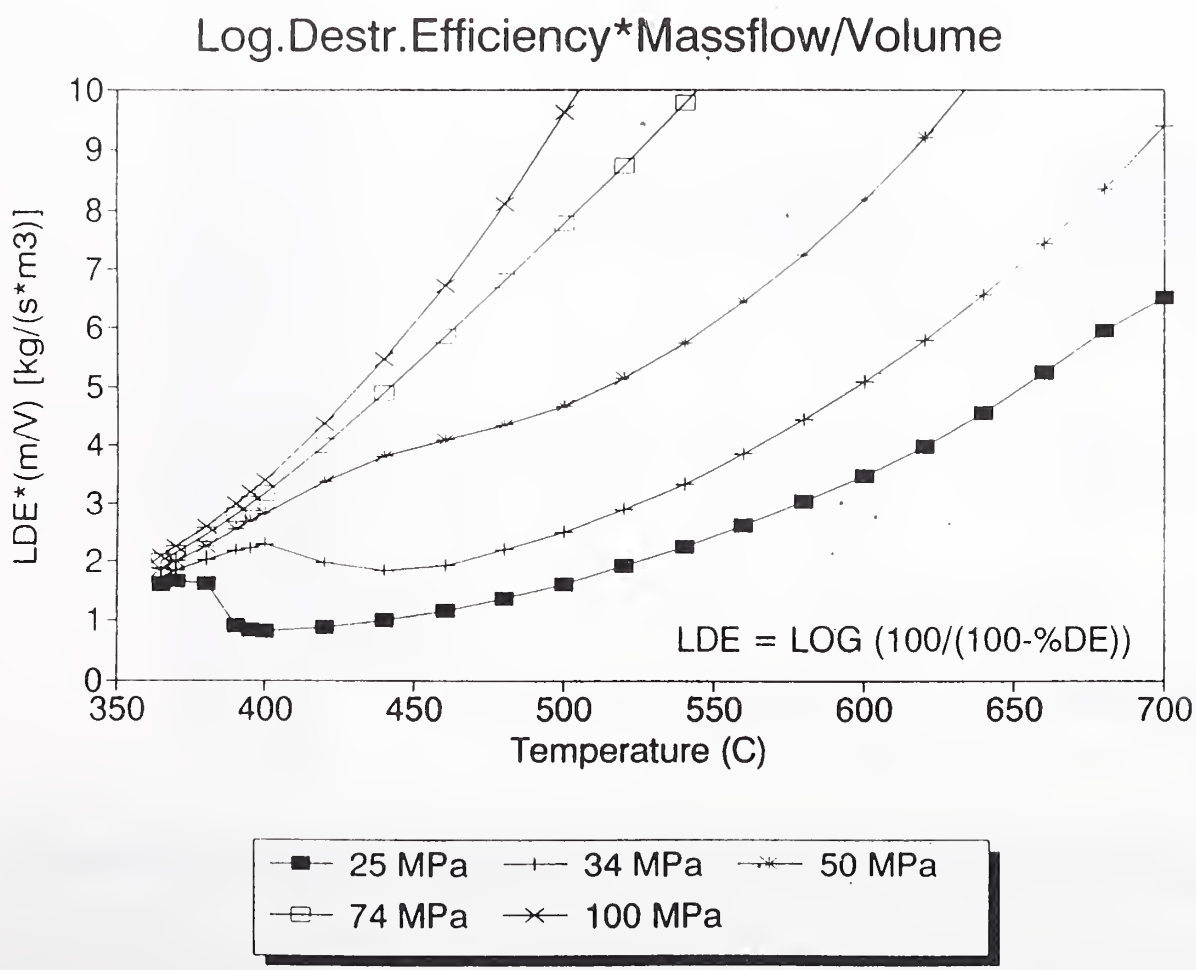




SCWO DEVELOPMENT

PROGRESS

KINETIC MODEL SUMMARY



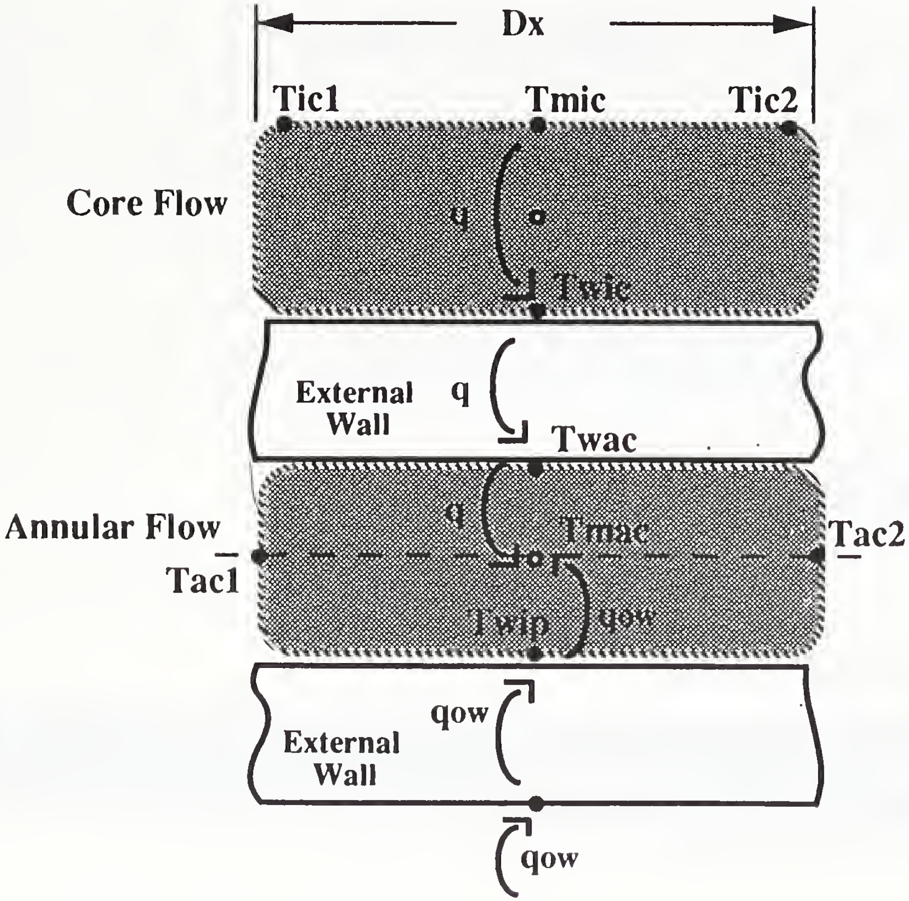
Model Runs :

Kinetic Arrhenius R. Fits
Residence Time
Reactor Volume
Destruction Efficiency
P & T Effects on Kinetics
P & T Effects on Density

SCWO DEVELOPMENT

PROGRESS

HEAT TRANSFER MODEL:
HEAT EXCHANGER, HEATER, REACTOR MODELS



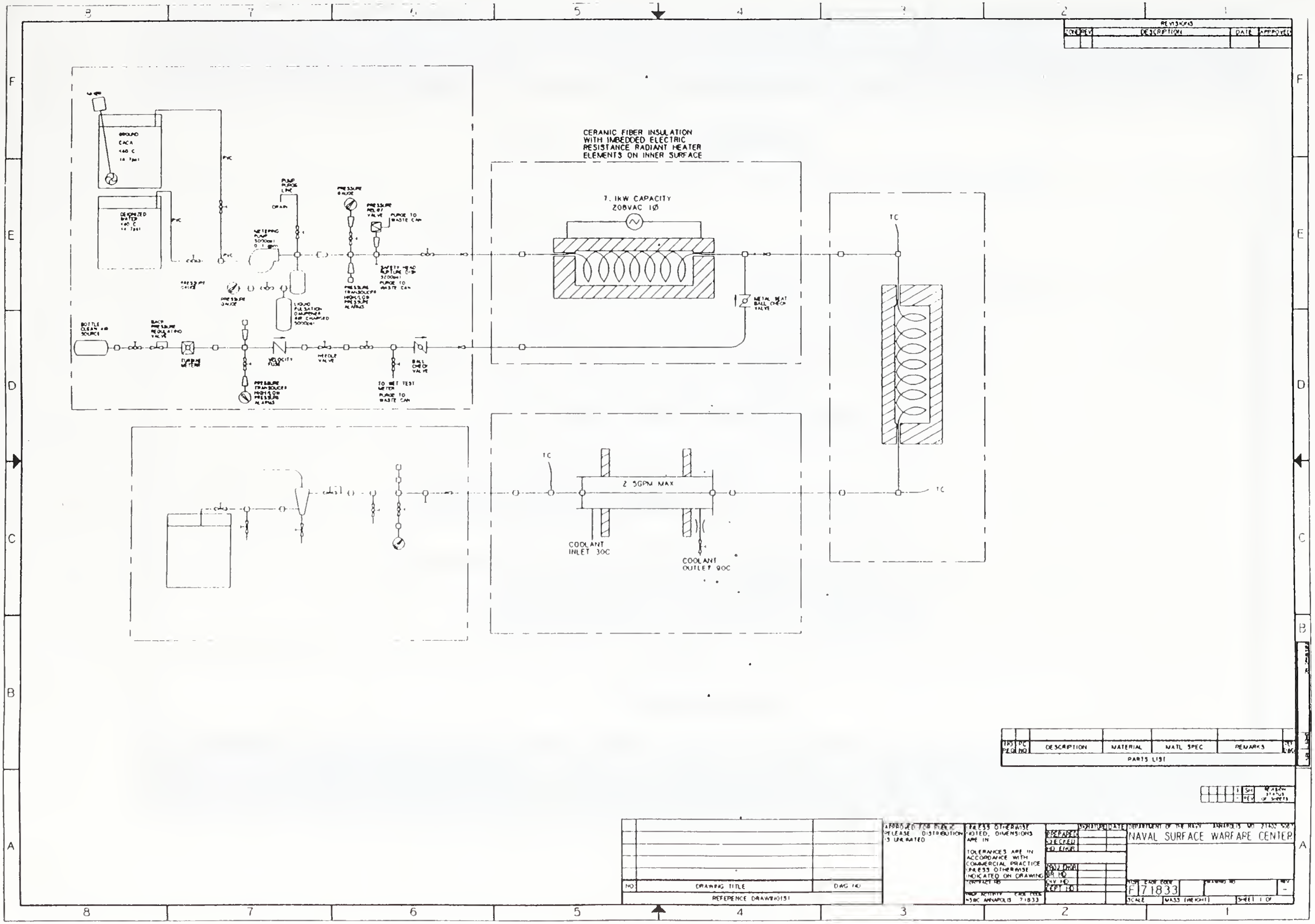
- o Simultaneous Solution of Equations at Stations
- o Results of Station i become intial condition for $i + 1$
- o Thermophysical Properties of Fluids are Dynamic :
  - Specific Heat
  - Density
  - Viscosity
  - Thermal Conductivity

SCWO DEVELOPMENT

PROGRESS

BENCH TOP REACTOR DESIGN & FABRICATION

o CONTINUOUS FLOW UNIT	0 - 1.0 gallon / hour
o TEMPERATURE RANGE	500 - 600 ^{o}C
o PRESSURE RANGE	3300 - 5000 psi
o REACTOR VOLUME	19.3 in^{3} (317 ml)
o HEATER POWER	7.1 kW
o OXIDANT	4000 psi Bottle Air
o COMPONENTS DESIGNED FOR SCALE-UP	


CERANIC FIBER INSULATION
WITH IMBEDDED ELECTRIC
RESISTANCE RADIANT HEATER
ELEMENTS ON INNER SURFACE
7. IKW CAPACITY
208VAC 1Ø
METAL SEAT
BALL CHECK
VALVE
TC
2.5GPM MAX
COOLANT
INLET 30C
COOLANT
OUTLET 90C
BOTTLE
CLEAN AIR
SOURCE
VELOCITY
FUSE
NEEDLE
VALVE
BALL
CHECK
VALVE
TO WET TEST
METER
PURGE TO
WASTE CAN
PRESSURE
GAUGE
PRESSURE
RELIEF
VALVE
PURGE TO
WASTE CAN
PVC
DRAIN
REVISIONS
DESCRIPTION
DATE
APPROVED
DESCRIPTION
MATERIAL
MATL SPEC
REMARKS
PARTS LIST
APPROVED FOR PUBLIC
RELEASE DISTRIBUTION
IS UNLIMATED
UNLESS OTHERWISE
NOTED, DIMENSIONS
ARE IN
TOLERANCES ARE IN
ACCORDANCE WITH
COMMERCIAL PRACTICE
UNLESS OTHERWISE
INDICATED ON DRAWING
PREPARED
CHECKED
DEPARTMENT OF THE NAVY
NAVAL SURFACE WARFARE CENTER
F 71833
SCALE
SHEET 1 OF
DRAWING TITLE
DWG NO
REFERENCE DRAWING(S)

SCWO DEVELOPMENT

PROGRESS

SHIPBOARD MATERIALS STRATEGY

- o MATERIALS TESTING PROGRAM: Code 2813
  - Coupon Test Screening
  - Flow-Through Condition Tests
- o NIST SCWO: Micro-reactor with Window
- o DARPA BAA CONTRACT: GENERAL ATOMICS
  - Perform R&D and Design of Transportable SCWO Pilot Plant: Chemical Agents, Solid Propellants, DOD HW
  - Materials Studies
    - Designed and Assembled Materials Testing Loop
    - Selected Candidate Materials
- o CDNSWC INTERACTION with GA MATERIAL STUDIES

SCWO DEVELOPMENT

PROGRESS

PRELIMINARY HAZARDS ANALYSIS STUDY

- o IDENTIFICATION OF SAFETY ISSUES
  - Bench Top Research Unit
  - Conceptual Full Scale Shipboard Unit

- o INITIATION OF SAFETY STUDY
  - Design Safe Guards and Interlocks
  - Operational Safety Requirements
  - Compartment Assignment Limitations
  - Operator Training Requirements

SCWO DEVELOPMENT

PROGRESS

SHIPBOARD EQUIPMENT AND DESIGN ANALYSIS

o HIGH PRESSURE AIR DELIVERY

- Stand Alone High Pressure Air Supply
- Code 2722 Air Booster System Survey
- Hydraulically Driven Air Booster Testing

o HIGH PRESSURE WASTEWATER PUMP

- Code 2723 Survey of Supported Pumps
- Hydraulically Driven, Low Speed HP Sewage Pump

o AUXILIARY FUEL ADDITION

- Analysis of Supplimental Fuel Source to Reduce Electrical Power Consumption (Autogenic Operation)

- Aux. Fuel Requires Injection Pump, Larger Air Demand, and Reactor.

SCWO DEVELOPMENT

KEY ENGINEERING ISSUES

- o DESIGN POINT - OF - OPERATION
  - P & T Setpoint
  - Level of Destruction
- o MATERIALS and CORROSION
  - Affordable Materials & Suitable Techniques
  - Corrosion Control Strategy
- o HEAT TRANSFER PROPERTIES
  - Heat Transfer Coeffs.
  - Heater, Reactor, Heat Exchanger Design
- o DEFINITION OF CRITICAL SCALE-UP PARAMETERS
  - Physical / Chemical Processes
  - Mechanical Design
- o SYSTEM DESIGN FOR SAFETY

SCWO DEVELOPMENT

PLANS TO DECISION POINT

- o BENCH TOP UNIT FABRICATION (FY 92)
  - Fabrication and Assembly of 1.0 gph Unit
- o KINETIC MODEL VERIFICATION & REFINEMENT (FY 92)
  - Initial Calibration with Model Compounds
  - Proportionals Mixtures of Blackwater & Graywater
- o HEAT TRANSFER MODEL REFINEMENT (FY 92)
  - Refinement of Model Predictions Based on Empirical Data
- o PRELIMINARY HAZARDS ANALYSIS STUDY (FY 92)
- o GA MATERIALS STUDY PARTICIPATION
- o SHIPBOARD FULL SCALE UNIT DESIGN

SCWO DEVELOPMENT

PLANS TO DECISION POINT

- o SHIPBOARD FULL SCALE UNIT DESIGN
  - Component Design Based on Bench Top Test Results
  - System Capacity, Weight and Volume Predictions
  - Destruction Efficiency and Effluent Quality
  - Preliminary SOP and Design Guidelines

DEMILITARIZATION R&D TECHNOLOGY FOR CONVENTIONAL MUNITIONS

US ARMY
ARMAMENT MUNITIONS
AND CHEMICAL COMMAND
ARMAMENT RDE CENTER

US ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER (ARDEC)

CRANE ROBINSON
SMCAR-AES-P
(201) 724-5839

OUTLINE

- PURPOSE
- BACKGROUND
- PROBLEM
- DEMIL R&D TECHNOLOGY PROGRAM
  (5-YEAR PLAN)
- SUPERCRITICAL WATER OXIDATION
  - WHY
  - CURRENT STATUS
  - FY 92 DOWNLOADING EFFORT
  - PRELIMINARY RESULTS
- SUMMARY

PURPOSE

TO PROVIDE A BRIEF OVERVIEW OF THE DEMILITARIZATION R&D TECHNOLOGY PROGRAM FOR CONVENTIONAL AMMUNITION AND PROVIDE THE CURRENT STATUS OF THE SUPERCRITICAL WATER OXIDATION PROGRAM FOR CARCINOGENIC/TOXIC COLORED SMOKE/DYE AND PYROTECHNIC COMPOSITIONS.

BACKGROUND

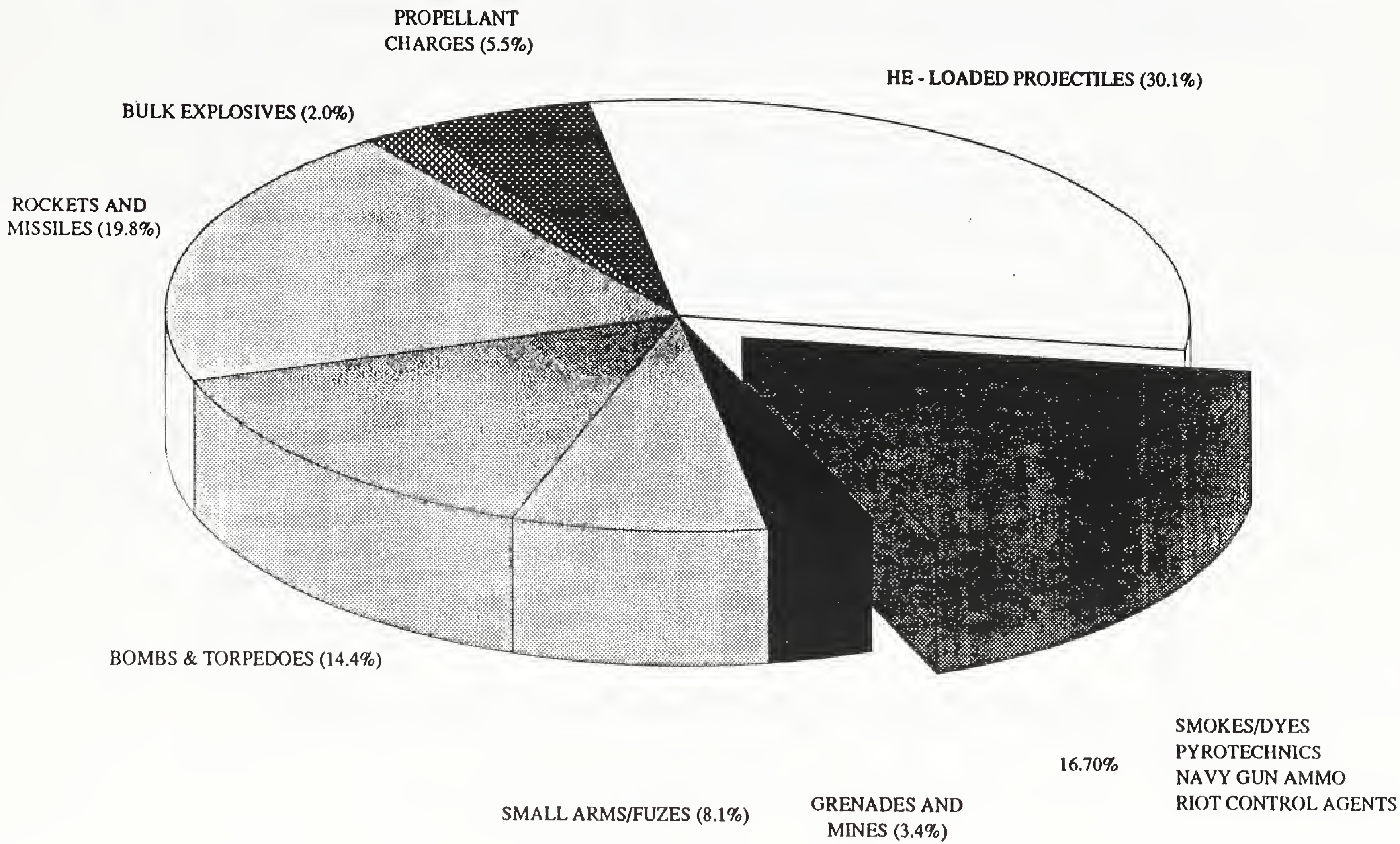
- WHO'S ACCOMPLISHING DEMILITARIZATION OF MUNITIONS?
  - CONVENTIONAL MUNITIONS
    - ✓ HQ AMCCOM : OB/OD, INCINERATION, STEAMOUT
    - ✓ ARDEC : NEW TECHNOLOGY DEVELOPMENT
  - LARGE ROCKET MOTORS : USADACS
  - SMALL ROCKET MOTORS : MICOM
  - CHEMICAL AGENT MUNITIONS : PM CHEM DEMIL

PROBLEM

- LARGE AND GROWING INVENTORY OF CONVENTIONAL MUNITIONS REQUIRING DEMILITARIZATION
- CURRENT STOCKPILE IS APPROXIMATELY 189,000 SHORT TONS (S/T) AND COULD EXPAND BY 952,500 S/T DUE TO WORST CASE RETROGRADE OF STOCKS FROM OCONUS
- ARMY AND SINGLE MANAGER CONTINUE TO RELY UPON OB/OD AS PRIMARY DEMILITARIZATION METHOD AT DEPOT SITES
- FEDERAL AND STATE ENVIRONMENTAL LEGISLATION MAY LIMIT OR ELIMINATE OB/OD IN THE FUTURE (CIRCA FY98)
  - INCREASING DEMILITARIZATION COSTS
  - LACK OF TECHNICAL SOLUTIONS FOR SEVERAL ITEMS (E.G., COLORED SMOKES/DYES, PYROTECHNICS)

DEMILITIZARATION INVENTORY

DATA AS OF 31 DEC 91



DEMIL R&D TECHNOLOGY PROGRAM
5-YEAR PLAN

- FY 92 PROGRAM
  - INITIATE EVALUATION OF NEW, EMERGING, INNOVATIVE TECHNOLOGIES FOR DEMILITARIZATION OF ITEMS IN THE INVENTORY WHERE NO TECHNOLOGY PRESENTLY EXISTS

- FY93-96 PROGRAM
  - COMPLETE TECHNOLOGY EVALUATIONS
  - FOCUS ON EVALUATING TECHNOLOGIES TO "PERMIT THE RECLAMATION AND REUSE OF ENERGETIC MATERIALS"

DEMIL TECHNOLOGY PROGRAM PLAN

FY 92 PROGRAM

- TECHNOLOGY ASSESSMENT OF ALTERNATIVES TO OB/OD FOR CONVENTIONAL MUNITIONS
- PLASMA ARC FURNACE EVALUATION
- SUPERCRITICAL WATER OXIDATION (SCWO) EVALUATION

FY 93-96 PROGRAM

- COMPLETE PLASMA ARC AND SCWO EFFORTS
- INITIATE EFFORTS ON OTHER ALTERNATIVE TECHNOLOGIES

WHY SUPERCRITICAL WATER OXIDATION?

- LARGE QUANTITY OF SPOTTING DYE PROJECTILES IN THE DEMIL INVENTORY REQUIRING TECHNOLOGY DEVELOPMENT
- INCINERATION OF SMOKE MUNITIONS PRODUCES LARGE QUANTITIES OF PARTICULATE MATTER THAT LOCKS-UP POLLUTION ABATEMENT EQUIPMENT
- INCINERATION OF PYROTECHNIC MUNITIONS EXCEED DESIGN TEMPERATURE LIMITATIONS ON ROTARY KILN DEACTIVATION FURNACES (APE 1236)
- CURRENT INCINERATION SYSTEMS ARE UNABLE TO MEET THE REQUIRED 99.9999% DESTRUCTION REMOVAL EFFICIENCY (DRE) FOR TOXIC CONTAMINANTS

CURRENT STATUS

- FY92 EFFORT FUNDED BY ARDEC AND BEING EXECUTED BY SNL, LIVERMORE, CA
- PROGRAM MANAGEMENT PLAN AND PROGRAM TEST PLAN HAVE BEEN SUBMITTED TO ARDEC BY SNL
- SIMULANT TESTING COMPLETED AT SNL ON LOW CONCENTRATION ORGANIC SOLUTIONS; HIGH DESTRUCTION REMOVAL EFFICIENCIES RECORDED
- TESTING HAS BEEN INITIATED ON CARCINOGENIC/TOXIC DYE COMPOSITIONS

FY92 DOWNLOADING EFFORT

- GREEN COLORED SMOKE COMPOSITION DOWNLOADED BY PINE BLUFF ARSENAL,
  - TOTAL OF EIGHT, 155-MM M116B1 GREEN SMOKE PROJECTILES WERE DISASSEMBLED AND MIX REMOVED FROM THE SMOKE CANISTERS.
  - MIX WAS GROUND IN WATER TO PRODUCE A SLURRY THAT CONSISTED OF A SUSPENSION OF PARTICLES LESS THAN 1-MM IN DIAMETER.
  - COMPOSITION TO BE SHIPPED TO SNL
- SPOTTING DYE COMPOSITONS DOWNLOADED BY McALESTER ARMY AMMUNITION PLANT
  - TOTAL OF 48, 6 INCH, 47 CALIBER MK35 EXPLOSIVE D LOADED PROJECTILES DISASSEMBLED.
  - CARCINOGENIC/TOXIC POWDERED DYE COMPOSITIONS (BLUE, GREEN, RED AND ORANGE) MANUALLY REMOVED, PACKAGED AND SHIPPED TO SNL

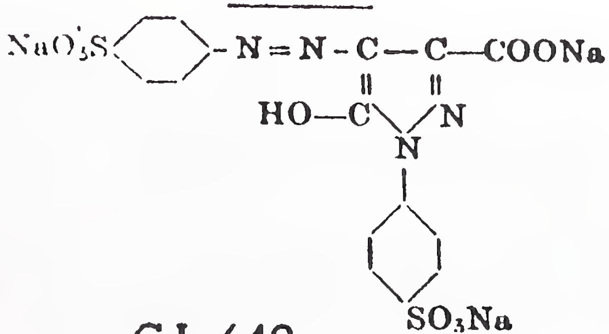
COMPOSITION OF STANDARD SPOTTING DYES

COLOR	INGREDIENT	C.I. NO. *	PERCENT
BLUE	ALPHAZURINE B CONC.	---	30.0
	ACID FAST VIOLET BG CONC 200 PERCENT OF NORMAL	699	20.0
	NACCOSOL A (WETTING AGENT)	---	2.0
	GRANULAR SUGAR	---	48.0
GREEN	WOOL YELLOW EXTRA CONC.	640	80.0
	ALPHAZURINE 2G	712	20.0
RED	NATIONAL FAST CRIMSON "R" CONC. 167 PERCENT OF NORMAL	---	80.0
	WOOL YELLOW EXTRA CONC.	640	20.0
ORANGE	WOOL ORANGE 2G CRYSTALS	27	100.0

* SOCIETY OF DYERS AND COLOURISTS
COLOR INDEX, JAN 1924

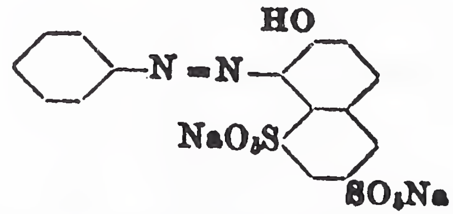
CHEMICAL DYE STRUCTURES

$C_{16}H_9N_4O_9S_2Na_3$



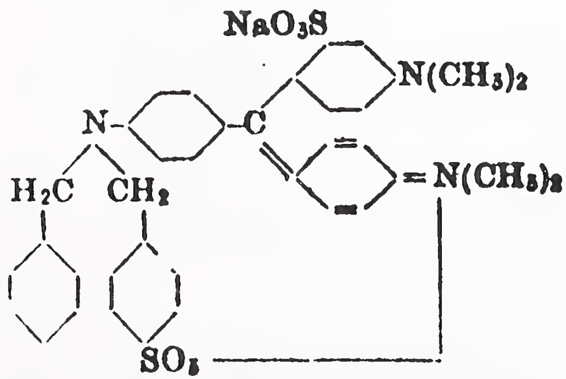
C.I. 640

$C_{16}H_{10}N_2O_7S_2Na_2$



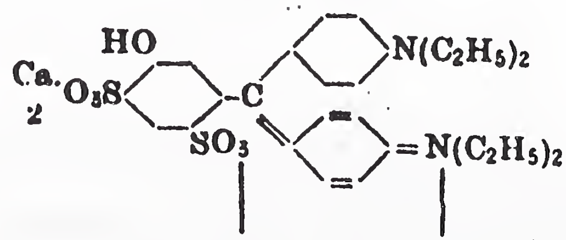
C.I. 27

$C_{37}H_{36}N_3O_6S_2Na$



C.I. 699

Calcium salt—$Ca(C_{27}H_{31}N_2O_7S_2)_2$ + 10 or 14 H_2O



C.I. 712

PRELIMINARY RESULTS

SNL HAS PROCESSED THE ORANGE DYE IN THE MER AT A VERY LOW CONCENTRATION

THE FOLLOWING DESTRUCTION EFFICIENCIES HAVE BEEN RECORDED (6/25/92).

Sample #	Temperature (°C)	TOC (ppm)	Residence Time (seconds)	Destruction Efficiency	Appearance
1	556	3.35	7.4	99.69	colorless
2	553	3.39	7.4	99.68	colorless
3	542	4.51	7.6	99.58	colorless
4	520	21.4	8.1	98.00	pale yellow
5	506	180	8.5	83.1	brown
6	484	247	9.2	76.9	brown/solids

Oxidizer: 5% Hydrogen Peroxide
Flow Rate: 0.75g/sec

Input concentration: 2140 ppm TOC by weight, 0.5% total dye by weight
Appearance: Dark orange

GREEN COLORED SMOKE COMPOSITION

COMPOUND	WEIGHT %
POTASSIUM CHLORATE(B)	31.5 ± 3.0
LACTOSE, TECHNICAL	18.0 ± 2.0
MAGNESIUM CARBONATE	3.5 ± 1.0
DYE, YELLOW (MIL-D-50029)	4.7 ± 0.5
DYE, BENZANTHRONE (MIL-D-50074)	9.4 ± 0.5
DYE, SOLVENT GREEN 3 (MIL-D-3277)	32.9 ± 1.0

SUMMARY

- SCWO APPEARS TO BE A VIABLE TECHNOLOGY FOR MUNITION ITEMS CONTAINING SELECTED SPOTTING DYES AND COLORED SMOKES
    - PLAN IS TO EXPAND EFFORTS TO DEMONSTRATE FEASIBILITY ON COMPOSITIONS CONTAINED IN CHEMICAL DYE MARINE MARKERS AND LARGE CALIBER PYROTECHNIC MUNITIONS.
- LEVERAGE TECHNOLOGY DEVELOPMENT EFFORTS BEING CONDUCTED BY DOD (e.g., LRM PROGRAM), ACADEMIA AND INDUSTRY.

SCWO DECOMPOSITION OF M31A1E1 TRIPLE BASE PROPELLANT

Roger L. Schneider

U.S. Army Corps of Engineers
Construction Engineering Research Laboratory

Champaign, IL 61824-9005

IDENTIFICATION AND ASSESSMENT OF ENVIRONMENTALLY SAFE ALTERNATIVE TECHNOLOGIES TO OPEN BURNING/OPEN DETONATION DESTRUCTION OF EXPLOSIVE AND PROPELLANT PRODUCTION WASTES

Roger L. Schneider and Bernard A. Donahue

U. S. Army Corps of Engineers
Construction Engineering Research Laboratory

Champaign, IL 61824-9005, 217-373-6733

ENERGETIC MATERIALS (PEP)

Propellants

Explosives

Pyrotechnics

USA CERL

ENVIRONMENTAL ENGINEERING DIVISION

Energetic Materials Research Programs include,

- Red Water / Pink Water

- Propellant Recycling (NC)

- Alternatives to OB/OD for contaminated production wastes

ENERGETIC MATERIAL DISPOSAL

- OB/OD

- Incineration

- Supercritical Water Oxidation (SCWO)

- Wet Air Oxidation (WAO)

- Biodegradation

- Electrochemical Oxidation / Reduction

- "Enclosed" Open Burning

EXPLOSIVE AND PROPELLANT WASTE CONTAMINANTS

- Tramp Metals

- Cementitious Materials e.g., gravel

- Glass

- Wood and other Cellulosics

- Plastics and Composites

- "Off-Spec"

CONTAMINATED EXPLOSIVE AND PROPELLANT PRODUCTION WASTE PRETREATMENTS

- Hydromilling

    - High Pressure, 35,000 - 55,000 psig

    - Lower Pressure, Abrasive Augmented, 2,000-10,000 psig

- Alkaline Hydrolysis

- Supercritical Fluid Extraction, e.g., CO_2

- Solvents

CH_2ONO_2

M31A1E1 TRIPLE BASE PROPELLANT

	%w/w
nitrocellulose (NC)	21.50
nitroglycerin (NG)	18.00
nitroguanidine (NQ)	54.70
dibutylphthalate	3.00
ethyl centralite	1.50
potassium sulfate	1.25
carbon black	0.05

Pu St

dip

Stab ge

Ce

Pure gel

dibu ph

DESTRUCTION OF WASTE PROPELLANTS, EXPLOSIVES, AND PYROTECHNICS USING SUPERCRITICAL WATER OXIDATION

Los Alamos National Laboratory

Project Goals

- Determine suitability of hydrolysis and supercritical carbon dioxide dissolution as pre-treatment of triple base propellant (M31A1E1) for supercritical water oxidation
- Design supercritical carbon dioxide feed system for supercritical water reactor
- Determine destruction efficiency and products

Los Alamos

CURRENT METHODS FOR TREATMENT

- Storage \$48/ton/year
  Not a solution
- Open Burning \$300/ton
  Uncontrolled air emissions
- Incineration \$2500-\$3000/ton
  Secondary treatment costs increasing
  Permit process is slow

Los Alamos

HIGH THROUGHPUT IS NECESSARY TO DECREASE COST

Solubility of many organic explosives
<100 milligrams/liter

- Co-solvents: Organic, carbon dioxide
- Slurries: <100μm particles
- Hydrolysis: Preprocess in alkaline solution

Los Alamos

MIXTURE OF CO-SOLVENT/EXPLOSIVE IS INJECTED INTO SUPERCRITICAL WATER

- Simple to implement
- Reduces amount of nitrate and nitrite
- Organic solvents: increase oxygen usage, increase heat release, possible fire hazard, may be toxic
- Many explosives have limited solubility in carbon dioxide

Los Alamos

USING SLURRIES REQUIRES NO ADDITIONAL CHEMICALS

- Particle size needs to be reduced to $< 100\ \mu m$
- Settling of explosive in feed lines can produce explosions
- Heterogeneous chemistry may make process control difficult

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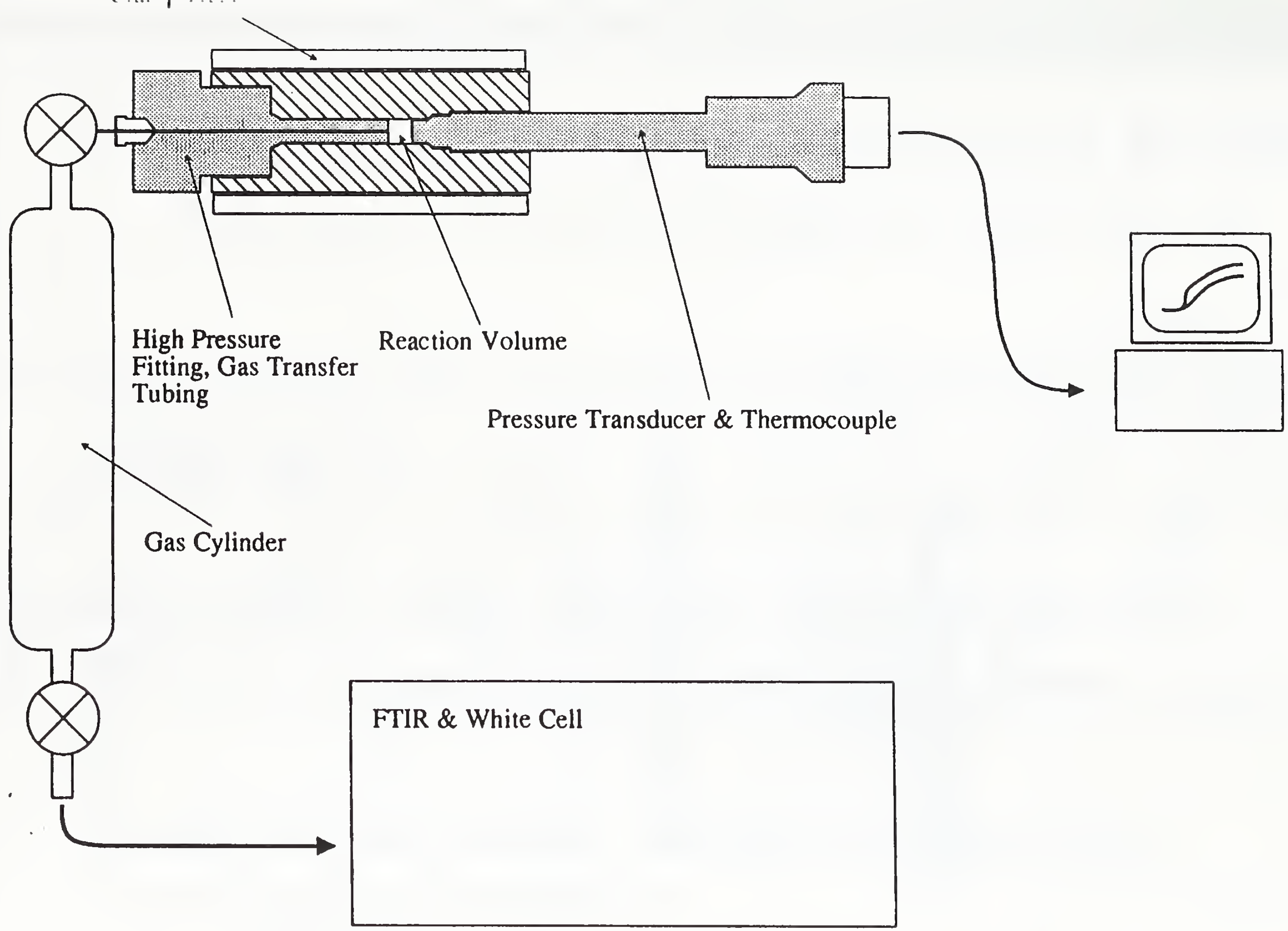
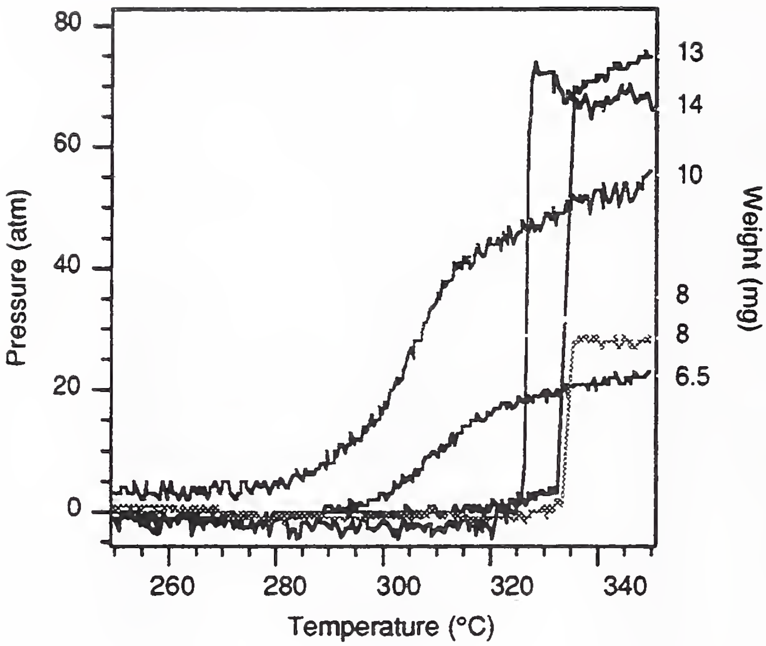
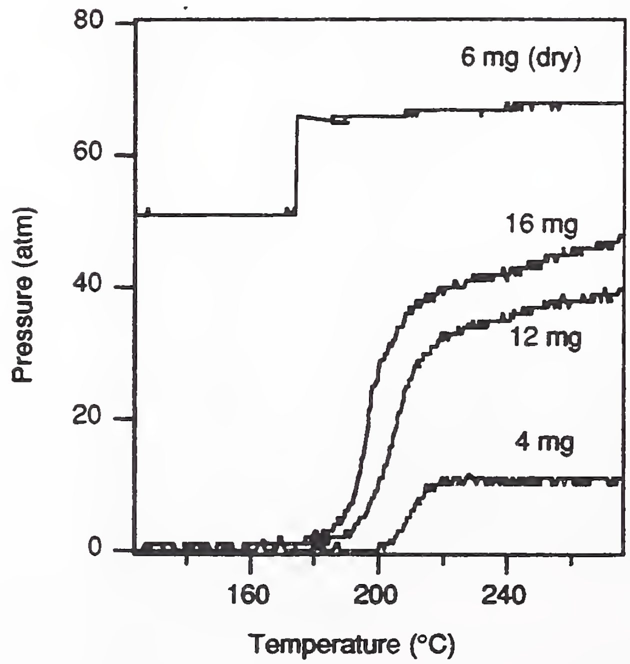


Schematic of the batch reactor experimental setup. The reaction volume used was 200 µl, but can be varied up to 2 ml. After completing the experiment the reactor volume is expanded into the evacuated gas cylindar for later analysis by FTIR.

TATB



Double Base Propellent



ALKALINE HYDROLYSIS PRODUCES WATER SOLUBLE NON-EXPLOSIVE PRODUCTS

- Explosives are heated (<100°C) in alkaline solution

- TNT, HMX, RDX, NG, NC, NQ, TATB, PBX, double base, triple base have been treated

- Supercritical water oxidation destroys hydrolysis products

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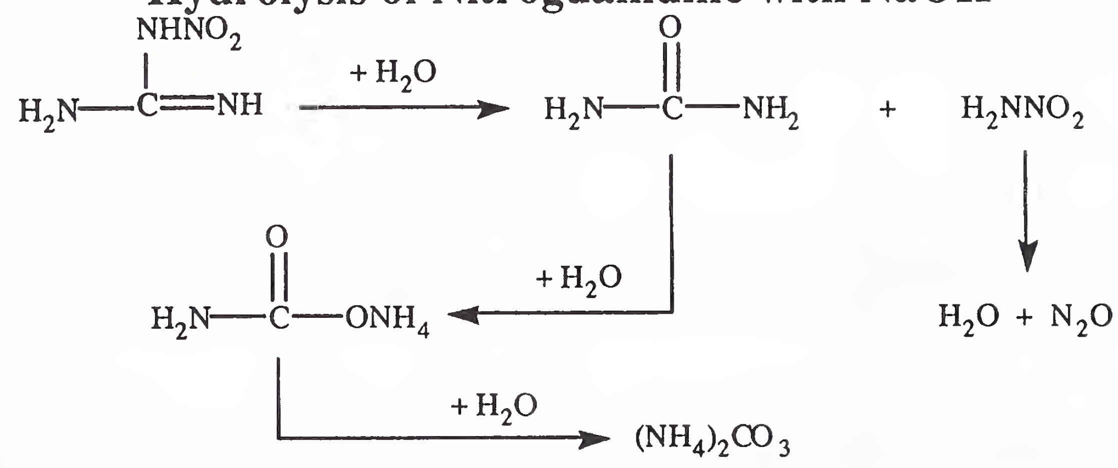
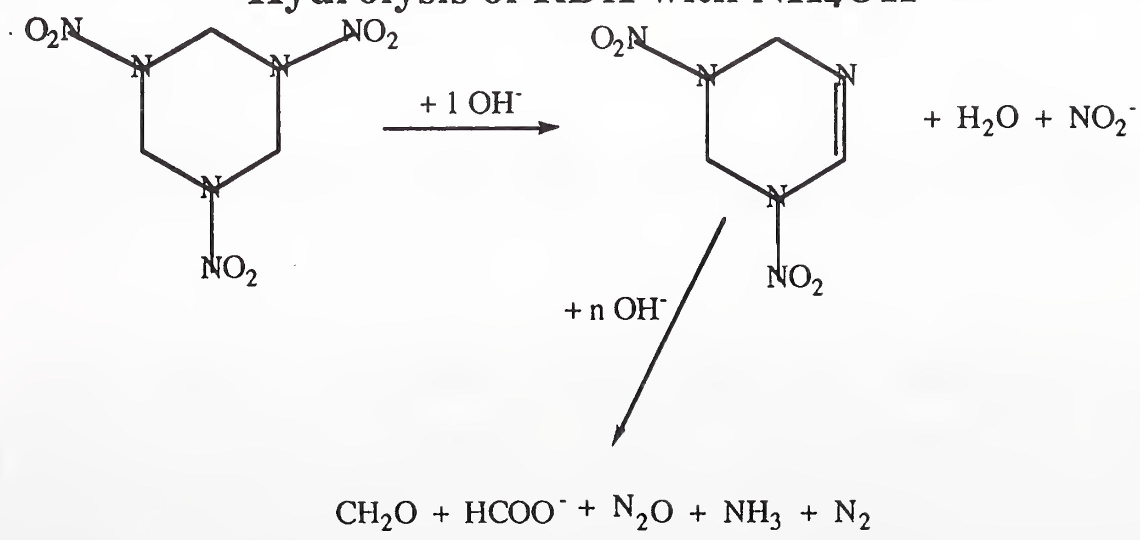
Hydrolysis of Nitroguanidine with NaOH



Hydrolysis of RDX with NH_4OH



HYDROLYSIS/SCWO OF HMX

	Initial Conc. ppm	Hydrolysis ppm (%)	SCWO ppm (%)
HMX	7000	22.5 (0.3)	<0.05 (<0.001)
TOC	1123	1026 (91)	0.7 (0.06)
TIC	0	<0.5 (<0.05)	0.2 (0.02)
N as Nitrite	0	184 (7)	0.09 (0.03)
N as Nitrate	0	80 (3)	30 (1.1)

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HYDROLYSIS/SCWO OF TNT

	Initial Conc. ppm	Hydrolysis ppm (%)	SCWO ppm (%)
TNT	14000	<2 (<0.02)	<0.05 (<0.0005)
TOC	5181	3380 (65)	<0.2 (<0.004)
TIC	0	1080 (21)	10 (0.2)
N as Nitrite	0	784 (30)	8.5 (0.3)
N as Nitrate	0	1 (0.04)	20 (0.8)

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PROCESS DESIGN WILL VARY

WITH WASTE FORM AND

EXPLOSIVE COMPOSITION

Los Alamos

PROGRESS TO DATE

- Demonstrated that M31A1E1 can be rapidly converted to non-explosive, water soluble products by hydrolysis in basic solutions at low temperatures(<100°C)
- Demonstrated that hydrolysis products can be rapidly destroyed by supercritical water oxidation
- Constructed supercritical carbon dioxide injection system for supercritical water reactor
- Demonstrated that supercritical carbon dioxide cosolvent does not decrease destruction efficiency for selected propellant components

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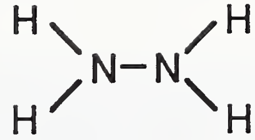
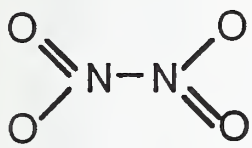
NH_4ClO_4

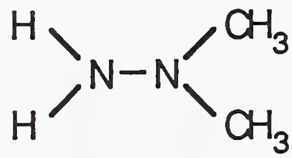
AMMONIUM PERCHLORATE



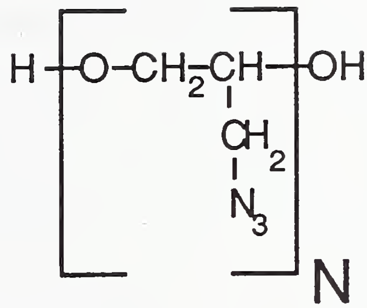
HYDRAZINE



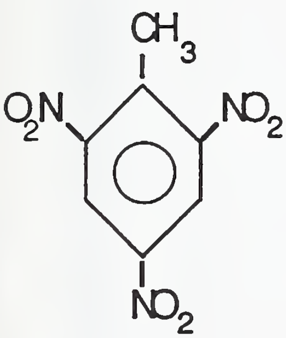
NITROGEN TETROXIDE



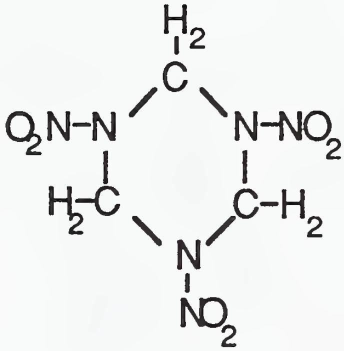
1,1 DIMETHYL HYDRAZINE



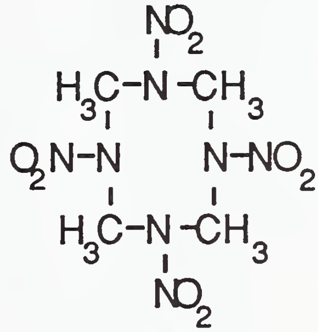
GLYCIDYL AZIDE POLYMER



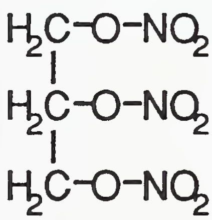
TNT



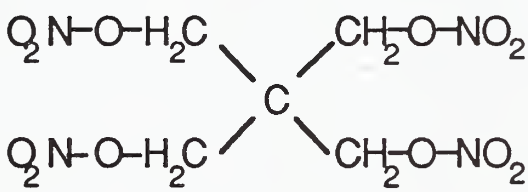
RDX



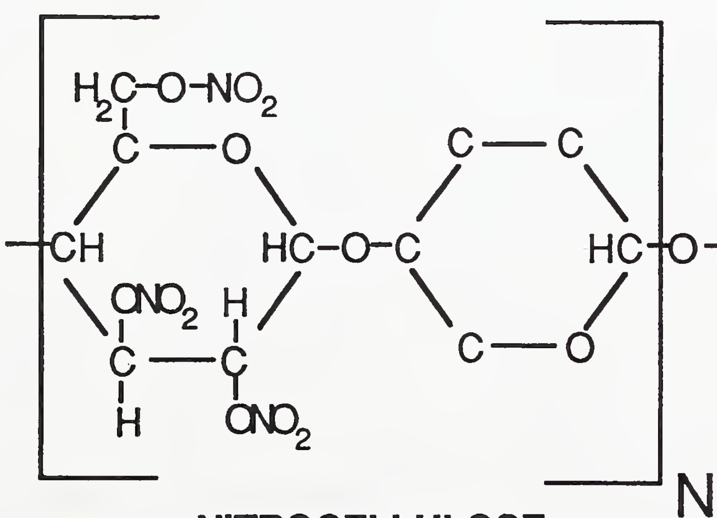
HMX



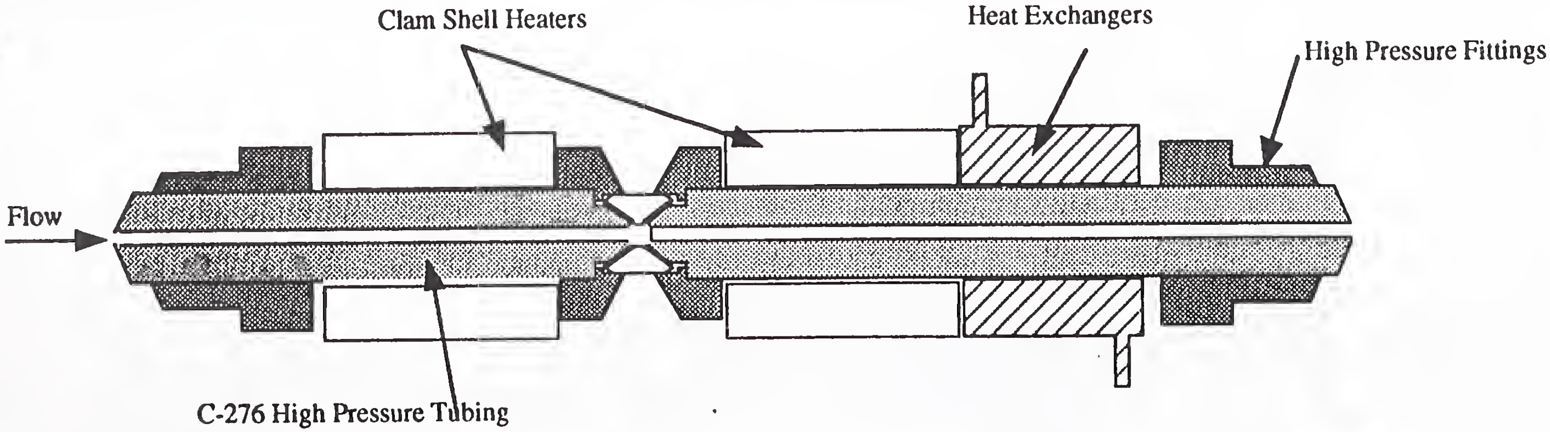
NG

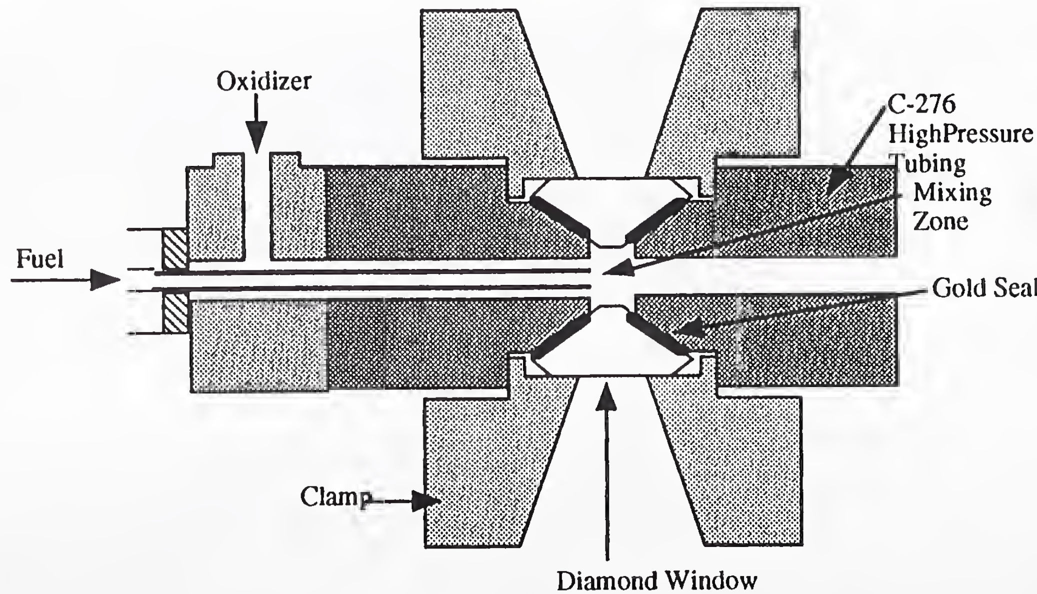


PETN



NITROCELLULOSE





FLOW REACTOR WITH DIAMOND WINDOWS

Los Alamos

Modeling Supercritical Water Oxidation Systems

Nina Bergan French, Sandia, Livermore

Prof. P. Barry Butler, Univ. of Iowa

Bob Schmitt, Univ. of Iowa

Charlie Westbrook, LLNL

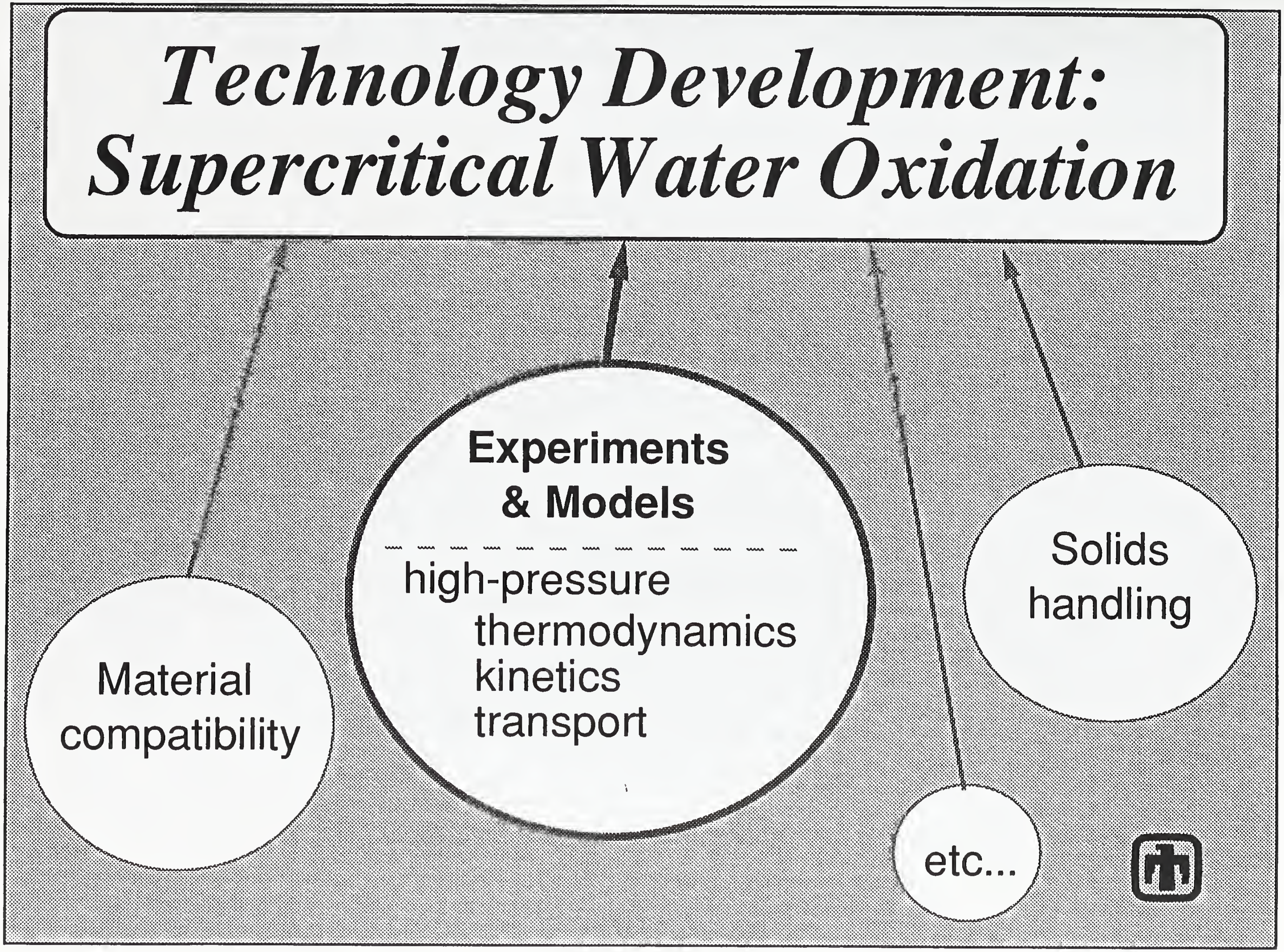
Bill Pitz, LLNL

Three important issues

System scale-up

Corrosion

Solids Separation


Technology Development:
Supercritical Water Oxidation
Experiments
& Models
high-pressure
thermodynamics
kinetics
transport
Material
compatibility
Solids
handling
etc...

System Model + Expt. Data = Engineering Solution

Real-gas thermodynamics

Representative chemical kinetics

Phase behavior

Transport (?)

We have developed several modules of system model for SCWO

Real-gas thermodynamics
and high-pressure chemical kinetics

- Two software packages
  - Chemkin Real-Gas (thermo.+kinetics)
  - Stanjan Real-Gas (equilibrium)
- Reaction mechanisms

Chemkin Real-Gas August, 1992

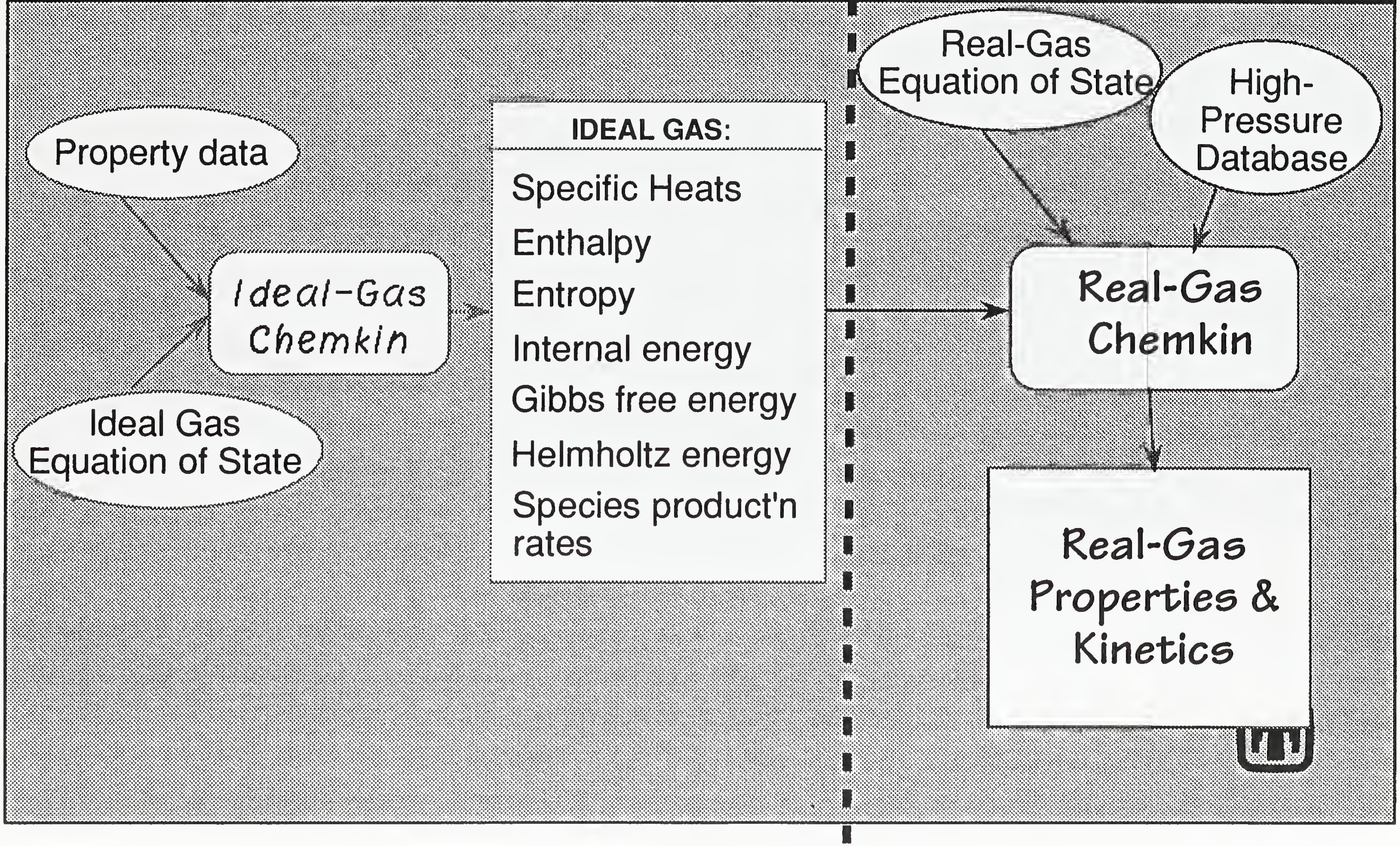
Based on Chemkin II (Bob Kee, et al, Sandia, 1989)

Problem-independent set of subroutines

Database for equation-of-state parameters (Cubic e.o.s. included)

Chemkin Real Gas

A Computer Code for Analysis of Thermodynamics and Chemical Kinetics in High-Pressure Systems

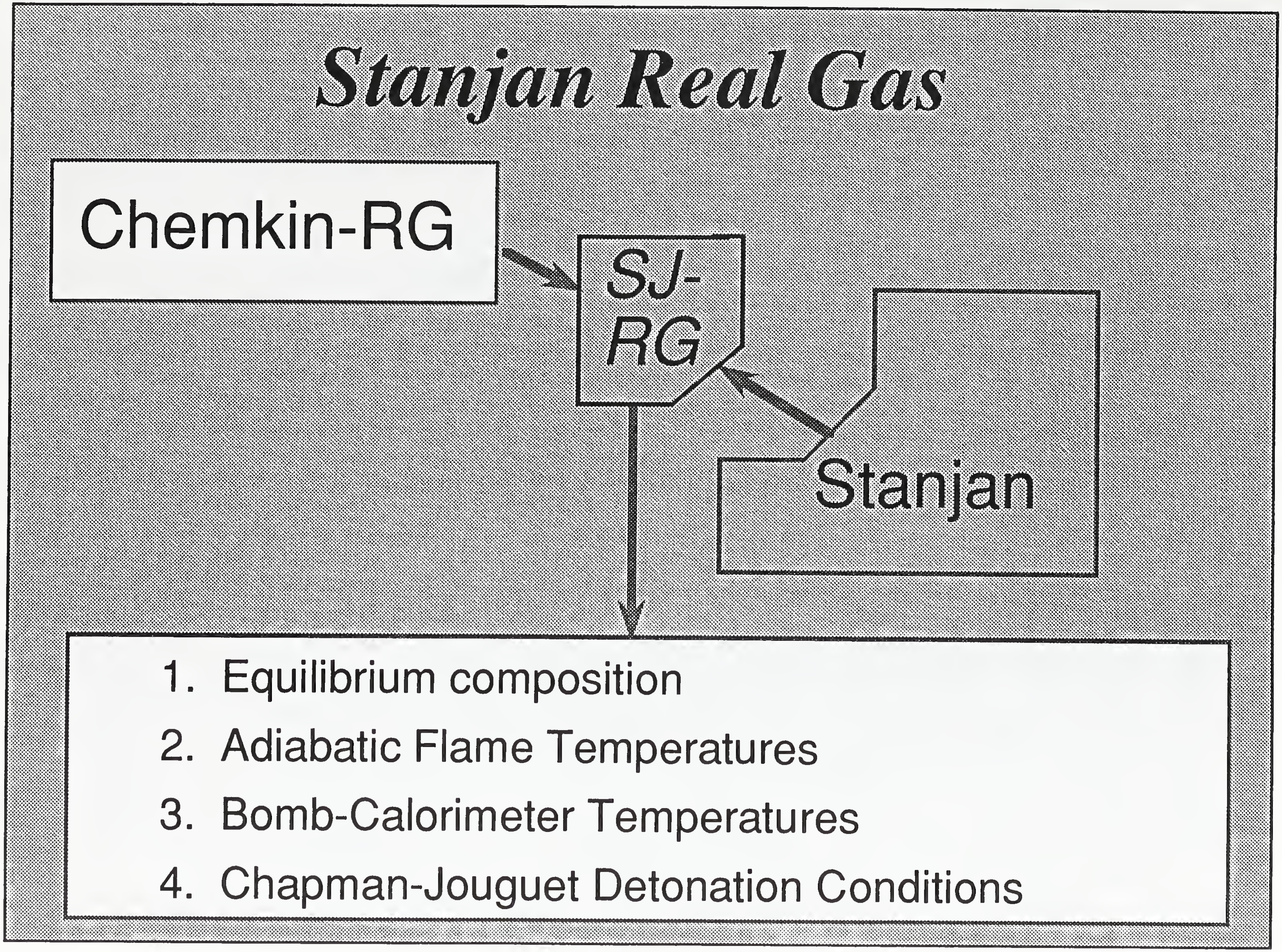


Stanjan Real-Gas

Based on Stanjan (Reynolds, 1986, Stanford Univ.)

Method of Lagrange Multipliers

Modified for real-gas thermodynamics

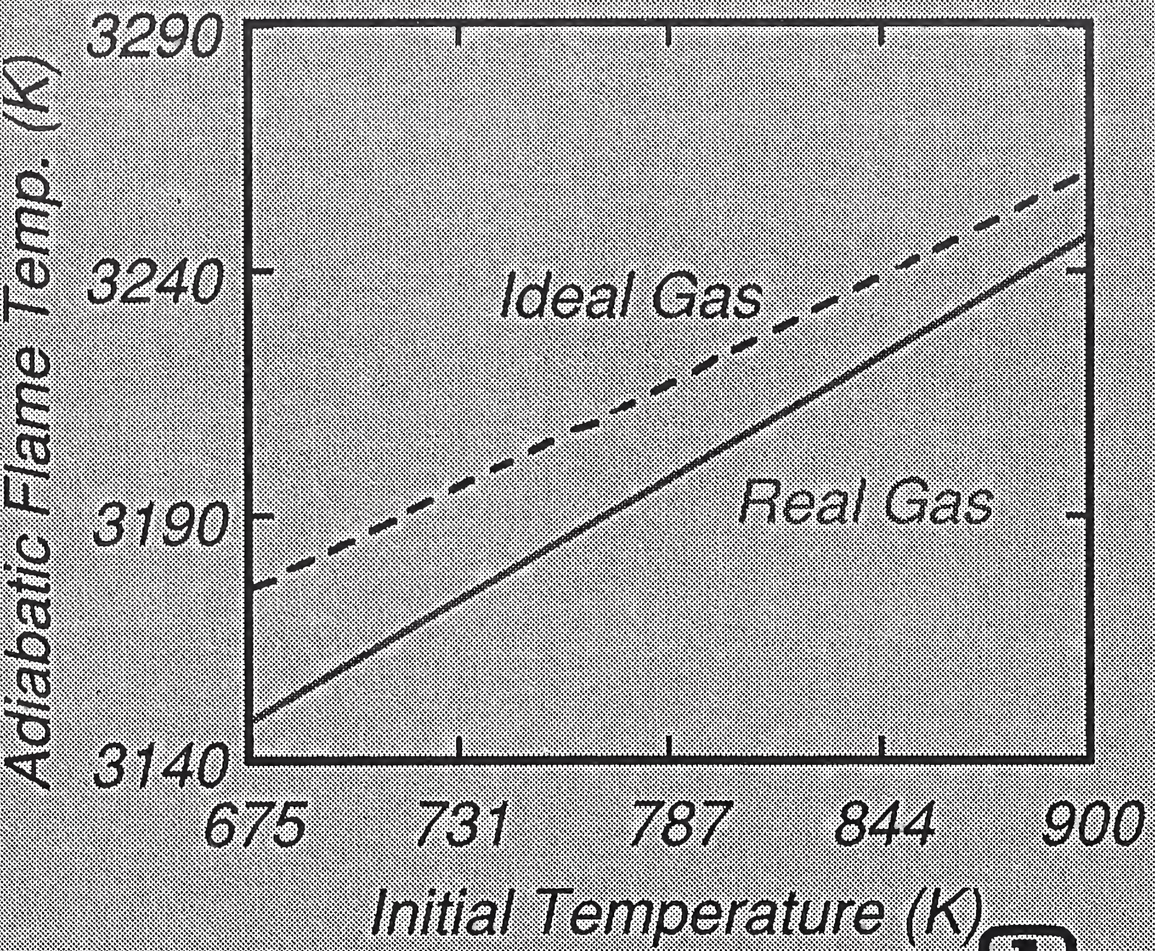

Stanjan Real Gas
Chemkin-RG
SJ-RG
Stanjan
1. Equilibrium composition
2. Adiabatic Flame Temperatures
3. Bomb-Calorimeter Temperatures
4. Chapman-Jouguet Detonation Conditions

Adiabatic Flame Temperature Calculations

30% CH_4 / H_2O
+ O_2

P=285 atm.

Average Temperature
= 3200 K

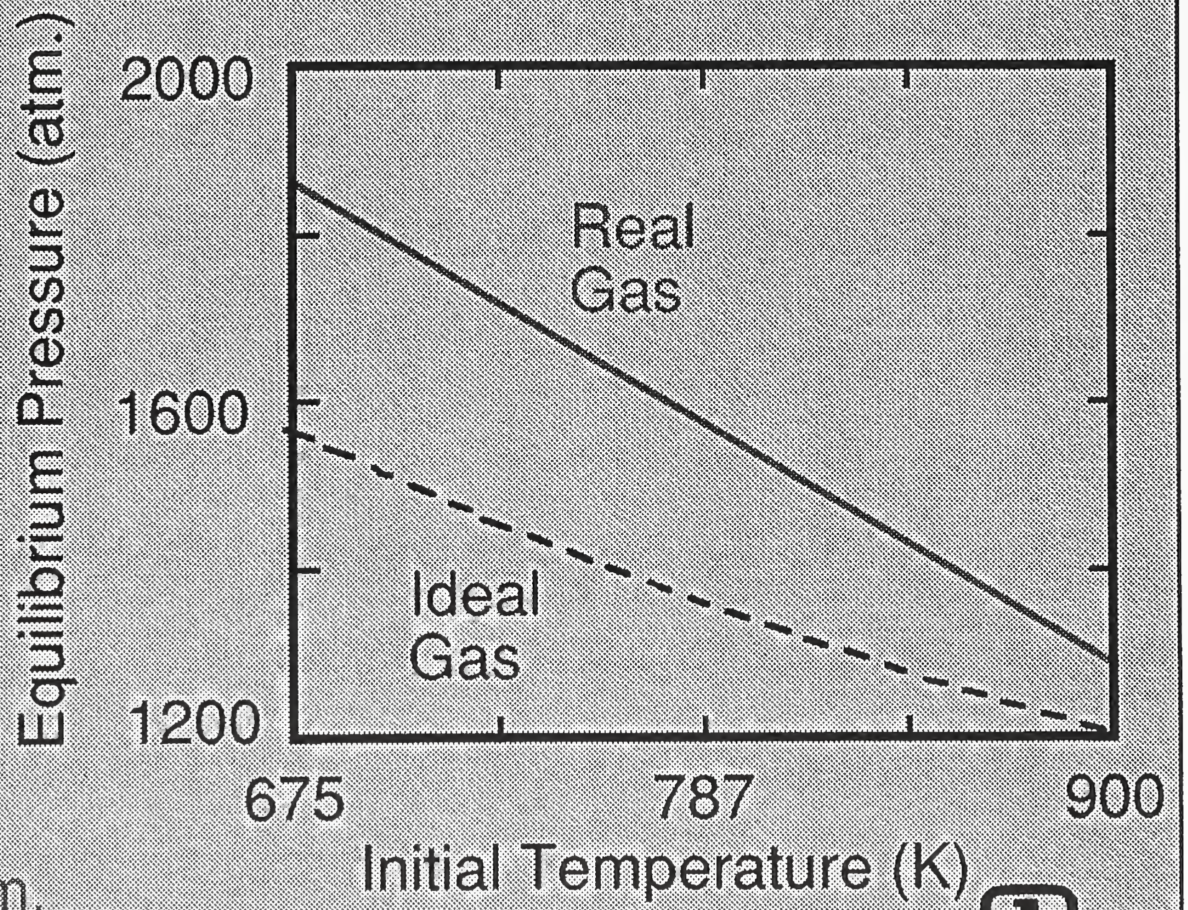


Enthalpy and Pressure Constant

Bomb-Calorimeter Equilibrium Pressures

30% CH_4 / H_2O
+ O_2

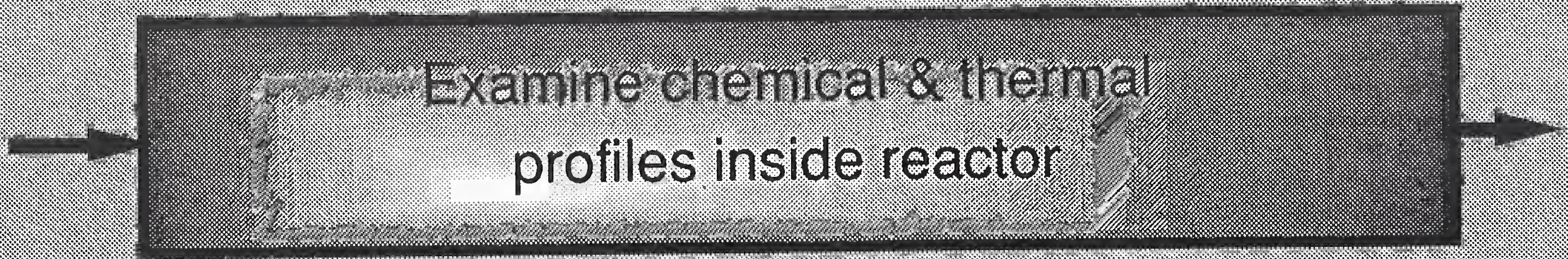
P(initial)
= 285 atm.



Avg. pressure
= 1300 to 1900 atm.

Internal Energy & Volume Constant

Simple Plug Flow Model



x=0.
X=0.

X=x/L

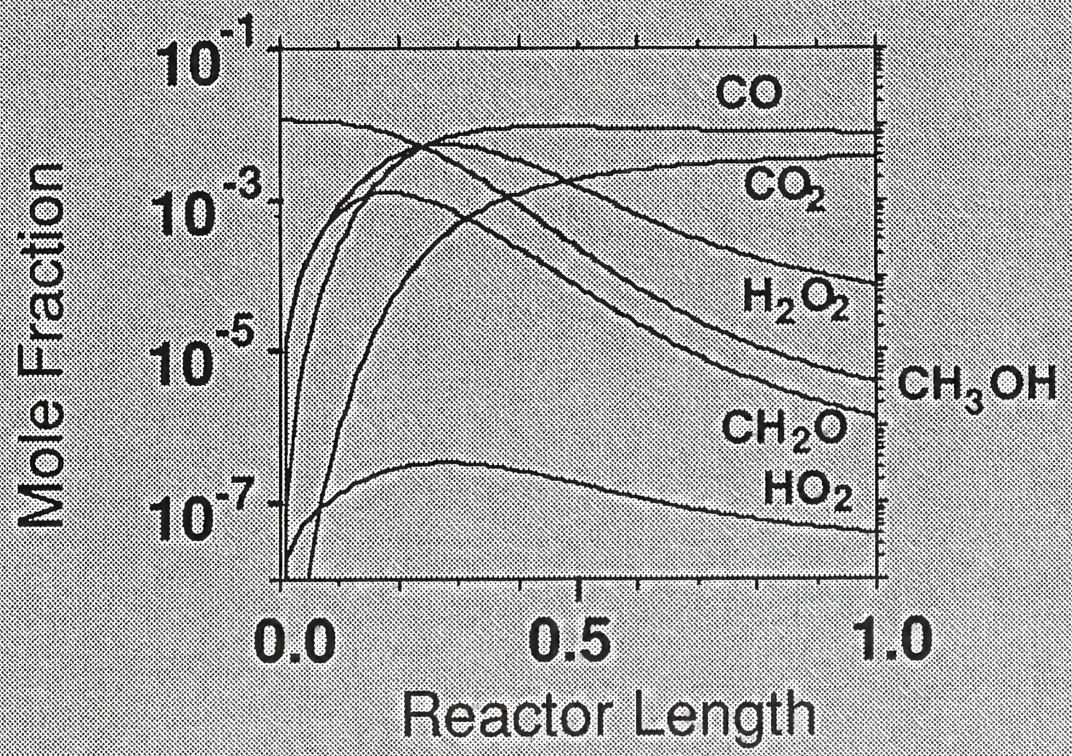
x=L
X=1.0

Species Conservation Eqns.

Energy Conservation Eqn. → Chemkin-RG with P-R EOS

High-pressure reaction mechanism

Calculated Species Profiles



690K, 246 atm

$Z_{99} = 0.57$

$t_{99} = 25.7$ sec

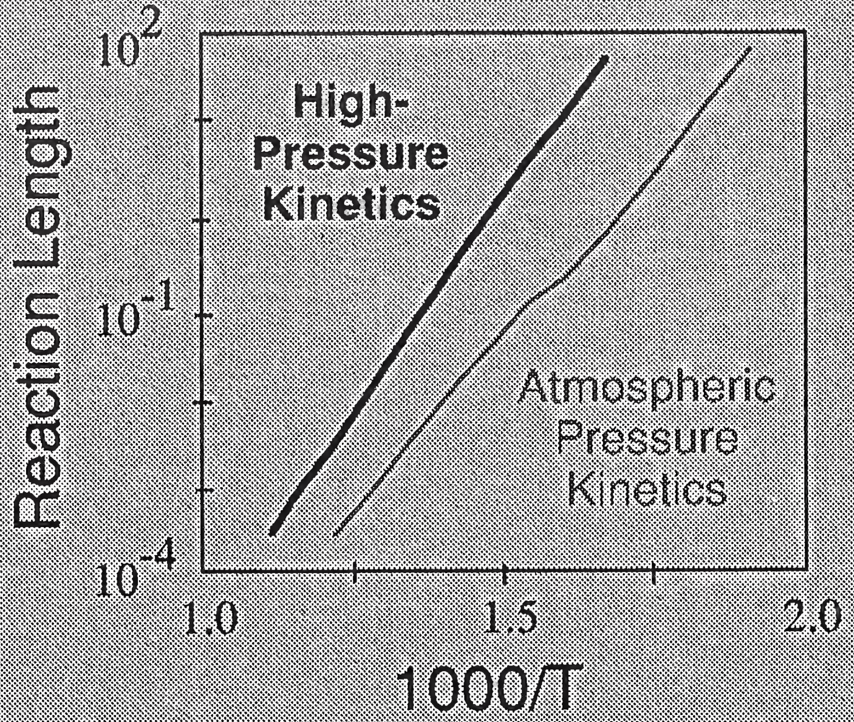
720K, 246 atm

$Z_{99} = 0.15$

$t_{99} = 6.6$ sec

Calculated Reaction Lengths

Atmospheric Pressure
and High Pressure Reaction Rates



Methanol Oxidation at 246 atm.

Future

Model Verification

System Scale-up Models

Design Optimization

Intelligent Process Control

WORKSHOP ON FEDERAL PROGRAMS
INVOLVING SUPERCRITICAL WATER OXIDATION
July 6-7, 1992 at NIST

THERMOPHYSICAL PROPERTIES

OF SUPERCRITICAL MULTICOMPONENT AQUEOUS SYSTEMS

J.M.H. Levelt Sengers
Thermophysics Division, NIST, Gaithersburg

Part I

(Part II, by Dan Friend, on interactive computing, follows next)

QUESTIONS WE ARE BEING ASKED

***Phase Boundaries**

Under what conditions does a solid salt separate out?

Under what conditions does a brine separate out?

Does the vapor phase contain salt?

What are the solubilities of gases such as CO_2, O_2, etc., in water at high temperatures and pressures?

***Thermophysical Properties for Reactor Design**

Enthalpy, density, heat capacity

Viscosity, thermal diffusivity

***Chemical Reactions in Highly Nonideal Mixtures**

Nonionic components

Ionic components

ATTACHMENTS
IAPWS releases on properties of steam
NIST SRD data base information

FACTS OF LIFE

***Water is a Unique Fluid**

Very wide coexistence curve

Very high T_c

Large variation of dielectric constant

***Phase Diagrams of Aqueous Systems are Complex and Varied**

$NaCl - H_2O$

$O_2 - H_2O$

$CO_2 - H_2O$

Alkanes - H_2O

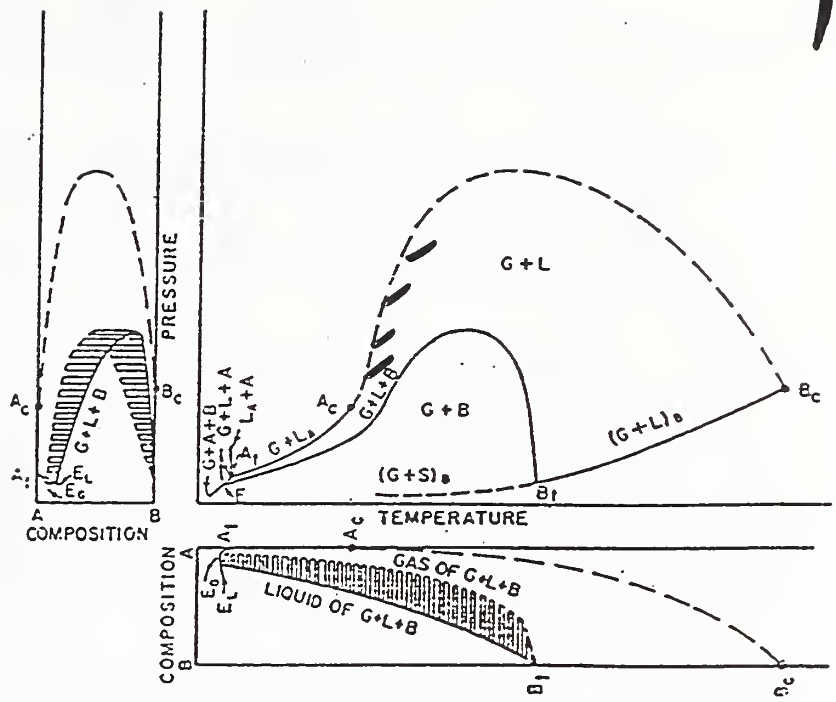
***Methods Developed for Liquid Mixtures Fail in this Regime**

Large anomalies in excess properties

Partial molar properties of solute, and related standard states, are highly anomalous.

COMPLEX PHASE DIAGRAMS OF AQUEOUS BINARY MIXTURES

NaCl-H_2O



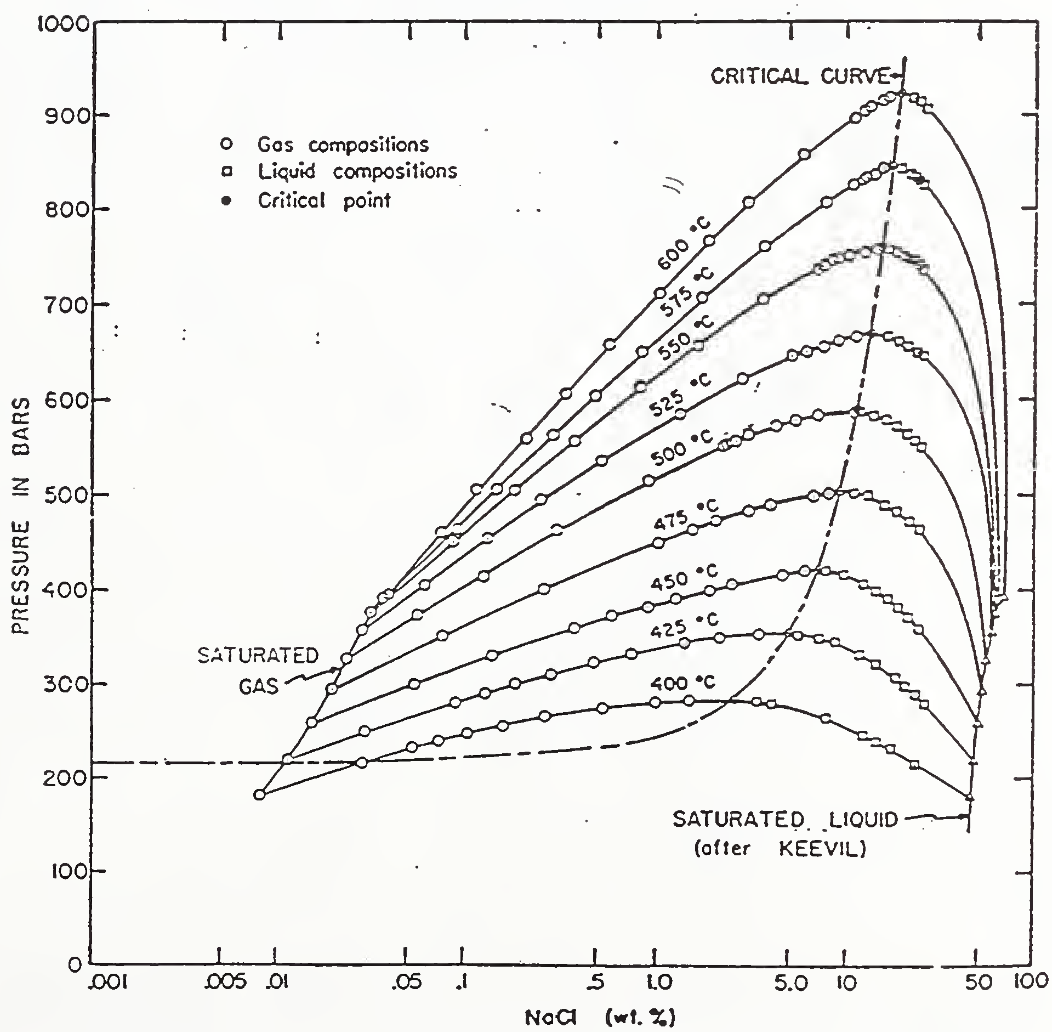
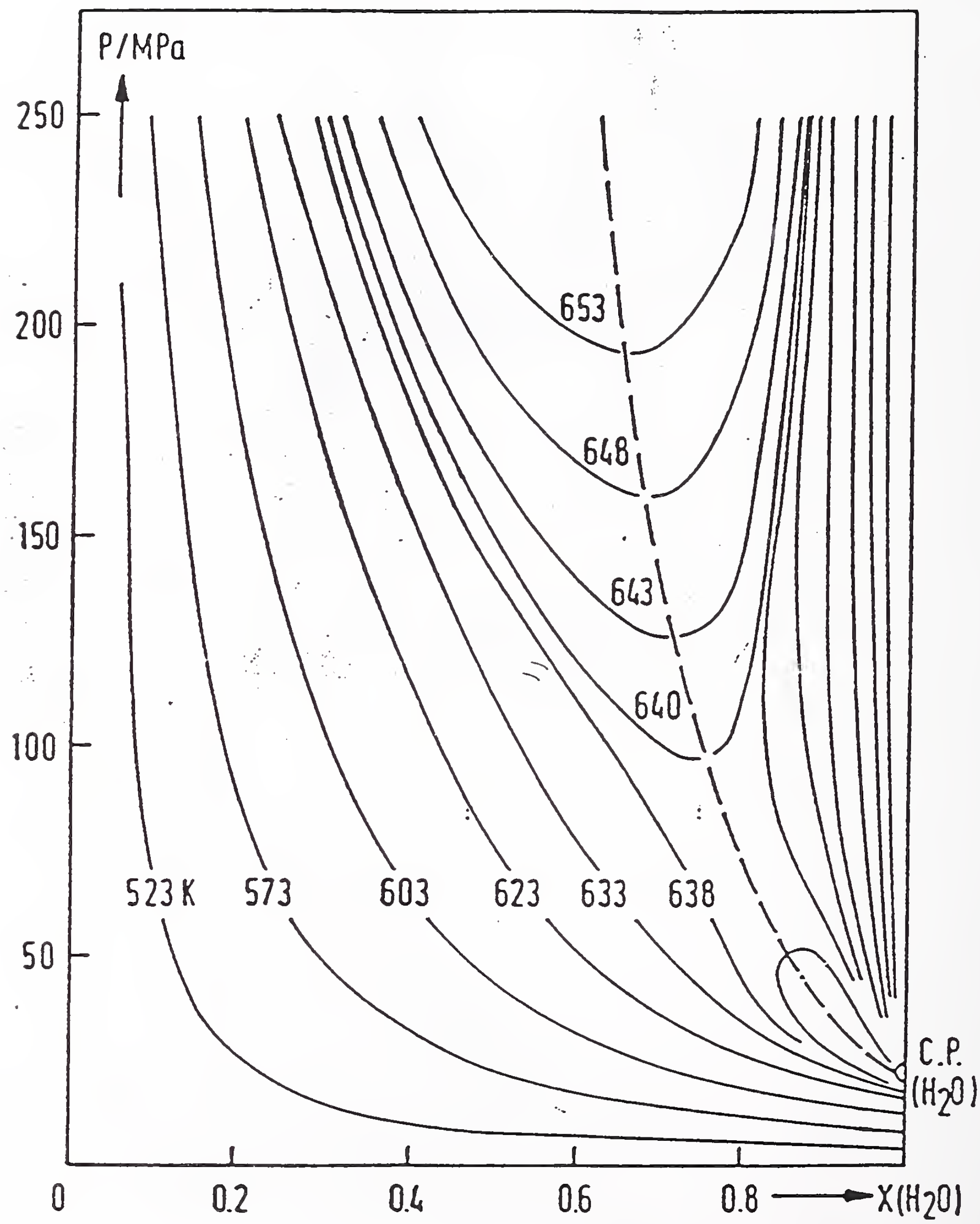


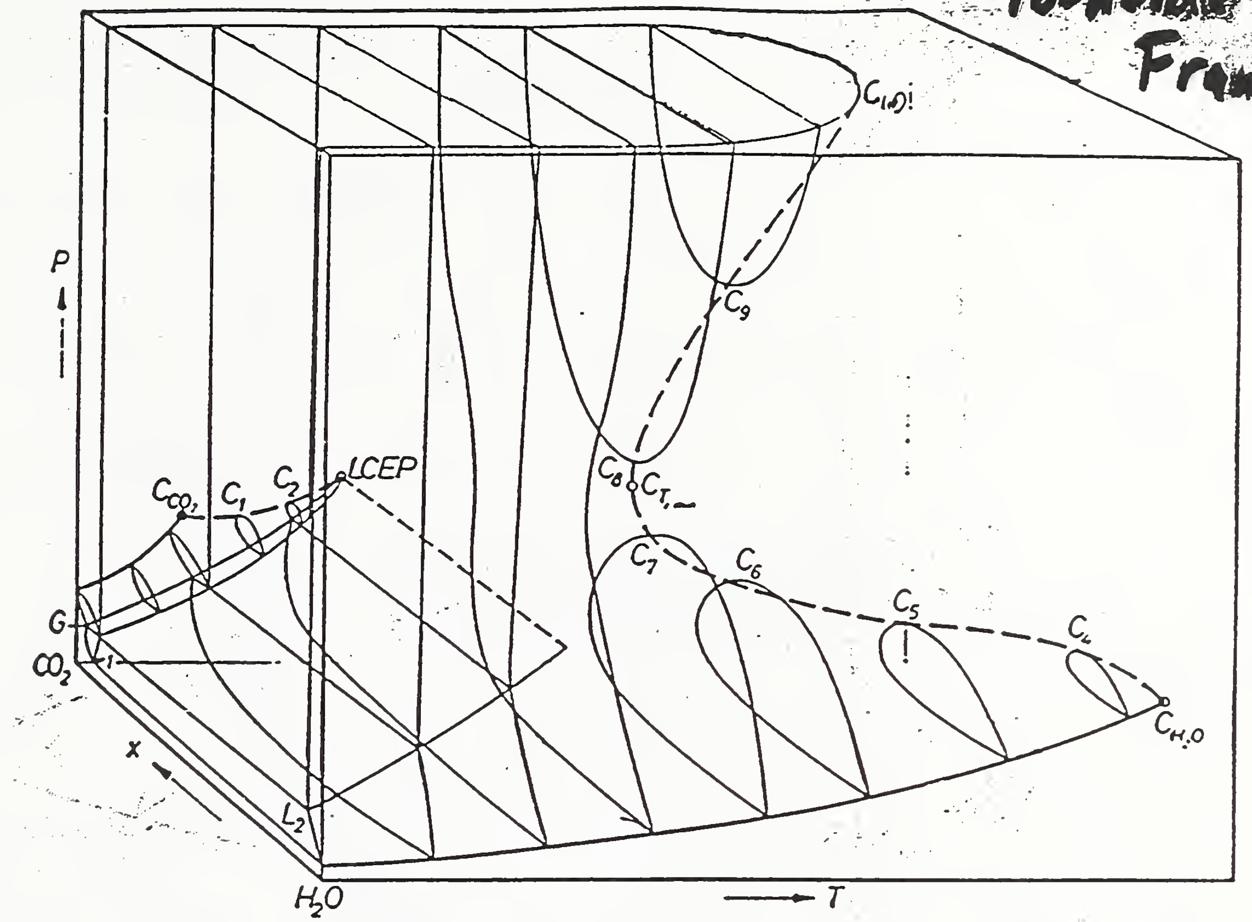
Fig. 13. Isotherms, 400°C-600°C, showing compositions of coexisting gases and liquids.

$O_2 - H_2O$

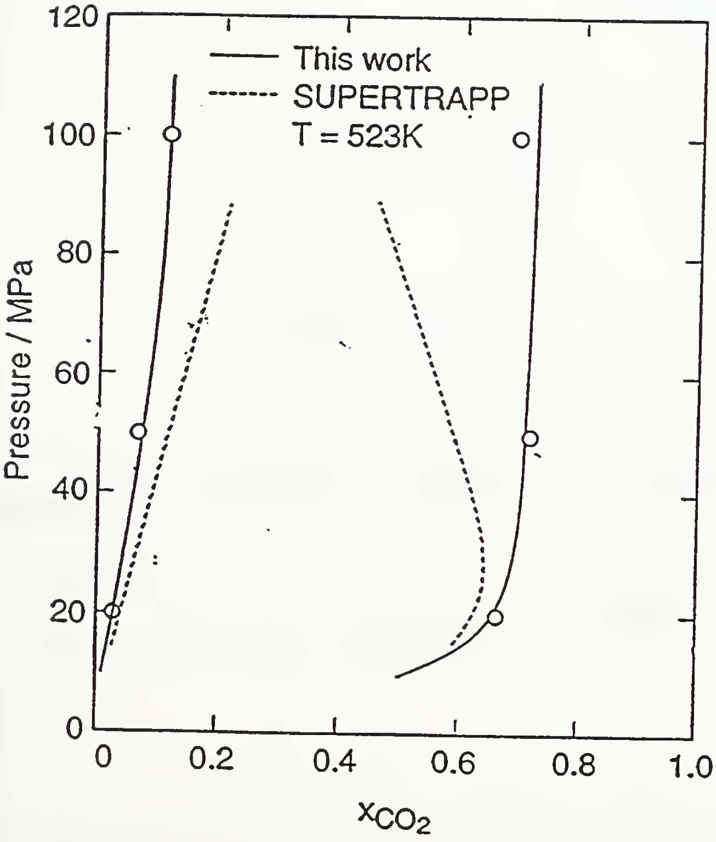


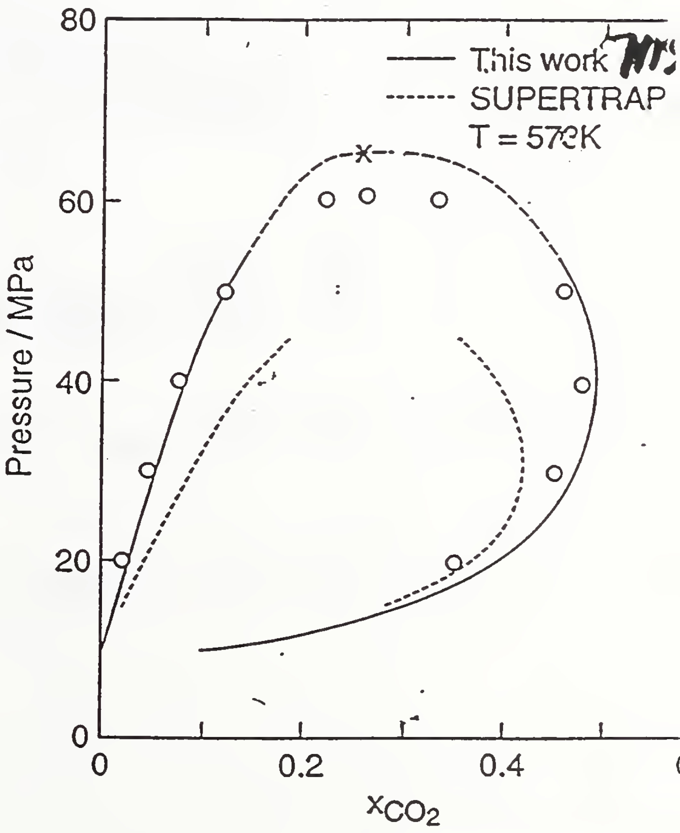
P/MPa
250
200
150
100
50
0
0.2
0.4
0.6
0.8
X(H2O)
653
648
643
640
523 K
573
603
623
633
638
C.P.
(H2O)

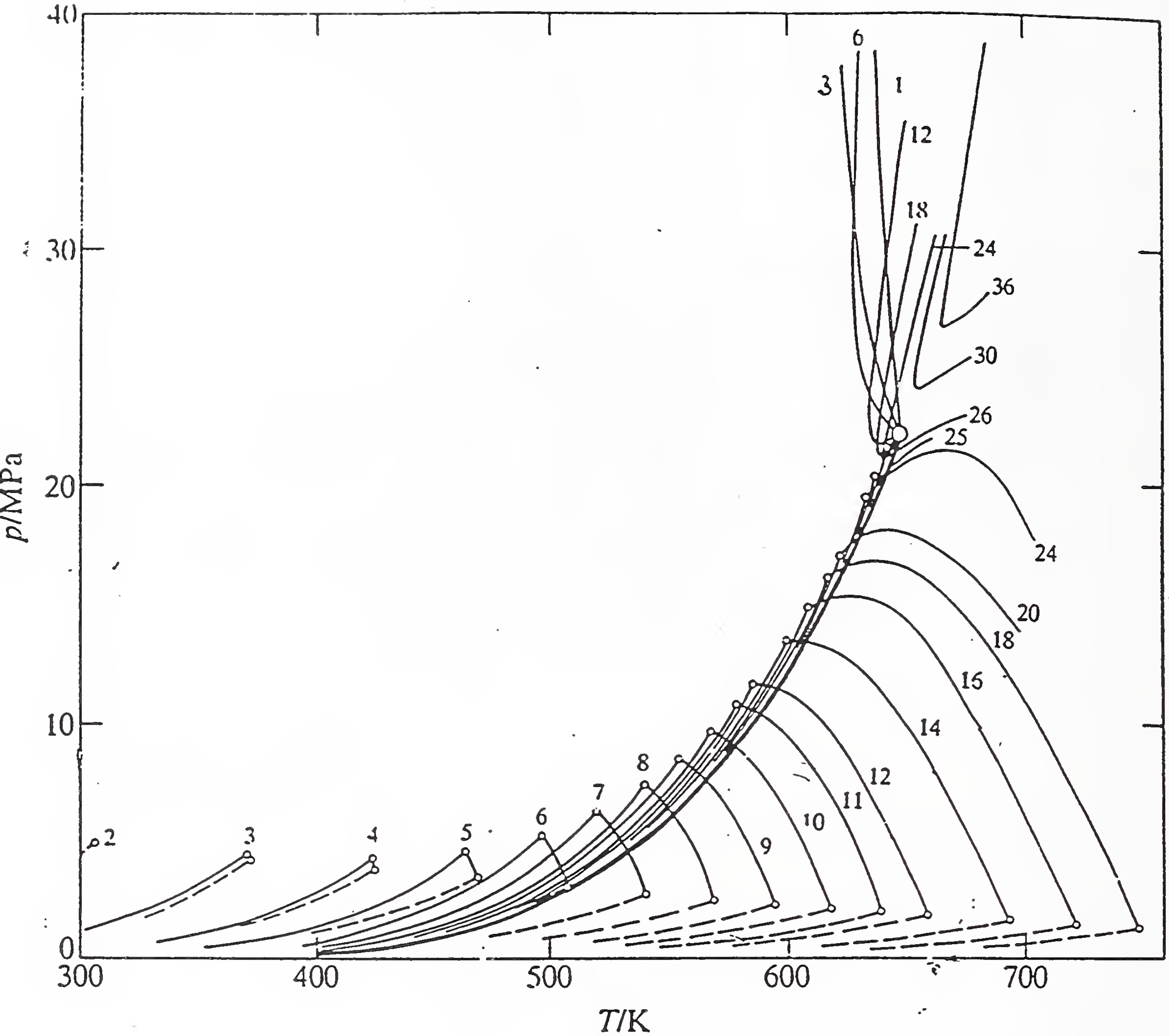
Tödheide + Franck



CO_2 - H_2O







n-alkanes in water

— critical lines and three-phase lines

---- pure-component vapor pressure

ANOMALOUS EXCESS ENTHALPIES

AND APPARENT MOLAR VOLUMES

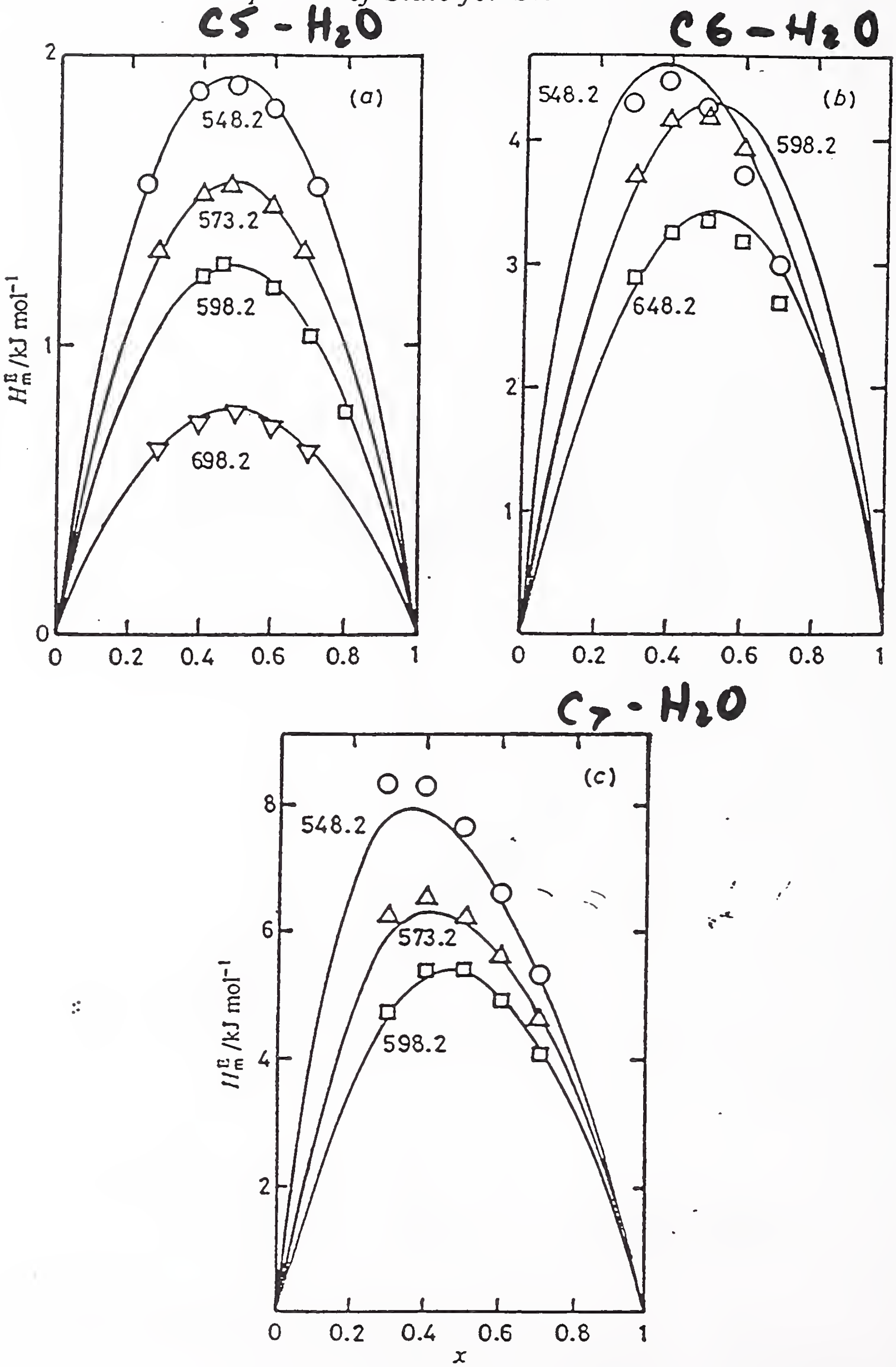
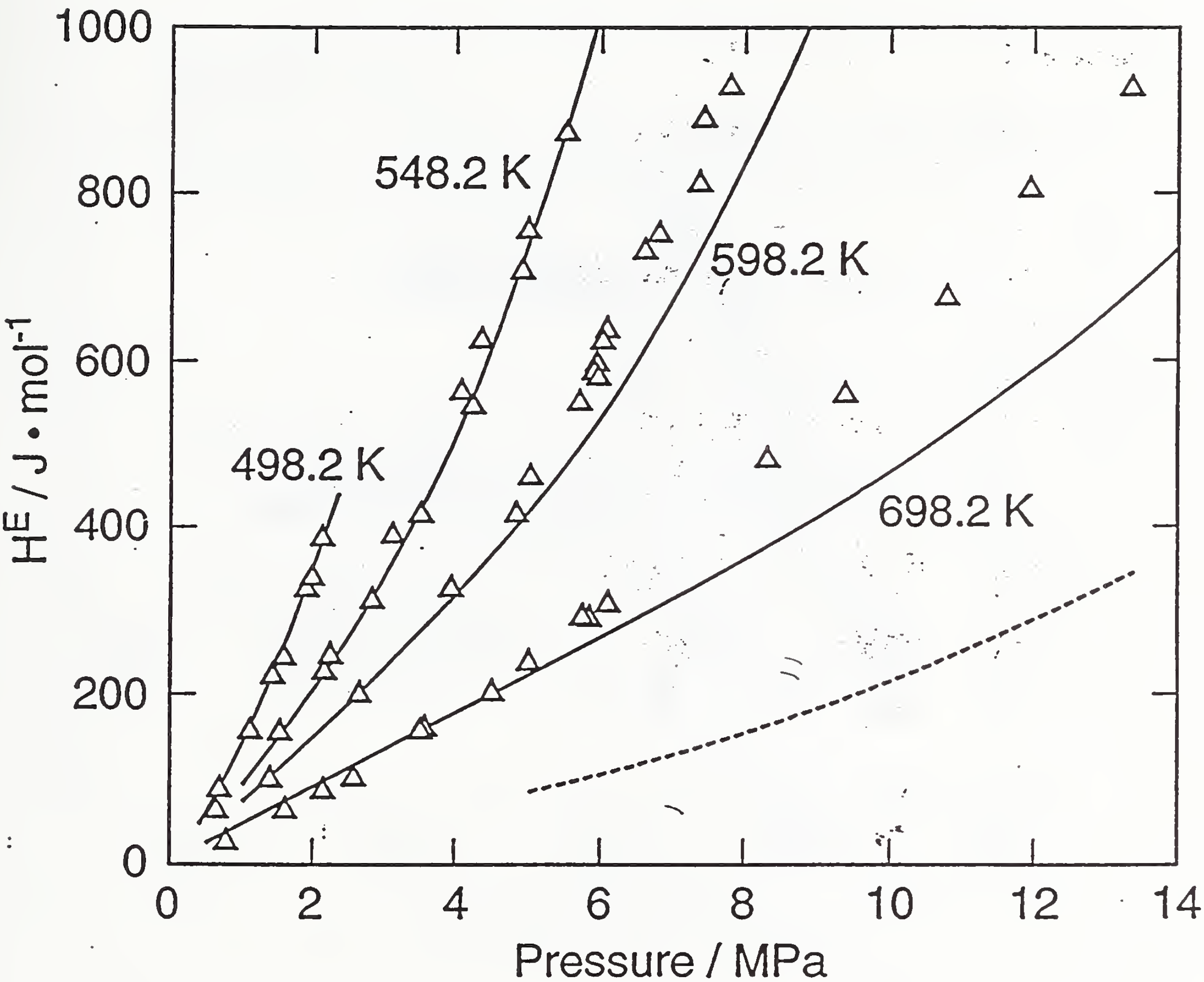


Fig. 3. Comparison of calculated and experimental excess molar enthalpies H_m^E of [$xH_2O+(1-x)C_nH_{2n+2}$] for $n = 5$–7. Solid curves were calculated from eqn (27) as described in the text. (*a*) [$xH_2O+(1-x)C_5H_{12}$],[18] all measurements at 4.50 MPa, (*b*) [$xH_2O+(1-x)C_6H_{14}$],[25] measurements at 548.2 K and 4.93 MPa, 598.2 K and 9.41 MPa, 648.2 K and 11.48 MPa, (*c*) [$xH_2O+(1-x)C_7H_{16}$],[25] measurements at 548.2 K and 4.58 MPa, 573.2 K and 6.00 MPa, 598.2 K and 7.68 MPa.

P 5-11 MPa

Wormald



$CO_2 - H_2O$

0.5 - 0.5 mol

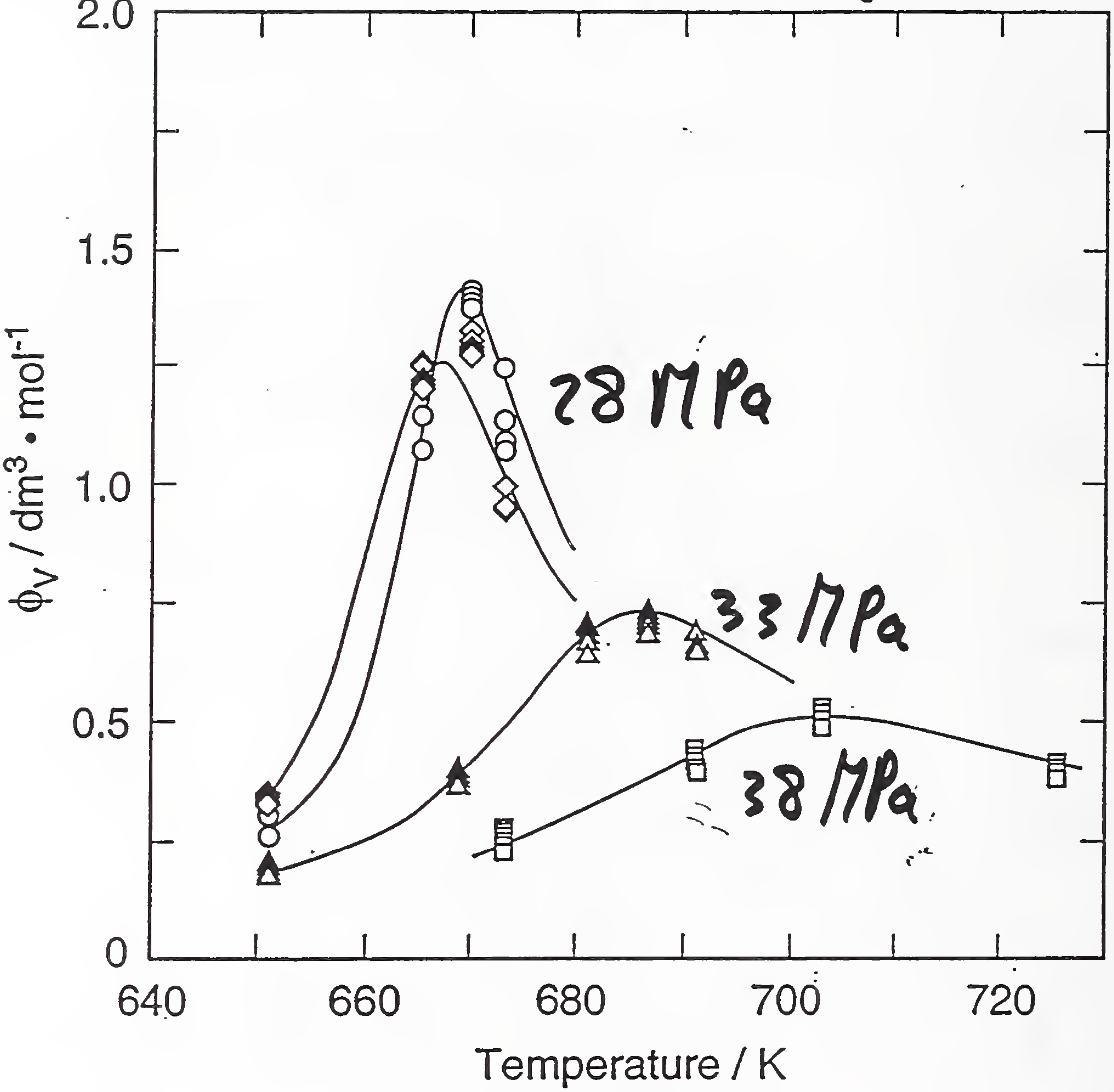
Δ Wormald

—— Model (NIST)

$CO_2 - H_2O$

◇ △ □ ○ Crovetto + Wood

——— model (NIST)



apparent molar volume near ∞ dilution for CO_2

3 supercritical isobars

WHAT TO DO?

*Use NBS/NRC Steam Tables, Hemisphere Publishers 1984, as a reference fluid

*Develop a Helmholtz free energy for multicomponent aqueous mixtures including phase boundaries, along the lines of the interactive programs to be discussed by Dan Friend.

THIS MUST ALSO BE DONE

*Predictive method for the viscosity of multicomponent aqueous systems

Incorporate nonionic chemical reactions

Extend to ionic components

REFERENCES

THERMOPHYSICAL PROPERTIES OF WATER AND STEAM

L. Haar, J. S. Gallagher and G. S. Kell, NBS/NRC Steam Tables, Hemisphere Publishing Company, 1984.
Programs available on disk from the Standard Reference Data Program at NIST, ordering information included here.

International Association for the Properties of Water and Steam;ordering information on property formulations ("releases") included here.

Properties include: density, dielectric constant, enthalpy, entropy, heat capacities, transport properties, ion product, electrical conductivity.

PHASE DIAGRAMS SHOWN HERE

NaCl - H_2O

S. Sourirajan and G.C. Kennedy, Am. J. Science 260, 115 (1962).

O_2 - H_2O

M.L. Japas and E.U. Franck, Ber. Bunsenges. Phys. Chem.89, 1268, (1985).

CO_2 - H_2O

K. Toedheide and E.U. Franck, Zeitsch. Physik. Chem. NF 37, 387 (1963). (data).

J.S. Gallagher, R. Crovetto and J.M.H. Levelt Sengers, submitted to J. Phys. Chem. Ref. Data. (model).

Alkanes - CO_2

E. Brunner, J. Chem. Thermodynamics 22, 335 (1990).

EXCESS ENTHALPIES

Alkanes - H_2O

C.J. Wormald and N.M. Lancaster, J. Chem. Soc. Faraday Trans. 85, 1315 (1989)

CO_2- H_2O

C.J. Wormald, N.M. Lancaster and A.J. Sellars, J. Chem. Thermodynamics 18, 279 (1987).

APPARENT MOLAR VOLUMES

R. Crovetto, R.H. Wood and V. Majer, J. Chem. Thermodynamics 23, 1079 (1991)

J.S. Gallagher, R. Crovetto and J.M.H. Levelt Sengers, submitted to J. Phys. Chem. Ref. Data.(model).

FAILURE OF STANDARD METHODS

J.M.H. Levelt Sengers, C.M. Everhart, G. Morrison and K.S. Pitzer, Chem. Eng. Comm. 47, 315 (1986).

J.M.H. Levelt Sengers, A.H. Harvey, R. Crovetto and J.S. Gallagher, accepted, Fluid Phase Equilibria.

IAPWS NEWS

International Association for the Properties of Water and Steam

President: J.M.H. Levelt Sengers **Vice President:** J.R. Cooper
Executive Secretary: R.B. Dooley

May 1992

President's Remarks

I would like to draw attention to an issue that has been repeatedly stressed by Professor Franck, namely the possibility of destroying hazardous waste and toxic products in oxygenated supercritical steam.

In the United States there is currently much interest in exploring this issue. Several universities and many Government agencies are doing research on the topic, while a number of companies are gearing up to build reactors. The December issue of Chemical and Engineering News is devoted to this topic, and IAPWS member Prof. Franck is one of the five authors of the feature article.

In my own organization, NIST, a team headed by Dr. Rosasco is building a prototype reactor with windows permitting spectroscopic studies. In my consulting activities with this team, I am becoming very aware of the similarities between this work and the principal concerns of IAPWS's working groups on Physical Chemistry of Aqueous Systems and on Chemistry in Power Cycles. The proposed reactors operate in a range comparable to that of supercritical power cycles, namely at about 250 bar and 400-600°C. Contrary to power plants, the water in the reactor is quite contaminated, but the compounds present are similar (oxygen, carbon dioxide, organics, salts) and the materials problems will overlap at least in part those encountered in the power industry. On the other hand, the research that is currently initiated in the field of supercritical aqueous hazardous waste destruction could indirectly benefit the power industry. Thus, for instance, the NIST reactor under construction will permit in-situ Raman studies of metal surfaces exposed to the supercritical water stream. Also, strenuous efforts are underway in many groups in the USA to model the chemical reactions taking place in the presence of excess water in a very nonideal state.

It is my hope that no opportunity will be missed for mutual fertilization between the field of power plant chemistry and this emerging technology. More may be needed than individual efforts of two or three IAPWS members happening to be active in both fields. I encourage the chairmen and members of PCAS and PCC to do some creative thinking about possible roles for IAPWS related to this new technology.

Russia Hosts 1992 IAPWS Meeting

Professor Alexandrov and his Russian National Committee are organizing the 1992 meetings for the executive committee and the working groups in St. Petersburg from Sunday, September 6 - Saturday, September 12, 1992. The program will start on Monday, September 7 with the Plenary Session at 9:00 AM. There will be a Symposium on Tuesday, September 8 covering the wide range of IAPWS activities and including presentations from Russian scientists, who do not usually attend the IAPWS meetings, and a number of IAPWS international members. The four working groups will meet throughout the week and the executive committee will meet all day Friday. Two visits are planned. The first on Wednesday will be to the Central Turbine and Boiler Institute (TsKTI) in St. Petersburg; this will be regarded as optional so that some working group members could also have a relaxed working session instead. The second visit, on Saturday, September 12, will be to the St. Petersburg Nuclear Plant which is about a two hour drive from the city; lunch will be provided.

All the meetings will be at the St. Petersburg Mining Institute. The Executive Secretary had the opportunity to visit with Professor N. Proskuryakov, the Rector, during a visit to St. Petersburg in March. The Institute is ideally situated on the Neva River and has all the required facilities to hold the IAPWS annual meetings. The Institute has its own Hotel, which is located about 2km away and transportation will be provided for the delegates. The rates are $95 for a single room or $130 for a double with all meals being provided. Alternatively, accommodation is available at the Pribaltiiskaya Hotel, ($160 single, no meals) which is located very close to the Institute's own hotel. Professor Proskuryakov also indicated that there will be some cultural activities included in the events.

We hope to see you in the magnificent city of St. Petersburg in September.

For further information on IAPWS or to request guidelines and releases, contact:
Dr. R.B. Dooley, Executive Secretary, EPRI, 3412 Hillview Ave., Palo Alto, California 94304, USA
Telephone: 415-855-2458 Fax: 415-855-8759 Telex: 82977 EPRI UF

Current IAPWS Guidelines and Releases

- "Release on the Refractive Index of Ordinary Water and Steam as a Function of Wavelength, Temperature and Pressure". (September 1991).
- "Electrolytic Conductivity (Specific Conductance) of Liquid and Dense Supercritical Water from 0°C to 800°C and Pressures up to 1000 MPa". (May 1990).
- "Solubility of Sodium Sulfate in Aqueous Mixtures of Sodium Chloride and Sulfuric Acid from Water to Concentrated Solutions, from 250°C to 350°C". (May 1990).
- "Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance". (September 1989).
- "Surface Tension of Heavy Water Substances (D_2O)". (September 1985).
- "IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance". (November 1985).
- "IAPS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substances". (November 1985).
- "IAPS Formulation 1985 for the Viscosity of Ordinary Water Substances". (November 1985).
- "IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance". (December 1984).
- "The IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use". (December 1984).
- "Viscosity and Thermal Conductivity of Heavy Water Substance". (February 1984).
- "1983 IAPS Statement, Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at their Respective Critical Points". (1983).
- "Ion Product of Water Substance". (May 1980).
- "Static Dielectric Constant of Water Substance". (1977).
- "Surface Tension of Water Substance". (1976).
- "The 1967 IFC Formulation for Industrial Use".
- IAPS Supplementary Release: "Saturation Properties of Ordinary Water Substance". (September 1986. Rev. November 1986)

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
STANDARD REFERENCE DATABASES

PRICE SCHEDULE

Databases of physical and chemical properties prepared by NIST's Standard Reference Data Program are available in magnetic tape, diskette, and CD ROM format under a license agreement. There are three types of licenses, applicable to an *Individual User*, to a *Distributor*, and to a *Subscription Search Service*.

#	NIST STANDARD REFERENCE DATABASE	FEE
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2.	NIST Chemical Thermodynamics (NBS Tech Note 270)	1,000
3.	NIST Crystal Data Identification File[1]	2,000
9.	NIST Thermophysical Properties of Hydrocarbon Mixtures	490
9.	NIST Electron and Positron Stopping Powers of Materials	350
9.	NIST X-Ray and Gamma-Ray Attenuation Coefficients and Cross Sections	400
9.	NIST Activity and Osmotic Coefficients of Aqueous Electrolyte Solutions	200
10.	NIST Thermophysical Properties of Water	300
18.	DIPPR Data Compilation of Pure Compound Properties[2]: Version 7.0	4,000
11A.	Student DIPPR	75
18.	NIST Thermophysical Properties of Fluids	490
13.	NIST JANAF Thermochemical Tables	1,200
13.	NIST Mixture Property Program[2]	400
18.	NIST/Sandia/ICDD Electron Diffraction[1]	3,000
16.	NIST Corrosion Performance[3]	240
18.	NIST Chemical Kinetics: PC Version 4.0	390
18.	NIST Estimation of the Thermodynamic Properties for Organic Compounds at 298.15 K	215
19A&B.	NIST Positive and Negative Ion Energetics	130
20.	NIST X-Ray Photoelectron Spectroscopy	495
21.	NIST/CARB Biological Macromolecule Crystallization Version 2.0	390
22.	Tribomaterials I[4]	350
23.	NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures: Version 3.0	390
24.	NIST Atomic Transition Probabilities Data File	215
25.	NIST Structures and Properties Database and Estimation Program	240

[1] Available from the JCPDS-International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081. Phone (215) 328-9400.
[2] Discount available to members of DIPPR. Discount available to GPA members for DDMIX.
[3] Available from NACE, P.O. Box 218340, Houston, TX 77218. Phone (713) 492-0535.
[4] Available from ACTIS Inc., 1118 Highgate Rd., Wilmington, DE 19808. Phone (302) 998-8240.

#	NIST STANDARD REFERENCE DATABASE	FEE
26.	NIST Vibrational Electronic Energy Levels of Small Polyatomic Transient Molecules Version 2.0	390
27.	NIST Molten Salts Version 2.0	240
30.	NIST Structural Ceramics	495
35.	NIST/EPA Gas Phase Infrared	415
36.	NIST/NIH Desktop Spectrum Analyzer Program and X-Ray Database	790
38.	NIST Spectroscopic Properties of Atoms and Atomic Ions	190

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Please contact:

Standard Reference Data
National Institute of Standards and Technology
221/A320
Gaithersburg, MD 20899
Telephone: (301) 975-2208
FAX: (301) 926-0416

THERMOPHSYICAL PROPERTIES OF FLUIDS: RESEARCH AT NIST

Thermophysics Division:

Dr. R. F. Kayser, Chief

- Gaithersburg, MD
- Boulder, CO

- Internal, OA, commercial sponsorship

- Standard reference data

- Liaison with industry for fluid properties

STANDARD REFERENCE DATA PROGRAM

Dr. M. W. Chase, Chief
Dr. J. Rumble, Jr., Program Manager

- Fluid Mixtures Data Center
  D.G. Friend

- Properties of Polar Fluids Project
  R.F. Kayser

COMPUTERIZED DATABASES FROM THE THERMOPHYSICS DIVISION

- NIST Thermophysical Properties of Hydrocarbon Mixtures Database (SUPERTRAPP, SRD 4)

- NIST Mixture Properties Database (DDMIX, SRD 14)

- NIST Thermophysical Properties of Pure Fluids Database (MIPROPS, SRD 12)

- NIST Thermodynamic Properties of Refrigerant and Refrigerant Mixtures Database (REFPROP, SRD 23)

- NIST Thermophysical Properties of Water Database (NBS/NRC Steam Tables, SRD 10)

GENESIS OF DDMIX

- NIST (NBS) Supercritical Fluid Properties Consortium

  - 14 companies primarily interested in supercritical CO_2 processes

  - 4 year project
    Experimental measurements
    Theory
    Modeling
    Computer package

  - Distribution by SRD

SUPERTRAPP
(SRD 4)

Dr. Marcia L. Huber

- Extended corresponding states (ECS)
- Transport property corresponding states
- Propane reference fluid
- 116 Fluids in database
  alkanes, alkenes, aromatics, cycloalkanes, common impurities
- Excess and residual properties easily calculated
- Ability to add new fluids
- User friendly

Thermophysical properties calculated by SUPERTRAPP

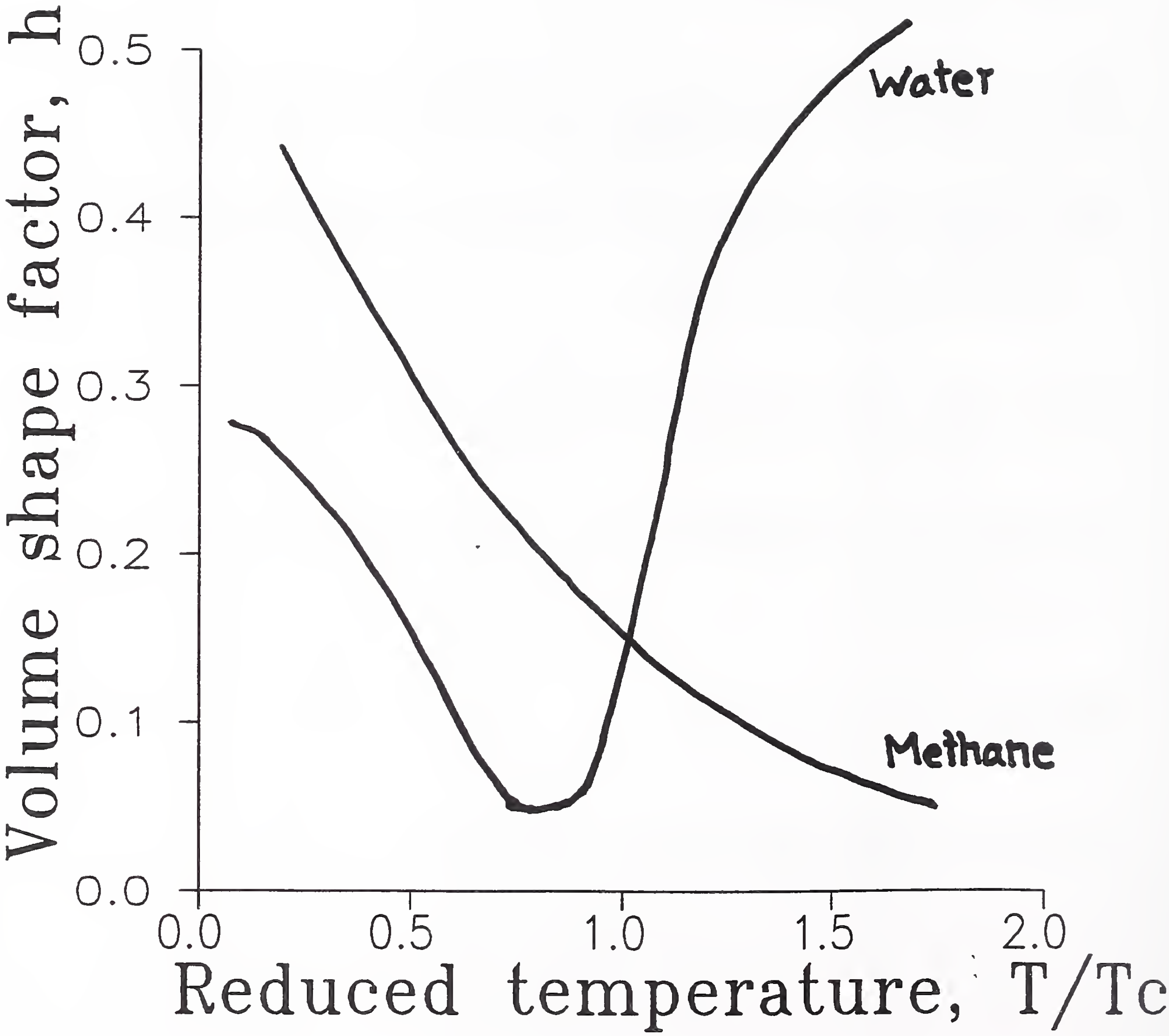
- phase boundaries
- density
- C_p
- Joule-Thomson coefficient
- enthalpy
- C_p/C_v
- viscosity
- entropy
- sound speed
- thermal conductivity
- compressibility factor
- molecular mass

Component database in SUPERTRAPP

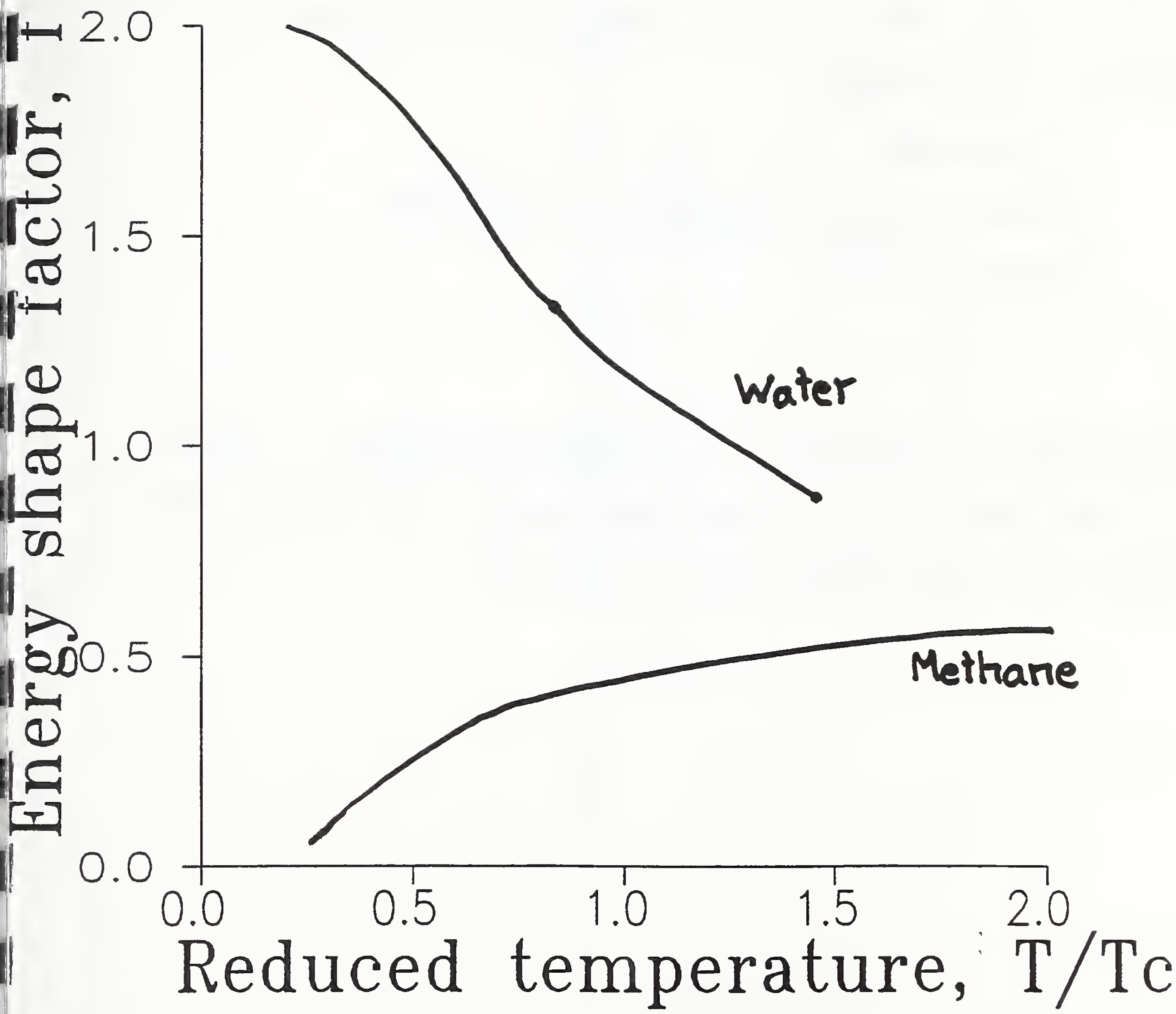
methane
ethane
propane
n-butane
isobutane
n-pentane
isopentane
neopentane
2,2-dimethylbutane
2,3-dimenthylbutane
3-methylpentane
2-methylpentane
n-hexane
2,2,3-trimethylbutane
3,3-dimethylpentane
2,4-dimethylpentane
2,3-dimethylpentane
2,2-dimethylpentane
3-ethylpentane
3-methylhexane
2-methylhexane
n-heptane
2,2,3,3-tetramethylbutane
2,3,4-trimethylpentane
2,3,3-trimethylpentane
2,2,4-trimethylpentane
2,2,3-trimethylpentane
3-methyl-3-ethylpentane
2-methyl-3-ethylpentane
3,4-dimethylhexane
3,3-dimethylhexane
2,5-dimethylhexane
2,4-dimethylhexane
2,3-dimethylhexane
2,2-dimethylhexane
3-ethylhexane
4-methylheptane
3-methylheptane
2-methylheptane
n-octane
2,3,3,4-tetramethylpentane
2,2,4,4-tetramethylpentane
2,2,3,4-tetramethylpentane
2,2,3,3-tetramethylpentane
2,2,5-trimethylhexane
2,2-dimethylheptane
2-methyloctane
n-nonane
2,2,5,5-tetramethylhexane
2,2,3,3-tetramethylhexane
3,3,5-trimethylheptane
n-decane
n-undecane
n-dodecane
n-tridecane
n-tetradecane
n-pentadecane
n-hexadecane
n-heptadecane
n-octadecane
n-nonadecane
n-eicosane
n-heneicosane
n-docosane
n-tricosane
n-tetracosane
ethylene
propylene
2-methylpropene
cis-2-butene
trans-2-butene
1-butene
2-methyl-2-butene
2-methyl-1-butene
3-methyl-1-butene
cis-2-pentene
trans-2-pentene
1-pentene
1-hexene
1-heptene
1-octene
1-nonene
1-decene
propadiene
1,3-butadiene
1,2-butadiene
cyclopropane
cyclopentane
methylcyclopentane
ethylcyclopentane
cyclohexane
methylcyclohexane
ethylcyclohexane
benzene
toluene
ethylbenzene
ortho-xylene
meta-xylene
para-xylene
propylbenzene
isopropylbenzene
butylbenzene
isobutylbenzene
t-butylbenzene
naphthalene
1-methylnapthalene
2-methylnapthalene
biphenyl
hydrogen
nitrogen
oxygen
water
carbon monoxide
carbon dioxide
sulfur dioxide
hydrogen sulfide

AQUEOUS SYSTEMS IN ECS MODELS

- Need Haar-Gallagher-Kell equation for reference states
- Refinement of phase boundary routines
- Further development of transport property corresponding states
- Structurally based ECS parameters
- Dielectric constant (or H-bonds) as ECS parameter
- Ionic components
- Chemically reacting systems



Volume shape factor, h
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.5
1.0
1.5
2.0
Reduced temperature, T/Tc
Water
Methane


Energy shape factor, f
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
Reduced temperature, T/Tc
Water
Methane

CONCLUSIONS

•There is a need for thermophsyical properties (phase diagrams, densities, viscosities, enthalpies, etc.) for a variety of supercritical aqueous systems:

- •accurate
- •thermodynamically consistent
- •easy to use

•Existing extended corresponding states models and computer packages can form the basis for fulfilling these needs.

NIST Programs Relevant to SCWO

Dr. Gregory J. Rosasco

Chemical Kinetics and Thermodynamics Division

Dr. Sharon G. Lias, Chief
301-975-2562

Equilibrium and reaction rate data for chemical reactions in vapor and liquid phases:

- reaction mechanisms
- reaction rate data
    - measurement
    - evaluation
    - estimation
- thermochemical equilibria
    - measurement
    - evaluation
    - estimation

Measured data and theory-based predictive models

Process Measurements Division

Dr. Andrej Maček, Acting Chief
301-975-2610

Optical diagnostics (P, T, species) and process simulators for multiphase reacting flows

- supercritical water flow reactors
- flow reactor (fluidized bed heating)
  - global kinetics
  - materials performance
- optically accessible flow reactor - *in situ* measurements
  - phase behavior
    - density, species
  - reaction intermediates
  - materials performance

Thermophysics Division

Dr. Rich F. Kayser, Chief
301-975-2483

Thermophysical property measurements for multi-component mixtures as functions of T and P :

heat capacity	vapor pressure
density	phase equilibria
viscosity	sound velocity
thermal conductivity	surface tension
thermal diffusivity	dielectric constant
diffusion coefficient	dipole moments

Theory-based predictive models:

NBS/NRC Steam Tables	REFPROP
SUPERTRAPP	MIPROPS
DDMIX	

Metallurgy Division-Corrosion Group

Dr. Richard E. Ricker, Leader
301-975-6023

Materials performance

- evaluated corrosion data
- expert systems for reactor design

Materials behavior (life-prediction)

- electrochemical evaluation of candidate materials
- alternate materials
- coatings

Measurement science

- instrumentation for *in situ* corrosion monitoring

NACE-NIST Corrosion Data Program

Materials Advisory Expert System for the Handling and Storage of Hydrogen Chloride

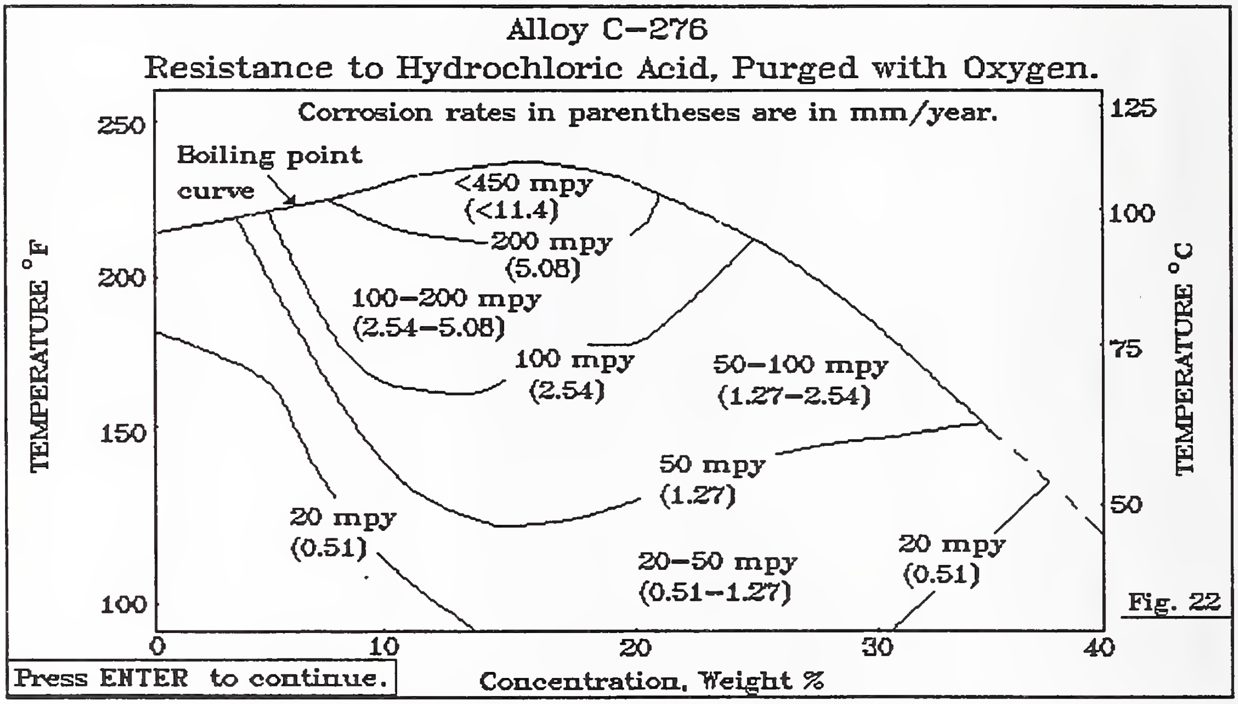


Fig. 22: Alloy C-276, resistance to HCl, purged with oxygen

Rule: If HCl concentration < = 12% or > = 20%
and Oxygen purge = true
and Temperature < = 50°C
then consider Alloy C-276
and Corrosion Rate < = 50 mpy

Army Research Office University Research Initiative in SCWO--Unofficial Summary

Dr. Gregory J. Rosasco

US ARMY UNIVERSITY RESEARCH INITIATIVE PROGRAM
FY 92-96

ENVIRONMENTAL SCIENCES ($13M/5y):

CHEMICAL REACTORS ($5.5M):

MIT	J. Tester, Chem Eng
U Delaware	M. Klein, Chem Eng
U Texas-Austin	K. Johnston, Chem Eng

COMBUSTION PROBES ($2.5M):

Cornell	F. Gouldin, Mech & Aero Eng

BIODEGRADATION ($2.4M):

Texas A&M	B. Dale, Ag Chem Eng

TRANSFER IN MIXED PHASES ($2.5M):

U N Carolina	C. Miller, Env Sci & Eng

ARO-University Research Initiative

Chemical Reactors

Massachusetts Institute of Technology

J. E. Tester
H. J. Herzog
J. B. Howard
R. M. Latanision
W. A. Peters
A. F. Sarofim

University of Delaware

M. T. Klein
T. B. Brill

University of Texas-Austin

K. Johnston
M. A. Fox
A. Bard

CHEMICAL REACTORS: SUPERCRITICAL WATER OXIDATION

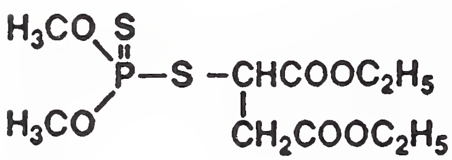
Massachusetts Institute of Technology:

Experiments: Global Kinetics of Destruction
Salts - Nucleation and Phase Separation
Corrosion

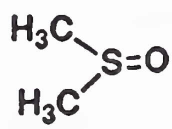
Modeling: Reactor Engineering
Process Simulation

Target Compounds:

Malathion

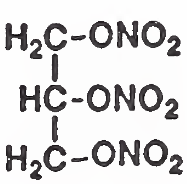


DiMethyl Sulfoxide

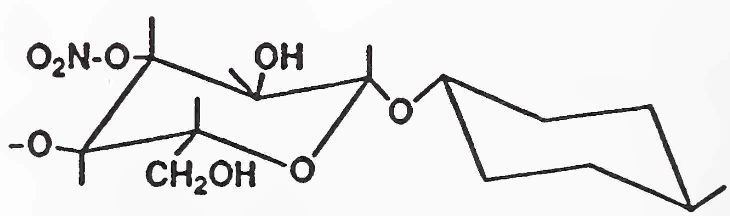


Ammonium Perchlorate NH_4ClO_4

Nitroglycerine



Nitrocellulose



CHEMICAL REACTORS: SUPERCRITICAL WATER OXIDATION

University of Delaware:

Experiments:	Identify Reactive Intermediates - FTIR, Raman
Modeling:	Detailed Reaction Kinetics

Target Compounds:

Nitrates	R-C-NO_2
Nitrate Esters	R-C-O-NO_2
Nitramines	R-C-N-NO_2
Nitrate, Perchlorate Salts	NH_4NO_3, NH_4ClO_4
High N Compounds - Azides	$Pb(N_3)_2$

CHEMICAL REACTORS:

SUPERCRITICAL WATER OXIDATION

University of Texas-Austin:

Experiments:	Spectroscopy of charge transfer reactions Redox Reactions with Metal Oxides Electrochemistry
Modeling:	Equation of State including H bonding Solvent effects on Reaction

DARPA

SUPERCRITICAL FLUID RELATED TASKS

by

Dr. Richard T. Loda
DARPA/DSO/MSD
(703) 696-2283, Fax - 2201

TECHNICAL EXCHANGE ON SUPERCRITICAL WATER OXIDATION
6-7 July 1992

NIST, Gaithersburg, Maryland

SCF TECHNOLOGY

- Clemson University (Thies)

  SCFE of pitch to remove inorganic contaminants and to select optimum molecular weight fraction(s) for producing low-cost and/or improved C-fibers and C-C composites.

- USC (Aklonis)

  Use supercritical fluids to aid processing of advanced polymers that are extremely difficult to fabricate or blend.

- J. L. McDaniel Enterprises, Inc. (Mitchell) - SBIR - II

  SCF CO_2 technique for the improved processing of high total solids rocket propellants (i.e., lower temperature, shorter mixing time, and smaller particle size for decreased hazards).

SUPERCRITICAL FLUID EXTRACTION: PREPARING MESOPHASE PITCH FOR THE MANUFACTURE OF HIGH-PERFORMANCE CARBON FIBERS

Clemson University, M. C. Thies and D. D. Edie

OBJECTIVES

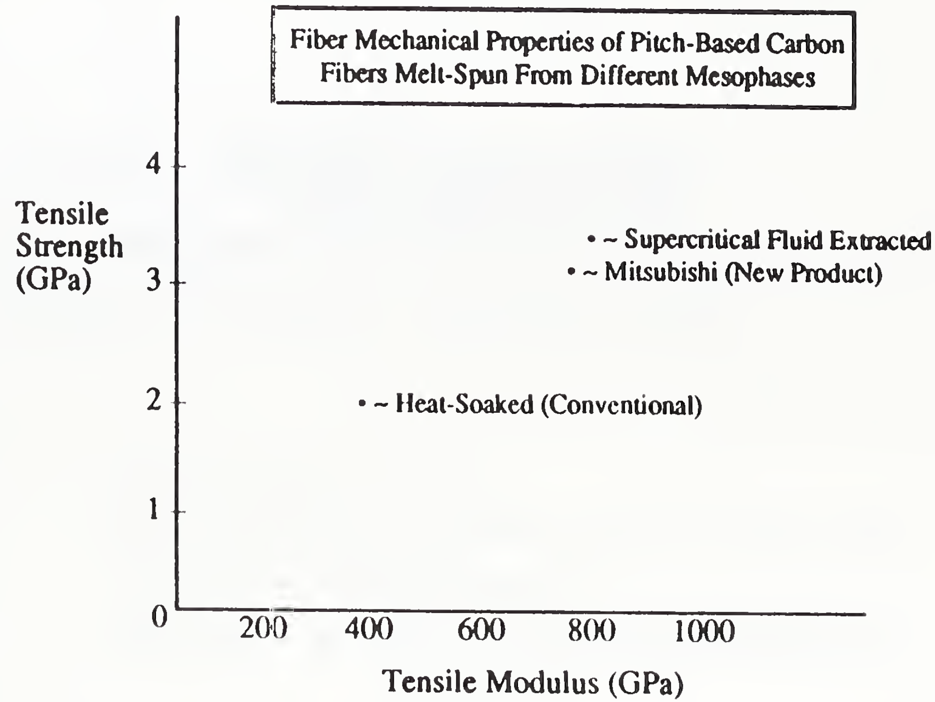
- Evaluate the potential of supercritical fluid (SCF) extraction for producing mesophase pitch.
- Produce fibers with strengths and moduli significantly superior to the best pitch-based fibers, at a production cost of $10/lb.
- Produce fibers with very high thermal conductivities.
- Establish relationships between fiber microstructure, mesophase properties, and SCF operating conditions.

ACCOMPLISHMENTS

- Early attempts on supercritical fluid extraction of carbon fibers melt-spun from mesophase showed strength and modulus values superior to the best known fibers (from Mitsubishi) which are pitch-based.
- Projections are for greater improvements and a low-cost pitch-based fiber by SCF extraction.

APPROACH

- Through changes in process variables, establish the relationships between fiber microstructure, mesophase properties, and SCF operating conditions.
- Fractionation of isotropic petroleum pitch into both isotropic and mesophase pitch fractions will be done in a liquid-liquid region from 300-400°C, 50-200 bar, and solvent-to-feed ratios of 1:1 to 5:1.
- Characterize the fractions by GPC, NMR, GC-MS, and FTIR.
- Spin, oxidize, and carbonize promising mesophase fractions into carbon fibers.
- Measure mechanical properties, thermal conductivities, and characterize by XRD, SEM, and TEM.
- Produce the most promising mesophases in pilot-scale quantities.



PROCESSING OF POLYMERS USING SUPERCRITICAL FLUIDS

University of Southern California, John J. Aklonis and Eric J. Amis

OBJECTIVES

- Use the properties of supercritical fluids (SCF) to assist in the fabrication or blending of difficult-to-process polymers.
- Employ SCF as solvents for the preparation of polymer fibers, polymer sheets, and other polymer solids (especially ultrafine fibers, powders, and films).

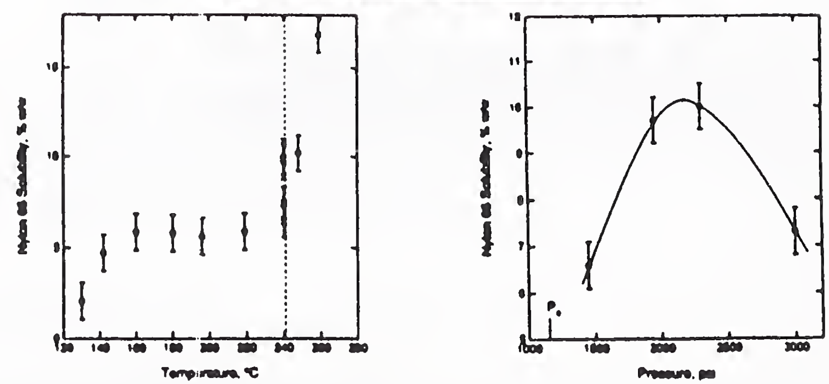
APPROACH

- Initial effort focused upon measuring the phase diagrams of homopolymers (e.g., PS, PMMA) in appropriate SCF solvents such as CO_2 and simple hydrocarbons.
- Prepare solid products of homopolymers and polymer blends and assess adequacy of mixing.

ACCOMPLISHMENTS

- Investigations of the solubilities of high MW polymers in SCF were expanded. PE, PS, PMMA, LEXAN, nylon 6, nylon 66, and PET have been studied in pure and mixed solvent systems. The maximum solubilities of some polymers in the SC regime were increased to as much as 15%.
- Fibers and powders of a number of homopolymers and polymer blends have been prepared by rapidly reducing the pressure of SCF polymer solutions. Fibers as long as 50 meters have been prepared by pressure drop spinning.

SOLUBILITY OF NYLON 6.6 IN SUPERCRITICAL METHANOL



Solubility increase with temperature at critical point

Maximum in solubility with increasing pressure above P_c. ($T = T_c$)

This is a model for highly crystalline materials; candidates are KEVLAR, UMWPE

SCF TECHNOLOGY

- CF Technologies, Inc. (Moses) - SBIR - II

  Supercritical fluid CO_2 processing of aerogels:
  - -- for high Tc superconductor precursors
  - -- for improving the strength and structural integrity of aerogel monoliths.

- CF Technologies, Inc. (Moses) - SBIR - II

  Chemical agent demilitarization using supercritical CO_2 with catalytic (γ - Fe_2O_3) or oxidative (H_2O_2) destruction.

MULTICOMPONENT AEROGEL PROCESSING IN SUPERCRITICAL FLUID MEDIA

J. M. MOSES , CF TECHnologies, Inc., Boston, MA

OBJECTIVES

Develop high quality multicomponent aerogels for various defense applications.

Determine the controlling mechanism in supercritical carbon dioxide exchange and drying of aerogels.

Produce gels for applications testing as aerospace materials, catalysts, and light-weight high-strength insulation.

Develop a cost effective process for the production of aerogels.

APPROACHES

Windowed pressure vessels are being used to observe the solvent exchange and drying processes.

Aerogel composition and processing are being modeled and tested to improve strength and other properties.

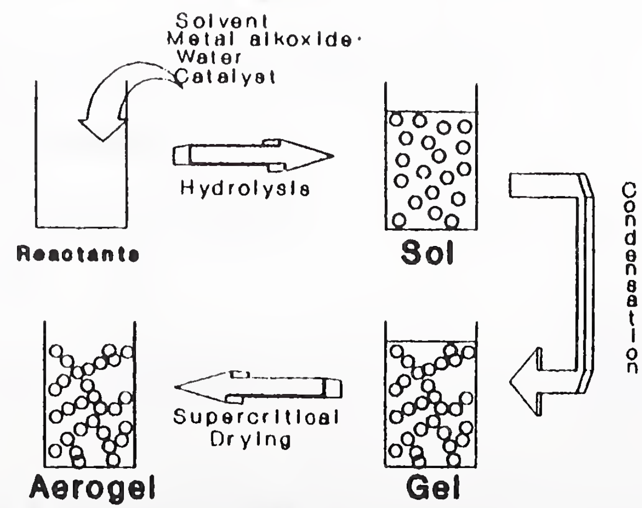
Laboratory production of large monoliths for process and application testing.

ACCOMPLISHMENTS

Production of an aerogel catalyst with destruction exceeding 99.5 % of the simulant DMMP at room temperature in a laboratory scale system.

Production of an aerogel monolith with 20 times the strength of conventional aerogels at the equivalent density of 0.12 g/ml.

Conceptual design of a system including the gel formation, critical fluid exchange and drying, and solvent recycling



EXTRACTION AND DESTRUCTION OF HAZARDOUS MATERIALS IN SUPERCRITICAL FLUID MEDIA

J. M. MOSES, CF TECHnologies, Inc., Boston, MA

OBJECTIVES

Extract and destroy hazardous materials in a critical fluid process.

Develop and demonstrate the technology in bench and pilot scale equipment using chemical warfare agent simulants.

Test other uses of the technology for defense environmental restoration and reclaimation applications.

Develop a cost effective process for the extraction and destruction of hazardous materials.

APPROACHES

Low temperature critical fluid extraction, reaction, and separation tests of simulants and hazardous materials in laboratory equipment.

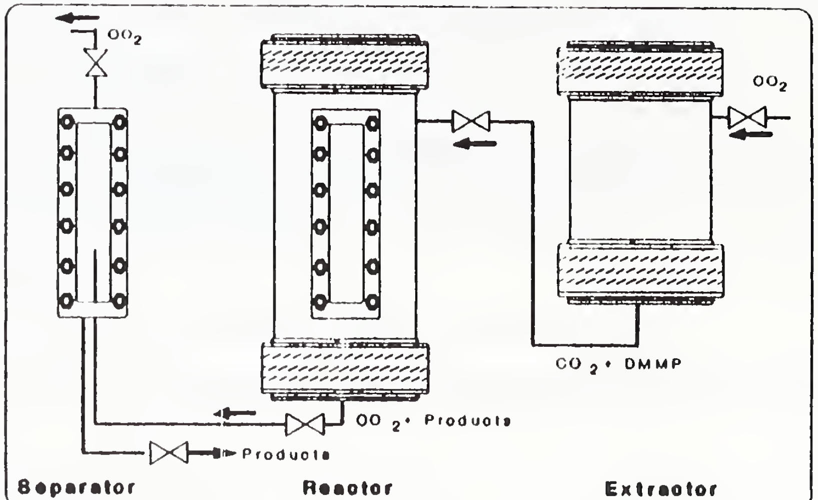
Carbon dioxide is the critical fluid being tested, Dimmethyl Methyl Phosphate (DMMP) is the simulant and aerogel monolithic catalysts are used for the destruction reaction.

ACCOMPLISHMENTS

Destruction exceeding 99.5 % of the simulant DMMP at room temperature in a laboratory scale system.

Conceptual design of a system including the critical fluid extractor, reactor, and separator.

Extraction of DMMP and various solvents and oils to non detectable levels.



SCWO TASKS

- University of New Orleans (Politzer)

  Theoretical studies aimed at the mechanisms by which supercritical fluids can influence the rates and equilibria of chemical reactions. Also, to develop data and predictive capability for controlled oxidations in supercritical fluids of chemical warfare agents and energetic materials.

- Harvard (Herschbach) (Computational Mathematics Program)

  Develop the method of dimensional scaling and apply it to electronic structure calculations which are intractable using currently available theoretical methods for multi-electron atoms and molecules. Enable theoretical prediction of reaction pathways for the decomposition of chemical species and enhance the capability to develop equations of state for supercritical fluids.

SCWO TASKS

- MODEC (Modell) - SBIR - II.
  - Remotely controlled SCWO System for High-Risk DoD Wastes. Destruction tests on simulated agents, system automated for remote operation. AF to fund Option B, field demonstration of safe HMX oxidation. (Transition).
  - In-situ neutralization of Acids Generated by SCWO (non-SBIR)

- Sandia (Johnston)

  Theoretical and experimental investigations of the chemical kinetics of oxidation in supercritical water

  theory -- oxidative reaction mechanisms and real-gas effects of water on the rate constants.

  experimental -- laser diagnostic techniques to detect reactants, intermediates, and products in SCW.

SCFO DESTRUCTION EFFICIENCY

SCWO Destruction Tests On Simulated Chemical Agents

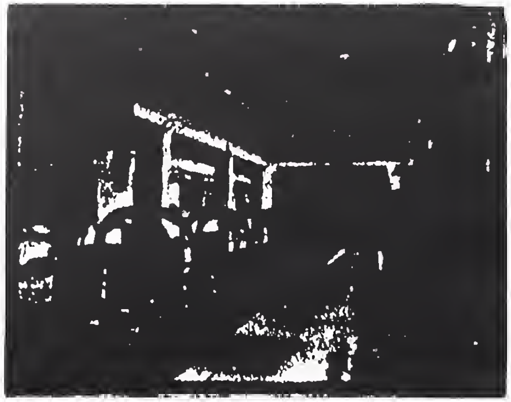
	Feed Concentration (wt-%)	Temperature (C)	Destruction Efficiency (%)
HD Simulants			
1,5-Dichloropentane	0.1	524	99.99995
Ethyl-2-hydroxyethyl sulfide	0.1	524	99.9997
GB Simulants			
4-Fluorobenzyl alcohol	1.0	563	99.99992
Diethylmethyl phosphate	1.0	563	99.99993
VX Simulants			
2-(DiIsopropylamino ethanol)	0.5	645	>99.99998
Diethylmethyl phosphonate	0.5	563	>99.99998

1296 3-28 90 6

SCWO PILOT PLANT DEMONSTRATION PROGRAM

- DARPA BAA. Goal to build and demonstrate a > 1000 gallon/day transportable pilot plant for the destruction of chemical agents, propellants, and other hazardous or toxic materials.
- 20 preproposals received, 4 final proposals. General Atomics (GA) team contracted. Contract initiated 16 March 1992.
- Two phase, 4 year program (FY92-95)

CRYOFRACTURE SYSTEM APPLIED TO U.S. CHEMICAL DEMILITARIZATION PLANT



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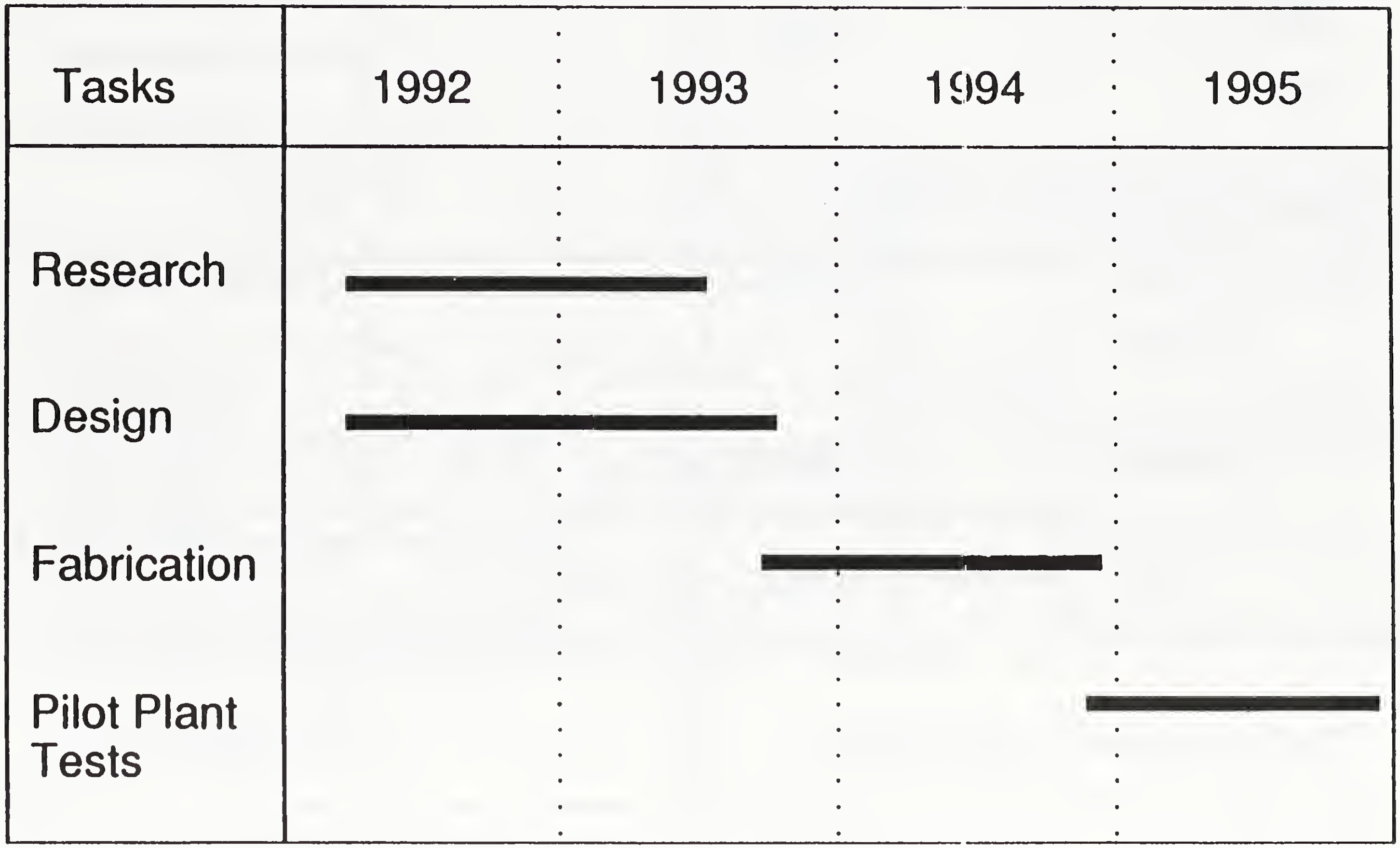
GENERAL ATOMICS

DARPA SCWO PROGRAM SCHEDULE ANTICIPATES PILOT PLANT DEMONSTRATION IN 1995



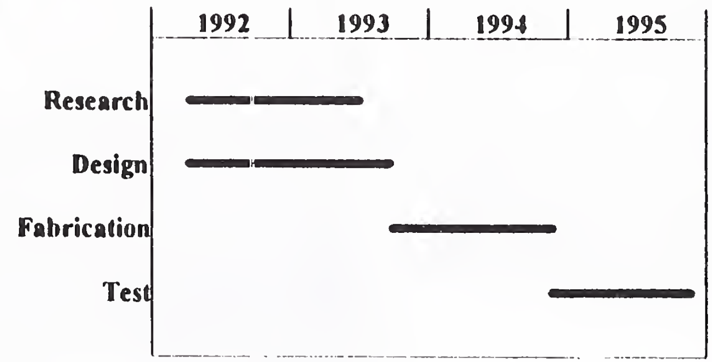
GENERAL ATOMICS

DARPA SCWO PROGRAM UNDERWAY

Objectives

1. Identify optimum materials of construction, operating conditions, and destruction and removal efficiencies during Research Phase of program.
2. Design transportable system capable of treating chemical agents, propellants, and other DoD wastes.
3. Provide SCWO system capable of processing >1000 gal/day.
4. Meet all regulatory requirements.
5. Ensure high reliability, availability, and maintainability.

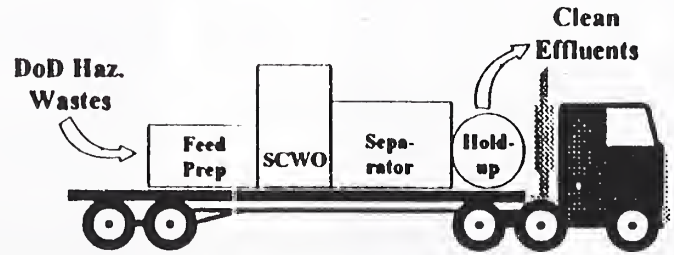
Anticipated Accomplishments



Approach

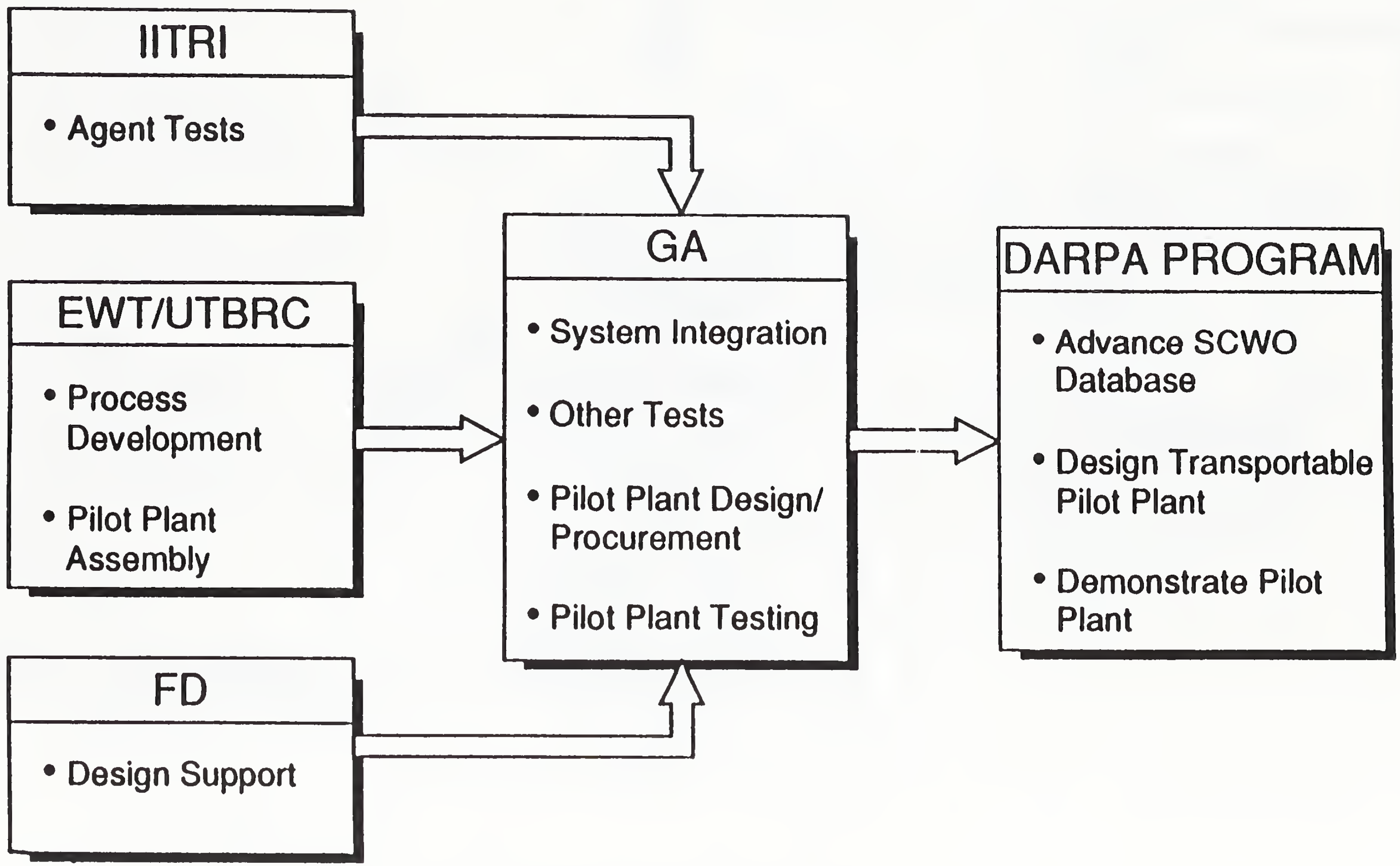
1. Assemble well qualified research and design team (GA, EWT/UT, IITRI, Fluor Daniel).
2. Survey available technology.
3. Integrate research and design tasks.
4. Use research results to drive design.
5. Emphasize Systems Engineering (Safety, RAM).
6. Plan broad design verification test program.

Transportable SCWO System



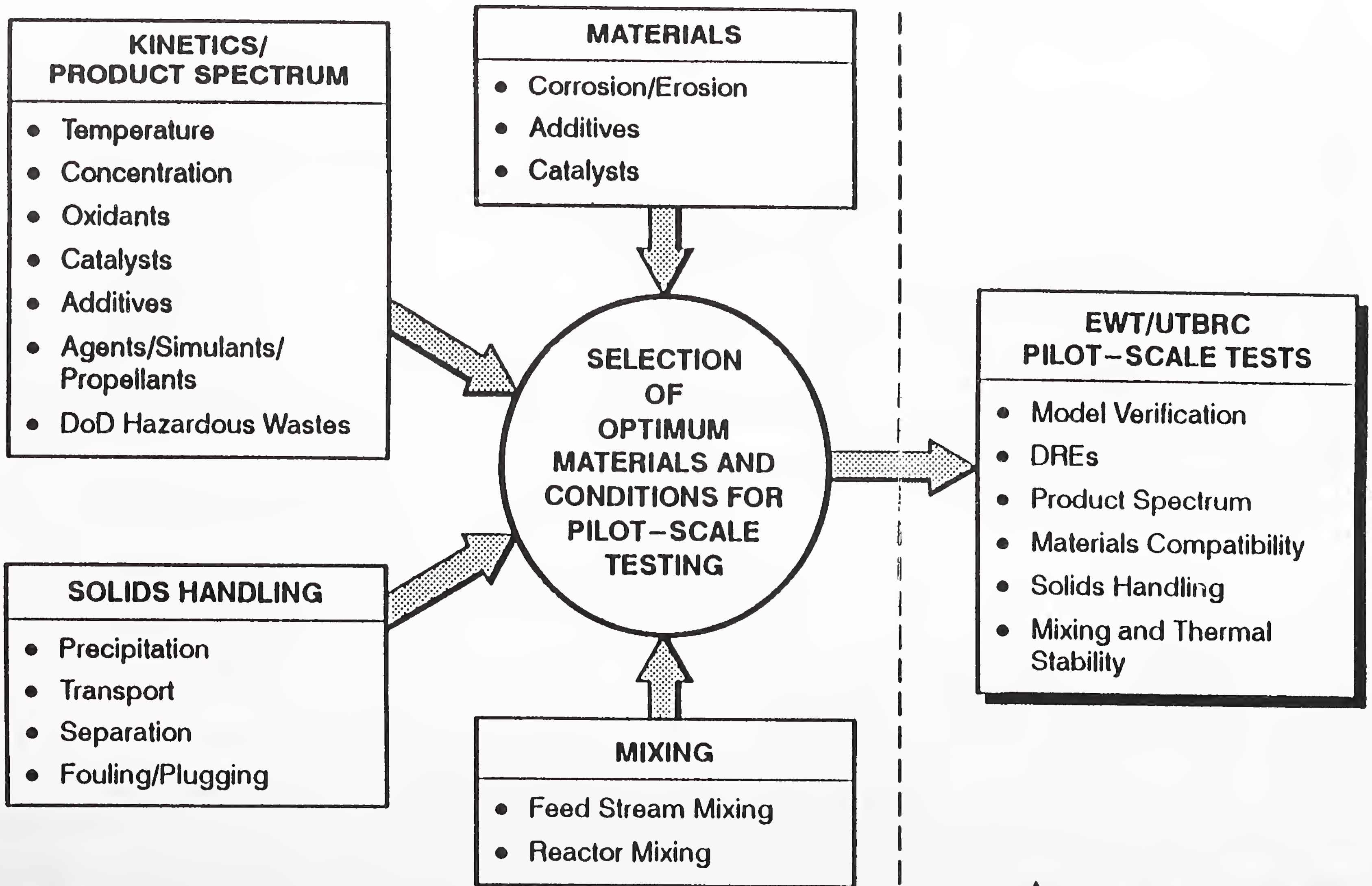
GENERAL ATOMICS

GA's TEAM APPROACH



GENERAL ATOMICS

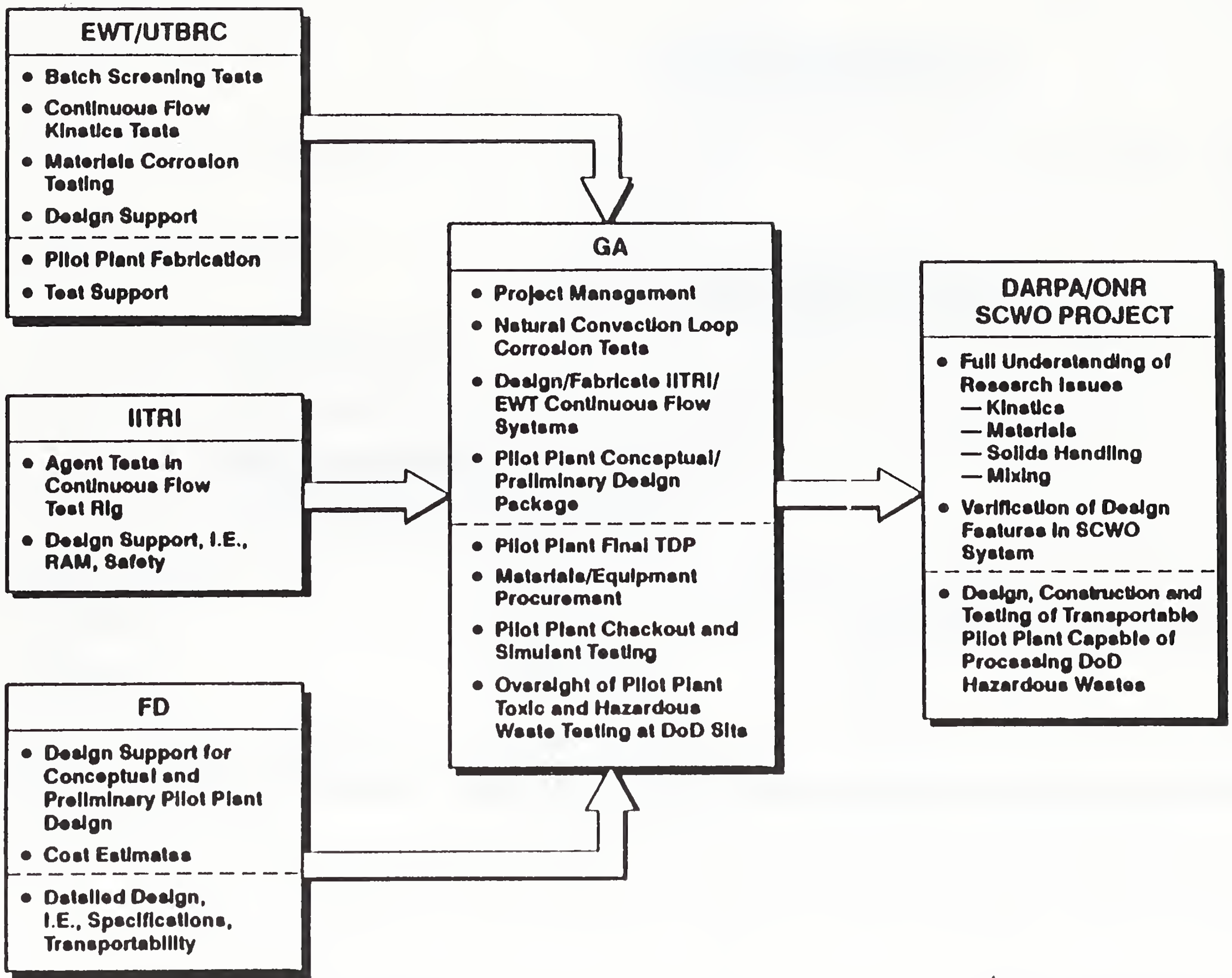
RESEARCH PROGRAM FOCUSED ON MAJOR SCWO TECHNICAL ISSUES



K-018(11)(I-01)
4-26-91

GENERAL ATOMICS

GA SCWO TEAM ASSIGNMENTS DEFINED



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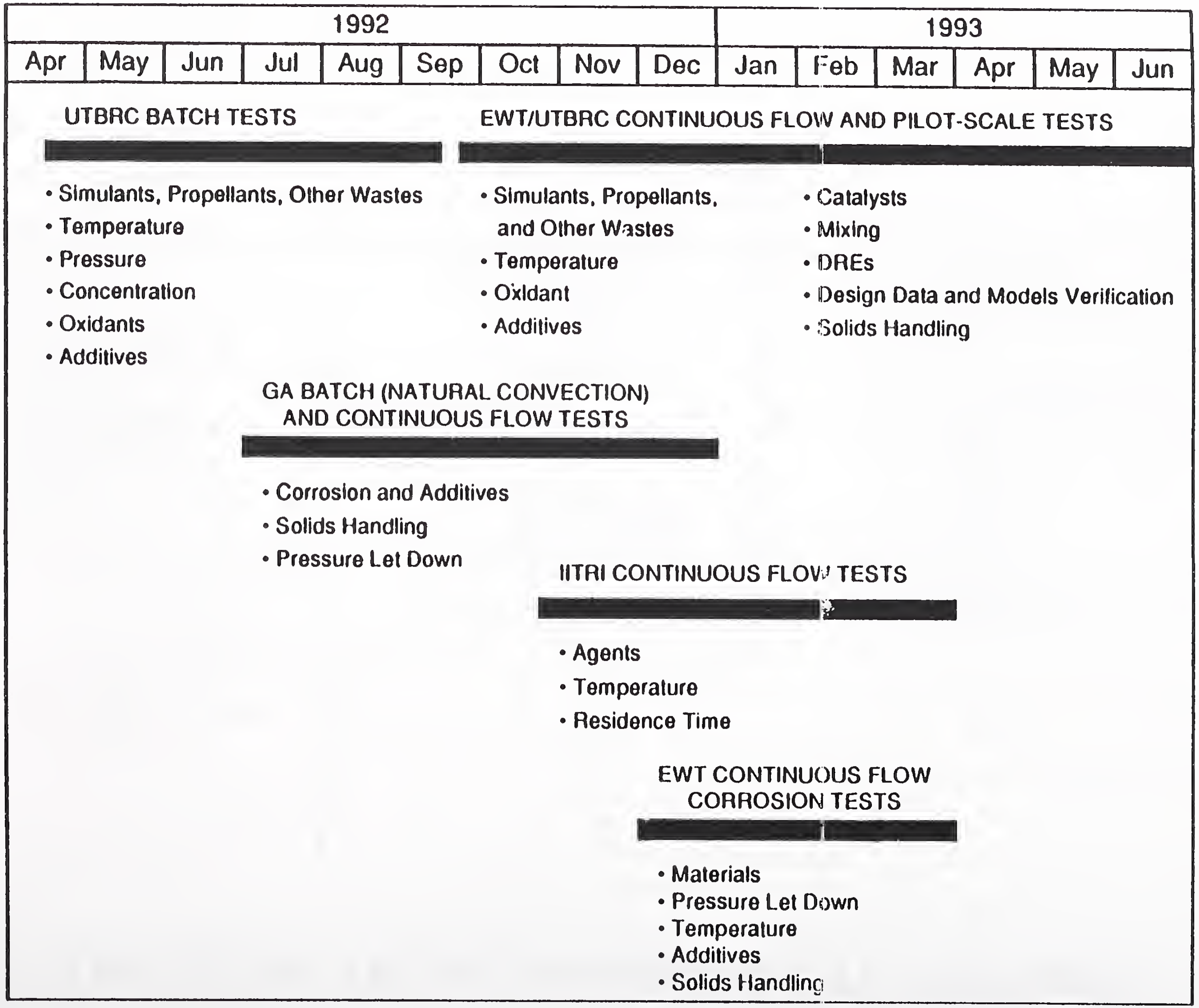
GENERAL ATOMICS

SCWO DATA TO BE OBTAINED FROM A VARIETY OF TEST BEDS



CANDIDATE MATERIALS SELECTED FOR CORROSION SCREENING

Class	Candidate Materials
Nickel-base Alloys	C-276, C-22, B-2, G-3, 625, 825
Reactive Metals	Zircadyne 704, Ti
Refractory Metals	Nb-1%Zr, Ta-10%W, Mo
Noble Metal Liners	Pt-10%Ir, Pt-10%Rh, Pt
Polymer Coatings	PBI
Ceramics	SiC, Si_3N_4
Others	?

MATERIALS COMPATIBILITY INITIAL TEST MATRIX DEFINED

<u>Test Parameters</u>	
Temperature	350°C, 425°C, 500°C
Pressure	25 to 30 MPa
Exposure time	5, 20, and 100 hours
Oxidant Concentration	7 weight % H_2O_2
<u>Test Media</u>	
GB	0.7% HF, 3.5% H_3PO_4, 6.3% CO_2
VX	1.8% H_2SO_4, 1.8% H_3PO_4, 0.3% NH_3, 9.1% CO_2
HD	3.1% H_2SO_4, 2.3% HCl, 5.5% CO_2
Type 1.1 Propellant	3.4% HNO_3, 1.0% NH_4ClO_4, 3.0% CO_2
Type 1.3 Propellant	3.9% NH_4ClO_4, 2.8% CO_2
Chlorinated Compounds	3.5% HCl, 5.0% CO_2

EWT/UTBRC RESEARCH ACTIVITIES

- Assist GA in technology review
- Perform 300 batch SCWO tests
- Perform 235 continuous flow SCWO tests
- Perform three 30 day continuous flow SCWO corrosion tests
- Design, fabricate, and test a slurry pressure reduction device
- Test solids separation with hydrocyclone
- Develop and verify reactor system model
- Design, fabricate, and operate pilot plant scale SCWO with catalyst bed
- Perform system integration and kinetic tests on SCWO pilot plant

UTBRC INITIAL BATCH TEST MATRIX BEING DEFINED

<u>Test Constants</u>	
Concentration	Up to 10,000 ppm
Oxidant	O_2 , 200% excess
Pressure	25 to 30 MPa
<u>Test Parameters</u>	
Compound	3 agent simulants, 2 propellants, 2 other waste simulants
Temperature	425°C, 500°C
Residence time	1, 2, and 3 minutes

UTBRC FOLLOW-ON BATCH TEST MATRIX BEING DEFINED

<u>Test Parameters</u>	
Compound	1 agent simulant, 1 propellant or other waste simulant
Concentration	5,000 ppm; 10,000 ppm; 50,000 ppm
Temperature	350, 425°C, 500°C
Pressure	25 MPa, 30 MPa, and two other pressures
Residence time	1 and 3 minutes
Oxidant	O_2, H_2O_2
Oxidant Concentration	20% excess, 200% excess
Additive	KOH, NaOH, Na_2CO_3
Additive Concentration	0% excess, 100% excess

UTBRC CONTINUOUS FLOW TEST MATRIX BEING DEFINED

Test Constants	
Concentration	10,000 ppm
Pressure	25 to 30 MPa
Test Parameters	
Compound	3 agent simulants, 1 propellant, 1 other waste simulant
Temperature	425°C, 460°C, 500°C
Residence time	1, 2, and 3 minutes
Oxidant	O_2, H_2O_2 (200% excess)
Additive	2 additives
Catalyst	3 catalysts
Mixing	2 static mixers

IITRI RESEARCH & DESIGN ACTIVITIES

- Ensure SCWO test system compliance with chemical agent requirements
- Preparation and approval of SCWO test system SOPs
- Synthesize chemical agents
- Install SCWO test system provided by GA
- Perform 40 continuous flow SCWO tests with chemical agents
- Analyze liquid and gaseous effluents from SCWO tests
- Decontaminate selected components of SCWO test system
- SCWO pilot plant design input specific to chemical agents

CHEMICAL AGENT TEST MATRIX BEING DEFINED

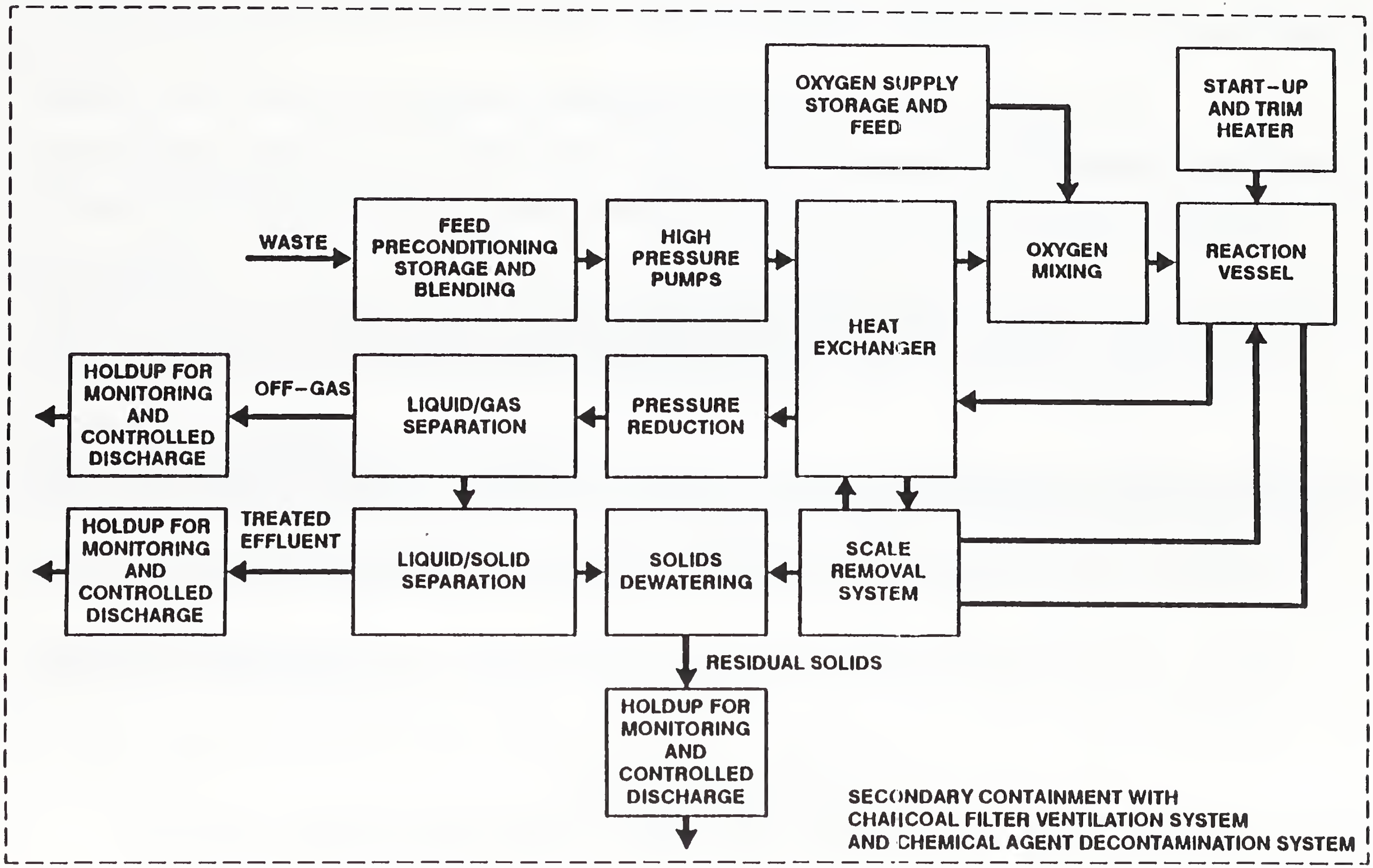
<u>Test Constants:</u>

Concentration	Up to 10,000 ppm
Oxidant	H_2O_2 , 100% excess
Pressure	25 to 30 MPa

<u>Test Parameters:</u>

Chemical agent	GB, VX, HD
Temperature	425°C, 460°C, 500°C
Residence time	1, 2, and 3 minutes

TRANSPORTABLE PILOT PLANT BLOCK FLOW DIAGRAM



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4-17-92

GENERAL ATOMICS

SCWO PILOT PLANT INCORPORATES MULTIPLE SUBSYSTEMS

- Feed System: provide consistently blended and metered feed stream
- Oxygen Supply System: pump high pressure oxidant to feed system
- Main Process System: contains reactor, heat exchangers, and pressure reduction system
- Effluent Storage and Disposal System: provides storage capacity for verification of agent destruction prior to disposal
- Control and Data Acquisition System: remotely located for operator protection; computer control of reactor parameters, oxygen/waste feed rates, and solid/liquid/gas separation and storage conditions
- Contamination Control System: agent related decon/monitoring equipment

SCWO TEAM SUPPORTS PILOT PLANT DESIGN

General Atomics

- Lead and coordinate team design activities
- Perform designs based on R&D background and chem demil experience

Fluor Daniel

- Provide A-E design support; modular, transportable, and SCWO design experience, and review design documents

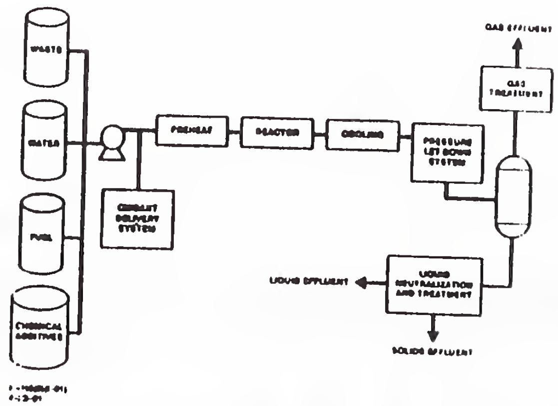
Eco Waste Technologies/UTBRC

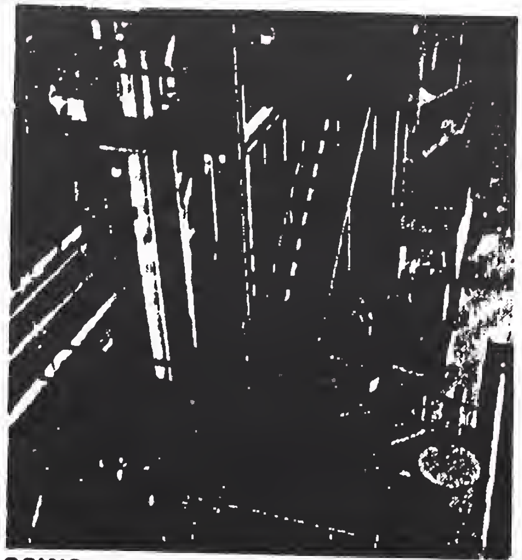
- Provide SCWO pilot-scale design expertise, hands-on experience, and review design documents

IIT Research Institute

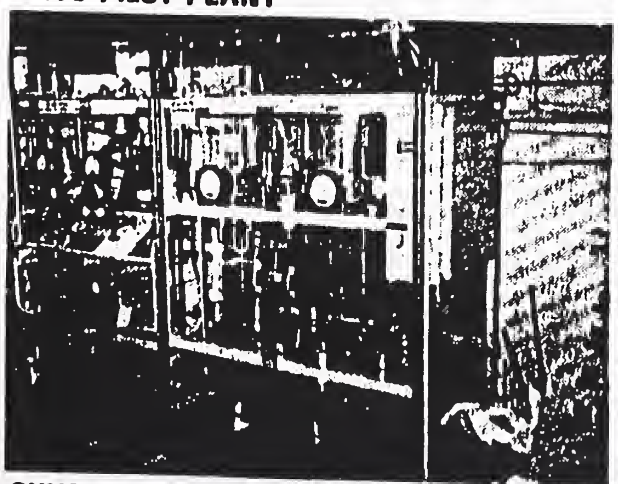
Provide agent-specific design support experience and review design documents

SUPERCRITICAL WATER OXIDATION



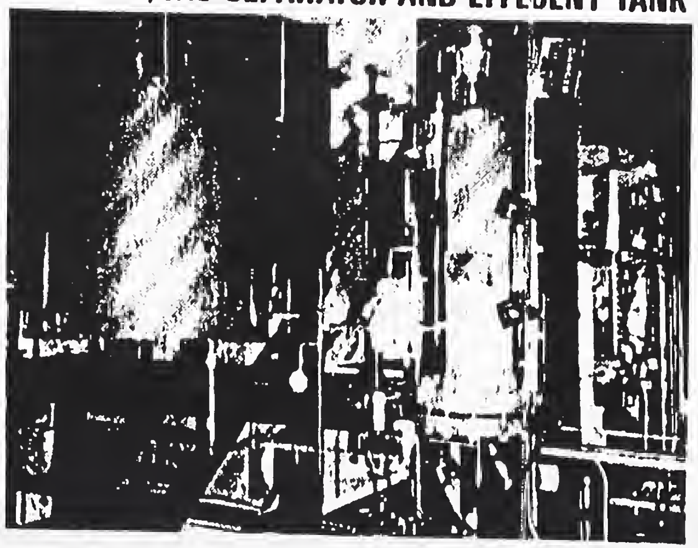


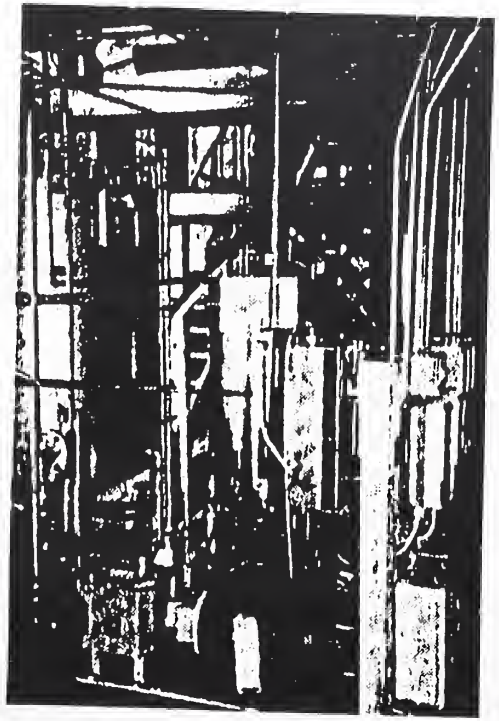
SCWO PILOT PLANT



OXYGEN SUPPLY SYSTEM

LIQUID/GAS SEPARATOR AND EFFLUENT TANK



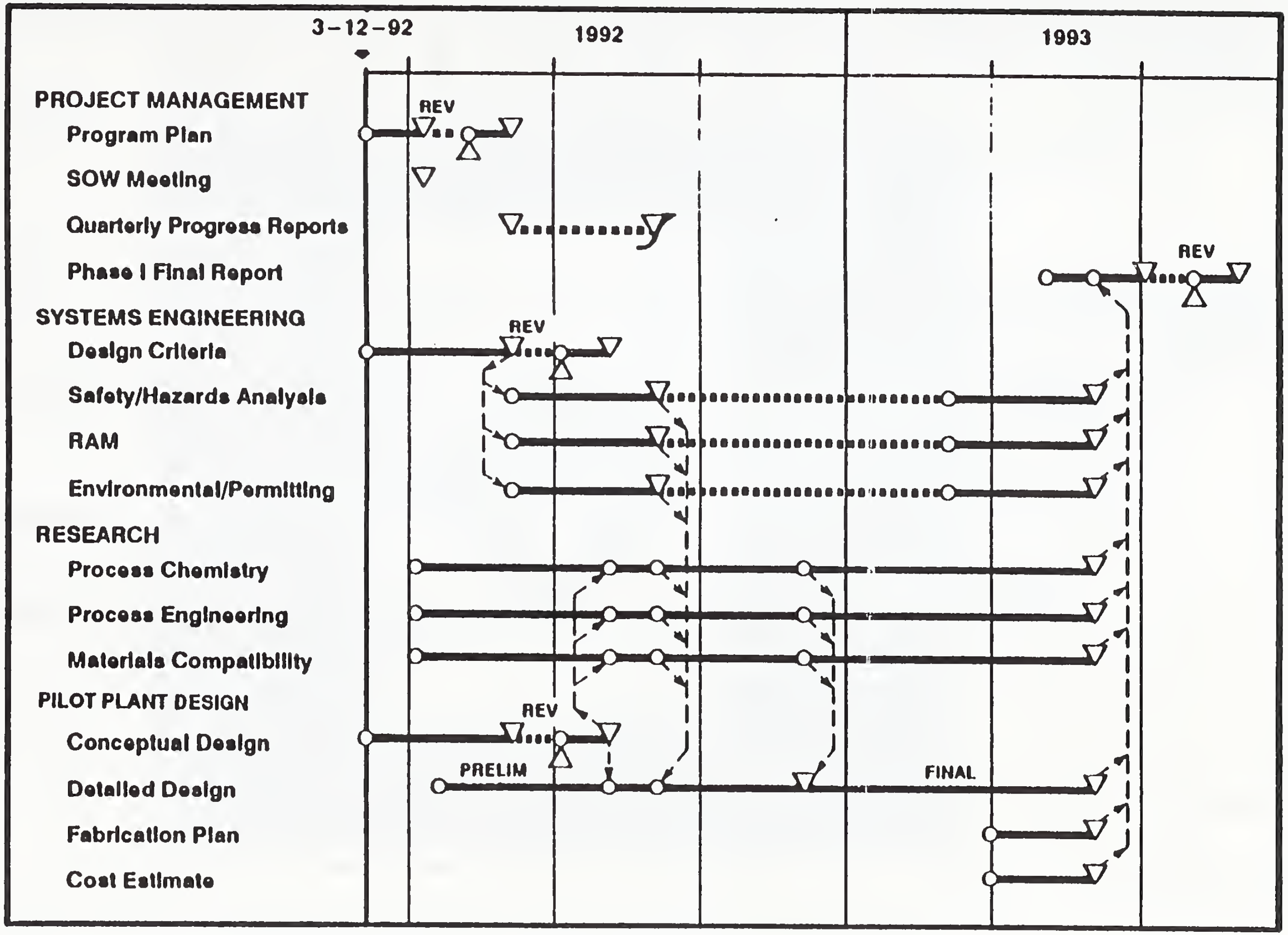


FEED SYSTEM

K-071(3)
5-29-91

GENERAL ATOMICS

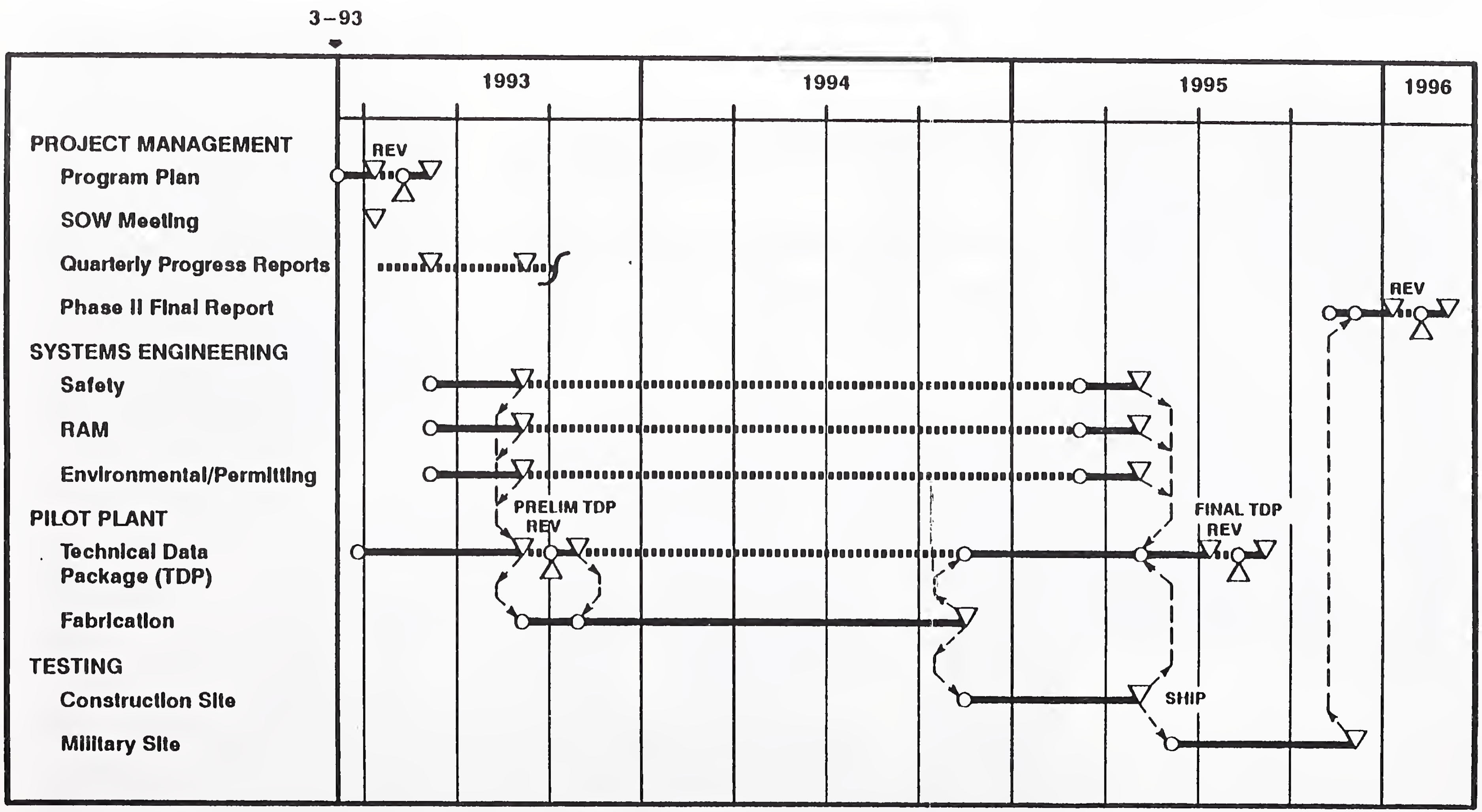
SCWO PHASE 1 PROJECT SCHEDULE



J-915(2a)(I-11)
4-17-92

GENERAL ATOMICS

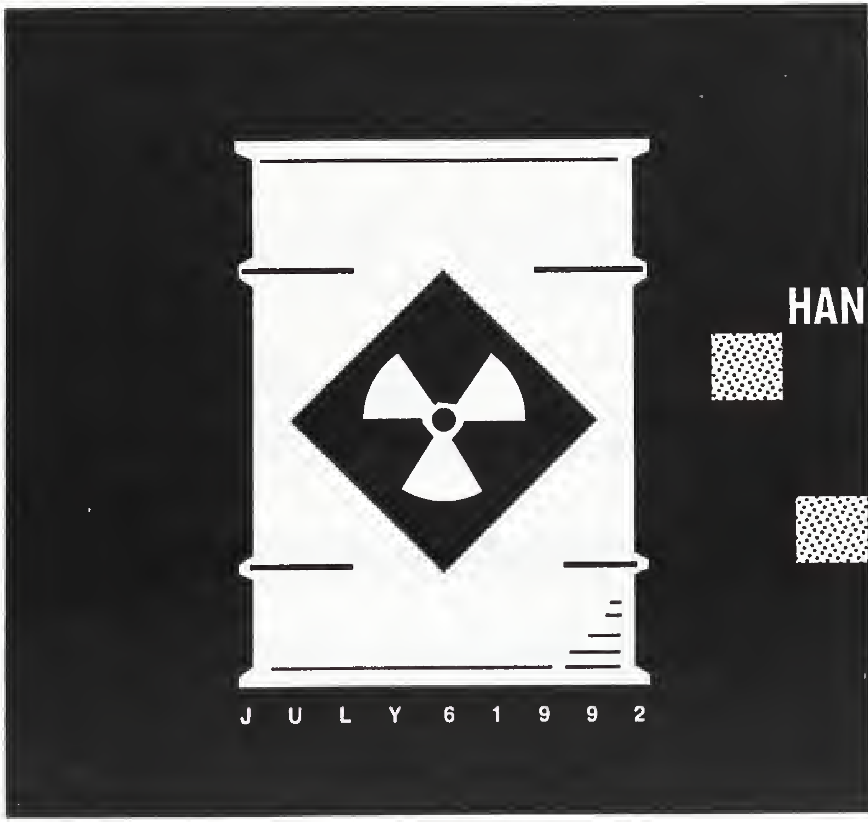
SCWO PHASE 2 PROJECT SCHEDULE



J-915(3)(I-01)
4-17-92

GENERAL ATOMICS

OFFICE OF ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT INITIATIVES IN SCWO



HANK STRAUCH

WORKSHOP ON SUPERCRITICAL FLUID PROCESSING

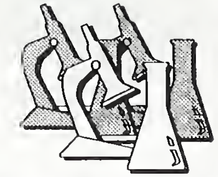
G A I T H E R S B U R G M D

M92-GT-0456-01

Major Regulatory Drivers for Technology Development:

- RCRA LDR Prohibit Land Disposal of MW after May 1992
- Pending Federal Facility Compliance Act does not allow variance beyond July 1997
- Case-by-Case Extension Proposes Schedule for Plant Availability
- FFCA have Individual Site Specific Requirements Specific Technology Development Requirements
- The amended Clean Air Act has very stringent requirements phasing in for new treatment facilities

Advantages to SCWO



- Nonpolar organics are completely miscible
- Many inorganic salts are insoluble and may be precipitated
- Oxidation reactions occur at lower temperatures than conventional combustion processes
- Gas-like transport properties
- Liquid-like densities
- Effectively oxidize a broad spectrum of organic compounds
- Recovery of the heat of combustion as high temperature process heat or power
- Closed system ~ complete control of emissions and meets EPA's concept of a "Totally Enclosed Treatment" facility
- SCWO needs lower carbon content than incineration to be energy-sufficient
- Single Phase – two phase systems have concentration gradients and mass transfer limitations across phase boundaries

M92-GT-0456-03

Disadvantages to SCWO

- Is similar to incineration in that it is not applicable to most inorganic wastes
- Conducting efforts to solve problems in treating aqueous wastes with high salt content
- Conducting efforts to solve problems in treating corrosive waste
- Continuous operation unproven – Batch operation could leave an accumulation of inorganic waste, including radionuclides
- Many inorganic salts are insoluable and may be precipitated

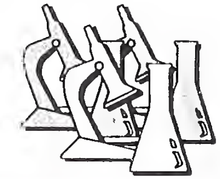
M92-GT-0456-04

Potential Applicability of SCWO to DOE

- Study Applicability of SCWO to Treat Mixed Waste to Destroy Organics
- Study Applicability of SCWO to Treat USTs for organic and ferrocyanide destruction and nitrate reduction
- Study Applicability of SCWO to Treat other materials – explosives, propellants, and explosives contaminated solvents
- Determine if SCWO is an Incineration Alternative - Economical, Public Acceptance, Offgas
- Stage Demonstrations: Halogenated Hydrocarbons, Hydrocarbons, Mixed Waste, TRU Waste, PCB/Oils

M92-GT-0456-05

Various Problem Areas



- Underground Storage Tanks
- Groundwater
- Mixed Waste/Rocky Flats

M92-GT-0456-06

Underground Storage Tanks

- Study kinetics of oxidation processes in SCWO
- Testing on surrogate wastes
- Use nitrates already in waste as oxidizing agents
- Clean, safe, and complete destruction and separation of organics, ferrocyanides, and nitrates

M92-GT-0456-07

Groundwater

- Treatment is ex-situ for groundwater
- No preprocessing for groundwater
- Contaminated groundwater treatment can be more cost effective by mixing with concentrated organic waste especially instead of an added fuel

M92-GT-0456-08

Mixed Waste

- Test surrogate waste in 30 gpd reactor
- Establish list of candidate wastes
- If successful testing would support procurement of 300-500 gpd nuclear SCWO unit

M92-GT-0456-09

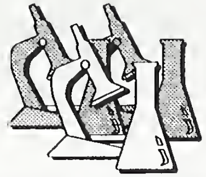
Mixed Waste Integrated Program

700 waste streams are divided into 7 categories

Mixed Wastes

- **100 Aqueous Liquids**
  - 110 Corrosive – Acids
  - 120 Corrosive – Bases
  - 130 Reactives – Cyanide
  - 140 Reactives – Other
  - 150 TC – Metals
  - 160 TC – Organics
  - 180 Hg Containing Solutions
- **200 Organic Liquids**
  - 210 Non-Halogenated Organic
  - 220 Halogenated Organic
  - 230 Scintillation Cocktails
  - 280 Hg Containing Organic
- **300 Inorganic Wastes**
  - 310 Sludges, Filter Cakes, & Residues
  - 320 Absorbed Liquids
  - 330 Ion Exchange Resins
  - 340 Salt Cakes
  - 350 Processing Salts
  - 360 Cemented Sludges
  - 370 Ash & Dusts
  - 380 Soils and Particulate
  - 390 Glass
  - 3A0 Ceramic Crucibles, Bricks, & Media
- **400 Metal Wastes**
  - 410 Ferrous Metals
  - 420 Non-Ferrous Metals
  - 430 Mercury
  - 440 Lead Shapes
  - 450 Activated Lead
- **500 Organic Solids**
  - 510 Absorbed Combustibles
  - 520 Paint & Residues
  - 530 Resins
  - 540 Animal Carcasses
  - 550 Sewage Sludges
  - 560 Wood
  - 570 Plastic & Rubber
  - 580 Paper, Cloth & Rags
  - 590 Heavy Sludges & Asphalt
  - 5A0 Graphite and Carbon
- **600 Heterogeneous Wastes**
  - 610 Construction, Cleanup, and Process Debris
  - 620 Lab Packs
  - 630 Equipment and Gloveboxes
  - 640 Filters
  - 650 Reactor Equipment, Experimental Hardware & Fuel
  - 660 Other Toxic Metal Containing Materials
  - 670 Lead Containing Components and Materials
  - 680 Hg Contaminated Materials
- **700 Potential Problem Wastes**
  - 710 Tritium Wastes
  - 720 Pyrophorics
  - 730 Nitrated Pages and Filters
  - 740 Unstable Organics
  - 750 Compressed Gases
  - 760 Beryllium Wastes
  - 770 PCB Contaminated

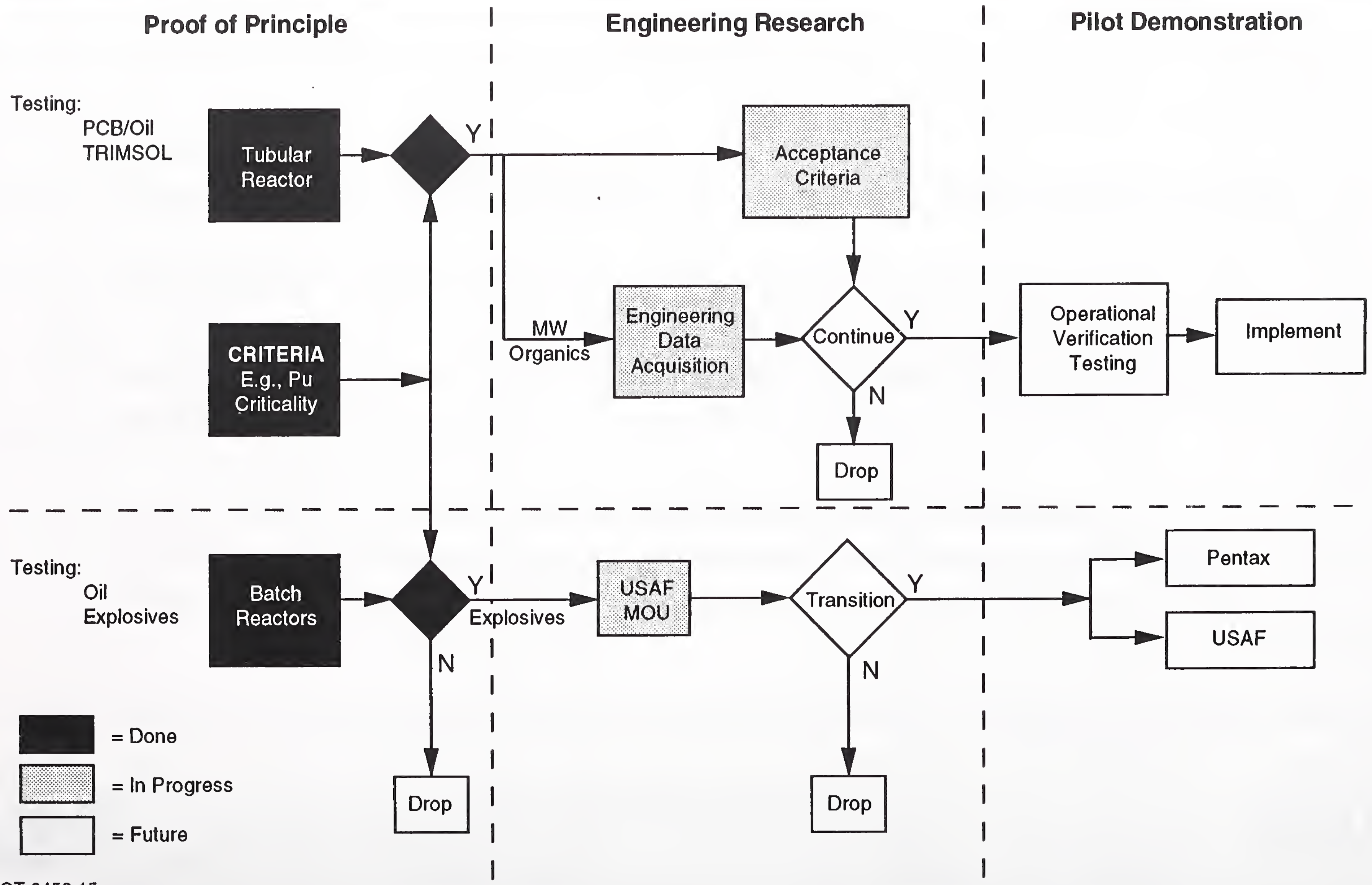
Accomplishments



- Designed, built, and operated reactors of different types and scale for technology evaluation, including chemistry, mixing, materials, system control, components, safety, system engineering, data for scaleup and operational experience
- Developed and validated elementary reaction models showing correlation of oxidation chemistry in supercritical water to low-temperature gas-phase oxidation
- Developed and adapted computer codes for evaluation, design and scaleup
- Shown preliminary feasibility of destruction of a number of propellant and explosive components
- Destroyed selected wastes with high efficiency
- Initiated scoping of flame formation parameters with model componds (subcontract to Sandia)

M92-GT-0456-14

Supercritical Water Oxidation



M92-GT-0456-15

Summary

- SCWO may effectively minimize waste and detoxify contaminants
- SCWO may be cheaper than incineration
- SCWO can give a high efficiency for destruction
- SCWO is a fast process

M92-GT-0456-16

WORKSHOP ON FEDERAL PROGRAMS INVOLVING
SUPERCRITICAL WATER OXIDATION

National Institute of Standards and Technology
Gaithersburg, MD 20899
Administration Bldg. July 6-7, 1992

List of participants

Dr. Steven J. Buelow
Los Alamos National Laboratory
Mail Stop J567
Los Alamos, NM 87545
Phone 505-667-1178
FAX 505-665-4817

Dr. Ugo Bertocci
National Institute of Standards and Technology
Bldg. 223 Rm. B254
Gaithersburg, MD 20899
Phone 301-975-6017
FAX 301-926-7975

Mr. Bob Chappell
DoE Idaho Operations
785 DoE Place - Mail Stop 1230
Idaho Falls, ID 83402
Phone 208-526-0085
FAX 208-526-5964

Dr. Philippe Chastagner
Westinghouse Savannah River
735AD106
P.O. Box 616
Aiken, SC 29808
Phone 803-725-3293
FAX 803-725-5377

Dr. Nina Bergan French
Sandia National Laboratories
Livermore, CA 94551-0969
Phone 510-294-3185
FAX 510-294-1015

Dr. Daniel Friend
National Institute of Standards and Technology
Bldg. 2 Rm. 1305
Boulder, CO
Phone 303-497-5424
FAX 303-497-5224

Mr. T. Mark Hightower
NASA Ames Research Center
M/S 239-11
Moffett Field, CA 94035
Phone 415-604-4443
FAX 415-604-1092

Mr. James A. Hurley
National Institute of Standards and Technology
Bldg. 2 MS 832.01
Boulder, CO 80303
Phone 303-497-3758
FAX 303-497-5044

Dr. Sheridan Johnston
Sandia National Laboratories
Organization 8103
Livermore, CA 94551-0969
Phone 510-294-2138
FAX 510-294-1004

Dr. Richard F. Kayser
National Institute of Standards and Technology
Bldg. 221 Rm. A105
Gaithersburg, MD 20899
Phone 301-975-2483
FAX 301-869-4020

Mr. Richard E. Kirts
Naval Civil Engineering Laboratory
Code L74B
Port Hueneme, CA 93043
Phone 805-982-1334
FAX 805-982-1409

Dr. Richard Loda
DARPA/DSO/MSD
3701 N. Fairfax Drive
Arlington, VA 22303-1714
Phone 703-696-2283
FAX 703-696-2201

Dr. Andrej Macek
National Institute of Standards and Technology
Bldg. 221 Rm. B306
Gaithersburg, MD 20899
Phone 301-975-2610
FAX 301-926-5002

Dr. Robert Mesmer
Oak Ridge National Laboratory
Bldg. 4500-S MS 6110
P.O. Box 2008
Oak Ridge, TN 37831-6110
Phone 615-574-4958
FAX 615-576-5235

Mr. Dennis Miller
U.S. Dept. of Energy, EM-50
Mail Stop GEO-45
1000 Independence Ave.
Washington, DC 20285
Phone 202-586-3022
FAX 202-586-8872

Ms. Grace Ordaz
U.S. Department of Energy
Mail Stop EM-541
1001 Independence Ave.
Washington, DC 20285
Phone 301-903-7440
FAX

Mr. Chris Otten
Federal Office for Military Technology and Procurement
SG III-3
5400 Koblenz
Germany
c/o Naval Surface Warfare Center, Carderock Division
Annapolis, MD 21402
Phone 410-267-3732
Fax 410-267-4874

Mr. Kevin T. Price
U.S. Department of Energy
Idaho Field Office
Idaho Falls, ID 83402
Phone 208-526-5192
FAX 208-526-1184

Lt. Janine Ramirez
WL/MNME
Eglin AFB, FL 32542-5434
Phone 904-882-4212
FAX 904-882-3540

Dr. Richard E. Ricker
National Institute of Standards and Technology
Bldg. 223 Rm. B254
Gaithersburg, MD 20899
Phone 301-975-6023
FAX 301-926-7975

Dr. Michael Rigdon
Institute for Defense Analysis
1801 North Beauregard St.
Alexandria, VA 22311-1772
Phone 703-578-2870
FAX 703-578-2877

Mr. Crane Robinson
U.S. Army Armament Research, Development and Engineering Center
SMCARAES-P
Picatinny Arsenal, NJ 07806-5000
Phone 201-724-5839
FAX 201-724-3162

Mr. Anthony T. Rodriguez
David Taylor Research Center
Code 2834
Annapolis, MD 21402-5067
Phone 410-267-2157
FAX 410-267-4874

Dr. Gregory J. Rosasco
National Institute of Standards and Technology
Bldg. 221 Rm. B306
Gaithersburg, MD 20899
Phone 301-975-4813
FAX 301-926-5002

Dr. Roger Schneider
Rho Sigma Associates
4906 N. Idlewild Ave.
Whitefish Bay, WI 53217-5968
Phone 414-332-0138
FAX 414-332-0015

Dr. Hratch G. Semerjian
National Institute of Standards and Technology
Bldg. 222 Rm. A317
Gaithersburg, MD 20899
Phone 301-975-3145
FAX 301-975-3845

Dr. J.M.H. Levelt Sengers
National Institute of Standards and Technology
Bldg. 221 Rm. A105
Gaithersburg, MD 20899
Phone 301-975-2463
FAX 301-869-4020

Ms. Carolyn Shapiro
EG&G Idaho
P.O. Box 1625
Idaha Fall, ID 83415-3416
Phone 208-526-8688
FAX 208-526-9779

Mr. Richard Steeper
Sandia National Laboratories
Div. 8364
P.O. Box 764
Livermore, CA 94551
Phone 510-294-2618
FAX 510-294-1004

Dr. Hank Strauch
BDM International
12850 Middlebrook Rd.
Suite 300
Germantown, MD 20874
Phone 301-601-1113
FAX 301-601-1107

Dr. Wing Tsang
National Institute of Standards and Technology
Bldg. 222 Rm. A260
Gaithersburg, MD 20899
Phone 301-975-2507
FAX 301-926-4513

Dr. Gideon Varga, CE221
U.S. Department of Energy
1000 Independence Ave. S.W.
Washington, DC 20585
Phone 202-586-0082
FAX 202-586-7114/8134

Dr. James F. Welch
National Institute of Standards and Technology
Bldg. 2 MS 832.01
Boulder, CO 80303-3328
Phone 303-497-3758
FAX 303-497-5044

Dr. Robert E. Zier
BDM International
12850 Middlebrook Rd
Suite 300
Germantown, MD 20874
Phone 301-601-1152
FAX 301-601-1107

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10. SUPPLEMENTARY NOTES

N/A

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

The Workshop on Federal Programs Involving Supercritical Water Oxidation, held July 6 & 7, 1992 at NIST Gaithersburg, was a follow-on to previous informal meetings held to discuss work in this area. The first was held at the Naval Civil Engineering Laboratory, Port Hueneme, CA in March 1990 and the second at Tyndall Air Force Base, FL in April 1991. As with past meetings, the focus of this Workshop was primarily programmatic not technical. These proceedings include the following:

- An Executive Summary
- List of the attendees, their addresses and phone numbers
- Schedule, including the laboratory visits at NIST, of this two day workshop
- Copies of the speakers' viewgraphs. Some speakers submitted additional material which also is included.
- an SCWO Track Chart which summarizes some of the organizations involved in SCWO technology development and their activities.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

Chemical agents, chemical kinetics, explosives, hazardous wastes, industrial wastes, materials performance, nuclear mixed wastes, phase behavior, propellants, supercritical water

13. AVAILABILITY

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