REC-ERC-84-8

OXIDATION OF FORMALDEHYDE SOLUTIONS USED FOR THE PRESERVATION OF REVERSE OSMOSIS MEMBRANES

December 1984

Engineering and Research Center

U. S. Department of the Interior

Bureau of Reclamation

7-2090 (4-81)
Bureau of Reclamation

TECHNICAL REPORT STANDARD TITLE PAGE

1. REPORT NO. REC-ERC-84-8	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.

4. TITLE AND SUBTITLE Oxidation of Formaldehyde Solutions Used for the Preservation of Reverse Osmosis Membranes	5. REPORT DATE December 1984 6. PERFORMING ORGANIZATION CODE D-1523C
7. AUTHOR(S) W. J. Boegli, A. P. Murphy, and M. K. Price	8. PERFORMING ORGANIZATION REPORT NO. REC-ERC-84-8
9. PERFORMING ORGANIZATION NAME AND ADDRESS Bureau of Reclamation Engineering and Research Center Denver, Colorado 80225	10. WORK UNIT NO. 11. CONTRACT OR GRANT NO. 13. TYPE OF REPORT AND PERIOD COVERED
12. SPONSORING AGENCY NAME AND ADDRESS Same	14. SPONSORING AGENCY CODE DIBR

15. SUPPLEMENTARY NOTES

Microfiche and/or hard copy available at the Engineering and Research Center, Denver, CO

Ed: JC

16. ABSTRACT

This report presents the results of an experimental study of a new process for the catalytic oxidation, at ambient temperatures, of dilute formaldehyde used in aqueous solutions for the preservation of cellulose acetate reverse osmosis membranes. The oxidation, involving hydrogen peroxide and an iron (ferric chloride) catalyst, was first tested in a bench-scale adiabatic reactor to develop operating curves for several concentrations of formaldehyde and to show the total oxidation time as a function of selected variables. These variables included initial solution temperature, reactant concentration, stirring rate, and the type of purge gas used above the reaction. In a subsequent series of tests, isothermal data were generated for fitting a temperature and concentration-dependent rate equation.

The reaction, which proceeds by formic acid production, was shown to be effective in completely oxidizing formaldehyde solutions at concentrations at, or greater than, 250 mg/L to carbon dioxide and water (with formaldehyde vapor detected in the product gas stream at less than 0.4 mg/m^3). The oxidation was found to be rate rather than mass diffusion controlled and, based on chemical similitude considerations, can be scaled up directly.

Based on the results of the study, recommendations are made for the design and operation of a full-scale reactor for the Yuma Desalting Plant (now being constructed for the Bureau of Reclamation at Yuma, Arizona). An estimate is also provided for the cost of chemicals used in oxidizing a single flushing from a control block (45 000 L) at an assumed concentration of 1200 mg/L.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. *DESCRIPTORS*-- *desalination/ *reverse osmosis membranes/ ion exchange/ water purification/ *water treatment/ *formaldehyde oxidation/ formaldehyde disposal/ *membrane preservation/ cellulose acetate membranes/ bacteriostat/ pesticide/ organic oxidation

b. *IDENTIFIERS*-- Yuma Desalting Test Facility, Arizona/ *Yuma Desalting Plant/ Wellton-Mohawk Irrigation District/

c. *COSATI Field/Group* 13B *COWRR:* 1302.5 *SRIM:*

18. DISTRIBUTION STATEMENT *Available from the National Technical Information Service, Operations Division, 5285 Port Royal Road, Springfield, Virginia 22161.* (Microfiche and/or hard copy available from NTIS)	19. SECURITY CLASS (THIS REPORT) *UNCLASSIFIED* 20. SECURITY CLASS (THIS PAGE) *UNCLASSIFIED*	21. NO. OF PAGES 57 22. PRICE

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UNITED STATES DEPARTMENT OF THE INTERIOR ★ BUREAU OF RECLAMATION

ACKNOWLEDGMENTS

The authors would like to thank Dr. John Vaughn, Professor of Chemistry, Colorado State University, for his helpful suggestions on kinetics; and Ken Williams, Chemist, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, Maryland, for providing operating conditions for the formaldehyde analysis by ion chromatography.

The research covered by this report was funded jointly by the Bureau's Lower Colorado Regional Office and the Office of Water Research.

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LETTER SYMBOLS AND QUANTITIES

a	Order of the reaction with respect to hydrogen peroxide (formaldehyde to formate)
b	Order of the reaction with respect to hydrogen ion
c	Order of the reaction with respect to ferric chloride
d	Order of the reaction with respect to ionic strength
C	Concentration, mol/ft^3
%C	Percent carbon, carbon concentration/initial carbon concentration
C_p	Heat capacity, Btu/(lb·°F)
D	Diffusivity, ft^2/s
F	Efficiency correction
H°_{298}	Enthalpy, cal/mol
k_4	Thermal conductivity, Btu/(s·ft^2) (°F/ft)
k	Rate constant
k_ψ	$k\,[H_2O_2]^a\,[H^+]^b\,[Fe^{+3}]^c\,[\text{ionic strength}]^d$
L	Length of reactor, ft
m	Order of the reaction with respect to hydrogen peroxide (formate to carbon dioxide)
Q	Heat generated by reaction, cal or Btu/mol
r	Rate expression, mol/(ft^3·s)
R	Radius of reactor, ft
S	Conductance, siemens
T	Temperature, °F
$\triangle T$	Temperature in excess of the wall temperature, °F
u	Linear velocity, ft/s
$\triangle V$	Volume change per unit disappearance of the reactant

α	Wall surface per unit of reactor volume, ft^{-1}
ε	Emissivity or absorptivity of the reactor wall, dimensionless
μ	Viscosity, lb/(ft·s)
ρ	Density, lb/ft^3
γ	Proportionality constant of 0.484, Btu/(s·ft^2) (°F)^4
τ	Torque, g·cm^2/s^2

CHEMICAL FORMULAS

C	Carbon
^{14}C	Radioisotope of carbon
CHO_2^-	Formate ion
CH_2O	Formaldehyde
CH_2O_2	Formic acid
CH_2O_3	Performic acid
CH_3OH	Methyl alcohol or methanol
$CH_2(NaSO_3)OH$	Sodium formaldehydebisulfite
CO	Carbon monoxide
CO_2	Carbon dioxide
$^{14}CO_2$	Carbon fourteen-tagged carbon dioxide
Fe^{+3}	Ferric ion
$FeCl_3$	Ferric chloride
HCl	Hydrochloric acid
$H^{14}CO_3^-$	Carbon fourteen-tagged bicarbonate ion
H_2O	Water
H_2O_2	Hydrogen peroxide
HSO_3^-	Bisulfite ion
N_2	Nitrogen
Na^+	Sodium ion
$NaHCO_3$	Sodium bicarbonate
$NaOH$	Sodium hydroxide
Na_2SO_3	Sodium sulfite
O_2	Oxygen

SUMMARY

This report discusses experimental studies of a new process [1]* for the catalytic oxidation to carbon dioxide and water of the dilute formaldehyde used in the preservation of cellulose acetate membranes. From these studies, conclusions and recommendations are made for the design of a formaldehyde oxidation reactor for the YDP (Yuma Desalting Plant).

One method, suggested by membrane manufacturers, to prevent biological degradation of stored reverse osmosis membranes is the use of a 0.5-percent (5000-mg/L) formaldehyde solution. However, the spent "pickling" solution, anticipated to be between 50- and 1200-mg/L formaldehyde for the YDP after flushing, cannot be discharged into the environment. This paper demonstrates that the Bureau (Bureau of Reclamation) has a safe, workable system for the oxidation of formaldehyde, which would support a petition to obtain a permit for the use of formaldehyde under FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act). The oxidation studies show that use of ferric chloride and hydrogen peroxide will quantitatively oxidize formaldehyde to carbon dioxide and water via formic acid production.

The principal objectives of the oxidation studies were to show that formaldehyde can be oxidized to safe levels, to provide preliminary design data on the process for a full-scale system for the YDP, and to support a request for a permit under FIFRA.

Testing was divided into adiabatic (no heat loss or gain) and isothermal (constant temperature) reactions. The adiabatic tests were used to develop operating curves for several concentrations of formaldehyde and to show total oxidation time as a function of selected variables including initial solution temperature, stirring rate, reactant concentrations, and atmospheric conditions over the reacting solution. The isothermal tests were used to generate data that would fit a temperature- and concentration-dependent rate expression.

Design recommendations are based on thermodynamic calculations for the known oxidations and side reactions, scale-up considerations, and the flushing and disposal requirements for formaldehyde solutions at the YDP. Using thermodynamic calculations, estimates were made of the temperature rise under certain oxidation conditions. The scale-up considerations determined that the oxidation reaction was a rate-controlled rather than a diffusion-controlled process. The conditions for the flushing and disposal of formaldehyde solutions are presented along with estimates of the chemical costs in the appendix.

INTRODUCTION

A reverse osmosis desalting plant is being constructed in Yuma, Arizona, for the Bureau. This plant will be treating water from irrigation returns in the Wellton-Mohawk area and returning it to mix with Colorado River water. Suppliers have recommended that when the reverse osmosis membranes are not in use, e.g., during scheduled plant shutdown or routine plant maintenance, they be stored in a 5000-mg/L formaldehyde solution to prevent microbial attack. Because formaldehyde is a bacteriostat, its use may require a pesticide registration label under FIFRA.

The Impact of FIFRA

The provisions of FIFRA (as amended by 86 Statute 973, 89 Statute 751, 7 U.S. Congress 136, et seq.) regarding registration may be applicable to the proposed use of formaldehyde. However, compliance may not be necessary because the Bureau will not sell, ship, or deliver formaldehyde. Although the Bureau will receive deliveries of formaldehyde, these will be in an essentially closed system, and waste formaldehyde solutions will be safely oxidized to carbon dioxide.

Formaldehyde Disposal Methods

A neutralization process has been developed at the Bureau's Engineering and Research Center in Denver that uses an iron catalyst and hydrogen peroxide at ambient temperature to oxidize formaldehyde to carbon dioxide and water. Earlier, other methods had been reviewed by the Bureau [2]. Two methods are commonly used to prevent stream pollution from formaldehyde. The first [3] is a reaction of the formaldehyde waste with hydrogen peroxide and sodium hydroxide. The reaction products are sodium formate and hydrogen gas. This reaction has been somewhat effective for dilute levels of formaldehyde such as those that would be present in the Yuma plant. However, the formaldehyde oxidation remains incomplete after a considerable reaction time, requires substantial chemical costs, and presents a potential sodium formate and hydrogen gas disposal problem.

The second conventional method [3] requires heating the waste stream to between 100 and 350 °C at a pressure of 200 to 2,500 lb/in^2. At this point, a platinum catalyst and oxygen gas are introduced to achieve oxidation. However, the high temperature and operation pressure make this process unattractive.

ADIABATIC TESTING

The adiabatic testing involved containing the heat of the reaction with an insulated reactor. Although

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* Numbers in brackets refer to entries in the bibliography.

some heat loss would be realized in this experimental apparatus as well as in a full-size plant, results under these conditions are to be contrasted with isothermal testing, where the reaction temperature was adjusted to remain as constant as possible.

The adiabatic testing consisted of five phases. "Beaker tests" determined the range of iron catalyst needed for the matrix (parametric) tests. "Matrix tests" predicted the treatment levels and times needed for quantitative formaldehyde oxidation in a full-scale plant. "Further testing at standard conditions" consisted of monitoring the pH of the reaction and the gas effluent for toxic gases and formaldehyde vapor. "Other considerations of the reaction" involved: (1) studies of the methyl alcohol in the reaction (methyl alcohol is present in formaldehyde solutions as a stabilizer), (2) characterization of the reaction at zero catalyst concentration, and (3) measurements of carbon dioxide in solution. Finally, "Studies of parameters kept constant in the matrix tests" examined the results obtained by varying some of the parameters that had been held constant in the matrix tests.

Beaker Tests

Varying the iron catalyst, while leaving other parameters constant, affected the reaction rate. The purpose of the beaker tests was to find a working range of iron catalyst concentrations that would cause formaldehyde oxidation in a reasonable time (less than 2 hours), during the matrix tests.

Experimental apparatus. – The experimental apparatus consisted of 50-mL beakers with known volumes of formaldehyde solution, hydrogen peroxide, and iron catalyst. The formaldehyde solution used throughout this report contained approximately 12.5 percent methyl alcohol. No attempts were made to remove the methyl alcohol because it would be present in the actual formaldehyde waste.

Experimental procedure. – First, 25 mL of 1000 mg/L formaldehyde was pipetted into each of several test breakers. This formaldehyde solution had been made radioactive beforehand by the addition of radioactive labeled formaldehyde (^{14}C formaldehyde). Next, the desired amount of iron catalyst was mixed into each beaker followed by the addition of hydrogen peroxide at time zero. At specified times, samples (0.25 mL) were pipetted from the reaction beakers into corresponding vials containing a known volume of scintillation cocktail (necessary to measure ^{14}C radioactivity) and immediately mixed. After a sufficient number of samples had been collected, the radioactivity of each sample was measured using a scintillation counter.

Results and discussion. – Figures 1 and 2 show the results of beaker tests performed with varying concentrations of iron catalyst and hydrogen peroxide. The ^{14}C radioactivity is reported as formaldehyde. These tests show that a 0.2-Fe/CH_2O molar ratio would be close to a preferred catalyst level for the reaction.

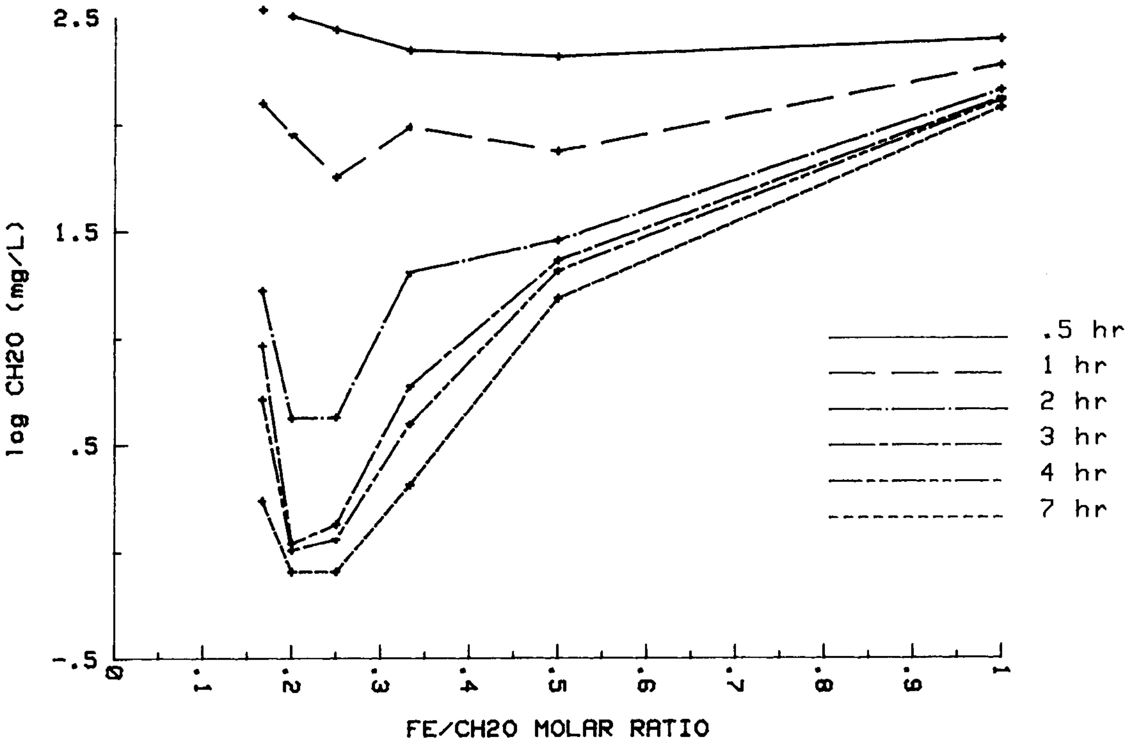
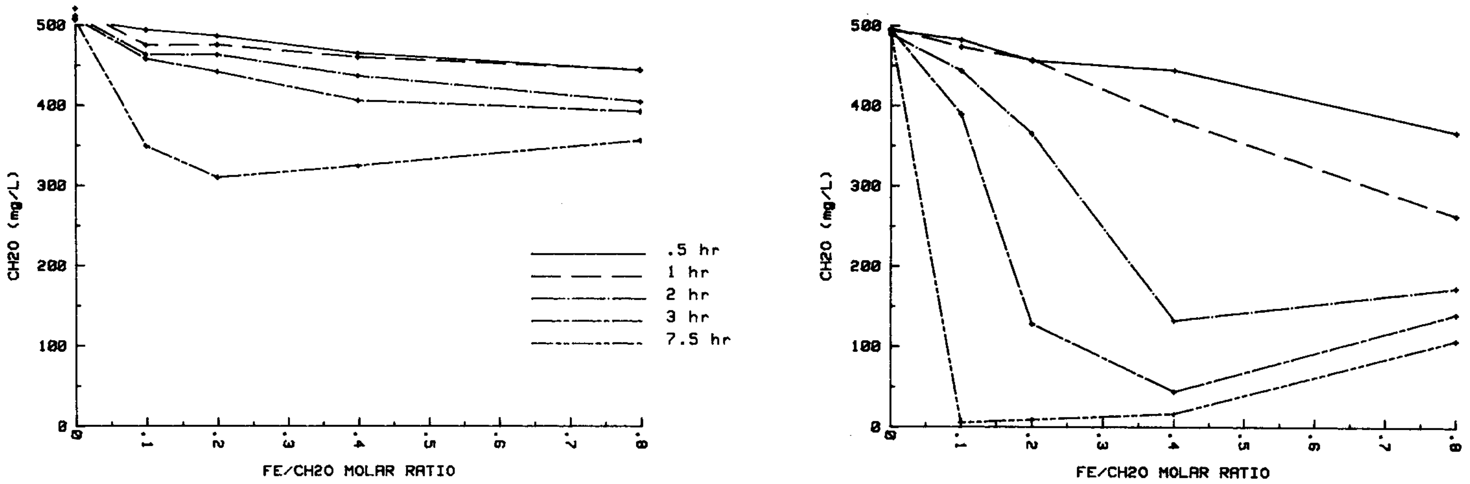
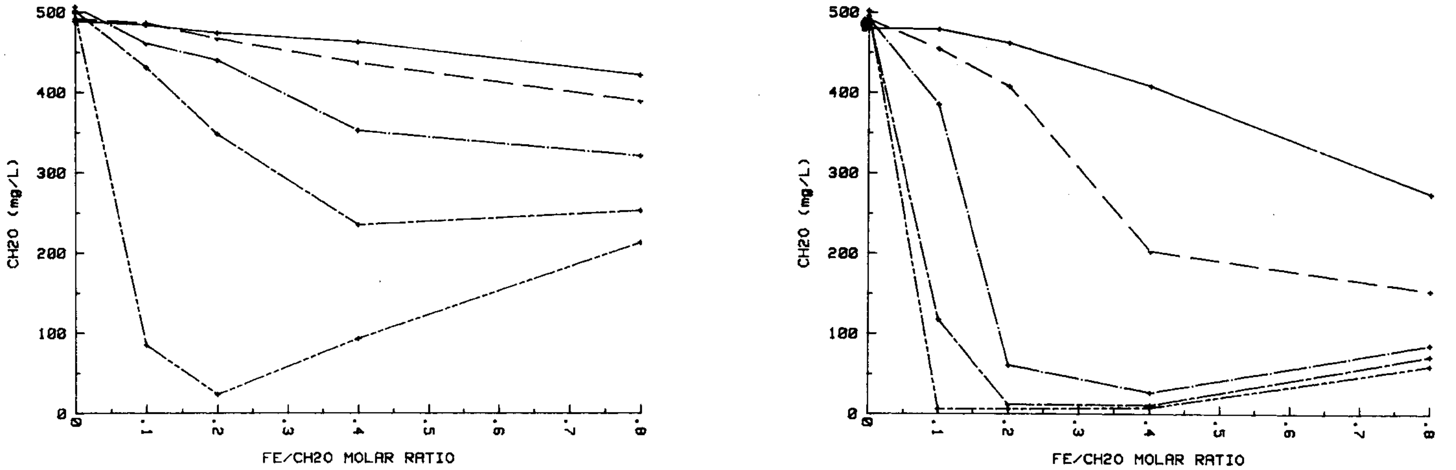


Figure 1. – Relationship of catalyst to formaldehyde revealing an optimum catalyst/formaldehyde ratio (3-times stoichiometric H_2O_2).



(a) 1-times stoichiometric H_2O_2

(c) 3-times stoichiometric H_2O_2



(b) 2-times stoichiometric H_2O_2

(d) 4-times stoichiometric H_2O_2

Figure 2. – Optimum catalyst concentration for varying H_2O_2 concentrations.

The chemistry of the iron catalyst is not well understood except that it behaves as a true catalyst in these experiments. That is, the reaction can proceed again [5], in a similar fashion, with previously used catalyst. Hence, the iron is not consumed but is available again. It has also been shown in later test results that the iron catalyst is necessary to oxidize dilute aqueous formaldehyde to carbon dioxide gas and water within a reasonable time frame.

In investigating various concentrations of iron catalyst, the following two reactions are important:

$$CH_2O + 2H_2O_2 \xrightarrow{Fe^{+3}} CO_2 + 3H_2O \qquad (1)$$

$$2H_2O_2 \xrightarrow{Fe^{+3}} O_2 + 2H_2O \qquad (2)$$

The first reaction is the foundation of this work. The second shows the undesirable autodecomposition of hydrogen peroxide and may explain the optimum catalyst concentration. The autodecomposition of hydrogen peroxide in the presence of heavy metal salts, such as iron, is a well-known chemical reaction [6]. Therefore, increasing the iron catalyst concentration may favor the second reaction, and a point of diminishing returns might be reached where only a small decrease in reaction time would be achieved, at the expense of increased levels of hydrogen peroxide decomposition. This appears to be the case in our testing.

In developing the breaker test experiments, it seemed reasonable to increase the iron-formaldehyde ratio in a molar fashion. Because iron is known [7] to form octahedral complexes in water, there would be available, at most, six possible ligand sites for formaldehyde (or an oxidized carbon species derived from this). Iron (Fe^{+3}) complexes in water are known to have their greatest affinity [8] for oxygen-coordinated ligands, such as phosphate ions, sugars, and presumably formaldehyde and formate.

The aqueous chemistry [9] of iron shows a hydrolysis that can be represented by the following equilibriums:

$$[Fe(H_2O)_6]^{+3} = [Fe(H_2O)_5(OH)]^{+2} + H^+ \qquad (3)$$

$$[Fe(H_2O)_5(OH)]^{+2} = [Fe(H_2O)_4(OH)_2]^+ + H^+ \qquad (4)$$

$$2[Fe(H_2O)_6]^{+3} = [Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{+4} + 2H^+ \qquad (5)$$

The hydrolysis in (4) takes place at acidic pH's of 2 to 3, and to have the hexaquo ion present in appreciable amounts, the pH must be about zero. Hence, the simplest and presumably most abundant species present under the pH conditions of the reaction would be $[Fe(H_2O)_5(OH)]^{+2}$. This means that if the aquo ligands could be displaced by formaldehyde (or perhaps a short-lived species having a formaldehyde carbon nucleus), the ideal 0.2 Fe/CH_2O ratio would be realized.

Figure 3 shows some condensation products that might exist in the reactor. It can be shown that the Fe/aquo ratio must reach a limit since an equation could be written such that if L = number of ligands and a = number of Fe sites, then:

$$\text{for } a > 1$$

$$L = 2(a - 2) + 8$$

$$\text{or } L = 2a + 4$$

and since the limiting ratio of Fe/aquo is desired:

$$\lim_{a\to\infty} \frac{a}{2a+4} = \frac{\lim\limits_{a\to\infty} 1}{\lim\limits_{a\to\infty} \frac{2a+4}{a}} = \frac{1}{2} = 0.500$$

Thus, the maximum value for this relationship must be 0.500. Based on the beaker tests, it seems that the catalyst must be either the mononuclear or binuclear iron condensation product, and the larger polynuclear species are not important in the reactions.

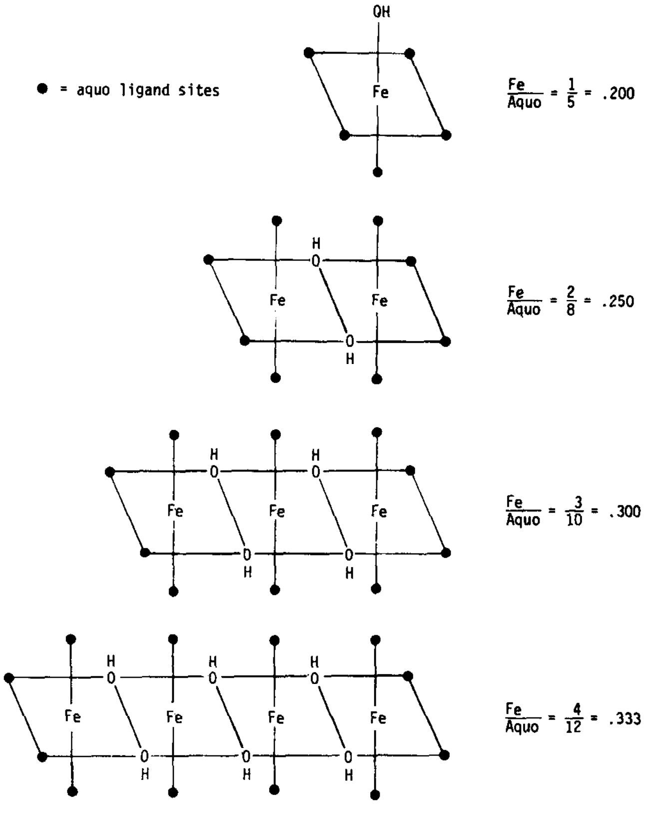


Figure 3. – Iron condensation products.

Matrix Tests

The matrix tests were designed to provide the reactant level data needed for the reaction to operate effectively at the YDP. Because an ideal catalyst-to-formaldehyde ratio was determined from the beaker tests, the catalyst was not varied in the matrix test program. This greatly reduced the amount of data needed. The variables used in the testing were the concentrations of hydrogen peroxide and formaldehyde. Other parameters were held constant. Reactant levels used in test 10 (3-times stoichiometric H_2O_2, 500-mg/L CH_2O, and a 0.2-molar ratio of Fe/CH_2O) became known as the "standard or midpoint conditions," a reference point with which later tests results were compared.

Experimental apparatus. – The matrix test apparatus is shown on figure 4a. The adiabatic reactor (fig. 4b) consisted of an insulated three-angle-neck round-bottom flask. One neck was attached to a three-way connecting tube with two outer and one inner ground glass joints. A 400-mm-long Graham condenser, used to vent product gases into a hood, was connected to one of the outer joints. The second outer joint was fitted with a machined Teflon stopper containing a thermowell. This thermowell was a dead-ended glass tube extending about 2.5 cm into the reaction mixture, which contained approximately 1 mL of water to enhance heat transfer. Temperatures were measured with a platinum RTD (resistance thermal device) sensor connected to a Stow Laboratories electric thermometer, model 911 PL. The temperatures were recorded by a calibrated 10-inch Beckman chart recorder.

The middle neck contained the stirrer with a glass shaft (Curtis Matheson Scientific, 271-593) and a Teflon blade (see fig. 5), connected to a Caframo RZR-1 variable-speed drive. A machined Teflon stopper, with a glass tube inserted, was placed into the third neck, through which a nitrogen atmosphere was introduced to strip out any carbon dioxide gas formed over the solution. Compressed air might have served the same purpose, but concern was expressed over oxygen contributing to the reaction. Gas flow was adjusted and monitored using a Lab Crest ⅛-inch flowmeter.

Fomofill urethane foam was used to insulate the round-bottom flask. The foam and flask were placed in a container 220-by 220-by 175-mm in depth, with the foam rising to the top of the outer necks. Splitting the foam by sawing along the lengths of the necks allowed for easy disassembly after each test. A laboratory jack was used to support the insulated vessel and to allow vertical adjustment and disassembly.

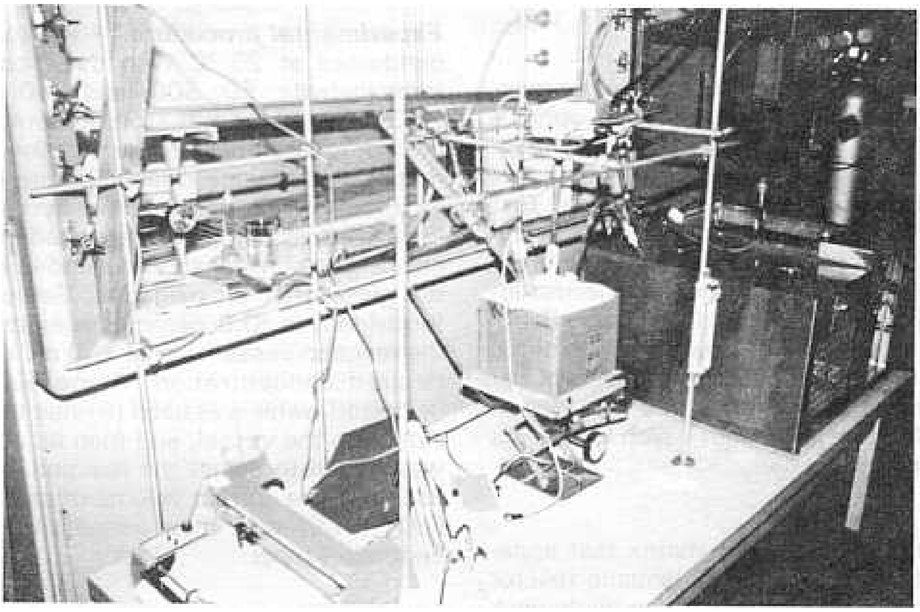
Experimental procedure. – The matrix tests were conducted at 25 °C with three concentrations of formaldehyde, 50, 500, and 950 mg/L, and with 2-, 3-, 4-, and 5-times stoichiometric concentrations of hydrogen peroxide. The reaction vessel and stirring assembly were cleaned before each test with a 2- to 4-molar concentration of hydrochloric acid, followed by rinsing with deionized water. The acid cleaning was necessary to remove iron deposits on the glass after an oxidation. Sufficient ^{14}C tagged formaldehyde (0.5 percent) solution was added to the reaction vessel to give 250 mL of solution at the desired concentration. A measured quantity of deionized water was used to rinse the graduated cylinder into the vessel, and then an additional amount was added to adjust the reaction vessel volume to 250 mL. The correct volume of catalyst (20 percent $FeCl_3 \cdot 6H_2O$) was then added using an adjustable Eppendorf pipet.

Just before each test, the electric thermometer and chart recorder were calibrated against a solution of deionized water at a known temperature. The stirrer was turned on and a 250-mL/min flow of nitrogen was introduced into the vessel.

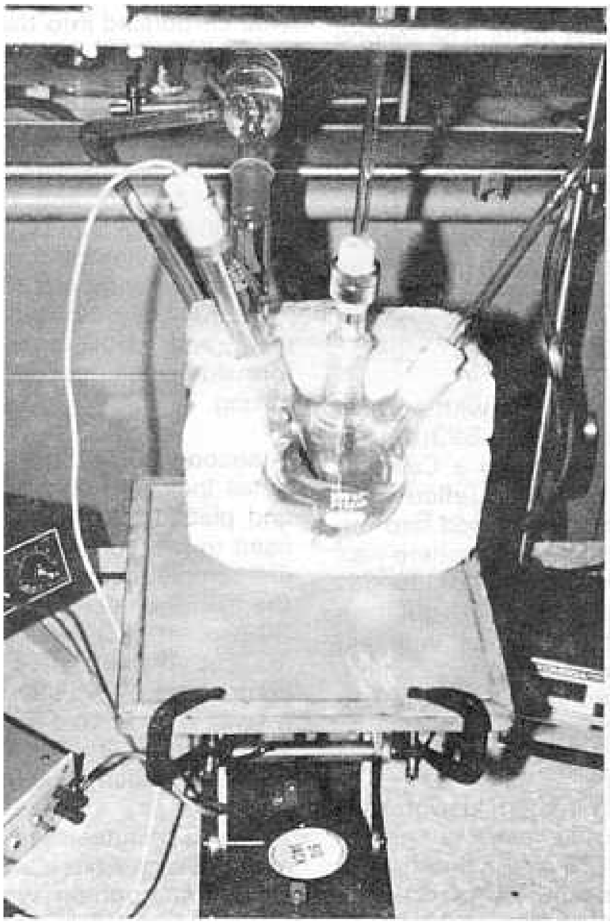
The reaction began with the addition of hydrogen peroxide from an Oxford Laboratories Macro-Set adjustable pipet, which had been calibrated with water. Samples were collected at times of 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, and 144 minutes (a Fibonacci sequence) with a 500-µL pipet. A sample from each of these times was introduced into a 100-mL volumetric flask filled with a sodium bisulfite solution (100 mg/L for the 50-mg/L formaldehyde concentration tests, and 1,000 mg/L for the 500- and 950-mg/L formaldehyde concentration tests) followed by rapid mixing.

A second 500-µL sample was taken at each of the times indicated above, as well as at 200 minutes, and placed into 10 mL of the scintillation cocktail used to measure ^{14}C radioactivity. In addition, an initial sample for ^{14}C was taken at time zero just before the hydrogen peroxide was added. Later, 0.2 mL of 30-percent H_2O_2 was added to each of the eleven 100-mL volumetric flasks and shaken. The same concentrations of bisulfite and peroxide were added to a twelfth flask to serve as a blank. A more dilute solution of H_2O_2, 3 percent, was used for the 50-mg/L formaldehyde concentration reaction samples.

After 15 minutes, samples from each of the volumetric flasks were placed in an autosampler for the ion chromatograph with an S-4 anion column to measure formaldehyde and formate concentration. In addition, the samples were analyzed for ^{14}C concentration. Appendix A gives an explanation of the ion chromatograph and the analytical techniques used.



(a) Experimental equipment. P801-D-80819



(b) Insulated reactor on an adjustable stand. P801-D-80820

Figure 4. – Matrix test apparatus.

Results and discussion. – The matrix was examined varying the hydrogen peroxide and formaldehyde concentrations.

Varying hydrogen peroxide concentration. – The rate of formaldehyde oxidation can be increased by strengthening the concentration of hydrogen peroxide in the reactor. As figure 6 shows, the time needed for the quantitative oxidation of a 50-mg/L formaldehyde solution can vary from 34 to 144 minutes, depending on the initial concentration of hydrogen peroxide. A similar result is shown on figure 7 for the 500-mg/L formaldehyde concentration. At 950 mg/L of formaldehyde (see fig. 8), the rate of formaldehyde oxidation does not vary as much, but continues to show that oxidation occurs faster with increased hydrogen peroxide concentration.

Formate oxidation data as a function of the hydrogen peroxide concentration are also shown on figures 7 and 8. Although no information is available for the 50-mg/L formaldehyde test because of a sampling error, the other samples show the trend of increased oxidation rates with increased peroxide concentration. At 950 mg/L of formaldehyde, the formate oxidation is incomplete even at 144 minutes with 2-times the stoichiometric amount of peroxide, but total oxidation is realized at 34 minutes with 5-times the stoichiometric amount.

The overall temperature change for each test shows that at 50 mg/L of formaldehyde, the reaction proceeded almost isothermally. However, at the 500- and 950-mg/L formaldehyde levels, the temperature change was directly related to the amount of peroxide present. At 950 mg/L of formaldehyde, the increase in temperature correlates strongly with hydrogen peroxide concentration.

The rate of ^{14}C loss correlates with increased levels of peroxide at all three formaldehyde concentrations. In general, a major change in the ^{14}C slope occurs as the formate curve shows a decline. There is also a steady temperature increase as the reaction proceeds, but after the reactants (formaldehyde and formate) are gone, the solution begins to cool off.

The increased reaction rates resulting from higher starting hydrogen peroxide concentrations seem to indicate that the reaction order with respect to hydrogen peroxide is greater than zero. However, another factor to consider is that the tests proceeded adiabatically; therefore, the additional heat generated by the autodecomposition of the hydrogen peroxide to oxygen and water was retained in solution. The data on changing initial temperature (see fig. 20) show that the reaction proceeds faster at higher temperatures. It might also explain the much slower rate of oxidation achieved in the 50-mg/L formaldehyde tests, because there was a much smaller temperature rise.

Varying formaldehyde concentration. – Figure 9 presents the information on figures 6, 7, and 8 in a condensed form. All of the formaldehyde and formate concentrations at a given hydrogen peroxide level are graphed to show more vividly the effects of increasing the hydrogen peroxide concentration. The rate of formate oxidation increases significantly, whereas, the rate of formaldehyde oxidation to formate appears less dramatic. Further information on the oxidation sequence can be found in the section "Other Considerations of the Reaction."

Figure 10 shows the oxidation of 250-mg/L formaldehyde at 3-times stoichiometric hydrogen perioxide. This test was not a part of the matrix tests, but was performed to see if the oxidation behaved more like the 500- or 50-mg/L formaldehyde oxidations. At 200 minutes, the formaldehyde had exited the solution as gaseous carbon dioxide, in contrast to 90 minutes for total conversion at 500 mg/L and only 25-percent conversion after 200 minutes at 50 mg/L. There was concern that reaction times might

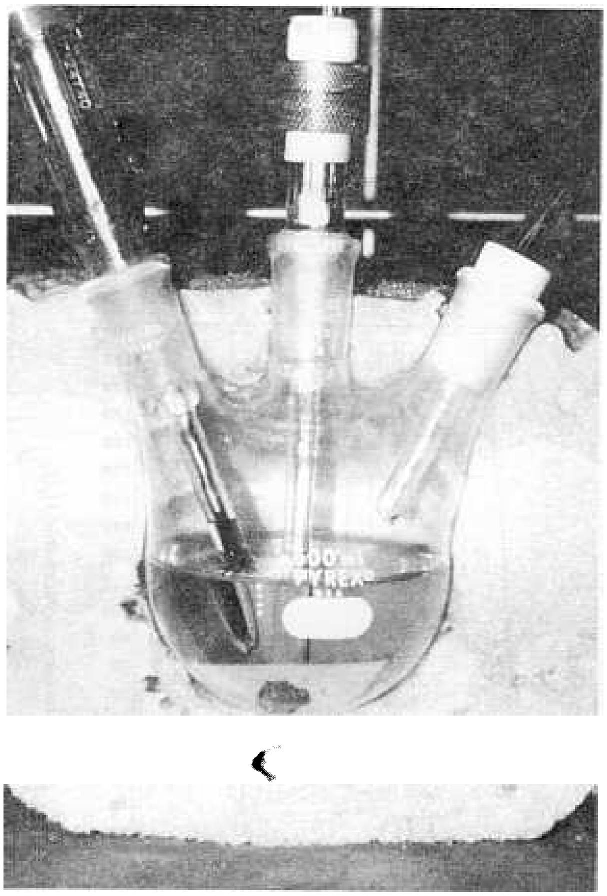


Figure 5. – Reactor showing Teflon stirring blade.
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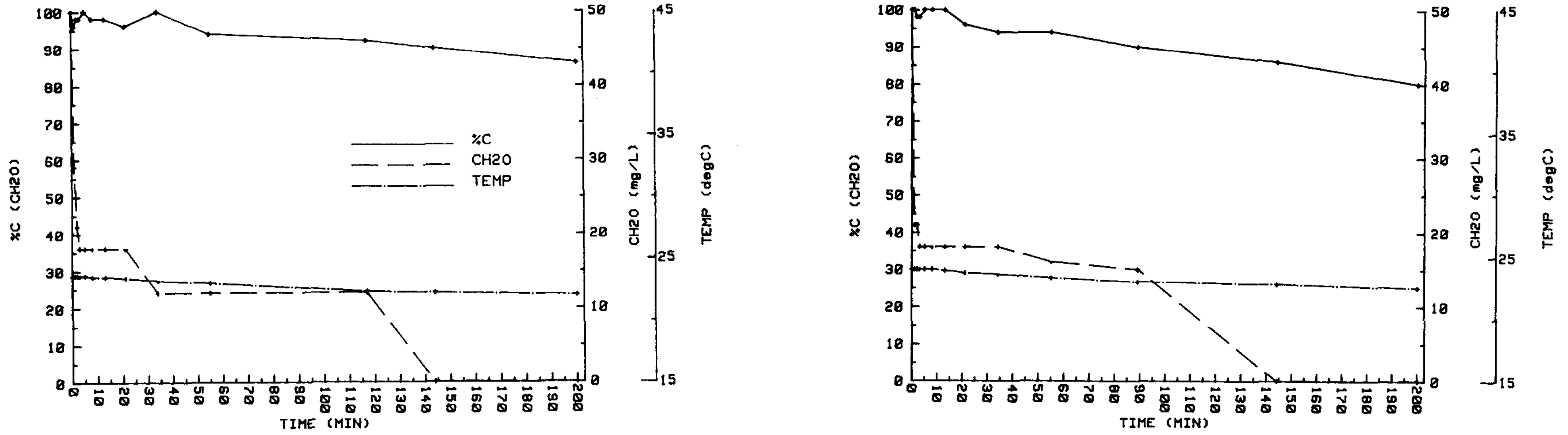
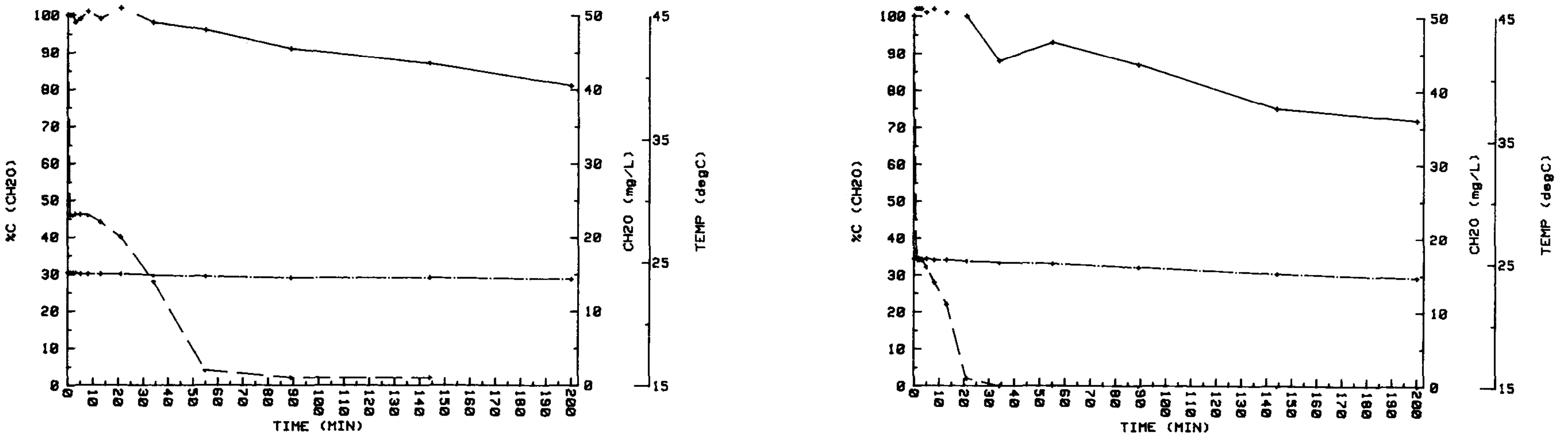


(a) 2-times stoichiometric H_2O_2

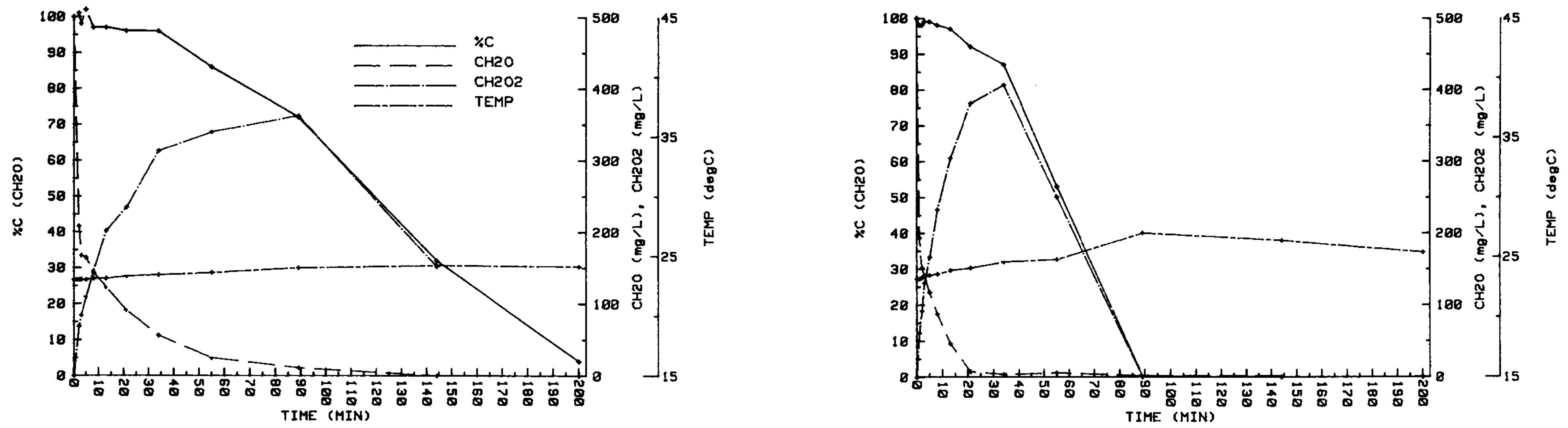
(c) 4-times stoichiometric H_2O_2



(b) 3-times stoichiometric H_2O_2

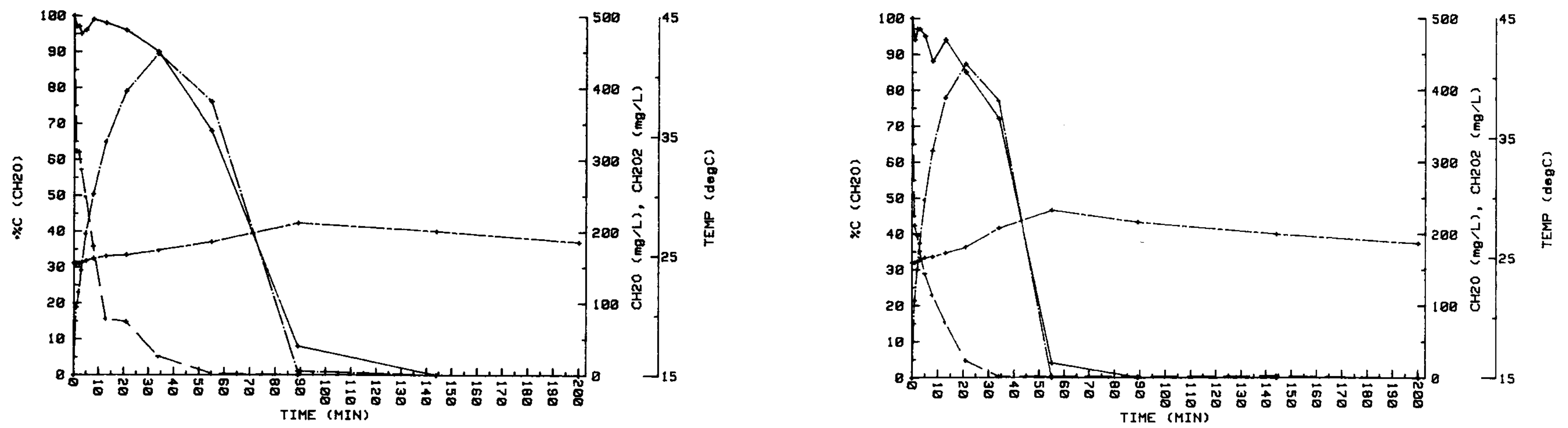
(d) 5-times stoichiometric H_2O_2

Figure 6. – Oxidation with varying H_2O_2 concentration at 50-mg/L CH_2O (Fe/CH_2O = 0.2, 250-mL/min N_2).



(a) 2-times stoichiometric H_2O_2

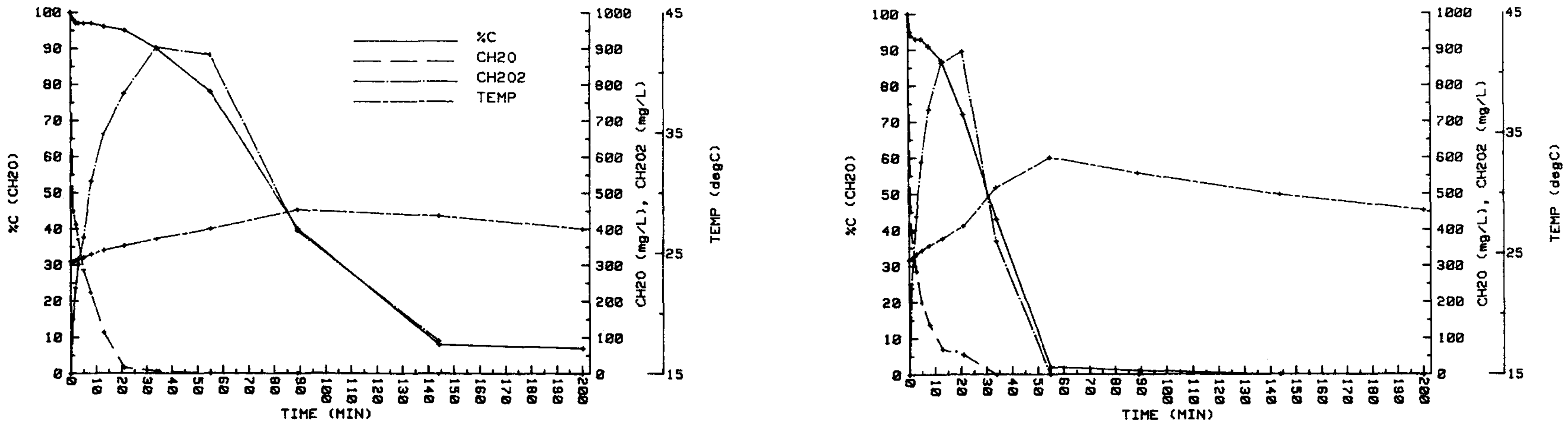
(c) 4-times stoichiometric H_2O_2



(b) 3-times stoichiometric H_2O_2

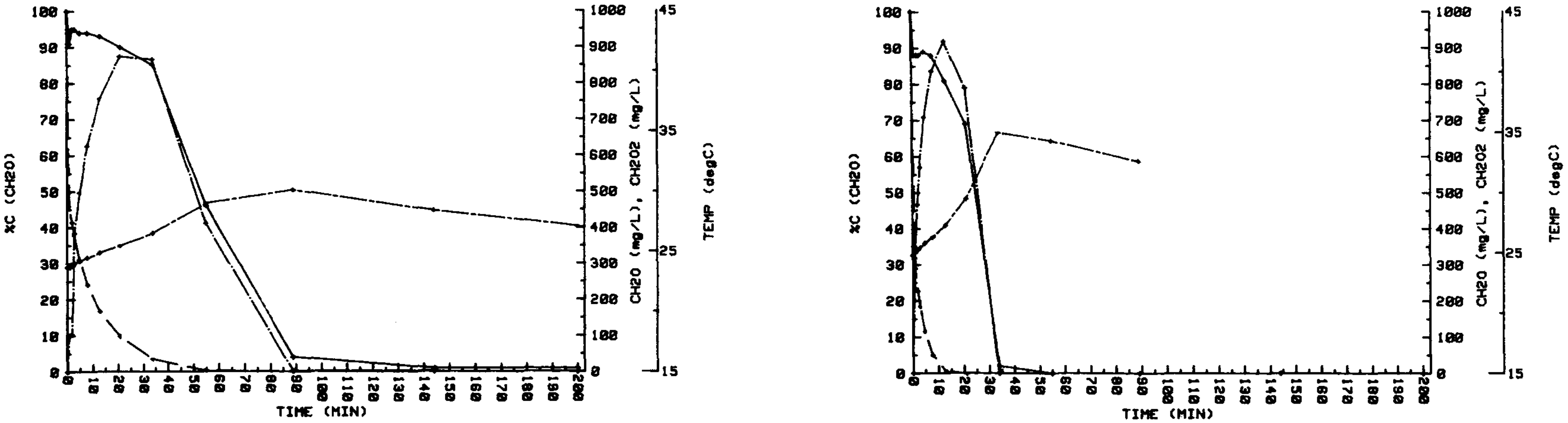
(d) 5-times stoichiometric H_2O_2

Figure 7. – Oxidation with varying H_2O_2 concentration at 500-mg/L CH_2O (Fe/CH_2O = 0.2, 250-mL/min N_2).



(a) 2-times stoichiometric H_2O_2

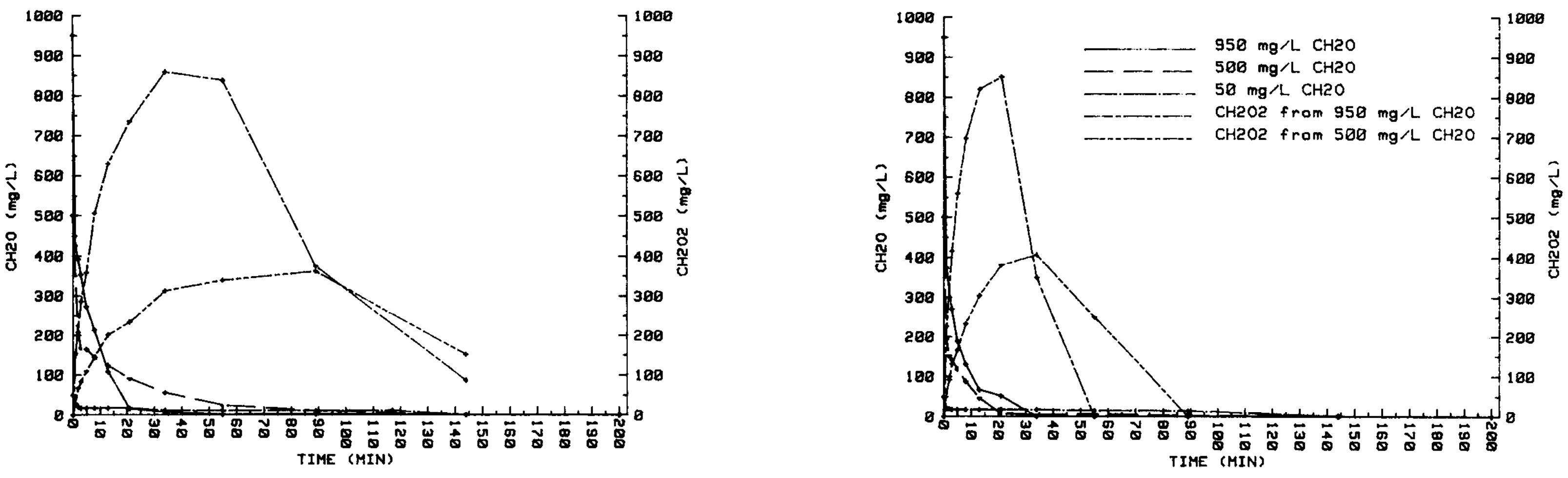
(c) 4-times stoichiometric H_2O_2



(b) 3-times stoichiometric H_2O_2

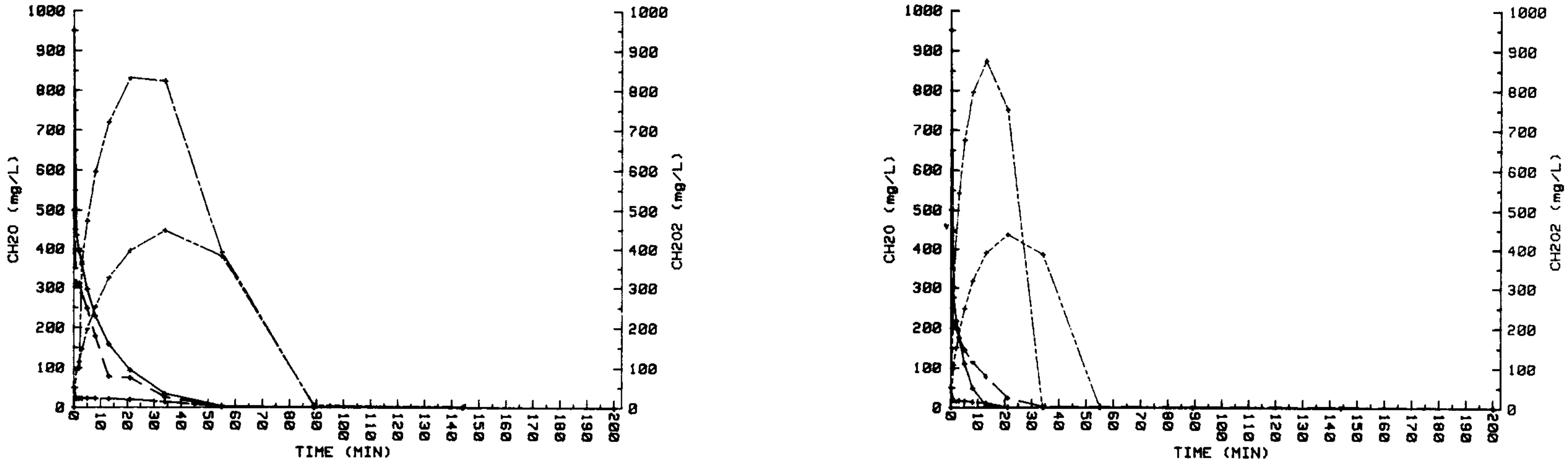
(d) 5-times stoichiometric H_2O_2

Figure 8. – Oxidation with varying H_2O_2 concentration at 950-mg/L CH_2O (Fe/CH_2O = 0.2, 250-mL/min N_2).



(a) 2-times stoichiometric H_2O_2

(c) 4-times stoichiometric H_2O_2



(b) 3-times stoichiometric H_2O_2

(d) 5-times stoichiometric H_2O_2

Figure 9. – Oxidation with varying H_2O_2 and CH_2O concentrations (Fe/CH_2O = 0.2, 250-mL/min N_2).

be too lengthy much below the initial 500-mg/L formaldehyde concentration.

Further Testing at Standard Conditions

Measurements were made of the reaction pH, the nature of the effluent gases, and the amount of formaldehyde vapor escaping the reactor.

Reaction pH. – pH measurements were conducted in the matrix test apparatus with a pH probe inserted in the reactor neck previously used to introduce nitrogen gas. Nitrogen was not used during these tests. The pH was measured with an Orion Research Ionalyzer, model 601A, using a Sargent Welch pH probe, model S-30072-15.

Figure 11a shows the reaction pH as a function of time for the midpoint test conditions. During the first 10 minutes of the reaction, the pH increases, but then remains relatively constant to 55 minutes. The pH then increases from 55 to 89 minutes, and during this time the largest pH change takes place. After 89 minutes the pH begins to decrease towards its original value at time zero. At 200 minutes, the pH meter was turned off.

As the reaction proceeds the pH increases with the greatest rate of change occurring during the time that the formate to carbon dioxide reaction is taking place (see fig. 11b). This could be caused by formic acid (low pH) leaving the aqueous phase as carbon dioxide, which would cause the pH to begin to rise and then drop close to the initial pH, where little formic acid was present. Of course, many factors could contribute to the pH change, such as the hydrolysis of the ferric ion.

Tables 1 and 2 show the pH to be about the same during the 500- and 950-mg/L formaldehyde tests. However, the 50-mg/L tests show a significantly different pH. The small decreases in percent C recorded during oxidation periods might indicate a preferred pH for the reaction or may relate to carbon dioxide solubility. No pH adjustment was tried at 50-mg/L formaldehyde.

Gas effluent testing for product gases. – Figure 12 shows a gas chromatography analysis on the product gases. Oxygen and carbon dioxide were the principal product gases released from the reaction. A relatively small amount of carbon monoxide (less than 27 p/m by volume) was also released. The oxygen probably resulted from a side reaction involving the autodecomposition of hydrogen peroxide. The trace amount of carbon monoxide, detected after the reaction had proceeded for approximately 10 minutes, might be significant in understanding the reaction mechanism.

Gas effluent testing for formaldehyde vapor. – Gas phase measurements of formaldehyde vapor

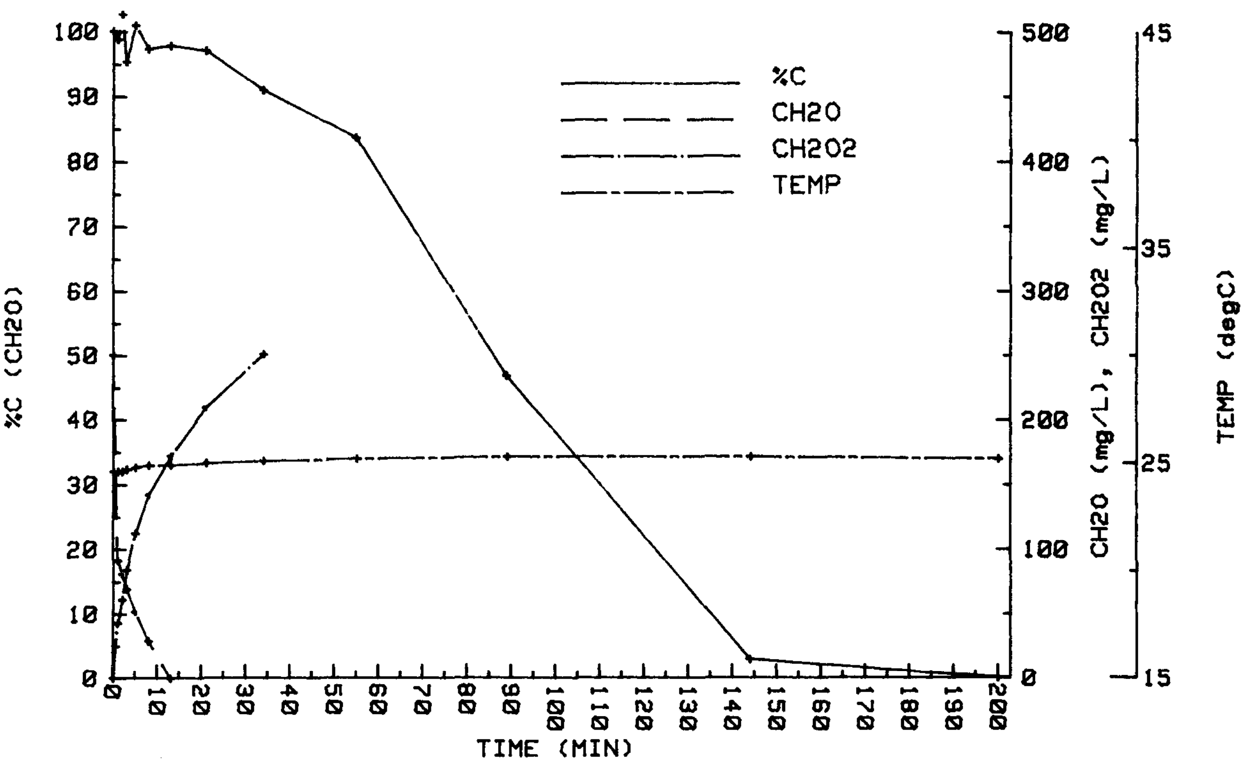
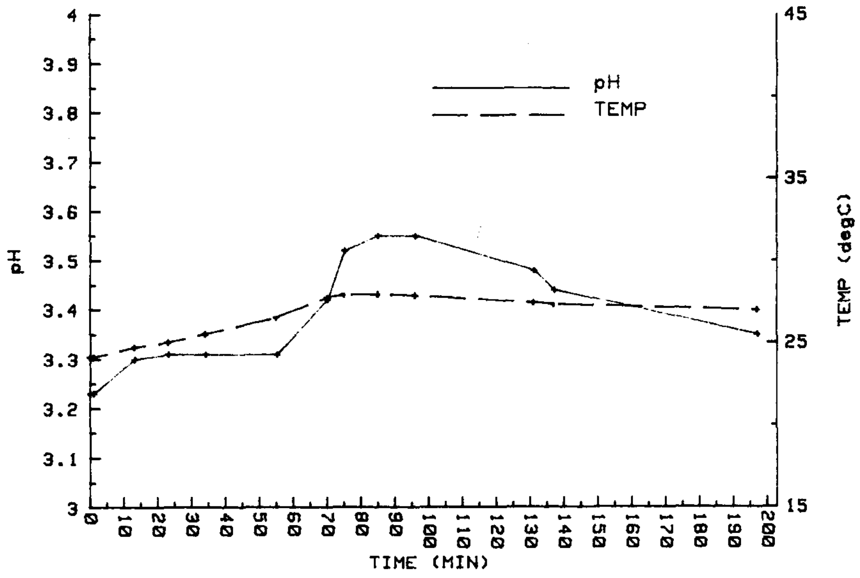
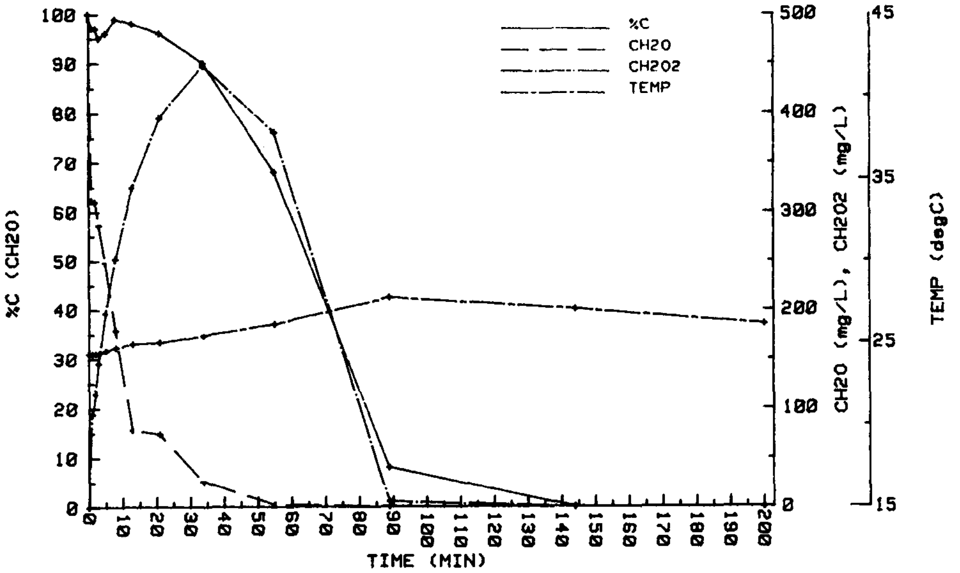


Figure 10. – Oxidation of a 250-mg/L CH_2O solution with 3-times the stoichiometric amount of H_2O_2 (Fe/CH_2O = 0.2, 250-mL/min N_2).



(a) Reaction pH



(b) Chemical species present during the pH measurements

Figure 11. – pH variation at midpoint conditions.

were conducted to determine the concentration of formaldehyde that would exit the reactor and whether these would present a potential health concern for workers in the vicinity. A machined Teflon stopper with a glass tube through the center was placed in the outlet of the condenser. From the condenser, gas flowed through Tygon tubing to a 50-mL bubbler, which was vented into a hood and contained a 1000-mg/L solution of sodium bisulfite used to trap CH_2O vapor. Results of the analyses showed less than 0.4-mg/m^3 formaldehyde in the gas phase at the midpoint test conditions.

Table 1. – Solution pH before and after hydrogen peroxide addition.

CH_2O mg/L	Fe/CH_2O molar catalyst ratio	pH before H_2O_2 addition	pH after H_2O_2 addition
50	0.2	3.70	3.70
500	0.2	3.07	3.14
950	0.2	2.94	2.99

Table 2. – Reaction pH at different formaldehyde concentrations based on beaker experiments.

Time min	50 mg/L	500 mg/L	950 mg/L
0	3.70	3.14	2.99
10	3.70	3.16	3.19
33	3.65	3.26	3.14
55	3.63	3.26	3.25
75	3.55	3.30	3.21

Formaldehyde vapor and carbon monoxide. – The only known concern from the product gases would be escaping formaldehyde vapor and carbon monoxide gas. OSHA (Occupation Safety and Health Administration) has set the permissible exposure limits for the workplace at an 8-hour time-weighted average of 3 p/m or 4.5 mg/m^3 for formaldehyde and 50 p/m or 55 mg/m^3 for carbon monoxide. The TLV's (threshold limit values) as established by the ACGIH (American Conference of Governmental Industrial Hygienists) are 2 and 50 p/m for formaldehyde and carbon monoxide, respectively. These TLV's compare with the one-time maximum readings determined in our testing — 0.4 and 27 p/m for formaldehyde and carbon monoxide, respectively. These numbers, arrived at by sampling directly from the exit port of the condenser, indicate that dangerous levels of toxic gases would not evolve from the reactor. With subsequent dilution by atmospheric air in the workplace, these levels would be considerably lower.

Methyl alcohol. – The formaldehyde solution anticipated to be used at the YDP contains 37-percent formaldehyde with 7-percent methyl alcohol to stabilize the formaldehyde. Concern with the fate of the methyl alcohol through the reaction led to a test on the ^{14}C tagged methyl alcohol to determine the extent of its oxidation. The result of this test is seen on figure 13a and should be compared with the formaldehyde oxidation shown on figure 13b. Both graphs

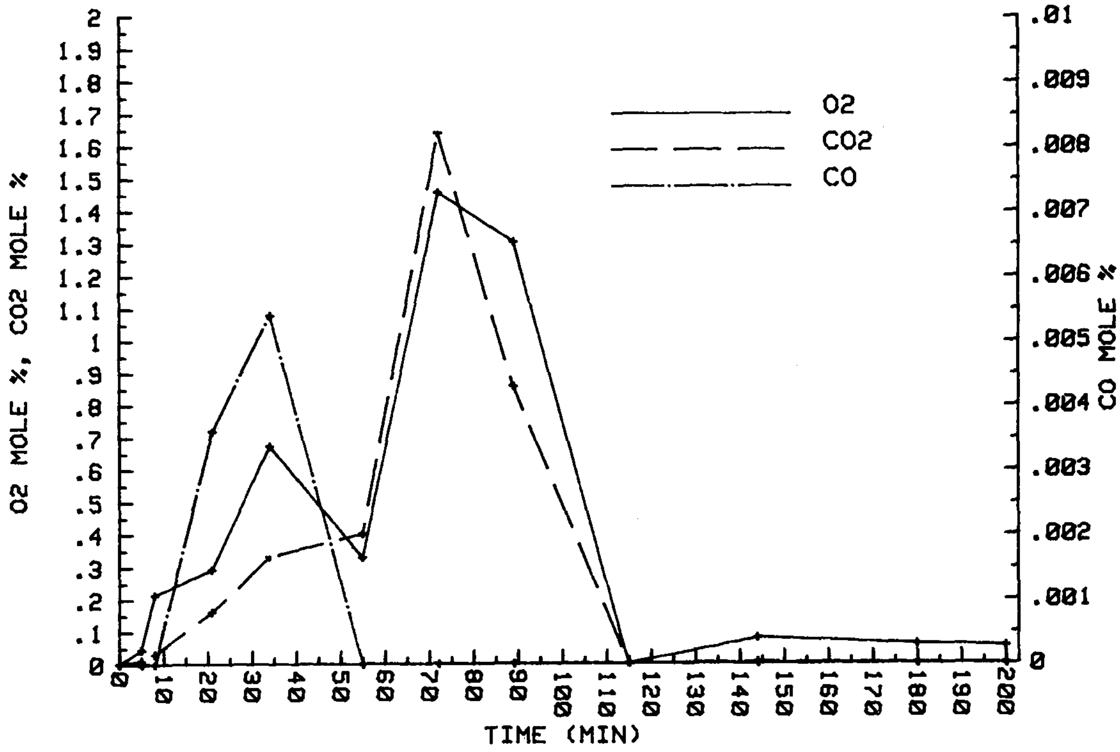
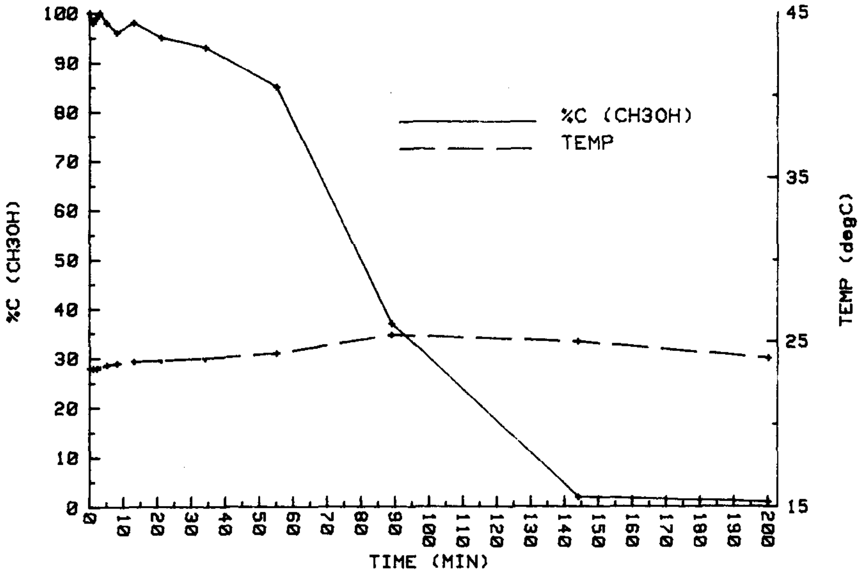
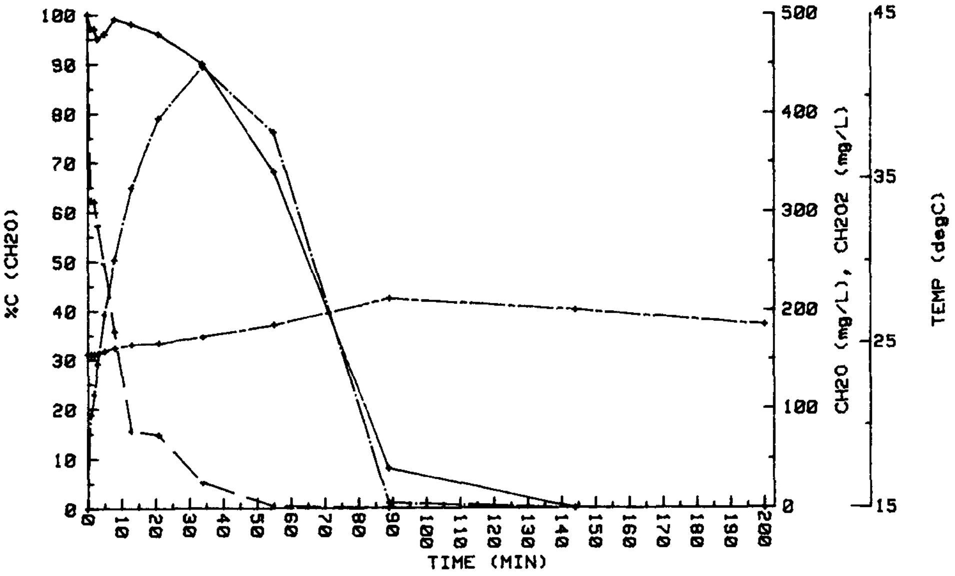


Figure 12. — Gas chromatography of the product gases.



(a) Methyl alcohol oxidation



(b) Formaldehyde oxidation

Figure 13. – Comparison of methyl alcohol oxidation and formaldehyde oxidation at midpoint conditions.

represent data taken at midpoint conditions. Figure 13a shows almost total loss of ^{14}C radioactivity, and the gas phase analysis shows only oxygen and carbon dioxide as the product gases. This indicates that the methyl alcohol is completely oxidized to carbon dioxide in this reaction.

The oxidation of methyl alcohol in the reaction has been demonstrated; however, the details of this oxidation are not known at this time. Methanol may go through a series of oxidations, from formaldehyde to formate and then to carbon dioxide, or it may go directly to any one of these products.

Other Considerations of the Reaction

Two specific areas of interest pertaining to the oxidation related to: first, the presence of residual carbon dioxide in solution (as indicated by ^{14}C measurements) after the disappearance of both formaldehyde and formate, and second, the extent of the reaction without a catalyst or hydrogen peroxide.

Carbon dioxide in solution. – Figure 14 is divided into regions A, B, and C, based on midpoint test data. Region A, beginning at time zero, shows the rapid oxidation of formaldehyde as the principal reaction. Region B begins with the formaldehyde totally oxidized. In region B the principal reaction appears to be the oxidation of formate. Region C begins with formaldehyde and formate essentially oxidized, and as the reaction proceeds through this region, the radioactivity gradually drops until it reaches zero at approximately 144 minutes.

Region C was of special interest because no formaldehyde and little formate was present at the start of region C. If it could be shown that only carbon dioxide is left at the beginning of region C, the reaction solution could be discharged from the YDP at this point with no residual organic carbon in the effluent. However, there was the possibility that other residual organics, such as performic acid, remained in solution.

Performic acid is known to form from hydrogen peroxide and formate. Since the stoichiometry is two peroxides to one formaldehyde, the reactions could be written as:

$$\underset{\text{(formaldehyde)}}{CH_2O\ (aq)} + H_2O_2 \xrightarrow{Fe^{+3}} \underset{\text{(formic acid)}}{CH_2O_2} + H_2O \quad (6)$$

$$CH_2O_2 + H_2O_2 \xrightarrow{Fe^{+3}} \underset{\text{(performic acid)}}{CH_2O_3} + H_2O \quad (7)$$

$$CH_2O_3 \longrightarrow CO_2(aq) + H_2O \quad (8)$$

$$+\ CO_2(aq) \longrightarrow CO_2(g) \quad (9)$$

$$CH_2O\ (aq) + 2H_2O_2 \xrightarrow{Fe^{+3}} CO_2(g) + 3H_2O$$

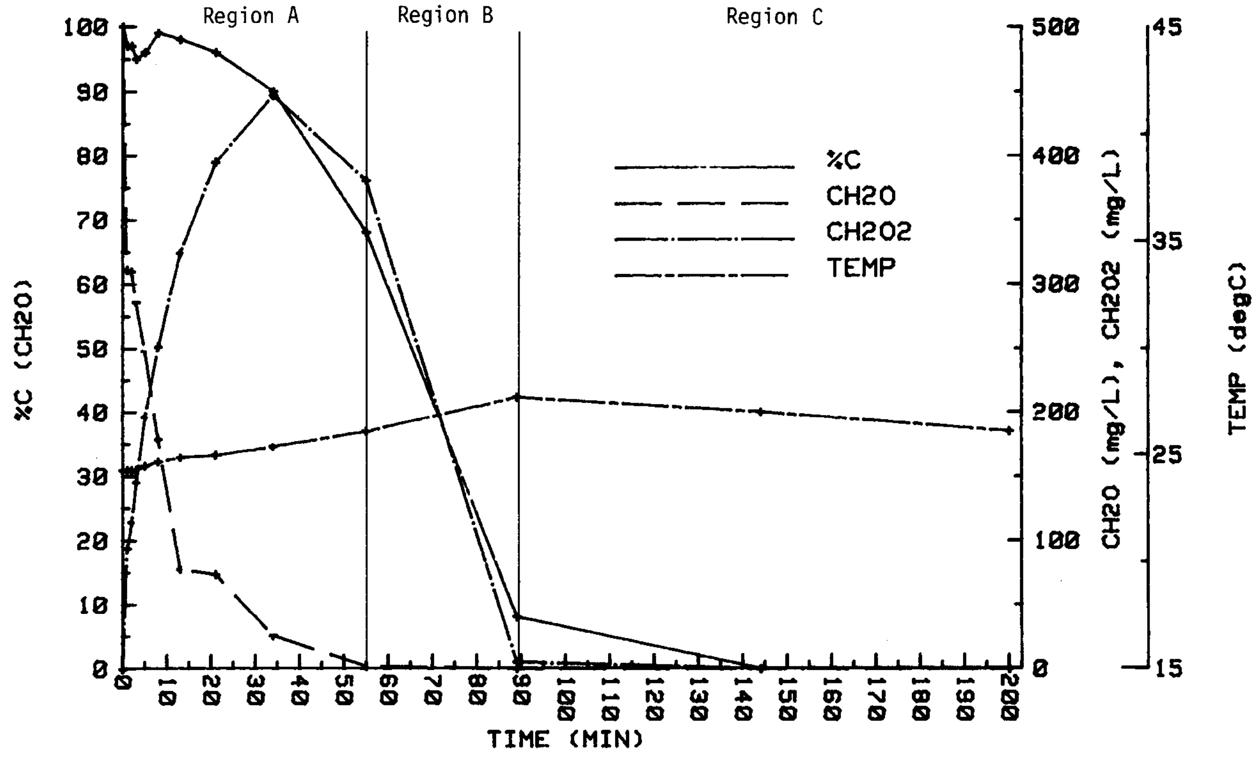


Figure 14. – Regional breakdown of the reaction.

But if performic acid does not form, an equally plausible explanation is the dissipation of CO_2. This set of reactions could be written as:

$$CH_2O\,(aq) + H_2O_2 \xrightarrow{Fe^{+3}} CH_2O_2 + H_2O \quad (10)$$

$$CH_2O_2 + H_2O_2 \xrightarrow{Fe^{+3}} CO_2(aq) + 2H_2O \quad (11)$$

$$+\ CO_2(aq) \longrightarrow CO_2(g) \quad (12)$$

$$CH_2O\,(aq) + 2H_2O_2 \xrightarrow{Fe^{+3}} CO_2(g) + 3H_2O$$

The reaction could also continue in region C with other unknown carbon compounds. The most direct approach to solving this problem was to attempt to show that residual carbon dioxide was the form of carbon in solution.

Two experiments were performed to establish that the product in region C was carbon dioxide. The first experiment studied the dissipation of carbon dioxide from the reaction solution. A reaction using midpoint conditions was run for 200 minutes. Next, 0.3 mL of extremely dilute but radioactive $NaHCO_3$ was introduced below the surface of the reaction solution. The small amount of $NaHCO_3$ used was assumed to have no effect on the reaction chemistry. Because the reaction solution is acidic, pH about 3.0, the $NaHCO_3$ was expected to form carbon dioxide as follows:

$$Na^+ + H^{14}CO_3^- + H^+ \longrightarrow Na^+ + {}^{14}CO_2 + H_2O$$

The N_2 flow to the reactor was closed off, and samples of the aqueous phase were taken at various times. Table 3 shows the results of this study to 135 minutes total reaction time. As can be seen, carbon dioxide gas diffuses from the solution very slowly, despite the midpoint stirring rate of 100 r/min. After the 100-minute sample was taken, N_2 gas was allowed to flow across the surface of the reacting solution. The last two samples show the decrease in radioactivity caused by replacing the $^{14}CO_2$ atmosphere over the solution with N_2. The results of this work seem to indicate that the residual radioactivity was carbon dioxide, as anticipated.

Table 3. – Carbon dioxide dissipation study.

Time min	Percent C (CO_2)
0	100
1.5	90
3.0	84
5.0	76
10.0	66
20.0	50
30.0	42
60.0	32
100.0	33
*105.0	23
*135.0	11

* After N_2 purge.

The second experiment, known as "rapid mix," was designed to cause the rapid transfer of all gases from the reaction solution into the gaseous phase above the solution and from there quickly into a vented hood. This was achieved by carrying out the reaction in a fleaker (similar to a breaker but with a more tapered top) with an extremely high mix rate causing a large vortex. Nitrogen gas was introduced into the vortex region to displace all gas products formed.

The rapid mixing test was run at the midpoint conditions: 500-mg/L CH_2O, H_2O_2 at three times the stoichiometric relationship, and a 0.2 molar ratio of Fe/CH_2O. A known weight of ^{14}C tagged formaldehyde was poured into a fleaker followed by deionized water at 25 °C to obtain the desired concentration of formaldehyde. IC (ion chromatography) and scintillation analyses were done on samples collected every 5 minutes for 85 minutes. The method of data collection was the same as that described for the matrix test with the following exceptions: no 30 percent H_2O_2 was added to the 100-mL bisulfite volumetric flasks after the sample was taken for IC analysis, and stirring was stopped momentarily to collect each sample.

The thought behind the "rapid mix" experiment was that if the reaction in equation 11 takes place (formate oxidized to carbon dioxide), then the decrease in radioactivity should closely correlate with the decrease in formate, with both values reaching zero together. If this is not the case, then something other than a gaseous product must be forming as a result of the reaction between hydrogen peroxide and formate. Table 4 and figure 15 show the results of this test. Based on both this and the previous (CO_2 dissipation) test, it appears that the reaction sequences in equations 10, 11, and 12 are being followed and that carbon dioxide is, as hypothesized, the main product.

The reaction with no catalyst and no peroxide. – Figure 16 shows the results of two tests: one using no catalyst and the other with no hydrogen peroxide. As seen in the reaction without a catalyst, the hydrogen peroxide itself caused no carbon dioxide formation, even after a 22-hour waiting period. Similar results are shown for the reaction without hydrogen peroxide.

Table 4. – Rapid mix experiment.

Time min	Formate moles C x 10^3	^{14}C moles C x 10^3
0	0	1.67
5	0.25	1.58
10	0.44	1.55
15	0.54	1.50
20	0.69	1.47
25	0.82	1.38
30	0.86	1.30
35	0.87	1.20
40	0.80	1.10
45	0.78	0.95
55	0.49	0.57
65	0.07	0.17
75	0	0.02
85	0	0.005

Studies of Parameters Kept Constant in the Matrix Tests

Stirring rate, initial temperature, catalyst concentration, and the rate of nitrogen gas flow over the surface of the reaction were all kept constant during the matrix tests. The results of varying each of these parameters were also examined in a separate set of studies.

Stirring rate. – Figure 17 shows the effect stirring rate has on the formaldehyde oxidation with all other test parameters fixed. The curves show that the rate of formaldehyde oxidation is generally independent of stirring over the range of rates evaluated (0 to 125 r/min). At all four stirring rates, the formaldehyde is completely oxidized to carbon dioxide by the time the 89-minute sample is taken.

Formate analyses at stirring rates of 0, 75, and 100 r/min show about the same rate of formate production, reaching a maximum concentration at the 34-minute sample and then oxidizing fairly rapidly. The 89-minute sample shows that the formate has been completely oxidized.

Samples stirred at 125 r/min show that the formate oxidation has been drawn out somewhat and that total oxidation has been achieved at 144 minutes.

Sample temperatures at stirring rates of 0, 75, and 100 r/min reach a maximum at 89 minutes and then proceed to cool slightly. The cooling is probably due to the positive value for the Joule-Thompson coefficient (μ_{JT}) for nitrogen gas. At a stirring rate of 125 r/min temperature is almost constant.

The ^{14}C data were affected by the stirring rate. At 0 and 75 r/min, there is residual carbon at 144 minutes. At stirring rates of 100 and 125 r/min, however, the ^{14}C has returned to zero after 144 minutes.

Another observation on increased stirring rate is the correlation between the formate oxidation and ^{14}C

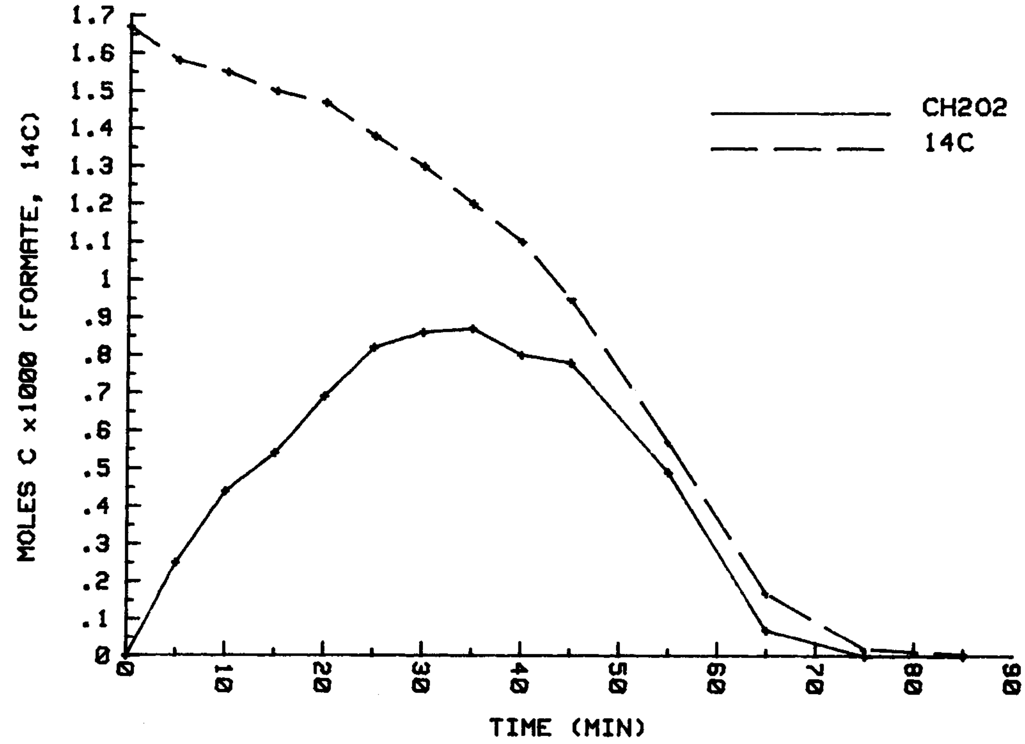
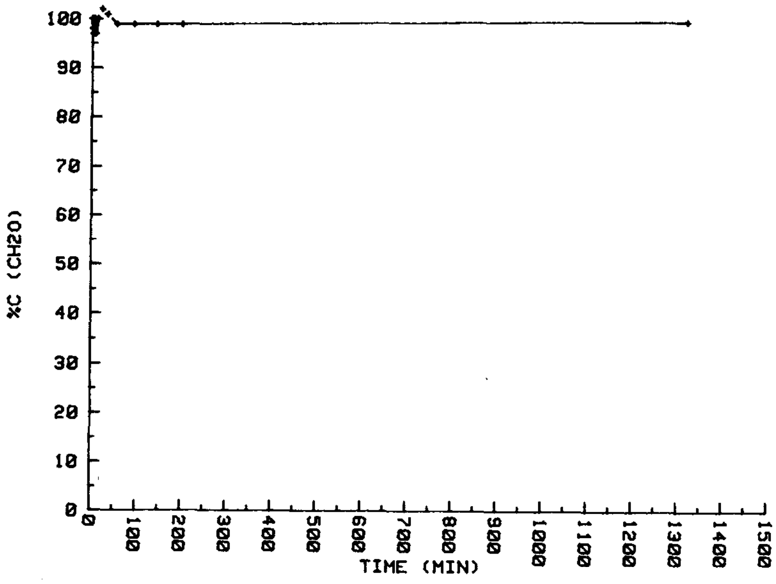
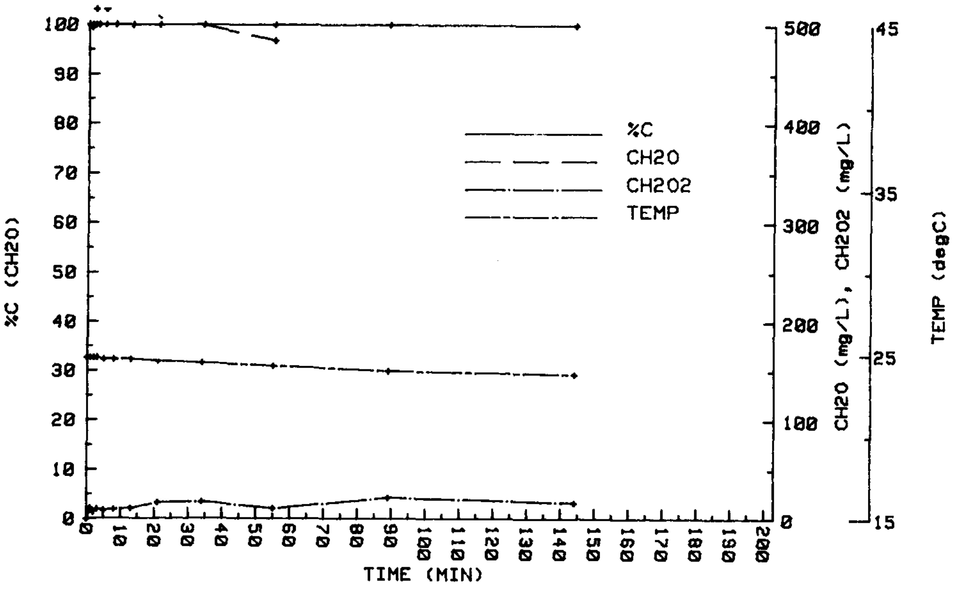


Figure 15. – Rapid mix experiment showing the simultaneous decline of formate and carbon in solution.

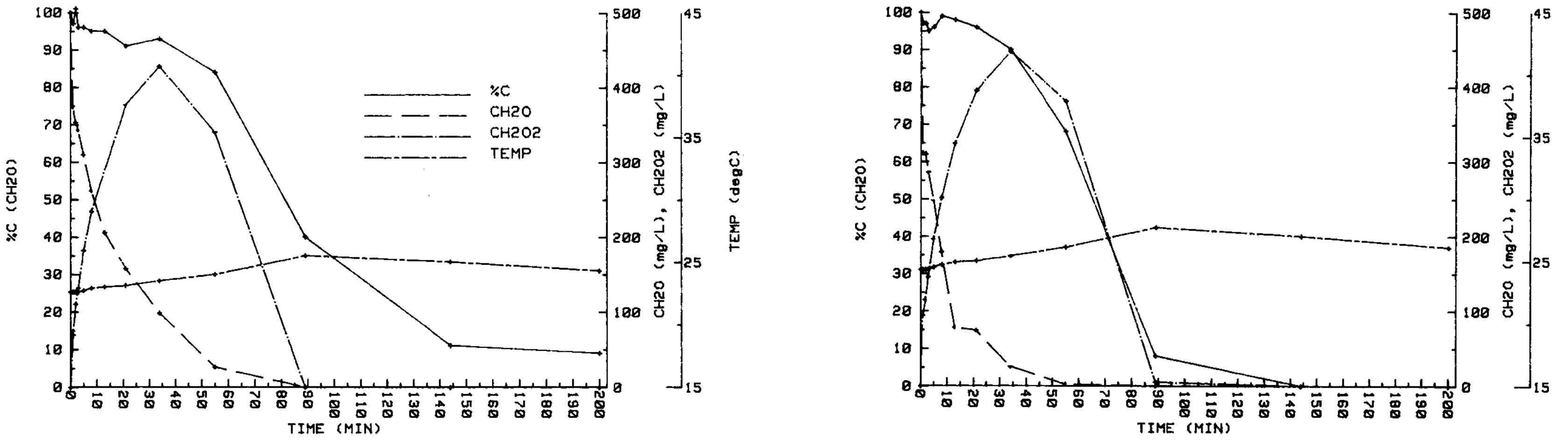


(a) Oxidation without Fe^{+3} catalyst



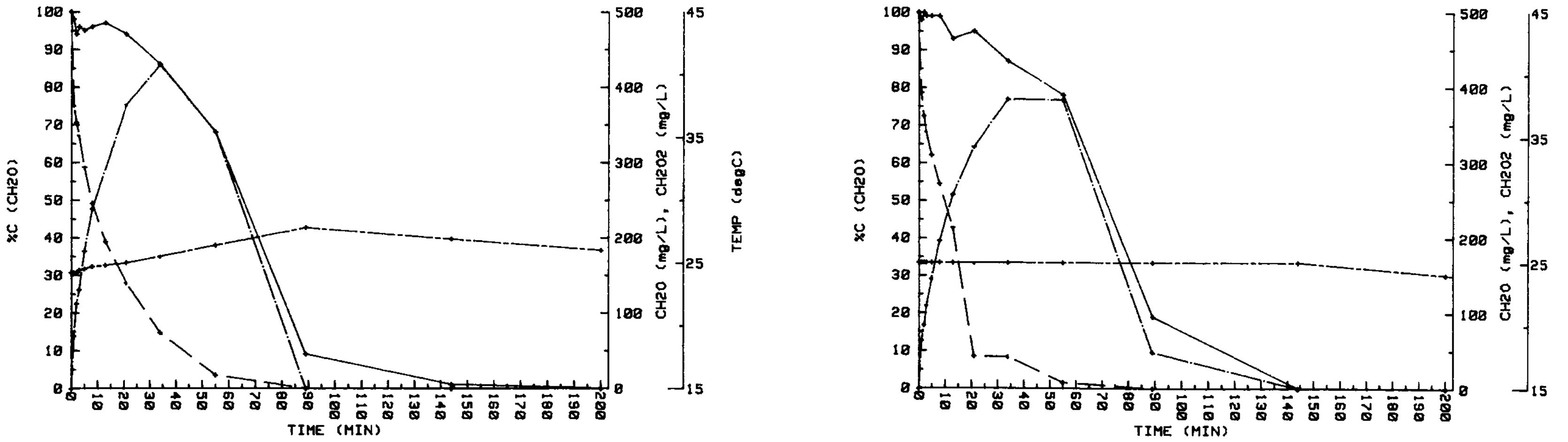
(b) Reaction without H_2O_2

Figure 16. – Reaction at midpoint conditions showing the effects of oxidation without catalyst and without H_2O_2.



(a) Stirring rate at 0 r/min

(c) Stirring rate at 100 r/min



(b) Stirring rate at 75 r/min

(d) Stirring rate at 125 r/min

Figure 17. – Effects of stirring rate on oxidation at midpoint conditions.

data. As the stirring rate is increased the formate oxidation tracks more closely to the ^{14}C loss. At a stirring rate of 125 r/min the formate and ^{14}C both reach zero at 144 minutes.

The stirring rate probably affects the reaction by increasing both the heat and mass transfer coefficients and the liquid-vapor boundary (as liquid is forced up the sides of the reactor vessel). This provides a feasible explanation for the rapid decline in the ^{14}C slope with respect to the stirring rate where the formate-to-carbon dioxide reaction predominates. It might also explain the reduction in the reaction rates due to cooling.

The formate oxidation is complete at 89 minutes with stirring rates of 0, 75, and 100 r/min, and tests show that at this point only residual carbon dioxide remains. When the curves of formate oxidation are examined for all four tests, the rate of oxidation to carbon dioxide appears to be generally independent of the stirring rate, with the possible exception of the somewhat retarded reaction at 125 r/min. The dissipation of carbon dioxide does correlate somewhat with stirring rate based on ^{14}C data. This indicates that stirring is an important variable when residual carbon dioxide in the effluent is a concern. The reaction

$$CH_2O_2 + H_2O_2 \xrightarrow{Fe^{+3}} CO_2\,(aq) + 2H_2O \qquad (13)$$

must proceed in the forward direction with the carbon dioxide product gas having little inhibiting effect. Data shown in the next section, in which pure carbon dioxide gas is used as a purge gas in place of nitrogen, indicate only a minimal change in the oxidation rate.

The atmosphere over the reacting solution. – One of the concerns in setting up the experimental procedure was the effect of gaseous products in a reversible reaction. If a step in the oxidation was reversible, then preventing the escape of that product from the reactor would not allow as complete a reaction in the forward direction, i.e., the product would eventually exist in equilibrium with the reactants. As a precaution, the matrix tests were run with a nitrogen purge that continuously replaced the gas above the reacting solution.

In the early phases of these experiments, significant differences in the data began to show when compared with that obtained in the beaker tests (reactor experiments were based on the beaker test results shown on figures 1 and 2). The problem was residual ^{14}C, which was of considerable concern since the desire was to quantitatively oxidize formaldehyde to carbon dioxide gas. Figure 18 shows this residual radioactivity from early matrix testing using no N_2 flow. It was concluded that one significant difference between the two sets of experiments was that the

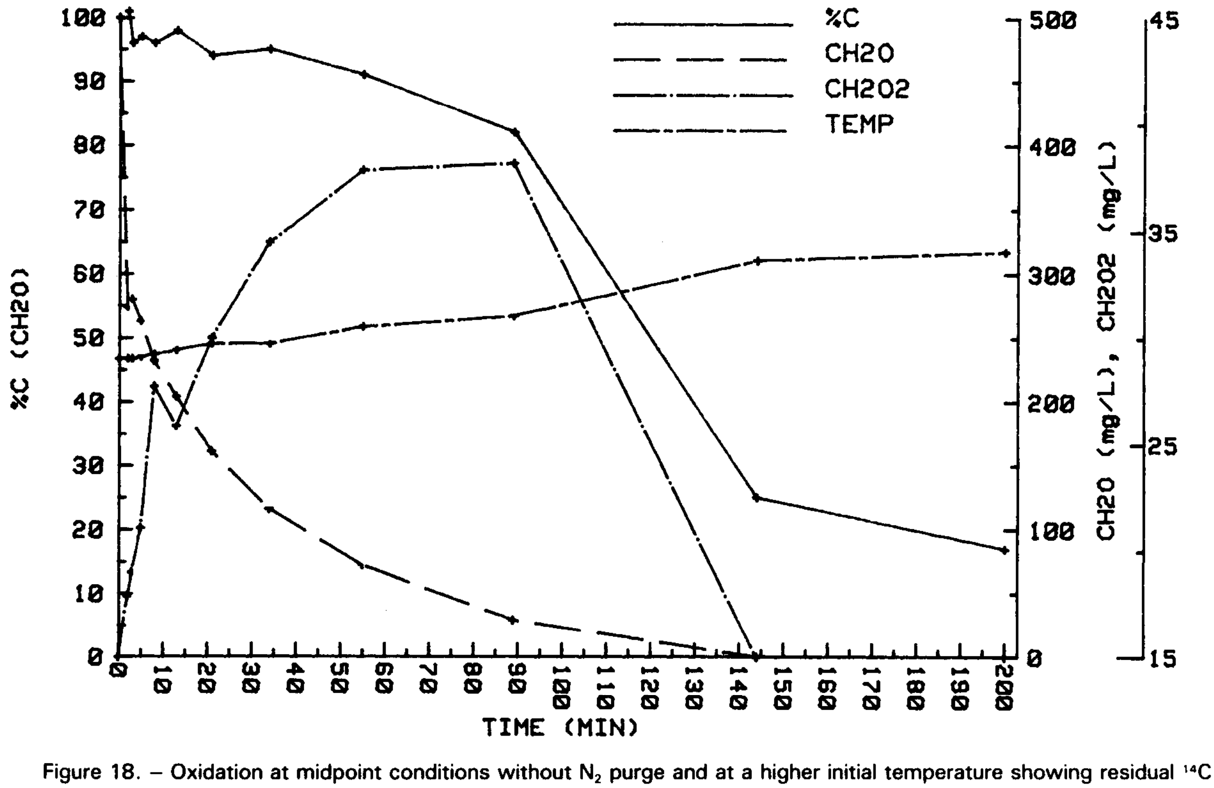
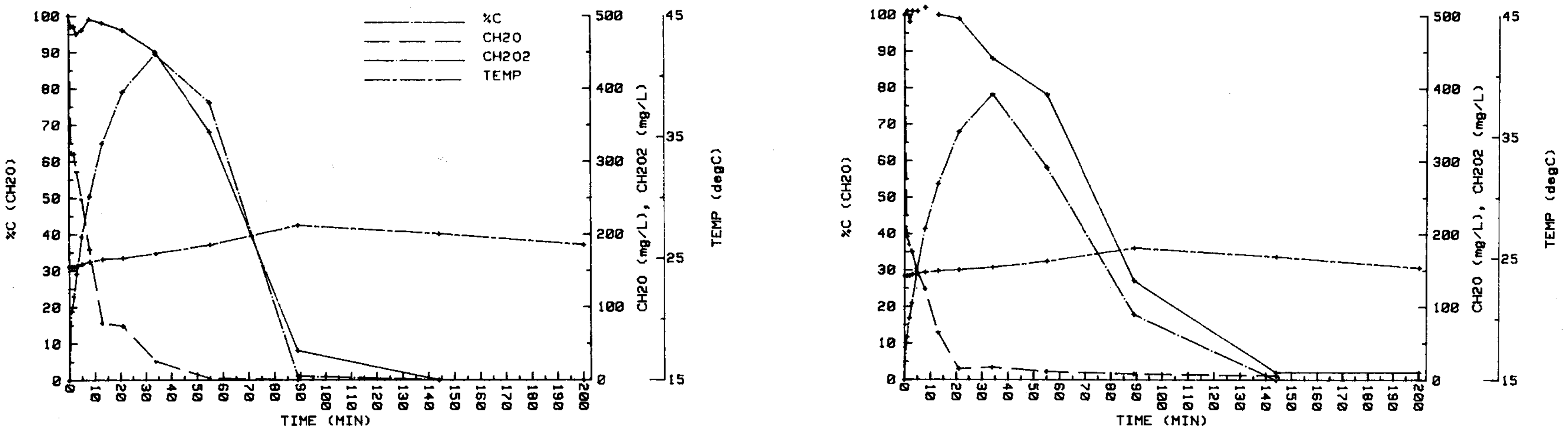
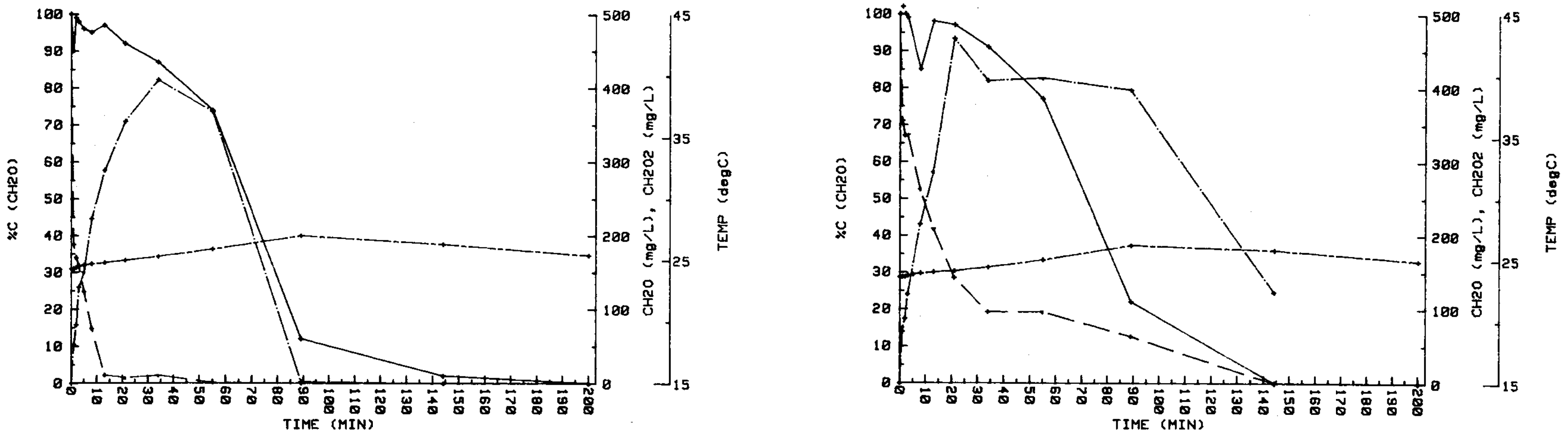


Figure 18. – Oxidation at midpoint conditions without N_2 purge and at a higher initial temperature showing residual ^{14}C.



(a) Oxidation using N_2 purge gas

(c) Oxidation using CO_2 purge gas



(b) Oxidation using O_2 purge gas

(d) Oxidation using CO purge gas

Figure 19. – Effects of different purge gases on oxidation at midpoint conditions.

beakers were open and air passed across the top, replacing product gases, whereas, in the matrix tests product gases were vented. Product gases may be responsible for ^{14}C residuals for one or more of the following reasons: equilibrium shifting backward in the reaction; a particular gaseous product having a strong inhibiting effect (trace levels of carbon monoxide were measured in the product gases); and finally, carbon dioxide gas generated in the reaction diffusing slowly from the liquid phase.

The gases commonly found in air as well as the gases known to form as the result of the reaction were used in the reactor in place of nitrogen to determine the effect, if any, on the reaction rate. Figure 19 compares the effects of using O_2, CO_2, and CO with those of N_2. The curves for N_2 and O_2 are similar, with both formaldehyde and formate reaching zero at 55 and 89 minutes, respectively. This is noteworthy because oxygen is one of the product gases, whereas nitrogen should be inert. Carbon dioxide retarded the reaction somewhat; nevertheless, quantitative oxidation was almost realized at 144 minutes, the total reaction time required with the use of the N_2 purge. The most notable result was with carbon monoxide, a minor product gas of the reaction. Although its effect is not significant enough to cause concern, it did inhibit the reaction somewhat. This inhibition is reflected in the existence of formate at 144 minutes and the fact that both formaldehyde and ^{14}C data tend to track each other, approaching zero at 144 minutes. It should be emphasized that these results were obtained using pure gases as opposed to those naturally evolving from the reaction.

Figure 19c shows the reaction with carbon dioxide used instead of nitrogen. Since the reaction proceeded essentially as it did with nitrogen, it must be concluded that carbon dioxide does not cause any appreciable shift in equilibrium. Next, assuming that carbon monoxide might inhibit the reaction, it was substituted for nitrogen with the results shown in figure 19d. Although carbon monoxide affected the rate of formaldehyde oxidation, quantitative oxidation to carbon dioxide was achieved in the same time frame. Therefore, carbon monoxide at the trace level was determined to have no significant effect. As discussed earlier, the diffusion of carbon dioxide from the gas phase into the liquid seems to be the cause of the residual radioactivity.

Changing initial temperature. – The effect of changing initial temperature for the reaction is seen on figure 20. Initial temperature has a major effect on the reaction rate over the range of temperatures investigated (17.1 to 31.0 °C). This appears similar to the results obtained with increasing peroxide levels. Residual carbon is noted at 200 minutes at 17.1 °C, but reaches zero by the time the 89-minute sample is taken at 31.0 °C. Temperature seems to have a stronger effect than concentration on the ^{14}C and formate data. Because most chemical reaction rates increase exponentially with temperature, these results were not unexpected.

Varying the catalyst concentration. – Figure 21 shows the effect of varying the catalyst concentration by plus or minus 50 percent of the previously determined 0.2 Fe/CH_2O molar ratio. Although an increase in catalyst affects the oxidation rate of formaldehyde and formate, the net effect on the reaction rates is greater where 50-percent less catalyst is used. This can be seen in the formate data that show quantitative oxidation at 89 minutes for the 0.2 and 0.3 Fe/CH_2O molar tests. In contrast, the 0.1 Fe/CH_2O molar test shows 144 minutes were needed for formate oxidation. This is significant because other tests show that when the formate goes to zero, the residual carbon is only carbon dioxide. These data substantiate earlier findings that a molar ratio of 0.2 Fe/CH_2O is close to the optimum catalyst concentration for the reaction.

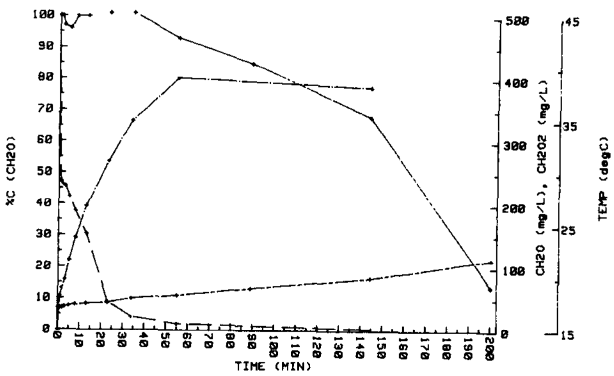
ISOTHERMAL TESTING

Isothermal test results were to be used in the development of a temperature and concentration-dependent rate expression for the formaldehyde oxidation. By measuring the change in the concentration of reactants and intermediates at selected temperatures, it would have been possible to use a multiple regression analysis to solve for the temperature-dependent rate constant. To test a simple proposed mechanism, data were collected using a "pseudo-first-order" or isolation method [10], but the hypothesis did not fit the data. This led to the conclusion that the reaction mechanism was much more complicated than previously envisioned. Work was ended when insufficient time and funds remained to develop the necessary analytical procedures for more complicated pseudo-first-order tests, and it was decided that this information was not absolutely necessary for the design and operation of the formaldehyde oxidation reactor.

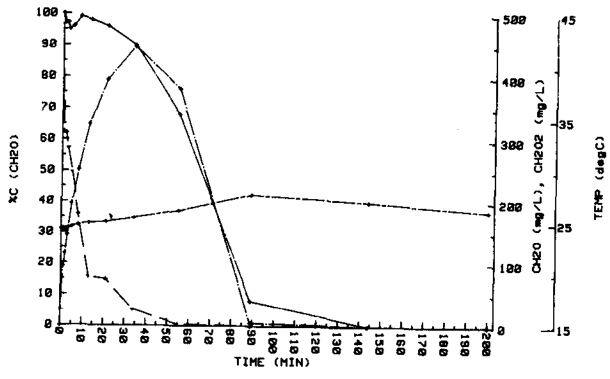
Experimental Apparatus and Procedure

The experimental apparatus was almost the same as that used in the matrix tests, except that rather than insulating the vessel, it was placed into a constant-temperature bath to provide isothermal conditions (see fig. 22).

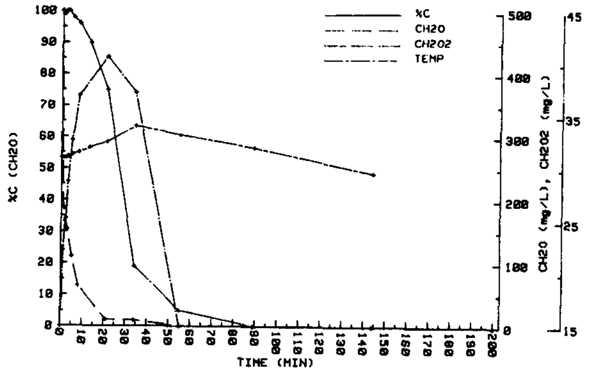
Three types of tests had been planned for the isolation method. Initially, the order with respect to the formaldehyde was to be determined by keeping the ionic strength, hydrogen peroxide concentration, catalyst concentration, and pH constant (all except pH



(a) Initial temperature of 17.1 °C

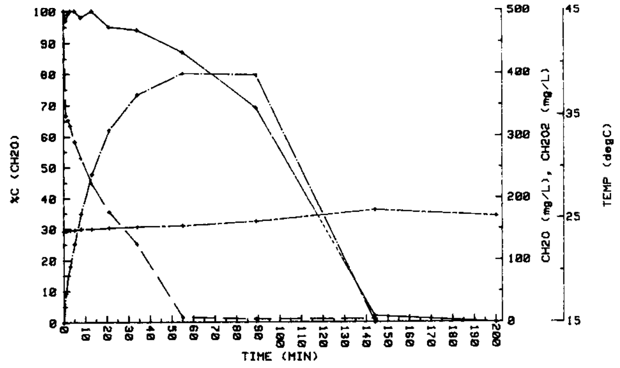


(b) Initial temperature of 25.0 °C

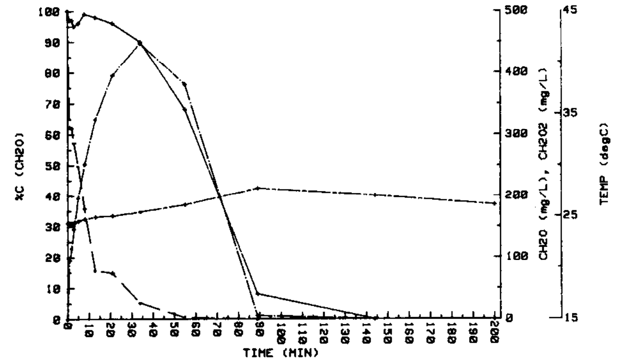


(c) Initial temperature of 31.0 °C

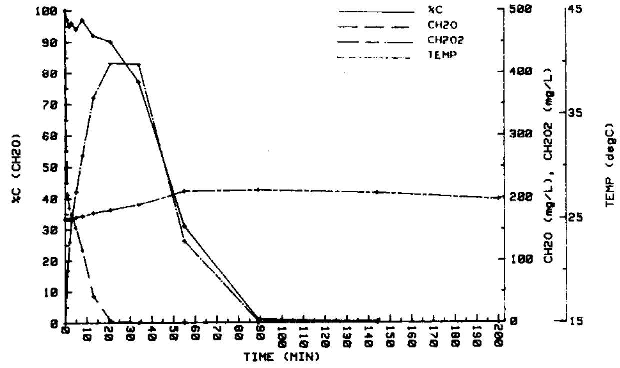
Figure 20. – Effects of initial temperature on oxidation at mid-point conditions.



(a) Catalyst at 0.1-Fe/CH_2O molar ratio

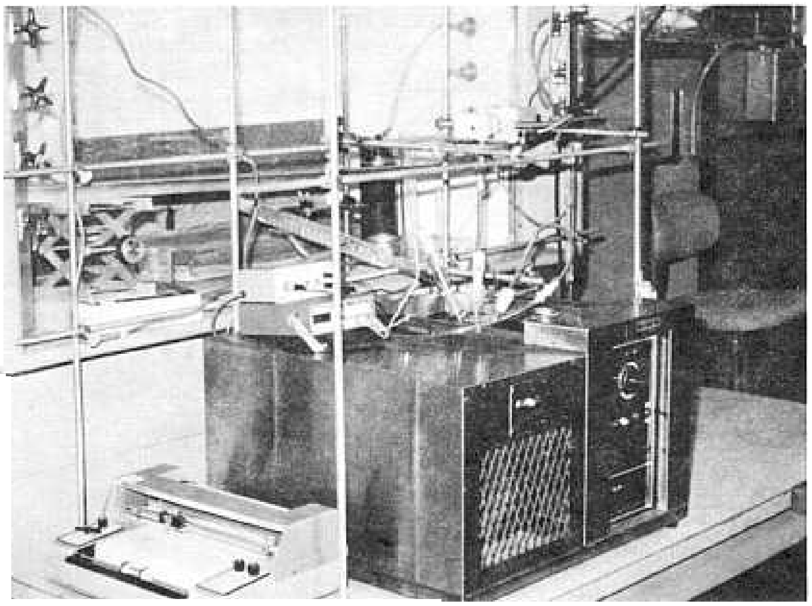


(b) Catalyst at 0.2-Fe/CH_2O molar ratio

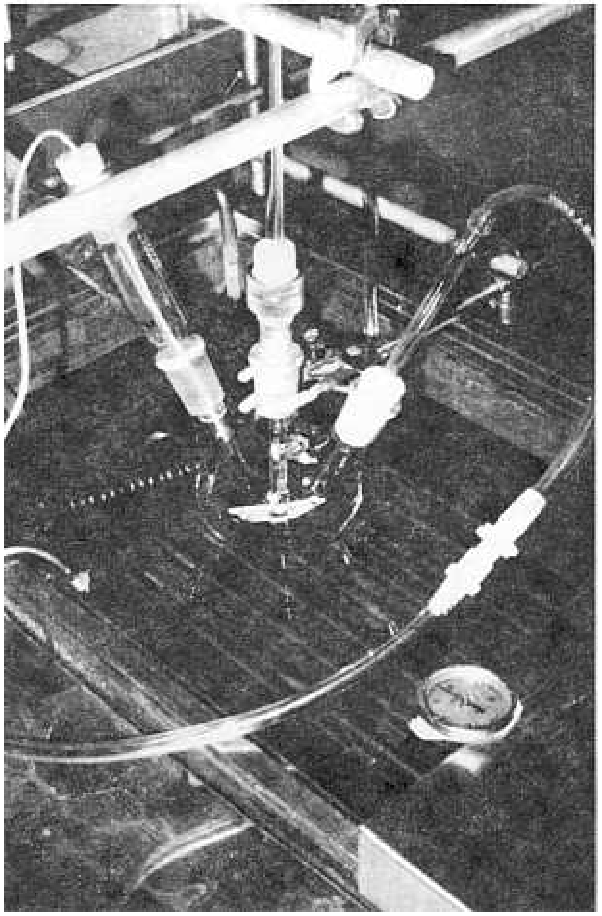


(c) Catalyst 0.3-Fe/CH_2O molar ratio

Figure 21. – Effects of catalyst concentration on oxidation at midpoint conditions.



(a) Isothermal test apparatus. P801-D-80822



(b) Isothermal reactor. P801-D-80823

Figure 22 Isothermal apparatus used in kinetics experiments.

would be in excess). At those conditions, concentration versus time data was to have been collected for several tests with different initial concentrations of formaldehyde.

A second group of tests was to have determined the order with respect to hydrogen peroxide, H^+, Fe^{+3}, and ionic strength. In each test, one of the "reactants" was to be varied while the rest remained constant, including the formaldehyde. A third set of tests was to have determined temperature dependence. The concentration of formaldehyde was to be varied at only 15 and 35 °C (25 °C data would have been collected in the first set of tests).

Two tests were performed where hydrogen peroxide was in excess of the stoichiometric amount by 40 and 100 times. The conditions for each of these tests were: formaldehyde at 250 mg/L, catalyst at a 0.2-Fe/CH_2O molar ratio, temperature at 25 °C, nitrogen flow at 250 mL/min, and stirring rate at 100 r/min. The test results are shown in figure 23.

Results and Discussion

A discussion of pseudo-first-order kinetics will be presented first, to facilitate understanding the attempt to develop a kinetic expression.

Pseudo-first-order kinetics. – The experiment originally planned would have developed the kinetics and mechanism using the initial rate method. However, this was changed to a pseudo-first-order method [10] because several problems are associated with the initial rate method. Foremost among these is the difficulty of including consecutive reactions in the rate expression because only the initial rate, or change in reactant with time, in the first reaction is measured.

A simplified example of the complexity of the proposed mechanism is a competitive, consecutive, second-order reaction:

$$A + B \xrightarrow{k_1} C + E$$

$$A + C \xrightarrow{k_2} D + E$$

where A equals H_2O_2, B equals CH_2O, C equals CH_2O_2, D equals CO_2 (g), and E equals H_2O. The rate expression for $[B]$, the formaldehyde concentration, is:

$$\frac{d[B]}{dt} = -k_1 [A][B] \qquad (14)$$

This model assumes that the order with respect to both A and B is 1.

Another simplification is that the oxidation of the methyl alcohol is not accounted for, and yet is used as a stabilizer, present at 7 percent, in the formaldehyde solution. Another competitive reaction involves the autodecomposition of hydrogen peroxide with the catalyst to form oxygen and water. Thus, the overall oxidation may include the following reactions:

$$2H_2O_2 \xrightarrow{Fe^{+3}} 2H_2O + O_2$$

$$CH_2O + H_2O_2 \xrightarrow{Fe^{+3}} CH_2O_2 + H_2O$$

$$CH_2O_2 + H_2O_2 \xrightarrow{Fe^{+3}} CO_2\ (aq) + 2H_2O$$

$$CO_2\ (aq) \longrightarrow CO_2\ (g)$$

$$CH_3OH + H_2O_2 \xrightarrow{Fe^{+3}} CH_2O + 2H_2O \qquad (15)$$

Complicated reactions, such as the oxidation of the formaldehyde solution to be used at the YDP, are better characterized by using a pseudo-first-order or isolation method. Pseudo-first-order kinetics assumes that the order with respect to any of the components is one. Assuming formaldehyde is first order, the rate equation can be written as:

$$-\frac{d[CH_2O]}{dt} = k[CH_2O][H_2O_2]^a[H^+]^b[Fe^{+3}]^c[\text{ionic strength}]^d \qquad (16)$$

Preliminary work indicated that the order with respect to formaldehyde was one. The rate constant, k, is temperature dependent, while a, b, c, and d are determined by a multiple linear regression. Equation 16 is simplified by having H_2O_2 in excess, a pH buffer, and constant ionic strength, and by knowing that Fe^{+3} is a catalyst.

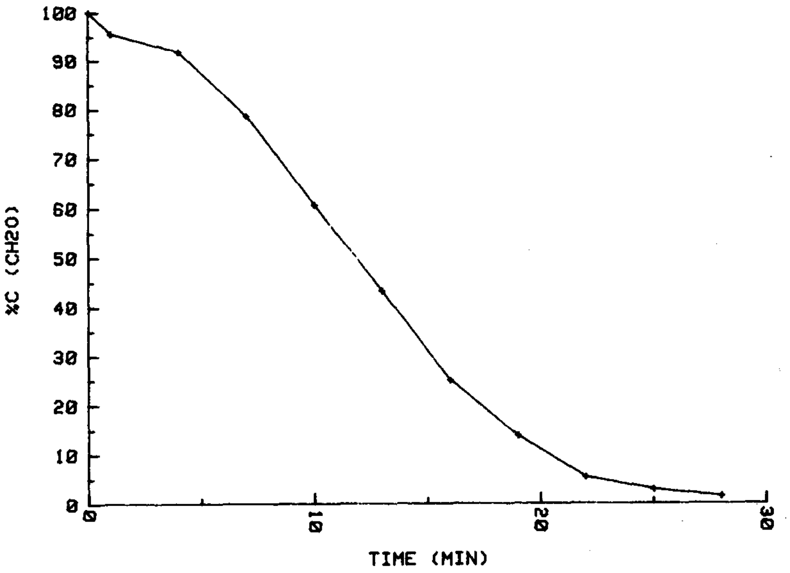
Under these conditions, it can be assumed that only the formaldehyde concentration $[CH_2O]$ varies with time. Equation 16 becomes:

$$-\frac{d[CH_2O]}{dt} = k_\psi[CH_2O], \qquad (17)$$

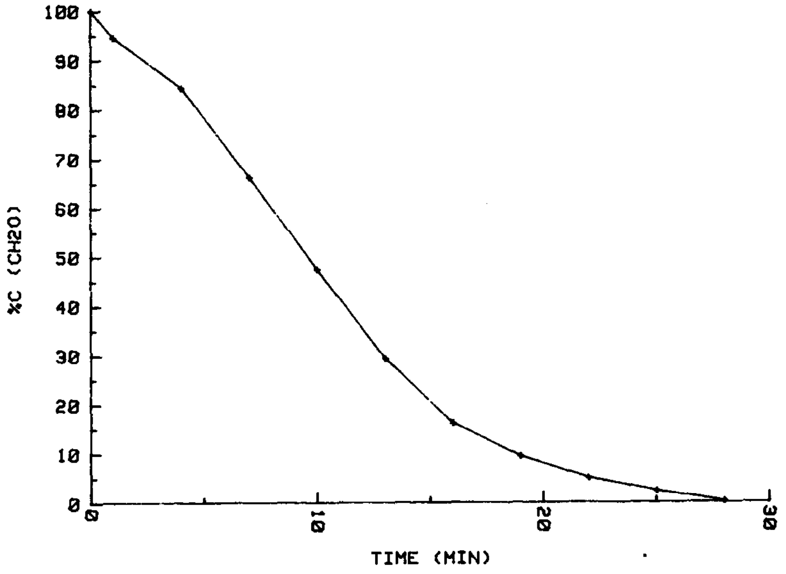
where $k_\psi = k[H_2O_2]^a[H^+]^b[Fe^{+3}]^c[\text{ionic strength}]^d$.

A multiple linear regression can be done on the log of k_ψ, as shown in equation 18.

$$\log k_\psi = \log k + a \cdot \log [H_2O_2] + b \cdot \log [H^+] + c \cdot \log [Fe^{+3}] + d \cdot \log [\text{ionic strength}] \qquad (18)$$



(a) 40-times stoichiometric H_2O_2



(b) 100-times stoichiometric H_2O_2

Figure 23. – Isothermal test results showing the decline of ^{14}C under pseudo-first-order conditions.

Of the unknown variables, k_ψ, k, a, b, c, and d, all except k_ψ are determined by the multiple regression. The variable k_ψ would be equal to the slope of the rate of change of formaldehyde concentration versus formaldehyde concentration.

Attempts to develop a kinetic expression. – It was hoped that a rate equation might be developed from the ^{14}C data, shown on figure 23, using the following assumptions: (1) ^{14}C is involved in the two-step reaction shown in equation 19, (2) initially only $^{14}CH_2O$ is present, (3) H_2O_2 is present in considerable excess, and (4) formaldehyde and formate are first order. These assumptions were a shortcut used to satisfy the three types of tests needed in the isolation method. The following is a derivation of a model based on these four assumptions,

$$CH_2O + 2H_2O_2 \xrightarrow{k_1} CH_2O_2 + H_2O_2 + H_2O \xrightarrow{k_2} CO_2 + 3H_2O \qquad (19)$$

$$-\frac{d[CH_2O]}{dt} = k_1 [CH_2O][H_2O_2]^a \qquad (20)$$

$$-\frac{d[CH_2O_2]}{dt} = k_2 [H_2O_2]^m [CH_2O_2] - k_1 [CH_2O][H_2O_2]^a \qquad (21)$$

$$\frac{d[CO_2]}{dt} = k_2 [CH_2O_2][H_2O_2]^m \qquad (22)$$

Since H_2O_2 is in excess:

$$\frac{d[CH_2O]}{dt} = -k_1' [CH_2O] \qquad (23)$$

$$\frac{d[CH_2O_2]}{dt} = k_1' [CH_2O] - k_2' [CH_2O_2] \qquad (24)$$

$$\frac{d[CO_2]}{dt} = k_2' [CH_2O_2] \qquad (25)$$

Integrating equation 23:

$$[CH_2O]_t = [CH_2O]_o\, e^{-k_1' t} \qquad (26)$$

Substituting equation 26 into equation 24 when $[CH_2O_2] = 0$ at $t = 0$:

$$[CH_2O_2]_t = [CH_2O]_o \frac{k_1'}{k_2' - k_1'}\left(e^{-k_1' t} - e^{-k_2' t}\right)$$

Since the model must fit ^{14}C data:

$$[^{14}C]_t = [CH_2O]_t + [CH_2O_2]_t$$

$$= [CH_2O]_o\, e^{-k_1' t} + [CH_2O]_o \frac{k_1'}{k_2' - k_1'}\left(e^{-k_1' t} - e^{-k_2' t}\right) \qquad (28)$$

Letting:

$$k_3 = \frac{k_1'}{k_2' - k_1'}$$

$$[^{14}C]_t = [CH_2O]_o\left[e^{-k_1' t} + k_3 \left(e^{-k_1' t} - e^{-k_2' t}\right)\right] \qquad (29)$$

Then,

$$\%C = \frac{[^{14}C]_t}{[CH_2O]_o} = (1 + k_3)\, e^{-k_1' t} - k_3 e^{-k_2' t} \qquad (30)$$

Equation 30 can be written in a more simplified form and compared with the data in figure 23:

$$y = A\left(e^{-Bt}\right) + C\left(e^{-Dt}\right) \qquad (31)$$

Both a nonlinear software package and a curve, fit by hand, were used to select the parameters A, B, C and D. Because neither method was successful in fitting the data to equation 31, it was concluded that one or more of the assumptions used was incorrect. Therefore, a rate expression would have to be found by going back to the beginning and using a pseudo-first-order method, after showing that the order with respect to formaldehyde is one. At this point, time and funding ran out, and the kinetic experiments were set aside.

DESIGN DATA FOR THE YUMA DESALTING PLANT

Several areas were investigated to aid in the design of the formaldehyde oxidation process. From adiabatic tests, the heat of reaction was measured. Thermodynamic calculations of the heat of reaction for the formaldehyde oxidation, the methanol oxidation, and the hydrogen peroxide decomposition were then summed and compared with the experimental values.

Tests were conducted to determine an appropriate method for scale-up. Torques applied to the reacting solution were calculated to compare power input to the oxidation results. A complementary analysis, involving chemical similitude [11] was used to check for controlling parameters, i.e., those relating to the geometry of the reactor, fluid velocities, and dynamic forces, such as diffusion, heat transfer, and reaction rate. From this analysis controlling dimensionless groups could be directly applied to the scale-up of the oxidation reactor.

Another area investigated was the conditions at the YDP for flushing and disposal of formaldehyde solutions. A formaldehyde concentration was calculated for the spent flushing solution from a mass balance.

Thermodynamics for the Known Oxidations

Heats of formation were calculated for the formaldehyde oxidation, methyl alcohol oxidation, and peroxide decomposition. From these values, estimates were made of the temperature rise for the 500- and 950-mg/L formaldehyde (0.2 Fe/CH_2O, 3-times stoichiometric H_2O_2) oxidations. The observed value for the 500-mg/L reaction with 250-mL/min nitrogen flow was 3.4 °C, compared with a calculated value of 4.66 °C. In the 950-mg/L test, the observed value was 6.9 °C, and the calculated value was 8.7 °C (see app. F for the calculations).

There were two probable causes for the observed values being low. First, there was a 250-mL/min nitrogen purge across the top of the solution. When another test was performed at 500 mg/L with no purge gas, the observed value was 5 °C, much closer to the calculated 4.66 °C rise. Second, the reactor was not totally adiabatic; it lost approximately 3 °C every 60 minutes when the room and solution temperatures were at 23 and 40 °C, respectively.

Scale-up

Scale-up considerations consisted of power input to the oxidation solution and chemical similitude. Intuitively, it was thought that the reaction was rate rather than diffusion controlled. Stirring rate would be important in a diffusion-controlled heterogeneous reaction where reactants must diffuse through a concentration gradient to a substrate and then diffuse back into the solution as products. However, the formaldehyde oxidation occurs in a homogeneous solution. Therefore, the controlling mechanism can be determined by comparing either the loss of reactants or formation of products with the power introduced into the solution through stirring. Chemical similitude was used to check dimensionless parameters that could be important in the scale-up process.

Power input from stirring. – Power input was calculated as the product of the torque and shaft rotation (radians per second). Torque was measured using a model 781-B-10 Power Instruments, Inc. Torqmeter. This meter was connected to a variable-speed stirrer at one end, and a shortened glass shaft

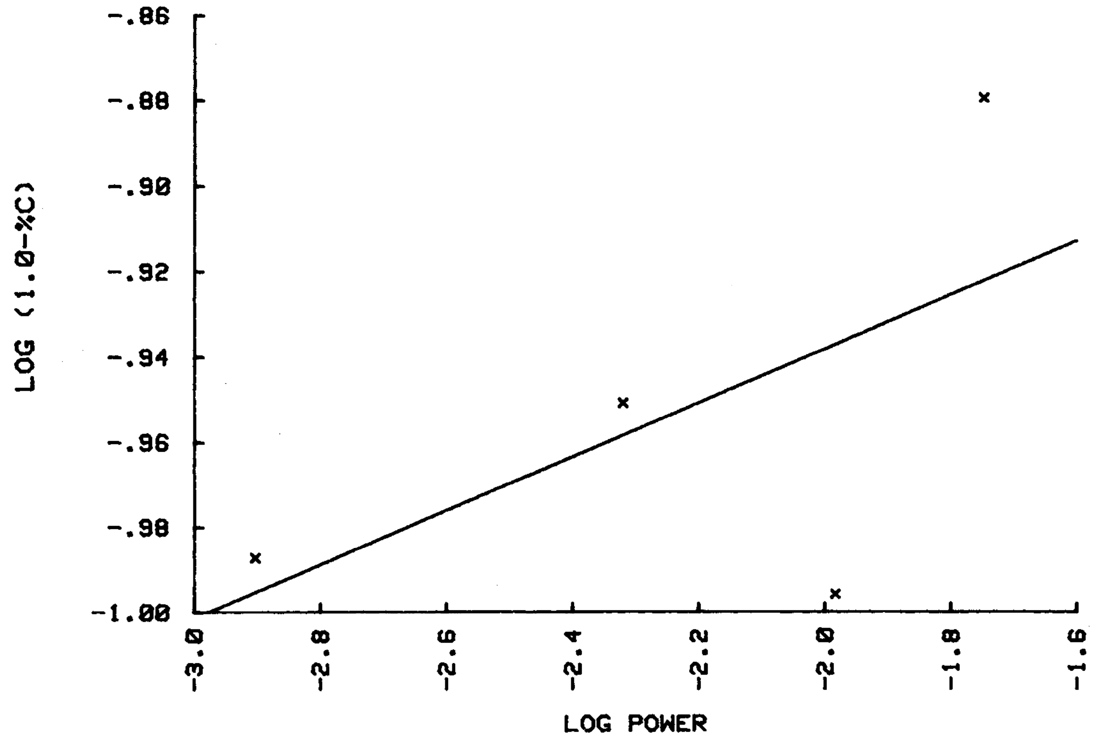


Figure 24. – Correlation between stirring power input and ^{14}C reduction.

at the other, attached to the same Teflon blade that was used during the oxidation experiments. The glass shaft and Teflon blade were placed into a three-neck, round-bottomed flask containing 250 mL of water. An electrical connector on the torquemeter was attached to a chart recorder to record revolutions per minute. Readings were taken at different stirrer settings by using a strobe light to "freeze" the motion of the torquemeter scale.

Specifics relating to the determination of power applied to the reaction solution can be found in appendix G. The measurements indicated a low power input from stirring. For most of the matrix tests, the stirring rate was set at 2 (equivalent to 100 r/min), which corresponds to a power input of 1.25×10^{-3} watts. Higher stirring rates for the matrix tests were considered unnecessary because there were no appreciable changes in the oxidation results above the 2 setting (see fig. 17).

Perry's "Chemical Engineer's Handbook" [12] suggests plotting the log of the oxidation results (function of percent C) versus the log of power to establish whether the controlling mechanism is the reaction rate or mass transfer. The ^{14}C-tagged formaldehyde oxidations at midpoint conditions were conducted isothermally at selected settings over the full range of the stirrer. An initial sample and another after 20 minutes of reaction time were taken for each stirring rate. Then the percent ^{14}C evolved as CO_2 was calculated for each setting by subtracting the percent ^{14}C remaining at the end of 20 minutes from 100 percent. Table 5 presents the results of these calculations with the corresponding power inputs. Figure 24 shows a linear regression fit of the data plotted as the log (1.0 - percent C) versus log power.

Table 5. – Stirring power input data.*

Stirring rate r/min	Power watts	1.0 - %C
100	1.25×10^{-3}	0.103
150	4.79×10^{-3}	0.112
200	1.04×10^{-2}	0.101
250	1.79×10^{-2}	0.132

* See table G-1 for actual torquemeter readings.

According to Perry's Handbook, mass-transfer effects are important when the slope is greater than 0.4, whereas a slope between 0 and 0.1 usually indicates that the chemical reaction is controlling. The slope of the linear fit from figure 24 is 0.063 with a correlation coefficient of 0.6, which would indicate reaction control. If the data point associated with setting 6 is discarded, the slope becomes 0.093 (correlation coefficient of 0.98), which would also indicate a reaction-controlled process.

Other evidence to support reaction control over diffusion control was shown in both the adiabatic stirring tests and the tests in which purge gases were varied. Figures 17(a), (b), and (c) show very similar formate concentrations at corresponding times for the different stirring rates [fig. 17(d) is somewhat modified because of the cooling effect at a high stirring rate discussed earlier]. These similarities indicate that an increased stirring rate has no effect on the reaction rate.

Figure 19 shows the reaction results using different purge gases. If $CO_2(aq)$ were an equilibrium product in one of the oxidation steps, then a purge would be expected to slow the overall oxidation by increasing the dissolved CO_2 in solution. However, the $CO_2(g)$ has an effect similar to the other gas purges, which shows that an equilibrium is unlikely and the diffusion of CO_2 does not limit the rate.

Chemical similitude. – Chemical similitude, described by Walas [11], leads to seven dimensionless parameters used for homogeneous reactions (see table 6), which must be considered in the reactor scale-up.

Table 6. – Dimensionless parameters for homogeneous reactions.

Homogeneous reaction	
$\frac{rL}{uC}$	(a)
$\frac{rR^2}{DC}$	(b)
$\frac{u}{rL(\Delta V)}$	(c)
$\frac{Ru\rho}{\mu}$	(d)
$\frac{C_p u R^2 \rho}{k_4 L}$	(e)
$\frac{QrR^2}{k_4(\Delta T)}$	(f)
$\frac{Qr}{\Delta T(4\alpha\varepsilon\gamma T^3 - C_p \rho r \Delta V)}$	(g)

The variables are defined as follows: C, concentration in mol/ft^3; C_p, heat capacity in Btu/(lb·°F); D, diffusivity in ft^2/s; k_4, thermal conductivity in Btu/(s·ft^2)(°F/ft); L, length of the reactor in feet; Q, heat generated by the reaction in Btu/mol reacted; r, rate expression = $-(1/v)dn/dt$ in mol/(ft^3·s); R, radius of reactor in feet; T, temperature in °F; ΔT, temperature in excess of the wall temperature in °F; u, linear velocity in ft/s; ΔV, volume change per unit disappearance of the reactant; α, wall surface per unit of reactor volume (ft^{-1}); ε, emissivity or absorptivity of the reactor wall (dimensionless); μ, viscosity in lb/(ft·s); ρ, density in lb/ft^3; and γ, proportionality constant of 0.484 Btu/(s·ft^2)(°F)^4.

In certain cases, such as the formaldehyde oxidation, selected dimensionless groups can be ignored: parameters *(a)*, *(c)*, *(d)*, and *(e)*, for batch reactions or those involving low flow rates; *(b)*, where small diffusional resistance is encountered, i.e., rate-controlled reactions; and *(c)* and *(g)*, for constant volume reactions. Parameter *(f)*, involving the heat of reaction, is the only dimensionless group remaining. When the heat of reaction is small, *(f)* can be ignored as well. The formaldehyde oxidation is exothermic but has a moderately small heat of reaction when the reactants are dilute, as was seen in the 4 to 5 °C rise during the matrix test at midpoint (adiabatic) conditions. Therefore, parameter *(f)* is expected to have only limited effect on scale-up. When parameter *(f)* is the controlling condition and the vessel is adiabatic and homogenous (representative of our matrix tests), scale-up can be direct. The reaction rate and reaction times would not be expected to vary with the scale of the reactor assuming that the same concentrations of reactants are used, i.e., the heat generated per unit volume would be independent of total reactor volume. Total power input to the larger reactor must be increased to assure homogeneity.

The heat of reaction generated in nonadiabatic reactors introduces more complexity in scale-up. Heat transfer is dependent upon several parameters including reactor surface area, wall thickness, inside and outside temperatures, thermal conductivities, and heat transfer coefficients. A larger reactor has less surface area per unit volume, which would result in greater heat retention, and thus, an increase in the temperature-dependent reaction rate.

Flushing and Disposal of Formaldehyde Solutions

Estimate of final formaldehyde concentrations. – Appendix H contains a previously proposed flushing scenario based on data collected at the YDTF (Yuma Desalting Test Facility). Using this scenario, it was possible to calculate both the total flushing volume and the final concentration of formaldehyde, from one control block.

The total flushing volume for a Hydranautics control block is 45 000 L (11 890 gal) (see table 7); values for Fluid Systems control blocks are similar. The final concentration of 1210-mg/L formaldehyde was calculated using a mass balance, where the control block contains 5000-mg/L formaldehyde in a total volume of 10 890 L. Initially, one control block contains 1815 moles of formaldehyde that are then diluted by the flushing to 1210 mg/L in 45 000 L.

Higher formaldehyde concentrations are desired because they create a greater heat of reaction, and thus, a faster reaction. A higher heat of reaction could be used to advantage by decreasing the amount of hydrogen peroxide. By balancing the hydrogen peroxide concentration against the increased heat of reaction available at higher formaldehyde concentrations, the oxidation cost could be lowered. Formaldehyde concentrations much lower than 250 mg/L are undesirable, as can be seen on figure 6, where the 50-mg/L formaldehyde did not completely oxidize to carbon dioxide.

Table 7. – Flushing volumes and concentrations.

Type of operation		Volume	
Step 1:	3-min flush	11 350 L	(3 000 gal)
Step 2:	Drain	7 000 L	(1 850 gal)
Step 3:	3-min flush	11 350 L	(3 000 gal)
Step 4:	Drain	7 000 L	(1 850 gal)
Step 5:	3-min flush	8 290 L	(2 190 gal)
Total		45 000 L	(11 890 gal)

An estimate of the chemical costs (January 1983) for a single control block is presented in appendix I. When the waste from one control block, 45 000 L at 1200-mg/L CH_2O, is oxidized, the formaldehyde cost will be $82; the peroxide cost, $1100; and the ferric chloride cost, $74.

Two suggestions can be made regarding the design of the oxidation system. The primary suggestion is to oxidize as high a formaldehyde concentration as possible, preferably higher than 500 mg/L, remembering that scale-up will become dependent on the heat of reaction. This would give total oxidation times of 90 minutes or less when the initial solution temperature is 25 °C or higher, the hydrogen peroxide is 2-times stoichiometric, and the Fe^{+3}/CH_2O molar ratio is 0.2. Secondly, add heat and/or peroxide to decrease the total oxidation time.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. In the matrix tests the rate of oxidation was affected by the initial temperature, the hydrogen peroxide concentration, and the formaldehyde

concentration. Higher initial temperatures or hydrogen peroxide levels caused the oxidation to occur at a faster rate. Formaldehyde concentrations of 250 mg/L or higher were completely oxidized to carbon dioxide, but the 50-mg/L formaldehyde concentration was not totally oxidized.

2. Methyl alcohol and formic acid (formate) were present in the formaldehyde. They were oxidized to carbon dioxide at the same time as the formaldehyde, rendering the solution free of these organics.

3. The reaction rate, not the mass diffusion, was the controlling mechanism. This was shown through analysis of input power and through chemical similitude.

4. The beaker tests showed that the optimum molar ratio between the catalyst and formaldehyde concentrations was approximately 0.2.

5. Ferric chloride was a nonprecipitating catalyst, necessary for the reaction to occur. With no catalyst and all other reaction conditions met, the oxidation to carbon dioxide did not occur within 25 hours.

6. The product gases from the oxidation were found to consist of carbon dioxide, oxygen, and trace levels of carbon monoxide. Formaldehyde vapor was also detected in the product gas stream at less than 0.4 mg/m^3.

7. Varying the rate of stirring and the blanketing of the reaction with product gases did not appreciably affect the reaction rate.

8. Residual ^{14}C present in solution after the oxidation of formic acid (formate) was shown to be carbon dioxide.

9. Thermodynamic calculations of the temperature rise during an adiabatic reaction gave results that were close to the experimental values.

10. The development of a temperature and concentration-dependent rate expression from kinetic theory was not successful because the simple mechanism hypothesized did not fit the experimental data. Further work with the pseudo-first-order method requires developing analytical methods that give accurate concentrations of selected reactants while other reactants are in excess.

Recommendations

1. The order in which chemicals are added for the oxidation should be consistent with that used during the matrix testing.

2. The formaldehyde waste to be oxidized should be as concentrated as possible, preferably above 500 mg/L.

3. Necessary safety precautions should be taken when adding reactants to waste formaldehyde solutions to avoid problems caused by the liberation of excess gases.

4. Ferric chloride is the recommended catalyst.

5. A preferred 0.2 molar ratio of iron catalyst to formaldehyde should be maintained.

6. The reaction should be continued until all formic acid (formate) has been oxidized.

7. Proper venting of the reactor is required to ensure safe operation.

8. An inert material such as polyethylene, polypropylene, or FRP (fiberglass-reinforced plastic) should be used to contain the reaction.

9. Stirring is needed only to mix the reactants and evenly distribute the heat of reaction to avoid a temperature gradient.

10. It is not recommended that the Bureau perform further studies of the kinetics of the formaldehyde oxidation, but an empirical relationship should be developed instead.

11. A pilot plant study should be made before the full-scale design to verify the conclusions regarding scale-up and to better define and optimize operating procedures.

12. Further testing of the formaldehyde oxidation should address the possibility of interference from contaminants in the YDP process water.

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APPENDIX A
ION CHROMATOGRAPHY

The various ionic constituents in water may be measured by a technique known as IC (ion chromatography). Although the basic principle of chromatographic separation of ions in water has been known for some time [1], it was not until 1972 that a prototype ion chromatograph was built using a conductivity cell as the detector. Today, with the advances in microprocessors, completely automated systems exist that, after proper calibration, can continuously generate data with an autosampler.

Over a dozen different colorimetric methods were considered for the formaldehyde analysis on this project. Nevertheless, each of these methods was abandoned in favor of ion chromatography for one or more of the following reasons.

Chemical interferences were a problem with most colorimetric methods. For example, iron is listed as an interferent in most methods at the concentration anticipated from our reaction solution. In contrast, IC elutes the iron species prior to formaldehyde detection. The analysis time would be lengthy for some methods. For example, many methods require freshly prepared reagents daily. In contrast, IC requires no new chemicals daily, relying on large carboys of eluents that can be used for several days and sometimes months under suitable conditions. A lengthy methods development program would be needed to fit a colorimetric method to the unique matrix of our reaction solution. However, IC separates the formaldehyde bisulfite adduct from other species present and, therefore, requires less development time.

Colorimetric methods have limited working ranges primarily due to Beer's law limitations. Thus, colorimetric methods are generally linear to less than one order of magnitude, while IC can be considered linear to several orders of magnitude, depending on the dissociation constant for the cation or anion. Hence, bisulfite (the anion of a moderately strong acid, $K_{25°}$ for $H_2SO_3 = 1.54 \times 10^{-2}$), which was the actual species measured for formaldehyde, has a greater linear range than formate (the anion of a weak acid, $K_{25°}$ for $CH_2O_2 = 1.77 \times 10^{-4}$).

Some methods were discarded due to insensitivity. To overcome this would require larger sample sizes from our reactor, which would disrupt our experiments. The IC work, on the other hand, required a relatively small sample size with respect to the total reactor volume.

Finally, spectral interferences may have presented a problem because the reactor solution is colored. However, IC is not affected by the color of the solution.

IC was also chosen because it provides a means of formate and carbon dioxide analysis. Because formate analyses done with a colorimetric method would be subject to problems similar to those that plagued formaldehyde, IC was a better choice. Carbon dioxide can be measured as the bicarbonate or carbonate ion, but because the use of a ^{14}C formaldehyde tag became standard in our testing procedure, and because it can be shown that the ^{14}C exits the solution as CO_2 gas, measuring the radioactivity became the means of CO_2 analysis.

The final purpose of IC, and perhaps the most important from a mechanistic standpoint, was using the chromatograms with the hope of locating other ions, which were crucial to understanding the reaction mechanism.

It should be noted, at this point, that although the chemistry of the reaction is not fully understood, information found by IC could characterize the reaction. Intermediary products, however, are generally short-lived and show no significant unknown peaks.

1. **Formaldehyde Analysis by IC**

Because formaldehyde is not ionic, it cannot be measured directly by IC. Two approaches to the formaldehyde analysis were considered. The first was oxidizing the formaldehyde to formate, then measuring the increased level of formate to determine the original formaldehyde present. The EPA (Environmental Protection Agency) uses this method to measure formaldehyde in air. The second approach was similar to the work of Dolzine, et al. [2], who first suggested the use of sodium bisulfite with formaldehyde to form the addition product, sodium formaldehydebisulfite. This addition product can then be ionized into sodium ions and formaldehydebisulfite ions. This method was an improvement over the first (EPA) method and was, therefore, the method we used.

One reason the sodium bisulfite method was selected over the formate method was that the preferred configuration for the formate analysis required the use of an ICE (ion chromatography exclusion) with a silver suppressor. This made an analysis troublesome and lengthy compared with using an S-4 column with a fiber suppressor. Also, the formate method would provide only a limited working range on the ICE column because formic acid is a weak acid, and the dissociation constant is small. The degree of conversion was another consideration; i.e., whether total conversion to formate would take place, or whether some formate would, in time, be further oxidized to carbon dioxide.

Finally, if the formate levels of samples were also desired, two entirely different analyses would be needed to obtain levels for formaldehyde and formate.

Our approach to the analysis of formaldehyde in the reaction solution was similar to an existing procedure for measuring formaldehyde vapor in air using a sodium bisulfite solution. Basically, the rapid introduction of a small sample from the reactor into a dilute solution of sodium bisulfite achieved two purposes: the analyses of formaldehyde and formate with a single sample injection and the "freezing" of the sample prior to analysis. Ongoing chemical reactions are generally "frozen" by an instantaneous dilution, chemical neutralization, or rapid freezing of samples. Because sodium bisulfite is a reducing agent, excess amounts would neutralize hydrogen peroxide and shut down the reaction. In our sampling procedure, the combination of chemical neutralization and rapid dilution was shown to be effective in "freezing" the reaction.

The excess bisulfite was destroyed by adding a slight excess of hydrogen peroxide. This procedure is similar to that of Dolzine, et al., and we observed similar results, noting that the retention times for bisulfite and the proposed formaldehyde bisulfite ion were the same. However, we were not confident that the formaldehyde bisulfite ion peaks were only bisulfite peaks. Using ^{14}C-tagged formaldehyde and going through the above-described procedure, we sampled the effluent from the IC every 12 seconds and measured the collected samples for ^{14}C. Figure A-1 shows that formaldehyde elutes well before the bisulfite peak. Thus, we concluded that the peak is bisulfite and that this complex probably splits prior to detection. In spite of this, good analytical data were obtained using this method.

2. **Formate Detection**

Two methods were used for formate detection with IC. The first method, preferred by the manufacturer, requires the use of a column based on the ion exclusion principle. This column is used for weak organic acids that are retained while the other anions travel through unaffected. The eluent is dilute HCl, and before it reaches the conductivity cell, a silver suppressor column removes the highly conductive chloride ion. The drawbacks, compared with the S-4 column, are a much more lengthy analysis time, 30 minutes versus 12 minutes; limited working range; and the troublesome replacement or cutting away of the disposable silver suppressor column.

The second method uses the standard S-4 column with fiber suppressor. A typical chromatogram from this type of analysis is shown on figure A-2. The baseline is nearly constant, and there are no interfering peaks nearby. The retention time of formate on this column is similar to that of other ions commonly found in water. This method requires prior knowledge that the water is free of these ions or that their concentrations remain constant; otherwise, the

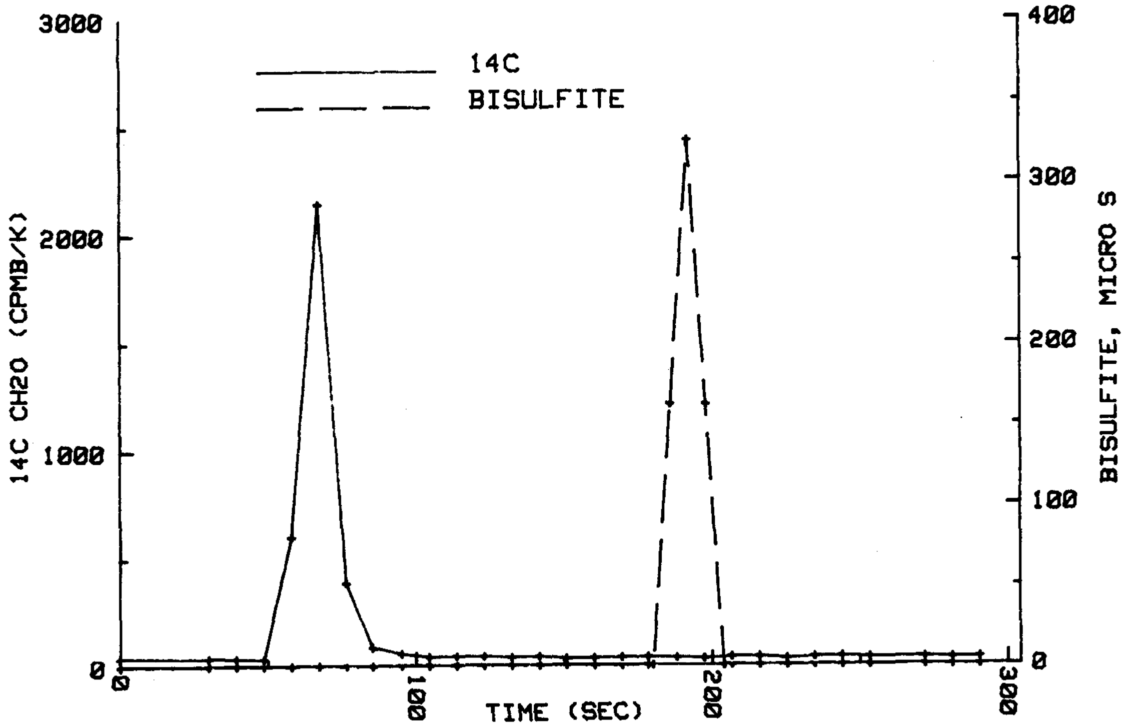

Figure A-1. – Splitting of formaldehydebisulfite anion through the IC column.

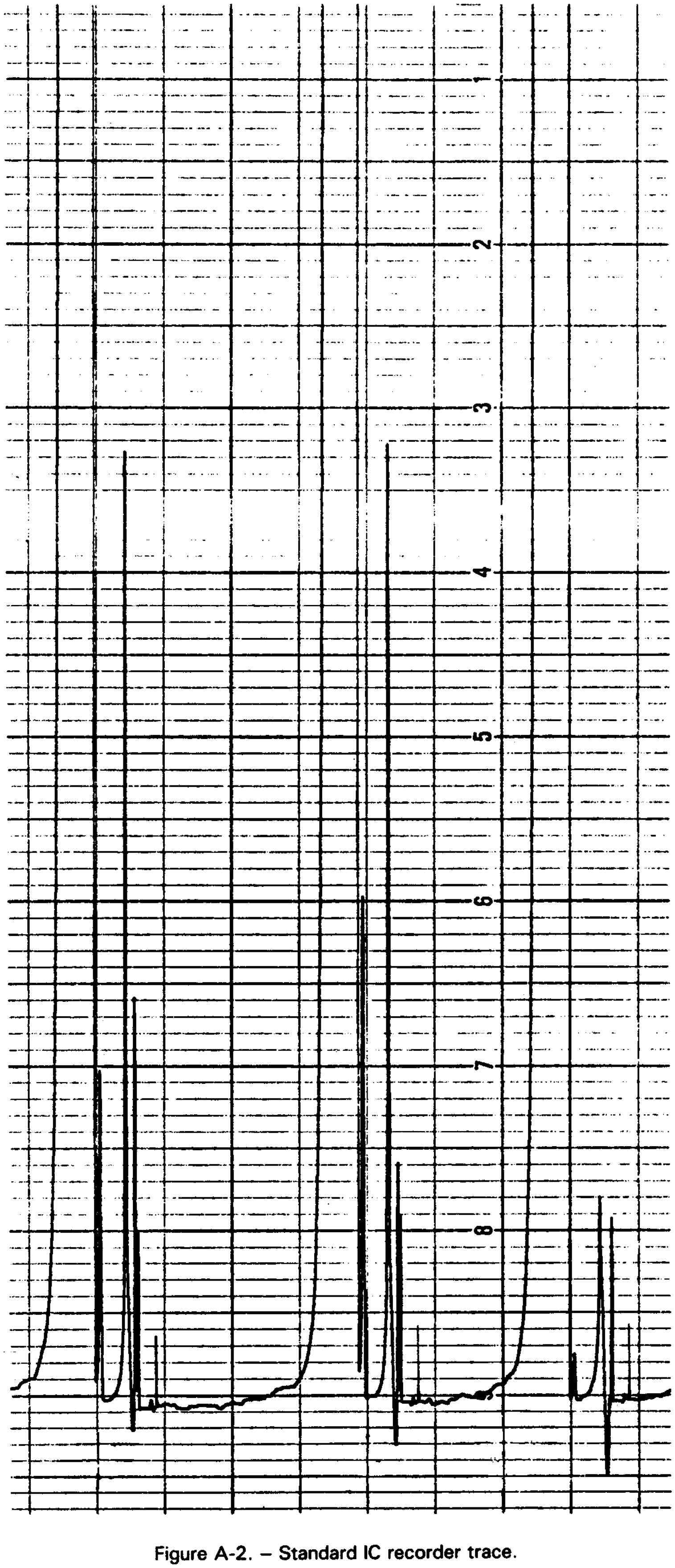

Figure A-2. – Standard IC recorder trace.

measurement of formate could not be done. Fortunately, the reaction solution is artificially made, and the ions that could cause interference with formate are not present. Therefore, the S-4 column was used to provide formate data. Although the S-4 chromatography for formate was acceptable when compared with the ICE column, the baseline was not as stable.

3. IC Chromatogram

Figure A-2 shows the chromatograms for several samples from a reaction having the conditions; 0.2-Fe/CH_2O ratio, 3-times stoichiometric H_2O_2, 500-mg/L CH_2O, 250-mL/min nitrogen, initial temperature of 25 °C, and a stirring rate of 100 r/min. All the chromatographic information was recorded from right to left with a chart speed of 0.25 cm/min. Thus, the first grouping of five peaks, on the right, are for the blank. The center grouping, six peaks, is the 3-minute sample, and the left grouping is for the 8-minute sample. In the blank, the first peak (from the right) is a signal produced by the IC indicating the time of sample injection into the system. The second peak is unknown, but has been observed to remain constant for all samples during a reaction. An exception to this was the 50-mg/L CH_2O tests where neither the first nor the second peaks were observed. The third peak, up against the second, can be seen in the 3- and 8-minute groupings and was identified as formate. The fourth peak was chloride; the fifth peak, bisulfite; and the sixth peak, sulfate.

Identification of the peaks was done in various ways. The formate peak was determined by standard additions, and the data were used to develop a standardized curve for formate. The fourth peak, chloride, was determined by adding NaCl to reaction samples, but no attempt was made to develop a standardized curve. Bisulfite was the fifth peak and was used to develop a standardization curve for the formaldehyde. An explanation of the relationship of bisulfite to formaldehyde was presented earlier in this appendix. The final peak was identified as sulfate. Sulfate became a problem at low concentrations of bisulfite because it tended to merge with the bisulfite peak. Care was taken that the procedures used did not create so much sulfate that the bisulfite peak would be obscured.

4. Water Contamination

A sample blank was used in calculating formaldehyde over time in the reactor. The blank typically yielded a small signal indicating the presence of formaldehyde. This value was subtracted from the other data points for the test. Since the blank was treated exactly like the samples, except for the addition of reactor solution, it was concluded that the contamination must be from either the water, hydrogen peroxide, sodium bisulfite, or the environment. Steps were taken to systematically check for each possible source of contamination, such as comparing the results obtained using plastic pipet tips and weighing paper with those obtained using glass pipets and aluminum foil weighing dishes. Relief was finally realized by using HPLC (high pressure liquid chromatography) water in place of the laboratory's deionized water. This caused the blank to drop by 85 percent. A possible explanation for this relates to the plasticizers found in our laboratory deionized water. At one point, glass-distilled water was used with only slight improvement. On a more careful inspection of the glass still, it was discovered that the warm distilled water comes into contact with tygon tubing, possibly causing the plasticizers to be leached out.

5. Daily Operation of the IC

The IC generally worked well during the testing period. Figure A-3 is the program for the Autoion 100 controller on the IC. Usually, the samples were analyzed without problems, but several times the controller automatically shut down. Later, it was found that the pump and autosampler caused voltage surges when turned on and off. This was corrected by representatives from the Dionex Corporation.

Another problem with the instrument was the extensive damage caused by a drip from one air-controlled valve onto another. The Dionex Corporation was able to solve the problem but not until the completion of the test program. Consequently, the H_2SO_4 feed to the fiber suppressor had to remain shut off at the reservoir during testing to avoid using the air valve.

One problem that seems to have been solved was the steady rise in system pressure over the testing period. It was suggested that the iron catalyst was precipitating in the S-4 anion column. The system pressure was lowered about 150 lb/in^2 by using a 1-percent HCl solution for eluent. The HCl was run through the system for about 4 hours, then the usual carbonate bicarbonate eluent was run for 4 hours. By the next morning the base line had smoothed out at the lower pressures.

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AutoIon™ 100 Controller Programming Form

SYSTEM NO. 1

PROGRAM NO. 3

REMARKS 2.0 ml/min 10 µS scale, charter recorder at .25 cm/min

SAMPLE Formaldehyde Analysis

COLUMNS S4 with concentrator and fiber suppressor

ELUENT .0028 M $NaHCO_3$ / .00225 M Na_2CO_3

DATE 10/21/82

REV 12/1/82

STEP	TIME (min)	ANALYTICAL PUMP		CHROMATOGRAPHY MODULE				CONDUCTIVITY DETECTOR				RELAYS				AC OUTLETS	
		Flow Rate (mL min^{-1})	Eluent No.	Temp Select	LOAD INJ	A OFF/ON	B OFF/ON	Temp Comp (%/°C)	Auto Offset OFF/ON	Mark OFF/ON	Range	1	2	3	4	1	2
												Auto S				Pump	Chart
1	0.0	2.0	1	0	LOAD	ON	OFF	1.7	OFF	OFF	3	OFF				OFF	ON
2	0.1	"	"	"	"	"	"	"	ON	"	"	ON				"	"
3	0.2	"	"	"	"	"	"	"	"	"	"	"				ON	"
4	0.7	"	"	"	"	"	"	"	"	"	"	"				OFF	"
5	0.8	"	"	"	INJ	"	"	"	"	ON	"	"				"	"
6	0.9	"	"	"	"	"	"	"	"	OFF	"	"				"	"
7	10.9	"	"	"	LOAD	"	"	"	"	"	"	"				"	"
END 8	11.0	"	"	"	"	"	"	"	"	"	"	"				"	"
9																	
10																	
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13																	
14																	
15																	

Figure A-3. – IC controller program.

APPENDIX B
RELIABILITY OF ANALYTICAL PROCEDURES

Reliabilities associated with each of the analytical procedures used in the test program were estimated and are presented in table B-1.

The methods used for formaldehyde analysis are described in appendixes A.1 and D, entitled "Formaldehyde Analysis by I.C." and "Assaying Stock Formaldehyde Solutions," respectively.

The accuracy of the formaldehyde analysis, based on an established titrametric procedure (see app. D), has been reported [1] to be within 0.02 percent for commercial formaldehyde solutions (37 percent); therefore, it can be assumed to be similar for 5000-mg/L (0.5-percent) solutions. In rows 1 and 2 of table B-1, different uncertainties in formaldehyde analysis are listed. No accuracy value was given for IC formaldehyde work because the accuracy is ultimately based on the titration. Precision for both methods includes consideration of the total uncertainty from start to finish. Confidence in the precision of the IC method can be obtained from the linear calibration curves for the standards, which reproduced virtually the same over a period of at least 1 week. From this information, the instrument's response to the formaldehyde concentration was predictable, and sample concentrations were determined from the linear equation shown in figure C-1. In addition, the many duplicate samples tested by IC throughout the test program confirmed the precision. Recovery experiments were also performed. Detection limit values varied for IC work based on initial formaldehyde concentrations because of operator choice of instrument sensitivity.

Table B-1. – Estimated uncertainty in measurements.

Row No.	Method	Accuracy	Precision	Detection limit
1	Titrametric CH_2O	0.02%	2.4	68 mg/L (for a 2.0-g CH_2O sample)*
2	IC CH_2O	—	0.9	0.96 mg/L at 500 or 950-mg/L CH_2O 0.08 mg/L at 50-mg/L CH_2O
3	IC formate	1%	3.0	2.4 mg/L
4	^{14}C analysis	—	2.0	1.8 mg/L at 500 or 950-mg/L CH_2O 0.11 mg/L at 50-mg/L CH_2O
5	G.C. analysis	5%	5.0	—
6	Sampling reactor	—	0.5	—
7	Freezing	—	±1 sec.	—
8	Temperature	±0.1 °C	±0.1 °C	—

* Estimated detection limit based on titrant concentration used to assay 5000-mg/L formaldehyde stock solutions.

Because the IC analysis was an indirect method; a potential problem existed with other organics present that might "protect" the bisulfite against H_2O_2 attack and cause high readings. Fortunately, the reactor was inert, consisting of only glass and Teflon parts, and the reaction solution was simple, consisting of only ferric chloride, hydrogen peroxide, and formaldehyde. In addition, deionized water was used to make up reactor solutions. Consequently, any interference from other organics was minimal. However, it was interesting in following this source of error, that some organic contaminates were present in the deionized water source, causing difficulties with the reaction (see app. A). The data were adjusted to correct for this error by subtracting a blank value for each experimental run.

The method of formate analysis is outlined in appendix A-2, "Formate Detection." Row 3 of table B-1 shows the estimated uncertainties for the formate work with the accuracy assumed from the assay on the bottle of formic acid. The same quality control procedures were used as with the formaldehyde work, including duplicate runs and recovery work. The calibration curve for formate is shown on figure C-2. Stock solutions were prepared by diluting ACS-grade formic acid to the desired concentration and adding a small amount of chloroform to prevent biological attack. No other assay was done on the stock solutions. Formate returned to zero on the chromatogram at the beginning and end of the reaction, indicating no interfering neighboring peaks.

Radioactive carbon work was performed using a Packard Tri-Carb 300C Liquid Scintillation Counter; sample calculations are shown in appendix C, "Percent Carbon from ^{14}C." This is a microprocessor-based, dual-region system, with an autosampler capacity of 300. The region for ^{14}C was preset in the instrument and was selected in the program that measured the ^{14}C of the samples.

A reactor solution of 0.5 mL was introduced into 10 mL of a liquid cocktail for scintillation counting. Almost all samples had an efficiency of 90 percent or greater. Based on the efficiency correlation curve for ^{14}C obtained with this instrument, there was no need to correct the counts on these samples. At higher catalyst concentrations the efficiency was not as high, and a correlation factor was used to adjust the reported values. In all experiments an initial sample was taken, and subsequent ^{14}C readings on the reaction were referenced to this data point. This compensated for any concentration effects that would have altered the counting efficiency. Uncertainties associated with the ^{14}C work are shown in table B-1, row 4.

Gas chromatography work was performed on the product gases using a Hewlett-Packard model 5830A chromatograph. A Porapak N column with both FID (flame ionization detector) and TCD (thermoconductivity detector) was used. The instrument was run isothermally. Carbon monoxide was converted to methane with a nickel catalyst tube, supplied with hydrogen. The carbon monoxide was then measured as methane. The chromatograph is routinely used to measure the gas in oil and is standardized against a known gas mixture at atmospheric pressure. Sample calculations are shown in appendix C-1, "Gas Chromatography." Uncertainties relating to the gas chromatography work are shown in table B-1, row 5.

Sampling from the reactor was achieved by pipetting 0.5 mL of solution with a 0.5-mL Eppendorf pipet. Because gaseous products are formed as the reaction proceeds, an accurate liquid volume had to be established. To confirm the accuracy of sample volumes, a test was performed by pipetting samples from the reactor into small cups, which were then weighed with a Mettler 4HK160 analytical balance. Results, shown in row 6 of table B-1, indicate good agreement with the sampling techniques used; therefore, the pipetting method was determined to have adequate precision.

It is important that the sampling method be able to "freeze" the reaction in time. This was confirmed by repeating analyses of the same samples over an extended period. The results of this procedure indicated no change in either formaldehyde or formate concentrations over a 24-hour time interval. Because the samples for each experiment were analyzed quickly, in less than 4 hours, results should be accurate. The estimated uncertainties associated with sampling and "freezing" the reaction are shown in rows 6 and 7 of table B-1.

Uncertainties relating to temperature measurements are shown in table B-1, row 8.

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[1] Walker, J. Federic, *Formaldehyde,* 3d edition, p. 486, Robert E. Krieger Publishing Company, New York, N.Y., 1975.

APPENDIX C
CALCULATIONS

1. Gas Chromatography

A known volume of standard gas mixture is injected into the GC (gas chromatograph) at local atmospheric pressure. A response, in arbitrary area units, is given for each gas. This response must be corrected for STP (standard temperature, 0 °C; and pressure, 1 atmosphere) as follows:

$$V_{STP} = a \times V_s \qquad (1)$$

where V_{STP} = gas volume at STP

a = STP correction factor

V_s = gas volume at laboratory temperature and pressure

and

$$a = \frac{b \times c}{273 \times 5700} \qquad (2)$$

where b = sample temperature (K)

c = sample pressure (kPa)

The total sample volume used was 1 mL. Since each gas has an area response, the partial volume of the unknown gas sample is determined as follows:

$$V_u = A_u \times \frac{V_{STP}}{A_{STP}}$$

where V_u = partial volume of the gas in the 1-mL sample

A_u = area response of sample gas at given retention time

V_{STP} = corrected volume at STP for gas standard

A_{STP} = area response from standard gas

This gives the partial volume of the gas (in mL) in the 1-mL gas sample, which, in turn, can be expressed as microliters/liter or molar fractions of gas.

2. Percent Carbon from ^{14}C

The calculation used to determine percent C is:

$$\%C = \frac{(C_T - C_B)}{(C_I - C_B)} \times 100 \times F$$

where C_I = initial counts on sample

C_T = counts on test data point

C_B = background counts on sample set

F = efficiency correction

In many cases, the samples were clean enough that the efficiency correction, F, could be considered to be 1. Depending on what tag was used, results were expressed either as %C (CH_2O) or %C (CH_3OH).

3. Formaldehyde and Formate

Formaldehyde and formate peaks were measured from the chromatograms in microsiemens per centimeter (µS/cm). Originally a computer was interfaced with the IC by a program that reported microsiemens. However, there were some technical difficulties with this setup; therefore, we later switched to measuring the peak heights directly from the chart recorder. These values were then entered into a calculator programmed with the equations for both standard formaldehyde and formate calibration curves, which are shown in figures C-1 and C-2, respectively. Formate concentrations were low (less than 30 mg/L); consequently, the linear section of this curve was used. The program took into account the dilution factor for the samples. The equations used are as follows:

$$\text{mg/L } CH_2O = [1.0392\,(\mu S_s - \mu S_B) - 0.0059] \times G$$

where G = dilution factor, and

μS_s = conductance of sample in microsiemens

μS_B = conductance of blank in microsiemens

and

$$\text{mg/L } COOH^- = [0.00508\,(\mu S_s - \mu S_B) - 0.0145] \times H$$

where H = dilution factor

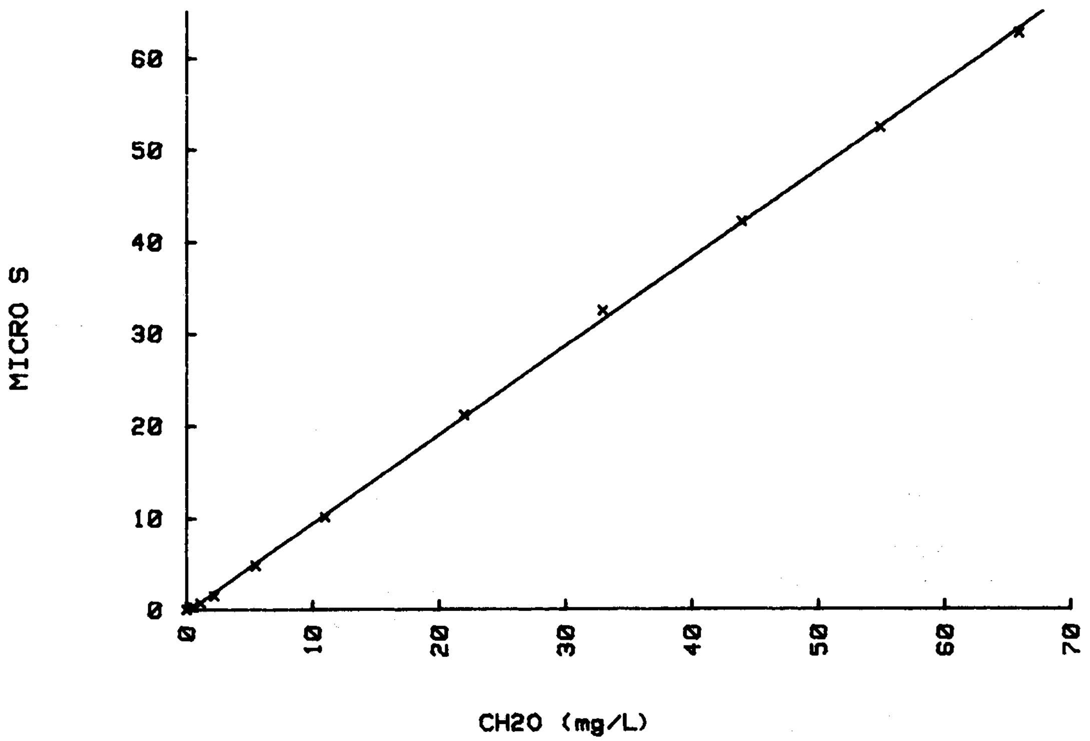

Figure C-1. – Formaldehyde calibration curve.

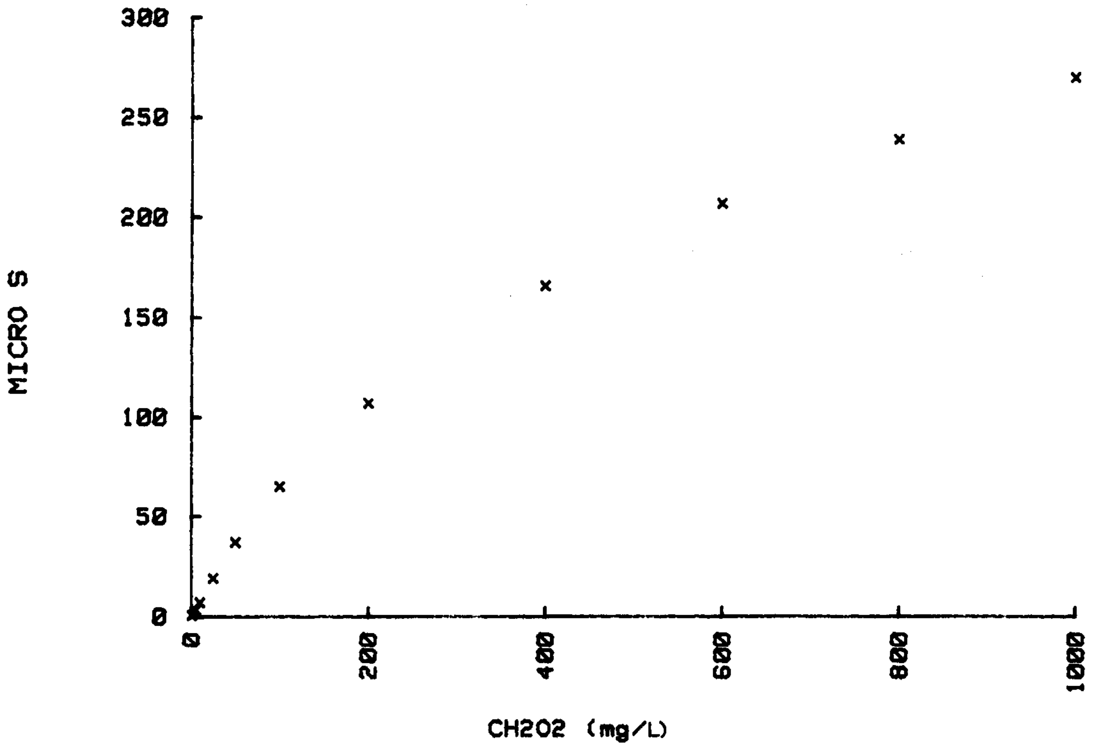

Figure C-2. – Formate standard curve with S-4 anion column.

APPENDIX D
ASSAYING STOCK FORMALDEHYDE SOLUTIONS

A method was needed to assay stock formaldehyde to establish a working calibration curve for the IC. The method must be suitable for the high concentration of a stock solution needed to make the various standards and testing concentrations. Because the accuracy of IC analysis is relative to standards, the formaldehyde assay must ultimately be based on a well-accepted and well-documented method, or the IC measurements must be based on some certified, commercially available standard.

The 0.5-percent CH_2O concentration selected for the stock solution is the same as that planned for the preservation of membranes at Yuma. This concentration was selected because dilute solutions (2 percent or less) of formaldehyde are completely hydrated [1], losing their carbonyl functionality and existing as methylene glycol, the first in the series of glycols. Because solutions in the dilute range have been verified by ultraviolet and Raman spectra to be free of the carbonyl (C = O) functional groups [2], and because cryoscopic measurements [3] confirm the existence of a completely monomeric species, this 0.5 percent CH_2O is an ideal concentration, which presents no precipitation problems and does not experience many of the degradation reactions common with concentrated aldehyde solutions.

Stock solutions were given at least 24 hours hydration time after being prepared from 37 percent formaldehyde. Iliceto [4, 5] showed that a 24-hour hydration time is needed prior to the analysis of formaldehyde. This waiting period also was followed for all reactor tests to ensure that the presence of formaldehyde polymers did not alter the reaction times.

The sodium sulfite method, first developed by Lemme [6] and later improved by Seyewetz and Gibello [7] and Gadtler [8], was used to assay stock formaldehyde. This method is a titrametric analysis that uses standard solutions prepared gravimetrically. It is derived from the quantitative liberation of sodium hydroxide known to occur when formaldehyde reacts with sodium sulfite to form the formaldehydebisulfite addition product.

$$CH_2O\ (aq) + Na_2SO_3 + H_2O \longrightarrow NaOH + CH_2(NaSO_3)OH$$

There were no changes made to this method except for different volume sizes and concentrations to optimize the titration. The equation used was:

$$\text{mg/L } CH_2O = \frac{\text{acid titer x normality of acid x } 3.003 \text{ x } 10^4}{\text{weight of sample}}$$

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APPENDIX E
CARBON-14 FORMALDEHYDE AND METHYL ALCOHOL

Radioactive tracers for formaldehyde and methyl alcohol (methanol) were used throughout this work. Two separate 2-L stock solutions of approximately 5000-mg/L CH_2O were prepared from a carboy of 37-percent formaldehyde obtained from the YDTF. Because formaldehyde can differ in the concentration of methyl alcohol, the additives used, and the contaminants from one manufacturer to another, a sample of formaldehyde was shipped from Yuma for our tests. One stock solution was tagged with ^{14}C formaldehyde and the other with ^{14}C methyl alcohol. Because the vials with the radioactive carbon contained only extremely small amounts of the chemicals, the stock solutions were made radioactive without appreciably changing the concentration of formaldehyde or methyl alcohol. These stock solutions were then used to perform the testing needed to follow the reaction pathway of the two compounds.

APPENDIX F
THERMODYNAMICS

Reactions

1. $CH_2O + 2H_2O_2 \longrightarrow CO_2 + 3H_2O$
2. $CH_3OH + 3H_2O_2 \longrightarrow CO_2 + 5H_2O$
3. $2H_2O_2 \longrightarrow 2H_2O + O_2$

Heats of Formation

1. $CH_2O \longrightarrow C + H_2 + \frac{1}{2}O_2$		42,800	
$2H_2O_2 \longrightarrow 2O_2 + 2H_2$		2 (45,800)	
$C + O_2 \longrightarrow CO_2$		−94,051	
$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$		3 (−68,317)	
$CH_2O + 2H_2O_2 \longrightarrow 3H_2O + CO_2$	$H^{\circ}_{298} =$	−164,602	cal/mol

2. $CH_3OH \longrightarrow C + 2H_2 + \frac{1}{2}O_2$		57,110	
$3H_2O_2 \longrightarrow 3H_2 + 3O_2$		3 (45,800)	
$C + O_2 \longrightarrow CO_2$		−94,051	
$5H_2 + \frac{5}{2}O_2 \longrightarrow 5H_2O$		5 (−68,317)	
$CH_3OH + 3H_2O_2 \longrightarrow CO_2 + 5H_2O$	$H^{\circ}_{298} =$	−241,126	cal/mol

3. $2H_2O_2 \longrightarrow 2O_2 + 2H_2$		2 (45,800)	
$2H_2 + O_2 \longrightarrow 2H_2O$		2 (−68,317)	
$2H_2O_2 \longrightarrow O_2 + 2H_2O$	$H^{\circ}_{298} =$	−45,034	cal/mol

Calculations

Assume midpoint conditions for the reaction, i.e., 500-mg/L CH_2O, 3-times stoichiometric H_2O_2, and a 250-mL solution.

$$CH_2O\text{:}\ \frac{0.5\text{ g }CH_2O}{L} \times \frac{1\text{ mol }CH_2O}{30\text{ g}} \times \frac{0.25\text{ L}}{250\text{ mL}} = \frac{4.167 \times 10^{-3}\text{ mol }CH_2O}{250\text{ mL}}$$

$$H_2O_2\text{:}\ a \times b \times 4.167 \times 10^{-3} = 2.5 \times 10^{-2}\ \frac{\text{mol }H_2O_2}{250\text{ mL}}$$

where a = 3 times stoichiometric
b = stoichiometric coefficient for H_2O_2 = 2

$$CH_3OH\text{:}\ c \times d \times \frac{1\text{ mol }CH_3OH}{32\text{ g }CH_3OH} = \frac{7.39 \times 10^{-4}\text{ mol }CH_3OH}{250\text{ mL}}$$

where CH_2O is 37 percent and CH_3OH is 7 percent by weight of the formaldehyde in solution

$$c = \frac{7\text{ g }CH_3OH}{37\text{ g }CH_2O}$$

$$d = \frac{0.5\text{ g }CH_2O}{L} \times \frac{0.25\text{ L}}{250\text{ mL}}$$

Heating of water

$$T = \frac{Q}{\text{mol}\cdot C_p}$$

where Q = calories transferred

$$C_p = \frac{1\text{ cal}}{\text{g}\cdot{}^\circ\text{C}}$$

1. $164{,}602\dfrac{\text{cal}}{\text{mol }CH_2O} \times \dfrac{4.167 \times 10^{-3}\text{ mol }CH_2O}{250\text{ mL}} \times \dfrac{1\text{ g}\cdot{}^\circ\text{C}}{\text{cal}} \times \dfrac{1\text{ mL}}{\text{g}} = 2.7\ {}^\circ\text{C}$

2. $241{,}126\dfrac{\text{cal}}{\text{mol }CH_3OH} \times \dfrac{7.39 \times 10^{-4}\text{ mol }CH_3OH}{250\text{ mL}} \times \dfrac{1\text{ g}\cdot{}^\circ\text{C}}{\text{cal}} \times \dfrac{1\text{ mL}}{\text{g}} = 0.71{}^\circ\text{C}$

3. Total H_2O_2 − H_2O_2 used in previous reactions = H_2O_2 left for decomposition

$$2.5 \times 10^{-2}\text{ mol }H_2O_2 - (2 \times 4.167 \times 10^{-3}) - (3 \times 9.11 \times 10^{-4})$$

$$= 1.39 \times 10^{-2}\text{ mol }H_2O_2\text{ remaining}$$

$$\frac{45{,}034\text{ cal}}{2\text{ mol }H_2O_2} \times \frac{1.39 \times 10^{-2}\text{ mol }H_2O_2}{250\text{ mL}} \times \frac{1\text{ g}\cdot{}^\circ\text{C}}{\text{cal}} \times \frac{1\text{ mL}}{\text{g}} = 1.25\ {}^\circ\text{C}$$

Total temperature rise in the reaction at midpoint conditions:
2.7 + 0.71 + 1.25 = 4.66 °C

Actual measurement in test 10 (with N_2 flow):
27.7 − 24.3 = 3.4 °C

Actual measurement in test 4 (without N_2 flow):
34.0 − 29.0 = 5.0 °C

Calculations

Assume 950-mg/L CH_2O, 3-times stoichiometric H_2O_2, and a 250-mL solution.

$$CH_2O\text{:}\ \frac{0.95\text{ g }CH_2O}{L} \times \frac{1\text{ mol }CH_2O}{30\text{ g}} \times \frac{0.25\text{ L}}{250\text{ mL}} = \frac{7.92 \times 10^{-3}\text{ mol }CH_2O}{250\text{ mL}}$$

$$H_2O_2\text{: } 3 \times 2 \times 7.92 \times 10^{-3} = \frac{4.75 \times 10^{-2}\text{ mol }H_2O_2}{250\text{ mL}}$$

$$CH_3OH\text{:}\ \frac{7\text{ g }CH_3OH}{37\text{ g }CH_2O} \times 2.38 \times 10^{-1}\text{ g }CH_2O \times \frac{1\text{ mol }CH_3OH}{32\text{ g }CH_3OH}$$

$$= \frac{1.41 \times 10^{-3}\text{ mol }CH_3OH}{250\text{ mL}}$$

Heating of water

1. $\frac{154{,}602\text{ cal}}{\text{mol }CH_2O} \times \frac{7.92 \times 10^{-3}\text{ mol }CH_2O}{250\text{ mL}} \times \frac{1\text{ g}\cdot{}^\circ C}{\text{cal}} \times \frac{1\text{ mL}}{\text{g}} = 4.9\ {}^\circ C$

2. $\frac{241{,}126\text{ cal}}{\text{mol }CH_3OH} \times \frac{1.41 \times 10^{-3}\text{ mol }CH_3OH}{250\text{ mL}} \times \frac{1\text{ g}\cdot{}^\circ C}{\text{cal}} \times \frac{1\text{ mL}}{\text{g}} = 1.36\ {}^\circ C$

3. $4.75 \times 10^{-2} - (2 \times 7.92 \times 10^{-3}) - (3 \times 1.73 \times 10^{-3}) = 2.65 \times 10^{-2}$ mol H_2O_2

   remaining

   $\frac{45{,}034\text{ cal}}{2\text{ mol }H_2O_2} \times \frac{2.65 \times 10^{-2}\text{ mol }H_2O_2}{250\text{ mL}} \times \frac{1\text{ g}\cdot{}^\circ C}{\text{cal}} \times \frac{1\text{ mL}}{\text{g}} = 2.4\ {}^\circ C$

Total temperature rise in reaction at 950-mg/L CH_2O:
$4.9 + 1.36 + 2.4 = 8.7$ °C

Actual measurement in test 19 (with N_2 flow):
$30.6 - 23.7 = 6.9$ °C

APPENDIX G
POWER INPUT

Power input was determined by using a Power Instruments, Inc. Torqmeter, model 781-B-10. Because the reliability of this instrument was in question, it was calibrated using a thread and weights. One end of the thread was wrapped around the shaft of the instrument, and various masses were suspended from the other end. Readings of the needle deflection on the instrument dial were recorded. The torque was then calculated by multiplying the force exerted (the mass times acceleration due to gravity) by the distance from the shaft centerline to the force vector of the weights. With this information a least-squares analysis was used to fit a calibration curve that related the dial readings to torque (see fig. G-1). Another curve (see fig. G-2) shows the correlation between the stirrer setting and the Torqmeter reading, which is directly related to the torque. A third graph (see fig. G-3) shows the relationship between stirrer setting and rotational velocity. The above information was used to calculate the power, log power, and torque, as a function of the stirrer setting (see table G-1).

Table G-1. – Calculations of the log of power.

Stirrer setting	Torquemeter reading	Torque $g \cdot cm^2/s^2$	Velocity r/min	Power mW	Log power
2	0.643	1 159	103	1.25	−2.9
4	2.605	2 935	156	4.79	−2.32
6	4.567	4 710	210	10.4	−1.98
8	6.529	6 486	263	17.9	−1.75

$$P = \text{torque} \times \text{r/min} = 1159\ \frac{g \cdot cm^2}{s^2} \times 103\ \frac{r}{min} \times \frac{2\pi rad}{r} \times \frac{1\ min}{60\ s} \times \frac{kg}{1000\ g} \times \frac{m^2}{10\ 000\ cm^2} = \text{watts}$$

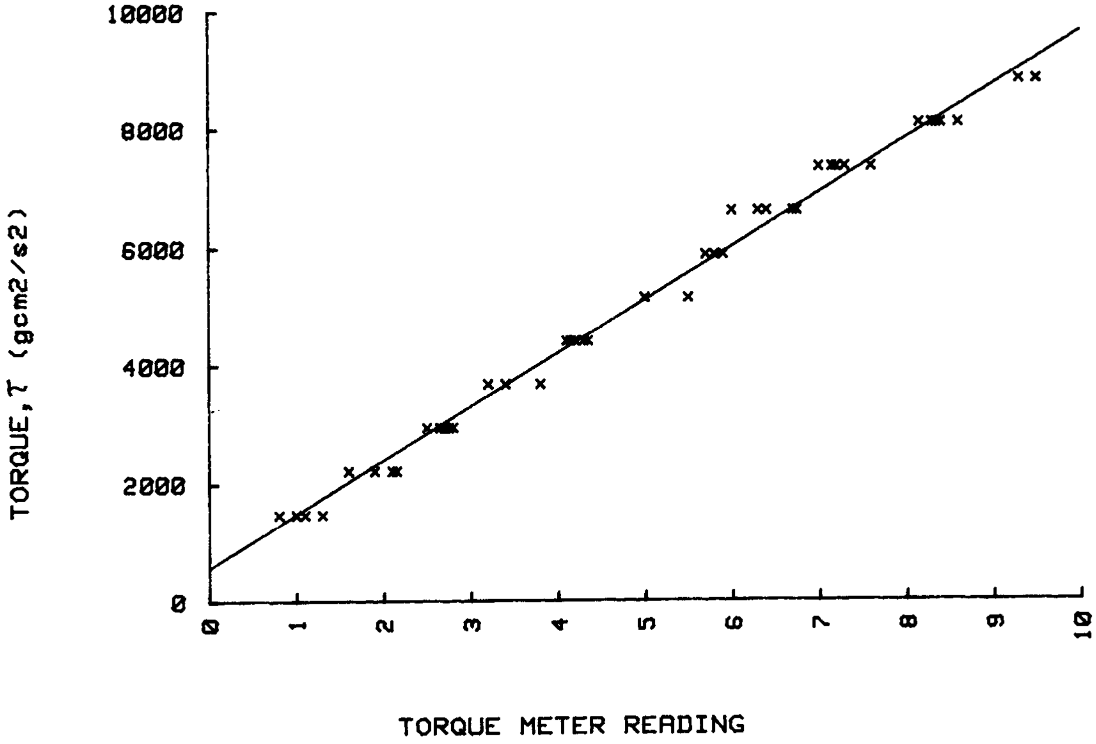

Figure G-1. – Torquemeter calibration curve.

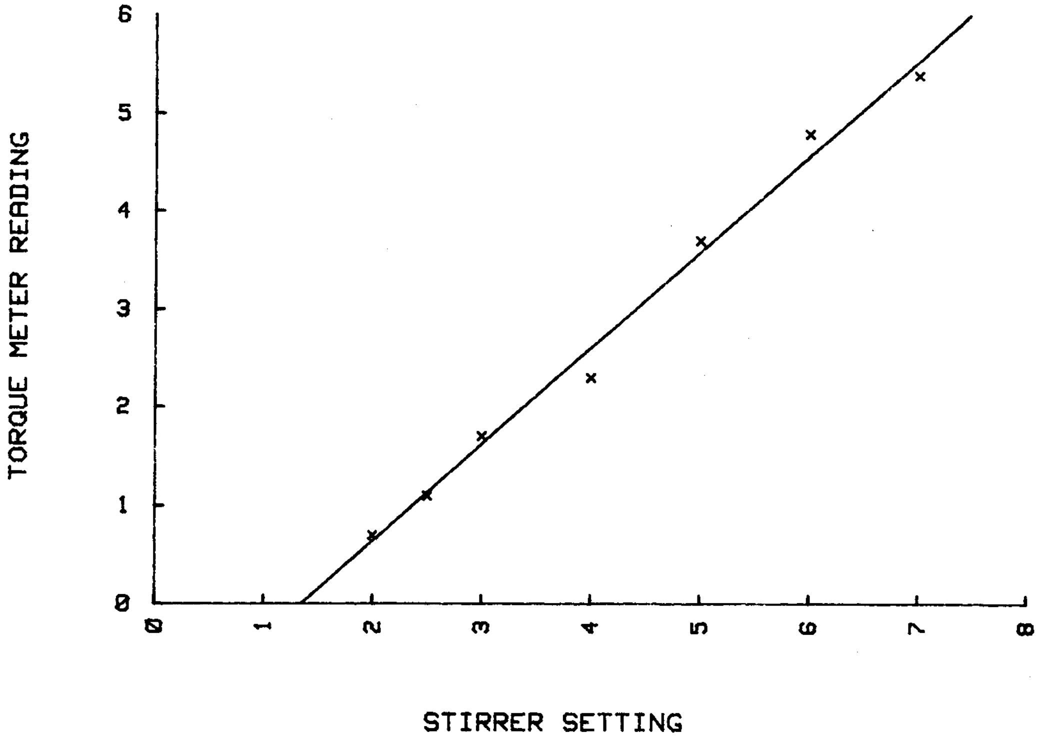

Figure G-2. – Correlation between stirrer setting and torquemeter reading.

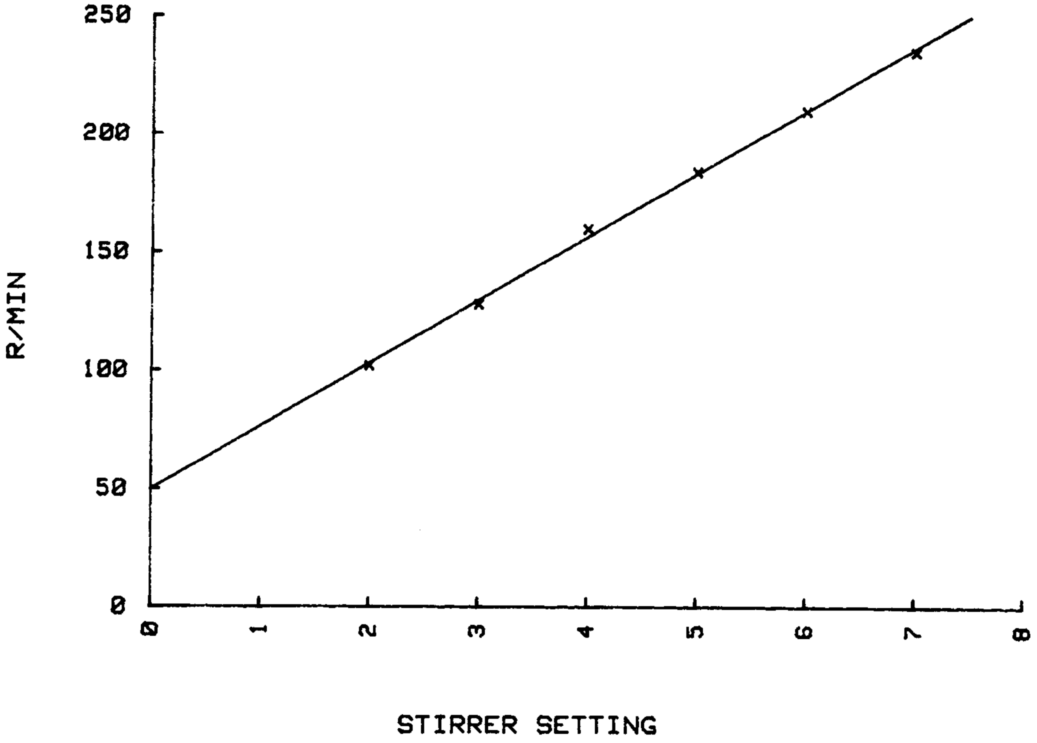

Figure G-3. – Plot of r/min versus stirrer setting.

APPENDIX H
FORMALDEHYDE FLUSHING AND DISPOSAL

When the desalting plant shuts down for more than 10 days, one of the options to preserve the membranes is "pickling" the control blocks with 0.5-percent formaldehyde solution. This appendix outlines a planned method for flushing the formaldehyde to nondetectable levels and for disposal of the flushed solution.

Hydranautics control blocks consist of 48 vessels, each with an internal diameter of 21.6 cm (8.5 in) and a length of about 7.62 m (25 ft). Each vessel has a volume of approximately 178 L (47 gal) made up of the following:

Reject flow space in elements	79.5 L (21 gal)
Product flow space in elements	45.4 L (12 gal)
Reject in outer annular space	41.6 L (11 gal)
Reject between elements	11.4 L (3 gal)

Fluid Systems control blocks consist of 24 vessels (note: this is based on the assumption that the present empty space will be filled under contract modification), each with an internal diameter of 32.4 cm (12.75 in) and a length of about 6.7 m (22 ft). Each vessel has a volume of approximately 322 L (85 gal) made up of the following:

Reject flow space in elements	178 L (47 gal)
Product flow space in elements	38 L (10 gal)
Reject in outer annular space	57 L (15 gal)
Reject between elements	49 L (13 gal)

Based on these data, the following control block results were obtained:

Table H-1. – Control block data.

	Hydranautics L (gal)	Fluid Systems L (gal)
Active reject volume in vessels	4361 (1152)	5470 (1445)
Active product volume in vessels	2180 (576)	908 (240)
"Dead" reject volume in vessels	1999 (528)	1363 (360)
Feed/reject volume in piping to trench	1703 (450)	1703 (450)
Product volume in piping to trench	644 (170)	644 (170)

From flushing data gathered at the YDTF, it can be deduced that a 1-volume flush reduces the formaldehyde level in the reject by 85 percent. Flushing with 689-kPa (100-lb/in^2) service water at 3785 L/min (1000 gal/min) results in a product flow of about 1022 L/min (270 gal/min) and a reject flow of 2763 L/min (730 gal/min), a ratio that is well suited to flush out the reject and product volumes in approximately equal times.

For instance, to get a 1-volume flush for a Hydranautics control block, 6064 L (1602 gal) have to be replaced in the feed/reject volume, and 2824 L (746 gal) have to be flushed from the product space. This results in a 3-minute flush at 3785 L/min (1000 gal/min). Fluid Systems control blocks have similar flushing requirements.

After such a 3-minute flush, formaldehyde levels in the reject stream would be reduced from 5000 to 750 mg/L, and in the product stream, from 5000 to 115 mg/L, based on YDTF data. This flush would add 11 356 L (3000 gal) per control block to the disposal system.

Next, the control block would be drained, assisted by a compressed air purge, which would force out about 60 percent of the stored volume, and, thus, remove at least 60 percent of the residual formaldehyde from the dead annular space. Such draining would add about 7003 L (1850 gal) to the disposal system. The control block would then be filled with service water followed by a 3-minute flush. This will add 11 356 (3000 gal) to the disposal system. The formaldehyde levels expected after this flush are 38 mg/L in the reject stream and 1 mg/L in the product.

Another draining, followed by a 3-minute flush with the product directed to the product pipe, will result in about 2-mg/L formaldehyde in the reject stream and about 15 152 L (4000 gal) going to the disposal system. This results in a total disposal volume of 45 425 L (12 000 gal) per control block.

The formaldehyde solution will be collected in a 15 152-L (4000-gal) covered sump and pumped to the disposal system at 757 L/min (200 gal/min). If this flushing/draining/disposal process is carried on continuously, the entire formaldehyde load in the desalting plant will be neutralized in about 4 days.

Proposed Disposal System

The disposal system proposed previously consisted of a 4-inch pipe from the desalting plant sump to the disposal area; two 56 781 L (15 000 gal) FRP (fiberglass-reinforced plastic) neutralization tanks (buried); one buried FRP hydrogen peroxide tank; and a ferric chloride bin with solutioning equipment, metering pumps, two 10.2-cm (4-inch) static mixers, vapor traps, flowmeters, level sensors, valves and other miscellaneous equipment.

APPENDIX I
COST OF PROCESS

Van Waters Rogers quote, January 1983 (relatively small quantities):

CH_2O	37 percent	485-lb drum	$122.55
H_2O_2	35 percent	500-lb drum	$237.00
$FeCl_3 \cdot 6H_2O$	39 to 43 percent	600-lb drum	$ 96.30

For one control block flushing at 1200 mg/L;

Moles of reactants needed for process.

$$CH_2O\text{:}\quad \frac{10\,887\text{ L}}{1\text{ control block}} \times \frac{5000\text{ mg}}{\text{L}} \times \frac{1\text{ mol }CH_2O}{30\text{ g}} = 1815\text{ mol}$$

$$H_2O_2\text{:}\quad a \times b \times 1815\text{ mol} = 10\,890\text{ mol}$$

where a = 3-times stoichiometric
b = stoichiometric coefficient for H_2O_2 = 2

$$FeCl_3 \cdot 6H_2O\text{:}\quad \frac{Fe^{+3}}{CH_2O} = 0.2$$

$$Fe^{+3} = 0.2 \times 1815\text{ mol} = 363\text{ mol}$$

Cost of reactants.

$$CH_2O\text{:}\quad \frac{\$122.55}{0.37 \times 485\text{ lb}} \times \frac{1\text{ lb}}{453.6\text{ g}} \times \frac{30\text{ g}}{\text{mol }CH_2O} \times 1815\text{ mol} = \$82$$

$$H_2O_2\text{:}\quad \frac{\$237}{0.35 \times 500\text{ lb}} \times \frac{1\text{ lb}}{453.6\text{ g}} \times \frac{34\text{ g}}{\text{mol }H_2O_2} \times 10\,890\text{ mol} = \$1100$$

$$FeCl_3 \cdot 6H_2O\text{:}\quad \frac{\$96.30}{0.41 \times 600\text{ lb}} \times \frac{1\text{ lb}}{453.6\text{ g}} \times \frac{237.0\text{ g}}{\text{mol}} \times 363\text{ mol} = \$74$$

GPO 845-605

Mission of the Bureau of Reclamation

The Bureau of Reclamation of the U.S. Department of the Interior is responsible for the development and conservation of the Nation's water resources in the Western United States.

The Bureau's original purpose "to provide for the reclamation of arid and semiarid lands in the West" today covers a wide range of interrelated functions. These include providing municipal and industrial water supplies; hydroelectric power generation; irrigation water for agriculture; water quality improvement; flood control; river navigation; river regulation and control; fish and wildlife enhancement; outdoor recreation; and research on water-related design, construction, materials, atmospheric management, and wind and solar power.

Bureau programs most frequently are the result of close cooperation with the U.S. Congress, other Federal agencies, States, local governments, academic institutions, water-user organizations, and other concerned groups.

A free pamphlet is available from the Bureau entitled "Publications for Sale." It describes some of the technical publications currently available, their cost, and how to order them. The pamphlet can be obtained upon request from the Bureau of Reclamation, Attn D-922, P O Box 25007, Denver Federal Center, Denver CO 80225-0007.