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Effect of pH on the Destruction of Complexants With Ozone in Hanford Nuclear Waste

W.I. Winters

Prepared for the United States
Department of Energy
Under Contract DE-AC06-77RL01030

Rockwell International

Rockwell Hanford Operations
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Richland, WA 99352

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ABSTRACT

Chemical processing of nuclear waste at Hanford has generated some waste solutions with high concentration (0.1 to 0.5M) of N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), and other organic complexing agents. These complexants must be destroyed because they affect radionuclide migration in soils, waste concentration, radionuclide removal, and other waste storage and processing considerations. Previous studies on actual waste solutions demonstrated that preozonation of the alkaline waste significantly improved radionuclide removal. A series of bench-scale experiments using synthetic waste has been performed to determine the optimum pH for most efficient ozone destruction of EDTA. Ozonation of EDTA in synthetic waste was carried out over the pH range of 1 to 14. Potential catalytic materials were examined at different pH levels. The EDTA-ozone reaction rates and stoichiometric requirements were compared and evaluated for the varying conditions.

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INTRODUCTION

Large amounts of organic complexants have been introduced into Hanford waste from the Hanford B Plant process for separation and concentration of fission products.(1,2) Complexants in Hanford waste may significantly impact waste processing and storage considerations. Organic chelating agents can increase the potential for radionuclide migration in soils.(3,4) Radiolysis and oxidation of complexants in the waste generate gases which increase waste volume and affect long-term storage requirements for these wastes.(5) Complexants complicate the present vacuum evaporator-crystallizer operations by decreasing crystal growth and increasing amounts of entrained water. Other proposed future waste solidification processes may be affected adversely by these reagents.

In this and previous studies, complexant destruction has been directed at evaluating ozone (O_3) oxidation of complexants, particularly ethylenediaminetetraacetic acid (EDTA), to satisfy the requirements for a radionuclide removal process being developed at Hanford.(6,7) This process requires reducing complexant concentration to $< 0.005\underline{M}$ in order to remove long-lived radionuclides to less than 10 nCi/g levels. Ozone was chosen because (1) it has excellent oxidizing power in alkaline solutions, (2) it does not increase volume or introduce undesirable materials, and (3) technology for processing large volumes of solution is established. These earlier studies showed that O_3 could oxidize complexants in actual waste, freeing cationic radionuclides for removal by sodium titanate ion exchangers. Scoping studies of waste and ozonation variables showed that the oxidation of EDTA by O_3 was influenced by the following variables:(6)

$$\left[\text{nitrite} \ \left(NO_2^-\right)\right] > \text{temperature} > \left[Al(OH)_4^-\right] > \left[\text{hydroxide} \ \left(OH^-\right)\right] > \text{UV light}$$

However, only NO_2^- concentration and temperature were determined to be significant at the 95% confidence level over the ranges studied.

The mechanism for O_3 oxidation of organics is known to vary considerably with pH.(8) The primary objective of this study was to determine the effect of pH on the oxidation of EDTA in waste in order to determine the optimum pH for designing an ozonation process. In addition to pH, various additives were investigated that potentially could enhance the reaction. A synthetic residual liquor waste containing only EDTA and tartrate as complexants was used for the study. The complexant of interest chosen was EDTA since it was the strongest complexant introduced into the waste in significant quantities and has a high degree of thermal and radiological stability.

Reaction rates and stoichiometry for the O_3 and EDTA reaction were used as the basis to evaluate pH effects. Because of progressive improvements in the experimental configuration and procedures, the experimental conditions for studying the O_3-EDTA reaction are described in detail. In addition to the evaluation of pH, an attempt has been made to document and consolidate additional information on complexant conditions in waste and possible products of the EDTA oxidation. This information may be significant in planning future complexant studies where the criteria for complexant destruction may be dependent not only on radionuclide removal capabilities but also on factors which would affect near-surface, in situ disposal of the wastes such as gas generation, radionuclide migration in soils, and waste solidifications processes.

SUMMARY AND CONCLUSIONS

The ozonation of EDTA in a synthetic residual liquor waste was studied over the pH range of 1 to >14 in order to determine the optimum pH condition for destroying complexants in Hanford nuclear waste. The O_3-EDTA reaction in this synthetic waste was found to exhibit a different behavior for three pH regions.

In the high pH region (pH 10 to 14+)*, a two-stage reaction was observed in which the reaction rate increased from $\sim 0.56 hr^{-1}$ to $\sim 1.2 hr^{-1}$ and the O_3 consumption increased from 30 moles O_3 per mole EDTA to $\sim$60 moles O_3 per mole EDTA. The optimum reaction rate occurred at pH 11 to 12 and the lowest O_3 consumption at pH 14+. Ozonation at high pH levels is characterized by an initial rapid decrease in EDTA molarity and then a slower decrease at lower EDTA concentrations. The reaction is probably controlled by the decomposition of O_3 to a hydroxyl free radical which reacts nonselectively with EDTA and other constituents $[(NO_2^-$, tartrate, carbonate $(CO_3^{-2})]$ in the waste. Kinetics of the ozonations at all pH levels were characteristic of pseudo-first-order reactions. Once steady state O_3 concentration is reached, the reaction rate becomes solely a function of EDTA concentration.

In many cases, the reaction rate will decrease during the ozonation of organics due to the formation of less reactive oxidation products. The increase in the second-stage reaction rate at high pH levels is believed to be caused by an effective increase in the steady-state O_3 concentration once the NO_2^- ion concentration has been significantly reduced by oxidation to nitrate (NO_3^-).

Addition of cupric nitrate $[Cu(NO_3)_2]$ to the synthetic waste at pH 14+ did not improve the kinetics or stoichiometry of the reaction. The addition of calcium hydroxide $[Ca(OH)_2]$ to remove CO_3^{-2} ion

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*"pH 14+" denotes tests carried out on unneutralized synthetic residual liquor in which the OH^- ion concentration was between 1 and 1.5<u>M</u>.

from the synthetic waste at pH 14+ failed to reduce the CO_3^{-2} ion concentration and resulted in a poorer reaction rate and O_3 usage. Carbonate ion is known to reduce the concentration of the hydroxyl free radical and thus the effectiveness of the reaction. Ozonations of a simple EDTA-water matrix at pH 12 with and without CO_3^{-2} showed that CO_3^{-2} ion had no effect on the reaction rate (4.75 hr^{-1}) but did increase O_3 consumption by 50% to 7.25 moles O_3 per mole EDTA. Since both of these values for the EDTA-water system are 3 to 4 times better than the results for the synthetic waste, it would indicate that other components of the waste, such as NO_2^- and tartrate, have a more significant effect on the reaction than carbonate. However, if it becomes necessary to reduce complexants to concentrations $<10^{-4}\underline{M}$, the CO_3^{-2} ion may have a significant impact on the O_3 requirement.

Ozonation in the high pH region is optimized at the lowest OH^- concentration that prevents aluminum precipitation. Based on these studies, ozonation at high pH levels would provide the highest reaction rate and lowest O_3 requirement without the need for a large solids separation process. Significant improvements in the ozonation of waste at high pH levels could be realized if the nitrite concentration first could be reduced by some cheaper, simpler method.

The intermediate pH region (pH 3 to 10) is undesirable for ozonation of the synthetic waste since large amounts (~50 vol%) of aluminum solids are formed over the entire pH range. Ozone reactions with EDTA in this pH region were characterized by a slow initial reduction in the EDTA molarity, followed by a faster oxidation of the EDTA. A two-stage reaction was observed in which the rate increased from ~0.12 hr^{-1} to 0.70 hr^{-1} and the O_3 consumption decreased from 120 moles O_3 per mole EDTA to ~10 moles O_3 per mole EDTA. This change in reaction characteristics is believed to be caused by a change in the O_3 oxidation mechanism from one based on the formation of hydroxyl free radical to one in which the O_3 molecule directly attacks the oxidizable material. Unlike the hydroxyl free radical reaction, direct O_3 attack is very selective. It is hypothesized that the O_3 initially attacks only NO_2^- ions, resulting in a slow EDTA reaction rate and a large O_3 consumption value. After all of the NO_2^- is oxidized, O_3 rapidly and efficiently oxidizes EDTA.

Continuous addition of hydrogen peroxide (H_2O_2) during the ozonation of synthetic waste at pH 7 showed the same reaction characteristics as the other intermediate pH level tests. The H_2O_2 did increase the second stage reaction rate to 2.0 hr^{-1}.

These studies on a synthetic waste did not show any significant advantages of operating in the intermediate pH range. However, it may be possible to adjust the pH of actual waste to 3 or 4 without a large amount of solids forming. If so, NO_2^- may be removed by a more economical process and thus take advantage of the improved use of O_3 found in the second stage of these reactions.

Ozonation of the synthetic waste in the low pH region, $<$pH 3, was characterized by a very slow single-stage reaction which consumed very little O_3. At low pH values, NO_2^- and CO_3^{-2} have decomposed to NO_x and carbon dioxide (CO_2) gases and are not important factors in the reaction. The reaction rate in this pH region was ~0.047 hr^{-1} and consumed about 12 moles of O_3 per mole of EDTA.

Aluminum was found to cause the slow reaction rate. Ozonation of a solution containing an EDTA and iron at pH 1.2 had a single-stage reaction rate of 1.07 hr^{-1} and used only one mole of O_3 per mole of EDTA. The addition of tartrate to the matrix made the ozonation a two-stage reaction with a slower second-stage rate of 0.45 hr^{-1}. The slower reaction rate is probably caused by competitive reaction of tartrates for the O_3. In the presence of tartrates, O_3 consumption increased to ~5 moles O_3 per mole EDTA. Results from the addition of chromium to the matrix were inconclusive since different results were obtained for different iron levels suggesting that both iron and chromium may affect the reaction. Only the addition of aluminum ion caused the reaction rate to decrease to 0.1 hr^{-1}. Since EDTA is easily oxidized by H_2O_2 at low pH values, an aluminum-EDTA complex is suspected of hindering the mechanism for the O_3 oxidation of EDTA.

Catalysis of the oxidation by the addition of silver nitrate ($AgNO_3$) at low pH levels was unsuccessful. Manganese nitrate ($Mn(NO_3)_2$) was added with the intention of continuously producing permanganate, which would have a more favorable EDTA oxidation mechanism. The Mn^{+2} ion only increased the reaction rate to 0.124 hr^{-1} with no significant improvements in O_3 consumption. Larger quantities of Mn^{+2} may produce more favorable results.

Raising the ozonation temperature from 60°C to 85°C produced a two-stage reaction at pH 1.2. The first-stage reaction rate at 85°C was initially 0.40 hr^{-1} and then decreased to 0.18 hr^{-1}. Only 3 moles of O_3 per mole of EDTA were consumed for the first stage of the reaction. The O_3 consumption rate increased to 20 for the final stage. Increasing the temperature made the O_3-EDTA reaction rate at low pH values comparable to those in the high pH region. High temperature ozonations at low pH also significantly improved O_3 utilization.

An advantage of ozonation at a low pH level is that no solids processing would be required. However, acidification of the waste requires a large amount of acid and may make other methods for destroying complexants economically competitive with the O_3 process. Before seriously considering ozonation of waste at low pH levels, other oxidants such as H_2O_2 should be evaluated.

Based on these studies, ozonation of waste at high pH levels appears to be the most advantageous because of its reasonable reaction rates, stoichiometry, and simplicity. However, before an accurate economic evaluation of the ozonation can be performed, more laboratory work is needed in order to:

- evaluate the mass transfer kinetics of the reaction
- determine the efficiency of ozone for destroying other complexants in Hanford waste

- study the fundamental chemistry of O_3-complexant reactions by (1) determining the products formed, and (2) by determining more accurately matrix and reaction condition effects with simpler reaction systems
- verify reaction parameters on actual waste.

All these studies should be directed at providing the necessary information for meeting not only radionuclide removal criteria, but also new criteria for the near-surface in situ disposal of Hanford wastes.

EXPERIMENTAL

EQUIPMENT AND PROCEDURES

The experimental arrangement underwent numerous modifications to improve the accuracy and reliability of the experiment. The final flow diagram and hood arrangement are shown in Figures 1 and 2. A detailed description of the equipment is discussed in Appendix A.

Ozone was generated from oxygen using a Linde Model SG-4060 ozone generator. The O_3 concentration in the gas entering and leaving the reactor was measured using Daisibi Model 1003HC O_3 monitors.* The volume of gas reacting with the synthetic waste mixture was measured using wet test meters (WTM). Ozone was destroyed using Westgate Ultrox+ catalytic O_3 decomposers.

A glass reactor similar to the one shown in Figures 3 and 4 was used for all the tests. The reactor used for these studies had a glass frit with 1 mm holes in place of the Teflon frit shown in Figure 3. The pot has provisions for sampling and continuous reagent addition without the loss of gas. A temperature probe monitors changes in the reaction temperature.

Normally, 2 l of a 1:1 diluted synthetic residual liquor with the composition shown in Table 1 was adjusted to the desired pH level and ozonated for 5 to 6 hours with continuous stirring in the reaction vessel. Tests made at pH values between 3 and 13 normally required filtration of the feed before ozonation.

Further details of the feed preparation process are described in Appendix A. A detailed procedure for preparing the synthetic residual liquor is provided in Appendix B.

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*Dasibi Environmental Corporation, 616 E. Colorado Street, Glendale California, 91205.

+Westgate Research Corporation, 1931 Pontius Avenue, West Los Angeles, California, 90025.

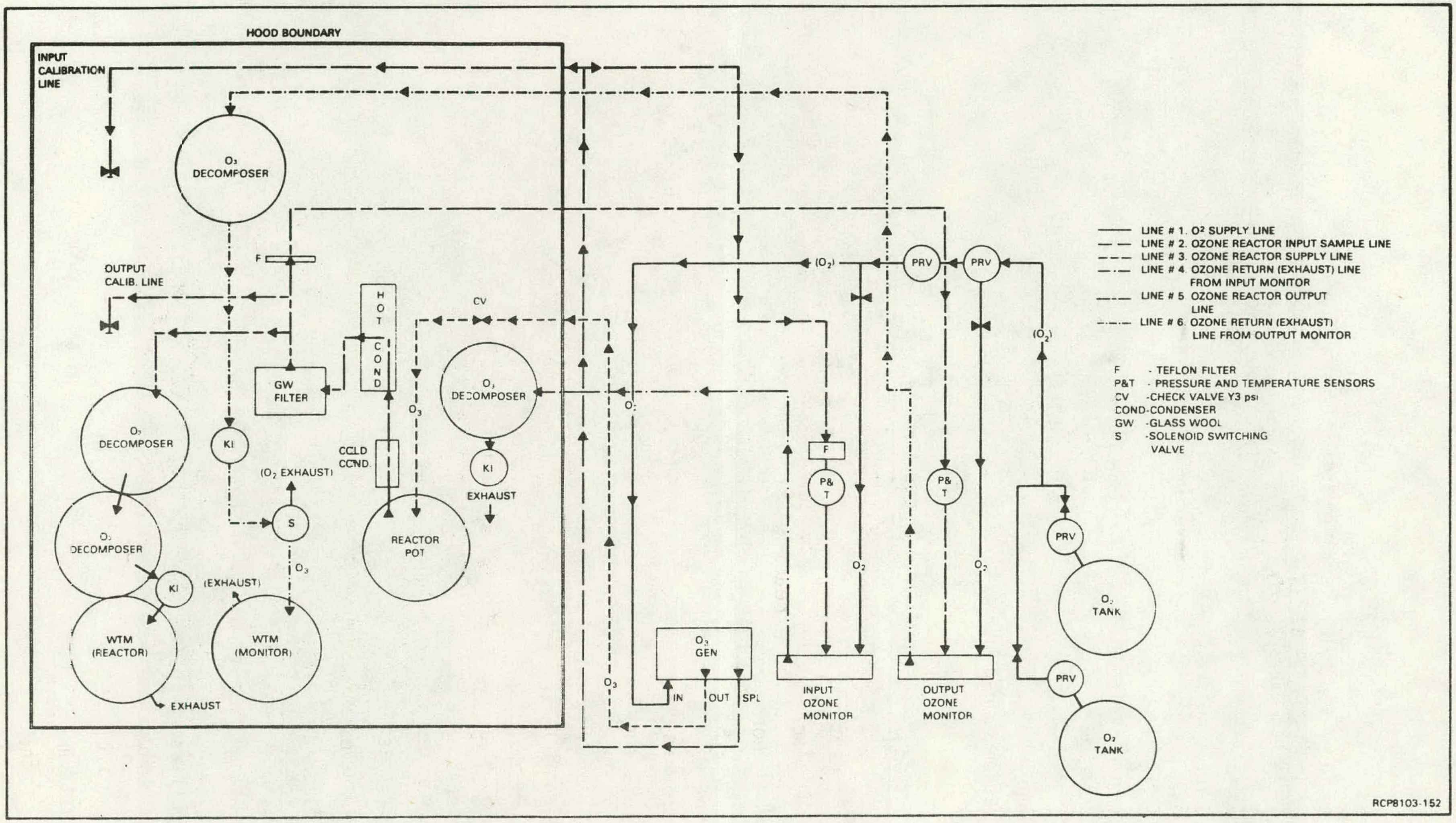

FIGURE 1. Flow Diagram of Ozonation System.

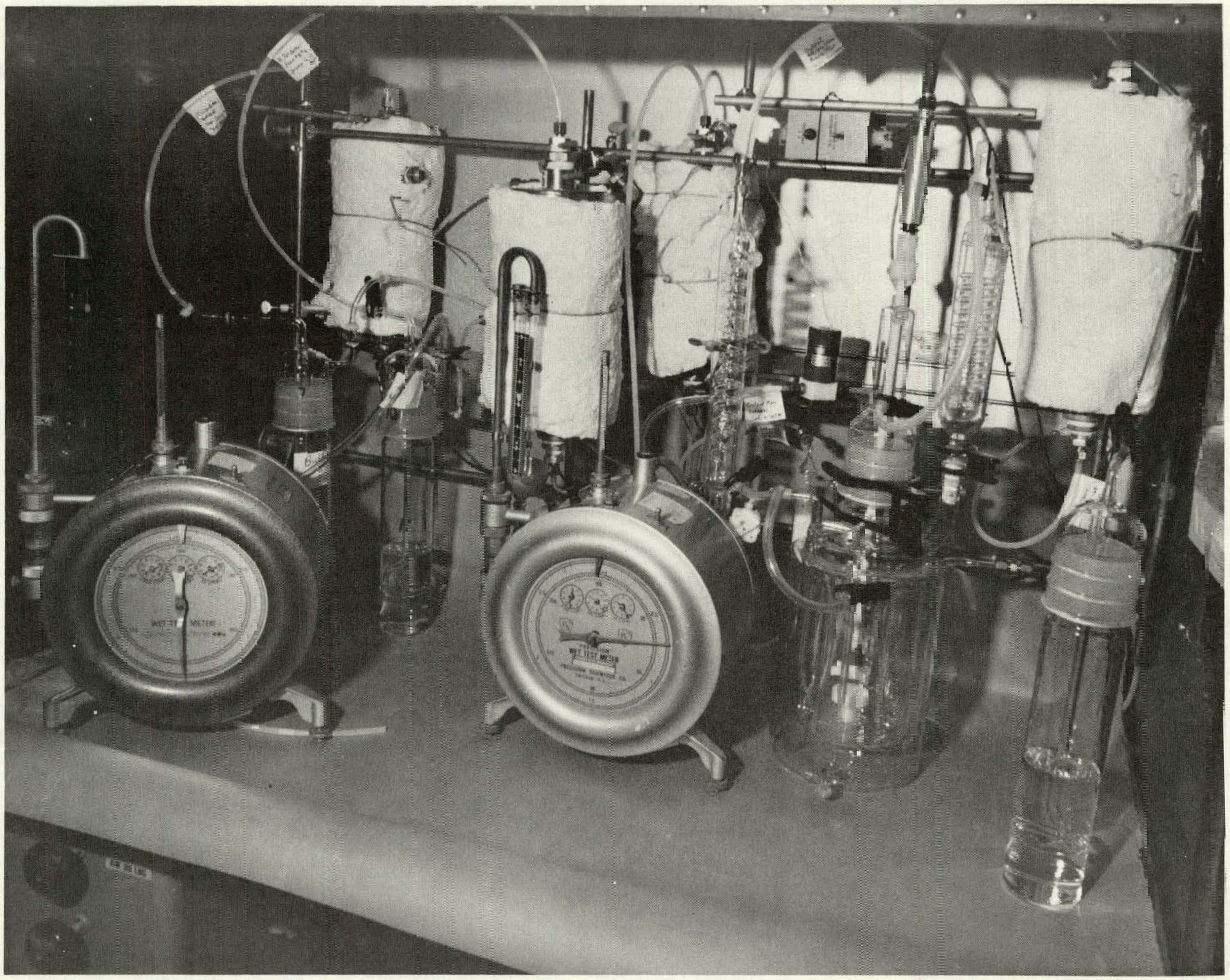

FIGURE 2. Ozonation System.

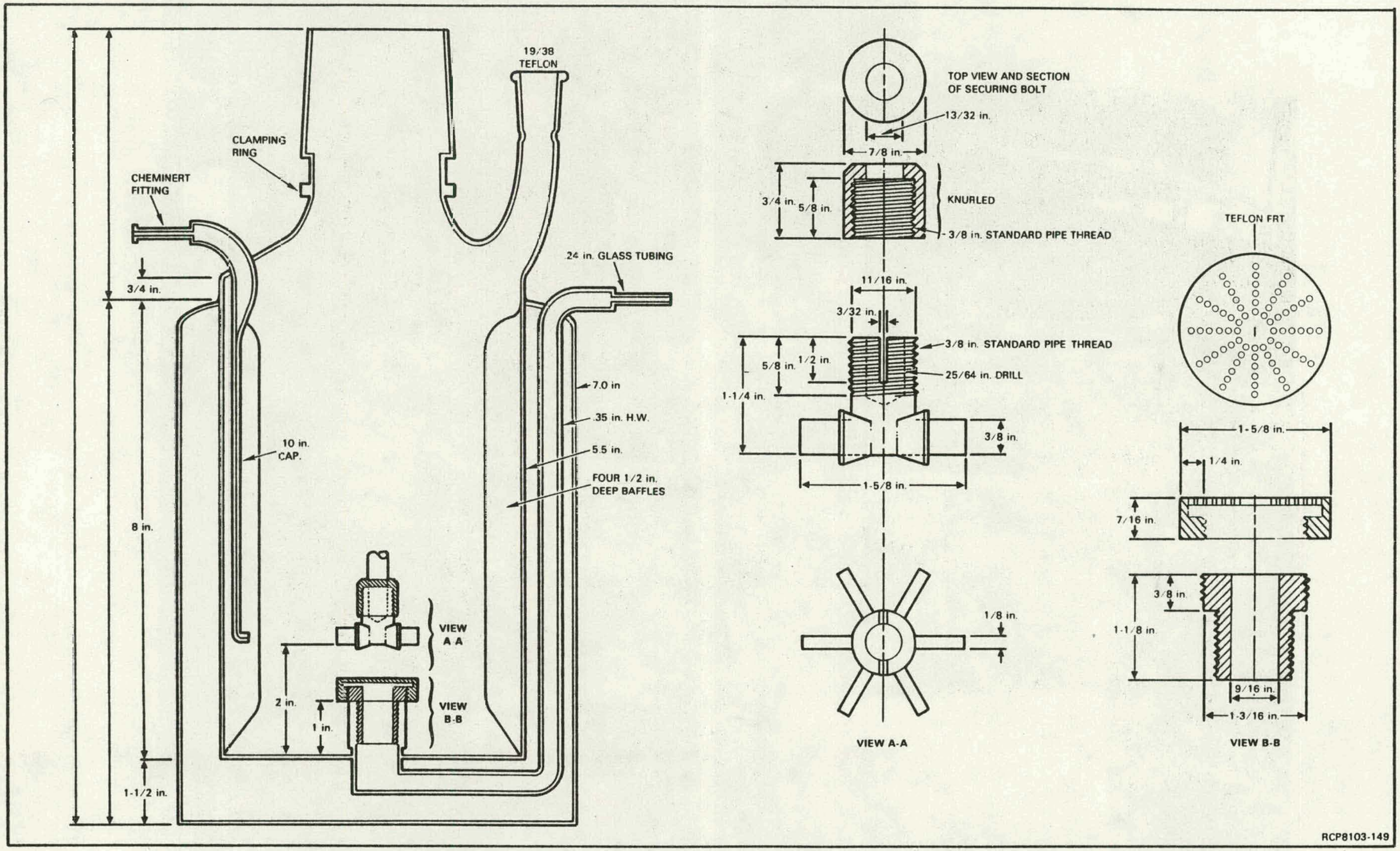

FIGURE 3. Reactor Pot and Teflon Frit.

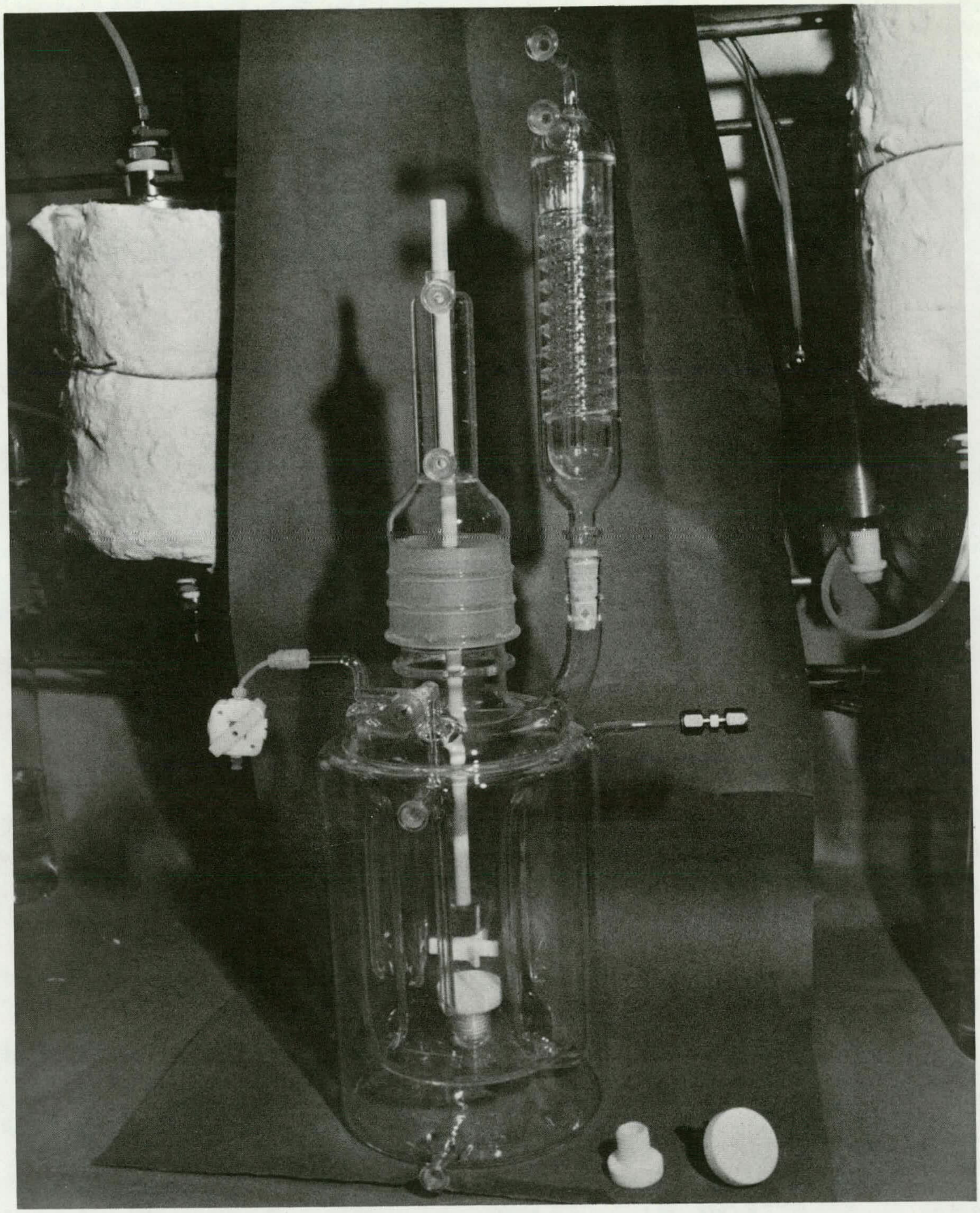

FIGURE 4. Reactor Pot.

TABLE 1. Synthetic Residual Liquor Waste Composition.

Component	Molarity
$NaAlO_2$	0.85
NaOH	1.30
$NaNO_3$	1.45
$NaNO_2$	1.35
Na_2CO_3	0.12
Na_2CrO_4	0.10
$Fe(NO_3)_3$	0.0075 (as Fe)
Sodium Tartrate	0.05
EDTA	0.031

Samples of the residual liquor were normally taken for EDTA, NO_2^-, CO_3^{-2}, and pH analysis every 15 minutes for the first 2 to 3 hours and then every 30 minutes until the test was completed. The volume and O_3 concentration of the gas entering and leaving the reactor was measured each time a sample was taken. These measurements, along with the temperature and pressure conditions for the gas at the various measurement points, were recorded on the data record shown in Appendix C.

The calculations for the analysis of these data are described in detail in Appendix D. They consist of a series of pressure-temperature correction calculations to determine the O_3 concentration and gas volume at standard conditions. A set of material balance calculations are used to determine the quantities of O_3 and EDTA reacting. The pseudo-first-order reaction rates were determined from the slope derived from least square analysis of the plot of -ln $EDTA/EDTA_0$ versus time. The O_3 consumption rate was determined from the slope of the line resulting by plotting the cumulative amount of O_3 reacted against the moles of EDTA reacted.

Numerous methods have been used to analyze O_3 and calibrate O_3 monitors.(9-14) The potassium iodide (KI) method described in Appendix E was used to calibrate the O_3 monitors. Low results were obtained if more than 6 l of gas were trapped when calibrating high O_3 concentrations. This is believed to be caused by the formation of iodates(15) and higher oxidized forms of iodine such as I_2O_9. Calibration of the O_3 monitors based on the UV principles described in Appendix F is recommended to overcome KI titration problems.(14)

ANALYSES

In earlier work, a spectrophotometric method was used to determine EDTA in ozonated solutions.(6,16) All EDTA results in this study were obtained using a recently developed high performance liquid chromatographic (HPLC) method.(17) This method is based on the formation, isolation, and quantification of the iron-EDTA complex. The complete formation of the iron-EDTA complex required 2 hours because of the slow ligand exchange of the aluminum complexes.(18,19)

Total organic carbon (TOC) and CO_3^{-2} analyses were determined using a modified Oceanography International TOC system.* Nitrite was determined spectrophotometrically using a procedure based on diazotization. Iron and aluminum were analyzed by standard atomic absorption techniques.

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*Oceanography International Corporation, 512 West Loop, College Station, Texas.

RESULTS AND DISCUSSION

pH TEST CONDITIONS

The effect of pH on the oxidation of EDTA by O_3 was studied over the pH range 1 to 14+. These tests, and tests where additives were introduced to improve the reaction, were carried out over a period of a year and are listed in Table 2. Some of the varying conditions during the tests have also been tabulated.

TABLE 2. pH and Additive Test Conditions.

Test	Reactor	Synthetic Waste Batch	Ozonator	Comment
pH 14+	1st	1st	1st	Shutdown - 45 min Small leak problem
pH 14+	2nd	2nd	1st	Flow stoppage
pH 14+ + $Cu(NO_3)_2$	2nd	2nd	1st	
pH 14+ + $Ca(OH)_2$	1st	2nd	1st	
pH 13	2nd	3rd	2nd	
pH 12	2nd	3rd	2nd	
pH 10	1st	1st	1st	Shutdown 3 hr 30 min
pH 8.5	1st	1st	1st	Shutdown 2 hr 15 min
pH 7 + H_2O_2	2nd	2nd	1st	
pH 4.5	1st	1st	1st	
pH 2.8	2nd	2nd	1st	
pH 2 + $AgNO_3$	2nd	2nd	1st	
pH 1.2 - 10 hr	2nd	2nd	1st	
pH 1.2 - 85°C	2nd	3rd	2nd	
pH 1.2 + $Mn(NO_3)_2$	2nd	3rd	2nd	

As explained in the equipment discussion, an improved reactor was built similar to Figure 3 but with a bubbler made of glass rather than Teflon. The second reactor permitted addition of solutions and removal of samples without loss of the ozonating gas. However, the bubbler on the second pot had fewer holes and was farther from the stirring shaft, giving poorer gas distribution. The total volume of gas reacting and the moles of O_3 reacting per mole of EDTA may be biased low for the first reactor because of gas losses during sampling. Reaction rates for the second reactor are lower because of the poorer gas distribution. Tests on unneutralized synthetic waste (pH 14+) were performed with both reactors for comparison.

Three 20-l batches of synthetic residual liquor were prepared. Even though the makeup procedure differed slightly for Batch 1, no significant differences were observed in the ozonation tests due to changes in batches of synthetic waste.

During one test, liquid siphoned back into the first ozonator, which then needed to be replaced. A substantial difference was observed in the flow rate of the second ozonator compared to the WTM results. In order to obtain the same flow through the reactor, it was necessary to operate with a higher flow through the ozonator. This caused the weight percent of O_3 generated to be lower than tests with the first ozonator. The change in flow and O_3 concentration with ozonators may have caused some change in reaction rates and O_3 consumption.

When the stirrer was connected directly to the motor, it would frequently vibrate loose and shut down (See Table 2). Reduced stirring capability from binding or loosening normally could be observed by an increase of O_3 in the gas coming off the reactor. There were frequent variations in the data after startup until a steady-state condition was reached.

On the pH 14+ test with the second reactor, solids plugged the holes in the glass bubbler, causing erratic and reduced flows through the ozonator and reactor. These reduced flows caused the weight percent of O_3 produced for this test to increase and fluctuate, reducing the accuracy of the O_3 analyses.

The results of the ozonation tests are summarized in Table 3. The data are organized in order of decreasing pH for seven different data areas of the ozonation test: preparation, O_3, EDTA, reaction data,

TABLE 3. Summary of Ozonation Data.

	pH 14+ 1st Reactor	pH 14+ 2nd Reactor	pH 14+ $+Cu(NO_3)_2$	pH 14+ $+Ca(OH)_2$	pH 13	pH 12	pH 10	pH 8.5
PREPARATION								
Vol. Ozonated (l)	1.5	2.0	2.0	2.0	1.7	2.0	1.5	1.7
Vol. HNO_3 to pH (ml)	-	-	-	-	350	701	324	412
Additive	-	-	5 g	26.3 g	-	-	-	-
OZONE DATA								
Length of Run (hr)	5.5	6.0	5.0	5.0	5.0	5.0	5.0	4.0
Av. wt% In	3.577±.08	3.896±.25	3.457±09	3.385±.03	3.109±.08	3.348±.08	3.268±.03	3.410±.03
Av. wt% Out	0.682	0.844	0.390	0.330	0.788	0.551	0.993	0.997
Total Vol. Added (l)	2923	2735	2768	2835	2578	2751	2894	2060
Moles Added/hr	0.58	0.54	0.58	0.58	0.48	0.56	0.57	0.56
Moles Added	3.179	3.220	2.905	2.903	2.422	2.791	2.862	2.245
Moles Unreacted	0.707	0.719	0.352	0.311	0.582	0.583	1.150	0.834
Moles Reacted	2.470	2.501	2.553	2.592	1.840	2.288	1.712	1.411
EDTA DATA								
Initial (M)	0.290	0.0280	0.0298	0.0331	0.0270	0.0236	0.0224	0.0234
Final (M)	0.0003	0.0014	0.0027	0.0065	0.0006	0.0006	0.0001	0.0042
Moles Reacted	0.0428	0.0531	0.0542	0.0530	0.0448	0.0461	0.0334	0.0328
% Reacted	98.4	94.8	90.6	80.1	97.6	97.7	99.4	82.4
REACTION DATA								
1st Rate	0.76	0.38	0.44	0.26	0.51	0.57	0.67	0.11
2nd Rate	$1.70^{(2-25)a}$	$0.55^{(3-0)a}$	$0.55^{(3.0)a}$	$0.47^{(3-30)a}$	$1.02^{(3-0)a}$	$0.99^{(2-45)a}$	$2.40^{(2-10)a}$	$0.82^{(1-45)a}$
$\Delta O_3/\Delta EDTA$ - 1st	27.61	23.65	31.42	53.7	20.30	36.72	39.35	115.2
$\Delta O_3/\Delta EDTA$ - 2nd	51.63	43.85	54.70	-	65.87	85.02	60.01	10.5
CO_3^{-2}								
Initial (M)	0.120	0.120	0.120	0.120	0.065	0.048	0.038	0.002
Final (M)	0.580	0.300	0.330	0.290	0.110	0.100	0.11	0.027
Rate of Increase	0.103	~0.02	0.043	(0.(06)b 0.02	0.02	0.008	0.017	NA
NO_2^-								
Initial (M)	1.28	1.33	1.41	1.30	1.290	0.966	1.13	0.43
Final (M)	0.04	0.21	0.14	0.14	0.023	ND	0.004	ND
Rate of Decrease	0.32	0.18	0.313	0.265	0.220	0.184	0.363	NA
pH								
Initial	>14	>14	>14	>14	12.84	11.89	9.98	$8.52 \rightarrow 9.4^{e}$
Final	>14	>14	>14	>14	12.54	9.52	9.07	8.59

[a]( ) - time when reaction rate changed

[b] - appears to undergo rate change

[d]ND - non-detectable

[c]NA - not analyzed

[e]highest pH

TABLE 3. Summary of Ozonation Data (Continued).

	pH 7 $+H_2O_2$	pH 4.5	pH 2.8	pH 2.1 +Ag	pH 2.1 10 hr test	pH 1.2 85°C	pH 1.2 $+Mn(NO_3^-)_2$
PREPARATION							
Vol. Ozonated (l)	2.0	1.5	2.0	2.0	2.0	2.0	2.0
Vol. HNO_3 to pH (ml)	490	460	639	640	628	915	908
Additive	0.26 mol/hr	-	-	4/g	-	-	4/g
OZONE DATA							
Length of Run (hr)	5.0	4.75	5.0	5.0	10.0	5.0	5.0
Av. wt% In	3.327±07	3.549±.04	3.335±.12	3.328±.04	3.563±.09	3.139±.07	3.396±.12
Av. wt% Out	0.980	2.079	3.219	3.178	3.490	3.000	3.193
Total Vol. Added (l)	3109	2354	2901	2795	5470	2585	2595
Moles Added/hr	0.63	0.53	0.58	0.56	0.59	0.49	0.54
Moles Added	3.140	2.537	2.904	2.806	5.902	2.460	2.675
Moles Unreacted	1.133	1.756	2.815	2.680	5.778	2.342	2.516
Moles Reacted	2.007	0.811	0.089	0.126	0.124	0.118	0.159
EDTA DATA							
Initial (M)	0.0195	0.0117	0.0204	0.0195	0.0133	0.0148	0.0167
Final (M)	0.0003	0.0023	0.0172	0.0166	0.0072	0.0047	0.0101
Moles Reacted	0.0384	0.0141	0.0066	0.0056	0.0122	0.0203	0.0133
% Reacted	98.4	80.3	16.2	14.9	45.9	68.6	39.8
REACTION DATA							
1st Rate	0.12	0.05	0.034	0.043	0.065	0.395	0.124
2nd Rate	2.04 (2-45)	0.60 (1-30)	-	-	-	0.184 (1-45)	0.035
O_3/ EDTA - 1st	118.0	499	12.1	15.7	9.4	2.9	9.73
O_3 / EDTA - 2nd	7.3	7.4	-	-	-	20.0	-
CO_3^{-2}							
Initial (M)	<0.04	ND	ND	ND	ND	ND	ND
Final (M)	0.023	ND	ND	ND	ND	ND	ND
Rate of Increase	0.03	NA	NA	NA	NA	NA	NA
NO_2^-							
Initial (M)	0.82	0.39	0.01	ND	ND	ND	ND
Final (M)	ND	0.0012	ND	ND	ND	ND	ND
Rate of Decrease	0.307	NA	NA	NA	NA	NA	NA
pH							
Initial	6.99	4.46→5.19	2.78	2.06	1.23	1.30	1.29
Final	8.57	4.83	2.79	2.10	1.58	1.49	1.72

[a] ( ) - time when reaction rate changed
b - appears to undergo rate change
[c] NA - not analyzed
[d] ND - non-detectable
[e] highest pH

$\left[CO_3^{-2}\right]$, $\left[NO_2^{-2}\right]$, and pH. Most of these topics are self-explanatory. The "Av. wt% In" is the average weight percent of O_3 going into the reactor for the entire reaction. It normally was very constant as can be seen from the standard deviations for the data. The "Av. wt% Out" data, on the other hand, varied continuously with the reaction and only roughly indicates the amount of O_3 not reacting for the test. The average weight percent O_3 entering the reactor for all tests varied only about ±6%. The average flow rate for these tests was 540 l/hr ±40 l or ±8%. Many of the reactions appeared to have more than one stage, as noted by changes in the reaction rate. Normally, for high pH values, the EDTA was almost completely destroyed by the end of the second stage. For tests at pH values greater than 7, the CO_3^{-2} concentration increased and the NO_2^- concentration decreased because of oxidation. At lower pH levels, the carbonic acid (H_2CO_3) and nitrous acid (HNO_2) decomposed to CO_2 and NO_x and were normally too low to be measured.

Effect of pH on Reaction Rate

The change in the rate of reaction as a function of time and pH is shown in Figures 5 and 6. The O_3 reaction appears to show three behavior patterns as a function of pH. At high pH levels (pH 10-14+), the EDTA concentration initially decreases very rapidly and the reaction rate is constant for almost 3 hours before increasing. For intermediate pH levels (pH 4.5-10), the EDTA concentration decreases slowly for the first 2 hours and then decreases at about the same rate as the first stage of the high pH reactions. Low pH (pH 1.2-4.5) reactions are much slower and do not show any changes in reaction rate with time.

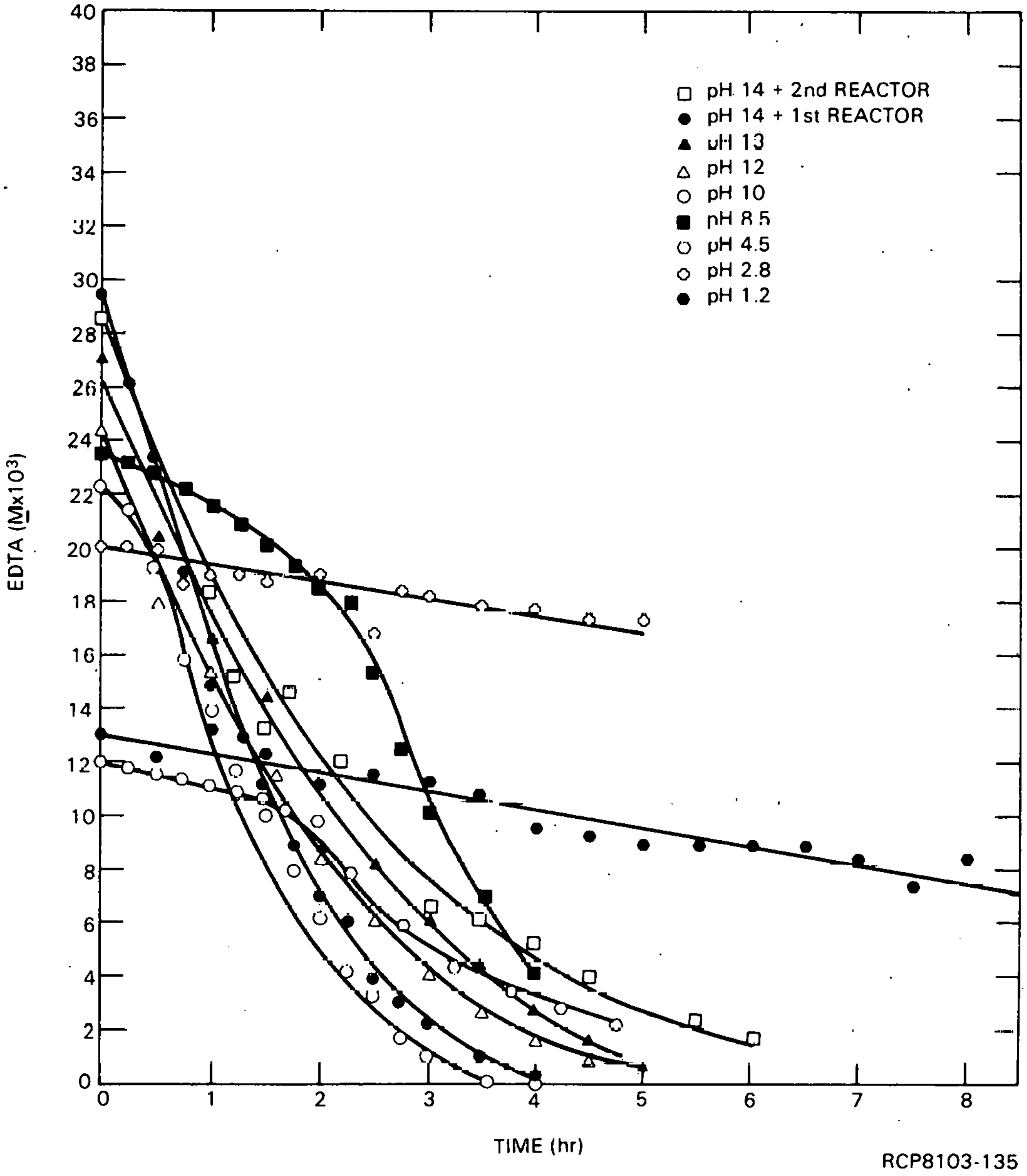

FIGURE 5. EDTA Molarity versus Time.

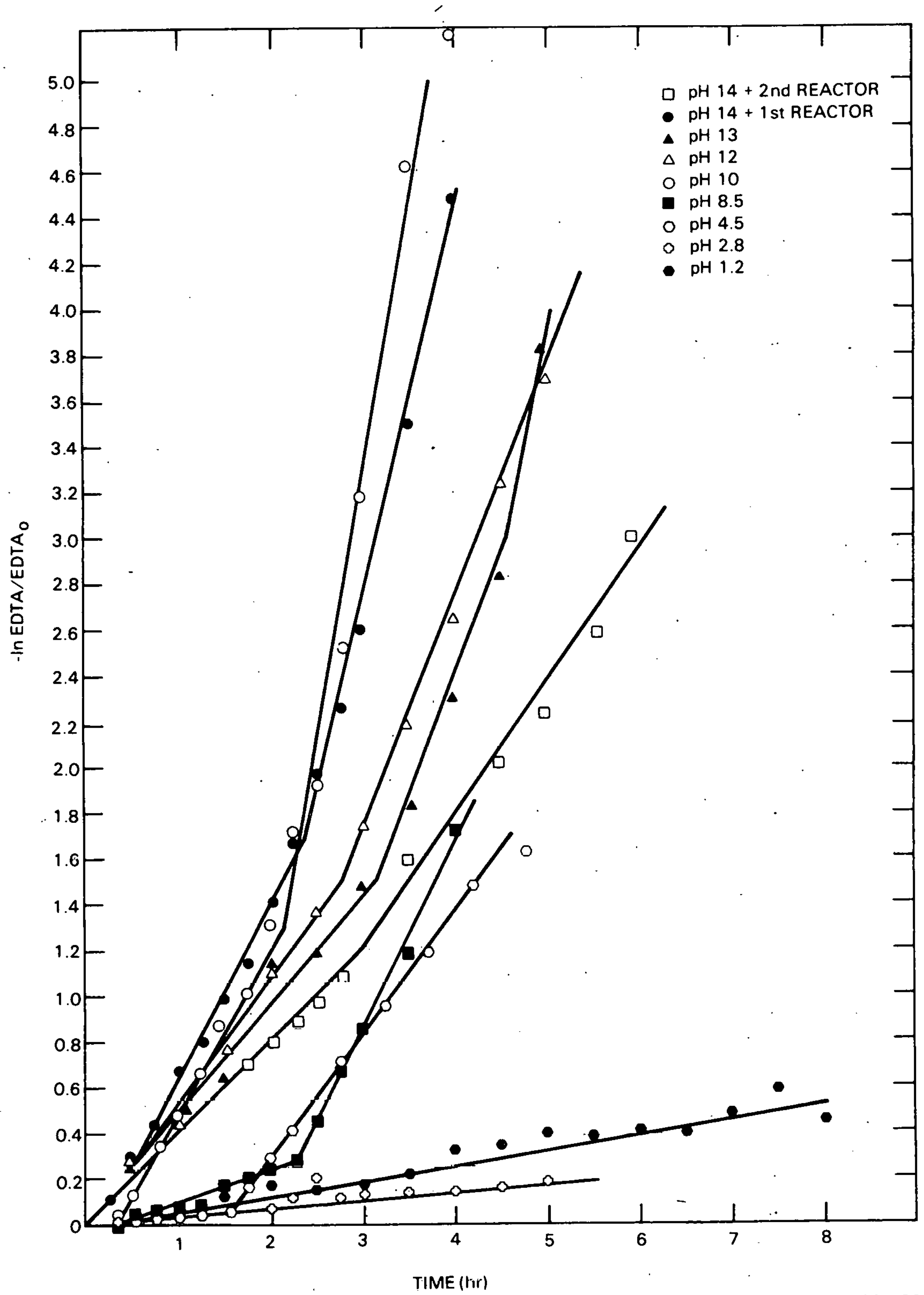

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FIGURE 6. $-\ln EDTA/EDTA_0$ versus Time.

Explanation of High pH Results

The O_3 reaction with EDTA is believed to be second order like most other organic $O_3^{(8)}$ reactions

where:

$$- \frac{d[EDTA]}{dt} = k_{EDTA} \left[O_3\right] [EDTA] \qquad (2)$$

The continuous addition of O_3 creates steady-state conditions in which the O_3 concentration $\left[O_3\right]$ becomes constant and the reaction becomes a pseudo-first-order reaction

where:

$$- \frac{d\ EDTA}{dt} = k^1_{EDTA} [EDTA] \qquad (3)$$

Changes in organic-O_3 reaction rate have been observed by other investigators.(20) In these reports, the rate decreased because of the formation of oxidation products which were less reactive than the original organic. In these studies, the second reaction rate is faster. A possible explanation for this observation is that the steady-state concentration of O_3 is smaller during the first part of the reaction because the very rapid reaction of O_3 with NO_2^- in the synthetic waste decreases the effective O_3 concentration.(21) Once most of the NO_2^- has been oxidized, the steady-state concentration of O_3 rises and the pseudo-first-order reaction rates constant of EDTA increases. This effect may be explained through the following equations. The rate of change in the concentration of O_3 in solution (O_s) is a function of the concentration of dissolved O_3 at the interface $(O_s)^*$ in equilibrium with the O_3 gas interface

where:

$$\frac{d\ O_s}{dt} = k_s \left(O_s{}^* - O_s\right) \qquad (4)$$

The O_3 concentration in solution is also affected by:

1) Decomposition$^{(19,22)}$

$$\frac{d\ O_s}{dt} = -k_D\ (O_s) \tag{5}$$

2) Reaction with (NO_2^-)

$$\frac{d\ O_s}{dt} = -k_{NO_2^-}\ (O_s)(NO_2^-) \tag{6}$$

3) Other oxidizable or free radical scavenging ion reactions such as CO_3^{-2}.$^{(23)}$

The rate of change of O_3 with time under these conditions is as follows:

$$\frac{d\ O_s}{dt} = k_s\ (O_s{*} - O_s) - k_d\ (O_s) - k_{NO_2^-}(O_s)\ (NO_2^-) \tag{7}$$

At steady state, $dO_s/d_t=0$, and the O_3 concentration in solution becomes:

$$O_s = \frac{k_s\ O_s{*}}{k_s + k_D + k_{NO_2^-}\ (NO_2^-)} \tag{8}$$

The NO_2^- oxidation by O_3 appears to be a zero-order reaction at all pH levels as seen in Figure 7. This indicates that it may be controlled by the O_3 feed rate or by mass transfer conditions. The NO_2^- oxidation rate varied from 0.32 to 0.18 moles/hour. The highest rates occurred with the first reactor, which was believed to have superior mass transfer capabilities. No NO_2^- data were collected for the pH 4.5 and 8.5 tests.

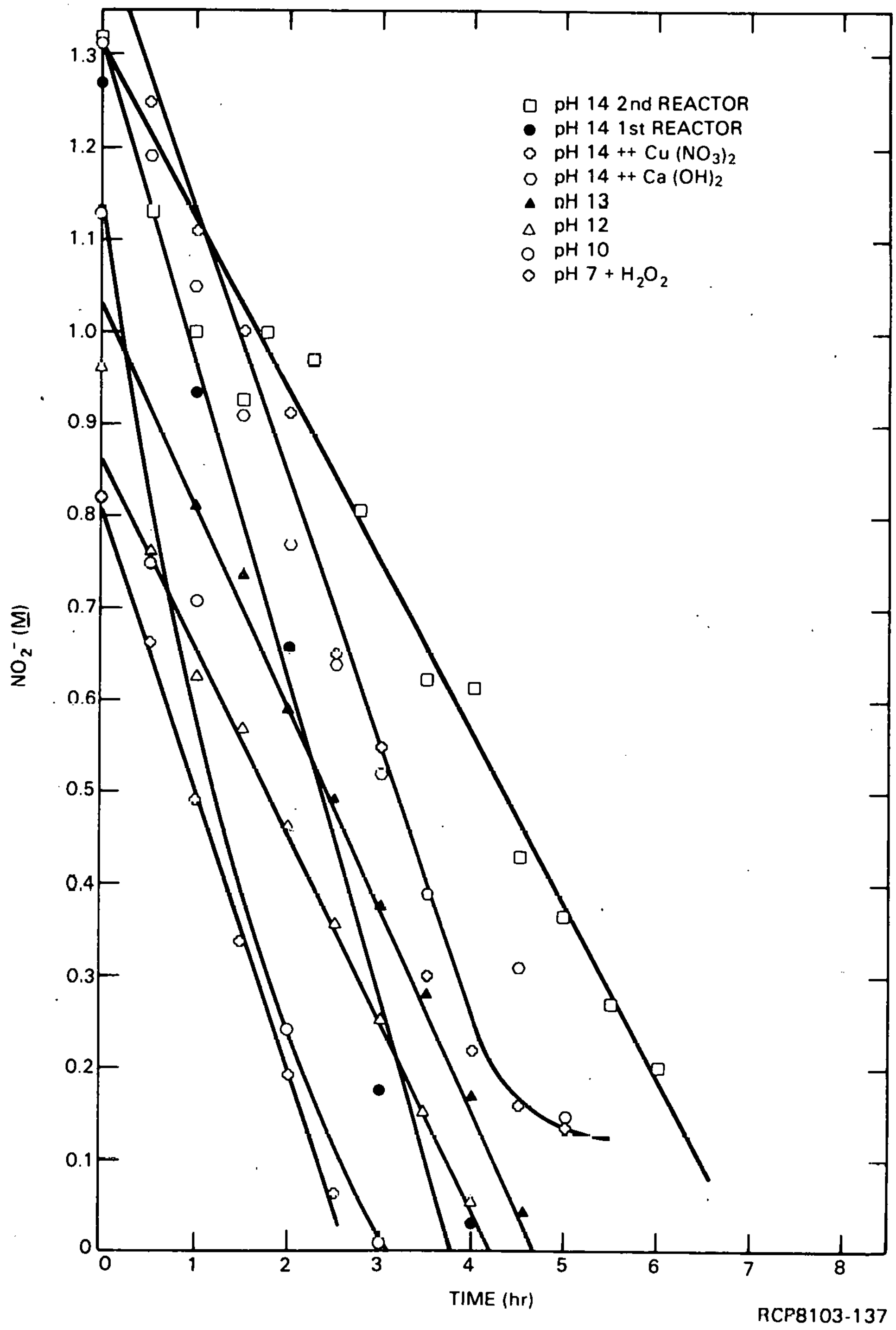

FIGURE 7. Nitrite Molarity versus Time.

Explanation of Intermediate pH Results

• Reaction rates for the intermediate pH tests were initially slow and later increased to about the same rate as the first stage of the reaction at high pH levels. This effect may be explained by a change in the mechanism for the O_3 reaction, or by retardation of the ligand oxidation because of metal coordination. The latter effect is believed to be significant for the oxidation of EDTA in synthetic waste at low pH levels. However, since most metal ions (aluminum, iron) precipitate as hydrous oxides in the intermediate pH range, their effect on the reaction is probably insignificant.

Hoigné and Bader have proposed that O_3 reacts directly with a substance in solution, or decomposes above a critical pH to form a hydroxyl free radical ($OH^\bullet$) which then becomes the important oxidant and controls the reaction.(8,22,23) The two paths of this reaction scheme have different characteristics (Figure 8). The direct method is slower and highly selective and the $OH^\bullet$ reaction is fast and less selective. The critical pH value above which the $OH^\bullet$ radical reaction predominates depends on the rate at which a substance reacts directly with O_3, and on other components in the solution, including reaction products, that may enhance or retard O_3 decomposition.

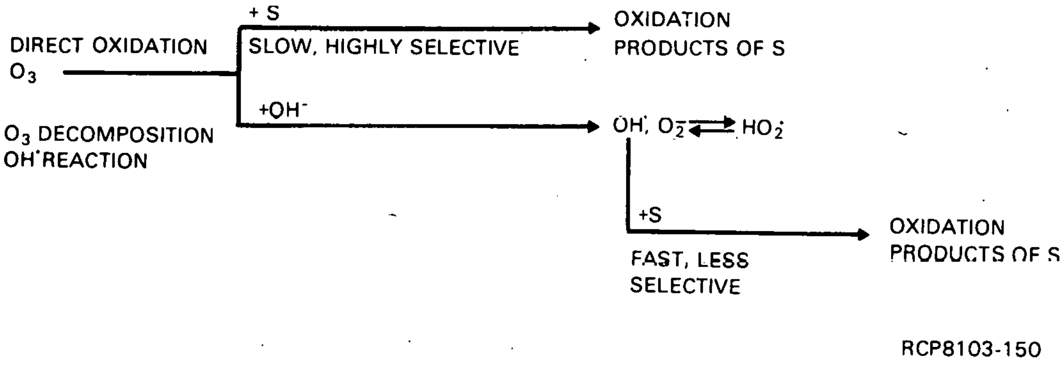

FIGURE 8. Ozone Reaction Paths.

The high selectivity of the direct O_3 oxidation of NO_2^- could explain the slower first stage reaction rates for the intermediate pH tests. Since the pH for the 8.5 test almost immediately went to 9.1, and since the pH 10 test is the same as other high pH tests, the critical pH for the reaction mechanism to switch from a hydroxyl radical controlled reaction to a direct ozonation reaction is probably between 9.0 and 10.0. Below this pH level, the fast direct oxidation of NO_2^- by O_3 predominates the reaction until all the NO_2^- is destroyed. Then, the next easiest oxidizable material, EDTA, is attacked. The first and second stage reaction rates appear to decrease as the pH is lowered from 8.5 to 4.5. An increasing effect from oxidation retardation by metal ion complexation, as was found in the low pH region, may cause this shift.

Explanation of Low pH Results

Initially, it was believed that ozonation of the synthetic waste at low pH levels would be significantly improved over ozonations for high pH since essentially all the NO_2^- and CO_3^{-2} in the synthetic waste would be destroyed by decomposition of their acids, HNO_2 and H_2CO_3, leaving the O_3 free to react with only EDTA or tartrate. However, the reaction rate for the pH 2.8 test was 20 times lower than the rate at high pH levels. The slow reaction rate resulted in very small changes in the O_3 and EDTA concentrations, which increased the error in the rate and stoichiometric determinations. Experiments with increasingly complex matrices were carried out to determine the cause of the slow reaction rates. In addition, a 10-hour test at pH 1.2 was made to ensure that a more rapid reaction observed for intermediate pH ozonations did not occur later in the reaction.

The first ozonation test was done with only iron and EDTA present in the system. A greater than normal amount of iron was needed to keep EDTA in solution at pH 2 because of the insolubility of the acid form of EDTA. Final adjustments resulted in a mixture that had a pH of 1.2. This pH was used for the study of more complex matrices. The next system studied contained EDTA, iron and tartrate. Chromium addition to the matrix in the next test caused additional makeup problems since chromium exists as Cr^{+6} or chromate ion in the basic solution, and as Cr^{+3} ion in the acidified solution. The Cr^{+6} is reduced to Cr^{+3} by HNO_2 during neutralization. Therefore, in order to simulate this process, $0.5\underline{M}$ sodium nitrite ($NaNO_2$) and $0.5\underline{M}$ sodium hydroxide (NaOH) were added to the matrix. Chromium (III) is known to form very labile complexes which made it suspect as an oxidation inhibitor.(24) Therefore, when the first test indicated that the Cr^{+3} did not cause the slow reaction rates at pH 1.2, a second chrome test was conducted in which the iron concentration was reduced to a lower and more normal level relative to the chrome concentration. Finally, aluminum was added to the system to determine its effect. The matrix components and their approximate concentrations for each test are listed in Table 4.

TABLE 4. Low pH Matrices Test Compositions.

Test	Component[a]	Concentration
	EDTA	$0.05\underline{M}$
Test 1	$Fe(NO_3)_3$	$0.05\underline{M}$ (high), $0.005\underline{M}$ (low)
Test 2	Sodium Tartrate	$0.05\underline{M}$
	NaOH	$0.5\underline{M}$
	$NaNO_2$	$0.5\underline{M}$
Test 3 and 4	Na_2CrO_4	$0.1\underline{M}$
Test 5	$NaAlO_2$	$0.5\underline{M}$

[a] Components are added cumulatively; i.e., Test 5 contains all components listed.

The results of these tests are summarized in Table 5 and Figures 9, 10, and 11. Results are compared to the long 10-hour pH 1.2 test in synthetic waste and to a simple test at pH 1.2 with only aluminum and EDTA. Test 1 used only iron and EDTA at pH 1.2 and contained higher than normal initial amounts of EDTA. On the other hand, Test 4 had an exceptionally low initial concentration of EDTA. This may have resulted from EDTA oxidation from HNO_2 or Cr^{+6} during acidification. Because of this low EDTA concentration, the information is more questionable. Ozone data for the first 75 minutes of Test 2 are affected by an undetected gas leak on a reactor connection.

TABLE 5. Summary of Ozonation Tests at pH 1.2 with Increasingly Complex Matrices.

	Test 1 EDTA +Fe	Test 2 EDTA + Fe +tartrate	Test 3 EDTA + Fe (High)+tart. +Cr	Test 4 EDTA + Fe (Low)+tart. +Cr	Test 5 EDTA + Fe +tart+Cr +Al	Test 6 Synthetic Waste 10 hr pH 1.2	Test 7 Al + EDTA
OZONE DATA							
Length of Run (hr)	5	5	5	5	5	10	3.5
Av. wt% In	3.422±.039	3.469±.015	3.405±.067	3.366±.047	3.328±.105	3.563±.09	3.331±.081
Av. wt% Out	2.760	2.354	3.040	2.980	3.137	3.490	3.243
Total Vol. Added	2906	2735	2965	2933	2911	5470	2021
Moles Added/hr	0.60	0.57	0.61	0.60	0.59	0.59	0.58
Moles Added	3.005	2.874	3.060	2.988	2.941	5.902	2.043
Moles Unreacted	2.423	1.970	2.736	2.639	2.756	5.778	1.927
Moles Reacted	0.582	0.904	0.324	0.349	0.185	0.124	0.116
EDTA DATA							
Initial ($\underline{M}$)	0.1240	0.0584	0.0347	0.0075	0.0474	0.0133	0.0496
Final ($\underline{M}$)	8.1×10^{-4}	3.3×10^{-3}	4.3×10^{-3}	8.2×10^{-4}[a]	0.0251	0.0072	0.0337
Moles Reacted	0.246	0.110	0.061	0.0134	0.0446	0.0122	0.0317
% Reacted	99.3	94.3	87.2	89.0	47.1	45.9	32.0
REACTION DATA							
1st Rate	1.07	0.951	0.444	0.80	0.113	0.065	0.105
2nd Rate	-	0.449	-	0.42	-	-	-
O_3/ EDTA - 1st	1.07	5.51	4.92	10.5	6.10	9.4	4.43
O_3/ EDTA - 2nd	21.3	13.92	-	29.3	4.02	-	-
pH							
Initial	1.18	1.23	1.24	1.21	1.27	1.23	1.23
Final	2.31	2.74	1.79	1.16	1.50	1.58	1.68

[a] Lowest measurement after 4 hr 30 min.

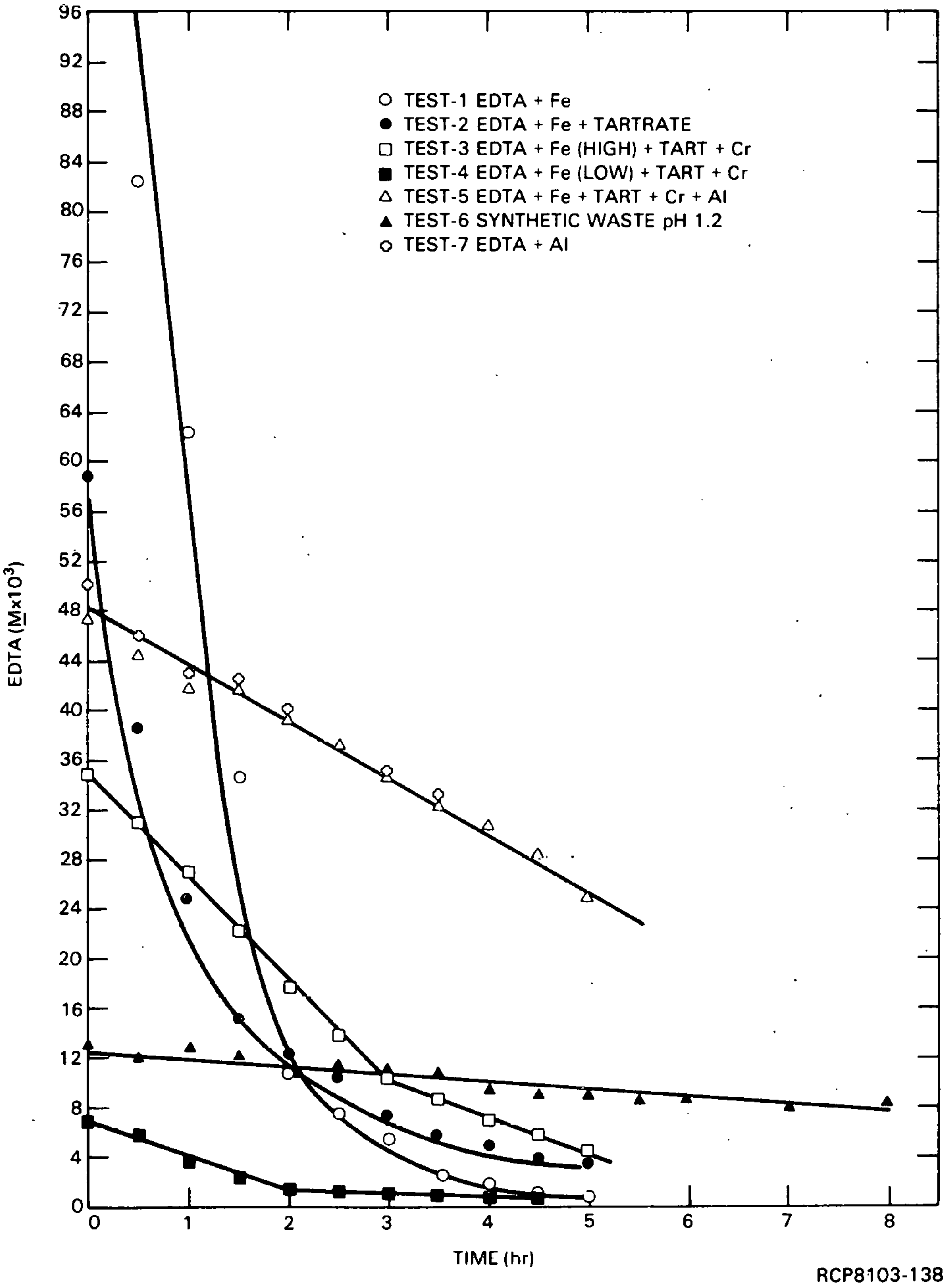

FIGURE 9. EDTA Molarity versus Time (Low pH Matrices Tests)

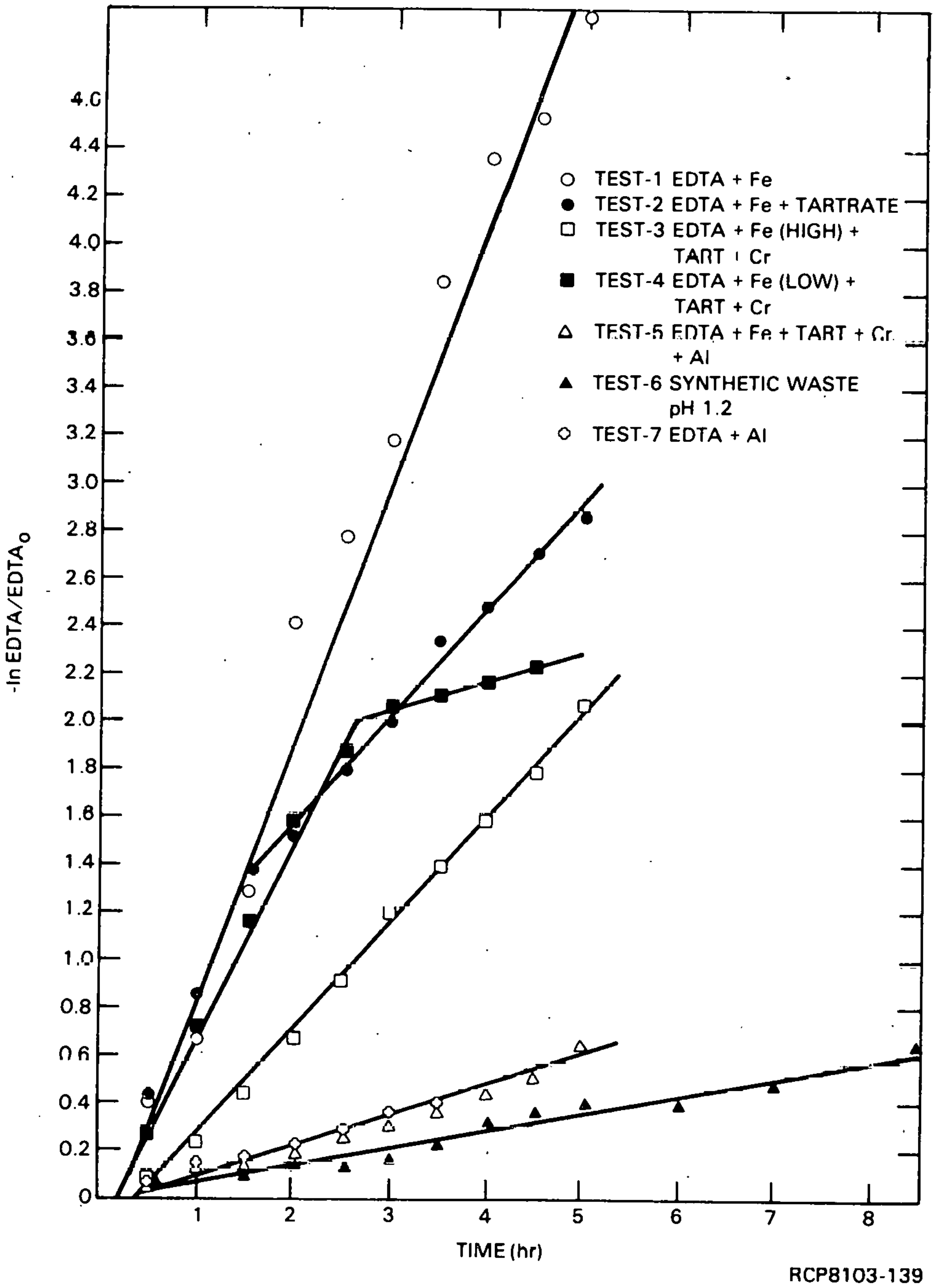

FIGURE 10. -ln EDTA/EDTA$_0$ versus Time (Low pH Matrices Test).

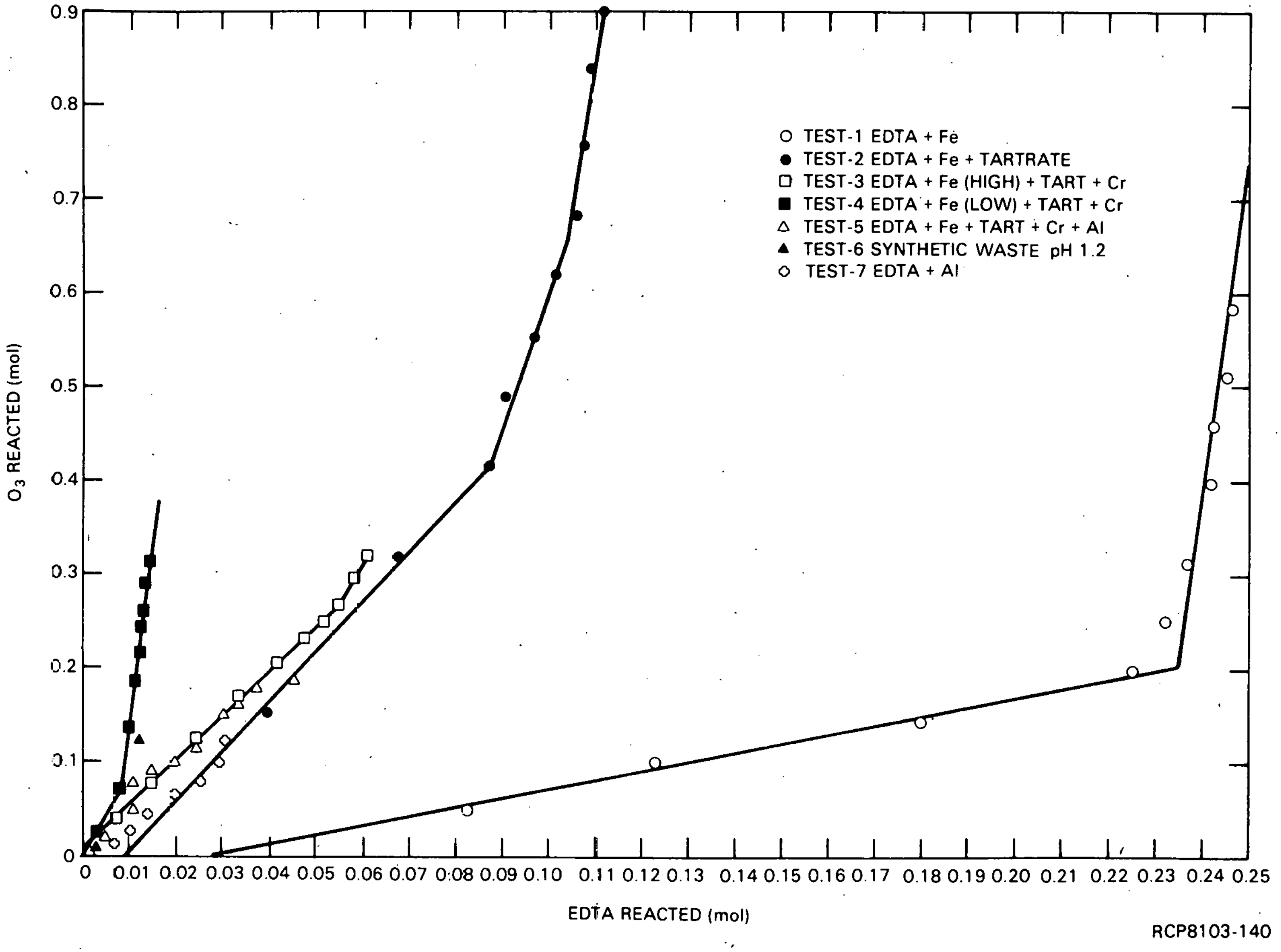

FIGURE 11. Moles Ozone Reacted versus Moles EDTA Reacted (Low pH Matrices Tests).

Data from these tests show clearly that the slow reaction was not caused by the low pH levels. The O_3-EDTA reaction rate at pH 1.2 with only iron and EDTA present was faster than the reaction rate in synthetic waste at high pH levels. When tartrate was added, the initial reaction rate was the same as the iron and EDTA test; however, after 90 min, the reaction rate changed to half its original value. At this point in the reaction, the EDTA concentration had been reduced to 0.015M and the tartrate (0.05M)-O_3 reaction probably becames the dominant rate-controlling reaction.

The effect of chrome on the reaction is difficult to interpret. When the chrome was added to a matrix containing a larger concentration of iron (0.05M), the reaction occurred in only one stage with a reaction rate (0.44 hr^{-1}) equal to the second stage of the tartrate addition test. When the iron concentration was reduced to 0.005M, the reaction rates were similar to the tartrate test. Unfortunately the low initial EDTA concentration for the low iron tests may have affected the results. If this was not a factor, it would appear that the iron concentration may also affect the rate. In the two tests (4 and 6) in which the iron and EDTA concentration were low, the O_3 consumption, $\Delta O_3/\Delta$EDTA, was higher (Figure 11). This may indicate that complexes of iron with EDTA or tartrate are affecting the reaction. Further work is required to clarify these experiments with chrome and iron.

Tests 5, 6, and 7 contain large concentrations of aluminum which caused the reaction rate to decrease by a factor of 10. The even lower rates for the synthetic waste may be the result of the complex equilibria associated with the metal ions and the organic ligands.

These results indicate that an aluminum-EDTA chelate complex may be inhibiting the oxidation by O_3. This could be the result of either the slow kinetics for ligand exchange for aluminum complexes, or from a steric hindrance effect caused by chelation.(18,19,25) In addition to chelation of aluminum, there is also evidence of the formation of an aluminum-

(EDTA) dimer. Hydrogen peroxide has rapidly oxidized EDTA at pH 1.2 in the same synthetic waste matrix. This would suggest that the O_3 reaction mechanism rather than ligand exchange kinetics limits the O_3 reaction.

Summary of pH Effects on Reaction Rate

Comparing the rate of reaction of O_3 and EDTA at different pH levels is complicated by changes in the experimental design and conditions such as reactor pot, flows, and ozonator variations. From Figure 12, several observations can be made concerning the effect of pH on reaction rate. The reaction rate increases significantly when the pH is raised from pH 8.5 to pH 10. This increase appears to peak at pH 11. A further increase in the pH results in a decrease in the reaction rate. Second-stage reaction rates follow a similar pattern in this pH range. Reaction rates at low pH levels are very slow. Based on these results, the maximum first-stage reaction rate for O_3-EDTA in synthetic residual liquor is between pH 11 and 12. Higher second-stage rates are possible in the intermediate pH range. However, the problems associated with the solids that formed in the range of pH 3 to 13 outweigh any benefits gained from improved reaction rates in this pH region. Therefore ozonation at high pH levels still appears to offer the best reaction rate conditions for destroying EDTA.

Effect of pH on Stoichiometry

The moles of O_3 required to oxidize a mole of EDTA at various pH values are shown in Figures 13 and 14. The change in O_3 consumption (slope = $\Delta O_3/\Delta$EDTA) as the reaction progressed is shown in Figure 13. The data also may be classified into three pH regions. At pH 10 or greater, the O_3 consumption remains approximately 20-30 moles of O_3 per mole of EDTA for most of the reaction and then approximately doubles for the last stage of the reaction. This trend reverses in the intermediate pH range (pH 3-10) with extremely high O_3 consumption (100-500 moles O_3/mole EDTA) observed during the short first stage of the reaction, and a very low (7-10 moles O_3 moles/mole EDTA) consumption for

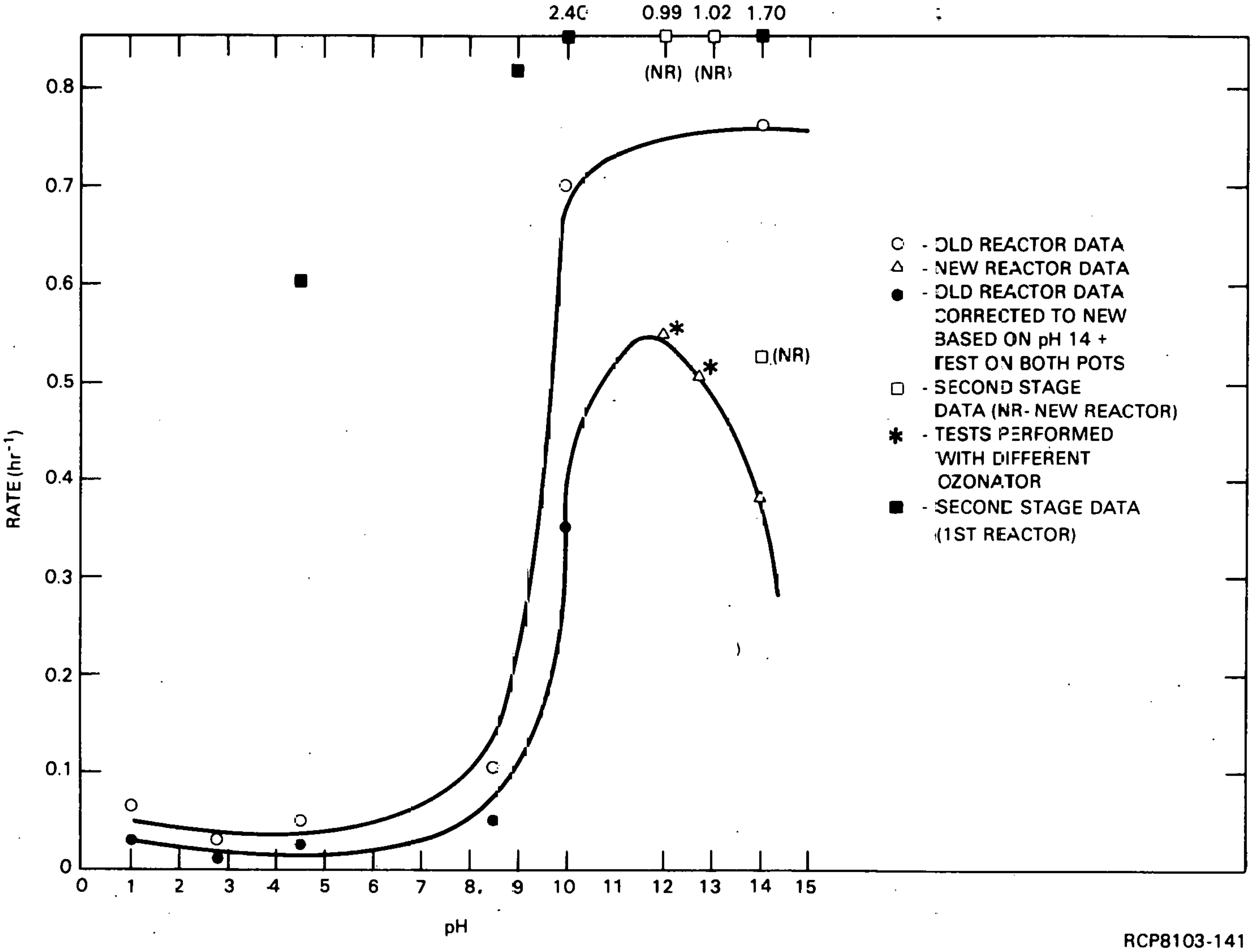

FIGURE 12. Rate of Ozone-EDTA Reaction versus pH.

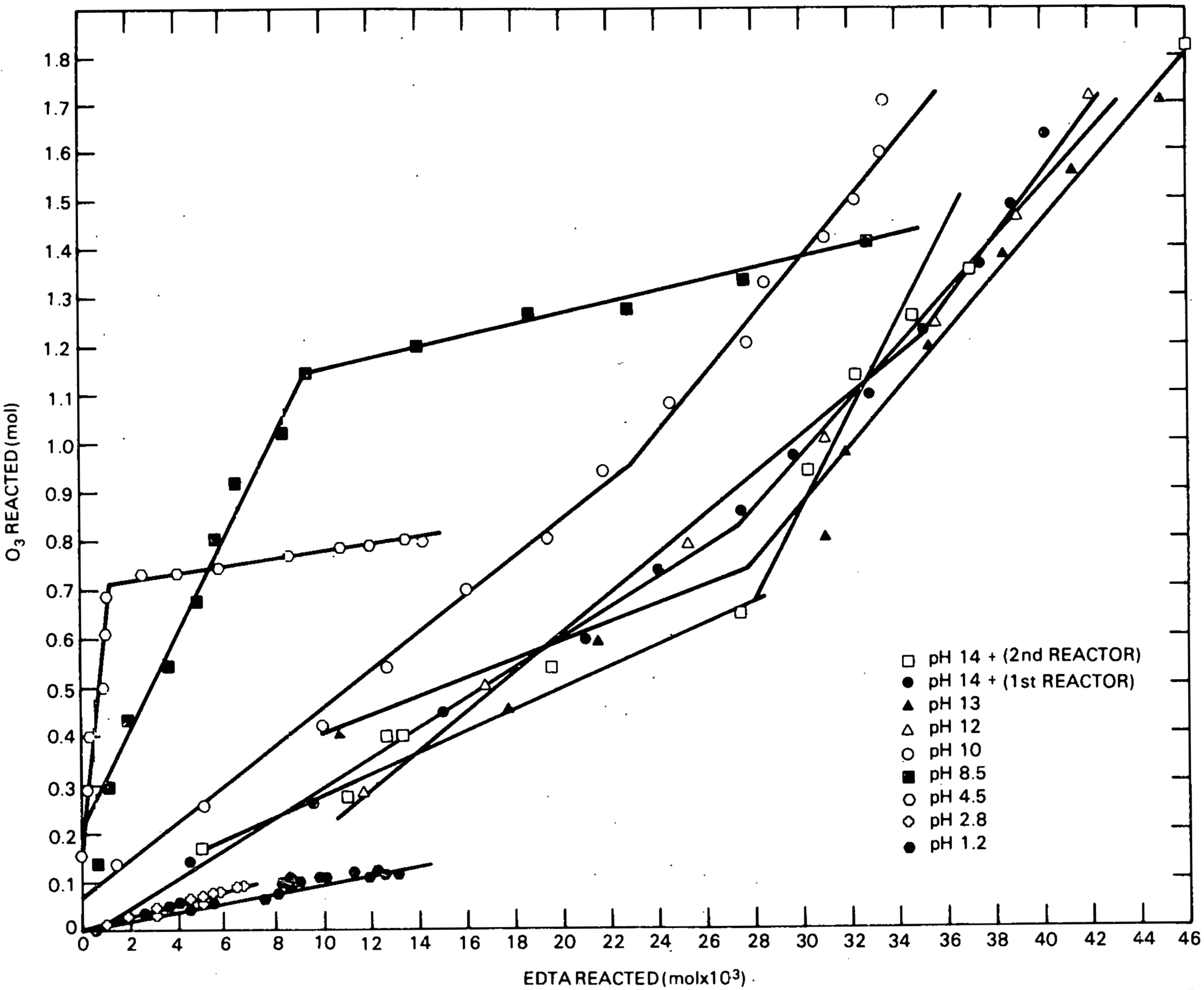

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FIGURE 13. Moles Ozone Reacted versus Moles EDTA Reacted.

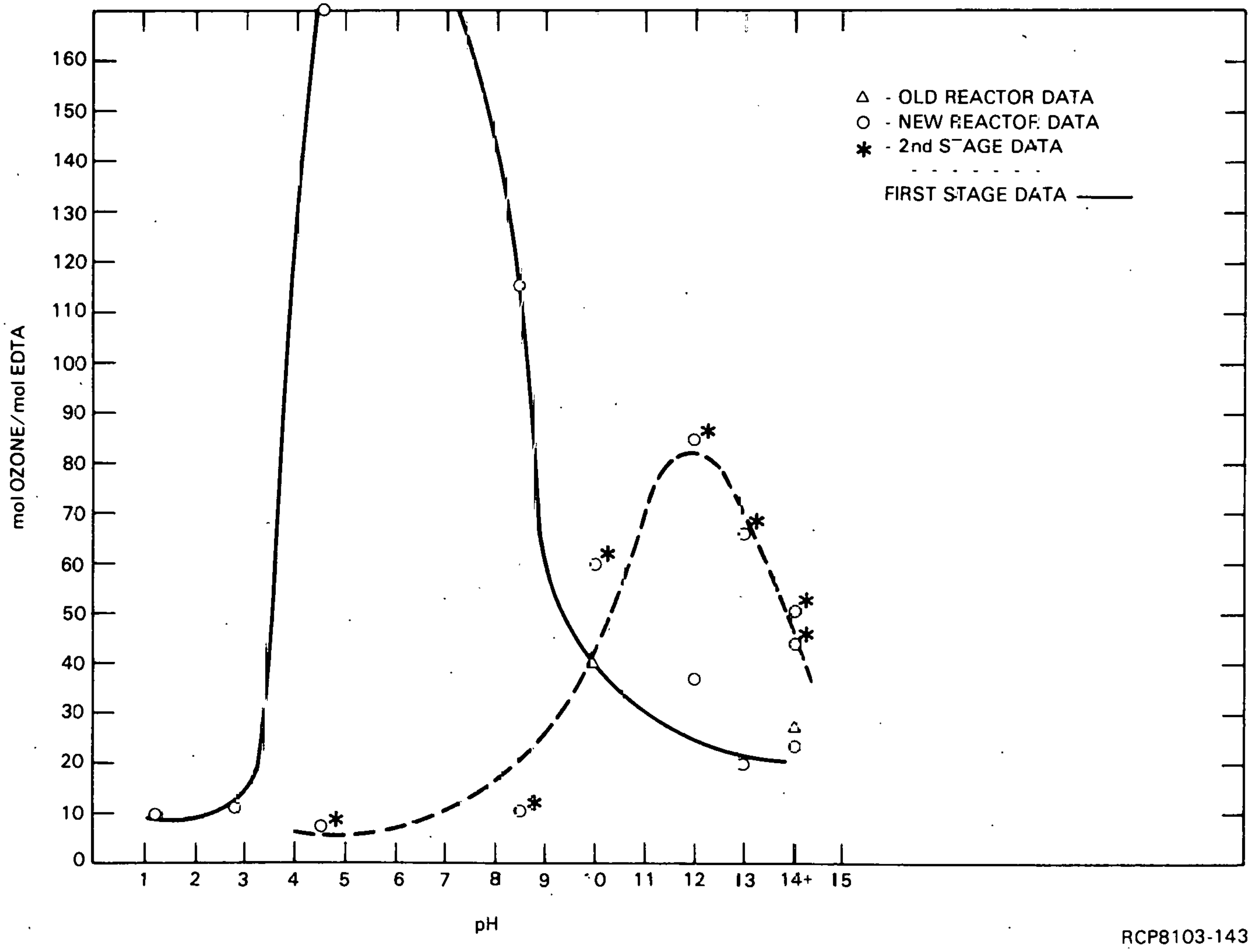

FIGURE 14. Moles of Ozone per Mole EDTA Reacted versus pH.

the second stage. The O_3 consumption at low pH levels is low and constant at about 10 moles O_3/mole EDTA. The small amounts of O_3 consumed makes the low pH very appealing economically. This advantage is offset by a very slow reaction rate. The first stage O_3 consumption appears to approach a minimum at pH 14+. Increasing the OH^- concentration appears to reduce the reaction rate but improve the O_3 stoichiometry. New experiments at higher and better defined hydroxide concentrations are needed to determine reaction rate and O_3 consumption limitations of the high pH region.

The stoichimetry of the O_3-EDTA reaction is a function of the mechanism (direct attack or hydroxyl free radical reaction) and the concentration of other species in competing with the EDTA for the O_3.(23) The reaction order of O_3 decomposition varies with pH.(26) In natural water with pH ∿8, one mole of O_3 decomposes to 0.5 moles of hydroxyl free radical ($OH^\bullet$).(22) At elevated pH levels, an even higher percentage of the O_3 is decomposed. The effective $OH^\bullet$ radical concentration will also be reduced by the presence of more easily oxidizable organic materials and free radical scavengers such as CO_3^{-2} ion.

The O_3 consumption rate changed with time (Figure 15). For high pH values, the O_3 consumption ($\Delta O_3/\Delta EDTA$) continually increased, while for intermediate pH values, it decreased very rapidly, leveling off at a low O_3 use. There is some evidence that at lower flow rates and high pH levels, $\Delta O_3/\Delta EDTA$ did not increase as rapidly with time, and may result in a lower overall consumption of O_3. However, as will be seen in later data, the increase in O_3 use could be the result of increased CO_3^{-2} concentration. Because the $\Delta O_3/\Delta EDTA$ values in Figure 15 are derived from smaller time intervals than Figure 13, the data points have a greater degree of scatter.

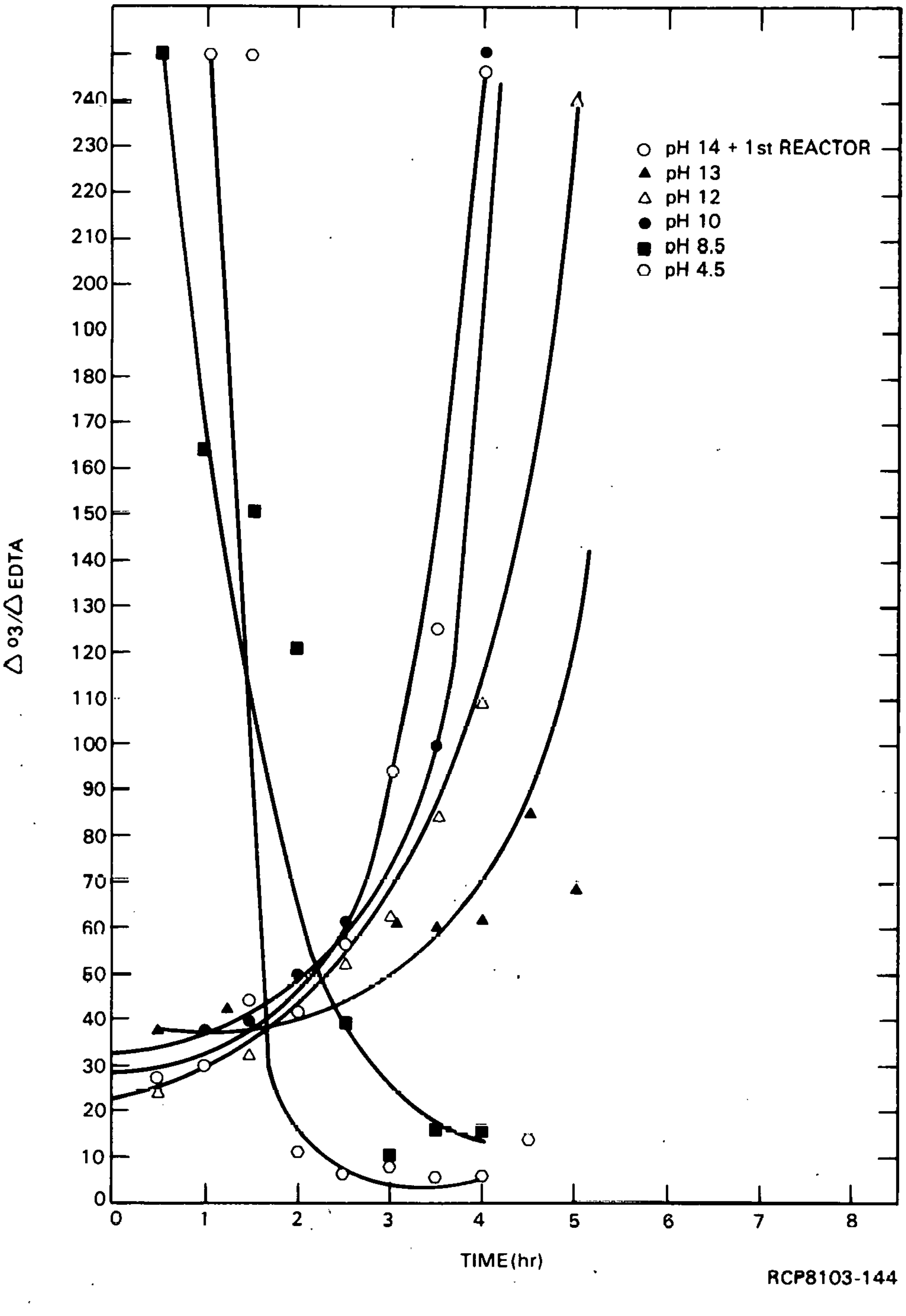

FIGURE 15. Change in Ozone per Change in EDTA versus Time.

The rate at which O_3 was consumed or decomposed can also be estimated by determining the percent of O_3 reacted based on the weight percent O_3 going into the reactor and the weight percent going out (Figure 16). The poorer O_3 transfer efficiency for the second reactor can be seen in these plots. As the pH decreases from 14+ to 4.5, the percent of O_3 reacting decreases more rapidly with time. At low pH levels, O_3 reacts and decomposes very slowly at a constant rate. Future mass transfer-kinetic studies are planned in which a solution O_3 monitor will be used to determine O_3 concentrations in solution. These studies should help to explain some of these observations and optimize the experimental conditions for the O_3 reaction. Based on present data, the best O_3 stoichiometry is obtained at the low or intermediate pH range. However, the slow reaction rates at low pH levels and the large amounts of solids formed at intermediate pH levels make the pH 14+ condition still the most favorable for destruction of EDTA.

ADDITIVE TESTS

Various materials were added to the synthetic waste mixture in an attempt to improve the reaction rate or O_3 consumption requirements. The additives were used to catalyze the oxidation or remove components which were believed to interfere in the reaction.

Cupric Nitrate

Five grams of $Cu(NO_3)_2$ were dissolved in a small amount of water and added to 2 l of the synthetic waste mixture. The solution changed color from its characteristic yellow to green and stayed this color throughout the test. As shown in Table 3, the reaction rate with Cu^{+2} present was only slightly higher than the pH 14+ test without Cu^{+2} (0.44 versus 0.38 hr^{-1}). The O_3 consumption was higher (31.42) with Cu^{+2} than without (23.65). However, this may have been the result of constricted flow during the test without Cu^{+2}. The NO_2^- destruction and CO_3^{-2} generation rates appear better when Cu^{+2} was added. However, these also may have been the function of an increased flow during the Cu^{+2} test. It was concluded that the addition of Cu^{+2} would not significantly improve the ozonation process.

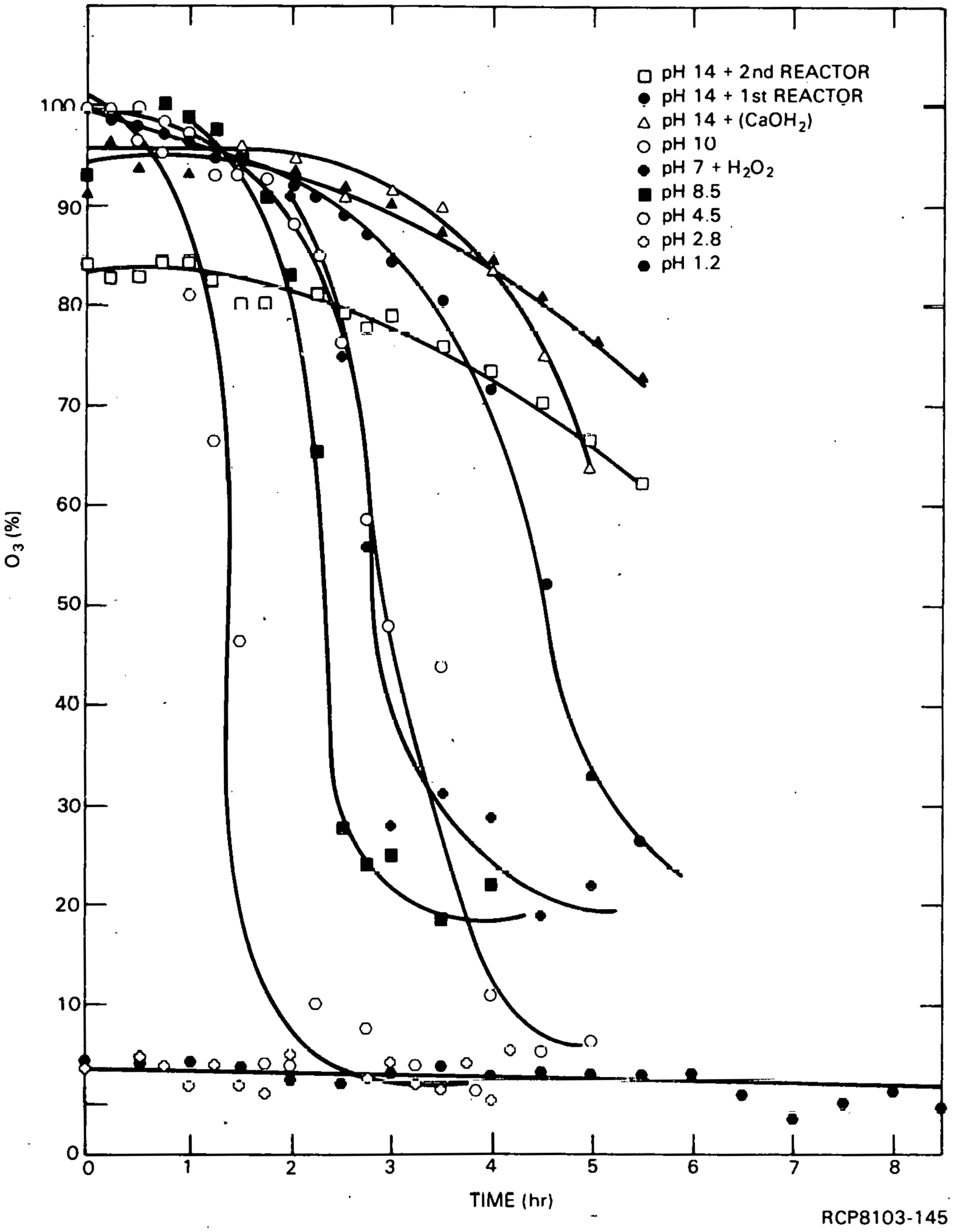

FIGURE 16. Percent Ozone Reacted versus Time.

Calcium Hydroxide (Carbonate Effects)

Hoigné and Bader have described the hydroxyl free radical scavenging effects of the CO_3^{-2} ion and shown its influence on oxidation of organics in water.(18,23,26) The carbonate concentration in Hanford residual liquor waste is high (0.5M) and becomes even higher during the oxidation of EDTA by O_3 as shown in Figure 17. Calcium hydroxide had been added in other ozonation studies.(28) Therefore $Ca(OH)_2$ was added to remove the CO_3^{-2} from solution and thus prevent its interference with the hydroxyl free radical reaction.

Calcium hydroxide is very insoluble and since solids had been causing flow problems in the second reactor, only 23.7 g of $Ca(OH)_2$ were added to 2 l of synthetic waste using the first reaction vessel.

As seen in the carbonate analysis for various tests (Figure 17), the $Ca(OH)_2$ did not reduce the original CO_3^{-2} concentration or significantly affect the increasing CO_3^{-2} level during the test. The O_3-EDTA reaction rate with $Ca(OH)_2$ present was 2 to 3 times slower than in the test without $Ca(OH)_2$. The O_3 consumption was also two times higher in the presence of $Ca(OH)_2$. The reasons for these detrimental results are not understood but may be due to reduced transport of O_3 through the $Ca(OH)_2$ solids or decomposition of O_3 on the less reactive solids.

Data from many of the ozonation runs indicated that the reaction rate increased even though the CO_3^{-2} also increased (all high pH tests). However, the O_3 consumption, for the high pH tests, increased with increasing CO_3^{-2} concentration. For the intermediate pH range, the O_3 consumption decreased even though the CO_3^{-2} level increased. Because of these opposing trends two tests were carried out to determine the magnitude of the CO_3^{-2} effect for our system.

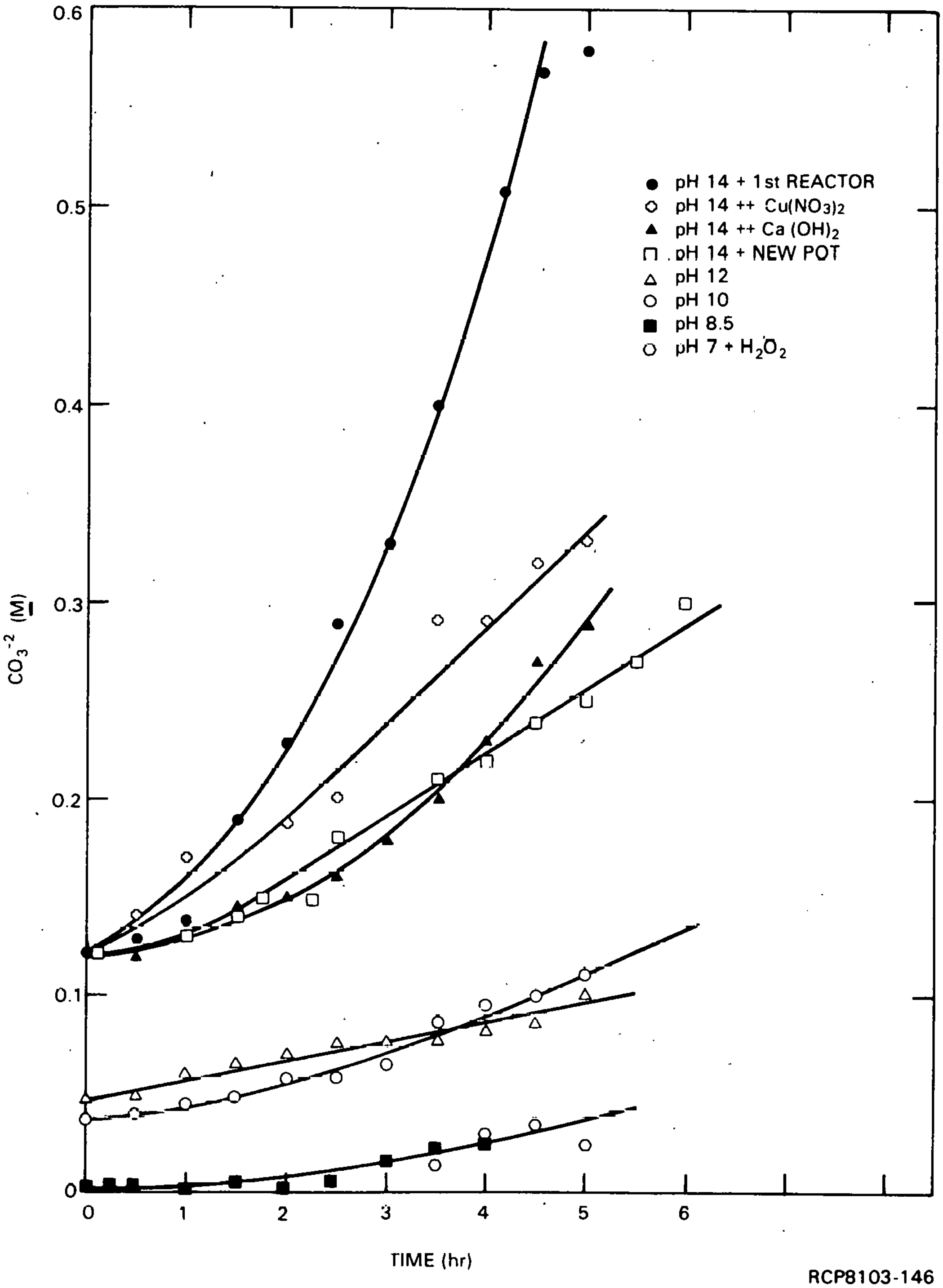

FIGURE 17. Molarity of Carbonate versus Time.

In these tests, a simple EDTA solution at pH 12 was ozonated with 0.2M Na_2CO_3 present and without carbonate initially present. Ozonation of these simple EDTA solutions caused the solutions to change to a yellow color. Liquid chromatograms showed two degradation peaks which disappeared after 20 minutes for the EDTA tests and 40 minutes for the CO_3^{-2}-EDTA test (Figure 18). The disappearance of the peaks corresponds to the time the reaction enters the second higher O_3-consuming stage of the reaction. During the tests, samples were taken for TOC. A plot of the percent of TOC and EDTA reacted versus time shows that even though the EDTA is 98% destroyed after 3 hours, 38% of the carbon is still present as some organic degradation product (Figure 19). The CO_3^{-2} in this test increased from 0 to 0.1M. This means about 20% of the EDTA was oxidized to CO_3^{-2}. The reaction rate for both these tests was 4.75 hr^{-1}. This is 5 to 10 times greater than observed for test with synthetic waste. The O_3 consumption for the test with carbonate was 50% greater (7.25 moles O_3 per moles EDTA) for the first stage and 4 times greater for the second stage of the reaction. These tests show that CO_3^{-2} affects the O_3 consumption but not the reaction rate. Since the O_3 consumption rates for the synthetic waste are 3 to 4 times greater than those when only CO_3^{-2} is present, other factors such as NO_2^- and other organic concentrations may have a more significant effect on O_3 consumption than CO_3^{-2}. However, if it becomes necessary to reduce the complexant concentrations to very low levels (10^{-3}-10^{-4}M), the CO_3^{-2} ion could be a very important factor for economical use of O_3. If a convenient means could be found for removing NO_2^- and CO_3^{-2} prior to ozonation, significant economic benefits from better O_3 utilization should be possible.

Hydrogen Peroxide

Others have reported that the addition of H_2O_2 can catalyze the oxidation of organics in H_2O.(29) In this test, 20% H_2O_2 was added continuously at a rate of 0.26 moles (40 ml) per hour to 2 l of synthetic waste at pH 7. The results of this test followed the same EDTA destruction pattern as the test at pH 8.5 without H_2O_2. The reaction

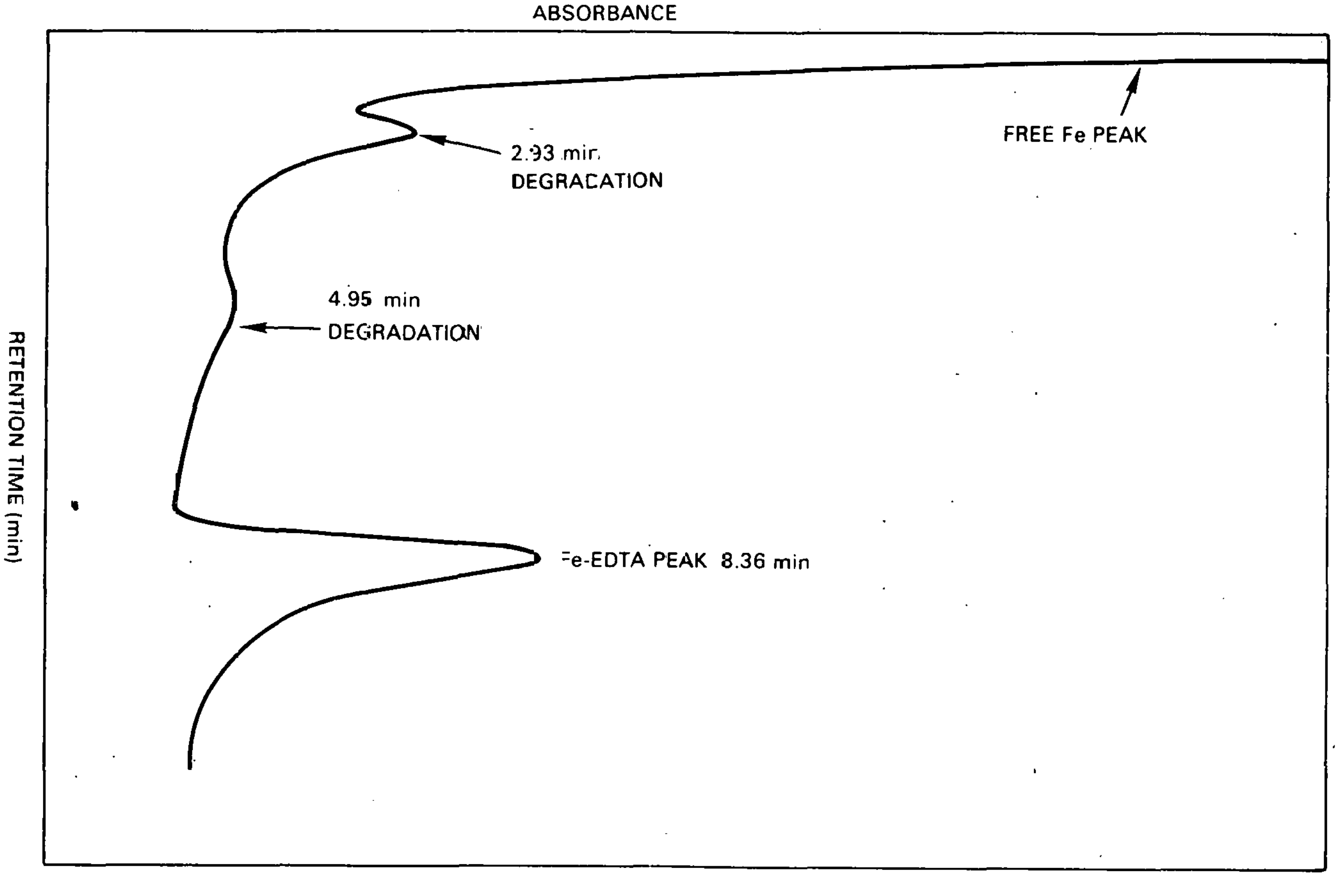

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FIGURE 18. Liquid Chromatogram of Ozonated EDTA Solution at pH 12.

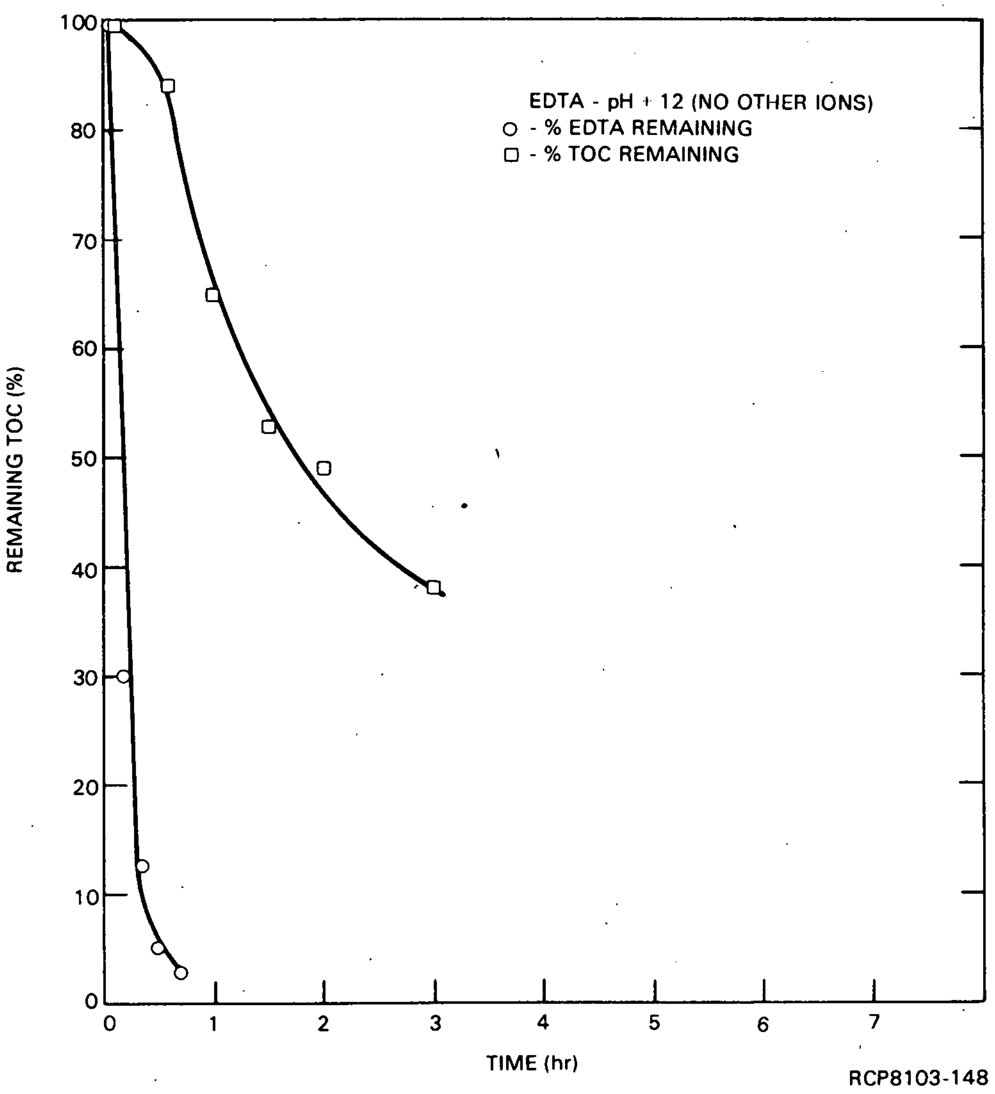


FIGURE 19. Total Organic Carbon Analysis of Ozonated EDTA.

was initially slow during NO_2^- oxidation and then fast during the second stage. The O_3 consumption for both stages of the pH 7 with H_2O_2 and pH 8.5 tests were essentially the same. However, the reaction rate of the rapid second stage was two times greater for the pH 7 test with H_2O_2 present. This does not appear to be a pH effect since it is also three times greater than the second stage rate at pH 4.5. Even though an improved reaction rate may be possible using H_2O_2, it probably is not significant enough to overcome the solids separation problems associated with operating at pH 7. Also, at the expense of only a little more concentrated HNO_3, it would be possible to use H_2O_2 as the oxidant in place of O_3 at a lower pH and at the same time overcome the solids problem by redissolving the aluminum hydroxide[$Al(OH)_3$].

Silver Nitrate

The catalytic effects of the silver ion was studied by adding 2 g of $AgNO_3$ to 2 l of synthetic waste at pH 2.1. A white precipitate formed when the $AgNO_3$ was added. This could have been silver chloride (AgCl) formation caused by chloride impurities in the materials used to make the synthetic waste. Based on the reaction rate and O_3 consumption results from this test, no improvements were observed by adding Ag^+. However if the silver ion was precipitated as a chloride it probably prevented the Ag^+ ion from acting as a catalyst by inhibiting oxidation to the argentic ion, Ag^{+2}.

Manganese Nitrate

Manganese ion was added to synthetic waste at pH 1.2 in an effort to improve the O_3 reaction rate at low pH values. Since H_2O_2 oxidations of EDTA at this low pH level were not affected by the aluminum complex interference, it was hoped than Mn^{+2} could catalyze the reaction by offering a different oxidation mechanism. This may be accomplished by continued O_3 oxidation of Mn^{+2} to permanganate. In this test, 4 g of $Mn(NO_3)_2$ were added to 2 l of synthetic waste at pH 1.2. The Mn^{+2} ion did not improve the O_3 consumption but did result in a two-fold increase in the reaction rate. Higher concentrations of Mn^{+2} may give further improvements. However, the rate is still 4 to 5 times slower than that obtained at high pH levels and additional costs of Mn^{+2} and acid would be required.

Effect of Temperature on the Ozone-EDTA Reaction at Low pH

A single ozonation test was carried out at a higher temperture (85°C) to see if the reaction rate at a low pH value could be improved. In this test, significant improvements in the reaction rate and O_3 consumption were observed. The reaction rate at 85°C was 0.395 hr^{-1} compared to 0.065 hr^{-1} at 60°C. The rate decreased to 0.184 hr^{-1} after about 105 min, indicating other reactants or products may be competing for the O_3. The O_3 consumption at 85°C was 2.9 moles of O_3 per mole of EDTA compared to 9.4 at 60°C. The second-stage O_3 consumption at 85°C was 20.0 moles O_3 per mole EDTA. This change did not occur until after 210 min when the EDTA molarity was <0.005M. Ozonations at low pH and higher temperatures might offer some significant cost benefits. Some problems were encountered during the test from condensation of water in the O_3 analysis lines. Better drying techniques may have to be implemented before additional high temperature tests can be performed.

FUTURE WORK

These ozonation studies have been directed specifically at destroying EDTA in Hanford nuclear waste in order to allow the removal of long-lived radionuclides from the waste prior to long-term disposal. Ozonation can meet the requirements for this application if EDTA concentrations can be reduced to $<0.005\underline{M}$. These studies show that this criterion can be met at almost any pH level. Even though ozonation of waste at low pH values and high temperature appears to require significantly lower amounts of O_3, the ozonation process at high pH offers reasonable O_3 use efficiency and simpler operating conditions. An accurate economical evaluation of these conditions will not be possible until the mass-transfer kinetics of the process are determined in next year's studies.

Recently, long-term waste management plans at Hanford have placed greater emphasis on in situ storage of the waste in a near-surface repositories. Under such a program, removal of long-lived radionuclides would most likely be limited to selected waste. For in situ disposal of the waste, the impact of complexants on radionuclide release scenarios such as water migration through soils becomes a significant factor. Criteria for near-surface disposal of complexed waste have not been established.

Some fundamental questions will have to be answered before these criteria can be developed.

- What is the effect of the different complexants in Hanford waste on the adsorption of radionuclides on the soil?
- At what concentrations are the complexant effects significant?
- What is the long-term risk of leaving the complexants in the waste?

If complexant destruction is required before in situ near-surface waste disposal, other factors must be considered in developing the destruction process.

- What are the reaction stoichiometry and kinetics for destroying all types of complexants in the wastes?
- How complete is the destruction of the complexants?
- What are the major products of the destruction process and how do they affect the adsorption of radionuclides and the risk assessment?

Obviously these limited O_3 studies have just begun to answer these questions about the complexant EDTA. Future work should be directed at:

- understanding the reaction of ozone with other complexants
- determining the completeness of the reaction for the different complexants
- identifying the major products of the reaction
- determining the radionuclide adsorption properties of ozonated waste.

This future work should include additional studies of synthetic systems as well as an increased emphasis on O_3 reaction studies with actual waste. Product identification and measurement will require the development of new analytical methods. Some of the other complexants and potential oxidation products of EDTA are described in the following sections.

HANFORD WASTE COMPLEXANTS

The major complexants added to the waste from the B Plant fission product recovery process are N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), EDTA, hydroxyacetic acid, and citric acid. In addition, smaller quantities of other complexants have also been added to the waste such as tartrate, oxalate, diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), acetate, and sucrose. Hanford wastes may contain extractants, diluents, and their chemical and radiolytic degradation products which could also act as complexants. Tributylphosphate (TBP), dibutylphosphate (DBP), monobutylphosphate (MBP), dibutylbutylphosphonate (DBBP), di-2-ethylhexylphosphoric acid (HDEHP), methyl isobutyl ketone NPH (normal paraffin hydrocarbons), and impurities and degradation products of these compounds are among these materials.(4) Knowledge of the complexants in Hanford wastes is based almost entirely on processing records of what has been added. Very little information from analysis of the actual waste is available.

The following estimates have been made for the amount of major complexants added to the waste:(30)

- Hydroxyacetic acid - 9.0×10^6 Moles
- Citric acid - 3.3×10^6 Moles
- HEDTA - 2.7×10^6 Moles
- EDTA - 0.57×10^6 Moles

These complexants represent only about 1% of the total weight of the waste inventory but may be as high as 24% of the B Plant and Purex waste.(31) It is believed that due to their high solubility, most of these complexants have been concentrated in the residual liquors from the waste concentration evaporators at Hanford.

The TOC analyses from the Hanford high-level defense waste characterization program are summarized in Table 6.(31) The TOC measurements were made on a water soluble and acid soluble fraction of the waste and are reported as the grams of carbon per gram of original sample. In a study on the removal of radionuclides from the waste the TOC of some salt cakes was found to be between 1 to 5 x 10^{-3}g/g.(7) Analysis of liquid waste for the study showed TOC ranged from 1 to 11M TOC with waste originating from B Plant having TOC values between 4 and 11M. These TOC numbers do not necessarily represent the levels of complexants since organic extractants, diluents, and their degradation products are also measured in the TOC analysis.

Recent HPLC analysis of a complexed residual liquor from the 241-AZ-102 tank found 0.09$\underline{M}$ EDTA and 0.13$\underline{M}$ HEDTA. This corresponds to ∿2.2$\underline{M}$ TOC. The TOC analysis of this waste was 7.4$\underline{M}$, indicating that other complexing agents, diluents, or degradation products were present in the waste. Characterizing these wastes and evaluating their effect on the long-term management of the waste will require more study.

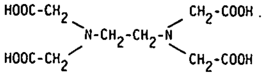
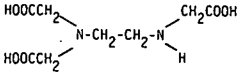
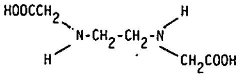
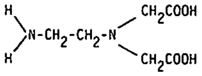
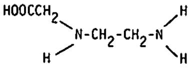
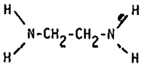
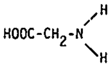
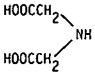
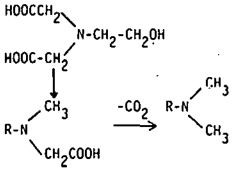
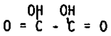
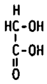
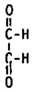
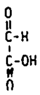
TABLE 6. Total Organic Carbon Analyses of Some Hanford Waste.

Tank No.	Type of Waste	TOC (g/g)	
		Water Soluble	Water Insoluble
107-BX	1st Cycle Bismuth Phosphate Sludge	--	7.3×10^{-4}
110-BX	Evaporator Bottom First Cycle Bismuth	1.69×10^{-4}	6.00×10^{-4}
112-BX	First Cycle Bismuth Phosphate Sludge	1.2×10^{-3}	8.9×10^{-3}
104-T	1st Cycle Bismuth Phosphate Sludge	2.9×10^{-3}	1.02×10^{-1}
102-TY	Evaporator Bottom	2×10^{-3}	--
104-TY	Tributylphosphate Sludge	1×10^{-3}	2.8×10^{-2}
106-TY	Tributylphosphate Sludge	9.18×10^{-4}	3.69×10^{-3}
105-TY	Tributylphosphate Sludge	$<1 \times 10^{-2}$	$<6 \times 10^{-3}$
106-C	Purex	0.02	--
103-TY	Tributylphosphate Sludge	1.1×10^{-3}	$<1.2 \times 10^{-3}$

EDTA Reaction Products

No specific references to ozonation of EDTA in which the products have been analyzed have been found. However, there are numerous references of the products formed from decomposition and oxidation of EDTA with other processes or chemical reagents.(32-40) Most of these products are formed by successive decarboxylation during thermal or photo decomposition, and oxidation by agents weaker than O_3 (Table 7). In addition, the products formed are a function of pH, particularly for O_3 where the mechanism changes from a direct O_3 reaction to a hydroxyl free radical reaction at high pH levels. Ozonation of other complexants, such as glycine, suggests that oxalic acid $(COOH)_2$, CO_2, and ammonia (NH_3) would be formed.(41) It is conceivable that incomplete oxidations could result in the formation of glyoxal, glyoxylic acid, or glycolic acid. The formation of NH_3 and CO_2 has been confirmed by X-ray diffraction identification of $(NH_4)_2CO_3$ solids in the hot condenser from the reactor pot. Lutton identified sodium oxalate solids as a product of some EDTA-O_3 reactions.(6) Ozonation of acetic acid resulted in the formation of glyoxylic and oxalic acid.(42) Glyoxylic, oxalic, formic, and acetic acids were the common ozonation intermediate products prior to oxidation to CO_2 for many organic materials.(36) Depending on conditions, complete oxidation of these end products to CO_2 by O_3 may be very slow and organic intermediates may remain to complex radionuclides in the waste. A considerable amount of literature exists on O_3-organic reactions.(43-47) Additional laboratory studies should be directed at specifically examining the products from ozonation of Hanford waste to determine if the products significantly increase the risk associated with near-surface disposal.

TABLE 7. Potential Products of EDTA Decomposition and/or Oxidation.

EDTA	
ED3A (N-carboxylmethyl-N,N'-ethylenediglycine)	
EDDA-N,N'(Symmetrical) (N,N'-ethylenediglycine)	
EDDA-NN(Unsymmetrical) (N-carboxymethyl-N-aminoethyleneglycine)	
EDMA (N-aminoethyleneglycine)	
EDA (Ethylenediamine)	
GL (Glycine)	
IMDA (iminodiacetic acid)	
Formaldehyde	HCHO
N-(2-hydroxyethyl)iminodiacetic acid (Thermal Decomposition)	 where R = CH_2CH_2OH or H
Formic Acid	 $HC(=O)-OH$
Oxalic Acid	 $O = C(OH) - C(OH) = O$
Gases	CO_2, NH_3
Glycolic Acid (hydroxyacetic acid)	 $HC(H)(OH)-C(=O)-OH$
Glyoxal	 $O=C(H)-C(H)=O$
Glyoxylic Acid	 $O=C(H)-C(OH)=O$

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APPENDIX A

EXPERIMENTAL AND PROCEDURES

EQUIPMENT

The experimental configuration for these tests underwent numerous modifications in order to improve the accuracy and reliability of the experiment. However, the flow pattern for these earlier experiments was essentially the same as that for the final arrangement shown in Figures 1 and 2. Stainless steel, Teflon, or glass components were used to prevent unwanted O_3 reactions. Dual KI traps were originally used to remove unreacted O_3. However, the traps were later replaced by Westgate Ultrox catalytic O_3 decomposers (6 in. diameter, 10 in. long) and a single trap was used in conjunction with the decomposers for cooling the gases and to indicate decomposer failure. Potassium iodide traps required frequent replacement at low pH values and caused additional problems such as plugging from KIO_3 formation, exploding from nitrogen triiodide (NI_3) formation, and generation of a noxious gas (I_2O_9). All experiments were performed in well ventilated hoods since O_3 tolerance levels are only about 0.1 ppm. A Dasibi Model 1003AH O_3 monitor monitored the room. Because of its strong oxidizing capability, shields were placed in front of the reactor pot in case of exothermic reactions.

Dual oxygen tanks supplied (Figure 1, Line 1) a Union Carbide Ozone Generator, Model SG-4060. The generator was operated at approximately 350 W power with a ∿12 l/min O_2 flow. Tests were normally run for 5-6 hr. The ozonator pressure was controlled at 12 psig. These conditions generated about 3.5 wt% O_3. Part of the oxygen going to the ozonator was split into two lines whose pressures were reduced to 8 psig. The oxygen was then introduced as a zero gas for the high-level O_3 monitors, which measured both input and output O_3 concentrations.

A small fraction of the O_3 generated (Figure 1, Line 2) was sent to the input O_3 monitor to measure the concentration of O_3 being introduced into the reactor pot. The monitor alternately measures the O_3 in the sample and zero gas by UV absorption principles and automatically reads out the net weight percent of O_3 in the sample.

The flows for both gases were controlled at 2 l/min. Since UV absorption is a function of the density of the gas, a type K thermocouple and a mercury manometer were placed in the line to measure the temperature and pressure of the gas. The O_3 concentration was corrected for temperature and pressure effects according to calculations described in Appendix D. A Teflon filter (5μ) was placed in the line to remove any particulates and to duplicate the O_3 monitor conditions. Another branch of this O_3 sample line was used to calibrate the O_3 monitor using the KI titration described in Appendix E. This branch was normally closed during an ozonation test. Because of the low flow, a single O_3 decomposer heated to 50°C by heating tapes removed the O_3 (Figure 1, Line 4) before discharging into the hood. The volume of this gas is not critical and was not measured since it does not enter into the reaction or calculations.

The major fraction of the O_3 generated was directed (Figure 1, Line 3) to the reactor pot for oxidizing the synthetic waste. The reaction pot underwent several modifications. The last arrangement is shown in Figures 3 and 4. The pot was maintained at a constant temperature, normally 60°C, with a waterjacket supplied by a constant temperature water circulator. Mixing was accomplished by a Teflon stirring shaft connected to an ACE Model 8081 flexible shaft motor drive assembly, through an ACE water-cooled, glass bearing (Model 8040).* The stirrer speeds for the test were controlled by setting the variable motor controller to approximately the same setting but were not measured. A direct drive to the stirring shaft was originally used but vibrations eventually resulted in the shaft binding and sometimes stopping. Four baffles were located on the glass walls to help disperse the O_3 gas bubbles. The gas was originally dispersed through a blown glass frit (2.5 in. dia.) with ~40 holes that were ~1 mm in dia. Because this design could not be easily reproduced, a removable, machined Teflon frit (Figure 3) with ~60 holes and variable diameters was fabricated and attached to the reactor with a glass-to-Teflon threaded fitting as shown.

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*ACE Glass Incorporated, Vineland, New Jersey, 08360.

Occasionally, solids would block the holes of the glass bubbler, causing flows to vary and making experimental conditions unreproducible. The Teflon frit is still being tested. The distance between the stirrer propeller and the frit was found to be critical for good gas dispersion and in later designs, the distance was limited to 1 in. Samples from the reactor were taken using a 2.5 mm glass capillary tube extended about 6 in. into the pot and connected to a plastic syringe via a Cheminert, Model CAV2031, two-way Teflon valve*. Liquid additives were introduced through another capillary line with a 3-mm Teflon stopcock valve. A stainless steel, sheaved, type K thermocouple to determine the pot temperature was introduced through a Teflon threaded fitting. In earlier experiments, significant gas losses were attributed to leaks around the two large glass fittings (71/60, 10/38) when the reactor was pressurized. Losses were minimized by placing spring clamps over the fittings. The 71/60 fitting required modification in order to accept an enlarged clamp.

The off-gas from the reactor (Figure 1, Line 5) was first passed through a 4°C, 8-in. condenser connected to the reactor's 10/38 fitting with a Teflon sleeve and clamp. The coolant, ethylene glycol, was supplied to the condenser and the ACE glass-Teflon bearing by a refrigerated circulator. Vibrations frequently caused the condenser connection to break. The condenser design should be modified in future models. The gases next flowed to a warm, 60°C, 12-in. downward spiral condenser before finally passing through a 6-in. tube of loosely packed glass wool. This gas treatment was primarily intended to remove moisture and particulates that could contaminate the optics of the output O_3 monitor. The efficiency of these filters and condensers is uncertain. During an 85°C ozonation test, moisture was found in the lines leading to the O_3 monitor, indicating more efficient drying may be required at higher temperatures. Any changes in the off-gas treatment must be done in a manner that will not affect the O_3 concentration of the off-gas.

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*Laboratory Data Control, Riviera Beach, Florida 33404.

After passing through the glass wool filter, the off-gas was spit into a sampling line and a major exhaust line. A small fraction, ∿2 l/min., of the off-gas was passed through a 5μ Teflon filter before entering the output O_3 monitor. The output O_3 monitor measures the O_3 concentration in the off-gas in the same manner as the input O_3 monitor. However, because the gas passing through the monitor also was used in the reaction, its volume had to be measured. This was complicated since the sample gas was not continually passing through the O_3 monitor but was alternating with the zero gas. In order to overcome this problem, another Teflon solenoid switching valve (S) was placed in the exhaust line (Figure 1, Line 6) from the output O_3 monitor and synchronized to the O_3 monitor logic through a solenoid control box fabricated in the lab. This permitted the exhausted off-gas to be directed through a Precision Scientific Model 63115 wet-test meter (WTM) and the zero gas to be exhausted to the hood. A single O_3 decomposer operated at 50°C and a trap containing 400 ml of 10% KI were placed in front of the control solenoid to remove the O_3 before entering the WTM.

The majority of the off-gas was directed through two O_3 decomposers operated at 50°C, and through a 10% KI trap to remove all the O_3, before passing through a WTM to measure its volume. Two decomposers were required to reduce the O_3 levels to a few parts per million for the higher volume of gas. The total volume of reacted gas equals the sum of the volumes measured by the two WTMs. Total gas volumes measured by the WTMs agreed to within 10% of the total volume as estimated from the flow meter readings of the ozonator. Another branch of the reactor output line (Figure 1, Line 5) was used to calibrate the O_3 monitor as well as measure the O_3 concentration of the reactor off-gas directly by KI titration.

Before beginning a test, the flows were balanced carefully by adjusting the control valves on the ozonator and on the O_3 monitors. Too much flow through the ozonator sample line (Figure 1, Line 2) resulted in too small of a flow through the reactor (Figure 1, Line 3) which in turn resulted in insufficient flow to the output O_3 monitor (Figure 1, Line 5). Oxygen flow to the O_3 monitors was controlled carefully so that it could be matched with the flow from the sample lines using the single flow meter on the O_3 monitor. In order to achieve accurate background correction, the supply pressures from the zero gas and sample lines were controlled to nearly the same value.

PROCEDURES

Synthetic Residual Liquor Feed Preparation

The formulation and detailed procedure for the synthetic residual liquor waste used in this study is given in Appendix B.

The mixture must be prepared carefully in order to keep iron in solution. Tartrate was added to help prevent the hydrolysis of iron. Small amounts of solids may form even when using the prescribed procedure. When the solids became more than a few volume percent, the solution was filtered to ensure that the samples taken were homogeneous.

For ozonation studies at OH^- concentrations less than ~0.1$\underline{M}$ (pH < 13), it was necessary to neutralize about 4 l of the waste with concentrated HNO_3. This neutralization resulted in the formation of a large volume of aluminum solids (~50 vol%) and copious amounts of NO_x. The aluminum concentration decreased from 0.6$\underline{M}$ to $10^{-2}\underline{M}$ and $10^{-4}\underline{M}$ for pH 10 and 4 tests respectively. Slow reactions associated with the aluminum precipitation and hydrolysis equilibria, residual NO_x, and decomposition of HNO_2 in the solution made it difficult to obtain a stable pH level. In general, the pH was adjusted as close as possible to the desired level with several additions of HNO_3 and thorough stirring. Sometimes the mixture would be allowed to equilibrate overnight or longer before removing the solids by centrifuging and/or filtering. After the solids were removed, small pH adjustments were made. New solids were sometimes formed which were removed if they were greater than a few volume percent. In some cases, oxygen was purged through the system to remove NO_x and to help stabilize the pH level. The pH was always analyzed immediately before ozonation because of the slow equilibria involved with the neutralization.

The solids formed were not filtered easily and centrifuging usually left some finely dispersed solids present. When the pH was adjusted below 3, the solids redissolved and oxygen purging of the NO_x from the solution was usually successful in stabilizing the pH level.

Neutralization of the waste caused some EDTA to precipitate with the solids. Small volumes (10 ml) of the synthetic were adjusted to pH 10, pH 7, and pH 4, and the solids were filtered. The filtrate was analyzed for EDTA and the solids were washed three times with water and redissolved in 1M NaOH. Results from these tests shown in Table A-1 indicate that increasing amounts of EDTA were precipitated with decreasing pH values. The data also indicate that the EDTA associated with the pH 4 solids may not be as easily removed as the EDTA at higher pH values. This could be the result of a different EDTA complex, or possibly formation of the acid form of the complexant.

TABLE A-1. Solids Washing Tests.

Solution	% Total EDTA		
	pH 10	pH 7	pH 4
Supernate	96.4	82.7	41.4
1st H_2O Wash	29.1	17.0	12.7
2nd H_2O Wash	1.3	3.5	1.2
3rd H_2O Wash	Not Detectable	1.0	1.0
1M NaOH Wash	2.1	5.9	62.7
Material Balance Percent	128.8	110.0	119.0

Another factor that must be considered in evaluating possible EDTA losses is oxidation by NO_x or Cr^{+6} at low pH levels. Based on a cursory examination of these possibilities, NO_2^- oxidation of EDTA was less than 10%, and Cr^{+6} was reduced to Cr^{+3} by HNO_2. Oxidation by Cr^{+6} is unlikely. The high material balances in Table A-1 are believed to be caused by inaccurate volume measurements of the supernate. Variations in the wash volumes were probably caused by carryover of solution by the solids. Because of EDTA losses, the starting EDTA concentration for some ozonation tests at intermediate and low pH levels were lower than would be expected from just dilution during neutralization.

SAMPLING AND DATA RECORDING AND ANALYSIS

After transferring between 1.5 to 2.0 l of the synthetic residual liquor into the pot, the oxygen flow was initiated and the flow through the reactor and O_3 monitors balanced. A 5-ml sample (t_0) was taken before turning on the power to the ozonator. The ozonator was then set to 350 w power. Samples were taken every 15 minutes for the first 2 to 3 hours and every 30 minutes until the test was completed. Occasionally the sampling schedule would be interrupted because of a power failure, stirrer failure, or a plugged gas flow from solids. In these circumstances, the ozonator was shut off and the tests resumed after the problem was alleviated. These unscheduled shutdowns sometimes caused fluctuations in the results because of the time required for the system to return to steady-state equilibrium.

A standard set of data was recorded for each sample. The weight percent and volume of O_3 entering and leaving the reactor were recorded, along with the temperature and pressures needed to make the corrections of the data to standard conditions. The data recording form, shown in Appendix C, was designed to simplify the input of the data into a UNIVAC Fortran IV computer program for calculating and plotting the results. Appendix C also explains the form and the variables of the experiment.

The calculations were performed in four steps described in detail in Appendix D. These were originally performed on a set of Hewlett Packard HP-97 calculator programs. Some of the last ozonation tests (pH 12, pH 13, the 85°C, and manganese addition tests) were calculated with the same equations using a UNIVAC (1100) computer with plotting capabilities.

The O_3 monitors were set to read out the weight percent O_3 of a gas in the absorption cell at 20^oC and 760 mm Hg. Since the temperature and the pressure of the gas in the UV absorption cell changes with each reading during operation, the reading from the O_3 monitors must be corrected to the operational temperature and pressure according to Equation 1D in Appendix D. The corrected weight percent O_3 is then converted to a volume percent (Equation 2D). The second step of the calculation is to determine the total volume of gas used in the reaction corrected to standard temperature and pressure (STP) conditions (0^oC, 760 mm Hg). This is done for both WTM volumes using Equations 3D and 4D in Appendix D. The next step in the calculation is to determine the material balance for the O_3 in the reaction. The grams of O_3 added (Equation 7D) for a sampling period was determined by the product of the volume of gas (STP) added times the average volume fraction of O_3 (Equation 6D) times the density of the gas at STP. The grams of O_3 leaving was calculated similarly (Equation 8D). The grams of O_3 reacted is the difference in these two quantities (Equation 9D). A cumulative amount for these quantities was also calculated so that the total amount of O_3 that had reacted at any time (t) could be determined.

The final step in the calculations is to determine the material balance for the EDTA. Once the molarity of the remaining EDTA was determined from a least-squares analysis of standards analyzed at the same time as the samples, this task was quite simple, as seen in Program D of Appendix D.

The stoichiometry or O_3 consumption ($\Delta O_3/\Delta$EDTA) for the reaction was determined by plotting the total moles of O_3 reacted versus the total moles of EDTA reacted for each sampling point and determining the slope or slopes by a linear least-squares calculation. The pseudo-first-order rate constant for the reaction was determined by plotting the negative logarithm of the ratio of the EDTA molarity at sample time (t_i) to the original feed EDTA molarity at (t_0) versus time. The slope of this plot determined by linear least-squares analysis is the first-order rate constant. Other functions of the EDTA and O_3 concentrations were also calculated and plotted in the evaluation of the ozonation test as noted in Appendix D. The percent O_3 reacted at any time was calculated by the following equation:

$$\%O_3 \text{ Reacted} = \frac{\text{wt\% } O_3 \text{ in} - \text{wt\% } O_3 \text{ out} \times 100}{\text{wt\% } O_3 \text{ in}} \quad (1)$$

and shows how O_3 consumption changes with time.

ANALYSES

Ozone Concentration

The O_3 concentration in the gas was determined using Dasibi O_3 monitors. They were calibrated using the KI titration procedure described in Appendix E. In this procedure, a known volume of gas containing O_3 is passed through two 2% KI traps where O_3 oxidizes the iodide to iodine. The iodine is then titrated with standard thiosulfate solution to a starch indicator endpoint. The weight percent O_3 for this gas is measured on the O_3 monitor with a recorded SPAN number (an instrumental calibration factor) setting and a known temperature (T) and pressure (P) for the gas. The recorded SPAN number was then corrected based on the slope of the plot of monitor readings versus the titration results. This is the correct SPAN number for a gas with the same T and P conditions as the gas on calibration day. The correct SPAN number is adjusted again to represent a gas at 20°C and 760 mm Hg (STP) and this standard value is used for all succeeding tests. The measured weight percent O_3 values during a test were then corrected for the T and P at the time of the monitor reading as described in Appendix D.

Even though the neutral buffered KI titration method is recognized by the Environmental Protection Agency (EPA) as a primary method for calibrating low-level O_3 monitors, there is a great deal of controversy about its stoichiometry and its reliability.(9,10) Other methods such as titration in borate buffers, or titrations with arsenite and formulas derived from first principles of UV absorption have been proposed as primary methods.(11-15)

When we attempted to collect greater than 6 l of 3-wt% O_3 in two 400-ml 2% KI traps, extremely low results were obtained. This was believed to be caused by the formation of iodate or higher oxidized forms of iodine such as I_2O_9.(15) This opinion is further supported by the formation of white solids, fading of the red I_2 color, and the formation of a dense white gas in the KI traps. Calibrations by KI titration have been developed for low-level O_3 monitoring and have not addressed some problems of high-level O_3 measurements.

Because of the problems associated with KI titrations at high O_3 concentrations, and since SPAN numbers from recent KI calibrations agree very well (within 1%) with theoretically calculated SPAN numbers, this latter method may be more accurate, reliable, and convenient than frequent KI calibrations. Therefore calculations of R. G. Clark for determining the SPAN numbers on high-level Dasibi monitors have also been included.(Appendix F) (14)

APPENDIX B

PROCEDURE FOR PREPARING SYNTHETIC RESIDUAL LIQUOR WASTE MIXTURE

The synthetic waste mixture is made up in 4-l batches which are combined in a large polyethylene carboy that contains 20 l. Table B-1 gives the chemical composition for a 4-l batch.

TABLE B-1.

Component	Molarity	Chemical Used	FW	Grams or ml used per 4 l
Al^{+3}	0.85	$NaAlO_2$	81.97	278.7 g
OH^-	1.30	NaOH	40.0	208 g
NO_3^-	1.45	$NaNO_3$	84.99	493 g
NO_2^-	1.35	$NaNO_2$	69	372.6 g
CO_3^{-2}	0.115	Na_2CO_3	105.99	48.7 g
CrO_4^{-2}	0.10	Na_2CrO_4	234.03	93.6 g
Fe^{+3}	0.0075	$Fe(NO_3)_3$	1.5 molar solution	18.66 ml
Tartrate	0.05	NaTartrate	230	46 g
EDTA	0.031	Na_2H_2EDTA	416.2	51.6 g

SYNTHETIC WASTE PREPARATION PROCEDURE

PROCEDURE	COMMENTS
1. Place 2 l of distilled water into a 4-l beaker.	
2. Add 208 g of NaOH and stir to dissolve.	
3. Add 278.7 g of $NaAlO_2$ and heat and stir until all dissolves.	
4. Add the following, dissolving each before adding the next. 493 g $NaNO_3$ 372.6 g $NaNO_2$ 936 g Na_2CrO_4 Stir on a cold stirrer.	4a) Be sure solution is cool before adding Na_2CO_3 in Step 5.
5. Adjust the volume to 3.5 l with distilled water and add 487 g of Na_2CO_3. Stir vigorously.	5a) The Na_2CO_3 is the most difficult to get into solution and requires a long stirring time.
6. In a separate 500-ml beaker, add 350 ml water and 46 g of Na tartrate and 51.6 g of Na_2EDTA. Add individually, stirring after each until dissolved.	6a) This may be done while Na_2CO_3 is being dissolved. 6b) Do not heat complexants to dissolve.
7. Add 18.6 ml $1.5\underline{M}$ $Fe(NO_3)_3$ to the solution of tartrate and EDTA in step 6. Rinse pipets in solution and stir to mix thoroughly.	
8. Add the contents of 500-ml beaker containing iron, EDTA and tartrate to the 4-l beaker. Rinse 500-ml beaker with a small amount of water and transfer to the 4-l beaker. Stir thoroughly.	
9. Transfer contents of 4-l beaker to a 4-l graduated cylinder and bring to volume with distilled water and mix well.	

PROCEDURE	COMMENTS
10. Transfer graduated cylinder contents to the 20-l carboy and mix with other 4-l batches.	10a) Mix the 20-l carboy well before removing portions for experimental tests.
	10b) Sometimes large amounts of iron may precipitate which will require fabrication and solution characterization prior to use.

APPENDIX C

DATA RECORD EXPLANATIONS

Block I	Computer directions for entering changes in test parameters (Block II) Also includes inputs for:	
	Title	Title of experiment
	Bar	Barometric Pressure for the day of the test in mm Hg
	S	Slope of HPLC calibration for EDTA
	I)	Intercept for HPLC calibration
Block II	Identifies parameters different from normal operating condition (Block III) and gives their new values for the test.	
Block III	Normal preset parameters used for an ozonation test.	
	SPANIN	Span number for the input O_3 monitor as determined by calibration by KI or by calculation.
	SPANOUT	Span number for the output O_3 monitor.
	SPANT	Temperature for which span was determined or is valid, in ^{o}K.
	SPANP	Pressure for which span was determined or is valid, in mm Hg.
		Note: The span number is a calibration factor which is a function of T and P. It is normally determined for the T and P for the day of calibration. The span number may be corrected and reset to the T and P for the day of a test or it may be set to a standard T and P (20^{o}C and 760 mm Hg) and each reading of weight percent O_3 corrected to the correct weight percent based on the T and P of the monitor at the time of measurement. This latter method was used for our tests since the T and P of the monitor changed during a run. This correction is based on the ideal gas law as seen in the calculation section.
	Vol	Volume of solution ozonated in liters.
	Power	Power level at which ozonator was operated, in watts.

O_2Flow	Flow in SCFH as recorded from ozonator flow meter. Setting varied 2 SCFH because of gas switching in O_3 monitor.
O_3STP	Density of O_3 at STP = 2.154 g/l.
O_2P	Oxygen pressure of ozonator.
I PLOT	Computer control parameter for plotting.

Block IV Sampling Data

Columns 1 & 11	Hrs	Length of time solution has been ozonated when sample is taken. Starts with 0. Recorded twice for computer input.
Columns 2 & 3	wt%	Weight percent O_3 on INput and OUTput O_3 monitors at sampling time.
Columns 4 & 5	TEMP-MON	Temperature of INput and OUTput O_3 monitors when wt% is read. (^{o}0 C).
Columns 6 & 7	DP-MON	Differential Pressure (mm Hg) of input and output O_3 monitors when wt% is read.
Column 8	VOL	Volume of gas recorded on WTM for the Reactor off-gas. Record WTM readings N-N-N convert to liters. Record when sample is taken.
Column 9	T	Temperature (^{o}C) of gas passing through WTM for Reactor off-gas.
Column 10	VP	Vapor pressure of water at "T" in mm Hg for gas passing through WTM for Reactor off-gas.

Columns 12, 13 & 14	Vol, T, VP	Same as columns 8, 9, and 10 except for the WTM used to measure the volume of gas from the output O_3 monitor.
Column 15	T React	Temperature of reactor solution when sample is taken.
Column 16	pH	pH of sample after it has cooled to room temperature.
Column 17	Peak Area	Integrated peak area from HPLC analysis for EDTA.
Column 18	DF	Dilution Factor for HPLC analysis of EDTA in sample.
Column 19	CO_3^2	Carbonate analysis of the sample. (Molarity)
Column 20	NO_2^-	Nitrite analysis for the sample (Molarity).
Column 21		Any other analysis on the sample. Note: Computer program limited to 20 columns of data.

DATE:

OZONE

TITLE:

I

PROGRAM STEPS
TEL-6-7641 (30) 6-7676 (120) @@ HOST SYSB DLT KRAT/RHO OXI (USER ID) OZONE PROJ ID) NAME/ADDRESS @USE O., OZONE @ ED, I, O. DATA RETURN - RETURN LNPI C /-/-/ (EDIT) EXI @ ADD, L O. CHKRUN @ ED, U O. DATA EXI @ ADD, L O CHKRUN @ ADD, L O. RUN @ ED, O. DATA, O. TESTN EXI @ PRT, T O. @ FIN @@ TERM

I

DATA ENTRY
YES OR NO $ PARAMS, P_1, P_2... $ END (TITLE) (BAR. P). (mm Hg) (S) = (I=!

II

NEW PARAMS
"P" =

III

PRESET	PARAMS
SPANIN=21.75	O_2 FLOW=.20
SPANOT=21.85	O_3 ST?=2.154
SPANT = 293	O_2P =" 1500/ 40/12
SPANP = 760	
VOL = 2.0	I PLOT = -1
POWER = 350	

IV

HR	WT% IN	WT% OUT	TEMP - MON IN	TEMP - MON OUT	DP - MON IN	DP - MON OUT	VOL WTM-R	T WTMR	VP R	☒	HR	VOL WTM-M	T WTM M	VP M	T REACT	pH	PEAK AREA	DF	CO_3^{-2} M	NO_2^- M	
										☒											
										☒											
										☒											
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DATA RECORD SHEET

APPENDIX D

CALCULATIONS

Calculations

The calculations for this study were done with four different programs using a Hewlett Packard 97 calculator. These calculations are described as follows:

Program A: Correction of Dasibi wt% Ozone to wt% at Test T and P.

$$\text{Corrected wt\% } O_3 = \frac{(\text{wt\% recorded})(760)(T^{o}K)}{(P_T)(293^{o}K)} \qquad (1\text{-D})$$

where:

760 mm Hg = standard pressure Dasibi span calibration setting.

$T^{o}K$ = temperature of Dasibi UV cell measured by thermocouple in ^{o}K

P_T = total pressure on Dasibi cell = barometric pressure + differential pressure (DP) measured by mercury manometer (mm Hg)

$293^{o}K$ = standard temperature in ^{o}K for Dasibi span calibration setting.

$$\text{Vol\%} = \frac{\text{Corr wt\%}}{\{150-0.5\ (\text{Corr. wt\%})\}} \times 100 \qquad (2\text{-D})$$

NOTE: 150 and 0.5 are derived values.

NOTE: Dasibi calibration span setting set for 20°C, and 760 mm Hg.

Program B: Corrected Volumes for WTM and Total volume of Gas

$$V_{STP} = \frac{V_{WTM}\ (273^{o}K)\ (P_B - V_P)}{(T^{o}K)_{WTM}(760\ \text{mm})}$$

where:

V_{WTM} - volume (liters) recorded on WTM
$271^{o}K = 0^{o}C$ = Standard Temperature
P_B =Barometric pressure mm Hg
VP = Vapor press of water at T^{o}_{WTM} of WTM gas
P_B-VP = Corrected pressure of gas being measured by WTM
760 mm = Standard Pressure (mm Hg)
Total $V_{STP} = V^{STP}_{Reactor} + V^{STP}_{Output\ Monitor}$

NOTE: Volumes corrected to STP conditions - $0^{o}C$ and 760 mm Hg
NOTE: Corrected pressure for WTM normally = $\left[P_B - P_{Man} - P_{Cor} - VP_{H_2O}\right]$

where:

P_{Man} = differential pressure on WTM normally 0 in our work
P_{Cor} = altitude, lattitude corrections not made in this work.

<u>Program C</u>: Determine Volume Change, gm O_3 added, gm O_3 out, gm O_3 Reacted for each time interval and total time lapsed.

1. Volume of gas reacted for time interval (t_i) to $\left(t_i + 1\right)$

$$\Delta V + \text{Total } V_i + {}_1 - \text{Total } V_i \qquad (5\text{-D})$$

where

i = time increment

2. Determine average volume percent ozone (volume fraction) added for a time interval for both input and output gas to reactor.

$$\text{Average Volume Fraction} = \frac{\text{vol\%}_i + {}_1\ \text{vol\%}_i}{2 \times 100} \qquad (6\text{-D})$$

3. Calculations for gm O_3 added, gm O_3 unreacted, gm O_3 reacted gm

O_3 Added = (ΔV)(Avg. Vol. Frac. In) $\left(\sigma_{O_3}\right)$ (7-D)

where:

σ_{O_3} = 2.154 = density of ozone at 0°C, 760 mm Hg

$$\text{gm } O_3 \text{ Unreacted} = \overset{\text{(out)}}{(\Delta V)}(\text{Avg. Vol. Frac. Out})\left(\sigma_{O_3}\right) \quad \text{(8-D)}$$

$$\text{gm } O_3 \text{ Reacted} = \text{gm } O_3(\text{In}) = \text{gm } O_3(\text{Out}) \quad \text{(9-D)}$$

NOTE: The total amount of ozone is stored and added to the amount of ozone for the next time interval to determine the total amounts of ozone at any time (t).

NOTE: The volume fraction of ozone is only an estimate since it is based only on two readings for a time interval. This estimate is accurate when the reaction is not undergoing any rate or stoichiometry changes. However; at some stages of the reaction these changes cause rapid changes in the volume percent O_3 in a time interval making the estimate less accurate.

Program D: Determination of EDTA Molarity Remaining and Other EDTA Functions.

1. Determine Slope and Intercept for LC calibration for EDTA.
X = mMoles EDTA Y = peak area.

2. Molarity EDTA = (Peak Area -I) $(^1/S)$ (DF)
Remaining

where: DF = dilution factor normally
250 µl-10ml with 100 µl injection into LC

DF - 400

Calculate:

3. $^1/\underline{M}$olarity Remaining - Used to test for 2nd order reaction

4. $$\% \text{ EDTA Remaining} = \frac{\text{M Remaining at (t)}^{\text{EDTA}}}{\text{M EDTA at }(t_o)} \times 100$$

5. % EDtA Reacted = 100-% Remaining

6. $-\ln \frac{\text{EDTA}(t)}{\text{EDTA}(t_o)}$ - used for measuring first order reactor rate.

7. Moles EDTA Remaining = $(\underline{M}\ \text{EDTA}_t)$(Total Volume)

8. Moles EDTA Reacted = $(\underline{M}\ \text{EDTA}_{t_o} - \underline{M}\ \text{EDTA}_t)$ (Total Volume)

APPENDIX E

CALIBRATION OF DASIBI OZONE MONITOR BY KI TITRATION

PROCEDURE	COMMENT
1. Checkout ozonation system before starting calibration. a) Record barometric pressure. b) Check O_3 monitor "sample" and "control" frequency record. c) Check WTM - zero and check fluid level. d) Set up 50-ml burrett with $0.1\underline{M}$ $Na_2S_2O_3$.	1a) Fill 20 trap bottles with 400 ml fresh 2% KI in distilled water and set traps on stirrers. Connect to calibration branch of ozonation system.
2. Set O_2 flow through system at approximately same level as operating condition.	
3. Turn ozonator for 30-minute warm up.	3a) Be sure valve to calibration branch is closed. (KI traps).
4. Turn ozonator to desired operating level (normally 350 W).	
5. After a couple minutes record O_3 monitor wt%, T, and DP.	
6. Open valve to calibration line permitting O_3 to pass through KI traps, WTM and O_3 monitor.	
7. Allow 3-6 l of gas (1 or 2 full revolutions) pass through traps and quickly turn valve off when WTM is at the 3-1 mark. Record WTM and WTM DP if >0. Record exact WTM volume.	7a) Attempts to collect larger volumes at 3 wt% O_3 may result in low titrations. 7b) Record as many O_3 monitor readings with T and P as possible during KI sampling.
8. Record a final O_3 monitor wt% reading with T and P.	8a) These O_3 monitor readings are compared and averaged for each titration.

9. Transfer contents of KI traps to a large (1000-ml) beaker as soon as possible to prevent I_2 reduction or loss.

9a) Rinse traps with deionized water and add to beaker.

10. Add 5 ml of concentrated H_2SO_4 and stir.

11. Titrate with standard $Na_2S_2O_3$ until the endpoint is near (fading red color) and add 2 ml of starch indicator. Finish titrating to characteristic blue endpoint and record volume of $Na_2S_2O_3$ used.

11a) Standard $Na_2S_2O_3$ was purchased from a vendor; however, it was frequently checked against a $K_2Cr_2O_7$ titration since $S_2O_3^{2}$ is unstable in air.

12. Repeat 4-5 more times at lower power levels to calibrate over a 0.5-4% range.

CALIBRATION CALCULATIONS

The titration weight percent is compared to the reading obtained on the O_3 monitor at a set SPAN number, T, and P. The SPAN number is a proportionality constant that can be changed to make the monitor read out directly in O_3 weight percent at the desired temperature and pressure. Assuming KI titration data as standard values, the monitor data are plotted on the Y-axis versus the titration data on the X-axis. If the SPAN number was properly set, the slope of this curve would be 1.000. If not, the new SPAN number is calculated as follows:

<u>NOTE</u>: A SPAN number should <u>always</u> be given for the T and P for which it is valid.

I. $$\text{Gram } O_2 = \frac{V(l) \times (293^{o}K) \times \left[P_{Bar} - P_{Man} - P_{Cor} - VP_{H_2O}\right] \times 1.3265}{(760 \text{ mm Hg})(T_2)}$$

Where:

V = Volume of gas passing through KI traps as measured on WTM
$293^{o}K$ = Standard Temperature ($20^{o}C$)
760 mm = Standard Pressure

1.3265 = Density of O_2 at 20°C, 760 mm
T = Temperature of gas through WTM
P_{Bar} = Barometric Pressure
P_{Man} = Differential Pressure on WTM
P_{Cor} = Altitude and Lattitude Correction not done in this work
VP H_2O = Vapor pressure of H_2O at T

II. $\text{Gram } O_3 = ml_{Na_2S_2O_3} \times N_{Na_2S_2O_3} \times \frac{0.024 gm O_3}{meq\ Na_2S_2O_3}$

III. $wt\%O_3 = \frac{gm\ O_3}{gm\ O_2 + gm\ O_3} \times 100$

IV. Plot O_3 wt% by titration (X) versus wt% O_3 by monitor (Y) and calculate a least squares fit to line. Record slope and intercept. See attached plot.

V. Calculate new SPAN number for T, P of monitor on calibration day.

$$\text{New SPAN at } T_c, P_c = \frac{\text{Old SPAN}}{\text{Slope}}$$

c = calibration day

VI. Determine the correct SPAN number for 20^oC, 760 mm Hg.

$$\text{SPAN No. } 20^oC, 760 \text{ mm Hg} = \text{SPAN No } T_c, P_c \times \left[\frac{(293^oK)}{T_c}\frac{(P_c)}{760}\right]$$

NOTE: If the temperature and pressure (T_c, P_c) on the monitor reading in (IV) fluctuate by more than 1°C or 4 mm Hg, convert each wt% reading at T_c, P_c from monitor to a wt% at 20°C, 760 mm Hg by substituting wt% for SPAN in the above equation. Calculate a new SPAN accordingly for 20°C, 760mmHg rather than T_c, P_c.

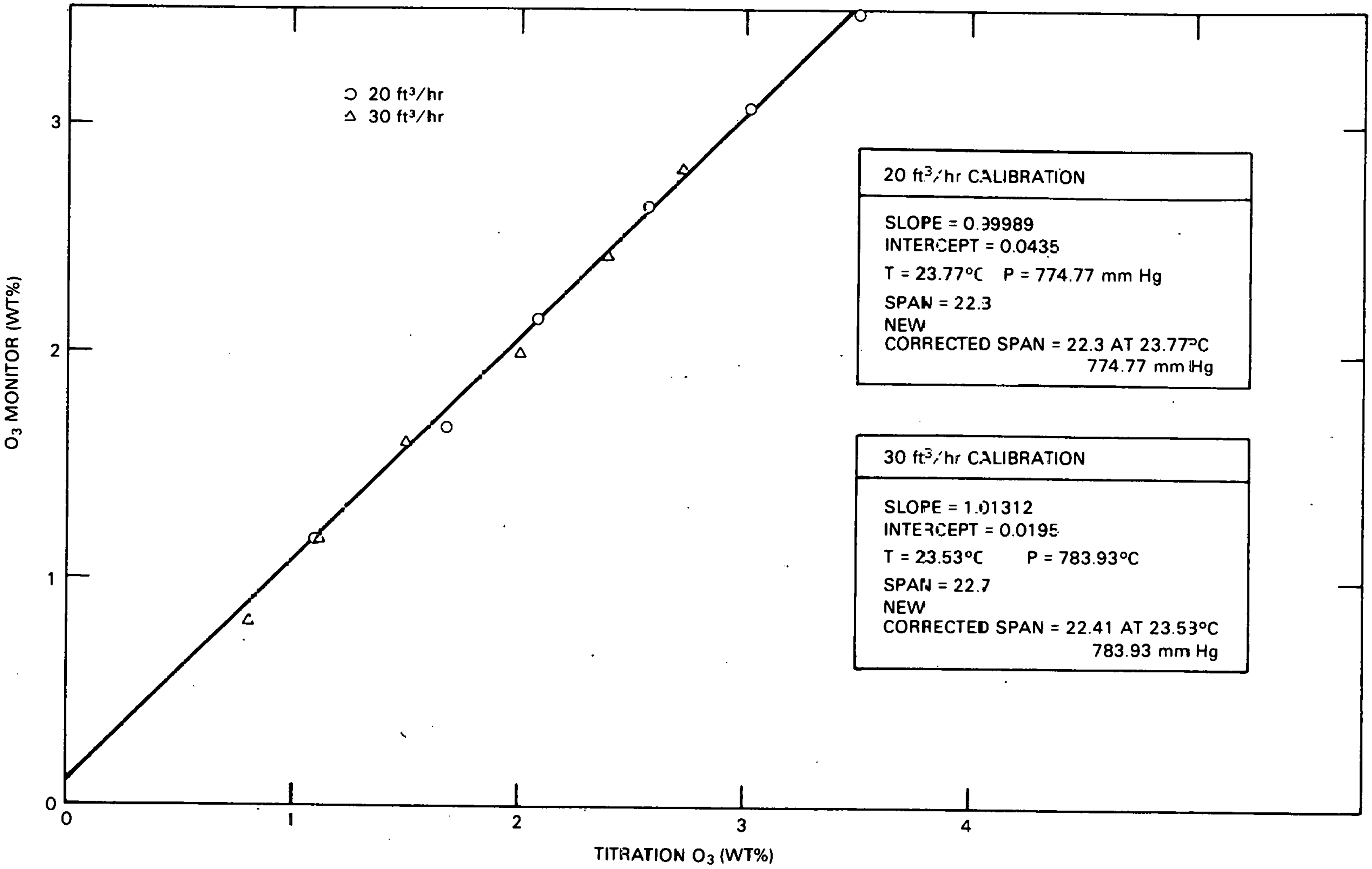

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FIGURE E-1. Calibration Data.

APPENDIX F

APPENDIX F

CALIBRATION OF DASIBI MONITOR BASED ON UV ABSORPTION PRINCIPLES

The following calculations are based on equations provided by Dr. R. G. Clark of Union Carbide Co. For these calculations he recommends a molar absorptivity of 133.9cm^{-1} at STP based on weighted average value determined by Dr. D. Pauer EPA, Research Triangle Park, North Carolina. The use of UV absorption principles for calibration of O_3 monitors is becoming more acceptable and may be simpler and more reliable than the controversial KI titration. Recent KI calibrations have agreed very well with theoretical SPAN number determinations.

Calculation of the SPAN Number

Equation 1. $$I_o = \frac{I_o - I}{1 - e^{-2.3026\ act}}$$

$$= \frac{R \times 10^3}{1 - e^{-2.3026\ act}}$$

Where: I_o = SPAN number

$I_o - I$ = $R \times 10^3$ = reading on O_3 monitor (3 wt% = 3000)

a = Absorption coefficient for O_3 at a given T.P.

b = Length of cell = 2.54×10^{-2} cm for O_3 monitor

c = O_3 concentration in atm where (atm = ppm (vol) x 10^{-6})

Equation 2. (Nonlinearity Factor)

$$\text{Factor} = \frac{\ln \frac{(1)}{\left(1 - \frac{R \times 10^3}{Io}\right)}}{2.3026 \times 0.0254 \times a \times R \times MW} \times 4800$$

This factor is multiplied by the monitor reading to get the true O_3 concentration.

Example: SPAN for O_3 in O_2 at 20°C, 760 mm Hg

Assume 3 wt% O_3

Calculation:

$$3 \text{ wt\% } O_3 = \frac{3gO_3}{97gO_2+3gO_3}$$

Volume of $3gO_3$ = PV = nRT

at 20°,760 mm Hg

$$V = \frac{(3g)}{(48)} (0.08205)(293) = 1.502 \text{ l}$$

$$\text{Volume of } 97\,g\,O_2 = \frac{97}{32} (0.08205)(293) = 72.873 \text{ l}$$

Total Volume = 74.375 l vol% O_3 = 2.019 = 20,190 ppm = 0.02019 atm

$$\text{a(absorption coefficent} = 133.9 \times \frac{273}{293} \times \frac{760}{760} = 124.76 \text{ cm}^{-1}$$

at 20°C,760 mm Hg

$$\text{SPAN No.} = I_0 = \frac{3000}{1-e^{-2.3026\,(124.76)(0.02019)(0.0254)}} = \frac{3000}{1-e^{-0.14732}} = 21900$$

$$\text{Factor} = \ln \frac{\left(\frac{1}{1-\frac{3000}{21900}}\right) \times 48000}{2.3026 \times 0.0254 \times 124.76 \times 3 \times 32.32} = 0.99966$$

$$\text{Where MW} = n_{\text{Total}} = n_{O_2} + n_{O_3}$$

$$\frac{g}{MW} = \frac{g}{MW_A} + \frac{g}{MW_B} = \frac{100}{X} = \frac{3}{48} + \frac{97}{32}$$

$$X = 32.32$$

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