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Investigation of the Applicability of Wet Air Oxidation to the Treatment of Hazardous Organic Wastes

for
Environmental Protection Service
Environment Canada
Ottawa, Ontario.

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(Proposal P-3470/G)

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1. SUMMARY

The applicability of wet air oxidation to the destruction of specific hazardous chemicals contained in aqueous waste water streams was investigated.

Three specific compounds were chosen as examples of hazardous organic materials containing chlorine, nitrogen and sulfur. These were:

Pentachlorophenol	PCP
Mercaptobenzothiazole	MBT
Diphenylamine	DPA

Destruction efficiencies of these compounds of greater than 99.9% were achieved in wet oxidation tests on streams consisting of both pure chemicals in water, and these same compounds as components of industrial waste streams.

Gas Chromatography/Mass Spectrometry (GC/MS) techniques were used to analyse both the starting compounds and the breakdown products from the oxidation reaction. Trace quantities of chlorinated organics were measured in the effluent from the oxidation of pentachlorophenol.

The majority of the chlorine appeared as inorganic chloride ion in the effluent. The major nitrogen containing breakdown products from the oxidation of both mercaptobenzothiazole and diphenylamine were aniline and nitrobenzene. No organic sulfur by-products were detected in the effluent from the oxidation of mercaptobenzothiazole.

Both aniline and nitrobenzene are steam strippable, and would, therefore, be removed from the aqueous solution as they are formed. Oxidation in the wet oxidation process occurs only in the aqueous phase. Temperatures and pressures are insufficient for efficient gas phase oxidation to occur.

It was concluded that wet oxidation would be an effective process for the destruction of the hazardous waste components studied. It was further concluded that no hazardous by-products were formed from the oxidation of pentachlorophenol, and that the only significant by-products of the oxidation of mercaptobenzothiazole and diphenylamine were aniline and nitrobenzene. Increasing reactor pressure and catalytic oxidation of the vapour phase are suggested as methods of eliminating these by-products.

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2. INTRODUCTION

Public concern over the safe treatment and transport of hazardous material has been increased by events such as the leaching of chemicals from the Love Canal chemical disposal site and the 1979 Mississauga train derailment. Management of hazardous wastes is improving, but the need for effective methods for detoxifying hazardous organic wastes economically still exists.

In responding to this need, lists of hazardous chemicals or pollutants have been established by various regulatory authorities in both the United States and Canada. In conjunction with chemical lists, the United States Environmental Protection Agency has defined sources and processes which generate these hazardous materials.

A task force on Hazardous Waste Definition, commissioned by Environment Canada, has been established to more thoroughly define and investigate hazardous waste types as well as the processes producing them. The term "Hazardous Waste" has been defined by this task force as follows(1):

> "Waste is any substance for which the owner/generator has no further use and which he discards.
>
> Hazardous wastes are those wastes, which, due to their nature and quantity, are potentially hazardous to human health and/or the environment which require special disposal techniques to eliminate or reduce the hazard."

Many of the wastes which may be defined as hazardous are organic. It is to the destruction of these waste materials that this study addresses itself.

The destruction of organic compounds is achieved by oxidizing them to form, ideally, carbon dioxide, water and inorganic forms of nitrogen, sulfur and/or chlorine. Established oxidation processes to realize this end include:

- Chemical oxidation (using chemical agents such as ozone or hydrogen peroxide)
- Biological oxidation

- Wet air oxidation
- Incineration

The choice of the process best suited to treat a particular waste depends upon the concentration and nature of the materials. For very, very low concentrations, chemical oxidation may be economically feasible. For rather stronger wastes, biological oxidation may be the preferred route, providing the species existing in the waste stream are not toxic to the bacteriological colony employed. For very concentrated wastes (say greater than 30% by weight of oxidizable species), incineration may be considered as a method of disposal. This approach may not be acceptable if high concentrations of chlorine, nitrogen or sulfur are present in the waste stream. These elements may give rise to unacceptable levels of air emissions from the incinerator.

For concentrations of waste between 1% and 30%, the cost of chemicals for chemical oxidation or the long retention times required for biological oxidation make both these processes expensive. Likewise, prior to incineration of such a stream, a proportion of the water must be evaporated, or sufficient fuel must be used in the incinerator to sustain combustion of these low level wastes. Both these approaches are expensive.

Wet air oxidation is best applied to streams containing between about 1 and 25% by weight of oxidizable material. Work has been undertaken on wet oxidation of sewage sludge, spent pulping liquors, and a number of other industrial wastes. The aim in these investigations was to determine the reduction in oxygen demand (COD, BOD) of the waste stream which can be achieved by the application of the wet air oxidation process to these wastes, the oxygen demand being the major detrimental effect of introducing such a waste stream to the environment. Less attention has been paid in these investigations to the fate of individual chemical species through the oxidation reactions. While gross reductions in COD or BOD of 75-90% are often acceptable in the wet air oxidation of wastes, these are unacceptable levels of destruction for chemicals which are regarded as hazardous.

Earlier work at ORF has examined the wet oxidation of a few specific chemicals. Overall destruction efficiencies for these are given in Table 1. These show quite high efficiency for the destruction of these species. There was, however, insufficient attention paid to determining what the reaction products were from the oxidative destruction of the specific chemicals tested.

One of the advantages of the wet oxidation approach to hazardous waste treatment is the fact that the inorganic elements, sulfur, chlorine and nitrogen, are retained in solution rather than giving rise to air pollution problems. Sulfur is converted to sulfate salt or sulfuric acid, chlorine to a chloride salt or hydrochloric acid and nitrogen ends up as ammonia. While the process has not destroyed these elements, they are more easily handled in a solution form than if they are emitted to the air stream to which an air pollution control process must be applied.

Ontario Research have, for the past 8 years, been investigating a specific wet air oxidation process known as the Wetox$^{(R)}$ Process. The reactor design utilized in this process allows for optimum mass transfer of oxygen to the oxidizable species at minimum temperature and pressure. The reactor design is a horizontal cylindrical compartmented vessel, with stirring in each compartment, which performs as though it were a series of continuous stirred tank reactors. Typical operating conditions are 230°C and 4 MPa pressure. Vapour and liquid phases are withdrawn separately from the reactor allowing for concentration of non-oxidizable species in the liquid phase. A more extensive description of the Wetox process is given in Appendix A to this report.

3. PROGRAM OBJECTIVES

The overall objective of the program was to assess the applicability of the wet air oxidation system, specifically the Wetox process, for the destruction of hazardous organic materials. More specific objectives of the experimental program were as follows:

(i) To determine the destruction efficiency of the Wetox process treating three specific hazardous chemicals.

(ii) To determine the by-products generated from incomplete combustion of the three compounds.

(iii) To determine the fate of each specific toxic chemical contained in an industrial waste stream.

4. WASTE SELECTION AND IDENTIFICATION

Selection of the three hazardous organic chemicals for testing under this program was based on a number of criteria which were divided into two major categories as follows:

(1) External Selection Criteria

- Material must be hazardous
- Material must be fairly prevalent in industry, and, therefore, be a potentially problem pollutant
- Material should be characteristic of a range or class of compounds (viz chlorinated organic, nitrogen containing organic, etc.)

(2) Internal Selection Criteria

- Personnel safety
- Soluble or miscible in water. This criterion was considered important to minimize any physical problems in withdrawing samples for analysis. (This is not a fundamental limitation of the wet air oxidation technology).

The three chemicals which were selected for evaluation in the program were:

1. Pentachlorophenol (PCP) [a chlorine containing waste]
2. Mercaptobenzothiazole (MBT) [a nitrogen + sulfur containing waste]
3. Diphenylamine Hydrochloride (DPA) [a nitrogen containing waste].

Difficulty was experienced in attempting to get permission to obtain samples of industrial waste streams containing either MBT or DPA within the time frame of this program. As a compromise, a mixed organic waste stream was secured from a large chemical producer. Commercial grade MBT or DPA was then artificially added to this stream, thus simulating a waste stream containing these compounds.

For the remainder of the program, the material being investigated will be identified as follows:

The Pure Compounds:

			Starting Chemical Oxygen Demand (ppm)	
Abbreviation	Chemical Formula	Measured COD/TOC	Batch	Semi-Batch
Pure PCP	C_6Cl_5OH	2.1	5,960	8,860
Pure MBT	$C_7H_5NS_2$	3.6	6,300	16,000
Pure DPA	$(C_6H_5)_2NH \cdot HCl$	3.7	6,000	16,300

The Waste Streams Containing the Pure Compounds:

		Starting Chemical Oxygen Demand (ppm)		
Waste Stream Abbreviation	Concentration of "Active" Ingredient (ppm)	Batch	Semi-Batch	Pilot Plant
Chemical Waste*	-	-	-	-
PCP Waste	∿ 847 (Batch) ∿ 400 (Pilot Plant & Semi-Batch)	6,000	4,000	∿ 4,200
MBT Waste	1,000	5,460	20,060	∿45,000
DPA Waste	1,000	5,650	20,250	∿45,000

*Received from chemical producer at COD ∿185,000 ppm. Contained in MBT Waste and DPA Waste.

5. EQUIPMENT & EXPERIMENTAL PROCEDURES

5.1 Wetox Testing Program

The selected pure organic chemicals, and the respective waste streams containing them, were investigated using three different reactors. Test procedures and experimental details for each are outlined individually in the following three sections:

5.1.1 Batch Scale Testing

The two-litre batch autoclave and its operation is described in Appendix B. This unit is capable of operation to a maximum temperature of 280°C. Starting COD concentration is limited to about 6000 ppm because of the unit's batch mode of operation.

Performances of the wet oxidation reaction were monitored via COD, TOC and inorganic chloride ion analyses as the following process conditions were varied:

Pressure (2.7 - 9 MPa)
Temperature (200° - 280°C)
Reactor Residence Time (5, 15, 30, 60, 90 minutes)
pH Adjustment (As received and at pH ∿ 2) Cu
Catalyst Addition (Copper as CuO) 200 ppm

Effluent samples from tests which showed the greatest reduction in COD and TOC were then subjected to a detailed organic analysis for an evaluation of the intermediate reaction by-products and unoxidized species.

5.1.2 Semi-Batch Experiments

Semi-batch tests were undertaken to provide a confirmation of the optimum reaction conditions established during the batch-scale testing portion of the program. The 10 litre semi-batch system is described more fully in Appendix C.

Conditions for all semi-batch tests in this program were 240°C, 625 psi for a 60-minute residence time. Samples were extracted for analysis at 5, 10, 15, 30 and 60 minutes.

5.1.3 Continuous Flow Pilot Tests

The mobile continuous flow reactor simulates completely a full-scale Wetox process for industrial and municipal wastewater treatment. Operation of this unit is discussed in more detail in Appendix D.

Only the industrial waste streams containing the hazardous organic chemicals were tested in this unit. Three tests were performed on PCP waste and two on each of MBT waste and DPA waste.

Besides providing a confirmation of the results obtained from the batch and semi-batch experiments, these tests were useful in determining the split of organic contaminants between the liquid and gaseous phases. In addition, some of the reaction kinetics required for the design of the Wetox system were developed.

5.2 Analytical Methods

The performance of the Wetox process in the treatment of hazardous organic materials was monitored via a variety of parameters. Measurement of these parameters was divided into two general classes:

- Routine Analyses
- Detailed Organic Analyses

5.2.1 Routine Analyses

Two different, but interrelated parameters were used to characterize the organic fraction of the waste. These two were as follows:

(i) Chemical Oxygen Demand (COD) - Measurement of the oxygen demand concentration of a waste stream.

(ii) Total Organic Carbon (TOC) - Measurement of the organic carbon concentration of a waste stream

Chloride ion concentration was the only inorganic parameter used in the program. This measurement was performed only on pure PCP.

Details of these analytical techniques can be found in Standard Methods for the Examination of Water and Wastewater(2).

5.2.2 Detailed Organic Analysis

The analytical scheme involved the analysis of those compounds that could be partitioned into an organic solvent using batch liquid/liquid extraction (BLLE). The procedure used involves extraction of a suitable aliquant of the aqueous sample with an organic solvent at two different pHs, in order to concentrate these so-called semi-volatile components into acidic and base neutral fractions. Each fraction has its own constraints in analysis by gas chromatography (GC) and GC-mass spectrometry (GC-MS) and are, therefore, analysed separately.

(i) Extraction

The following pure compounds:

(a) Pure DPA
(b) Pure MBT
(c) Pure PCP

and the following waste streams:

(a) Chemical Waste
(b) PCP Waste
(c) DPA Waste
(d) MBT Waste

after Wetox treatment (batch, semi-batch and pilot plant) were received in glass solvent bottles (4L capacity). The BLLE procedure followed is detailed as follows:

A sample aliquant (1 L) was transferred to a clean amber glass bottle (4 L capacity) containing a teflon stirring bar (2") which was used to stir the sample at maximum stable speed. The pH of the solution was adjusted to 11 or greater using sodium hydroxide (6N). Three solvent extractions, each of 40-minute duration, were made using 200 mL, 100 mL and 100 mL of methylene chloride (CH_2Cl_2; redistilled). The solvent was removed after each extraction with the aid of a separatory funnel (2 L capacity). The combined solvent extracts were concentrated on a rotary film evaporator (RFE) to a small volume (≃ 5 mL). The concentrate was transferred to a smaller RB flask (25 mL capacity), at which time it was dried by passage through a small plug of anhydrous sodium sulfate. The dried solution was concentrated by RFE to a small volume (≃ 5 mL) and then transferred to a volumetric flask (10 mL) and made up to the mark with CH_2Cl_2.

The pH of the aqueous phase was next adjusted to 2 or less using hydrochloric acid (6N). The solution was serially extracted with CH_2Cl_2 and the extracts treated as described above. The acidic extracts were all esterified with diazomethane (CH_2N_2; prepared from DIAZALD*) as follows:

The extract was concentrated to incipient dryness and any residue dissolved in methyl alcohol (anhydrous; 1 mL). Excess CH_2N_2/ether was added to the solution and left at room temperature for 20 minutes. The reaction mixture was transferred to Kuderna-Danish apparatus and concentrated to a small volume (1 mL or 0.5 mL).

(ii) Gas Chromatography

Aliquots of the BLLE were taken for gas chomatographic analysis. A Varian Model 3700 gas chromatograph was used with the following GC parameters:

1. Base neutrals:

Column:	0.5 m x 2 mm glass containing 5% OV-101 on Chromosorb G (HP; 100/120 mesh)
Column Temperature:	70°C - 250°C @ 15°C/min
Injector Temperature:	250°C
Detector Temperature:	350°C

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*DIAZALD$^{(T)}$ (N-methyl-N-nitroso-p-toluene sulfonanide) a product of Aldrich Chem. Co. Ltd., Milwaukee, Wisconsin, U.S.A.

Detector:	FID
Flow rates:	$N_2 \approx 25$ mL/min H_2 and Air adjusted for maximum sensitivity

2. Acidics (esterified):

Column:	1.8 m x 2 mm glass containing 30% OV-17 on Chromosorb G (HP; 100/120 mesh)
Column Temperature:	70°C - 320°C @ 8°C/min
Injector Temperature:	350°C
Detector:	FID
Flow rates:	$N_2 \approx 25$ mL/min H_2 and Air adjusted for maximum sensitivity

(iii) Gas Chromatography - Mass Spectrometry (GC-MS)

The GC-MS instrument used was a Hewlett Packard Model 5992 B equipped with a desk top calculator (9825A) with a flexible disk system (9885).

The GC parameters used for the GC-MS analyses were the same as detailed under the GC section.

The identifications made are of a tentative nature in most cases since standard compounds were not available for analysis on the system. Identifications were based on manual interpretation of the mass spectra followed by reference to the Compilation of Mass Spectral Data (and supplements) of A. Cornu and R. Massot(3). Where standards were available for confirmation, positive identification was achieved from the relative retention time in the GC profile and the matching mass spectrum.

6. RESULTS AND DISCUSSION

For the reader's convenience, this section is divided into three separate parts corresponding to the three materials studied:

Pentachlorophenol
Mercaptobenzothiazole
Diphenylamine

6.1 Pentachlorophenol (PCP)

6.1.1 Pure PCP

Ten batch-scale experiments and three semi-batch experiments were performed on reagent grade PCP. It was necessary to add sodium carbonate to promote the solubility of PCP in water.

A summary of the ultimate COD and TOC destruction, effluent COD/TOC ratios, and PCP destruction based on chloride ion generation, for all of the trials is presented in Table 2. From this table, it can be seen that temperature had a marked effect on COD and TOC reduction. This effect, for three temperatures, is tabulated in Table 3 and presented graphically in Figure 1.

Sulfuric acid addition (to a pH = 2) appeared to promote the destruction of COD and TOC of the pure PCP. At a 90-minute residence time, COD and TOC reductions were about 65.6 and 78.6% respectively, compared with reductions of 51.3% and 57.9% without acid addition. The addition of copper, a proven catalyst in wet oxidation, also promoted the oxidation reaction. The effect of these two parameters on the combustion efficiency of pure PCP is presented in Table 4 and in Figure 2.

From Table 2, it can be seen that addition of both copper and sulfuric acid further enhanced the COD and TOC destruction. However, PCP destruction (based on chloride ion generation) in this test was only 54%. Similarly, oxidation of pure PCP at pH $\sim$ 2 without copper liberated only 46% of the available chlorine as chloride ion. In contrast to this result, PCP destruction, as measured by chloride ion generation, in the test on pure PCP with copper only was apparently 99.4%.

Because of these curious differences, detailed organic analyses were performed on two effluent samples. The results of these analyses are presented in Table 5A (Acidic Extraction*) and Table 5B (Basic Extraction*). From Table 5A, it can be seen that 6.5 ppm of PCP was remaining in the Wetox effluent from pure PCP with copper only. Conversely, the effluent from pure PCP with CuO and acid still contained 364 ppm PCP. This corresponds to a PCP destruction of 99.94% and 96.89% for pure PCP/CuO only, and pure PCP/CuO + acid, respectively.

The semi-batch tests indicated much greater reductions in COD and TOC than were achieved during the equivalent batch-scale experiments. This disagrees with the amount of inorganic chloride liberated, which was, in all three semi-batch tests, less than 50%.

Three possible explanations for the apparent difference in destruction efficiencies between batch and semi-batch test results were examined:

(i) Oxygen concentration in the batch reactor was inadequate for completion of reaction. The semi-batch unit, with continuous oxidant flow,would not have this potential oxygen starvation condition.

(ii) Steam strippable or highly volatile compounds were swept out of the semi-batch reactor and not recondensed back in during reaction.

(iii) Sublimation of the PCP (or by-product of it) on the inside walls of the semi-batch autoclave. Because of this reactor's configuration, it is very difficult to observe and clean inside. However, the "open pot" design of the batch reactor makes it accessible for easy cleaning and visual observation.

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*See Section 5.2.2.

Visual observation of the semi-batch autoclave revealed some material adhering to the inside walls. Also, detailed organic analysis in subsequent tests revealed organic chlorine contamination (where none should have been present). Therefore, it was concluded that PCP, or some chlorinated by-product of it, was subliming to the walls of the autoclave.

Detailed organic analyses were performed on semi-batch effluents from the wet oxidation of pure PCP with copper catalyst and pure PCP with copper and acid. The results of these analyses are presented in Tables 5A and 5B.

It can be seen from Table 5A that residual concentrations of 409 ppm PCP and 447 ppm PCP were measured with wet oxidation effluents of pure PCP (CuO) and pure PCP (CuO + Acid) respectively. These represent PCP destruction efficiencies of 97.65% and 97.43%. Because of the previously discussed difficulties associated with the sublimation of the PCP in the semi-batch reactor, these results did not correlate well with the results from the batch tests.

6.1.2 <u>PCP Waste</u>

A summary of the ultimate COD and TOC removals from the eight batch and three semi-batch tests are presented in Table 7.

The effect of temperature on the destruction of COD and TOC of PCP waste is tabulated in Table 8. COD destruction versus time at various temperatures is shown graphically in Figure 3.

Sulfuric acid added to the PCP waste (to pH ∿ 2) appeared to have no effect on the COD and TOC reduction. Copper catalyst, however, increased the COD and TOC removals by about 6%. The effect of these two additives on the combustion efficiency of PCP waste is given in Table 9 and Figure 4.

A detailed organic analysis was carried out on the effluent from the oxidation of PCP waste with copper oxide catalyst. Results of this analysis are given in Tables 5A and 5B.

The initial concentration of PCP in the PCP waste was ∿ 847 ppm. After wet oxidation, the PCP content was 0.6 ppm (see Table 5A). This suggests a PCP destruction of 99.93%.

The results obtained from the semi-batch wet oxidation of PCP waste were comparable, within experimental error, to those obtained during the equivalent batch tests. A detailed organic analysis was performed on the effluent from the oxidation of PCP waste with CuO. These results are presented in Tables 6A and 6B.

The initial PCP concentration in this sample was ∿ 400 ppm. From Table 6A, it is evident that 5.7 ppm of PCP is remaining. This corresponds to a PCP destruction of 98.6%.

Three continuous flow pilot plant tests were undertaken in the unit described in Section 5.1.3.

The three tests were:

(1) PCP Waste, no addition
(2) PCP Waste, + 200 ppm Copper (as $CuSO_4$)
(3) PCP Waste, + Copper + $H_2SO_4 \rightarrow pH = 2$

The performance of a continuous flow system can be predicted from the reaction kinetics obtained from batch-scale testing. A graphical technique, established by R. W. Jones(4), was employed in this program to predict COD and TOC reductions in the 4-10 continuous flow reactor. A more detailed presentation of this method is given in Appendix E.

A comparison of the COD and TOC removals predicted by the Jones method and those actually achieved is tabulated in Table 10 for PCP waste with copper. Figure 5 also gives the COD reduction versus time predicted and achieved.

A detailed organic analysis was performed on the liquid and vapour phase effluents from the continuous flow experiment on PCP waste with copper. Results of this analysis are presented in Tables 11A and 11B. Based on a starting PCP concentration of ∿ 400 ppm, a destruction efficiency of 97.6% of PCP was achieved.

Detailed operating conditions and results of the three waste PCP continuous flow pilot plant tests are given in Appendix E.

6.1.3 Discussion

PCP destruction in the batch Wetox reactor, in the presence of a copper catalyst, was about 99.94%. When contained in an industrial waste stream under equivalent process conditions, PCP destruction was about 99.93%. Sulfuric acid addition (to pH ∿ 2) appeared to reduce the destruction of PCP, and, at the same time, increase the production of other chlorinated organic species.

Results from the semi-batch testing of pure PCP were unreliable because of suspected sublimation of PCP on the walls of the semi-batch autoclave.

Continuous flow and semi-batch testing of PCP waste with copper catalyst resulted in slightly lower destructions of PCP (∿ 97.6% and 98.58% respectively) than were observed during the equivalent batch experiments. In addition, concentrations of other reaction by-products were lower in the batch system.

It can be seen from Table 11A that about one third of the effluent PCP is contained in the vapour phase. This material is not subject to further oxidation. In the batch reactor it is very probable that the PCP in the vapour space would be absorbed back into the liquid phase. In contrast, the dynamic natures of the semi-batch and continuous flow systems may inhibit the absorption of the PCP back into the liquid fraction. It follows, therefore, that the PCP destruction in the batch unit would be slightly greater.

It would be expected, therefore, that decreasing the amount of steam generated would increase the destruction efficiency of PCP. This can be achieved by increasing total reactor pressure. However, due to equipment pressure limitations, it would not be verified in this program.

6.2 Mercaptobenzothiazole (MBT)

6.2.1 Pure MBT

Six batch and two semi-batch tests were performed on reagent grade MBT. A summary of the results from all of these experiments is presented in Table 12. It can be seen from this table that the COD reduction is, in all experiments, greater than the TOC reduction. This suggested that the organic sulfur and nitrogen was oxidized preferentially over the carbon in the compound.

Wet oxidation temperature had a pronounced effect on the achieved destruction of COD and TOC. Results of experiments carried out at 200°, 240° and 265°C are tabulated in Table 13 and presented graphically in Figure 6.

Pure MBT is soluble only in alkaline solutions. Therefore, tests with sulfuric acid addition were not undertaken with this material. Copper catalyst was added, however, and the effect of this catalyst on the results is given in Table 14 and Figure 7.

Detailed organic analyses on the effluent from this test are provided in Tables 15A and 15B. No MBT was detected in this sample following wet oxidation, suggesting, therefore, 100% destruction efficiency of MBT.

The semi-batch test on pure MBT with no addition gave results which were consistent with the batch test results. However, much reduced COD and TOC destructions were observed in the semi-batch experiment with copper catalyst relative to the equivalent batch test. Additional tests were undertaken to verify this anomaly. Evidently, COD and TOC removals were consistent between the batch and semi-batch system for the first fifteen minutes of reaction. However, beyond this point, COD reduction increased by about 20% in the batch system compared with only 2% in the semi-batch reactor.

The only plausible explanation for this discrepancy that can be offered is that oxidation by-products of pure MBT with CuO were more volatile (or steam strippable) than the by-products of pure MBT without CuO. These materials would remain in the vapour space and, thus, not be subject to further oxidation. Due to the dynamic nature of the semi-batch system, this would be more likely to occur than in the batch system.

Results of a detailed organic analysis performed on the effluent from the semi-batch oxidation of pure MBT with CuO is presented in Tables 15A and 15B. It can be seen from Table 15B that MBT was not detected in this sample.

6.2.2 MBT Waste

Eight batch tests were performed on one litre samples of chemical waste to which 1000 ppm reagent grade MBT was added. A summary of all of the results is tabulated in Table 16.

Increasing the temperature from 200°C to 240°C ~~significantly~~ increased the reduction of COD and TOC. Beyond this point, however, temperature had little effect on the reaction. The effect of temperature on the combustion efficiency of MBT waste is presented in Table 17 and Figure 8.

Although copper catalyst had a substantial effect on the destruction of COD and TOC of the pure MBT, it apparently had virtually no effect on the destruction efficiency of COD and TOC in the MBT waste. However, the COD contribution of MBT to the total COD of the waste mixture was only about 30%. Thus, the increased destruction of COD and TOC associated with the addition of copper to pure MBT may be masked by the effect of copper on the wet oxidation of the chemical waste.

Reducing the pH of the MBT waste to two almost doubled the reduction of COD and tripled the reduction of TOC. Because tests were not undertaken on pure MBT with sulfuric acid, the actual effect of acid on the destruction of MBT only could not be ascertained.

The effect of copper catalyst and sulfuric acid on the combustion efficiency is given in Table 18 and presented graphically in Figure 9.

The results of the detailed organic analysis performed on the effluent from the wet oxidation of MBT waste with copper are presented in Tables 15A and 15B. It can be seen from Table 15B that no MBT is detected in this sample. Thus, essentially 100% of the MBT is destroyed in the Wetox process.

Three semi-batch experiments were carried out on MBT waste. The initial COD concentration of the material was greater than that used for the batch experiments. However, the same quantity (1000 ppm) was added to the chemical waste in each reaction. Therefore, the COD contribution of the MBT to the total COD of the MBT waste was lower in the semi-batch unit than the batch unit. This imbalance was taken into account in comparing batch and semi-batch results. With this correction, it was found that the results of the semi-batch tests of MBT waste (no addition) and MBT waste (CuO) correlated well with the equivalent batch experiments.

One test was performed with sulfuric acid in the semi-batch reactor. The COD and TOC removals were substantially lower than those observed during the batch experiments. The acid apparently either increases the volatility of components of the chemical waste or promotes the production of volatile components during the wet oxidation reaction. These volatile (or steam strippable) components were carried into the vapour space for the duration of the reaction, and, therefore, were not subjected to further wet oxidation. Subsequent continuous flow experiments confirmed this explanation. The measured concentration of COD and TOC in the vapour phase was five times greater in the test on acidified waste, than the test undertaken without acid added.

To be consistent with batch testing, a detailed organic analysis was done on MBT waste, semi-batch with CuO catalyst. The results of this analysis is presented in Tables 15A and 15B.

The two continuous flow pilot plant tests which were carried out on MBT waste were:

(i) MBT waste with CuO
(ii) MBT waste with CuO + $H_2SO_4 \rightarrow pH = 2$

A comparison of the COD and TOC reduction predicted from batch kinetics using the Jones Method and those results actually achieved is presented in Table 19 for MBT waste with CuO. A plot of the predicted and achieved COD reduction versus time is given in Figure 10.

A testing of the concentrations of the oxidation by-products contained in both liquid and vapour phase Wetox effluents from this experiment is presented in Tables 20A and 20B. It can be seen from Table 20B that no MBT is detected in either the liquid or vapour phase effluents. It is apparent, however, that significant concentrations of reaction by-products were present in the effluents.

Detailed operating conditions and test results from both of the continuous flow experiments on MBT waste are given in Appendix E.

6.2.3 Discussion

The destruction of MBT in Wetox tests on pure and waste MBT were apparently 100%. Major oxidation by-products of the reaction included aniline, nitrobenzene and azobenzene.

A detailed organic analysis was undertaken on the Wetox effluent from the chemical waste. With the exception of nitrobenzene at 13.7 ppm, all other oxidation products were in relatively low concentrations. Therefore, the oxidation products of MBT waste can essentially be interpreted as being from the wet oxidation of MBT only.

It can be seen from Table 15B and 20B that the concentrations of the major by-products varied widely from test to test. This suggested that a reaction equilibrium between the compounds was never established.

The oxidation of MBT would likely proceed first to aniline and, thereafter, to nitrobenzene. Both of these compounds are steam strippable. Thus, because of the dynamic nature of the semi-batch system, it is likely that the first steam strippable compound produced, aniline, would be carried into the vapour phase. Therefore, the concentration of aniline would likely be less in the semi-batch system than in the batch. By comparison of the GC-MS analysis of the pure MBT for the batch and semi-batch systems, this appears to be the case.

This occurrence is further evident by noting the oxidation by-products present in the vapour phase effluent from the continuous flow system (see Table 20B). As MBT was being oxidized to aniline, it was carried into the vapour space. Because of the short vapour residence time in the reactor, only a small fraction of aniline precipitated back into the liquid state for further oxidation.

The concentration of aniline in the vapour phase would be reduced significantly if the pressure of the reactor system were to be increased. However, because of pressure limitations with the 4-10 Wetox reactor, this could not be undertaken in the program.

6.3 Diphenylamine (DPA)

6.3.1 Pure DPA

A total of eight batch and three semi-batch experiments were carried out on pure DPA. A summary of the test results from these experiments is presented in Table 21.

It can be seen from this table that COD and TOC removals were greater than 72% and 66% respectively, even at the low operating temperature of 200°C. Temperature was increased between 200°C and 265°C and the effect of this increase is presented in Table 22 and in Figure 11.

Copper catalyst increased the reduction of COD and TOC. Sulfuric acid addition, however, provided no improvement in combustion efficiency. The effect of these two additions on the destruction of COD and TOC is tabulated in Table 23 and presented graphically for COD only in Figure 12.

It can be seen from Table 24B that only a trace of DPA was detected in this sample. Therefore, DPA destruction was virtually 100%.

Semi-batch test results of the pure DPA did not correlate well with the results from the equivalent batch tests. In all three semi-batch experiments, COD and TOC reductions were 10-15% greater than those observed during the equivalent batch experiments. Two possible reasons for this discrepancy were:

(i) Experimental or analytical error

(ii) Certain by-products produced during the wet oxidation of DPA inhibited the oxidation (forward) reaction. Due to the dynamic nature of the semi-batch reactor, this compound was carried into the vapour space and not absorbed back into the liquid. Therefore, since the wet oxidation reaction occurs entirely in the liquid phase, this inhibitory compound would not affect the completion of the oxidation reaction.

Results of a detailed organic analysis performed on the effluent from the semi-batch wet oxidation of pure DPA with CuO catalyst is presented in Tables 24A and 24B.

6.3.2 DPA Waste

Eight batch wet oxidation tests were performed on one litre of chemical waste to which 1000 ppm DPA was added. The results from these tests, plus those from three semi-batch experiments, are summarized in Table 25.

Results of the tests on DPA waste correlated well with the results obtained from the MBT waste experiments. This is because the same chemical waste was used as the base to which both compounds of interest were added.

Increasing the reaction temperature from 200°C to 265°C produced only a moderate increase in COD and TOC destruction. Effect of this process parameter on the combustion efficiency of DPA waste is presented in Table 26 and Figure 13.

The addition of copper catalyst did not appear to significantly increase the COD and TOC removal of the DPA waste. Reducing the pH of the mixture to two greatly enhanced the combustion efficiency. However, previous results on pure DPA indicated that COD and TOC removals were not affected by solution pH. It follows, therefore, that the reduction of COD and TOC of the chemical waste fraction of the DPA waste is greatly enhanced at acidic pHs. The effect of copper and sulfuric acid on the combustion of DPA waste is compared in Table 27 and Figure 14.

A detailed organic analysis was undertaken on the effluent from the oxidation of DPA waste with CuO catalyst, the results of which are presented in Tables 24A and 24B. The destruction of DPA contained in the waste stream was evidently 100%.

Semi-batch test results were lower than the equivalent batch test results. However, the COD contribution of pure DPA to the COD of the total mixture in the semi-batch unit was lower than in the batch unit. When this was taken into account, results of the experiments in the two units were comparable.

The semi-batch experiment on DPA waste with both copper catalyst and sulfuric acid was subjected to a detailed organic analysis. Results of this are presented in Tables 24A and 24B.

One continuous flow test was performed on DPA waste with CuO and one on DPA waste with CuO + acid. Predicted and achieved continuous flow performance is presented in Table 28 and Figure 15 for DPA waste with copper. Both liquid and vapour phase effluent from this test were subjected to a detailed organic analysis. The results of these analyses are presented in Tables 29A and 29B.

Detailed operating conditions and results from the two pilot plant tests are given in Appendix E.

6.3.3 Discussion

The destruction of pure DPA was essentially 100% in both batch and semi-batch wet oxidation experiments.

Results from batch and semi-batch Wetox tests on DPA waste also indicate virtually 100% DPA destruction. In the continuous flow test on DPA waste, approximately 0.24% of the initial DPA was contained in the vapour phase effluent while no DPA was detected in the liquid phase effluent. This concentration, therefore, indicates 99.94% destruction of the DPA.

The major oxidation by-products from the wet oxidation of DPA appeared to be aniline, nitrobenzene and azobenzene. These were the same compounds evident in the wet oxidation effluent of MBT.

As indicated previously, nitrobenzene was the only significant residual compound remaining from the wet oxidation of the chemical waste. Therefore, by-products of waste DPA can be assumed to be essentially all derived from the oxidation of DPA alone.

Detailed organic analysis was performed on the effluent from the semi-batch wet oxidation of DPA waste with both copper and sulfuric acid. The remainder of the detailed analyses were undertaken on experiments without sulfuric acid. It can be seen from Table 24B that reducing the pH to two greatly enhanced the destruction of residual aniline and nitrobenzene.

A detailed organic analysis was undertaken on the continuous flow experiments of DPA with CuO only. Therefore, it is unknown what effect the sulfuric acid addition would have on the destruction of residual aniline and nitrobenzene in this unit. In addition to pH adjustment, the effect of increasing the 4-10 reactor pressure on the destruction of these materials was not assessed in the program. It would be expected, however, that increasing total reactor pressure would result in improved process performance.

7. CONCLUSIONS AND RECOMMENDATIONS

It was apparent from the results of the program that the Wetox Process would provide a means for effective destruction of the materials investigated. It was also found that the destruction of a compound of interest in a particular industrial waste stream could be assessed on the basis of that compound by itself.

The destruction of pentachlorophenol was greater than 99.9%, and only trace concentrations of other chlorinated materials were observed in the wet oxidation effluent.

The wet oxidation of both mercaptobenzothiazole and diphenylamine resulted in virtually 100% compound destruction. However, steam strippable compounds were generated (aniline and nitrobenzene) which were carried into the vapour space above the aqueous phase in the reactor. The temperatures and pressures at which wet oxidation is conducted are insufficient to achieve effective vapour phase oxidation. Operation of the wet oxidation reactor at higher pressures minimizes the steam production and is a possible solution to the problem of steam stripping. Other approaches include catalytic oxidation of the vapour phase or post treatment of the condensed vapour phase.

Previous work has utilized the destruction of chemical oxygen demand (COD) as a parameter to assess the effectiveness of the Wetox process. Typically, destruction efficiencies of 75-95% have been measured. The detailed analytical results from this study have shown that, while similar efficiencies have been recorded based on COD, the destruction efficiency of compounds considered hazardous or toxic was virtually complete. The study has also shown that only trace quantities of hazardous breakdown products were generated during the reaction.

One of the objectives of the program was to establish the major breakdown products from selected chlorine, sulfur and nitrogen containing organic materials and from that postulate in more general terms what might be expected from the destruction of similar compounds.

No sulfur, and only very small concentrations of chlorine were detected in an organic form as a breakdown product from the oxidation of, respectively, mercaptobenzothiazole or pentachlorophenol. This leads to the conclusion that these elements are present in the effluent as inorganic chloride and sulfate ions. As has been previously discussed, nitrogen was detected as aniline and nitrobenzene in the effluent from the wet oxidation process, but it was postulated that this is as a result of steam stripping of these compounds prior to their complete oxidation. The proportion of nitrogen appearing as nitrobenzene and aniline compared with the original organic nitrogen in diphenylamine and mercaptobenzothiazole was about 0.01% to < 2%. Previous work with wet oxidation of materials containing organic nitrogen compounds or cyanides has shown that much of the nitrogen is converted to ammonia and it is suggested that the remainder of the nitrogen from DPA and MBT is present in the effluent in this form.

The low concentrations of organic chlorine, sulfur and nitrogen containing materials in the effluent from the wet oxidation process compared to the relatively high concentration of residual TOC, suggests that the wet oxidation of carbon/chloride, carbon/sulfur and carbon/nitrogen bonds is more effective than the wet oxidation of carbon/carbon bonds. Oxidation of carbon/carbon bonds becomes increasingly difficult as the size of the molecule is reduced and also if it becomes partially oxidized. One of the major by-products of wet air oxidation is acetic acid, CH_3COOH.

Comparison of the destruction efficiencies for PCP, MBT and DPA in pure form and as part of a waste stream suggests that the behaviour of the compounds under wet oxidation conditions can be properly predicted by the simpler experiments using pure compounds in water. None of the experiments using waste mixtures suggested any antagonistic or synergistic effects.

Because the results of this preliminary program indicated that the Wetox process was extremely successful in destroying hazardous chemicals contained in wastewater streams, it is recommended that a follow-up project be supported. Some of the tasks which should be considered by such a program should include:

- Establish more precise reaction kinetics for the destruction of pure hazardous compounds, and the production of by-products.
- Complete a more precise mass balance particularly for chlorine, nitrogen and sulfur.
- Extend the investigation to other pure compounds to confirm that similar results are obtained.
- Investigate methods to improve the oxidation of steam strippable breakdown products such as nitrobenzene and aniline. This may be accomplished through increased reactor pressure or through vapour phase catalytic oxidation of these by-products.
- Investigate the efficacy of post treatment methods for the residual COD in the Wetox effluent. These might include biological oxidation, carbon adsorption, etc.
- Apply all of the information gained to the investigation of a specific hazardous waste containing stream (to be identified by Environment Canada). This investigation would include confirmatory oxidation tests, mass and energy balance, design, integration of the process into the plant producing the waste and an economic feasibility study.

REFERENCES

1. Public Hearings on Hazardous Waste Management in Alberta - Report and Recommendations p 37, Environment Council of Alberta, Edmonton, Alberta, December, 1980.

2. Standard Methods for the Examination of Water and Wastewater, 14th ed. 1975, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, D.C.

3. Compilation of Mass Spectral Data (Incl. Supplements), A. Cornu and R. Massot, Heyden & Son Ltd. (1966).

4. Jones, R. W., A General Graphical Analysis of Continuous Reactions in a Series of Agitated Vessels, Chemical Engineering Progress, Vol. 47, p 46 (1951).

TABLE 1 - Wet Oxidation of Specific Chemicals

Compound	Destruction Efficiency %
Phenol	99.9
Pentachlorphenol	99.99
Thiocyanate	99
Cyanides	98.8 - > 99.99
DDT	> 98

Source: Internal ORF investigations

TABLE 2 - Pure PCP - Summary of Batch & Semi-Batch Test Results

Run #	Mode	Residence Time (minutes)	Temp/Press. (°C/psi)	Additions	COD Red'n. (%)	TOC Red'n. (%)	Effluent COD/TOC*	PCP Destruction Based on Cl^- Generation (%)
1	Batch	90	200/400	None	48.0	47.4	2.1	94
2	Batch	90	220/500	None	51.3	48.2	2.0	96
3	Batch	90	240/650	None	51.3	57.9	2.3	96
4	Batch	90	250/700	None	78.2	78.9	2.2	-
5	Batch	90	265/950	None	83.6	88.6	3.0	93.5
6	Batch	90	280/1300	None	80.0	84.0	2.7	-
7**	Batch	90	240/650	250 ppm CuO	68.1	72.8	2.5	99.4
8	Batch	90	240/650	$H_2SO_4 \rightarrow pH = 2$	65.6	78.6	3.4	46
9**	Batch	90	240/650	$CuO + H_2SO_4$	77.3	86	3.4	54
10	Batch	90	240/650	2.5% NaOH	47.3	-	-	97
11	Semi-Batch	60	240/625	None	72.0	81.1	3.1	-
12**	Semi-Batch	60	240/625	250 ppm CuO	75.5	-	3.7	46
13**	Semi-Batch	60	240/625	$CuO + H_2SO_4$	92.3	95.9	3.9	38

Sodium Carbonate added to promote solubility
*Feed COD/TOC = 2.1
**Detailed organic analysis performed on this sample

TABLE 3 - Pure PCP - Effect of Temperature on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 200°C, 400 psi		Batch Test - 240°C, 650 psi		Batch Test - 265°C, 950 psi	
	COD	TOC	COD	TOC	COD	TOC
5	-	16.8	9.6	15.8	65.4	65.8
15	25.0	29.8	21.2	33.3	69.2	71.9
30	28.8	40.4	32.7	40.4	76.9	82.4
60	40.4	45.6	42.3	41.2	80.8	86.8
90	40.4	47.4	44.2	48.2	81.2	88.6

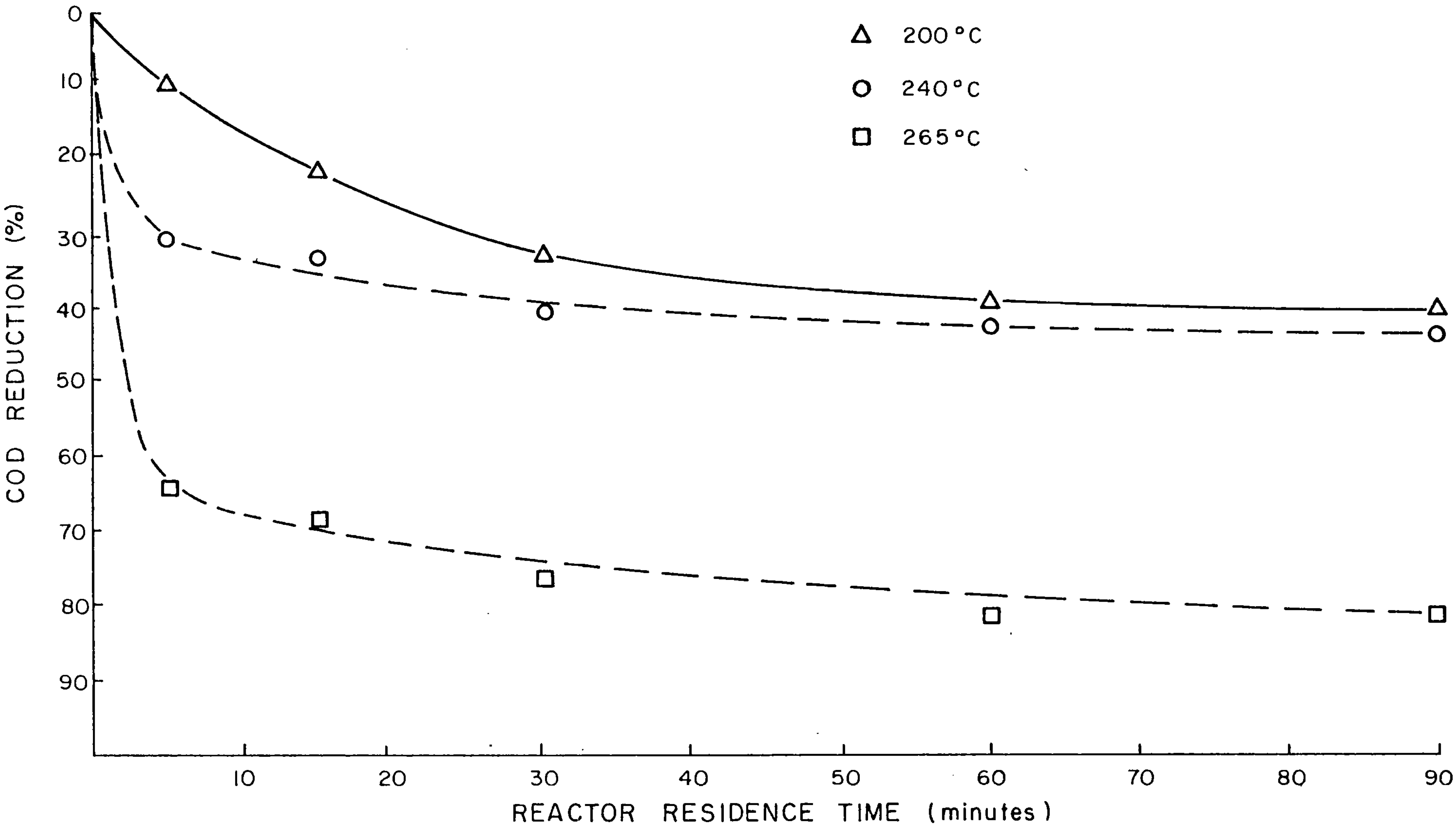


FIGURE I. PURE PCP - EFFECT OF TEMPERATURE ON COMBUSTION EFFICIENCY

TABLE 4 - Pure PCP - Effect of H_2SO_4 and CuO on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 240°C, 650 psi		Batch Test - 240°C, 650 psi, 250 ppm CuO		Batch Test - 240°C, 650 psi, $H_2SO_4 \rightarrow pH = 2$	
	COD	TOC	COD	TOC	COD	TOC
5	9.6	15.8	34.6	42.1	57.2	52.1
15	21.2	33.3	46.2	50.9	59.7	64.9
30	32.7	40.4	53.8	59.6	62.0	57.9
60	42.3	41.2	59.6	68.4	61.4	81.6
90	44.2	48.2	63.5	72.8	65.6	78.6

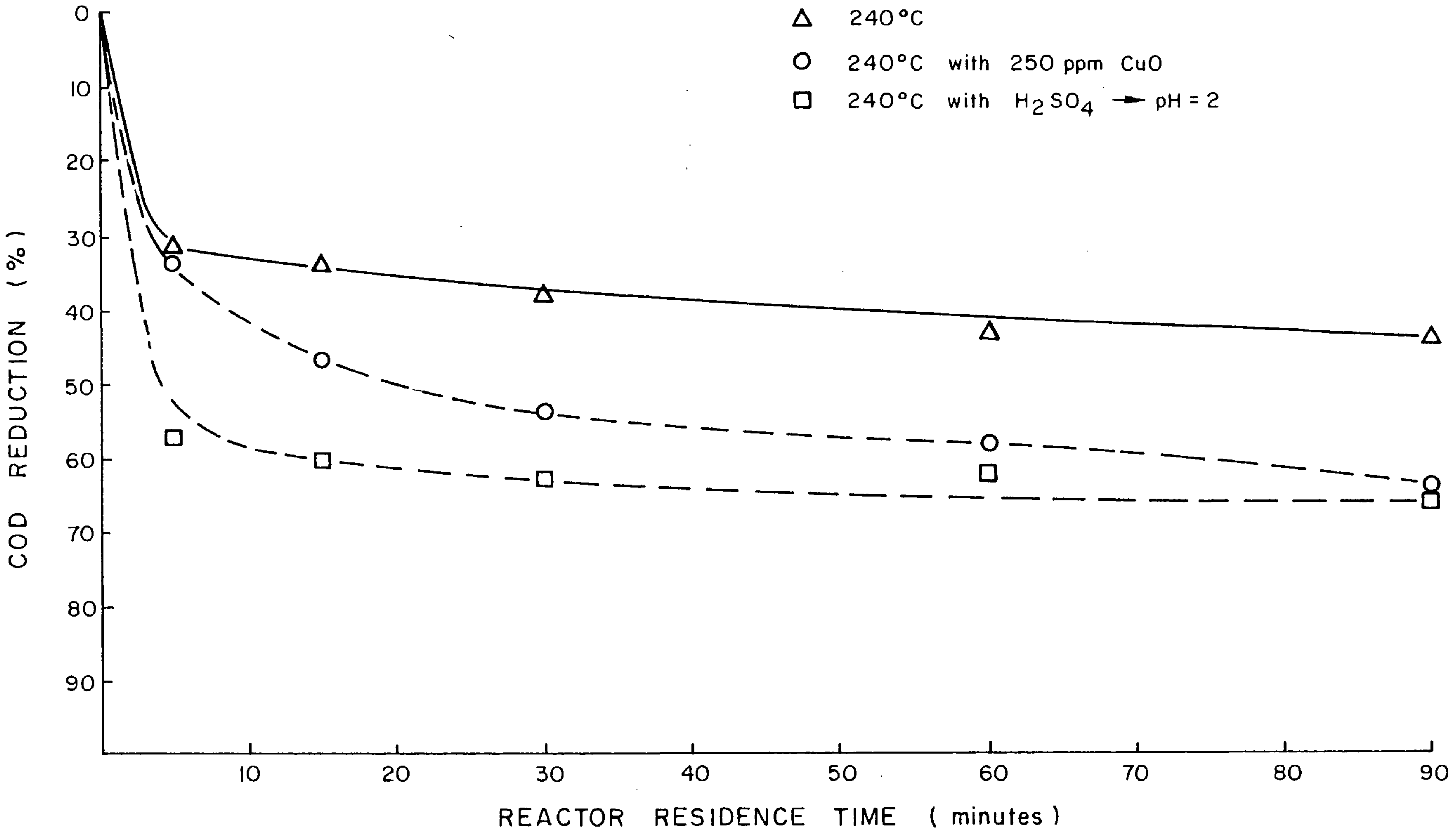


FIGURE 2. PURE PCP · EFFECT OF H_2SO_4 & CuO ON COMBUSTION EFFICIENCY.

TABLE 5A - Batch Experiments (Acidic Fractions)

Pentachlorophenol

Tentative Compound Identification	$[M]^+$	Pure PCP CuO	Pure PCP CuO/H_2SO_4	PCP Waste
Benzoic Acid	136	0.24*	0.49	0.52
Alkyl homologs				
C_1-	150	x	-	x
C_2-	164	x	-	x
C_3-	178	x	-	x
C_4-	192	x	-	x
C_5-	206	-	-	x
C_6-	220	-	-	x
Chloro-	170	-	-	x
Methyl chloro-	184	-	-	x
Salicylic acid	152	0.33++	-	0.75
C_3-	194	x	-	x
Hydroxybenzyl alcohol	166	-	-	x
"	194	-	-	x
"	208	-	-	x
Tetrachlorophenol	244	1.9		-
Pentachlorophenol	278	6.5**	364	0.6
Chlorinated (3)	278)			
Chlorinated (4)	312)	x	63.4	-
Chlorinated (4)	326)			

*Values in mg/L calculated from standard benzoic acid (GC-FID)
++Values in mg/L calculated from standard salicylic acid (GC-FID)
**Values in mg/L calculated from standard PCP (GC-FID)
- - Not present by visual inspection of GC-MS profiles
x - Less than 0.5 mg/L (abundances in GC-MS profiles)

TABLE 5B- Batch Experiments (Basic Fractions)

Pentachlorophenol

Tentative Compound Identification	$[M]^+$	Pure PCP CuO	Pure PCP CuO/H_2SO_4	PCP Waste
Benzaldehyde	106	x	-	x
C_1-	120	x	-	x
C_2-	134	x	-	x
C_3-	148	x	-	x
C_4-	162	-	-	x
Dichloro-	174	x	-	x
Phthalide	134	x	-	x
-	156	x	-	-
-	170	x	-	-
Trichlorobenzene	180	x	-	
Tetrachlorobenzene	214	x	x	x
Pentachlorobenzene	248	x	0.26*	x
Hexachlorobenzene	282	x	0.34*	-
Tetrachlorotoluene	228	x	-	-
Pentachlorotoluene	262	x	-	-
Tetrachlorophenol	230	x	0.20*	-
Pentachlorophenol	264	x	-	-
Chlorinated (3)	220	0.2*	-	-
Chlorinated (4)	254	x	-	-
Chlorinated (5)	263	-	-	-
Hydrocarbons (alkanes)	184	-	-	x
	198	-	-	x
	212	-	-	x
	226	-	-	x
	240	-	-	x
	254	-	-	x
	268	-	-	x
	282	-	-	x

*Values in mg/L calculated from standard pentachlorobenzene (GC-MS)
x - indicates less than 0.5 mg/L (abundances in GC-MS profiles)
- - not present by visual inspection of GC-MS profiles

TABLE 6A - Semi-Batch Experiments (Acidic Fractions)

Pentachlorophenol

Tentative Compound Identification	$[M]^+$	Pure PCP CuO	Pure PCP CuO/H_2SO_4	PCP Waste
Benzoic Acid	136	0.9*	0.8	1.76
Alkyl homologs				
C_1-	150	-	-	x
C_2-	164	-	-	x
C_3-	178	-	-	x
C_4-	192	-	-	x
C_5-	206	-	-	-
C_6-	220	-	-	-
Chloro-	170	-	-	x
Methyl chloro-	184	-	-	x
Salicylic Acid	152	-	-	1.24++
C_3-	194	-	-	
Hydrocybenzyl Alcohol	166	-	-	
"	194	-	-	
"	208	-	-	
Tetrachlorophenol	244			
Pentachlorophenol	278	409**	447	5.7
Chlorinated (3)	278)			
Chlorinated (4)	312)	12.6	5.9	x
Chlorinated (4)	326)			

*Values in mg/L calculated from standard benzoic acid (GC-FID)

++Values in mg/L calculated from standard salicylic acid (GC-FID)

**Values in mg/L calculated from standard PCP (GC-FID)

- - not present by visual inspection of GC-MS profiles

x - less than 1 mg/L (abundances in GC-MS profiles)

TABLE 6B - Semi-Batch Experiments (Basic Fractions)

Pentachlorophenol

Tentative Compound Identification	$[M]^+$	Pure PCP CuO	Pure PCP CuO/H_2SO_4	PCP Waste
Benzaldehyde	106	-	-	x
C_1-	120	-	-	x
C_2-	134	-	-	-
C_3-	148	-	-	-
C_4-	162	-	-	-
DichloroO	174	-	-	-
Phthalide	134	-	-	-
-	156	-	-	-
-	170	-	-	-
Tetrachlorobenzene	214	x	x	-
Pentachlorobenzene	248	0.12*	0.11*	
Hexachlorobenzene	282	0.16*	0.13*	
Tetrachlorophenol	230	-	-	
Pentachlorophenol	264	0.19*	x	x
Hydrocarbons (alkanes)	184			
	↓	-	-	x
	282			
Octyl phthalate	m/e 149	-	-	x

*Values in mg/L calculated from standard pentachlorobenzene (GC-MS)
x - Less than 0.1 mg/L (abundances in GC-MS profiles)
- - Not present by visual inspection of GC-MS profiles

TABLE 7 - PCP Waste - Summary of Batch & Semi-Batch Test Results

Run #	Mode	Residence Time (minutes)	Temp/Press. (°C/psi)	Additions	COD Red'n. (%)	TOC Red'n. (%)	Effluent COD/TOC*
1	Batch	90	200/400	None	69.0	53.0	2.8
2	Batch	90	240/650	None	73.3	59.3	2.9
3	Batch	90	250/750	None	73.3	60.0	2.9
4	Batch	90	265/950	None	79.6	65.8	2.6
5	Batch	90	280/1300	None	85.0	76.0	2.6
6**	Batch	90	240/650	25o ppm CuO	77.9	67.9	3.0
7	Batch	90	240/650	H_2SO_4 → pH = 2	70.0	54.2	2.9
8	Batch	90	240/650	CuO + H_2SO_4	76.7	67.6	3.1
9	Semi-Batch	60	240/625	None	70.0	48.9	2.5
10**	Semi-Batch	60	240/625	250 ppm CuO	67.9	44.0	2.5
11	Semi-Batch	60	240/625	CuO + H_2SO_4	74.9	61.1	2.8

*Feed COD/TOC = 4.3
**Detailed organic analysis performed on this sample

TABLE 8 - PCP Waste - Effect of Temperature on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 200°C, 400 psi		Batch Test - 240°C, 650 psi		Batch Test - 265°C, 950 psi	
	COD	TOC	COD	TOC	COD	TOC
5	31.0	5.0	29.2	11.2	62.9	45.5
15	41.0	15.0	51.7	32.3	70.0	54.2
30	54.0	27.0	60.0	40.4	73.3	57.8
60	58.0	33.3	58.3	44.0	77.5	63.6
90	69.2	53.0	73.3	59.3	79.6	65.8

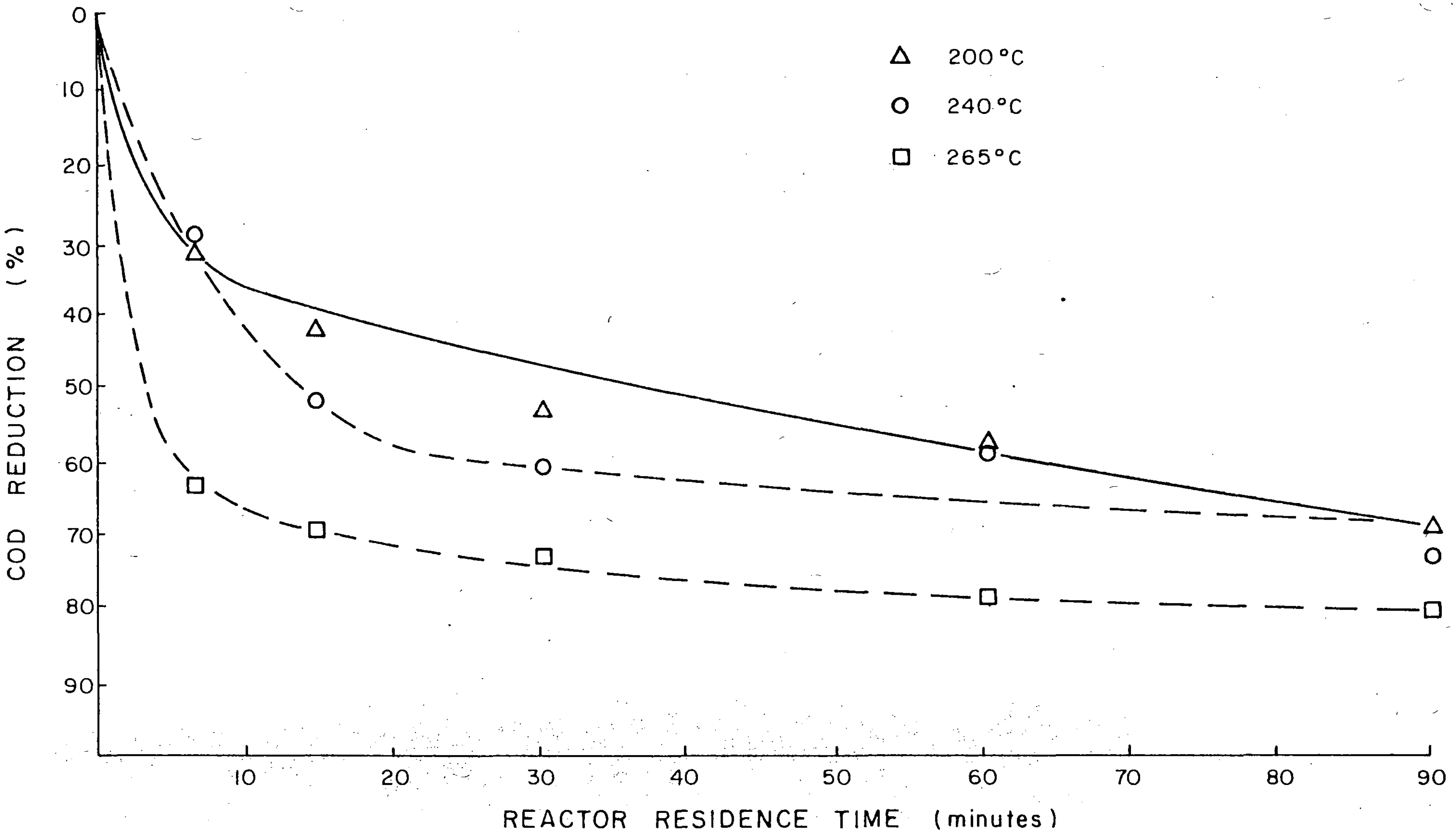


FIGURE 3 : PCP WASTE - EFFECT OF TEMPERATURE ON COMBUSTION EFFICIENCY.

TABLE 9 - PCP Waste - Effect of H_2SO_4 & CuO on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 240°C, 650 psi		Batch Test - 240°C, 650 psi, 250 ppm CuO		Batch Test - 240°C, 650 psi, $H_2SO_4 \rightarrow pH = 2$	
	COD	TOC	COD	TOC	COD	TOC
5	29.2	11.2	61.2	44.0	63.3	42.5
15	51.7	32.3	63.8	48.4	64.2	44.0
30	60.0	40.4	70.8	60.0	63.7	44.7
60	58.3	44.0	74.2	55.6	66.7	51.3
90	73.3	59.3	77.9	67.6	70.0	54.2

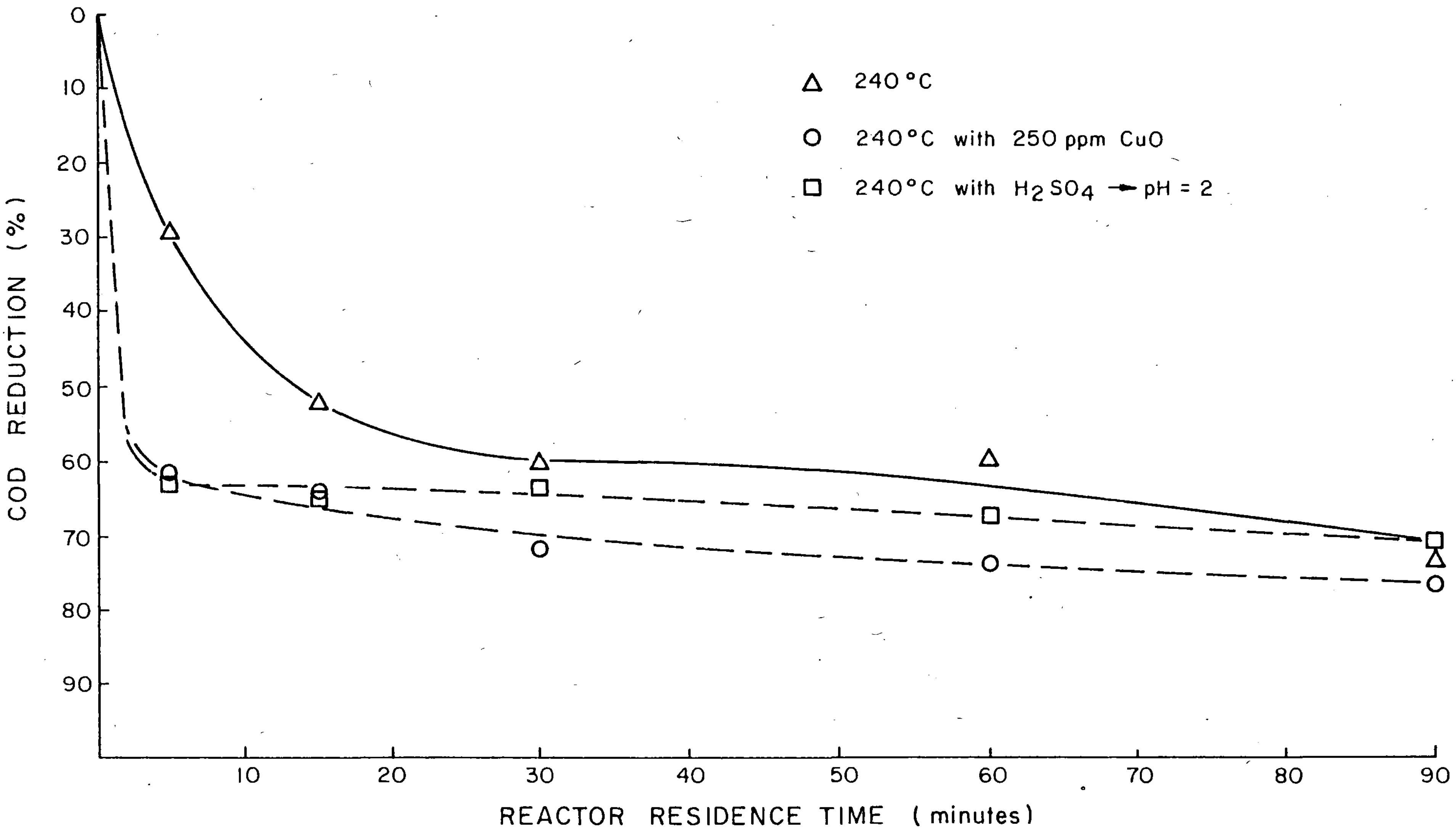


FIGURE 4. PCP WASTE - EFFECT OF H_2SO_4 & CuO ON COMBUSTION EFFICIENCY.

TABLE 10 - PCP Waste - Pilot Plant Test Results (with Copper)

Reactor Residence Time (minutes)	Percent Reduction			
	Predicted from Jones Plot		Achieved Results	
	COD	TOC	COD	TOC
20	66.7	-	77.9	50.7
33	70.0	-	80.0	58.2
46	71.7	-	81.0	60.0
60	73.3	-	81.0	71.3

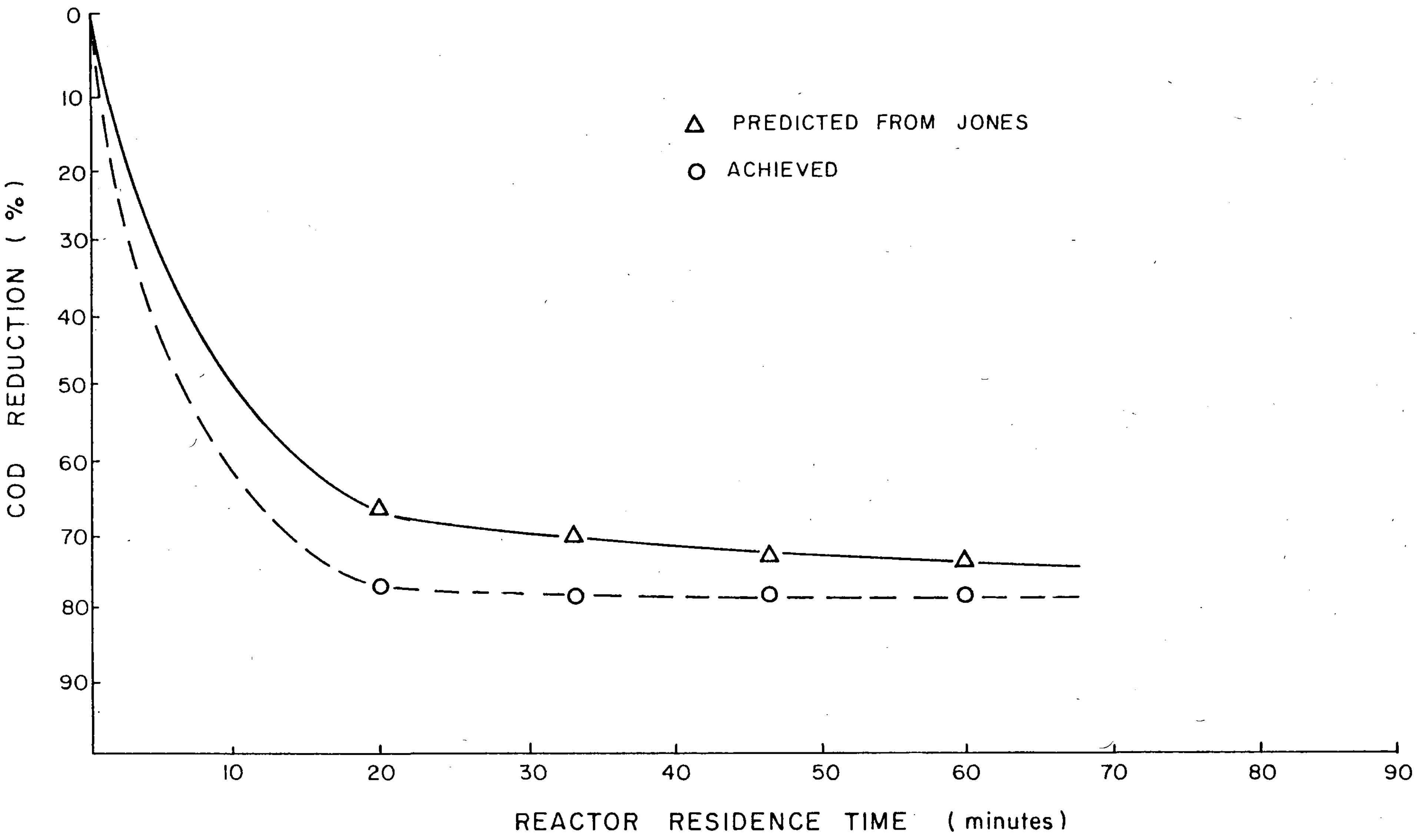


FIGURE 5. PCP WASTE - PILOT PLANT TEST RESULTS (WITH COPPER)

TABLE 11A- Pilot Plant Experiments (Acidic Fractions)

Pentachlorophenol

Tentative Compound Identification	$[M]^+$	Vapour Phase Concentrate	Liquid Phase Effluent
Benzoic Acid	136	0.5*	1.8
Alkyl Promologs			
C_1-	150	x	x
C_2-	164	-	x
C_3-	178	-	-
C_4-	192	-	x
C_5-	206	-	-
C_6-	220	-	-
Chloro-	170	0.3*	4.2
Methyl Chloro-	184	-	x
Dimethyl Chloro-	198	-	x
Hydroxybenzyl alcohol	166	-	-
"	194	-	-
"	208	-	-
Trichlorophenol	210	x	
Tetrachlorophenol	244	x	x
Pentachlorophenol	278	4.6**	9.8
Chlorinated	278)		
Chlorinated	312)	x	x
Chlorinated	326)		
Hydrocarbons (alkanes)	186 ↓ 324		
Octyl phthalate			x

*Values in mg/L calculated from standard benzoic acid (GC-FID)
**Values in mg/L calculated from standard PCP (GC-FID)
x - Less than 0.2 mg/L (abundances in GC-MS profiles)
- - Not present by visual inspection of GC-MS profiles

TABLE 11B - Pilot Plant Experiments (Basic Fractions)

Pentachlorophenol

Tentative Compound Identification	$[M]^+$	Vapour Phase Concentrate	Liquid Phase Effluent
Pyridine	79	1.3*	x
Methyl-pyridine	93	x	x
Chloro-pyridine	113	x	x
Aldehydo-pyridine	107	x	x
Benzonitrile	103	x	x
Benzaldehyde	106	1.3++	x
C_1-	120	1.8++	x
C_2-	134	x	x
C_3-	148	-	x
Phthalide	134	x	x
Hydrocybenzaldehyde	122	x	x
Tetrachlorobenzene	214	-**	x**
Pentachlorobenzene	248	-**	x**
Pentachlorophenol	264	x**	x**
Hydrocarbons (alkanes)	184	x	x
	↓	x	x
	282	x	x

* Values in mg/L calculated from standard pyridine (GC-FID)
++Values in mg/L calculated from standard benzaldehyde (GC-FID)
x - Indicates less than 0.5 mg/L (abundances in GC-MS profiles)
\- - Not present by visual inspection of GC-MS profiles
**Visual inspection of GC-MS profiles indicates chlorinated compounds are present in trace amounts < 0.1 ppm

TABLE 12 - Pure MBT - Summary of Batch & Semi-Batch Test Results

Run #	Mode	Residence Time (minutes)	Temp/Press. (°C/psi)	Additions	COD Red'n. (%)	TOC Red'n. (%)	Effluent COD/TOC*
1	Batch	90	200/400	None	46.0	22.2	2.5
2	Batch	90	220/500	None	51.6	35.7	2.7
3	Batch	90	240/650	None	64.8	44.3	2.3
4	Batch	90	250/750	None	69.8	52.6	2.3
5	Batch	90	265/950	None	74.8	62.3	2.4
6**	Batch	90	240/650	250 ppm CuO	78.0	54.8	2.0
7	Semi-Batch	60	240/625	None	58.3	48.2	2.9
8**	Semi-Batch	60	240/625	250 ppm CuO	60.0	40.5	2.7

NaOH Added to promote solubility
*Feed COD/TOC ≃ 3.6
**Detailed organic analysis performed on this sample

TABLE 13 - Pure MBT - Effect of Temperature on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 200°C, 650 psi		Batch Test - 240°C, 650 psi		Batch Test - 265°C, 650 psi	
	COD	TOC	COD	TOC	COD	TOC
5	31.0	9.0	37.0	21.1	56.7	46.3
15	37.0	16.0	49.2	28.6	66.0	52.1
30	37.0	18.0	56.3	36.0	69.0	58.6
60	42.0	20.0	62.2	38.3	74.0	62.3
90	46.0	22.2	64.8	44.3	74.8	62.3

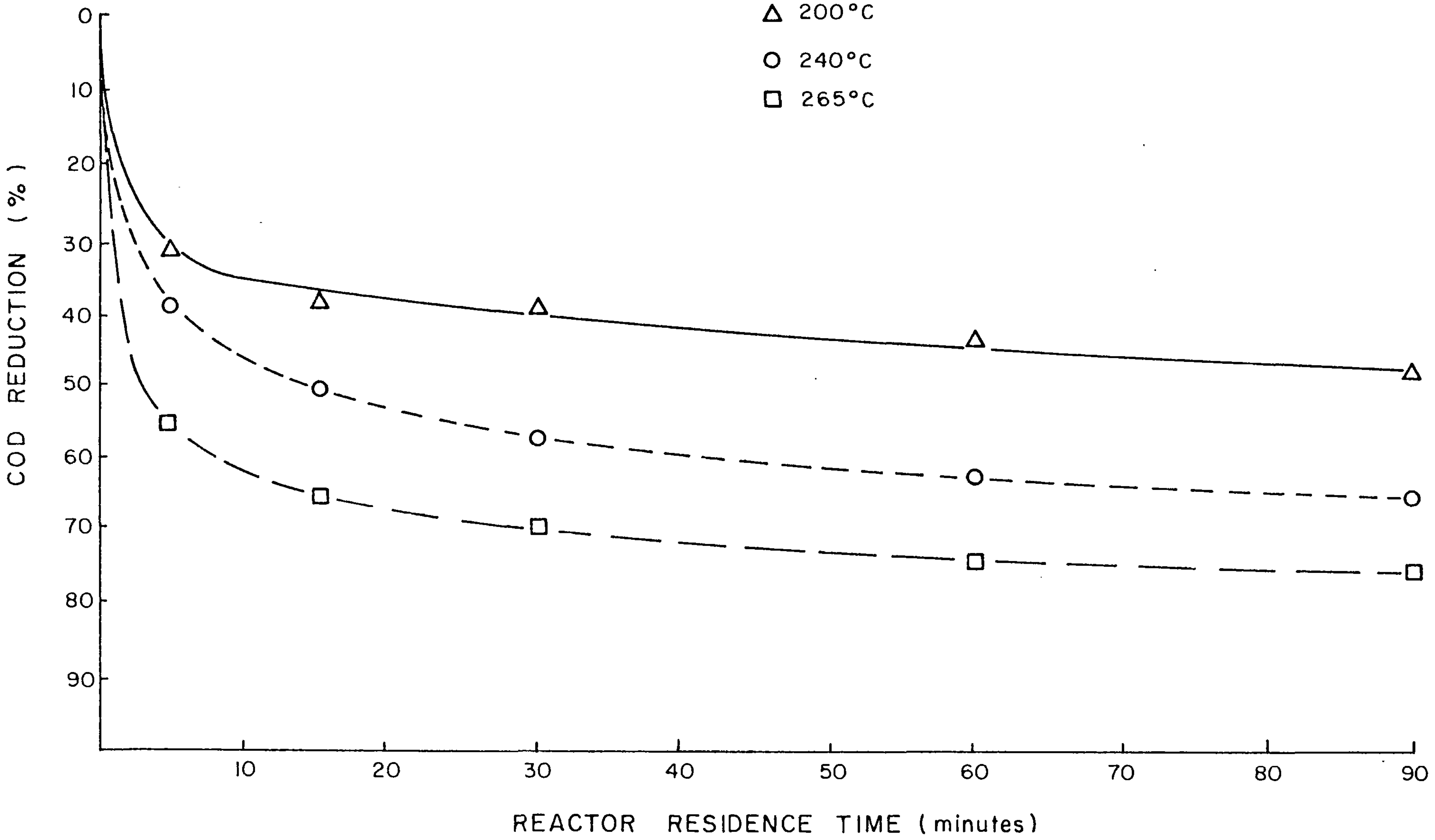


FIGURE 6. PURE MBT - EFFECT OF TEMPERATURE ON COMBUSTION EFFICIENCY.

TABLE 14 - Pure MBT - Effect of CuO on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction			
	Batch Test - 240°C, 650 psi		Batch Test - 240°C, 650 psi, 250 ppm CuO	
	COD	TOC	COD	TOC
5	37.0	21.1	51.7	47.7
15	49.2	28.6	61.1	36.6
30	56.3	36.0	69.8	45.6
60	62.2	38.3	75.0	54.9
90	64.8	44.3	78.0	58.0

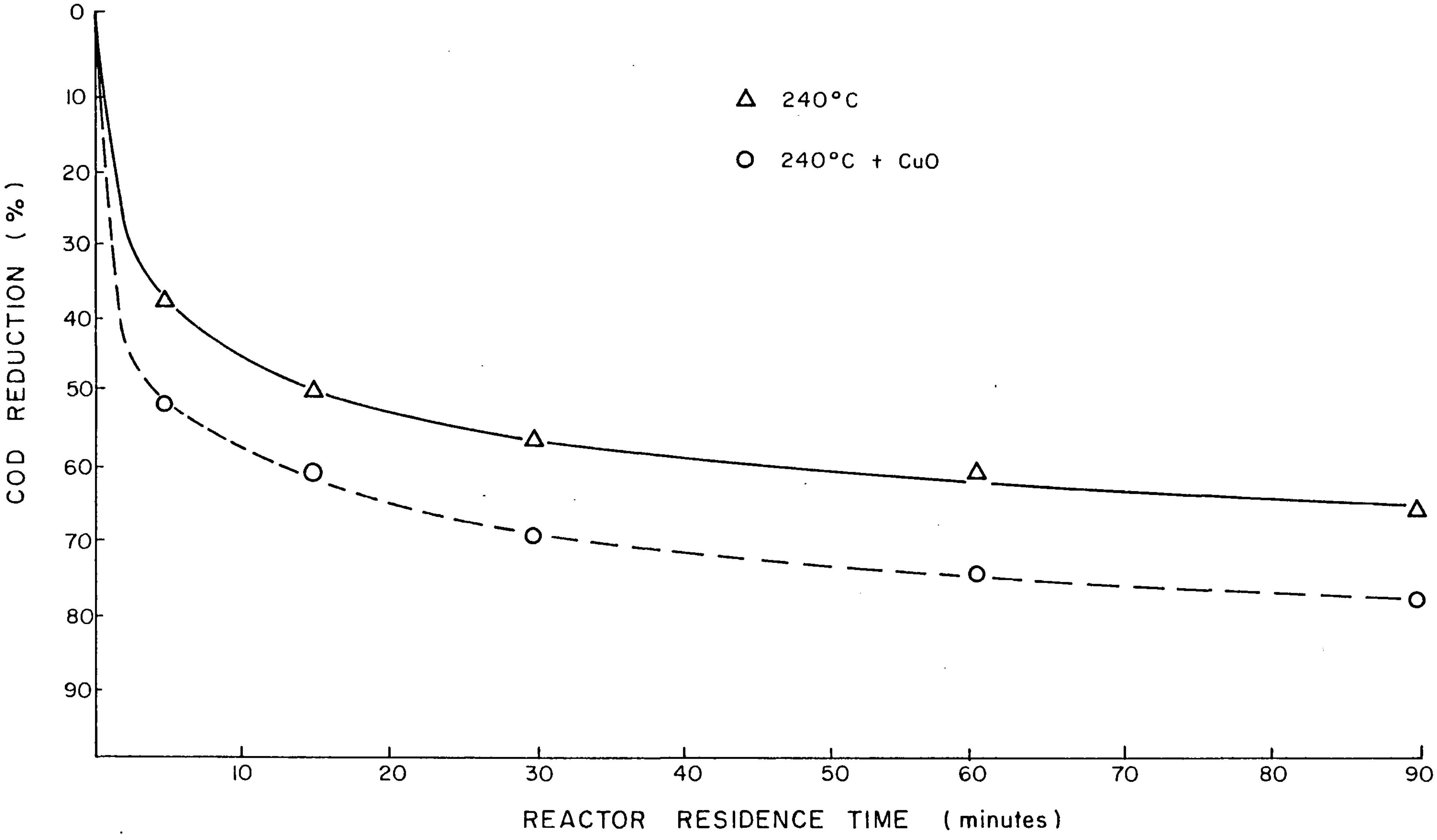


FIGURE 7. PURE MBT - EFFECT OF CuO ON COMBUSTION EFFICIENCY.

TABLE 15A - Batch & Semi-Batch Experiments (Acidic Fraction) - Mercaptobenzothiazole

Tentative Compound Identification	$[M]^+$	Pure MBT Batch	Pure MBT Semi-Batch	MBT Waste Batch	MBT Waste Semi-Batch
$(CH_3S)_2$	94	-	-	x	-
Methyl benzoate	136	0.3*	0.4	x	-
CH_3^-	150	x	-	-	-
$C_2H_5^-$	164	-	-	x	-
$C_4H_{11}^-$	192	-	-	-	-
Methyl salicylate	152	x	x	-	-
Methoxy nitrobenzene	153	x	-	-	-
Nitro-benzoate	181	x	-	-	-
Azobenzene-methyl carbocylate	240	x	-	x	-
-	202	x	-	x	-
-	238	-	-	-	-
-	258	-	-	-	-
-	129	x	x	x	-
-	229	-	-	-	-
-	136/ 135	-	-	-	-
-	166	-	-	-	-

*Concentration in mg/L calculated from GC-FID using a pure methyl benzoate standard

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- - not observed in GC-MS data

TABLE 15B - Batch & Semi-Batch Experiments
(Basic Fraction) - Mercaptobenzothiazole

Tentative Compound Identification	$[M]^+$	Pure MBT Batch	Pure MBT Semi-Batch	MBT Waste Batch	MBT Waste Semi-Batch
Aniline	93	x	6.3*	3.7	8.7
Nitrobenzene	123	30.0	<0.2	7.8	14.0
Azobenzene	182	5.4	0.4	2.3	-
-	180	3.3	3.8	2.0	2.5
Azoxybenzene	198	1.7	0.3	2.0	-
Dimethylazobenzene	210	-	0.3	-	1.3
Isoquinoline	129	x	-	-	1.0
-	121	-	-	-	2.8
-	171	-	10.7	1.8	-
-	194	-	-	-	2.1
Mercaptobenzothiazole	167	-	-	-	-

*Concentration in mg/L calculated from GC-FID using a pure anilene standard

- - Not observed in GC-MS data

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

TABLE 16 - MBT Waste - Summary of Batch & Semi-Batch Test Results

Run #	Mode	Residence Time (minutes)	Temp/Press. (°C/psi)	Additions	COD Red'n. (%)	TOC Red'n. (%)	Effluent COD/TOC*
1	Batch	90	200/400	None	33.2	12.0	2.5
2	Batch	90	220/500	None	40.5	27.7	2.7
3	Batch	90	240/650	None	47.8	29.5	2.4
4	Batch	90	250/750	None	53.8	37.7	2.4
5	Batch	90	265/950	None	51.0	29.8	2.3
6**	Batch	90	240/650	250 ppm CuO	49.3	35.8	2.6
7	Batch	90	240/650	H_2SO_4 → pH = 2	86.5	82.2	2.5
8	Batch	90	240/650	CuO + H_2SO_4	88.0	86.0	2.8
9	Semi-Batch	60	240/625	None	42.2	42.2	2.7
10**	Semi-Batch	60	240/625	250 ppm CuO	42.0	25.0	2.4
11	Semi-Batch	60	240/625	H_2SO_4 → pH = 2	63.3	54.5	2.5

*Feed COD/TOC = 3.3

**Detailed organic analysis performed on this sample

TABLE 17 - MBT Waste - Effect of Temperature on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 200°C, 400 psi		Batch Test - 240°C, 650 psi		Batch Test - 265°C, 950 psi	
	COD	TOC	COD	TOC	COD	TOC
5	18.9	5.0	37.2	9.6	37.9	11.1
15	26.5	8.0	39.0	16.0	43.5	21.7
30	27.1	11.0	44.5	24.1	46.1	25.9
60	30.0	11.4	44.5	27.0	47.0	25.9
90	33.2	12.0	47.8	29.5	51.0	29.8

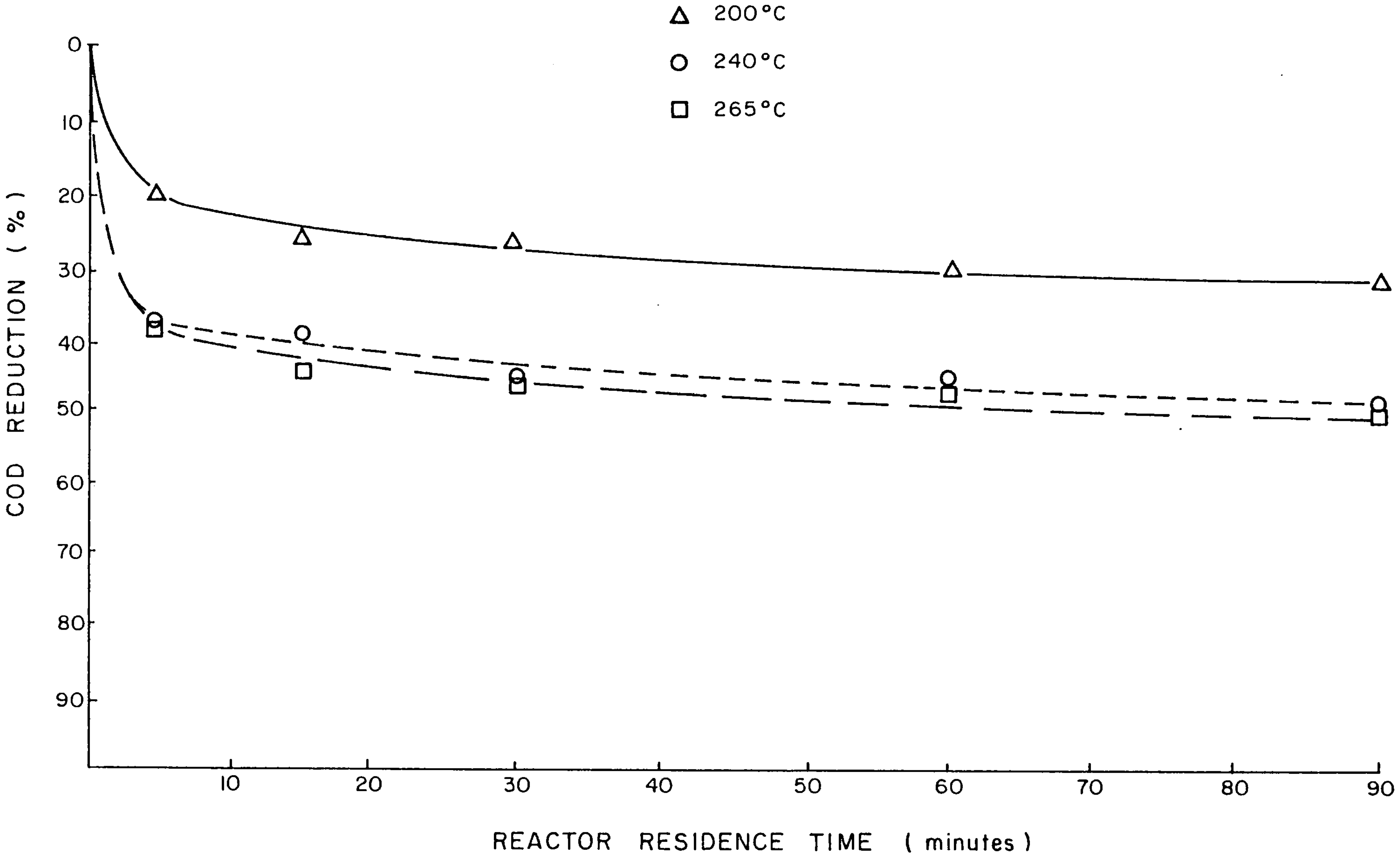


FIGURE 8. MBT WASTE - EFFECT OF TEMPERATURE ON COMBUSTION EFFICIENCY.

TABLE 18 - MBT Waste - Effect of H_2SO_4 & CuO on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 240°C, 650 psi		Batch Test - 240°C, 650 psi, 250 ppm CuO		Batch Tests - 240°C, 650 psi, $H_2SO_4 \rightarrow pH = 2$	
	COD	TOC	COD	TOC	COD	TOC
5	37.2	9.6	34.8	6.0	68.9	59.0
15	39.0	16.0	40.0	16.0	79.5	72.0
30	44.5	24.1	43.4	18.7	82.0	73.2
60	44.5	27.0	45.0	33.0	84.7	79.2
90	47.8	29.5	49.3	35.8	86.5	82.2

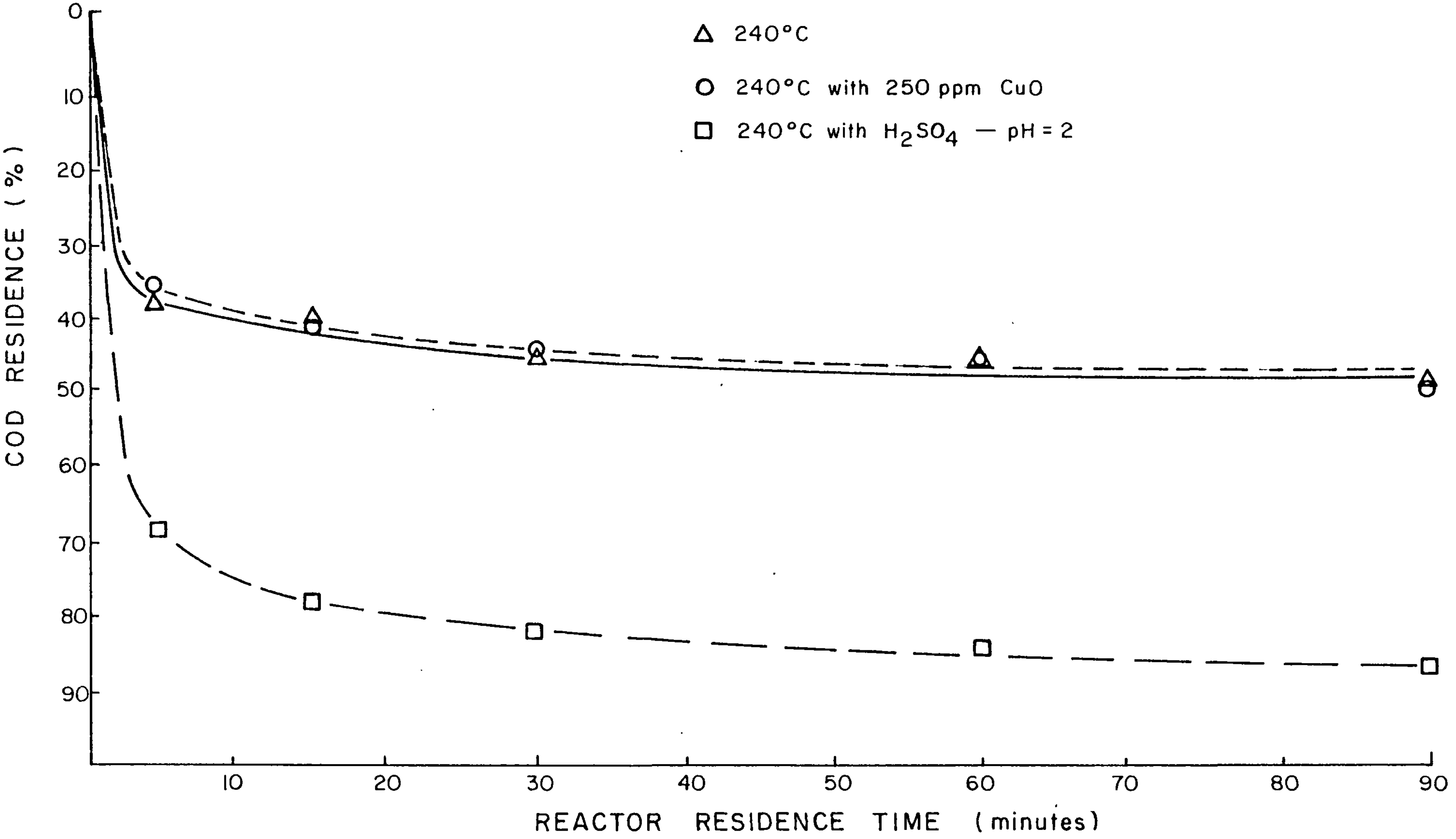


FIGURE 9. MBT WASTE - EFFECT OF H_2SO_4 & CuO ON COMBUSTION EFFICIENCY

TABLE 19 - MBT Waste - Pilot Plant Test Results (with Copper)

Reactor Residence Time (minutes)	Percent Reduction			
	Predicted from Jones Plot		Achieved Results	
	COD	TOC	COD	TOC
30	44.0	-	46.0	29.8
50	45.8	-	53.9	37.2
70	47.6	-	58.7	45.6
90	49.5	-	58.7	54.6

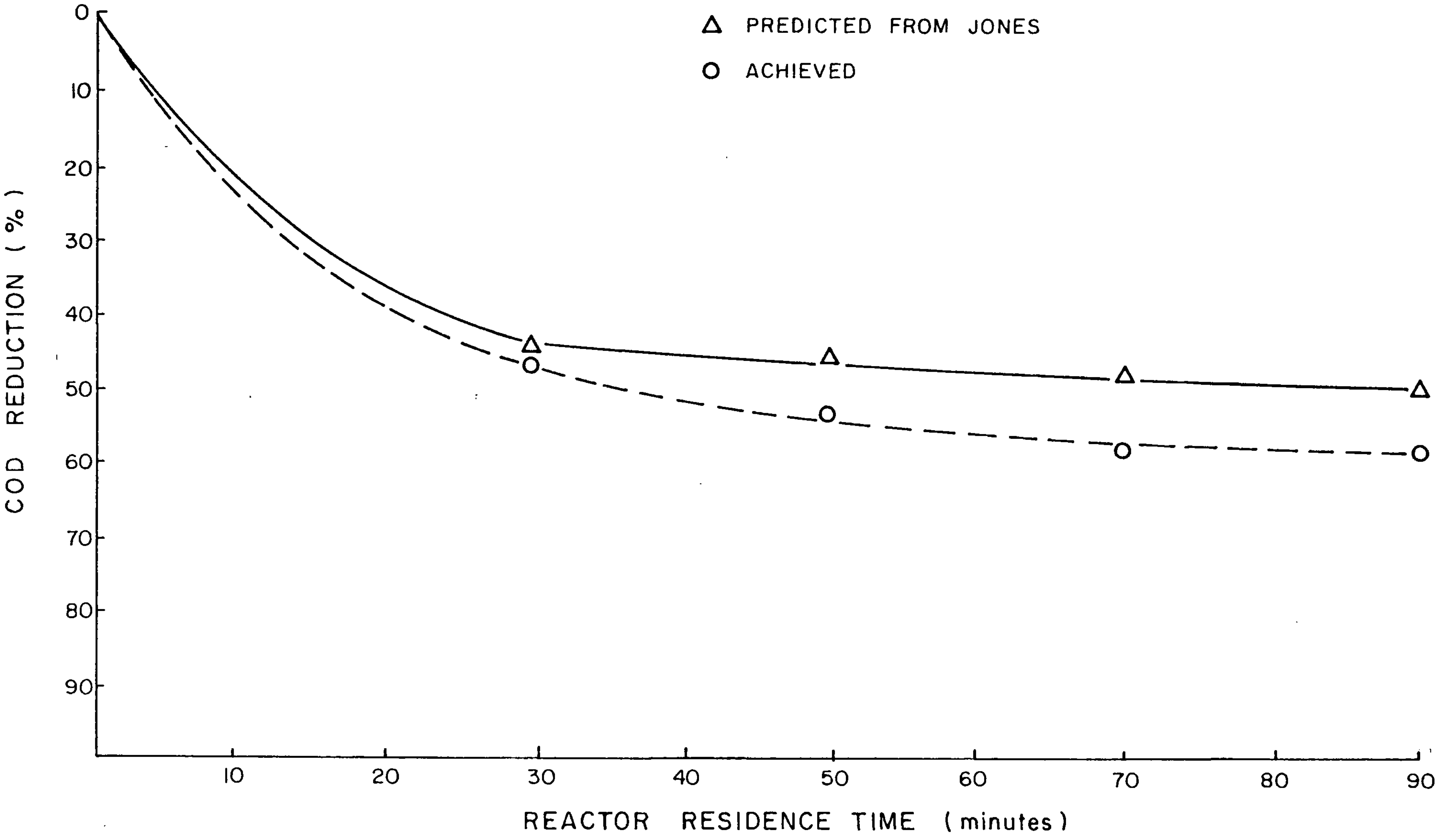


FIGURE 10. MBT WASTE - PILOT PLANT TEST RESULTS (WITH COPPER)

TABLE 20A - Pilot Plant Experiments (Acidic Fraction) - Mercaptobenzothiazole

Tentative Compound Identification	$[M]^+$	Vapour Phase Effluent	Liquid Phase Effluent
$(CH_3S)_2$	94	-	x
Methyl benzoate	136	-	2.9
CH_3^-	150	-	-
$C_2H_5^-$	164	-	-
$C_4H_{11}^-$	192	-	-
Methyl salicylate	152	-	1.4**
Methoxy nitrobenzene	153	-	-
Nitro-benzoate	181	-	-
Azobenzene-methyl carbocylate	240	-	12.0
-	202	-	-
-	238	-	-
-	258	-	2.5
-	129	-	-
-	229	-	2.1
-	136/ 135	-	1.7
-	166	-	1.0

**Concentration in mg/L calculated from GC-FID using methyl benzoate as standard

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- - Not observed in GC-MS data

TABLE 20B - Pilot Plant Experiments
(Basic Fraction) - Mercaptobenzothiazole

Tentative Compound Identification	$[M]^+$	Vapour Phase Effluent	Liquid Phase Effluent
Aniline	93	157.0	24.0
Nitrobenzene	123	16.0	2.5
Azobenzene	182	12.4	-
-	180	35.6	21.6
Azoxybenzene	198	-	10.7
Dimethylazobenzene	210	-	x
Isoquinoline	129	14.6	3.29
-	121	x	x
-	171	x	-
-	194	-	-
Mercaptobenzothiazole	167	-	-

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- - Not observed in GC-MS data

TABLE 21 - Pure DPA - Summary of Batch & Semi-Batch Test Results

Run #	Mode	Residence Time (minutes)	Temp/Press. (°C/psi)	Additions	COD Red'n. (%)	TOC Red'n. (%)	Effluent COD/TOC*
1	Batch	90	200/400	None	80.0	78.0	3.0
2	Batch	90	220/500	None	78.0	69.1	2.6
3	Batch	90	240/650	None	80.0	74.8	2.3
4	Batch	90	250/750	None	81.7	74.0	2.3
5	Batch	90	265/950	None	93.2	90.2	2.3
6**	Batch	90	240/650	250 ppm CuO	89.7	87.8	2.7
7	Batch	90	240/650	H_2SO_4 → pH = 2	75.2	66.7	2.4
8	Batch	90	240/650	CuO + H_2SO_4	72.3	73.2	3.3
9	Semi-Batch	60	240/625	None	90.6	92.8	2.4
10**	Semi-Batch	60	240/625	250 ppm CuO	96.3	95.1	2.6
11	Semi-Batch	60	240/625	H_2SO_4 → pH = 2	94.3	90.5	2.2

*Feed COD/TOC = 3.3

**Detailed organic analysis performed on this sample

TABLE 22 - Pure DPA - Effect of Temperature on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 220°C 500 psi		Batch Test - 240°C, 650 psi		Batch Test - 265°C, 950 psi	
	COD	TOC	COD	TOC	COD	TOC
5	72.3	62.6	62.5	70.7	62.3	56.0
15	73.8	67.5	78.3	81.3	82.0	76.7
30	75.2	68.0	81.0	78.3	87.5	82.7
60	77.6	69.1	76.3	74.5	89.0	85.1
90	77.8	69.1	80.0	74.8	93.2	90.2

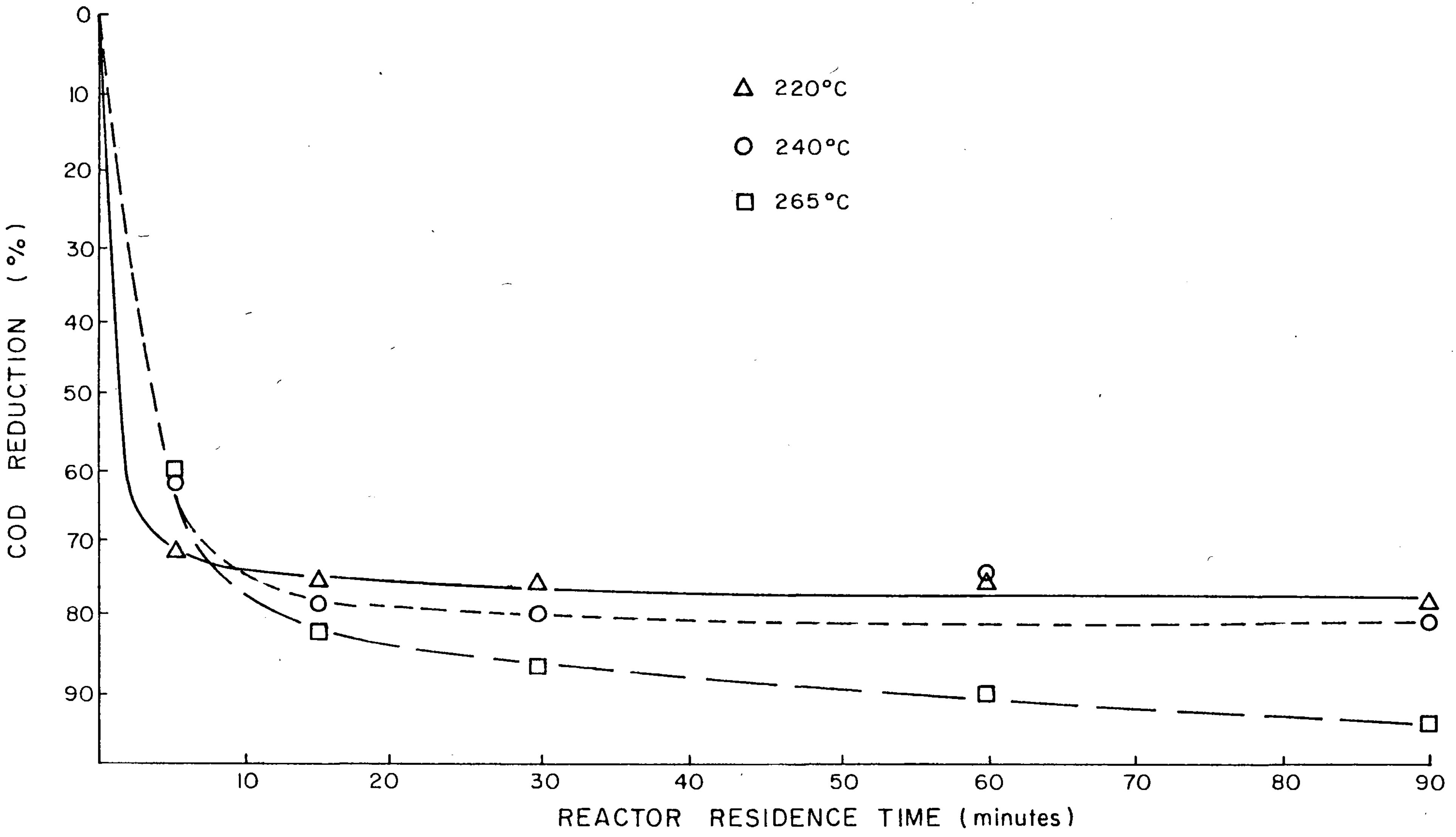


FIGURE II. PURE DPA - EFFECT OF TEMPERATURE ON COMBUSTION EFFICIENCY

TABLE 23 - Pure DPA - Effect of H_2SO_4 & CuO on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 240°C, 650 psi		Batch Test - 240°C, 650 psi, 250 ppm CuO		Batch Test - 240°C, 650 psi, $H_2SO_4 \rightarrow pH = 2$	
	COD	TOC	COD	TOC	COD	TOC
5	62.5	70.7	76.0	75.1	60.3	15.5
15	76.3	81.3	84.1	85.1	71.0	60.2
30	78.3	78.3	84.6	82.6	71.2	63.4
60	81.0	74.5	88.5	87.3	74.5	65.8
90	80.0	74.8	89.7	87.8	75.2	66.7

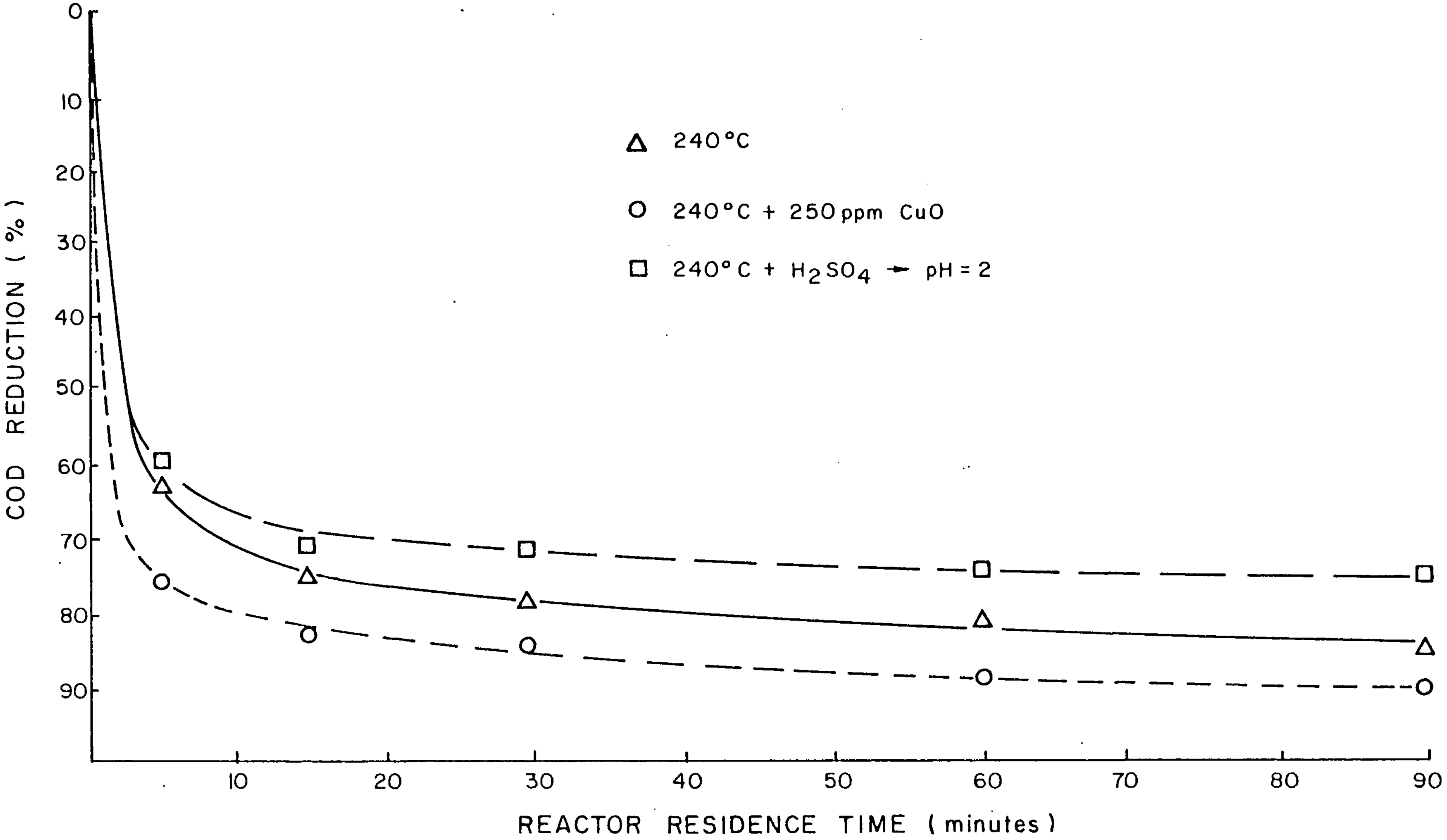


FIGURE 12. PURE DPA - EFFECT OF H_2SO_4 & CuO ON COMBUSTION EFFICIENCY.

TABLE 24A - Batch & Semi-Batch Experiments (Acidic Fraction) - Diphenylamine

Tentative Compound Identification	$[M]^+$	Pure DPA Batch	Pure DPA Semi-Batch	DPA Waste Batch	DPA Waste Semi-Batch
$(CH_3S)_2$	94	-	-	x	-
Methyl benzoate	136	0.25*	0.93	0.25	0.32
CH_3^-	150	-	-	-	-
C_2H_5	164	-	-	-	x
Methyl salicyclate	152	x	x	0.23	-
Amin-benzoate	151	-	-	-	-
Methoxy-nitrobenzene	153	-	-	x	-
Azobenzene-methyl carboxylate	240	-	-	x	-
-	188	-	-	x	-
-	202	-	-	x	-
-	238	-	-	x	-
-	256	-	-	x	-
-	282	x	-	x	-
-	286	x	-	-	-
-	258	-	-	x	-
-	129	-	-	x	-
-	171	x	x	-	x
-	229	x	-	-	-
-	251	-	-	x	-
-	279	x	-	-	-
-	136/ 135	-	-	x	x
-	319	-	-	-	-

*Concentration in mg/L calculated from GC-FID using a pure anilene standard

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- \- Not observed in GC-MS data

TABLE 24B - Batch & Semi-Batch Experiments (Basic Fraction) - Diphenylamine

Tentative Compound Identification	$[M]^+$	Pure DPA Batch	Pure DPA Semi-Batch	DPA Waste Batch	DPA Waste Semi-Batch
Aniline	93	0.6*	0.3	6.6	<0.1
Nitrobenzene	123	<0.1	<0.1	40.0	<0.1
Azobenzene	182	0.4	-	5.6	-
-	180	-	-	7.4	-
Azoxybenzene	198	-	-	8.3	-
Dimethylazobenzene	210	3.6	6.8	-	-
Chloropyridine	113	x	-	-	-
Chloro-aniline	127	0.6	x	-	-
Dichloroaniline	161	x	x	-	-
Trichloroaniline	195	-	-	-	-
-	121	-	-	-	x
Isoquinoline	129	-	-	-	-
DPA	169	x	-	-	-
-	194	-	-	2.6	-
-	?	-	-	3.2	-

*Concentration in mg/L calculated from GC-FID using a pure aniline standard

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- - Not observed in GC-MS data

TABLE 25 - DPA Waste - Summary of Batch & Semi-Batch Test Results

Run #	Mode	Residence Time (minutes)	Temp/Press. (°C/psi)	Additions	COD Red'n. (%)	TOC Red'n. (%)	Effluent COD/TOC*
1	Batch	90	200/650	None	45.7	36.0	2.7
2	Batch	90	220/650	None	46.4	36.4	2.7
3	Batch	90	240/650	None	55.0	41.5	2.5
4	Batch	90	250/750	None	58.6	41.5	2.3
5	Batch	90	265/950	None	57.8	38.0	2.3
6**	Batch	90	240/650	250 ppm CuO	52.9	44.9	2.7
7	Batch	90	240/650	H_2SO_4 → pH = 2	87.6	81.4	2.1
8	Batch	90	240/650	CuO + H_2SO_4	88.7	83.9	2.2
9	Semi-Batch	60	240/625	None	41.6	35.0	2.8
10	Semi-Batch	60	240/625	H_2SO_4 → pH = 2	64.0	45.3	3.1
11**	Semi-Batch	60	240/625	CuO + H_2SO_4	77.2	75.0	2.9

*Feed COD/TOC = 3.2
**Detailed organic analysis performed on this sample

TABLE 26 - DPA Waste - Effect of Temperature on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 200°C, 400 psi		Batch Test - 240°C, 650 psi		Batch Test - 265°C, 950 psi	
	COD	TOC	COD	TOC	COD	TOC
5	31.0	19.2	40.9	33.9	41.0	16.7
15	40.0	30.0	43.0	34.5	51.0	27.7
30	40.9	28.8	47.6	41.5	53.6	28.8
60	43.0	31.1	51.5	35.0	55.5	35.0
90	45.7	36.0	55.0	41.5	57.8	38.0

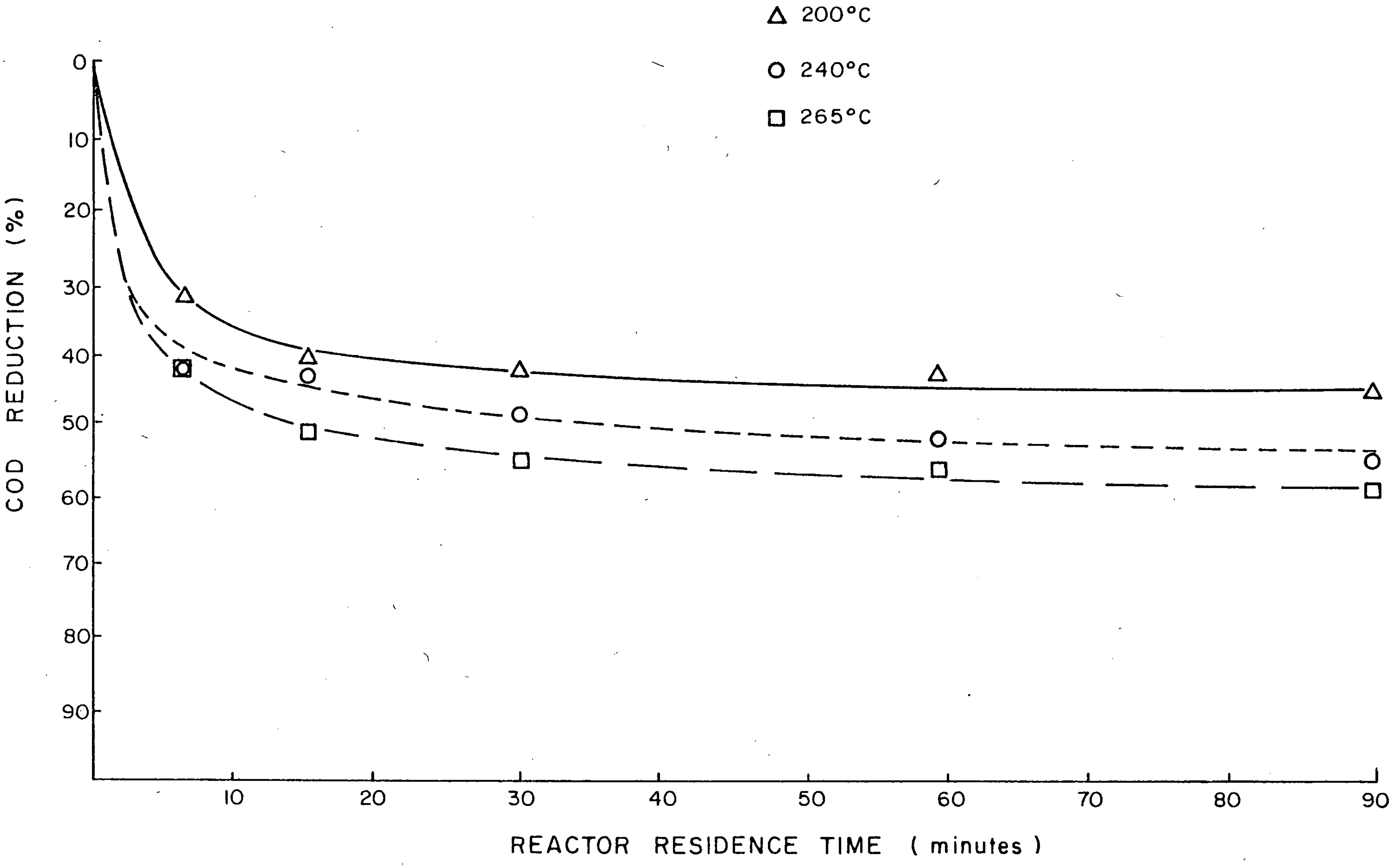


FIGURE 13. DPA WASTE - EFFECT OF TEMPERATURE ON COMBUSTION EFFICIENCY.

TABLE 27 - DPA Waste - Effect of H_2SO_4 & CuO on Combustion Efficiency

Reactor Residence Time (minutes)	Percent Reduction					
	Batch Test - 240°C, 650 psi		Batch Test - 240°C, 650 psi, 250 ppm CuO		Batch Test - 240°C, 650 psi, $H_2SO_4 \rightarrow pH = 2$	
	COD	TOC	COD	TOC	COD	TOC
5	40.9	33.9	39.8	20.3	70.0	59.9
15	43.0	34.5	42.1	35.0	75.3	62.8
30	47.6	41.5	47.1	39.0	80.0	63.9
60	51.5	35.0	50.8	42.0	85.0	71.0
90	55.0	41.5	52.9	44.9	87.6	81.4

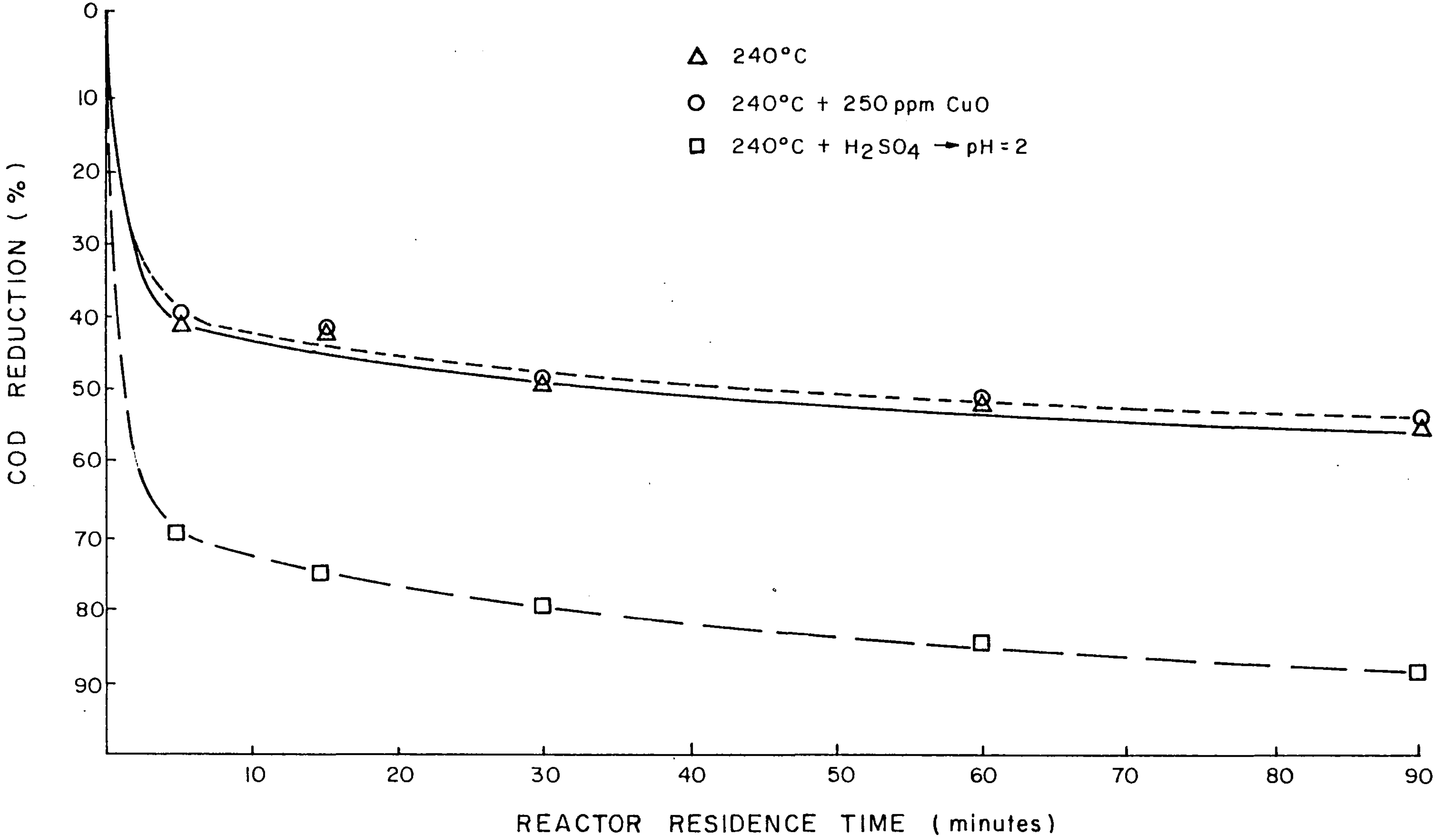


FIGURE 14. DPA WASTE - EFFECT OF H_2SO_4 & CuO ON COMBUSTION EFFICIENCY

TABLE 28 - DPA Waste - Pilot Plant Test Results (with Copper)

Reactor Residence Time (minutes)	Percent Reduction			
	Predicted from Jones Plot		Achieved Results	
	COD	TOC	COD	TOC
30	47.0	-	44.8	-
50	49.2	-	46.2	37.5
70	50.9	-	51.0	44.9
90	51.9	-	55.8	58.3

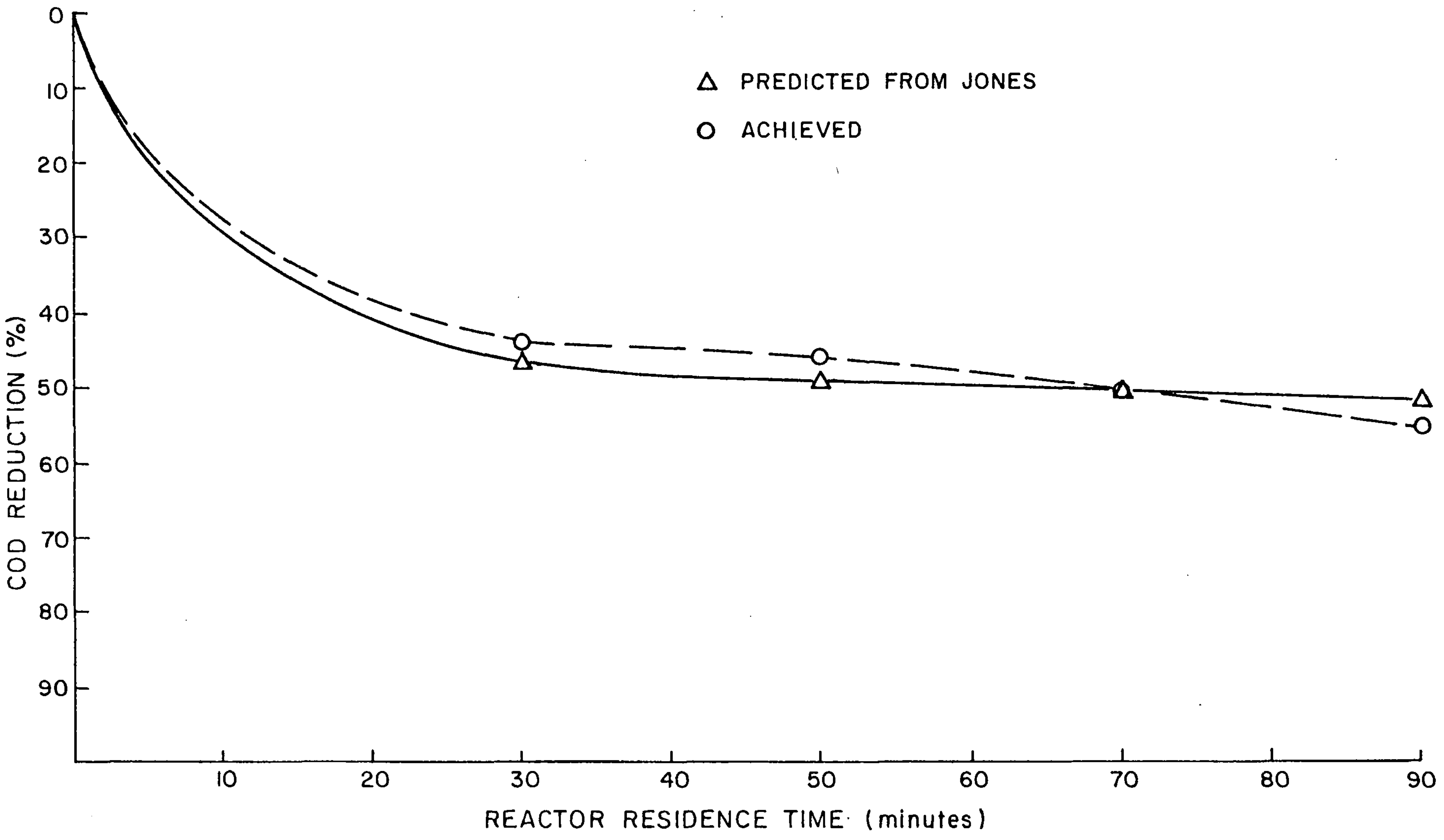


FIGURE 15. DPA WASTE - PILOT PLANT TEST RESULTS (WITH COPPER)

TABLE 29A - Pilot Plant Experiments (Acidic Fraction) - Diphenylamine

Tentative Compound Identification	$[M]^+$	Vapour Phase Effluent	Liquid Phase Effluent
$(CH_3S)_2$ $(CH_3)_2SO_2$	94	-	x
Methylbenzoate	136	-	3.0
CH_3^-	150	-	x
C_2H_5	164	-	x
Methyl salicyclate	152	-	1.6
Amino-benzoate	151	-	x
Methyoxy-nitrobenzene	153	-	-
Azobenzene-methyl carboxylate	240	-	4.5**
-	188	-	-
-	202	-	x
-	238	-	1.0
-	256	-	-
-	282	-	-
-	286	-	-
-	258	-	x
-	129	-	0.8
-	171	-	-
-	229	-	x
-	251	-	-
-	279	-	-
-	136/ 135	-	1.8
-	319	-	x

**Concentration in mg/L calculated from GC-FID using methyl benzoate as standard

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- - Not observed in GC-MS data

TABLE 29B - Pilot Plant Experiments (Basic Fraction) - Diphenylamine

Tentative Compound Identification	$[M]^+$	Vapour Phase Effluent	Liquid Phase Effluent
Aniline	93	149.0	26.0
Nitrobenzene	123	49.0	6.5
Azobenzene	182	2.6	16.7
-	180	32.5	5.2
Azoxybenzene	198	-	-
Dimethylazobenzene	210	-	0.8
Chloropyridine	113	-	-
Chloro-aniline	127	-	-
Dichloroaniline	161	-	-
Trichloroaniline	195	-	-
-	121	x	-
Isoquinoline	129	8.7	0.3
DPA	169	2.4	-
-	194	-	-
-	?	-	-

x - Indicates that molecular ion $[M]^+$ was observed in GC-MS and that GC-FID calculations based on a methyl benzoate standard gave concentrations less than 0.05 mg/L

- - Not observed in GC-MS data

on aniline

APPENDIX A

Wet Oxidation: a brief description

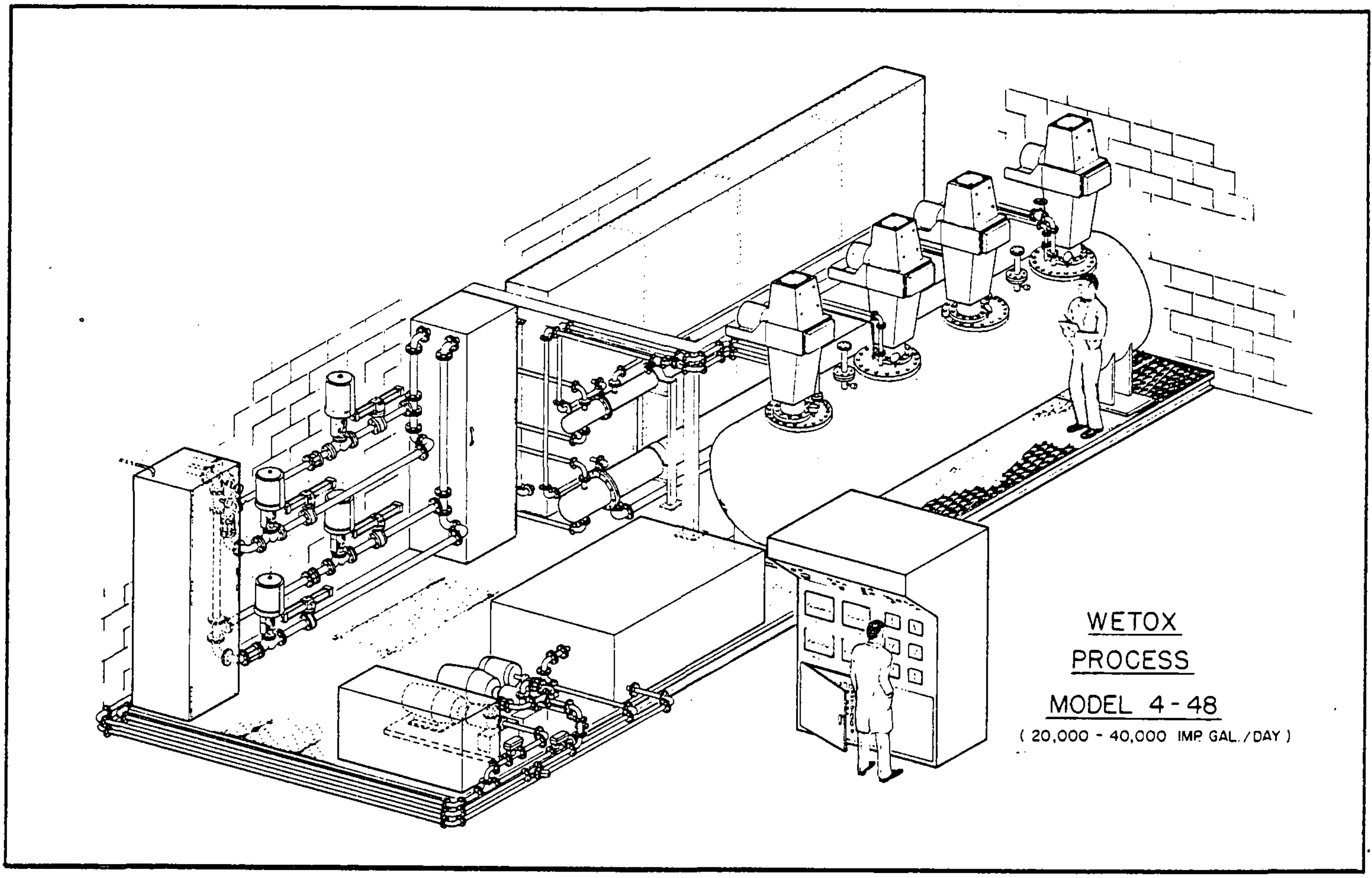
WET OXIDATION:
a brief description

1. History of wet air oxidation

Wet air oxidation is not a new process – patents in the fields of extractive metallurgy and waste treatment were granted at the turn of the century. The extractive metallurgical applications originated from the Bayer Process which was patented in 1888. The application of wet air oxidation to waste treatment proceeded from R. W. Strehlenert who, in 1912, patented a process for the treatment of spent pulping liquors with oxygen at elevated temperatures and pressures. Development of the process proceeded simultaneously in several fields and in many countries, including Sweden, Germany and U.S.A.

Cederquist, using a horizontal, agitated autoclave, investigated the use of wet oxidation for energy production from peat, wood, spent pulping liquor, etc. He began publishing his findings in 1953. It was at this time that W. K. Porteus was applying for patents concerning various applications of the Porteus Process or "heat treatment". In 1954, F. J. Zimmerman was granted a patent for the destructive oxidation of organic material in liquid waste effluents. Soon after, the Sterling Drug Company founded the Zimpro Division of that corporation to market the Zimmerman Process. In this process, the reaction is carried out in a vertical tower reactor.

In 1952, plans were announced by the



Chemical Construction Company, then a subsidiary of American Cyanamid Company, for the exploitation of a new process for the pressure leaching of metallurgical materials. Plants were under construction, at that time, for three firms: Sherritt Gordon Mines Ltd., National Lead Company and the Calera Mining Company. The Wetox® Process originated from the Calera Mining Company wet oxidation process constructed in 1954. The Calera process used a horizontal, multi-compartmented autoclave to react cobalt ore and oxygen at 400°F. The Calera autoclave routinely treated a slurry with a COD equivalent of greater than 30%.

2. Fundamentals of wet air oxidation

Wet air oxidation is a process in which combustible material is oxidized by air or oxygen in the presence of liquid water. Elevated temperatures are required to achieve a useful reaction rate and, therefore, to maintain a liquid phase, elevated pressures are required. The process is operated continuously with liquid and gas streams being introduced to the reactor simultaneously.

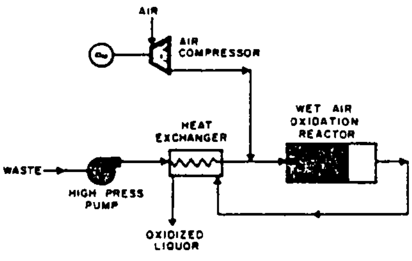


Figure 1 - General Wet Combustion Schematic

A basic flowsheet for the process is presented in Figure 1. The waste is pumped via a high pressure pump through a heat exchanger and then into a reactor where it is mixed with compressed air. The oxygen in the air reacts with the organic matter in the slurry to produce mainly carbon dioxide and water. Due to the exothermic nature of the reaction, heat is produced which raises the temperature of the reactor contents. The effluent from the wet oxidation reactor is heat exchanged with the incoming waste.

Almost any combustible material which remains in the liquid phase can be oxidized in the process. The destruction of the organic contaminants is achieved as well in water at elevated temperature and pressure as by concentrating the material and incinerating the dry residue. In either case the products are the same: carbon dioxide, water and ash. Since the products from wet air oxidation are automatically and thoroughly scrubbed, air and odour pollution are minimized.

The wet air oxidation process provides an efficient means for the recovery of the energy from relatively dilute waste streams. The reaction occurs and the energy is liberated in the liquid phase, with no barrier to the transfer. The energy can, therefore, be recovered with the highest degree of efficiency.

3. Physical parameters governing wet oxidation

The maximum extent of the oxidation is primarily a function of the maximum operating temperature within the reactor. A typical combustion curve is presented in Figure 2. The operating temperature effectively dictates the minimum operating pressure since confinement of the resulting steam and adequate oxygen partial pressure is required.

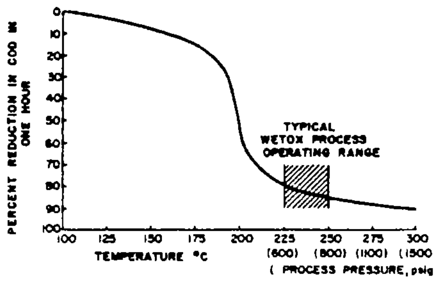


Figure 2 - Effect of Temperature

In wet air oxidation, oxidation and hydrolysis reactions proceed simultaneously depending on the availability of oxygen. Thus, with inadequate transfer of oxygen, hydrolysis reactions become significant and often generate products which are refractory to further oxidation in this process. Examples of these products are low molecular weight carboxylic acids; acetic, proprionic, etc. The mass transfer requirements must, therefore, be satisfied to achieve maximum conversions to carbon dioxide and water. The rate of transfer of oxygen into the solution at a given operating temperature is controlled by:

- The solubility of oxygen in the waste which is a function of the oxygen partial pressure or overpressure. Increased process pressures will, therefore, result in increased rates of mass transfer.
- The degree of mixing of the oxygen and the waste.

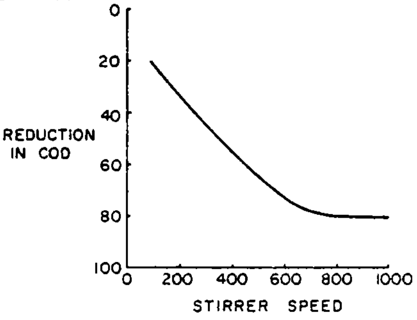


Figure 3 - Effect of Stirring

Increased process pressures result in increased capital costs for the reactor vessel, heat exchanger, compressor, etc., as well as increased operating costs, largely attributable to electrical power consumption. Effective mixing is, therefore, a most important parameter in economically optimizing the system, as shown in Figure 3.

4. Applications of wet air oxidation

The process is uniquely suited to the oxidation of waste liquors, slurries and sludges where the organic matter is but a few percent of the predominantly water stream. The relative position of wet air oxidation in relation to conventional wastewater treatment techniques is shown in Figure 4. It is the most economical process for wastes which have a concentration of oxidizable material between 2 and 20% by weight with water.

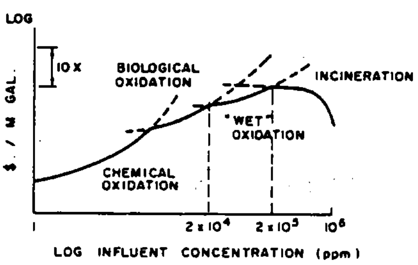


Figure 4 - Comparison of Total Waste Disposal Costs

In this range, sufficient material is available to react with the oxygen to generate enough heat to maintain the desired temperature and pressure in the reactor without external energy being supplied. Above about 1.5% concentration, excess heat is generally produced which can be efficiently and economically recovered. Above 20% concentration, incineration would generally be the most efficient method of disposal. Wet air oxidation is, therefore, most effective on wastes too concentrated for biological or chemical oxidation and too dilute for incineration.

Wet air oxidation can be applied to non-biodegradable materials as well as dangerous, toxic or obnoxious wastes. Valuable inorganic materials can be efficiently recovered from the liquid phase effluent. This is especially important for materials which after incineration would not be in a recoverable or reusable form. Because the oxidation takes place under water, the production of air and odour pollution is minimized. Potentially obnoxious materials remain in solution and exit the reactor in the liquid phase as salts or acids such as sulfates, chlorides, etc.

Examples of waste streams which can be effectively treated by wet air oxidation include:

Industry	Waste
Refinery & Petrochemical	Refinery Cyanide Waste
	Refinery Spent Sour Water
	Chlorinated Hydrocarbon Sludge
	Refinery API Separator Sludge
	Re—Refinery Acid Sludge
	Petrochemical Ammonium Chloride Waste
	Petrochemical Nitrate Waste
	Petrochemical HC1 Wash Stream
	Petrochemical NaOH Wash Stream
	Petrochemical Ammoniated Organic Waste
	Linear Alkyl Benzene Sulfonate Waste
	Refinery Spent Caustic
	Refinery Filter Backwash
	Refinery Biological Sludge
Pulp and Paper	Phenolic Waste Stream
	Paper Mill Fines
	Recycled Newsprint
	Wood Preservative Liquor
	Sodium Base Sulfite Liquor
	Calcium Base Sulfite Liquor
	Ammonium Base Sulfite Liquor
	Sodium Base Semi-Chemical Liquor
	Soda Base Liquor
	Clay Filler Sludge
Electroplating	Copper Stripping Solution
	Copper-Cyanide Plating Solutions
	Cadium-Cyanide Plating Solutions
	Alkaline-Cyanide Cleaner Waste
Food	Vegetable Hydrolysis Sludge
	Tomato Waste
	Bean Sludge and Bean Wastewater
	Cheese Whey
	Cornstarch Waste
	Coffee Grounds
	Fish Processing Waste
Iron and Steel	Thiocyanate Waste
	Cyanide Waste
Automotive	Mixed Paint Waste
	Mixed Waste Slurry
	Automotive Lagoon Waste
	Automotive Radiator Plant Sludge
Textile	Caprolactam Waste
	Nylon Manufacturing Waste
	Condensate from Polyester Resin Production
	Spinning Oil From Nylon Manufacture
Miscellaneous Wastes	Paint Manufacturing Waste
	Paint Stripping Sludge
	Drum Washing Effluent
	Metals Recovery Sludges
	Tanning Wastes Containing Chromate
	Sewage Sludge
	Gasification of Wood Effluent
	Manure
	Mixed Industrial Organic Waste
	PCB-containing Wastes
	Metal Grinding Sludges
	Palm Oil Mill Effluent
	Antifreeze
	Raw Sewage

Other Process Applications:

- Conversion of agricultural residues to single cell protein and/or methane via wet oxidation and biological treatment.
- Desulfurization of high sulfur fuels such as lignite, coal, coke, etc.
- Combustion of low-grade fuels such as peat, low-grade coal, waste paper, etc.
- Regeneration of activated carbon.

5. The Wetox Process

The heart of the Wetox Process (see Figure 5) is the reactor: a multi-compartmented horizontal unit with agitation and oxygen addition in each compartment. This design results in substantially increased reaction rates and makes possible efficient operation at relatively modest temperatures and pressures (∿230°C and ∿600 psi). The liquid and steam phases are withdrawn separately from the reactor. This feature improves the heat exchanger efficiency, increases the effective retention time of the liquid, and reduces the volume of liquid effluent for chemical recovery or treatment.

Detailed energy balance calculations for the Wetox Process have been performed and summarized in Figure 6.

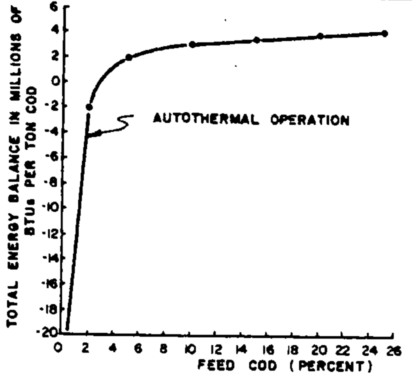


Figure 6 - Total Energy Balance of the Wetox Process

Above about 1.5% COD* the process is autothermal and above 3.0% COD the process is a net energy producer. A comparison to biological treatment and incineration is provided in Figure 7.

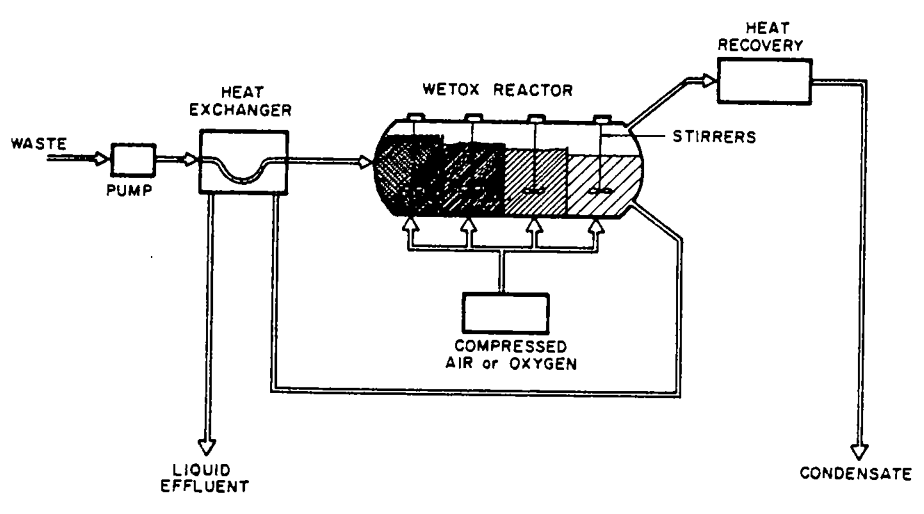


Figure 5 - Wetox Process Schematic

Capital cost comparisons have indicated that from 3% COD to about 30% COD, the capital cost of the Wetox Process is the same or less than the comparable biological or incineration system.

It would be expected, therefore, that the Wetox Process would be the most economical system for wastes with COD concentrations of from 3% to about 40% (volatile solids from 1.5% to 20%). Total system costs for the Wetox Process are generally in the 0.5c to 5.0c per Imperial gallon range.

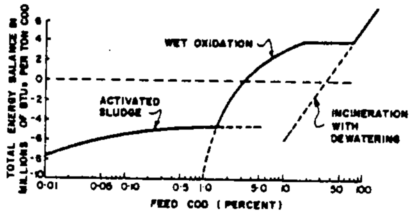


Figure 7 - Comparison of Total Energy Balances

6. Commercial Development

In 1978, WetCom Engineering Limited was established to market and manufacture the process.

Wetox Process units can be economically designed from about 3,000 Imperial gallons per day (2 feet diameter by 8 feet long) to about 400,000 Imperial gallons per day (8 feet diameter by 50 feet long). The Wetox Model 4–48 with a capacity of from 20,000 to 40,000 Imperial gallons per day is shown on page 1. This size of unit would, for example, provide sewage sludge disposal for a wastewater treatment plant treating from 5 to 10 million Imperial gallons per day of sewage.

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*COD is Chemical Oxygen Demand. This is a measure of the amount of oxygen which would be required to reduce the waste to carbon dioxide and water. Hence, a waste having a COD of 1% would require 1 lb of oxygen per 100 pounds of waste. Most undiluted organic compounds have a COD of between 1 and 3 lbs per pound of material. In a general description such as this a value of 2 lbs COD per lb of organic has been assumed. Thus a waste stream containing 1% organic material is assumed to have a COD of 2%.

APPENDIX B

2-Litre Batch Autoclave

1. EQUIPMENT

The 2-litre autoclave (Figure 1) has a total capacity of two litres with an active liquid volume of about one litre at the temperatures and pressures employed. The reactor is equipped with a variable speed stirrer mounted centrally in the vessel. The maximum operating temperature is 300°C.

The injection and sampling system is presented in Figure 2. Two injectors are used: one for diluent water addition and the other for concentrated waste addition. Two sample lines with two separate ice baths are used for liquid and vapour sampling. The system is equipped with two water cooling lines: stirrer bearing and reactor cooling coil.

2. PROCEDURE

A schematic of the 2-litre system is provided (Figure 3). Typical test operations include:

(1) The assembled reactor is placed into the heater and the following connections made:

  (a) the oxygen inlet line
  (b) the liquid sampling line and purge line
  (c) the vapour exit line
  (d) the cooling water lines (2) and the corresponding discharge lines (2).

(2) All valves are closed.

(3) The stirrer is connected to the pressure vessel.

(4) Valve V_{12} is opened allowing cooling water to flow through stirrer bearing assembly.

(5) Valves V_1, V_4 and V_5 are closed.

(6) The 1-litre washer-filler is charged with 880 ml of distilled water through the filler cap on the top of the vessel. By opening valves V_1, V_2 and V_{14}, the vessel is pressurized

(filler cap replaced). Valves V_1 and V_2 are then closed and valves V_{14}, V_3 and V_5 are opened forcing the water into the reactor (valve V_8 on reactor is vented to atmosphere). Valves V_3, V_8 and V_{14} are closed and valves V_1, V_4 and V_5 are opened and the reactor charged to 100 psig with oxygen. The stirrer is then set at a low-speed (approximately 300 rpm).

(7) The heaters are turned on and the temperature within the reactor raised to the desired temperature and maintained at that temperature ± 5°F.

(8) The injector is loaded with 60 ml of the concentrated test solution by means of a syringe through cap C, valves V_1 and V_2 are opened and the pressure within the injector raised to approximately 900 psi. Valves V_1 and V_2 are closed. Valves V_3, V_4 and V_5 are then opened and the concentrated test solution is injected into the reactor. Valves V_3, V_4 and V_5 are then opened and the concentrated test solution is injected into the reactor. Valves V_3, V_4 and V_5 are then closed. This is recorded at time 0 for test purposes. The stirrer is set at the desired operating speed at this time.

(9) Oxygen is added via valves V_1, V_4 and V_5 and the total pressure within the reactor is increased to the desired value. Valves V_1, V_4 and V_5 are then closed.

(10) Samples of the liquid-phase within the reactor are taken periodically throughout the experiment by opening valve V_6. The liquid is cooled in the ice bath and collected. The sample line is cleaned with alternate water and air purges through valves V_7, V_9 and V_{10}.

(11) After the required time at temperature, the heaters are turned off and the cooling water flow is started through the cooling coil within the reactor by opening valve V_{11}. The stirrer speed is reduced.

(12) At a reactor temperature of about 180°F, the spent gases are discharged from the reactor via valve V_8 and exit through

the vapour sampling line. The moisture is condensed in the ice bath and collected in the separator. The gases are collected in a Tedlar bag. The total pressure within the reactor is reduced to approximately 50 psi.

(13) Valve V_6 is opened and the liquid within the reactor is discharged through the ice bath to a suitable container.

(14) The exit gases in the bag sample are analyzed for O_2 and CO_2 via a Beckman O_2 meter, model 715, and a CO_2 meter, model MEXA 200 infrared analyzer by Horiba Limited.

(15) The liquid samples are analyzed for TOC using a Total Carbon Analyzer (model 915), manufactured by Beckman Instruments Incorporated. Additional analyses were performed in accordance with Standard Methods for the Examination of Water and Wastewater by APHA, AWWA and WPCF, 13th Edition.

(16) The reactor is rinsed thoroughly via the 1-litre injector with hot distilled water according to (6).

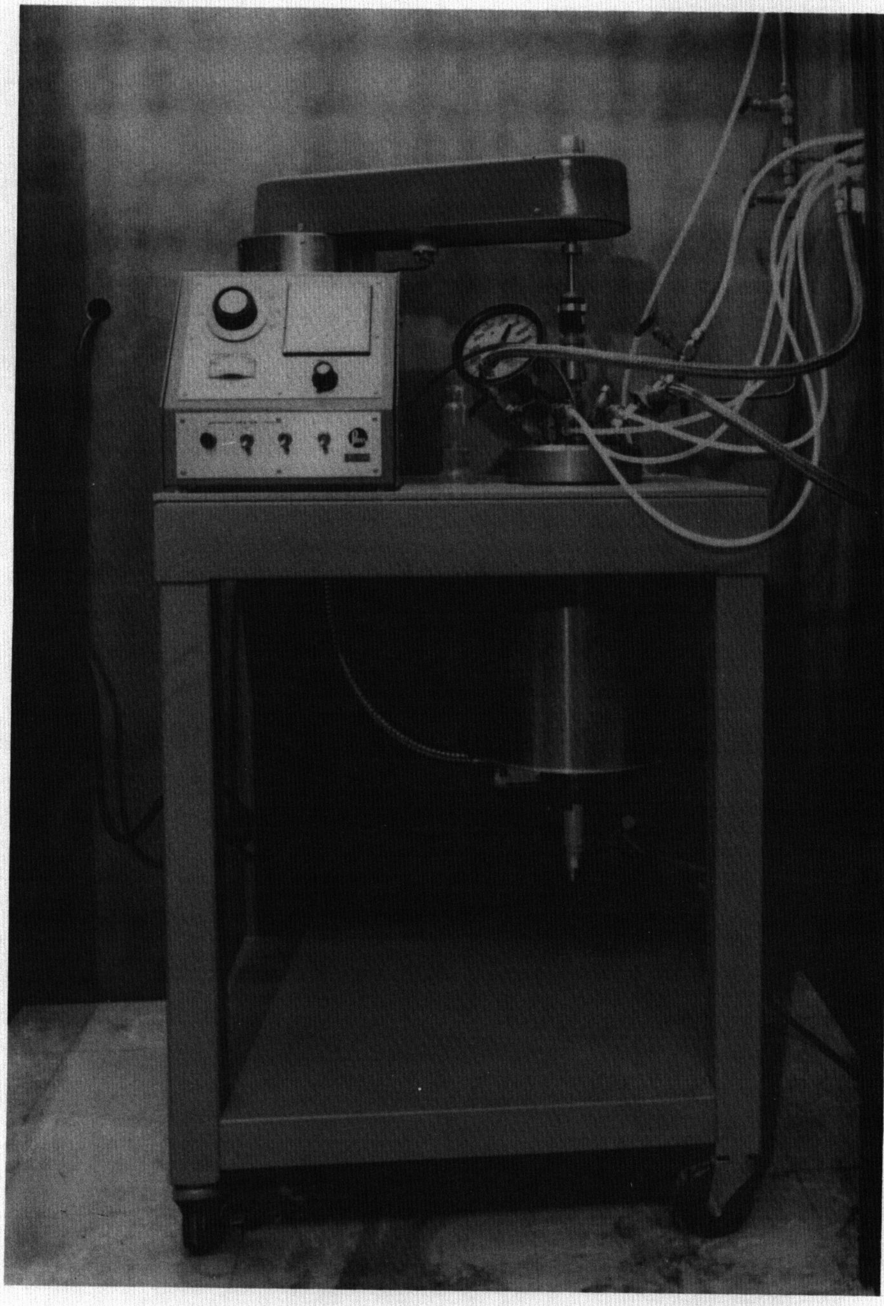


FIGURE 1 - 2-Litre Parr Reactor

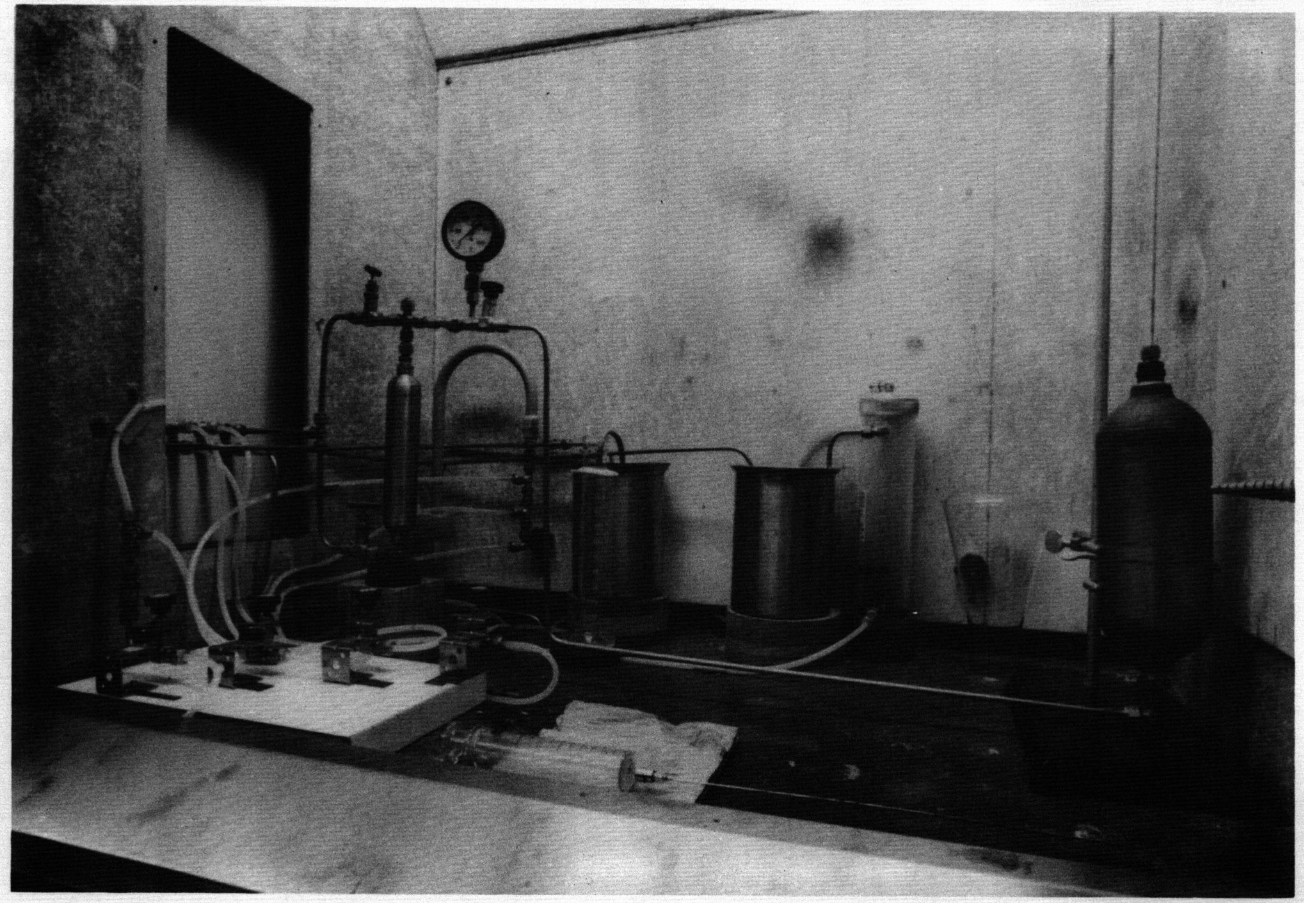


FIGURE 2 - Injection and Sampling System

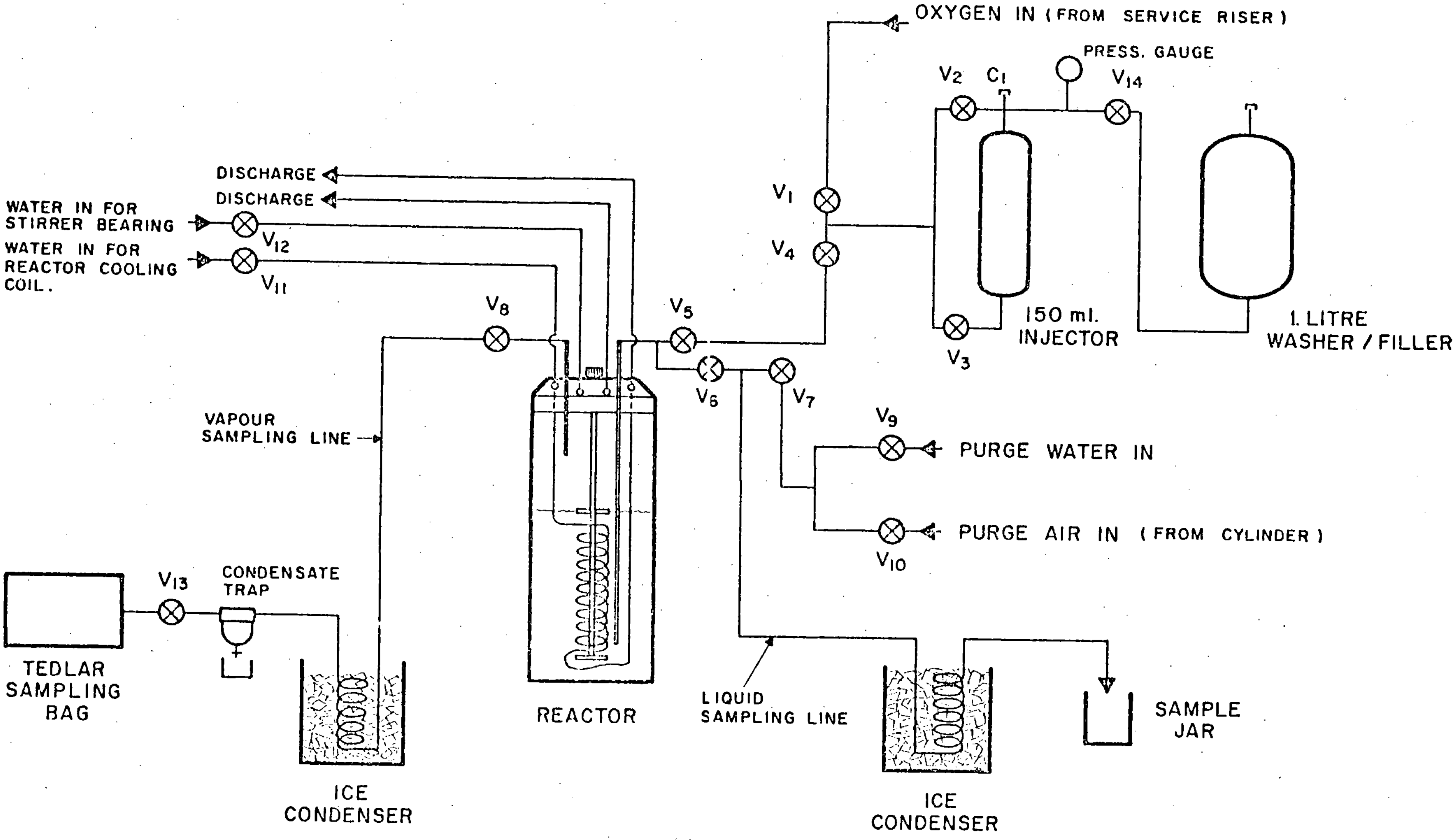


FIGURE 3 - Schematic for 2-Litre Autoclave

APPENDIX C

Semi-Batch System

1. EQUIPMENT

The semi-batch Wetox$^{(R)}$ 1-10 unit (see Figure 1) is equipped with two reactors. Each reactor (Figure 2) has a total volume of 10 litres with an active liquid capacity of ∿ 5 litres. The inside lining of the reactor, stirrer shafts, etc., are made of titanium. The process flowsheet is presented in Figure 3. The salient features of this unit are described in the following:

- Agitation

Each reactor is equipped with a 3/4-10-5000 MagneDrive stirrer with a maximum RPM of 1500. The stirrer speed is controlled by an SCR control, model 2M171 (manufactured by Dayton Electronic), which allows variable speeds from 0 to 1500. A tachometer (Autoclave Engineers, Model P910B) provides readout of the RPM.

- Heating and Cooling of the Reactor

A wide range liquid phase heat transfer fluid, Therminol 66 (Monsanto), is employed.

In the heating cycle, the heat transfer fluid is pumped through the heaters (Type C, Chromalox) and then through a jacket around the reactor and back to the heaters. The temperature of the Therminol is controlled by a Barber-Colman Controller (Model 72-G) which is equipped with a deviation indicator meter.

In the cooling cycle, the Therminol 66 is pumped through a water-cooled condenser and then through the reactor jacket.

- Reactor Temperature

A Barber-Colman Selector Switch is provided to enable measurements in either reactor. A Barber-Colman Recorder-Controller (Model RD11) provides a record of the temperature profile. The reactor temperature is controlled below a set point by the automatic heater override. Maximum operative temperature of the equipment is 500°F.

- Reactor Pressure and Air Supply

Compressed air is supplied from a bank of 5 cylinders. The inlet air flow is controlled by a micrometer inlet valve. The exit air flow, and hence pressure, is controlled by a Masoneilan Micropak, Series 29000 Control Valve. This valve is automatically controlled by a Masoneilan Controller, Model 2700, which, from comparison of the set point and reactor pressure, causes the valve to open or close. Rupture discs (1200 psi) are provided on each reactor. Maximum operative pressure of the equipment is 900 psi.

2. PROCESS DESCRIPTION

Compressed air from the cylinders is introduced into the reactor by passing through the micrometer valve to control its flowrate. It is then passed to the top of the agitator, down the hollow core of the stirrer shaft, exiting at the bottom of the shaft and is dispersed in the liquid phase. The flow of air is limited to below that equivalent to ∿ 25 - 30 cubic feet per hour (cfh) measured at room temperature and pressure, since, above this flow rate and with the violent agitation, entrainment of the liquid in the vapour stream occurs.

Normally during the experiment, the vapour effluent consisting of the spent air saturated with steam, is passed through the vapour cooler in order to condense the steam back into the reactor. The water in the vapour cooler may be turned off momentarily and a sample of the vapour effluent taken. The spent air exiting from the vapour cooler is then passed through the Masoneilan Controller and Micropak to control the system at the specified pressure. The condensed liquid is collected in a sample bucket which is fitted with a lid. A sample probe within the bucket allows the continuous monitoring of the exit gases.

A liquid phase sample line from the centre bottom portion of the reactor is provided. This is a 1/4" line, so designed to prevent blockage due to solids in the slurry. The pressure within the reactor forces liquid through a condenser to cool the sample and then through an ice bath. The sample is collected in a sample bottle within a bucket. Due to the large bore sample line, it is necessary to remove samples of approximately 25 to 50 ml each. Up to 10 samples may be taken successively in a run; thus, only 5% to 10% of the total liquid volume will be removed during an experiment.

3. PROCEDURE

The reactor is loaded with 5 litres of the sample to be oxidized via the feed port. The heating cycle is started and the contents of the reactor are brought up to the desired temperature. The temperature is automatically controlled at ± 5°F.

During the heat-up cycle, an air flowrate of 3 cfh was employed. The continuous presence of air inside the reactor is essential to this laboratory unit in order to maintain a thin layer of TiO_2 on the titanium lining to keep it free from corrosion. At the reaction temperature an air flowrate of 25 cfh is used for the specified period of reaction time. Liquid phase samples are withdrawn at specified intervals. The gaseous effluent is monitored continuously (effluent air flowrate and O_2). At the end of the specified reaction time the cooling cycle is started. The air flowrate has switched back to ∿ 3 cfh. After the reactor contents are cooled to about 100°F the remaining liquid is removed from the reactor.

4. ANALYSIS OF SAMPLES

The samples are cooled and stored. COD analyses are performed in accordance with Standard Methods for the Examination of Water and Wastewater by APHA, AWWA and WPCF, 13th Edition.

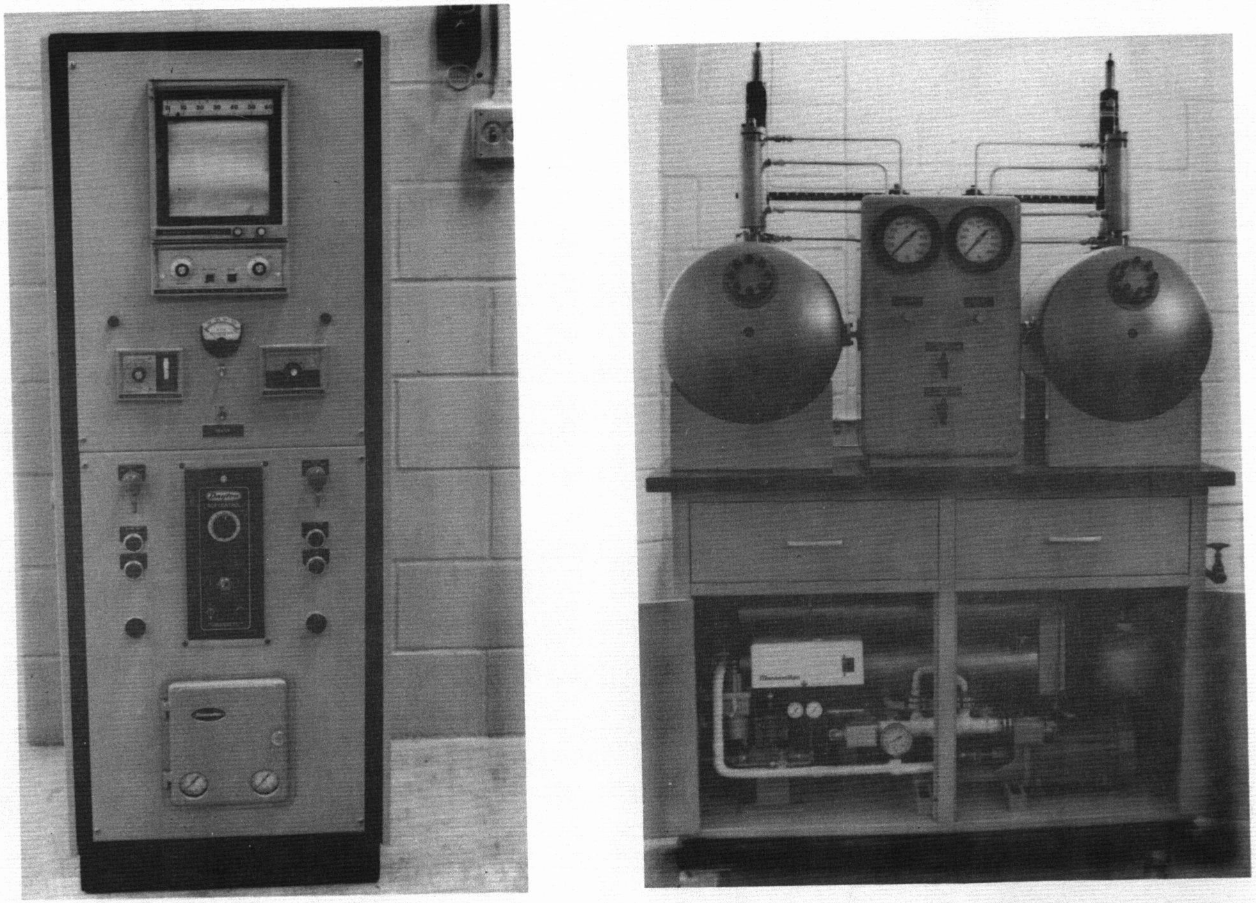


FIGURE 1 - Wetox(R) 1-10 Semi-Batch Unit

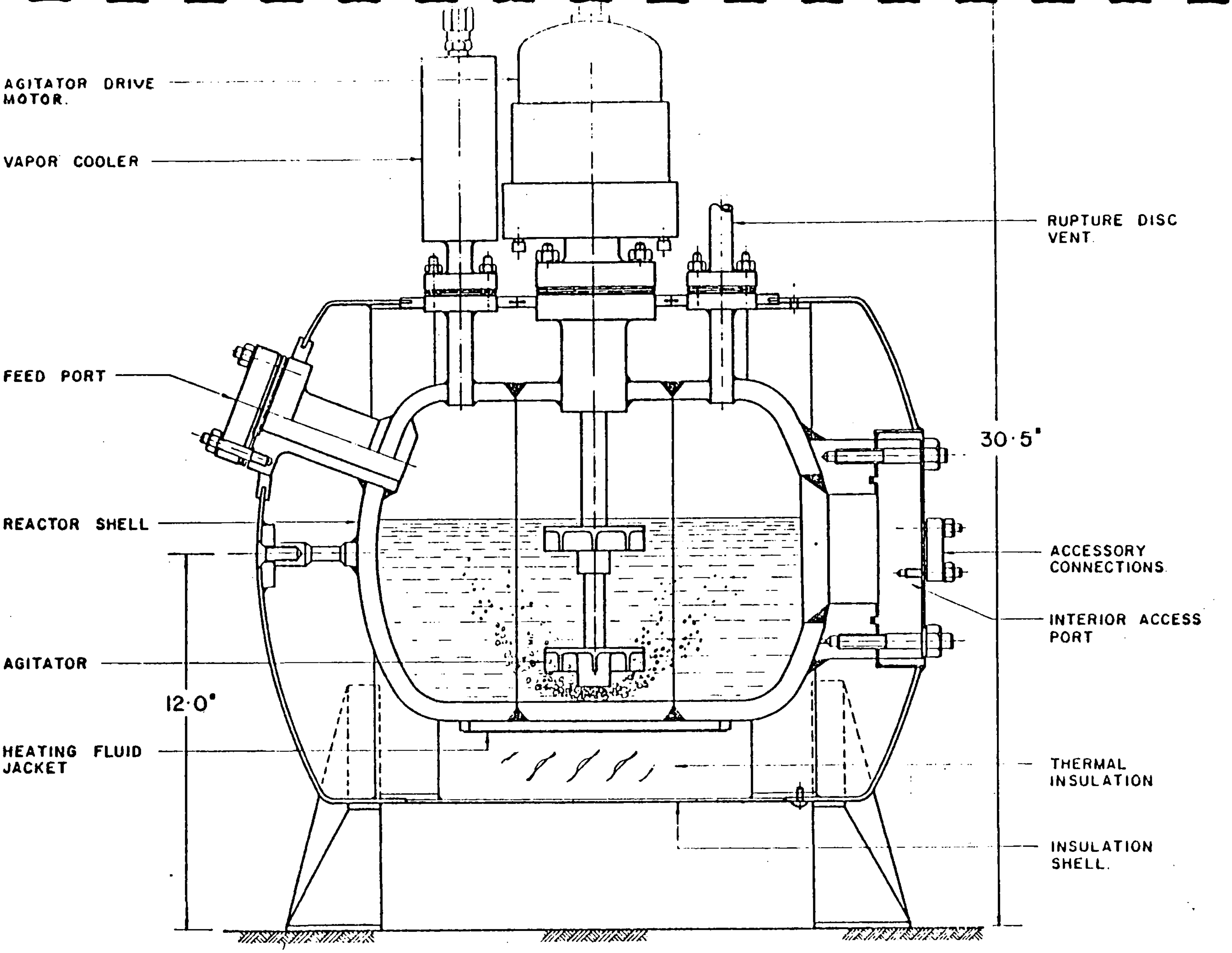


FIGURE 2 - Wetox 1-10 Batch Reactor

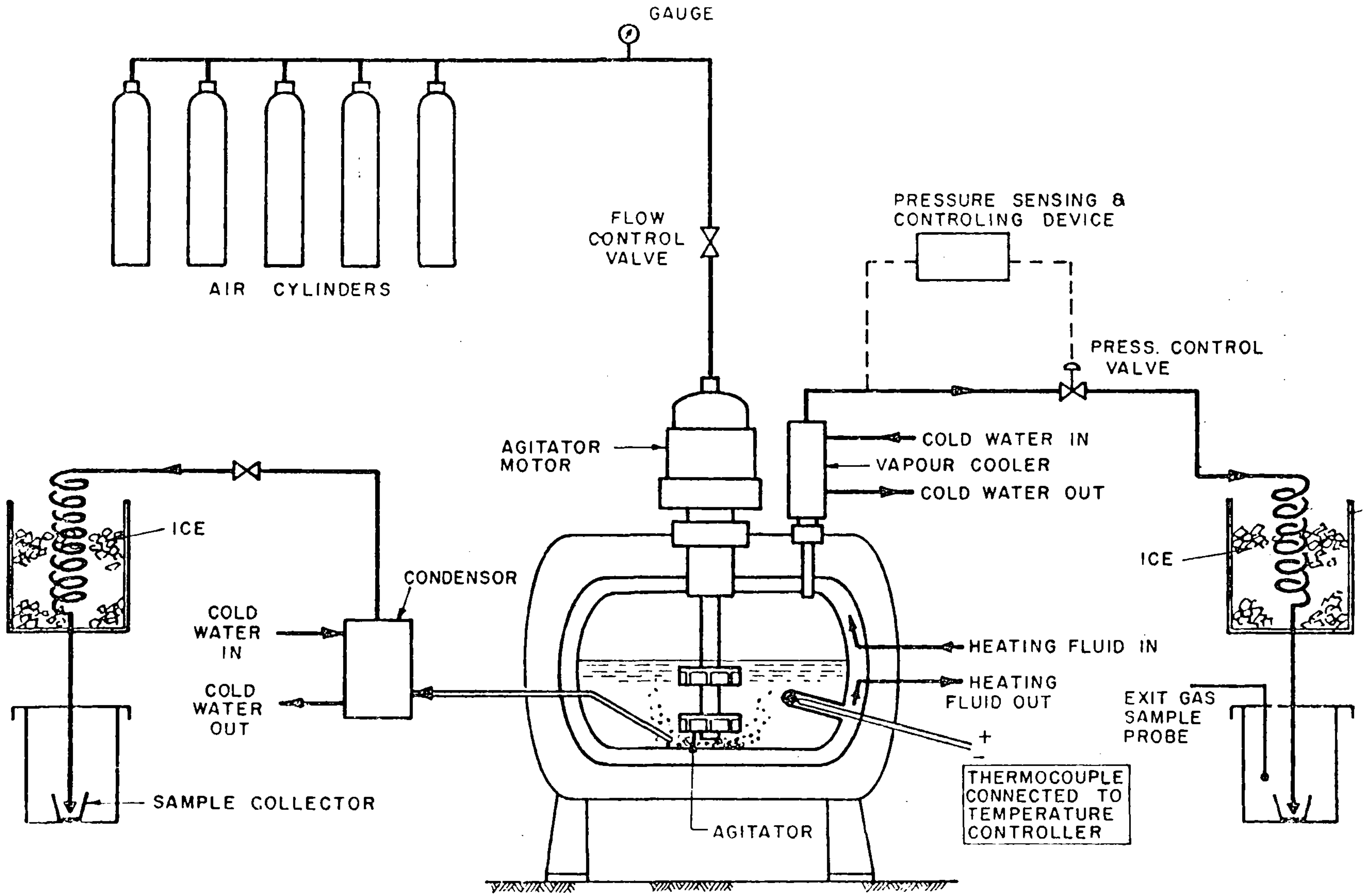


FIGURE 3 - Process Schematic Diagram

APPENDIX D

Mobile Continuous Flow Pilot Plant

1. INTRODUCTION

The Wetox 4-10 pilot plant is a continuous flow treatment system which is capable of processing from 200 to 600 Imperial gallons per day. The unit is mounted in a truck for on-site testing and demonstrations (see accompanying photograph). The truck also contains a small laboratory to provide analyses during operation.

A process schematic of the 4-10 pilot plant is provided. The assemblance of equipment includes devices to:

(1) feed (pressurized) reactants (air or oxygen and wastewater) to the reactor,

(2) perform wet oxidation in a continuous flow reactor at elevated temperature and pressure,

(3) sample the reactor during the test (while it is at elevated temperature and pressure),

(4) control and monitor the important operating conditions such as temperature and pressure,

(5) discharge and store (depressurized) liquid-phase effluent,

(6) condense and store steam and volatile matter vented with the spent gases from the reactor,

(7) monitor the oxidant level in the spent gases from the reactor.

2. PREPARATION AND STORAGE OF WASTE

The feed sample is pumped into a 200-litre head tank located outside of the truck. The centrifugal recirculation pump withdraws fluid from the bottom of the tank and provides a divided, valved discharge to the high-pressure pump and to the head tank surface. The line to the high pressure pump is also equipped with a valved fresh water line for rinsing purposes. Where necessary, the head tank is also equipped with an agitator.

3. FEED SYSTEM

The waste is pumped via a high pressure metering plunger pump (max. flow of 26 Imperial gallons per hour).

Compressed air from the 15 h.p. air cooled compressor (max. flow of 27 standard cubic feet per minute) is stored in a 2-foot long by 8 inch diameter cylinder or accumulator. The flow from the compressor is automatically controlled to maintain from 700 to 1000 psi in the accumulator. The discharge from the accumulator is in three parts:

- high pressure air (700 psi) for agitator pressure
- low pressure (100 psi) instrument air
- high pressure air (650 psi) to the reactor.

The latter flow is monitored via a strain-gage flow-meter and controlled. This total air flow is divided into 3 main flows: to compartment 1, to compartment 2 and to compartments 3 and 4. The flow to compartment 1 and to the combined compartments 3 and 4 is monitored via similar strain-gage flow meters. The line to compartments 3 and 4 is thereafter divided. The flow to each compartment is controlled via suitable needle valves. The air enters each compartment through inlets directly below the impellers.

4. WETOX REACTOR

Prints of the detailed drawings of the 4-10 reactor are provided.

Basically the Wetox reactor is a pressurized version of the continuous stirred tank reactor - the CSTR widely used in chemical engineering. The interior is divided into approximately equally sized compartments, each containing a vertically mounted agitator and separate air inlet. The reactants pass continuously through the series of compartments. The flow of reactants is much slower than the speed of mixing in the constantly stirred chambers or tanks, and incoming fluid immediately blends with the much larger mass of constantly stirred liquid already present in the vessel. As fresh wastewater is added to the first compartment, the level of the agitating liquid rises above the overflow opening in the barrier between the first and second compartments - a portion of the liquid spills over into the second compartment and, in so doing, causes a portion of the liquid in the second compartment to spill into the third and so on throughout the reactor. In this manner, the wastewaters cascade from compartment to compartment during treatment, undergoing intimate mixing continuously. At steady state, the concentrations of the reactants in individual compartments are invariant. The rate of reaction and extent (percentage reduction) depend on the mass flow through the reactor and the operating conditions.

The pilot plant reactor is a 10 inch OD, 48 inch long autoclave. The reactants are mixed sequentially in a series of four mixing chambers. The interior of the reactor is subdivided into 5 chambers, four of which are approximately equal in size and contain agitators. The fifth chamber located at the rear of the reactor is smaller than the others; it contains no agitator and serves as a phase-separation basin. Automatically controlled, separate vents for the vapour and liquid phases are located in the settling basin. The chambers or compartments are formed by four approximately equally spaced, vertically positioned plates of 1/4 inch thick titanium metal. Each plate (partition) is fastened securely to the periphery of the reactor shell to form a water-tight dam. Each partition has a small notch or weir at the liquid level, approximately 7.5 inches above the floor of the reactor. The weir in each partition is 0.25 inches lower than that in the preceding wall, causing liquid to cascade from compartment to compartment as fresh influent enters the first compartment.

Each mixing compartment contains a vertically mounted, motor-driven agitator. All impellers are six-bladed turbines. Two titanium, three inch diameter impellers are mounted on each shaft. In all compartments, one impeller is located within 1 inch of the floor of the reactor and the other barely below the surface of the liquid. Each agitator is equipped with double mechanical balanced seals. The speed of rotation is 900 rpm.

External heat can be supplied to the reactor by four electrically heated rods which are inserted externally into four tubular protrusions extending horizontally into the first compartment. Once the reactor is hot and the blow-case pump is operating, a substantial amount of heat is recovered by the heat exchanger described in a preceding paragraph. The two heaters located near the floor of the reactor well beneath the water level are activated as needed by an automatic controller.

Samples of the liquid phase can be removed from any of the mixing compartments as desired during the test by manually operated sampling tubes.

5. HEAT EXCHANGER

Influent exits from the high-pressure pump and enters the first compartment of the reactor via a tube-in-tube heat exchanger (see attached print of detailed drawing). The tubes comprising the heat exchanger are arranged in a horizontal array and enclosed in a thermally insulated rectangular box. The cold influent first is contacted by the vapours and gases vented from the reactor and then by the liquid-phase effluent. The vapour-liquid exchanger has a path length of 20 feet. The liquid-liquid exchanger path length is 70 feet. The surface area available for heat transfer is about 6 square feet in the combined exchangers. When cold water is pumped through the exchangers and into a 400°F reactor by a high-pressure pump, the influent and effluent approach nearly continuous flow. Under these conditions, the overall coefficient of heat transfer is about 150 $\text{Btu/hr-ft}^2\text{-°F}$.

6. VAPOUR-PHASE EFFLUENT

Compressed air or pure oxygen is fed continually to each compartment in proportion to the input COD. The incoming gas is introduced through small openings in the floor of each compartment beneath the liquid. Rising bubbles of gas are mixed thoroughly with the agitating liquid and become saturated with steam (and volatile organic species). As gas and wastewater are added to the reactor, its total pressure increases until it exceeds the desired maximum and a pressure-regulated valve is actuated. Each time the valve opens, steam (water-saturated gas and vapours) passes from the reactor through the vapour vent generally located in the rear.

All exiting gas (vapours and steam) are passed through the heat exchanger in which the vapours and steam are condensed. This vapour-phase condensate (VPC) is collected and sampled for each test.

7. LIQUID-PHASE EFFLUENT

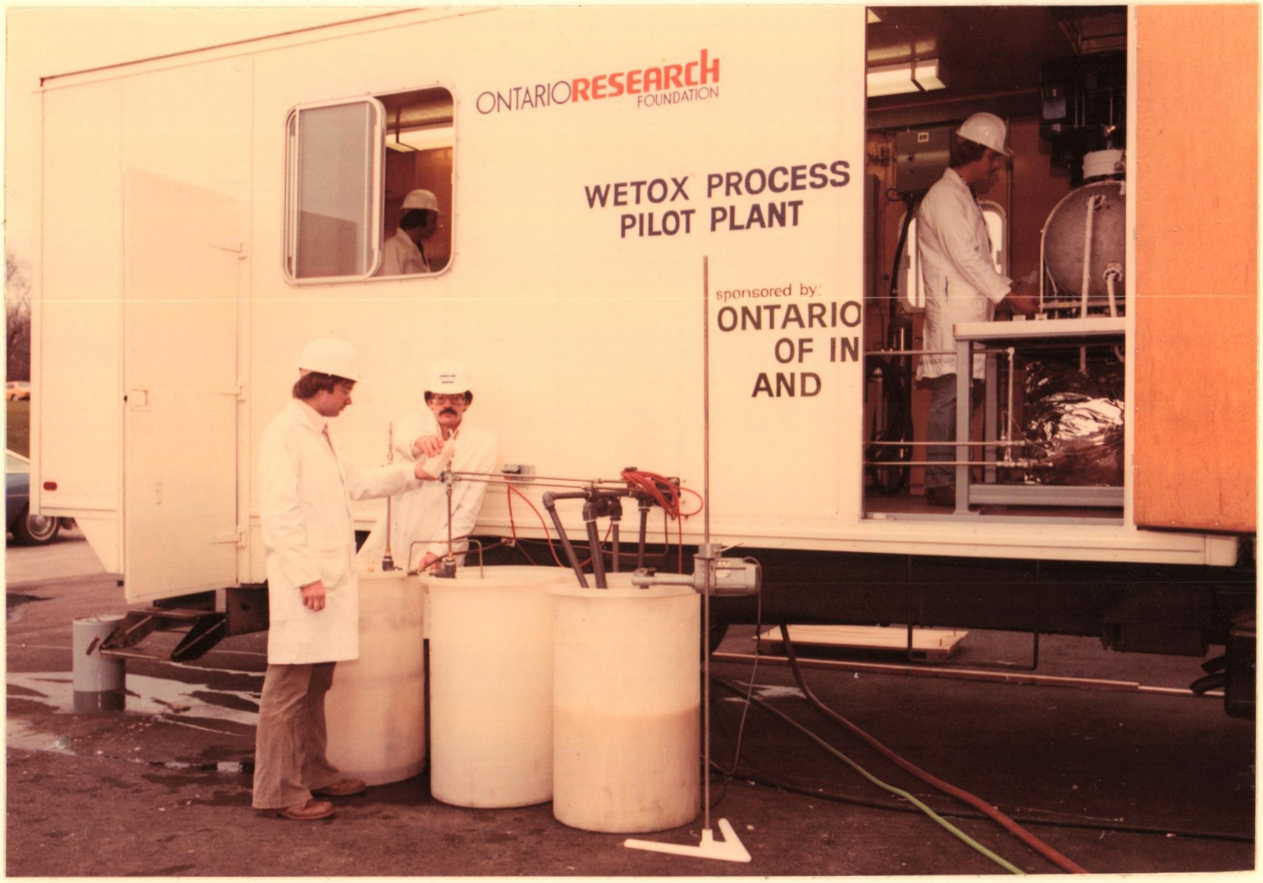
The liquid-phase discharge from the reactor is a slurry of insoluble solids suspended in a liquor containing residual water-soluble organic matter as well as dissolved inorganic salts and acid. This liquid-phase slurry generally is referred to as the liquid-phase effluent (LP). It is depressurized by a separate liquid let-down system and collected in a storage tank.

The liquid let-down system is activated by a conductivity probe located in the settling basin at the rear of the reactor adjacent to the fourth mixing compartment. Whenever the level of liquid in the settling basin rises above the probe, a ball-cock valve opens and liquid is forced out of the reactor. The liquid discharge from the autoclave passes through the tube-in-tube heat exchanger countercurrent to the flow of influent. Liquid enters the effluent storage tank at about 160°F.

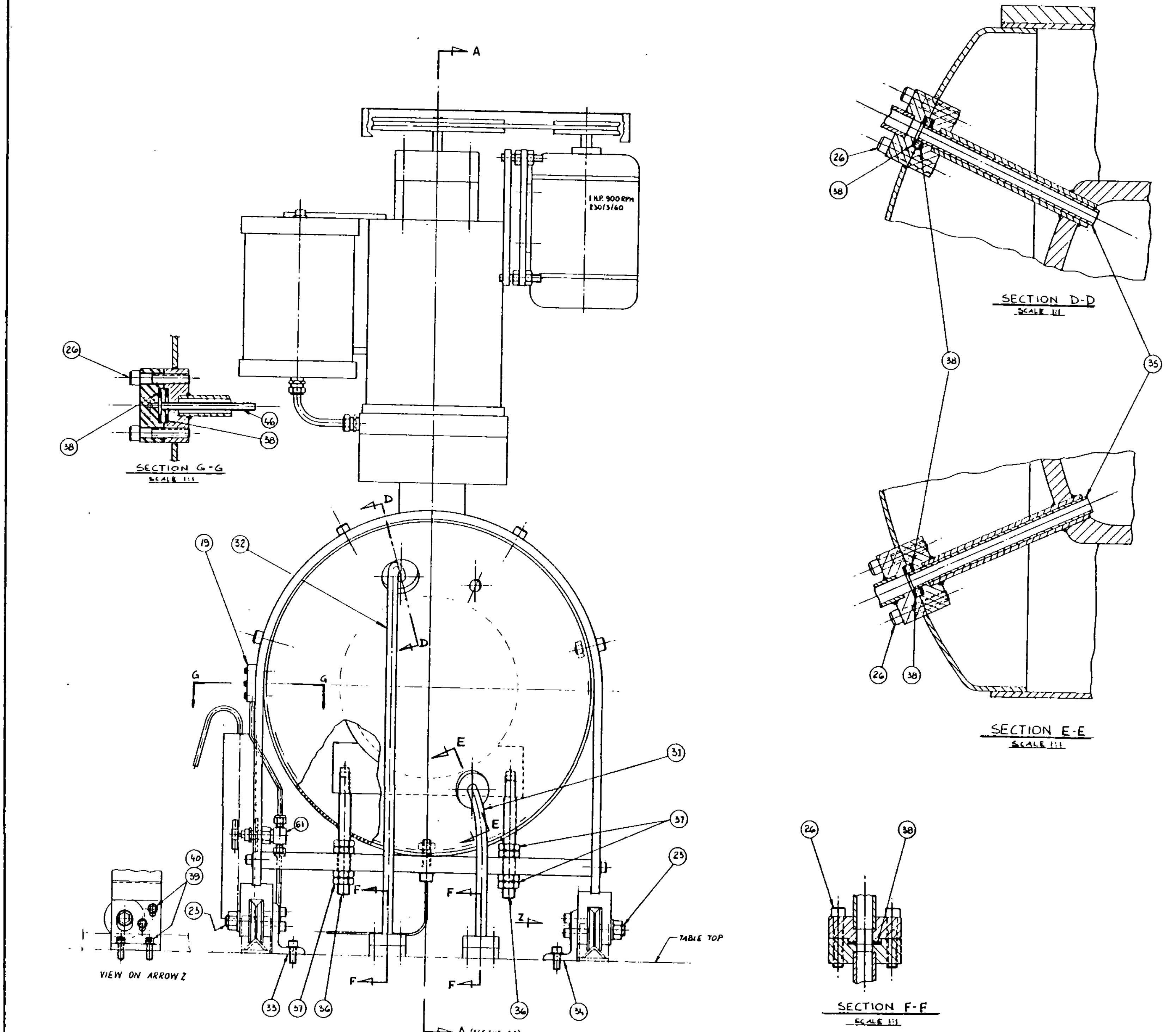
8. TEST PROCEDURE

The general test procedure includes the following steps:

- The reactor and agitator are pressurized.
- Fresh water is pumped into the reactor until the unit is filled.
- The heaters are then turned on and a small flow of air established to each compartment.
- After the reactor is at the desired temperature, waste is pumped at the desired rate through the heat exchanger and into the reactor. The air flow is adjusted accordingly. Steady-state temperatures throughout the process are generally achieved 60 to 90 minutes after pumping begins.
- The off-gas is monitored for oxygen concentration and adjustments to the oxidant flow made, if required.
- Feed is pumped for 2 to 3 reactor volumes (e.g. approximately 90 litres) to achieve steady-state concentrations throughout the process.
- Samples are then withdrawn from each compartment and from the feed, LPE and VPC.
- Temperatures and pressures are recorded throughout the process.


ONTARIO RESEARCH FOUNDATION
WETOX PROCESS
PILOT PLANT
sponsored by:
ONTARIO
OF IN
AND

[illegible]	Nº REQ'D	[illegible]	DE[illegible]ON	[illegible]
31	1	ORF-77152	LIQUID EFFLUENT OUTLET - AUTOCLAVE	.99
32	1	ORF-77153	VAPOR EFFLUENT OUTLET - AUTOCLAVE	1.76
33	1	ORF-77154	SUPPORT ANGLE	1.81
34	1	ORF-77155	SUPPORT ANGLE	1.37
35	2	ORF-77191	INSERT - EFFLUENT OUTLET STEM	.24
36	4	ORF-77192	STUD-AUTOCLAVE ENDS SUPPORT	1.52
△1 37	24		3/4-10 UNC HEX JAM NUT	.24
38	22		FLEXITALLIC GASKET [illegible]	–
39	8		3/8-16UNC-1 1/4 HEX SOC HD CAP SCREW	.30
40	8		3/8 FLAT WASHER	.08



VIEW ON ARROW 'G'
(SEE SHT Nº 1)

△1	APR 25 1978	E.K.	ITEM 37: WAS 3/4-10 UNC HEX. NUT
Nº	DATE	BY	DESCRIPTION

REVISION

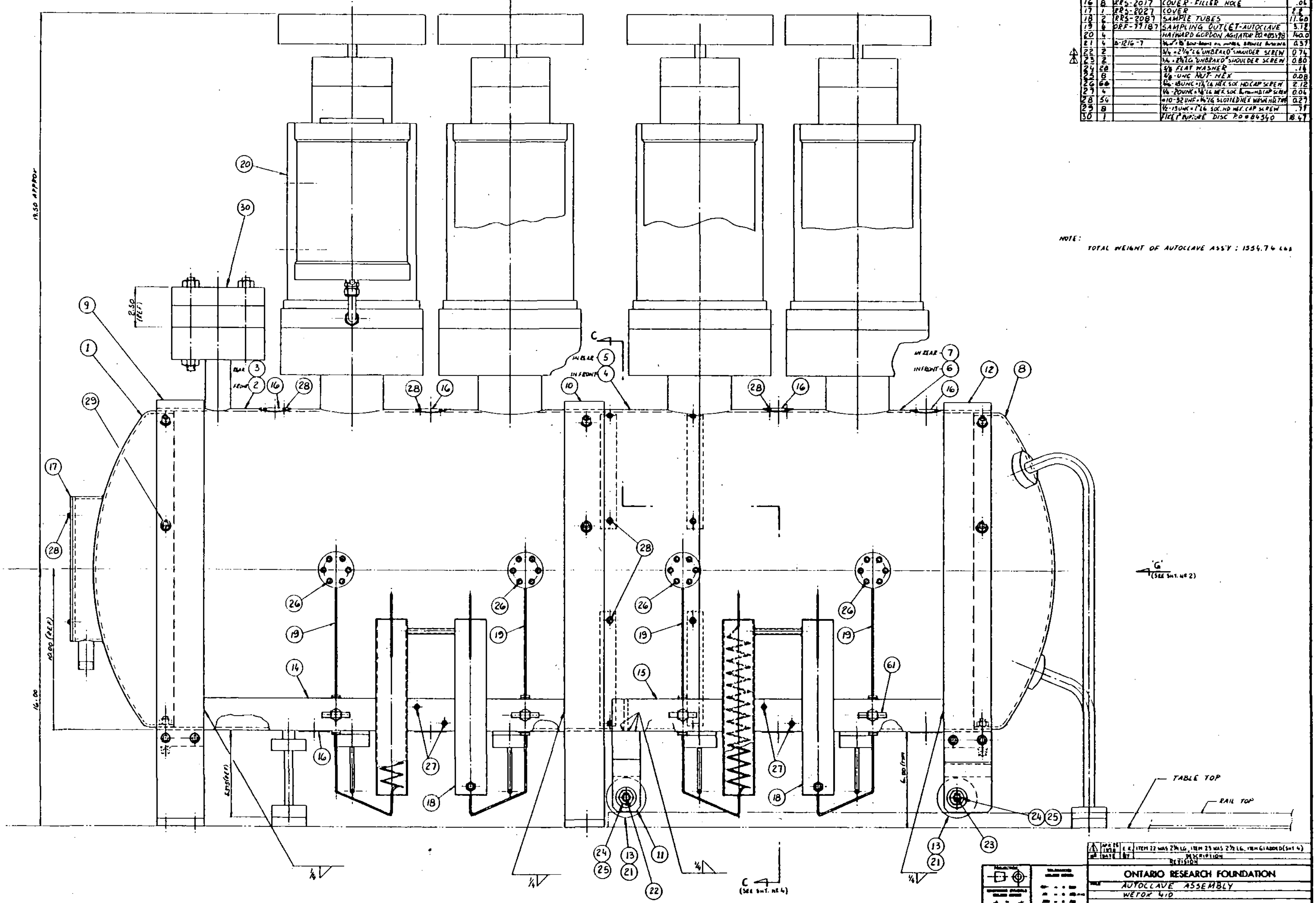
ONTARIO RESEARCH FOUNDATION

AUTOCLAVE ASSEMBLY
WETOX 410

SCALE 1:2
DRAWN BY R.D.R.
DATE DEC/17/77
ORF-77101
SHT 2 OF 4
E

ITEM Nº	Nº REQ'D	[illegible]	DES[illegible]N	[illegible]
1	1	ORF-77136	DISHED HEAD L.H	13.36
2	1	ORF-77137	OUTER SHELL L.H. FRONT	37.28
3	1	ORF-77138	OUTER SHELL L.H REAR	36.40
4	1	ORF-77139	OUTER SHELL INSERT FRONT	7.38
5	1	ORF-77140	OUTER SHELL INSERT REAR	7.11
6	1	ORF-77141	OUTER SHELL R.H. FRONT	25.60
7	1	ORF-77142	OUTER SHELL R.H. REAR	32.09
8	1	ORF-77143	DISHED HEAD R.H.	10.20
9	1	ORF-77144	END SUPPORT L.H.	45.56
10	1	ORF-77145	CENTRE SUPPORT	37.81
11	1	ORF-77146	CENTRE WHEEL BRACKET	22.95
12	1	ORF-77147	END SUPPORT R.H.	48.63
13	4	ORF-77148	WHEEL	6.00
14	1	ORF-77149	SAMPLE TUBES MOUNTING BKT L.H	3.23
15	1	ORF-77150	SAMPLE TUBES MOUNTING BRACKET R.H	3.08
16	8	RRS-2017	COVER-FILLER HOLE	.06
17	1	RRS-2027	COVER	2.8
18	2	RRS-2087	SAMPLE TUBES	11.60
19	6	ORF-77187	SAMPLING OUTLET-AUTOCLAVE	5.12
20	4		HAYWARD GORDON AGITATOR P.O.#83498	140.0
21	4	B-1216-7	3/4"×1/2" [illegible] OIL IMPREG. BRONZE BUSHING	0.37
22	2		3/4×2¾"LG "UNBRAKO" SHOULDER SCREW	0.74
23	2		3/4×2¾LG. "UNBRAKO" SHOULDER SCREW	0.80
24	28		5/8 FLAT WASHER	.16
25	8		5/8-UNC NUT-HEX	0.08
26	66		5/16-18UNC×1¼"LG HEX.SOC.HD.CAP SCREW.	2.12
27	4		1/4-20UNC×3/4"LG HEX.SOC.[illegible] HD.CAP SCREW	0.06
28	54		#10-32UNF×1/4"LG SLOTTED HEX WASH.HD.TAP	0.27
29	8		1/2-13UNC×1"LG. SOC.HD HEX.CAP SCREW	.77
30	1		FIKE RUPTURE DISC P.O.#84540	18.47

NOTE:
TOTAL WEIGHT OF AUTOCLAVE ASS'Y : 1554.74 LBS



Nº	DATE	BY	DESCRIPTION
1	APR 26 1978	E.K.	ITEM 22 WAS 2¾ LG, ITEM 23 WAS 2½ LG, ITEM 61 ADDED (SHT 4)

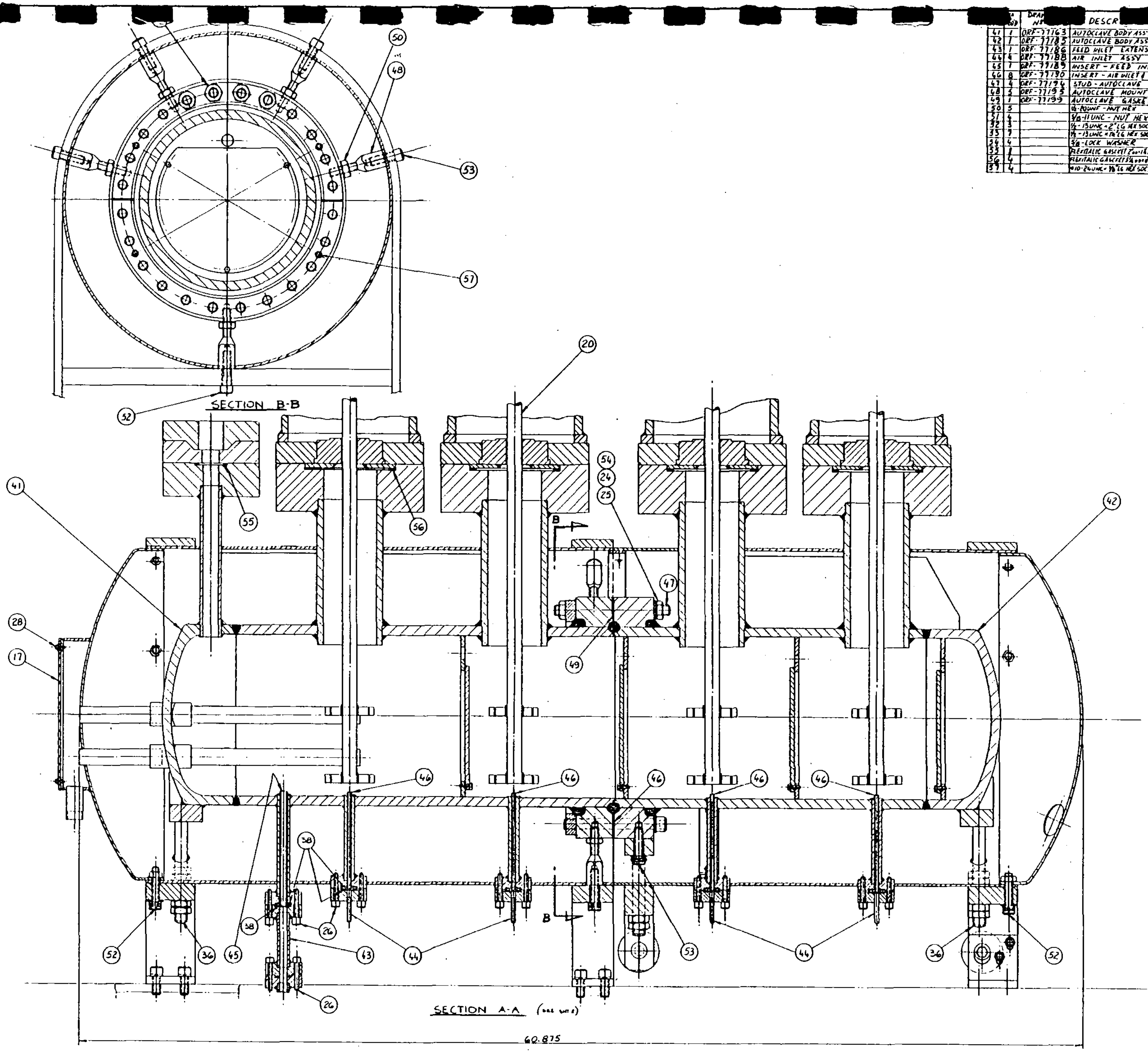
REVISION

ONTARIO RESEARCH FOUNDATION

TITLE AUTOCLAVE ASSEMBLY
WETOX 410

SCALE 1:2
DRAWN BY E.S.R.
DATE DEC/14/77
CHECKED
DATE
DWG NO. ORF-77101 E
SHEET 1 OF 4

ITEM	QTY REQ'D	DRA... N...	DESCR...	
41	1	ORF-77163	AUTOCLAVE BODY ASSY L.H.	215.13
42	1	ORF-77185	AUTOCLAVE BODY ASSY R.H	185.00
43	1	ORF-77186	FEED INLET EXTENSION	.18
44	4	ORF-77188	AIR INLET ASSY	5.92
45	1	ORF-77189	INSERT - FEED INLET	.12
46	8	ORF-77190	INSERT - AIR INLET & SAMPLING	1.20
47	4	ORF-77194	STUD - AUTOCLAVE	2.36
48	5	ORF-77195	AUTOCLAVE MOUNT LUG	2.20
49	1	ORF-77199	AUTOCLAVE GASKET	—
50	5		½-20UNF - NUT HEX	.05
51	4		⅝-11UNC - NUT HEX - JAM	.06
52	3		½-13UNC × 2" LG HEX SOC HD CAP SCREW	.44
53	7		½-13UNC × 1½" LG HEX SOC HD CAP SCREW	.88
54	4		⅝-LOCK WASHER	.06
55	1		FLEXITALLIC GASKET 2.00 × 1.5 × .125 10.84590	—
56	4		FLEXITALLIC GASKET ¾ × ... 10.84594	—
57	4		#10-24UNC × ⅝" LG HEX SOC HD CAP SCREW	.03



ONTARIO RESEARCH FOUNDATION

TITLE AUTOCLAVE ASSEMBLY
WETOX 410

SCALE 1:2
DRAWN BY P.I.R.
DATE DEC/18/77
CHECKED
DATE
DWG. NO. ORF-77101
SHEET 3 OF 4
E

APPENDIX E

Pilot Plant Operating Conditions & Results

PILOT PLANT TEST RESULTS

1. INTRODUCTION

The 4-10 continuous flow pilot plant was employed to establish reaction kinetics on three different wastes in the program. Operation and equipment descriptions of this unit are presented in detail in Appendix D.

The wet air oxidation reaction is typically two first order reactions in series, as depicted in Figure 1 for the batch test on PCP waste (CuO). From these batch scale kinetics, the performance of a series of continuous stirred tank reactors (i.e. the 4-10 Wetox reactor) can be predicted.

This prediction was undertaken in this program with the aid of a graphical technique originated by R. W. Jones(4). An example of this method is given in Figure 2.

A prediction of full-scale performance is useful for establishing optimum residence times for pilot testing, as well as determining necessary oxidant (air) flowrates to each of the reactor's four compartments.

2. TEST RESULTS

There are two tables provided for each of the seven continuous flow pilot plant tests.

The first table of each set outlines the specific operating conditions of the particular experiment. Data given include system parameters such as waste and air flowrates, compartment temperatures, etc.

The second table of each set tabulates the results obtained in the experiments. COD determinations were used to evaluate process performance. Terminology used in this table that has not been defined to this point is presented below:

LPE - Liquid Phase effluent from the reactor
VPC - Vapour Phase condensate from the reactor
Calculated COD - Based on air flowrate and compartment temperature and pressure, the flowrate of both the liquid and vapour can be calculated. Therefore, assuming that the COD of the vapour remains constant throughout the reactor, the calculated COD in compartment 'n' is:

$$\text{COD} = \frac{\text{VPC Flowrate} \times \text{COD}_{\text{VPC}} + \text{LPE Flowrate} \times \text{COD}_n}{\text{Total Waste Flowrate}}$$

where: COD_n is the measured COD from the n^{th} compartment

The results from three series of continuous flow experiments will be presented individually according to the material investigated:

Pentachlorophenol (PCP)
Mercaptobenziothiazole (MBT)
Diphenylamine (DPA)

2.1 PCP Waste

Three pilot experiments were undertaken on PCP waste. The operating conditions and results for PCP waste with no addition, copper catalyst and copper catalyst plus acid are presented in Tables 1a and 1b, 2a and 2b, and 3a and 3b respectively.

The air control valves into the third and fourth compartments of the reactor were grossly oversized because of the very low oxygen requirement. Therefore, accurate air flowrates into these compartments could not be made.

Two reasons for the very low oxygen requirements were:

(i) The reaction kinetics established from batch scale results indicated that about 90% of the total oxygen was required in the first compartment.

(ii) The waste was received at a COD lower than normally used in pilot plant operation. Therefore, total air flowrate was necessarily low.

On all of the tables, therefore, air flows into the third and fourth compartments are listed as approximately zero.

2.2 MBT Waste

The two continuous flow experiments undertaken on MBT waste were:

(i) MBT Waste + CuO catalyst
(ii) MBT Waste + CuO + H_2SO_4

Operating conditions and results are presented in Tables 4a and 4b and 5a and 5b for (i) and (ii) above respectively.

Due to reaction kinetics developed from batch scale test results, air requirements for the third and fourth compartments of the reactor were abnormally low. Although the residence time could have been decreased, it was desired to achieve maximum destruction within reasonable reactor residence times. Because of this, therefore, it was difficult to accurately establish air flowrates to these two compartments. Thus, the air flowrate to these compartments on all tables is indicated as being approximately zero.

From Table 5b, it can be seen that there is a COD increase in the last two compartments. Two reasons were suggested for this anomaly:

(i) Experimental or analytical error.

(ii) If insufficient air was admitted to the third and fourth compartments, the actual steam flowrate would decrease.

Therefore, volatile or steam strippable compounds which were carried into the vapour phase in the first half of the reactor may have precipitated back into the liquid phase in the last two compartments.

2.3 DPA Waste

Two continuous flow pilot plant experiments were performed on DPA waste. The conditions of the experiments were:

(i) DPA Waste + CuO
(ii) DPA Waste + CuO + H_2SO_4

The experimental operating conditions and results are presented in Tables 6a and 6b and 7a and 7b for (i) and (ii) above respectively.

The results and operating conditions for DPA waste were analogous to those for MBT waste. This is because the COD contribution of the pure chemical (i.e. MBT or DPA) to the COD of the pilot plant waste feed was less than 5%.

Again, due to very low oxygen requirements for the third and fourth compartments, the air flowrates are indicated on all tables as approximately zero.

It can be seen from Table 7b that the COD increased over the last two compartments. This phenomenon also occured during the pilot plant test on MBT waste with CuO and acid. Two explanations were suggested:

(i) Experimental or analytical error.
(ii) Volatile or steam strippable materials produced in the first two compartments precipitated out of the vapour and back into the liquid in the last two compartments.

Since this occurred on two separate occasions, the latter of these explanations is most realistic. This suggests, therefore, that air flow to these compartments was definitely too low.

TABLE 1a - Test Conditions - PCP Waste/No Additions

Waste Feed:	PCP Waste - no additions	
Waste Pumping Rate:	Water Flow Rate:	0.653 litres/min
	COD Flow Rate:	2.76 g/min
Reactor Residence Time:	55 mins	
Air Flow Rate:		scfm
	Compartment #1	0.4
	Compartment #2	0.2
	Compartment #3	~ 0
	Compartment #4	~ 0
	Total	0.6
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	458
	Compartment #2	443
	Compartment #3	435
	Compartment #4	430
	Mean Reactor Temperature	441.5
Water Balance:	Measured Liquid Produced:	0.623 L/min
	Measured Steam Produced:	0.030 L/min
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	16%
	Oxygen Consumed as Fraction of Supplied:	23.4%
	Total Oxygen Consumed:	1.1 g/min

TABLE 1b - Test Results - PCP Waste/No Additions

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	653		4220		2750				
Compartment #1	634.2	18.77	1230	1222	798	1958	71	3160	
Compartment #2	634.6	18.36	1080	1077	703	95	3.4	1600	
Compartment #3	637.9	15.10	930	931	608	95	3.4	∿ 0	
Compartment #4	639.3	13.67	900	901	588	19	0.7	∿ 0	
LPE	623		708						
VPC		30	953						
Totals						2167	78.6	4760	1100

TABLE 2a - Test Conditions - PCP Waste/Copper

Waste Feed:	PCP Waste + 145 g $CuSO_4$	
Waste Pumping Rate:	Water Flow Rate:	0.653 L/min
	COD Flow Rate:	2.8 g/min
Reactor Residence Time:	55 mins	
Air Flow Rate:		scfm
	Compartment #1	0.4
	Compartment #2	0.2
	Compartment #3	∿ 0
	Compartment #4	∿ 0
	Total	0.6
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	454
	Compartment #2	441
	Compartment #3	435
	Compartment #4	429
	Mean Reactor Temperature	439.8
Water Balance:	Measured Liquid Produced:	0.623 L/min
	Measured Steam Produced:	0.030 L/min
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	16%
	Oxygen Consumed as Fraction of Supplied:	23.4%
	Total Oxygen Consumed:	1.1 g/min

TABLE 2b - Test Results - PCP Waste/Copper

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	653		4340		2834				
Compartment #1	637	16	961	960	627	2206	77.9	3160	
Compartment #2	363	17	868	870	568	59	2.1	1600	
Compartment #3	638	15	831	833	544	23	0.8	∿ 0	
Compartment #4	640	13	837	835	545	∿ 0	∿ 0	∿ 0	
LPE	623		667						
VPC		30	953						
Totals						2288	80.8	4760	1100

TABLE 3a - Test Conditions - PCP Waste/Copper + Acid

Waste Feed:	PCP Waste + 145 g $CuSO_4$ + H_2SO_4 → pH = 2	
Waste Pumping Rate:	Water Flow Rate:	0.655 L/min
	COD Flow Rate:	2.74 g/min
Reactor Residence Time:	55 mins	
Air Flow Rate:		scfm
	Compartment #1	0.4
	Compartment #2	0.2
	Compartment #3	no
	Compartment #4	no
	Total	0.6
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	456
	Compartment #2	443.5
	Compartment #3	437.5
	Compartment #4	430.5
	Mean Reactor Temperature	442
Water Balance:	Measured Liquid Produced:	0.625 L/min
	Measured Steam Produced:	0.030 L/min
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	17%
	Oxygen Consumed as Fraction of Supplied:	18.6%
	Total Oxygen Consumed:	0.88 g/min

TABLE 3b - Test Results - PCP Waste/Copper + Acid

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	655		4190		2744				
Compartment #1	637.5	17.5	1080	1076	705	2039	74	3160	
Compartment #2	636.4	18.6	812	816	535	170	6.2	1580	
Compartment #3	638.9	16.1	722	727	476	58	∿0.2	∿ 0	
Compartment #4	651.3	13.7	656	662	434	42	1.5	∿ 0	
LPE	625		642						
VPC		30.0	953						
Totals						2310	84	4740	

TABLE 4a - Test Conditions
MBT Waste/Copper

Waste Feed: MBT Waste + 145 g $CuSO_4$

Waste Pumping Rate:	Water Flow Rate:	0.391 L/min
	COD Flow Rate:	18.4 g/min
Reactor Residence Time:	92 mins	
Air Flow Rate:		scfm
	Compartment #1	1.3
	Compartment #2	0.4
	Compartment #3	≃0.0
	Compartment #4	≃0.0
	Total	1.7
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	463
	Compartment #2	460
	Compartment #3	458
	Compartment #4	453
	Mean Reactor Temperature	458.5
Water Balance:	Measured Liquid Produced:	0.316 L/min
	Measured Steam Produced:	0.075 L/min
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	4.5%
	Oxygen Consumed as Fraction of Supplied:	78%
	Total Oxygen Consumed:	10.4 g/min

TABLE 4b - Test Results - MBT Waste/Copper

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	391		48,500		18,964				
Compartment #1	320	70	31,500	26,098	10,204	8760	46	10,300	
Compartment #2	306	85	27,900	22,280	8,711	1492	7.9	3,200	
Compartment #3	311	80	24,500	19,949	7,800	911	4.8	∿ 0	
Compartment #4	323	68	24,300	20,385	7,971	∿ 0	∿ 0	∿ 0	
LPE	316		21,300	18,000	7,100				
VPC		75	2,200						
Totals						11163	58.7	13,500	10,400

TABLE 5a - Test Conditions - MBT Waste/Copper & Acid

Waste Feed:	MBT Waste + 145 g $CuSO_4$ + H_2SO_4 → pH = 2	
Waste Pumping Rate:	Water Flow Rate:	0.412 L/min
	COD Flow Rate:	17.6 g/min
Reactor Residence Time:	87 mins	
Air Flow Rate:		scfm
	Compartment #1	1.3
	Compartment #2	0.2
	Compartment #3	≃ 0
	Compartment #4	≃ 0
	Total	1.5
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	458.5
	Compartment #2	455.5
	Compartment #3	453.5
	Compartment #4	448.5
	Mean Reactor Temperature	454
Water Balance:	Measured Liquid Produced:	0.287
	Measured Steam Produced:	0.125
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	4.5%
	Oxygen Consumed as Fraction of Supplied:	78.5%
	Total Oxygen Consumed:	9.3 g/min

TABLE 5b - Test Results - MBT Waste/Copper + Acid

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	412		42,700		17,592				
Compartment #1	350	62.0	12,800	12,550	5170.6	12,421.4	70.6	10,270	
Compartment #2	345.6	66.4	12,400	12,190	5022.3	148.3	0.8	1,580	
Compartment #3	350.7	61.3	13,200	12,880	5306.6	- 284.3	- 1.6	~ 0	
Compartment #4	358.9	53.1	14,200	13,790	5681.5	- 374.9	- 2.1	~ 0	
LPE	287		19,100						
VPC		125	11,100						
Totals						11,910	67.7	11,850	9,300

TABLE 6a - Test Conditions
- DPA Waste/Copper

Waste Feed:	DPA Waste + 145 g $CuSO_4$	
Waste Pumping Rate:	Water Flow Rate:	0.419 L/min
	COD Flow Rate:	20.3 g/min
Reactor Residence Time:		
Air Flow Rate:		scfm
	Compartment #1	1.5
	Compartment #2	0.4
	Compartment #3	≈ 0
	Compartment #4	≈ 0
	Total	1.9
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	460
	Compartment #2	456
	Compartment #3	454
	Compartment #4	449
	Mean Reactor Temperature	455
Water Balance:	Measured Liquid Produced:	0.312 L/min
	Measured Steam Produced:	0.107 L/min
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	8.7%
	Oxygen Consumed as Fraction of Supplied:	58%
	Total Oxygen Consumed:	8.7 g/min

TABLE 6b - Test Results - DPA Waste/Copper

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	419		84,500		20,322				
Compartment #1	343.9	75.1	32,200	26,778	11,220	9102	44.8	11,850	
Compartment #2	335.5	83.5	32,100	26,120	10,944	276	1.4	3,160	
Compartment #3	341.4	77.6	28,800	23,800	9,872	972	4.8	∿ 0	
Compartment #4	350.4	68.6	22,800	19,540	8,187	1785	8.8	∿ 0	
LPE	312		22,100						
VPC		107	2,100						
Totals						12,135	59.8	15,010	8700

TABLE 7a - Test Conditions - DPA Waste/Copper + Acid

Waste Feed:	DPA Waste + 145 g $CuSO_4$ + H_2SO_4 → pH = 2	
Waste Pumping Rate:	Water Flow Rate:	0.380 L/min
	COD Flow Rate:	16.3 g/min
Reactor Residence Time:		
Air Flow Rate:		scfm
	Compartment #1	1.5
	Compartment #2	0.4
	Compartment #3	≈ 0
	Compartment #4	≈ 0
	Total	1.9
Reactor Temperature Profile:		Temperature (°F)
	Compartment #1	460.5
	Compartment #2	457
	Compartment #3	455
	Compartment #4	451.5
	Mean Reactor Temperature	456
Water Balance:	Measured Liquid Produced:	0.260 L/min
	Measured Steam Produced:	0.12 L/min
Oxygen Balance:	Measured Oxygen Concentration in Exhaust:	5.0%
	Oxygen Consumed as Fraction of Supplied:	76%
	Total Oxygen Consumed:	11.4 g/min

TABLE 7b - Test Results - Waste DPA/Copper + Acid

	Water Balance		COD Balance					Oxygen Balance	
	Liquid mL/min	Steam mL/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	380		43,000		16,340				
Compartment #1	304.4	75.6	14,500	14,789	5616.4	10,723.6	66	11,850	
Compartment #2	283.95	86.05	14,100	14,520	5518	98.4	0.6	3,160	
Compartment #3	295.24	89.76	14,800	15,100	5738	- 220.0	- 1.3		
Compartment #4	306.9	73.1	14,800	15,120	5746	- 8.0	- 0.5		
LPE	260		17,900						
VPC		120	15,900						
Totals						11,050	64.8	15010	11,420

FIGURE 1 - PCP Waste

Semi Log Plot of COD Reduction with Time

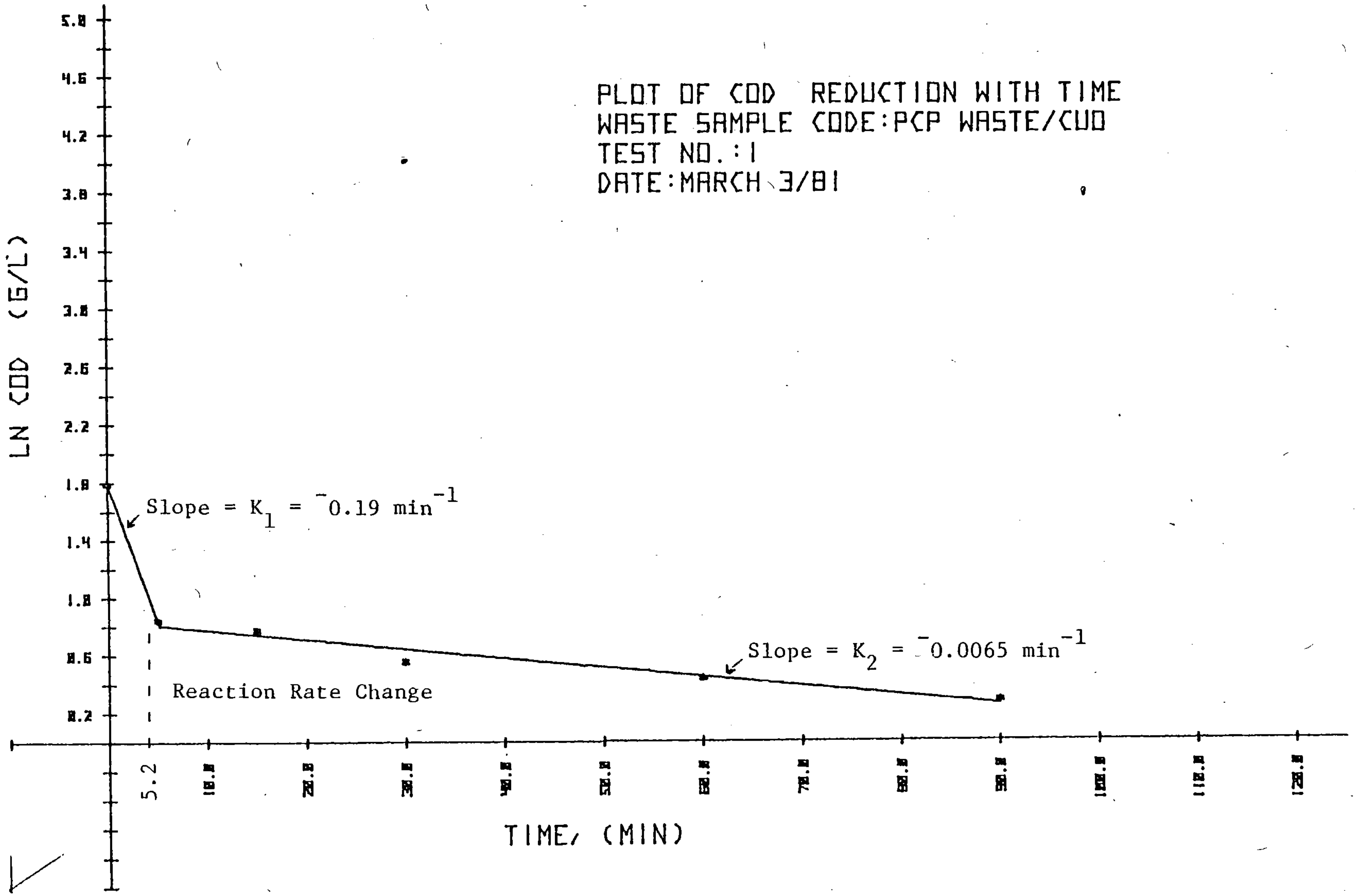
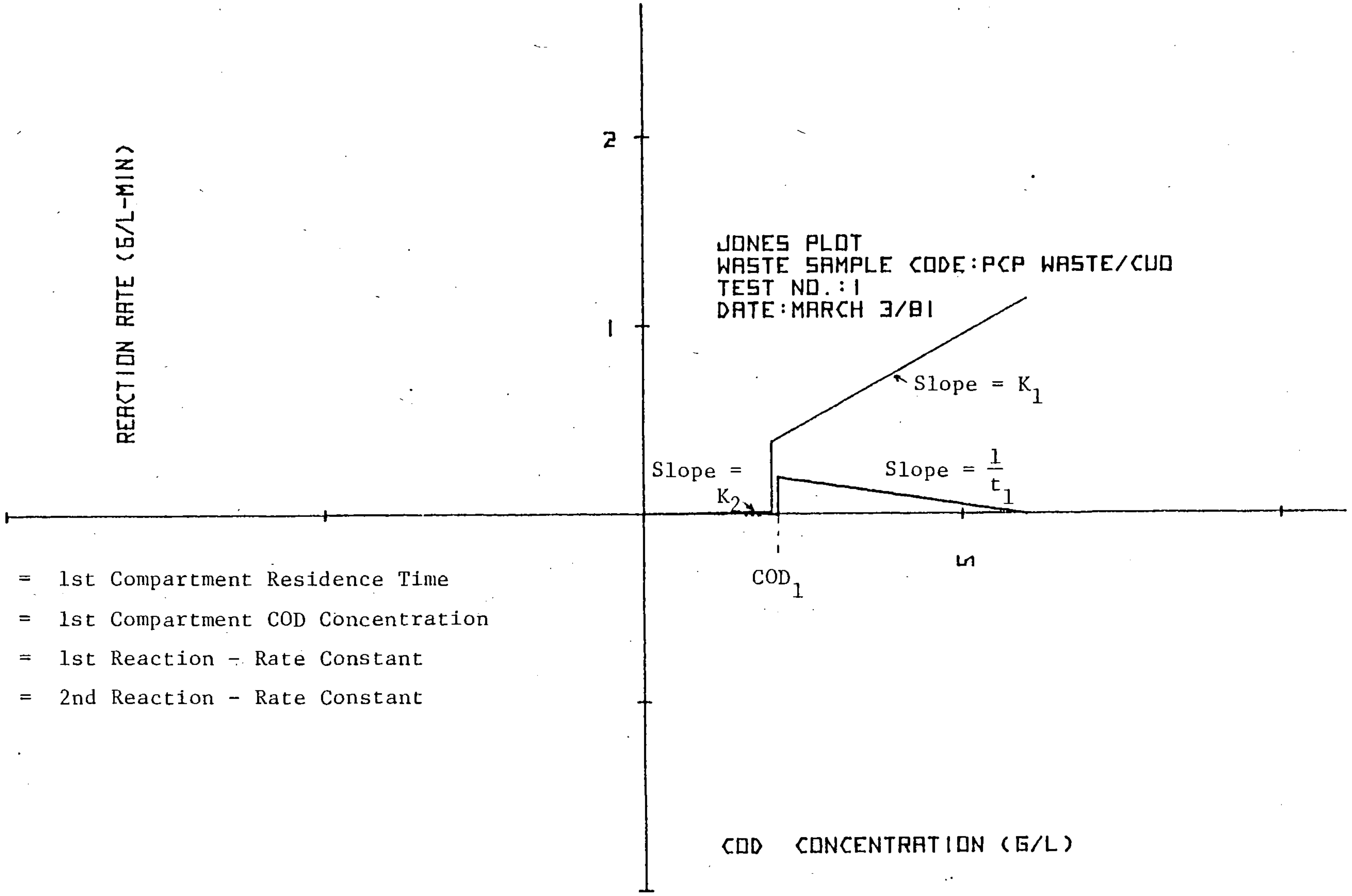


FIGURE 2 - PCP Waste

Jones Plot-Reaction Rate vs COD Concentration



t_1 = 1st Compartment Residence Time

COD_1 = 1st Compartment COD Concentration

K_1 = 1st Reaction - Rate Constant

K_2 = 2nd Reaction - Rate Constant

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