

DOE/MC/29107-93/C0184

Bench-Scale Operation of the DETOX Wet Oxidation Process for Mixed Waste

Authors:

P.M. Dhooge

DOE/MC/29107--93/C0184

DE93 009136

Contractor:

Delphi Research, Inc.  
701 Haines Ave. NW  
Albuquerque, NM 87102

OSTI

Contract Number:

DE-AC21-92MC29107

Conference Title:

Waste Management 93 Symposium

Conference Location:

Tucson, Arizona

Conference Dates:

March 3, 1993

Conference Sponsors:

University of Arizona, American Nuclear Society,  
U.S. Department of Energy, New Mexico State University  
Waste-Management Education Committee of the  
American Society of Mechanical Engineers  
etc.

MASTER

*ch*  
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

## BENCH SCALE OPERATION OF THE DETOX WET OXIDATION PROCESS FOR MIXED WASTES.

Patrick M. Dhooge  
Delphi Research, Inc.  
Albuquerque, New Mexico

### Abstract

Waste matrices containing organics, radionuclides, and metals pose difficult problems in waste treatment and disposal when the organic compounds and/or metals are considered to be hazardous. A means of destroying hazardous organic components while safely containing and concentrating metals would be extremely useful in mixed waste volume reduction or conversion to a radioactive-only form. Previous studies have found that DETOX, a patented process utilizing a novel catalytic wet oxidation by iron(III) oxidant, could have successful application to mixed wastes, and to many other waste types. This paper describes the results of bench scale studies of DETOX applied to the components of liquid mixed wastes, with the goal of establishing parameters for the design of a prototype waste treatment unit. Apparent organic reaction rate orders, and the dependence of apparent reaction rate on the contact area, were measured for vacuum pump oil, scintillation fluids, and trichloroethylene. It was found that reaction rate was proportional to contact area above about 2% w/w loading of organic. Oxidations in a 4 liter. volume, mixed bench top reactor have given destruction efficiencies of 99.9999+% for common organics. Reaction rates achieved in the mixed bench top reactor were one to two orders of magnitude greater than had been achieved in unmixed reactions; a thoroughly mixed reactor should be capable of oxidizing 10. to 100.+ grams of organic per liter-hour, depending on the nature and concentration of the organic. Results are also presented on the treatment of contaminated vermiculite, and the solvation efficiency of DETOX for mercury, cerium, and neodymium. Results of development to date have been encouraging. The next stage of development will be conversion of the bench top unit to continuous processing.

## INTRODUCTION

Wet oxidation processes can be valuable tools in the treatment/volume reduction of many waste types, including mixed wastes. The DETOX process utilizing iron(III) oxidant in an aqueous acid solution (1,2) has been shown in previous studies to have applicability to a variety of waste types, by oxidizing waste organics to carbon dioxide while containing and concentrating metals in the acidic catalyst solution. Since many mixed wastes contain very little radioactive material, the volume reductions which can be achieved are great, and in many instances the waste can be converted from a mixed waste to a radioactive-only waste. In order to further define the parameters of a practical waste treatment unit utilizing DETOX additional development studies have been conducted over the past year. The ability of the process solution to treat vermiculite, and to solvate the metals mercury, neodymium, and cerium, was investigated (More detailed metals studies are now in progress, as well as studies on the ability of the process to treat contaminated soils). The effects of organic loading, and contact area between the organic and the oxidizing solution, have been determined for vacuum pump oil, scintillation fluids, and trichloroethylene, in order to establish desirable organic loading values and mixing rates for a prototype waste treatment unit. A four liter volume, stirred bench top reactor was operated in batch mode to determine the reaction rates and destruction efficiencies for organics at larger process volume under mixed conditions. The bench top reactor also provided an opportunity to determine the suitability of some materials and components for a prototype waste treatment unit, and to measure the operating pressures and vapor composition of the DETOX solution. In the development studies described herein no major problems in the operation of the process were encountered, indicating that it will be desirable to proceed to continuous processing studies in the bench top unit as a test bed for engineering and design of the prototype waste treatment unit.

## EXPERIMENTAL

The reaction vessels used in these studies were of three types. Small test volumes were used in Parr Instrument Company (PIC) Model 4749, 23. ml general purpose bomb. Intermediate size studies were conducted in PIC Model 4751, 125. ml general purpose bombs. The bench scale studies were conducted in a PIC Model 4551, one gallon (~ 4. liter) pressure reaction apparatus with entrained gas stirrer.

The catalyst solution and other reagents were prepared from "reagent" or "ACS" grade materials and 10 Megohm-cm deionized water. Iron chloride solutions used in the bench top tests were prepared from electrolytic grade iron, reagent grade hydrochloric acid, and electronic grade hydrogen peroxide (to oxidize iron(II) to iron(III) before use). Samples of Hydrocount™ and Ready Value™ scintillation fluids, and Duoseal™ vacuum pump oil were provided by The University of California Los Alamos National Laboratory (LANL) and were used as is. Trichloroethylene was all "reagent" grade material from stock at Delphi Research, Inc. (Delphi). Organics spiked with metals were prepared using mercury metal, mercuric oxide, neodymium isopropoxide, and cerium naphthanate solution. A representative sample of the mixture was used for the metal solvation studies, or, for mercury metal, the entire mixture was used. Gases used in gas chromatography analysis were all "zero" grade. The oxygen used for pressuring the reaction vessels was standard grade.

Blank vermiculite was prepared by baking a commercial vermiculite at 523.0K for 24 hours, and was subsequently stored in a clean glass bottle; gas chromatographic purge/trap analysis of off-gas from the heated (453.0K) blank vermiculite demonstrated the absence of detectable volatile organics. Spiked vermiculite was prepared by suspending a small container of the blanked vermiculite in a sealed bottle containing Hydrocount™, Ready Value™, or trichloroethylene for at least 24. hours to achieve an equilibrium concentration of sorbed organic; gas chromatographic analysis was used to establish the pre-oxidation levels of sorbed organics.

For each oxidation the bombs were loaded with 10. ml, 50. ml, or 1500. ml of the primary catalyst solution, followed by addition of a weighed amount of cocatalyst and a measured amount of the organic. The 125. ml bombs and the bench top reactor were pressurized with 690. KPag (100. psig) of oxygen before heating. The 23. ml and 125. ml bombs were placed into an oven preheated to the desired temperature; at the end of the allotted reaction time the bombs were removed from the oven and allowed to cool in a shallow (about 1.0 cm) water bath. The bench top reactor was heated by a heater well into which the reactor body was placed; the bench top reactor was not actively cooled, and generally required several hours to cool to near room temperature from its operating temperature of 473.0K.

Iron(II) was titrated with cerium(IV), using 1,10-phenanthroline as an indicator. Gas chromatographic analysis for gases was performed using a gas sample injection loop into a Carbosphere™ column with detection by thermal conductivity. Gas chromatographic analysis for volatiles was performed by purge-trap technique, using a standard EPA Method 624 packed column and an FID detector; identification of the residual volatile material was by retention time. Volatiles and semivolatiles analyses for the destruction efficiency studies were conducted by EPA Methods 624 and 8270 at an independent commercial analytical laboratory. Analyses for mercury were conducted by cold vapor atomic absorption, with sample spiking to correct for matrix effects. Neodymium and cerium analyses were performed by inductively coupled plasma spectrophotometry at an independent commercial analytical laboratory.

## RESULTS

### Solubility of Mercury, Cerium, and Neodymium.

A variety of metals can be contaminants in mixed wastes, but the current studies have concentrated on three metals of interest in mixed waste at Los Alamos National Laboratory, namely mercury, plutonium, and uranium. Cerium and neodymium have been used in our studies to substitute for plutonium and uranium, as they have similar chemistries in the catalyst solution. Solubilities for neodymium and cerium appear to be in keeping with the solubilities to be expected from the chlorides of these metals, with neodymium soluble to the extent of about 80. g/liter catalyst solution, and cerium soluble to the extent of about 100. g/liter catalyst solution. When organics containing cerium and neodymium were oxidized in the catalyst solution, no amounts of cerium or neodymium were found in the solid residues (in fact, there was no significant solid residue after oxidations). The detection limits for the analytical method used for these two metals give a minimum of 97.% solvation, but the actual values are probably considerably higher. Mercury was tested as a contaminant in vacuum pump oil, at loadings of approximately 1.% w/w mercuric oxide (100. µg mercury in 10. mg of oil), and at 60. to 75.% w/w mercury metal (12. to 15. mg mercury in 10. mg oil). The amount of

mercury found in solids from the oxidation ranged from less than 0.15  $\mu\text{g}$  for the tests with 1.0% w/w loading to around 1.0  $\mu\text{g}$  for the tests with 60. to 75.0% w/w loading, or at least 99.98% solvation of the mercury. Mercury should be soluble to the extent of about 1.5 grams per liter of the catalyst solution, and in fact this was approximately the loading used in one of the solubility tests here. Further tests are planned to provide a more precise solubility value for mercury and to determine the ability to selectively remove mercury, lead, and cadmium from the catalyst solution as their chlorides.

### **Treatment of Contaminated Vermiculite**

Vermiculite and other similar sorbent materials contaminated with hazardous organics are a common problem waste. It was of interest to determine how effective the catalyst solution might be in destroying scintillation fluid solvents and trichloroethylene sorbed on vermiculite. After 24. hour oxidations in unmixed, 23. ml bombs, the amount of sorbed materials remaining on the vermiculite ranged from 0.5% for trichloroethylene to 0.02% for pseudocumene (1,2,4-trimethylbenzene) and o-xylene. It is believed that the actual amount remaining was less than analyzed, as the Teflon™ bomb liners absorb volatile organics and then release them back into the bomb upon cooling.

### **Effects of Organic Loading and Contact Area**

The dependence of oxidation rate in the catalyst solution on organic loading must be known to estimate the desirable organic loading for a treatment unit, and to estimate the time to a certain percentage destruction of the organic. Figure 1 shows an example of results obtained in studies of organic loading versus oxidation rate as reflected by generation of iron(II) in unmixed reaction bombs. The data is fitted by a logarithmic curve which gives the pseudo- order of the reaction in the organic (the exponential factor) and a multiplicative constant which is equal to the product of the apparent reaction rate and the iron(III) concentration. Pseudo-orders for the organics were 0.52 for Hydrocount™, 0.31 for Duoseal™, and 0.25 for TCE. Several factors complicate the relationships found in these studies. The amount of surface area contact between the catalyst solution and the organic (i.e., mixing), the solubility of the organic in the catalyst solution, the vapor pressure of the organic, and the head space volume of the reaction vessel should all affect the relationship between organic concentration and apparent oxidation rate. In these unmixed reaction bombs, oxidation rates at higher concentrations are undoubtedly lower than would be obtained under mixed conditions. Increased reaction rates at higher loadings would increase the organics' apparent reaction orders; coal gasification studies with iron(III) oxidation solutions in well mixed reactors have given a pseudo-order of near 1.0 for organics (3). In a thoroughly mixed reactor the solubility of the organic should have little effect on the apparent reaction rate unless the organic is quite soluble in the catalyst solution. Place Fig. 1 here.

The above results allow estimates of the time required to achieve a given amount of oxidation and of the time required to reduce the concentration of an organic to a given level. Calculations indicate that to reduce a catalyst solution from 1.0 gm/liter organic concentration to  $1 \times 10^{-6}$  gm/liter (1. ppb) organic concentration will require about 20. hours for Duoseal™, 6.3 hours for Hydrocount™, and 1.0 hour for TCE. This type of calculation would be valuable for estimating the time required to reduce organic concentrations to desirable levels at the conclusion of a waste processing run, although one would not normally be operating a waste treatment unit in such an organic-starved condition.

Further studies were conducted to determine the relationship between surface area of contact and apparent reaction rate. One series of studies utilized the 23. ml bombs, with the volume of catalyst solution varied from 10. ml to 1.0 ml while the amount of organic was kept constant; the surface area of the catalyst solution in contact with the organic was not changed by the variation in solution volume. In these tests, the total amount of oxidation, as measured by generation of iron(II), was not changed by variation in solution volume; this result tends to eliminate solution volume as a factor in the amount of reaction between the catalyst solution and organics. In order to further clarify the relationship between organic concentration, surface area of contact, and the reaction rate, a second series of tests were conducted using Hydrocount™ in the 125. ml bombs. By tilting the bombs at a 45° angle, an increase in contact area from 11.4 cm<sup>2</sup> to 16.1 cm<sup>2</sup> could be obtained. The bombs were loaded with 25. ml of catalyst solution and amounts of Hydrocount™ from 47.5. mg to 0.95 gm. Results of these tests are shown in Figure 2. At lower amounts of organic, the reaction rate appears to depend solely on the amount of the organic. At the higher amounts of organic, the reaction becomes dependent on contact surface area. These results are consistent with a surface area-dependent reaction; at lower organic loadings, much of the organic is in the vapor state and is at sufficiently low concentration that availability of organic at the catalyst solution surface controls the reaction rate, while at higher organic loadings the reaction begins to be controlled by the availability of iron(III) at the contact area. As the solution is unmixed, the availability of iron(III) at the surface is controlled by the rate of diffusion of iron(III) in the catalyst solution. The rate of mass transfer of iron(III) as reflected by the measured reaction rate is consistent with known diffusion rates for iron ions in aqueous solutions. From the data here, the reaction rate becomes dependent on iron(III) diffusion at about 100.-200. KPa organic vapor pressure. Thus, a great increase in reaction rate should be expected in a mixed reactor due to both thinner diffusion layers and, if the organic is a liquid or vapor, increased contact area. Figure 3 demonstrates this increase in reaction rate if the surface area to volume ratios obtained in the 23. ml bomb tests are converted to contact area for a given particle size of organic at a 5% w/w organic loading for Ready Value™ scintillation fluid. Place Fig 2 here. Place Fig. 3 here.

### **Oxidation Efficiencies**

Oxidation efficiency studies for Hydrocount™, Ready Value™, Duoseal™, and TCE were carried out in both unmixed, 125. ml bombs, and in the stirred 4. liter reactor.

The studies in the 125. ml bombs were carried out for 24. hours to obtain a fairly complete oxidation of the organics in these unmixed bombs. From 95. mg to 438. mg of the organics were oxidized in the 125. ml bombs. Results of oxygen consumption and carbon dioxide production measurements indicated that fairly complete oxidation to carbon dioxide had been achieved. Titrations of the post-oxidation solutions for iron(II) showed no, or negligible, amounts of iron(II), thus the iron was kept in the (III) state by the oxygen in the bombs. The post-oxidation catalyst solutions were analyzed for residual amounts of volatile and semivolatile organics by an independent analytical laboratory. Results showed that greater than 99.9997% of the o-xylene and 1,2,4-trimethylbenzene had been destroyed, and that 99.995% of the TCE had been destroyed. Some amounts of other organic intermediates were seen, giving absolute destruction efficiencies of about 99.% in these tests.

Studies in the 4. liter, stirred bench top reactor were conducted over much shorter time periods than those in the unmixed bombs, and with significantly greater amounts of organics. Preliminary tests with n-butyl acetate as the organic used from 7.875 gm to 13.125 gm of organic oxidized for one and three hours, respectively. No n-butyl acetate was detected after the oxidations, giving a destruction efficiency for the parent compound of >99.9999%. Some intermediates were seen in the catalyst solution, and absolute destruction of all organic material was about 99.9%. Apparent reaction rate constant for oxidation of n-butyl acetate was about  $1 \times 10^{-4} \text{ sec}^{-1}$  at 423.<sup>0</sup>K at a relatively low organic loading of 0.2% w/w. Organic loading was limited in these batch tests by the amount of oxygen which was loaded into the reactor headspace, and is in the realm of organic concentration-limited reaction rate. Oxidations of Duoseal<sup>TM</sup>, Hydrocount<sup>TM</sup>, Ready Value<sup>TM</sup> and TCE followed the preliminary tests. Three batch oxidations were conducted with each organic. The results obtained were quite good. Apparent average reaction rate constants for Duoseal<sup>TM</sup> and the other three organics were about  $1 \times 10^{-5} \text{ sec}^{-1}$ ; added mechanical agitation is probably responsible for the more rapid oxidation rates achieved. For Duoseal<sup>TM</sup> vacuum pump oil, the amount of residual organics in the catalyst solution after oxidation of over 7. grams of Duoseal<sup>TM</sup> for 2.-3. hours was less than in the freshly prepared catalyst solution alone. The amount of oxygen consumed was consistent with complete oxidation of the Duoseal<sup>TM</sup> to carbon dioxide, and the absolute destruction efficiency for all organic material in the reactor was 99.96%. For Hydrocount<sup>TM</sup> and Ready Value<sup>TM</sup>, oxygen consumption indicated complete oxidation of the organics. Greater than 99.9999% oxidation of the parent compounds, o-xylene and 1,2,4-trimethylbenzene, was achieved in 3. hours, and the absolute destruction efficiency for all organic materials was 99.5% after 3. hours. Oxidation of TCE proved to have unexpected consequences on the reactor materials; the entrained gas stirrer head was attacked and corroded, presumably by a corrosion/erosion mechanism, as the corrosion appeared only where there was rapid flow of catalyst solution past the parts. As a result, oxygen consumption indicated greater than 100% oxidation of the TCE, with the excess oxygen undoubtedly being used as the metal parts were oxidized. A destruction efficiency of 99.95% was achieved for TCE in three hours, and the absolute destruction efficiency for all organic materials was 99.5%. No buildup of significant amounts of unreacted byproducts were seen in any of the oxidations in the 4. liter reactor.

### Catalyst Solution Pressure and Composition

Of interest to design of a prototype waste treatment unit is the vapor pressure of the catalyst solution under typical operating conditions, and the composition of the catalyst solution vapors. Figure 4 gives the measured pressure versus temperature for the 4. liter bench top unit containing 1.5 liters of catalyst solution and pressurized with oxygen. The gases in the headspace contribute some of the pressure increase with temperature, and their pressure curve is also shown. The difference is the vapor pressure of the catalyst solution. Samples of the vapor taken at 473.<sup>0</sup>K were analyzed for water and HCl content; it was found that the vapor is approximately 0.04% v/v HCl, and essentially 100% water vapor when the permanent gas volume is subtracted. The HCl content of the headspace gases was somewhat lower than was expected, and is thus expected to be of less concern than was anticipated. Place Fig. 4 here.



## CONCLUSIONS

To date the development of DETOX has been successful. Reaction conditions have been identified which increase the oxidation rate for organics by several orders of magnitude. The catalyst solution appears to be capable of solvating metals as expected, and can remove organic contaminants from inert materials. Destruction efficiency studies have demonstrated that in a mixed reactor at least 99.9999% destruction of common hazardous organics can be achieved, and that there is no build up of non-reactive byproducts. Gas analysis studies have demonstrated complete oxidation to carbon dioxide. Results from the bench top unit indicate that there should be no reactivity concerns in scaling the process up to larger processing volumes. The next phase of development will be conversion of the 4. liter bench top unit to a continuous processing system which will be capable of oxidizing multiple gram quantities of organics per hour. The continuous unit will act as a test bed for prototype design concepts.

## ACKNOWLEDGEMENTS

We would like to express our sincere appreciation to The University of California Los Alamos National Laboratory and the Department of Energy Morgantown Energy Technology Center for sponsoring the DETOX development effort.

## REFERENCES

1. United States Patent Number 4,925,540, "Method For Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor".
2. United States Patent Number 5,047,224, "Method For Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor".
3. P.M. Dhooge, D.E. Stilwell, and S.-M. Park, Journal of The Electrochemical Society, 129, 1719 (1982), also P.M. Dhooge and S.-M. Park, *ibid.*, 130, 1029 (1983).

Figure 1 - Hydrocount Oxidation Rate vs Concentration in DETOX Soln. at 473 K.

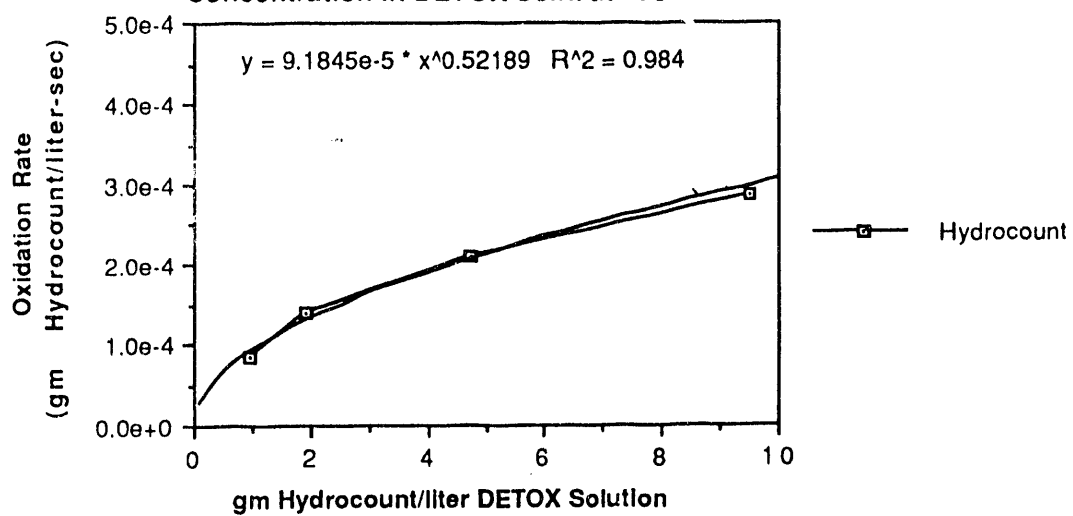


Figure 2 - Apparent Reaction Rate  
Constants vs Organic Loading at 473.K.

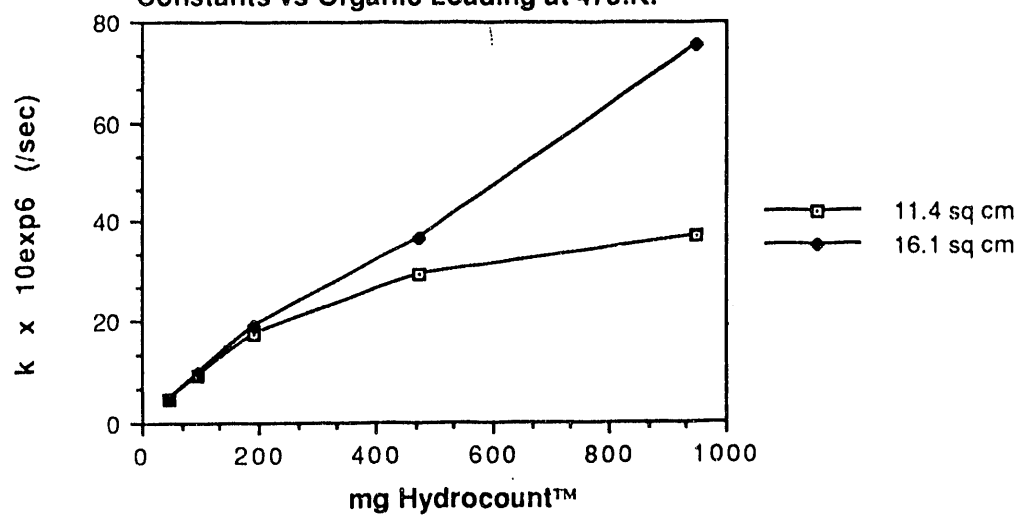


Figure 3 - Oxidation Rate Vs Particle Size  
for Ready Value at 5%v/v Loading and 473 K.

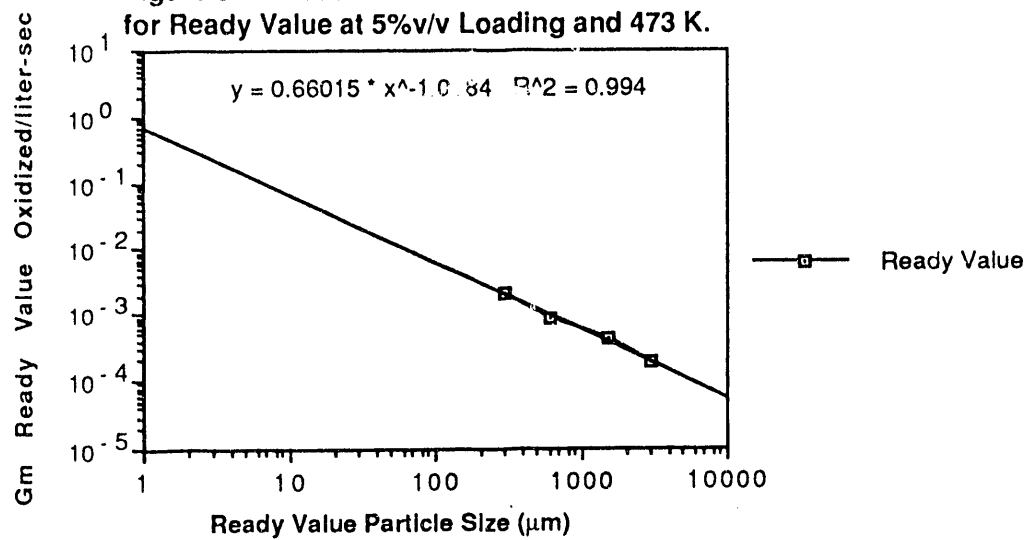
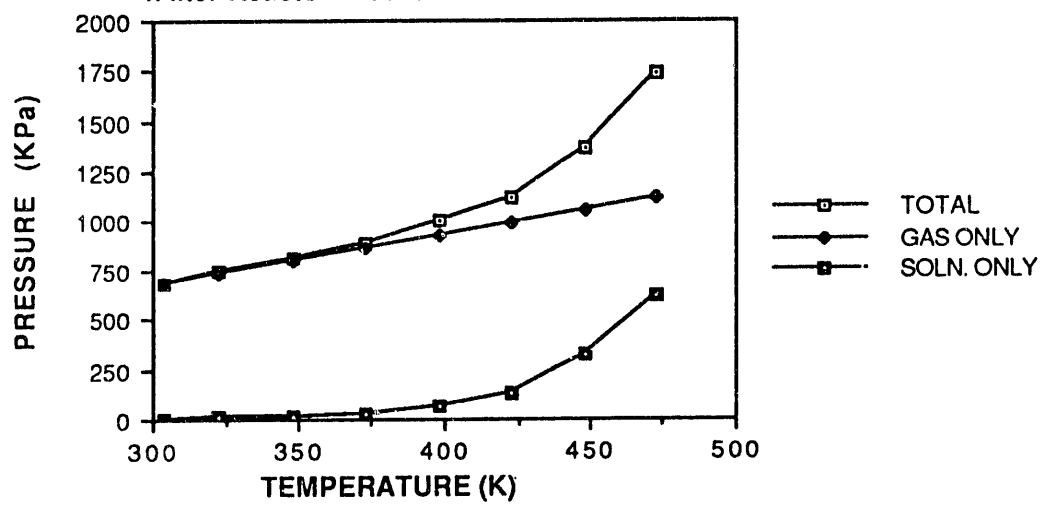


Figure 4 - P vs T for Catalyst Solution In  
4. liter Reactor Pressurized w/690. KPa O<sub>2</sub>





# END

---

DATE  
FILMED

5/03/93

