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September 1995

Prepared for Westinghouse Hanford Company and
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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(a) Zimpro Environmental, Inc.

Summary

Under the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project, Pacific Northwest Laboratory (PNL) is evaluating and developing organic destruction technologies that may be incorporated into the Initial Pretreatment Module (IPM) to treat Hanford tank waste. Organic (and ferrocyanide) destruction removes the compounds responsible for waste safety issues, and conditions the supernatant for low-level waste disposal by removing compounds that may be responsible for promoting strontium and transuranic (TRU) components solubility. Destruction or defunctionalization of complexing organics in tank wastes eliminates organic species that can reduce the efficiency of radionuclide (e.g., ^{90}Sr) separation processes, such as ion exchange, solvent extraction, and precipitation. The technologies being evaluated and tested for organic destruction are low-temperature hydrothermal processing (HTP) and wet air oxidation (WAO). Based on the results presented in this report and in FY 1993, the PNL HTP/WAO technology was selected by an independent panel as the baseline reference technology for IPM.

Low-temperature HTP is an autogenous thermal-chemical processing method to destroy organic constituents in Hanford tank waste using existing oxidants in the tank waste such as nitrite and nitrate. The process effectively destroys organics at temperatures from 250°C to 400°C to eliminate safety hazards and improve further processing. Processing of the tank waste with HTP can be done in a plug-flow, tubular reactor, or a continuous stirred-tank reactor system designed to accommodate the temperature, pressure, gas generation, and heat release associated with decomposition of the reactive species.

A similar hydrothermal process, wet air oxidation (WAO), has been practiced commercially for 30 years to destroy a wide variety of organics. Wet air oxidation is a liquid-phase reaction between oxygen from air and organics (and many oxidizable inorganics) in the waste stream. The waste stream is pumped to system pressure and passed through heat exchangers generating temperatures ranging from ~200°C to 400°C and pressures from ~1500 to 4000 psig. Air is injected from a compressor, and the oxidation takes place in a pressure vessel.

The FY 1994/95 activities to evaluate these technologies were continuations and extensions of the FY 1993 activities. Work involved batch testing with simulant, batch testing with actual waste samples, and continuous bench-scale testing with simulant.

The objectives of the batch testing with simulant (representing Tank 101-SY waste) were to test and demonstrate the effectiveness of HTP and WAO to 1) destroy a variety of organic components, and 2) remove strontium from solution. In addition, batch tests (no air addition) were conducted at temperatures between those of HTP and heat and digest (i.e., typically 100°C to 120°C and atmospheric pressure). These tests were conducted to gain more confidence in extrapolating the vast amount of HTP test results to supplement heat and digest testing that is currently being conducted by Westinghouse Hanford Company. The HTP simulant batch testing was conducted primarily by PNL, and the WAO simulant batch testing was conducted primarily by Zimpro Environmental, Inc., under a subcontract to PNL.

The HTP and WAO simulant batch tests were conducted using Tank 101-SY simulant with a variety of organics believed to exist in the actual tank waste, which were added to the simulant to make

up the TOC content. In the HTP testing, the relative destruction rates of EDTA (ethylenediamine-tetraacetic acid), HEDTA [N-(2-hydroxyethyl) ethylenediaminetriacetic acid]/EDTA (2:1 molar ratio), formate, citrate, acetate, and oxalate were evaluated. Acetate was by far the most difficult organic species to destroy, followed by citrate, oxalate, EDTA, HEDTA/EDTA (2:1 molar ratio), and formate, respectively. In the WAO testing, EDTA, acetate, formate, and potassium ferrocyanide were added to 101-SY simulant. As with the HTP testing, acetate was found to be the most difficult organic species to destroy, followed by EDTA, and then formate. In all WAO runs conducted with ferrocyanide, the cyanide content was reduced by over 99%. The relative destruction rate of EDTA via WAO appeared to be faster than EDTA destruction via HTP.

The simulant batch tests showed that HTP and WAO treatment is effective in removing strontium from solution. Upon treatment, the chelating organics appear to become "defunctionalized," releasing strontium, which can then be removed from solution via filtration. Furthermore, it was observed that complete organic destruction is not necessary; 50% TOC destruction (EDTA, HEDTA/EDTA, or citrate as the organic source) resulted in the removal of $\geq 94\%$ strontium from solution via filtration. Neither formate nor acetate complexed significant quantities of strontium in the supernatant.

The HTP/heat and digest temperature-bridging simulant tests were conducted at temperatures between 175°C and 250°C. The results obtained from these tests were in good agreement with what would be expected, based on previous HTP testing at higher temperatures. This is partial validation that the HTP test results can be applied to heat and digest conditions.

The objectives of the batch testing with actual waste were to test and demonstrate the effectiveness of HTP and WAO to 1) destroy the organic components present in the waste, and 2) remove strontium and TRU from solution. These test results were then compared to testing conducted using 101-SY simulant (EDTA as the organic source).

Three batch tests were conducted using actual waste from Tank 101-SY. The tests consisted of two HTP tests, conducted at 300°C and 350°C, and one WAO test, conducted at 280°C. Tests were also conducted at identical conditions, and in an identical reactor, using 101-SY simulant containing EDTA as the organic source for direct comparison with the actual waste testing. The batch testing with actual waste showed that HTP and WAO treatment is effective in reducing the TOC and in removing both strontium and TRU (e.g., ^{238}Pu and $^{239/240}\text{Pu}$) from the supernatant. In all three tests, $>90\%$ TOC destruction and $>90\%$ strontium and 80% to $>99\%$ ^{238}Pu and $^{239/240}\text{Pu}$ removal (via treatment and filtration) were achieved. The results from the tests on actual wastes were in good agreement with those obtained from simulant testing.

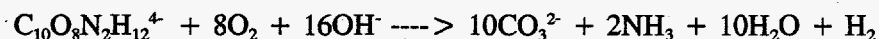
HTP testing conducted in FY 1993 showed that from 27 mol% to 53 mol% H_2 and 33 mol% to 56 mol% N_2O were present in the off-gas. In FY 1994, an off-gas safety evaluation was performed by PNL to evaluate the potential concern of having such high H_2 and N_2O levels in the off-gas. The results of this evaluation indicated that these levels of H_2 and N_2O were well within the flammable range, and possibly within the detonable range. As a part of this study, calculations were performed for a number of operating conditions and situations associated with bench-scale HTP testing. Two alternative methods of operation were recommended as an outcome of this evaluation: 1) operate by introducing an inert gas into the front end of the process or 2) inject air into the front end of the process. The injection of air not only alleviates the off-gas safety issue, it also provides faster kinetics (and lower operating temperatures and pressures) as compared with autogenous hydrothermal destruction. Thus, bench-scale continuous WAO simulant testing was vigorously pursued in FY 1994.

The objectives of the continuous WAO bench-scale testing with simulant were to 1) verify that the off-gas safety concerns associated with HTP could be minimized via WAO, 2) gain a better understanding of the WAO chemistry, 3) develop a WAO kinetic model to describe the destruction of EDTA in tank waste simulant and compare it with HTP kinetics, and 4) evaluate the overall operability of the system.

Thirteen different WAO test conditions were evaluated. In all tests, 3:1 (3 volumes water:1 volume simulant) diluted 101-SY simulant containing EDTA as the organic source was used as feed to the system. A modified version of the continuous reactor system that was used in the FY 1993 HTP testing was used here. The modification included the injection of air from an air cylinder at the bottom of the tubular reactor.

The WAO continuous test results verified that the off-gas safety concerns associated with HTP treatment are minimized with WAO treatment. Continuous WAO test results showed that nitrous oxide in the off-gas never exceeded 0.15%, and hydrogen gas levels were always less than 2.5%.

The experimental results indicated that the oxidation of EDTA via WAO treatment can be fairly well represented by the following overall reaction:



Less severe operating conditions are required for destruction of EDTA via WAO as compared with HTP treatment. Analytical results indicate that at approximately 280°C and a residence time of 6 to 9 min, a TOC destruction of 70% can be achieved. By comparison, with HTP, operation at approximately 350°C and a residence time of approximately 8 min would be required to achieve 70% TOC destruction. Based on the continuous tests, on the average, WAO can be operated at 77°C lower than autogenous HTP to achieve similar TOC destructions (with EDTA). Furthermore, in these temperature ranges, the system operating pressure can be decreased by more than 1000 psig if WAO treatment is used.

A kinetic model was developed to describe the global rate of destruction of EDTA via WAO treatment. The model is first order with respect to EDTA and zero order with respect to oxygen, with an activation energy of 11.4 Kcal/mole EDTA carbon. This relatively low activation energy may be indicative of mass transfer limitations in the reactor.

The studies conducted here have shown that HTP/WAO technology can be applied for treating Hanford tank waste to destroy organics and remove strontium and TRU components. Through commercial experience and PNL's technology development work, a large-scale system could be tailored and deployed within only 2 to 4 years.

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Abbreviations

AA	atomic absorption spectroscopy
AEA	alpha energy analysis
COD	chemical oxygen demand
CPDL	Chemical and Process Development Laboratory
CRS	continuous reactor system
DOE	U.S. Department of Energy
EDTA	ethylenediaminetetraacetic acid
GC	gas chromatograph
GEA	gamma energy analysis
GFAA	graphite furnace/atomic absorption analysis
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetic acid
HLW	high-level waste
HTP	low-temperature (autogenous) hydrothermal processing
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
IPM	Initial Pretreatment Module
LANL	Los Alamos National Laboratory
LFL	lower flammability limit
LLW	low-level waste
MS	mass spectrometry
PNL	Pacific Northwest Laboratory
SNL	Sandia National Laboratory
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
TS	total solids
TSS	total suspended solids
TWRS	Tank Waste Remediation System
WAO	wet air oxidation
WHC	Westinghouse Hanford Company

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1.0 Introduction

The U.S. Department of Energy (DOE) established the Tank Waste Remediation System (TWRS) to safely manage and dispose of high-level, transuranic, and low-level radioactive wastes stored in underground tanks at the Hanford Site in southeastern Washington State. Certain classes of the tanks are considered highest priority with respect to safety: the explosive gas (H_2) generating tanks, the organic tanks, and the ferrocyanide tanks. The problems associated with these types of tanks can be mitigated if the organic material and/or ferrocyanide could be destroyed or removed. Additionally, destruction or defunctionalization of complexing organics in tank wastes eliminates organic species that can reduce the efficiency of radionuclide (e.g., ^{90}Sr) separation processes, such as ion exchange, solvent extraction, and precipitation.

1.1 Project Description

Within the TWRS activities is the Pretreatment Technology Development Project, which is managed by Pacific Northwest Laboratory (PNL^(a)). In FY 1993, work began to experimentally develop and evaluate technologies for the destruction or defunctionalization of organics and ferrocyanides. The focus of this testing was on low-temperature hydrothermal processing (HTP). Batch and continuous testing with Hanford tank waste simulant was conducted to evaluate the chemistry and determine the kinetics for organic destruction via HTP (Orth et al. 1993). In FY 1994/95, the work emphasized the evaluation and development of hydrothermal organic destruction technologies for Hanford tank waste pretreatment. Wet air oxidation (WAO) was tested in addition to low-temperature HTP. During FY 1995, simulant testing to bridge the temperature gap between heat and digest treatment (i.e., 100°C to 120°C) and HTP (i.e., 300°C to 375°C) was also conducted.

Low-temperature HTP is an autogenous thermochemical processing method that can be used to accelerate the naturally occurring reactions in the tank waste in a controlled manner so that the safety hazards are eliminated and low-level waste (LLW) requirements can be satisfied. With HTP, organics react with oxidants such as nitrite and nitrate already present in the waste. No air or oxygen needs to be added to the system. Processing of the tank waste with HTP can be done in continuous tubular or stirred-tank reactor systems designed to accommodate the temperature, pressure, gas generation, and heat release associated with decomposition of the reactive species. Typical HTP operating conditions are 300°C to 375°C and 3000 psi. The low-temperature HTP technology is described in Orth et al. (1993) and Schmidt et al. (1993).

Wet air oxidation is a thermochemical process in which air or oxygen is added to the feedstock in a heated, pressurized reactor to oxidize organic and inorganic compounds. The technology is commercially available for wastewater treatment applications. In FY 1993, a subcontract was competitively bid and awarded to Zimpro Environmental, Inc. (Zimpro) by PNL to test the viability of treating simulated Hanford tank waste in commercially available WAO systems.

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The activities discussed here were integrated with a complementary high-temperature HTP program at Los Alamos National Laboratory (LANL). The LANL work involves reaction kinetics and system designs at operating temperatures of 375°C to 550°C and pressures from 4000 to 15,000 psi (Dell'Orco et al. 1993; Foy et al. 1993), while the bulk of PNL's tests have been conducted at 250°C to 375°C and 1500 to 3000 psig.

This report covers work performed in FY 1994 and FY 1995. Four activities are described: Batch HTP/WAO Testing with Actual Tank Waste (Section 3.0), Batch HTP Testing with Simulant (Section 4.0), Batch WAO Testing with Simulant (Section 5.0), and Continuous Bench-scale WAO Testing with Simulant (Section 6.0). For each of these activities, the objectives, test approach, results, status, and direction of future investigations are discussed. The background and history of the HTP/WAO technology is summarized below. Conclusions and Recommendations are provided in Section 2.0. A continuous HTP off-gas safety evaluation conducted in FY 1994 is included as Appendix A. The safety evaluation and the recommendation of the May 1993 Organic Destruction Technology Selection Panel to operate HTP at the lowest temperatures and pressures that can achieve target destruction objectives (Beeman and Hansroute 1993) are the basis for the testing and development of WAO processes within the PNL HTP program.

1.2 Project History and Developments

During early FY 1993, a number of organic destruction technologies were being developed and evaluated within the TWRS program for potential incorporation into the Initial Pretreatment Module (IPM). The number of technologies being investigated for this function was larger than could be adequately funded during the IPM conceptual design. To reduce the number of technologies, a criteria package was distributed that identified information that would be used to select the organic destruction technologies to be carried through the initial portion of the conceptual design process. Principal investigators of candidate technologies from LANL, Sandia National Laboratory (SNL), Westinghouse Hanford Company (WHC), and PNL were asked to respond to the criteria package and present information to an independent selection committee in Salt Lake City on May 24-27, 1993. Based on the recommendations of the selection committee, IPM ranked PNL's low-temperature HTP process as the most promising technology, and continued funding was provided for the remainder of FY 1993.

In October 1993, a new pretreatment strategy (Case Beta) was adopted and the need for organic destruction technology development for tank safety issues became uncertain. In accordance with the Case Beta strategy, the scope of organic destruction technology development was expanded to examine the destruction of organics that chelate or form complexes with ⁹⁰Sr and TRU in tank waste supernatant. By removing or defunctionalizing organics, anticipated downstream radionuclide separation processes (e.g., ion exchange, solvent extraction, and precipitation) are expected to perform more effectively. As a result of the change in the pretreatment strategy, activities in FY 1994 were expanded to evaluate the destruction of organics to facilitate strontium and TRU removal, as well as to resolve tank waste safety issues.

In June 1994, a second technology selection process was conducted to select the baseline organic destruction technology for resolving tank waste safety issues. The technologies evaluated in this process were Low-Temperature Hydrothermal/Wet Air Oxidation (PNL), Electrochemical Treatment (PNL), High-Temperature Hydrothermal Processing (LANL), Calcination/Dissolution (WHC), and

Steam Reforming (SNL). Based on results presented by PNL and Zimpro, the independent panel members selected the PNL HTP/WAO process as the baseline reference technology.

The following excerpt was taken from the report, Second IPM Technology Selection Meeting, June 27-29, 1994, Doubletree Hotel, Salt Lake City, Utah (Final Report: July 21, 1994):

Low-temperature Hydrothermal/Wet Air Oxidation was selected as the primary technology by the IPM downselect committee. The panel believes this technology has the highest potential to meet the minimum IPM requirements established for this selection process in a relatively short time frame and, accordingly, will meet the safety needs for IPM. Current commercial use of wet air oxidation for waste treatment was well documented. The process studies determined realistic operating ranges although some additional pilot studies may still be required before final design can be effected. The materials corrosion studies established confidence in the material of construction selection. The pressure vessel codes need to be reviewed to evaluate construction/inspection requirements in the high level radiation environment. There was a high degree of confidence that this technology can be engineered to perform in the Hanford environment and could be implemented in the shortest time.

During FY 1994, PNL investigated the destruction efficiency of low-temperature HTP for a variety of organics in tank simulant based on Tank 241-SY-101 (Tank 101-SY) using a batch autoclave reactor. An HTP test using actual waste from Tank 101-SY was also completed. Furthermore, a series of continuous bench-scale WAO tests showed that, with WAO, organic destruction efficiencies could be obtained at temperatures and pressures significantly lower than for low-temperature HTP. Off-gases generated from the WAO testing are much safer and easier to handle than those generated from autogenous HTP.

In FY 1995, additional HTP and WAO batch tests were conducted, using actual Hanford tank waste. In addition, batch tests using Hanford tank waste simulant were conducted at temperatures lower than those typically used in HTP. These tests were conducted to bridge the temperature gap between HTP and "heat and digest" processing. Heat and digest process conditions are typically 100°C to 120°C and near atmospheric pressure. With PNL support, heat and digest testing, using actual tank waste, was initiated by WHC in FY 1993, and continued through FY 1995. The HTP/heat and digest temperature bridging tests were conducted in FY 1995 to provide a greater confidence in the extrapolation of the vast amount of data obtained at HTP conditions to typical heat and digest temperatures. The HTP data were used in FY 1995 to supplement heat and digest data in an engineering evaluation of heat and digest for the destruction of organics in Hanford tank waste.

Through the use of air injection, PNL has mitigated the off-gas safety concerns and developed a technology with superior kinetics. With air injection, the system operating temperature and pressure have been significantly reduced to meet the IPM baseline criteria. By moving from low-temperature HTP to WAO, the operating temperature has been reduced from 350°C to 280°C, and the operating pressure has been decreased from 3000 psig to 2000 psig at residence times of 6 to 9 min for both processes.

2.0 Conclusions and Recommendations

2.1 Major Conclusions

The work completed in FY 1994 and FY 1995 led to the following major conclusions:

- HTP/WAO is a viable technology for the treatment of Hanford tank waste to facilitate the removal of key radionuclides. Significant technology development efforts with simulant tank waste and actual tank waste (confirmation testing) have been performed at PNL and Zimpro facilities with batch-, bench-, and pilot-scale systems. The WAO process has been commercially practiced for more than 30 years. Through commercial experience and PNL's technology development efforts, HTP/WAO can be tailored for deployment at Hanford for tank waste treatment.
- Based on continuous bench-scale testing at PNL, kinetic models have been developed to describe both autogenous HTP and WAO. These models can be used for evaluation of full-scale HTP/WAO systems for the treatment of Hanford tank waste.
- Complete (i.e., 100%) destruction of organic carbon is not necessary to achieve high levels of strontium removal. Partial destruction can defunctionalize the complexing ability of the chelators. With EDTA, HEDTA, and citrate (strong complexants), total organic carbon (TOC) destructions of approximately 50% led to the removal of more than 94% of the strontium from tank waste simulant supernatant.
- Testing with actual waste confirmed that both autogenous HTP and WAO are effective in significantly decreasing (i.e., > 90%) both the strontium and the TRU concentrations in the tank waste supernatant.
- Comparison of the results obtained from testing on actual tank waste with results from simulant testing showed consistency and good agreement. The extent of organic destruction and the removal of complexed strontium from supernatant was slightly greater during the actual waste testing, indicating results from simulant are conservative. This comparison demonstrates the value of simulant testing, which costs only a fraction of the cost of testing with actual wastes.
- HTP testing at low temperatures produced TOC destruction levels that were consistent with values predicted by the kinetic model developed from data collected at much higher temperatures. This testing supports the use of the kinetic model to predict organic destruction behavior at the near-ambient heat and digest conditions.

2.2 Significant Findings

2.2.1 Batch HTP Testing with Actual Tank Waste

Actual waste tests showed that HTP/WAO is capable of significantly reducing TOC and the solution concentrations of strontium and TRU (e.g., ^{238}Pu and $^{239/240}\text{Pu}$). It is presumed that some portion of the strontium and TRU content of the waste is solubilized by reaction with organic

complexants, such as EDTA, and that hydrothermal processing destroys or defunctionalizes those organics, thereby causing precipitation of the uncomplexed strontium and TRU. The results obtained from testing with actual waste were in agreement with tests conducted using simulant.

2.2.2 Batch HTP Testing with Simulant

With respect to relative ease of destruction via HTP, acetate is by far the most difficult organic species to destroy under the conditions evaluated (i.e., 300°C to 375°C). Citrate is the next most difficult, followed by oxalate, EDTA, HEDTA/EDTA (2:1 molar ratio), and formate, respectively. It was slightly more difficult to destroy EDTA in filtered simulant than in the unfiltered simulant. It has been speculated that solids may be playing a catalytic role in the HTP reactions.

For EDTA and HEDTA/EDTA in 3:1 (3 volumes water:1 volume simulant) diluted simulant, nitrite serves as the dominating oxidizing agent. Testing with citrate, formate, and acetate do not show a clear trend on whether nitrite or nitrate is preferentially consumed.

With EDTA, HEDTA/EDTA, and citrate, complete TOC destruction is not necessary to remove significant amounts of strontium from solution. TOC destruction of approximately 50% or greater results in more than 94% of the strontium being removed from the supernatant. Neither formate nor acetate complex significant quantities of strontium in the supernatant. Consequently, although acetate is difficult to destroy via HTP, from a complexant destruction perspective, acetate destruction is not required.

The total suspended solids content of 3:1 (3 volumes water:1 volume simulant) diluted 101-SY simulant was typically between 1.5 wt% and 2 wt%. After HTP treatment, the suspended solids content remained unchanged. Thus, HTP does not appear to have a negative impact on the amount of solids that will require high-level waste (HLW) disposal. For tanks in which chromium (in the solids) is a limiting constituent for HLW disposal, HTP treatment, might in fact be beneficial. Chromium concentrations in the supernatant increased with HTP treatment. This increase is mostly likely due to oxidation of insoluble Cr(III) to soluble Cr(VI).

Extrapolation of HTP test results to heat and digest conditions was partially validated. TOC and strontium removal results obtained from tests conducted at between 175°C and 250°C (i.e., between heat and digest and HTP conditions) were in good agreement with what would be expected based on previous HTP testing.

2.2.3 Batch WAO Testing with Simulant

Based on runs conducted by Zimpro without air addition (i.e., autogenous HTP), significant confidence was established that the Zimpro and PNL hydrothermal processing test results are consistent and comparable. Consistent with findings at both PNL and LANL, Zimpro's WAO testing showed that TOC reduction in simulant containing acetate is more difficult than any of the other organics tested. In all WAO runs with ferrocyanide (in the 101-SY simulant matrix), the cyanide content was reduced by over 99%.

Very little nitrite (within analytical error) was oxidized via WAO treatment. In addition, oxygen (from the injected air) was consumed, and essentially no nitrite or nitrate was being consumed under

the conditions tested, which indicates that the air was the primary oxidizer responsible for the destruction of organics.

The results of strontium removal versus TOC destruction from WAO testing with EDTA, formate, and acetate were consistent with the results obtained from PNL's HTP testing. Acetate did not appear to complex significant amounts of strontium, and 50% TOC destruction (EDTA as organic source) was adequate to achieve a strontium supernatant decontamination factor of approximately 10.

Only trace quantities of N_2O and NO_x were produced when treating 3:1 diluted simulant via WAO. The ratio of moles of hydrogen generated per mole of EDTA destroyed via WAO is similar to that obtained for HTP. However, because of the nitrogen present in air, with WAO, the hydrogen is diluted below the lower flammability limit.

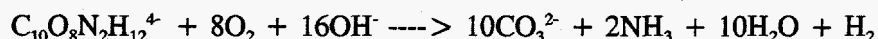
Based on the preliminary materials-of-construction corrosion evaluation, 316L, 304L, or Inconel 600 would be acceptable materials of construction for the components of WAO and HTP processing systems. (However, longer-term corrosion testing is recommended prior to the construction of a full-scale system.) From the corrosion tests, the general corrosion rates for these materials were less than 5.5 MPY in each test. Furthermore, the coupons constructed of these materials showed no evidence of localized or intergranular stress corrosion.

2.2.4 Continuous Bench-Scale WAO Testing with Simulant

Off-gas safety concerns associated with HTP treatment through the production of hydrogen and nitrous oxide gases exceeding the lower flammability limits are minimized with WAO treatment. Continuous WAO test results showed that nitrous oxide in the off-gas never exceeded 0.15%, and hydrogen gas levels were always less than 2.5%.

Less severe operating conditions are required for destruction of EDTA via WAO as compared with HTP treatment. Analytical results indicate that at approximately 280°C and a residence time of 6 to 9 min, a TOC destruction of 70% can be achieved. By comparison, with HTP, operation at approximately 350°C and a residence time of approximately 8 min would be required to achieve 70% TOC destruction. Based on the continuous tests, WAO can be operated, on the average, at 77°C lower than autogenous HTP to achieve similar TOC destructions (with EDTA). Furthermore, in these temperature ranges, the system operating pressure can be decreased by more than 1000 psig if WAO treatment is used.

The oxidation of EDTA via WAO treatment can be fairly well represented by the following reaction:



Analytical results showed that an average of 0.89 ± 0.1 mole of oxygen is consumed for each mole of TOC destroyed, and that essentially all of the organic nitrogen is being converted to ammonia.

A kinetic model was developed to describe the global rate of destruction of EDTA via WAO treatment. The model is first order with respect to EDTA and zero order with respect to oxygen, with

an activation energy of 11.4 Kcal/mole EDTA carbon. This relatively low activation energy may be indicative of mass transfer limitations in the reactor.

One test was conducted with the full 3:1 (3 volumes water:1 volume simulant) diluted simulant (i.e., unfiltered) to evaluate the effects of solids on system operability. No operational stability or plugging problems were observed during this run.

2.3 Recommendations

It is recommended that future testing be conducted with both actual and simulated wastes. Testing with actual waste is absolutely necessary; however, testing exclusively with actual waste is extremely expensive and time consuming. Accordingly, simulant testing should be conducted to 1) determine optimal test conditions for conducting the more costly actual waste tests, 2) provide an extensive data base for use in process development and design, and 3) provide a comparison between actual waste and simulant test results.

Provided simulant and actual waste tests compare favorably, an extensive data base can be obtained through simulant testing with a selected number of actual waste tests at a fraction of the cost and time required for exclusive actual waste testing. Testing with 101-SY simulant is substantiated by the FY 1995 HTP/WAO testing with simulant and actual waste and previously reported ozonation studies (Delegard et al. 1993), which showed that 101-SY simulant testing results were in good agreement with those obtained using actual 101-SY tank waste.

Specific recommendations for future HTP and WAO testing are given below.

2.3.1 Batch HTP Testing with Tank Waste

Although the comparison described here indicates good processing similarity between this particular waste and its simulant, it is recommended that additional testing be conducted with both actual and simulated wastes, especially with other tank wastes and their corresponding simulant compositions. Comprehensive analyses should be performed on untreated and HTP treated tank wastes to determine if (and to what extent) solids are being produced, to determine the organic species present, and to determine the changes in concentrations of TRU, strontium, and other analytes in the supernatant and solids phases.

2.3.2 Batch HTP Testing with Simulant

Batch HTP testing to date has focused primarily on 101-SY waste simulant and variants. Testing should be expanded to include HTP testing with simulants based on other tank waste compositions.

There is considerable uncertainty regarding the speciation and relative concentrations of organic constituents in the actual tank waste, and new species are likely to be identified as a result of ongoing tank waste characterization efforts. Consequently, there will be an ongoing need to perform testing to evaluate and determine conditions at which HTP can effectively destroy these new species and remove strontium and TRU from the supernatant.

Determining the effectiveness of heat and digest organic destruction requires significant time and funding as a result of the slow reaction rates at temperatures ranging from 65°C to 120°C. It would be more expedient and cost effective to perform additional batch HTP testing with simulants (other than 101-SY) at temperatures between 150°C and 250°C with a variety of organics, and then extrapolate the results to heat and digest conditions. Such testing should be repeated with actual waste.

2.3.3 Batch WAO Testing with Simulant

The range of batch WAO testing with simulant should be expanded to include other organics found in Hanford tank waste, simulant compositions, and test conditions. It is also recommended that batch WAO testing with actual waste be expanded to confirm the promising results obtained with the initial test with actual waste and the numerous tests with simulant.

Air addition should be examined as a means to enhance the kinetics of heat and digest organic destruction. As with HTP, it would be more expedient and cost effective to perform batch WAO testing with simulant at temperatures between 150°C and 250°C with a variety of organics and simulants and extrapolate the results to the lower-temperature heat and digest conditions.

2.3.4 Continuous Bench-Scale HTP/WAO Testing

During FY 1994, a kinetic expression was developed based on the WAO destruction of EDTA in 101-SY tank simulant. Additional continuous WAO and HTP testing should be conducted to further develop the kinetics (with a variety of organic-chelating species) and to investigate the overall operability of the process. The testing should focus on WAO testing under typical WAO conditions. However, additional HTP testing at temperatures lower than typical HTP conditions should also be conducted to obtain kinetic data to support ongoing heat and digest testing efforts.

The relatively low activation energy obtained from the WAO continuous tests indicate that mass transfer rather than the intrinsic reaction rate may be controlling the overall destruction of TOC. Testing in a high velocity reactor should be pursued to determine if mass transfer is limiting. The use of alternative reactor designs to enhance mixing/mass transfer should be evaluated.

The effects of feed dilution, temperature, pressure, and organic source should be further evaluated. Also, with respect to WAO, process upsets, component reliability, and the ability to stop and restart the system while maintaining process integrity should be examined. The effectiveness and need for off-gas scrubbing (i.e., caustic scrubbing of the off-gas) should be investigated in conjunction with this testing.

Future efforts should also include the design of a bench-scale continuous WAO system for testing with actual waste. The design and installation of a continuous bench-scale/pilot-scale WAO system for hot testing should be completed with testing scheduled to be initiated within 2 years.

2.3.5 Pilot-Scale HTP Testing with Simulant

Pilot-scale WAO demonstration is needed to provide proof of principle and the scalability of a continuous WAO process for the destruction of chelating organics. A pilot-scale demonstration test (24 to 40 hr at approximately 10 L/hr) should be conducted at PNL using Hanford tank waste simulant.

This testing, along with the bench-scale continuous WAO testing results, will be used to provide material balance, operation, and kinetic data for the design of a WAO continuous process. This run would be conducted in collaboration with Zimpro.

To provide further verification that the commercial WAO process is appropriate and applicable to the pretreatment of Hanford tank waste, additional pilot-scale WAO testing should be conducted at Zimpro's facilities, under subcontract to PNL. In the past, Zimpro has designed and operated numerous commercial WAO systems for various industrial applications. The objectives of the pilot-scale testing are to demonstrate the feasibility of processing simulant tank waste on a large scale, to support considerations on design of a large-scale treatment process, to obtain kinetic data, to obtain sufficient processing data to develop a heat and material balance, and to obtain a measure of plant corrosion behavior. For the pilot-scale testing, Zimpro would log 200 hr of continuous processing at a feed rate in the range of 2 to 6 L/min (0.5 to 1.5 gpm). Zimpro has estimated that 6-1/2 months would be required to complete the pilot-scale testing and report the results.

3.0 Batch HTP/WAO Testing with Actual Tank Waste Samples

3.1 Objectives

This testing investigated the capability of HTP/WAO to destroy organics in actual waste from Tank 101-SY by following changes in supernatant concentrations of TOC and certain radionuclides (e.g., strontium and plutonium). The purpose of the radioactive tests was to compare results using actual tank waste and specified processing conditions with results of comparable simulant tests. This comparison led to a greater degree of confidence in the simulant testing.

3.2 Test Approach

Testing was conducted using samples of actual tank waste in a small stirred batch reactor. A composite sample from Tank 101-SY (Window C sample) was used for this testing. Testing was performed in an available glovebox at the 325 Building in the Hanford Site's 300 Area. This building contains several laboratory facilities for radioactive testing. Approximately 25 to 30 mL of 3:1 diluted (3 volumes water:1 volume waste) 101-SY waste were used for each test. Batch tests were conducted at temperatures ranging from 280°C to 350°C in the reactor with an air (WAO) or an inert gas (HTP) overpressure. Samples of the waste were analyzed before and after the tests to determine organic destruction and radionuclide solubilities. Batch reactor tests were performed at conditions similar to, and the results then compared with, nonradioactive simulant tests.

In a test, the waste samples were first placed into the pressure vessel at ambient conditions. The reactor was sealed and purged with the selected cover gas (i.e., air or argon) and then pressurized to ~1000 psig to test for leaks. After leak testing, the reactor was vented to the desired initial overpressure. The reactor was then heated to the test temperature and held at that temperature for the duration of each test. The pressure at temperature in the reactor ranged from ~1000 to 4000 psig, depending on operating temperature and gas generation from organic destruction. Typically, the runs were terminated after ~15 min to 1 hr at the operating temperature.

At the end of each run, the reactor was cooled to ambient temperature and a gas sample was taken from the reactor head space. The reactor was then disassembled, and the remaining waste contents were sampled and analyzed. Organic destruction was measured by comparing before and after results of TOC analyses of the waste samples. Radionuclide analyses were generally performed by a radioactive decay counting procedure, such as beta counting, gamma energy analysis, etc. Other metal analyses were performed by inductively coupled plasma spectroscopy (ICP) or atomic absorption (AA) spectroscopy. Anions were analyzed by ion chromatography (IC). Other analyses or analytical techniques for better determining organic speciation/destruction were not used but may be identified and recommended for future efforts.

3.3 Test Apparatus/Facility Description

The reactor system procured and delivered in FY 1993 was installed in a glovebox during the first quarter of FY 1994. Operability testing was conducted using first water then simulated waste to verify operation of the reactor and associated equipment.

The glovebox containing the reactor is a lead-shielded enclosure designed for radioactive work connected to a filtered exhaust line for venting. The reactor system (50-mL batch stirred microautoclave from Autoclave Engineers, Inc.; see Figure 3.1) is set up in the glovebox and connected to an external gas bottle for purging and pressurizing the reactor.

Stirring is accomplished with an internal agitator magnetically coupled to a drive motor. The reactor is surrounded by an electrical heater capable of sustaining it at the desired temperature for the duration of the test. The heater is controlled by a thermocouple inserted along the outer wall of the reactor, and fluid temperature is monitored by a thermocouple in a thermowell submerged in the fluid. The gas supply is also connected to a cooling coil surrounding the body of the reactor, and air or inert gas is used at the conclusion of the experiment to rapidly quench the reactor from the test temperature to ambient prior to sampling. An identical reactor system was also used for conducting simulant tests for comparison with the actual waste tests.

Wetted parts of the reactor are fabricated from Hastelloy C-276, an alloy that is highly corrosion resistant under a wide variety of chemical environments, which was recommended by the reactor manufacturer for compatibility with these waste types. Subsequent corrosion testing with this alloy in simulated alkaline, nitrate, organic-bearing wastes indicated a susceptibility for stress cracking. The testing methods were very conservative (e.g., U-bend coupons and slow strain rate tensile tests), which produced stresses much greater than the hoop stresses in a reactor vessel under normal operating

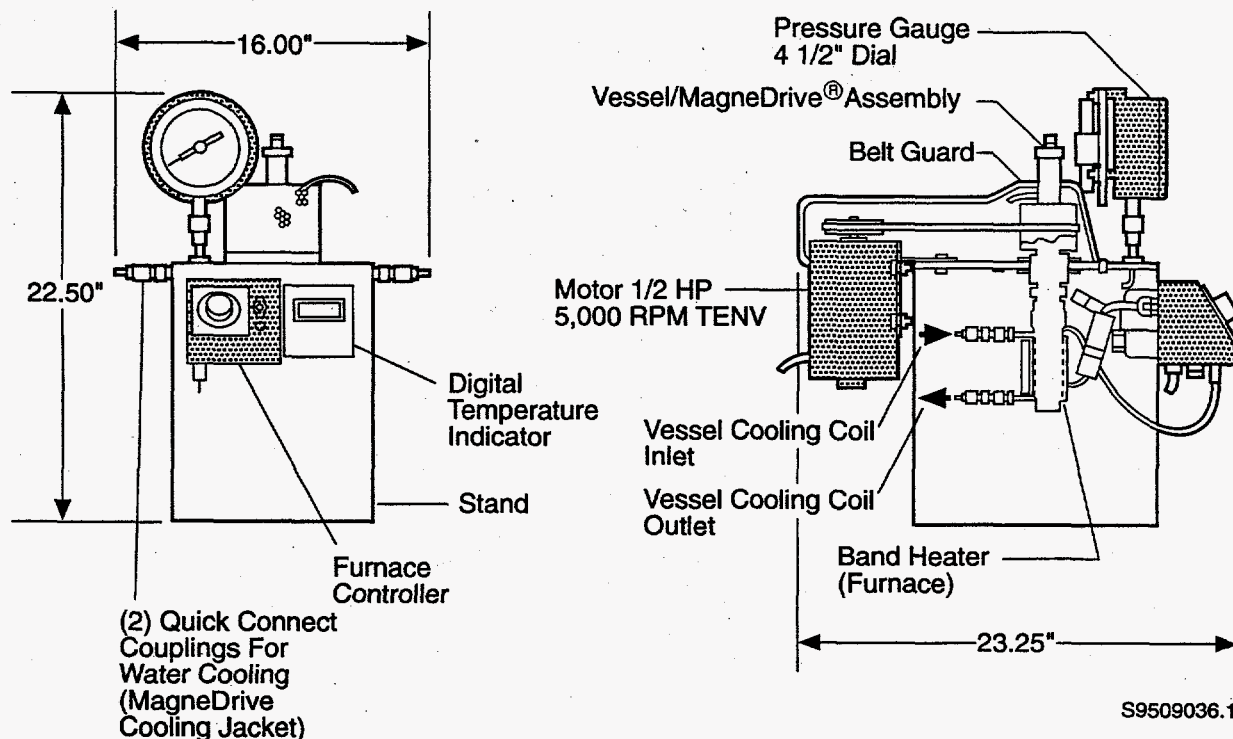


Figure 3.1. Microclave Reactor System (Autoclave Engineers) for HTP Batch Testing with Tank Wastes Samples

conditions. Therefore, although a possibility for failure apparently existed, the likelihood of a failed reactor under the range of test conditions seemed exceedingly small. The reactor was visually examined after cleaning following each test cycle to look for obvious degradation of the internal wetted parts. However, the difficulty of viewing the smaller components through the glovebox window prevented close inspection.

3.4 Results and Discussion

The first HTP test using actual Tank 101-SY waste was conducted in FY 1994. Because the 325 Building facility was shut down per a DOE mandate, this test was the only HTP test on actual waste conducted in FY 1994. One volume of the waste sample was diluted with three volumes of deionized water (3:1 diluted waste) to simulate anticipated dilution of tank waste caused by retrieval activities. The sample was thoroughly mixed and sampled. A 25-mL sample of the diluted waste was then moved from the hot cell to the glovebox and into the reactor vessel. The vessel was closed and repeatedly pressurized with argon and depressurized to purge much of the dissolved gases from the liquid. For this test, the initial argon pressure at ambient temperature was set at 500 psig. The agitator speed was set at 1000 RPM. Power was turned on to the vessel heater. After ~15 min the waste temperature had reached the target of 300°C, and the test was considered started at that point.

The reactor system was controlled at 300°C for 1 hr. Pressure was monitored and recorded throughout the test until power was turned off. When heater power was turned off at the end of the test (vessel agitator still running), argon gas was passed through the cooling coils surrounding the reactor. The waste temperature cooled to ambient in ~30 min.

After the reactor was cooled down, the gas sampling system was purged with off-gas from the reactor, and the off-gas was sampled with a typical gas chromatograph (GC) syringe. Gas samples were then taken to the mass spectrometer lab for analysis. Results of the gas analysis are shown in Table 3.1.

Based on off-gas analyses alone, hydrothermal processing of the actual waste sample appears to behave similarly to testing performed with simulated waste, although data are limited. The primary gases produced via HTP treatment of actual waste (H_2 , N_2O , N_2) are qualitatively in agreement with HTP testing using simulants (see appendix and Orth et al. 1993).

In FY 1995, following restart of operations in the 325 Building, the treated waste sample was removed from the reactor. The waste was thoroughly mixed, and a sample of the slurry was withdrawn for analysis. A sample of the "supernatant" liquid phase was taken by filtering the liquid through a 0.45- μ m filter and was submitted to the analytical chemistry laboratory along with the slurry sample for analysis. The basis for using a 0.45- μ m filter for this testing and the simulant testing (Sections 4.0 and 5.0) is provided in Appendix B. Corresponding supernatant and slurry samples of the diluted but untreated feed were submitted for chemical analysis along with the product samples from the FY 1994 test. Analyses included TOC; total inorganic carbon (TIC); anions by IC; ^{90}Sr by separation and beta counting; $^{238/239/240}Pu$ by alpha energy analysis (AEA); ^{154}Eu , ^{137}Cs , ^{241}Am , and ^{60}Co by gamma energy analysis (GEA); total cesium by graphite furnace/atomic absorption analysis (GFAA), and selected cations by ICP. Results of the supernatant liquid and slurry analyses for the feed and product samples are shown in Table 3.2.

Table 3.1. Off-Gas Analysis from Autogenous Hydrothermal Processing and Wet Air Oxidation Testing of Radioactive 101-SY Waste Samples

Species	Autogenous HTP		WAO
	300°C, 1 hr	350°C, 1 hr	280°C, 1 hr
Argon	87.93	93.53	1.68
Carbon Dioxide	<0.001	<0.01	0.025
Carbon Monoxide	<0.001	<0.01	<0.01
Helium	<0.001	<0.001	<0.001
Hydrogen	0.285	0.091	0.013
Methane	0.116	0.054	0.023
Nitrogen	7.69	4.38	78.3
Oxygen	1.67 (5.95)	0.359 (1.28)	20.0
Nitrous Oxide	2.13	1.58	0.027
Other Nitrogen Oxides	<0.05	<0.01	<0.01
Ethane	0.008	<0.001	0.003
Other Hydrocarbons	0.02	<0.01	<0.001
Ammonia (estimated)	0.17	<0.01	0.003

Total hydroxide by titration was also requested on initial samples. However, although the waste is a highly caustic slurry, the results from the laboratory indicated no free hydroxide. This appears to be a result of chemical interferences used in this particular method. Free OH⁻ analysis was dropped from subsequent sample analytical requests, since it appeared to be an unresolved issue that would require too much time and funding to investigate.

Two more tests were conducted in FY 1995 using (3:1-diluted) 101-SY waste, following essentially the same procedure as described for the FY 1994 test at 300°C. One test was an HTP test run at 350°C for 1 hr. The other test was a WAO test run at 280°C for 1 hr (900 psig air initial over-pressure). The off-gas analyses and supernatant liquid and slurry analyses (feed and product) are given in Tables 3.1 and 3.2, respectively.

These three radioactive test conditions were selected to compare with corresponding nonradioactive tests with simulated (3:1-diluted) 101-SY waste. Performance indicators (in terms of TOC destruction, nitrite destruction and strontium removal) are shown in Table 3.3 with the corresponding values from the simulant tests. The simulant and actual waste test results are in good agreement with each other for the three test conditions evaluated. In all cases, significant amounts of strontium (i.e., ≥93%) are removed from solution via treatment.

TRU surrogates were not included in the waste simulant testing. Therefore, TRU removal from solution could not be compared between testing with actual and simulated wastes. However, TRU (specifically ²³⁸Pu and ^{239/240}Pu) analyses were performed on feed and product samples from the actual

Table 3.2. Summary of Filtrate and Slurry Analytical Results from Radioactive HTP and WAO Testing

Species	Units	3:1-Diluted Feed ^(a)		HTP Test #1 ^(a)		HTP Test #2 ^(a)		WAO Test ^(a)	
		Filtrate	Slurry	Filtrate	Slurry	Filtrate	Slurry	Filtrate	Slurry
TOC	μg/ml	4060	NA ^(b)	120	NA	300 ^(c) (115) ^(d)	NA	100	NA
TIC	μg/ml	3130	NA	6150	NA	22000 ^(c) (13750) ^(d)	NA	8700	NA
TC	μg/ml	7190	NA	6260	NA	22300 ^(c) (8577) ^(d)	NA	8800	NA
NO ₂ ⁻	μg/ml	38300	37200	24900	24400	49300 ^(c) (18962) ^(d)	22000	34800	35900
NO ₃ ²⁻	μg/ml	39600	38500	37100	36200	71900 ^(c) (27654) ^(d)	31900	41800	42100
PO ₄ ³⁻	μg/ml	2500	2200	2700	2450	5950 ^(c) (2288) ^(d)	3150	2150	2250
SO ₄ ²⁻	μg/ml	1300	1300	1450	1450	3700 ^(c) (1423) ^(d)	1800	1700	1625
⁹⁰ Sr	μCi/g	1.37E+0	5.29E+0	<4.0E-2	2.00E+0	4.19E-2	6.75E+0	1.00E-1	3.87E+0
^{239/240} Pu	μCi/g	1.63E-3	1.83E-3	9.01E-5	3.31E-3	<2.0E-5	2.21E-2	4.24E-5	5.78E-3
²³⁸ Pu	μCi/g	2.70E-3	4.18E-4	6.00E-5	3.54E-4	<2.0E-5	2.70E-3	6.14E-6	8.56E-4
¹⁵⁴ Eu	μCi/g	ND ^(b)	1.51E-2	ND	1.00E-2	ND	ND	ND	ND
¹³⁷ Cs	μCi/g	1.08E+2	9.29E+1	9.55E+1	9.98E+1	1.30E+2	1.32E+2	1.24E+2	9.08E-1
²⁴¹ Am	μCi/g	ND	2.89E-2	ND	1.90E-2	ND	ND	ND	ND
⁶⁰ Co	μCi/g	1.71E-2	5.95E-3	ND	3.56E-3	ND	8.89E-3	ND	4.23E-3
Cs(total)	μg/ml	5260	5183	4465	4678	3381	3682	2859	3556
Al	μg/ml	3055	11031	2450	27913	5140	15020	469	8880
Cr	μg/ml	201	1215	<139	2266	503	1444	1455	1140

(a) Test Conditions: Feed diluted 3:1 by volume with deionized water, Spec.Grav._(slurry) = 1.17g/ml, Spec.Grav._(filtrate) = 1.135g/ml; HTP#1 = 300°C, 1 hr, 500 psig_(i) Ar; HTP#2 = 350°C, 1 hr, 500 psig_(i) Ar; WAO = 280°C, 1 hr, 900 psig_(i) air.

(b) NA = Not Analyzed, ND = Analyzed for but Not Detected

(c) Suspected dilution error in analytical laboratory. Actual value was believed to be reported value divided by approximately 2.6. Factor determined by comparing PO₄³⁻, SO₄²⁻, and TC values from this test with other tests.

(d) Suspected dilution factor error of 2.6 taken into account.

waste tests. Table 3.4 shows significant reductions in solution concentrations of these radionuclides following HTP treatment to destroy organic species. From these results it is presumed that, as with strontium, a portion of the TRU in the waste is solubilized by reacting with organic complexants. Hydrothermal processing apparently destroys or defunctionalizes these organics, causing the TRU to precipitate from solution in a manner similar to strontium behavior.

In summary, HTP/WAO results using actual waste were very encouraging. HTP and WAO treatment of actual waste not only was successful in removing strontium from solution, but also

Table 3.3. Percentage Changes of Certain Chemical Species Comparing HTP Treatment of Actual and Simulated 101-SY Waste

Test Conditions	Waste Type	TOC Destruction (%)	Nitrite Destruction (%)	Strontium Removal (%)
HTP, 300°C, 1 hr	Simulant	74	40	>97
	Actual	>98	35	>97
HTP, 350°C, 1 hr	Simulant	93	36	>97
	Actual	>93 ^(a) , 97 ^(b)	≤0 ^(a) , (50) ^(b)	97
WAO, 280°C, 1hr	Simulant	>99	4	>97
	Actual	>98	9	93

(a) Suspected dilution error in analytical laboratory. Actual value was believed to be reported value divided by approximately 2.6. Factor determined by comparing PO_4^{3-} , SO_4^{2-} and TC values from this test with other tests.

(b) Suspected dilution factor error of 2.6 taken into account.

Table 3.4. Removal of TRU from 101-SY Waste Supernatant by Hydrothermal Processing

Test Conditions	²³⁸ Pu Removal (%)	^{239/240} Pu Removal (%)
HTP, 300°C, 1 hr	85	83
HTP, 350°C, 1 hr	>99	>99
WAO, 280°C, 1 hr	>99	97

allowed for the removal of TRU (plutonium). In addition, the results from the actual waste testing were in good agreement with those obtained from simulant testing. This observation leads to more confidence in applying simulant testing results to actual waste processing.

3.5 Direction of Future Work

Future efforts should focus on conducting actual waste batch testing using other tank wastes that are available (e.g., Hanford Tanks AN-102, AN-107). Testing should also be conducted for different waste dilutions, and further investigation using WAO to destroy the organics should be pursued. In addition, a system should be assembled to conduct actual waste testing in a continuous manner. This system would allow for better determination of reaction kinetics and could be used to obtain information pertinent to the design and operation of a larger system.

4.0 Batch HTP Testing with Simulant

4.1 Objectives

The primary objective of the HTP batch testing with simulants was to evaluate the ability of HTP to remove complexed strontium from solution and destroy a variety of organic species expected to be present in Hanford tank waste at significant concentrations. Another objective was to bridge the temperature gap between heat and digest conditions (i.e., 100°C to 120°C) and typical HTP conditions (i.e., 300°C to 375°C) by conducting tests between 175°C and 250°C. In addition, the chemistry effects on nitrate, nitrite, and bulk metals were evaluated within the batch testing effort. Many of the results discussed below have also been reported elsewhere (Schmidt et al. 1994).

4.2 Test Approach

Most of the batch testing was conducted using a 1-L batch autoclave reactor (see Section 4.3), and a limited number of batch tests were conducted using a microautoclave identical to that described in Section 3.3. 101-SY simulant was used in this testing because Tank 101-SY is known to contain organic complexants. In most of the testing, 1 volume of simulated waste was diluted with 3 volumes of water (i.e., 3:1 diluted 101-SY simulant) to approximate dilution of the tank contents upon retrieval. The formulation of the 3:1 diluted 101-SY simulant (denoted as SYI-SIM-93A), using Na₄EDTA as the organic source, is given in Table 4.1. The simulant was made according to the composition and recipe documented by Hohl (1993).

The test conditions ranged from approximately 175°C to 410°C and 1100 to 4700 psig, with hold times (at temperature) from 0.25 to 144 hr. All of these batch tests were autogenous HTP tests (i.e., no air was added). In all cases, argon gas was added to the reactor so that an overpressure was always present.

Most of the higher-temperature tests ($\geq 300^\circ\text{C}$) were conducted using unfiltered 3:1 diluted 101-SY simulant. Some additional tests (using EDTA as the organic source) were conducted using 3:1 diluted 101-SY simulant that was filtered through 0.45- μm filters. One test was conducted using a 1:1 (1 volume water:1 volume simulant) diluted 101-SY simulant.

The effects of several different organic compounds, found in Hanford tank waste (Campbell 1994), were evaluated in this testing: EDTA, HEDTA/EDTA (2:1 molar ratio), formate, citrate, acetate, and oxalate. Thus, in some tests, these other organic compounds, rather than Na₄EDTA, were used to formulate the simulant. In all cases, however, a TOC content of approximately 5000 mg/kg was targeted for the 3:1 diluted simulant. Also in all cases, the organic species were added as sodium salts. The total suspended solids (TSS) content of the 3:1 diluted 101-SY simulant was typically between 1.5 wt% and 2 wt%. After hydrothermal treatment, the suspended solids content remained unchanged (i.e., within analytical limits).

Lower-temperature ($\leq 250^\circ\text{C}$) HTP/heat and digest bridging tests were conducted using unfiltered 101-SY simulant, with EDTA as the organic source. These tests were conducted primarily to extrapolate down from typical HTP conditions (300°C to 375°C) to heat and digest conditions (100°C

Table 4.1. Hanford Tank 101-SY Simulant Formulation (3:1 diluted)^(a) - (SYI-SIM-93A, Hohl 1993)

Component	Weight Percent
Na ₄ EDTA	1.67
Na ₃ PO ₄ • 12H ₂ O	0.88
NaNO ₂	5.42
NaNO ₃	4.49
Na ₂ CO ₃	1.91
Na ₂ SO ₄	0.20
NaCl	0.45
NaF	2.4x10 ⁻²
Ca(NO ₃) ₂ • 4H ₂ O	4.8x10 ⁻²
KNO ₃	0.29
ZnCl ₂	1.4x10 ⁻³
CsNO ₃	7.2x10 ⁻⁴
Sr(NO ₃) ₂ ^(b)	4.1x10 ⁻⁵
NaOH	2.02
Cr(NO ₃) ₃ • 9H ₂ O	1.09
Fe(NO ₃) ₃ • 9H ₂ O	6.9x10 ⁻²
Ni(NO ₃) ₂ • 6H ₂ O	2.4x10 ⁻²
NaAlO ₂ • 0.21NaOH • 1.33H ₂ O	4.72
H ₂ O	76.69
Total	100.00

(a) 3:1 diluted = 3 volumes water mixed with 1 volume simulant.

(b) In some cases, significant amounts of Sr were introduced into the simulant as an impurity in the Ca(NO₃)₂ • 4H₂O. Sr(NO₃)₂ value given here represents the minimum amount of Sr present in the simulant.

to 120°C). Ongoing heat and digest testing was conducted by WHC with undiluted actual waste; hence, most of this simulant testing was conducted with undiluted feed material as well. A limited number of these tests were conducted using 3:1 diluted 101-SY simulant.

4.3 Equipment/Facility Description

The 1-L batch autoclave reactor (manufactured by Autoclave Engineers, Inc.) is located at the Chemical and Process Development Laboratory (CPDL) at PNL. A diagram of the reactor system is given in Figure 4.1. The reactor is heated by a 1.7-kW heater, which has the capability to heat the reaction environment up to 500°C. The typical time required to heat 300 mL of solution to 350°C is approximately 60 min. The aqueous fluid and reaction gases are mixed inside the reactor by a

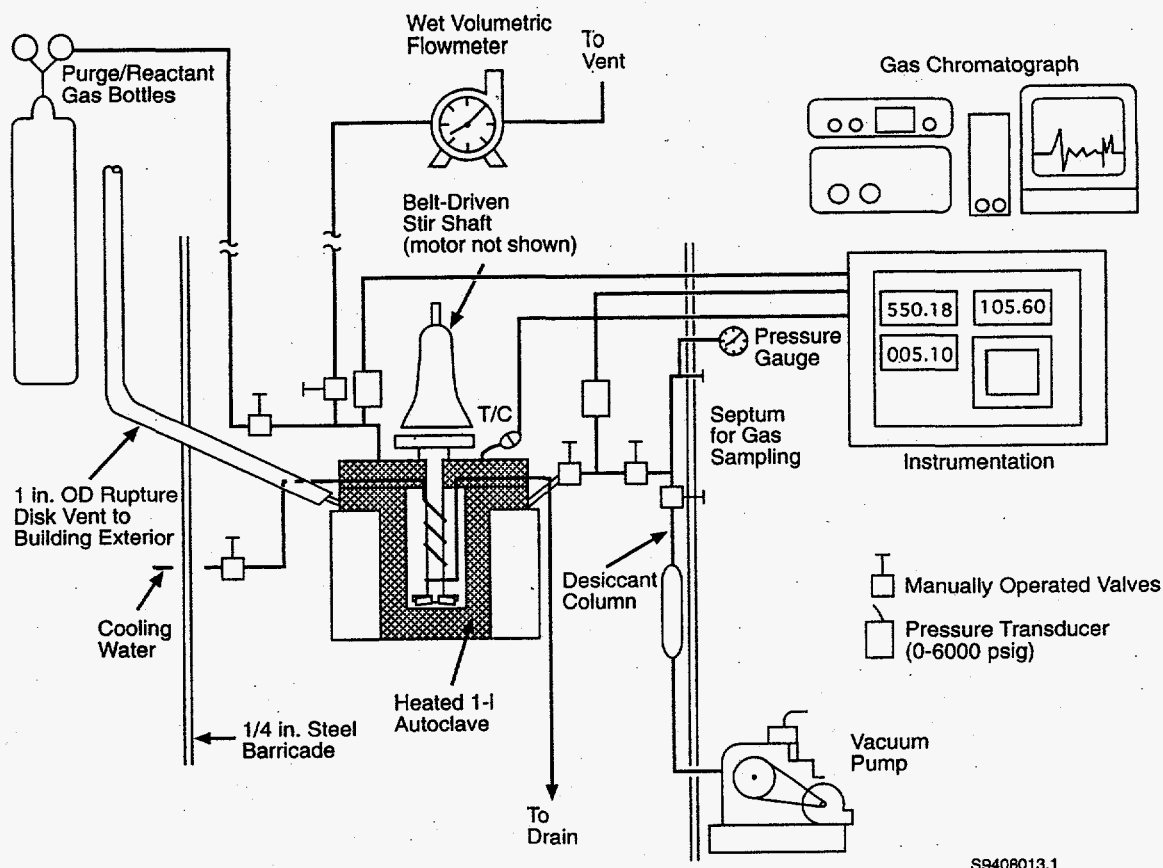


Figure 4.1. Schematic Diagram of the Batch Autoclave Reactor System

magnetic-coupled stirrer. The reactor has a cooling coil that is used to cool down its contents at the end of each experiment. The reactor and the majority of the ancillary equipment under pressure are contained inside a 1/4-in. steel barricade. Pressure indicators, temperature and stirrer controllers, and pressure and temperature alarms are located outside the barricade.

Gas samples are taken through a body wall port in the top of the reactor. The reactor and sample removal system are operated remotely after the reactor has been batch charged. The gas sample system employs a combination of a manually operated sampling valve and a pressure transducer on the sample loop. Typically, the sample loop is filled to a pressure of 50 psig. The sampling system allows the entire sample loop to be evacuated prior to taking a sample, which avoids contaminating the sample by previous samples. The system is equipped with an adsorbent column to collect any water and other liquids in the samples. This column is weighed before and after experiments for a quantitative determination of the mass of water collected.

4.4 Results and Discussion

4.4.1 TOC Destruction as a Function of Test Conditions and Organic Composition

The run conditions of the FY 1994/95 batch tests, and some FY 1993 batch tests that will also be discussed, are given in Table 4.2. The primary purpose of the FY 1993 and FY 1994 testing was to determine the effects of temperature and hold time on TOC destruction for a variety of different organics. The FY 1995 testing focused on conducting lower-temperature HPT/heat and digest bridging studies. Most of these lower-temperature tests were conducted using undiluted 101-SY simulant (Runs 31 through 35 in Table 4.2), since ongoing heat and digest testing is being conducted with undiluted 101-SY actual waste. However, a limited number of low-temperature tests were conducted in FY 1995 using 3:1 diluted 101-SY simulant (i.e., Runs 3, 4, and 5 in Table 4.2) to supplement two other low-temperature tests that had been conducted in FY 1994 (Runs 1 and 2 in Table 4.2).

The TOC, nitrate, and nitrite concentrations are given in Table 4.3 for the feed and products from the batch runs. In addition, the last two columns of the table show the moles nitrate and nitrite consumed per mole TOC destroyed.

When EDTA was used as the organic source, nitrite was, in general, consumed preferentially over nitrate. The average nitrate/TOC consumption (mol/mol) was approximately 0.15 compared with approximately 0.75 mol nitrite consumed/mol TOC destroyed for the first 17 runs listed in Table 4.3.

Runs 18 through 20 were conducted using 3:1 diluted 101-SY simulant and HEDTA/EDTA (2:1 mole ratio) as the organic source. Use of this ratio of HEDTA/EDTA was based on successful demonstration that it behaved essentially the same as the organics in actual 101-SY tank waste samples during ozonation organic destruction testing (Delegard 1993). The nitrate/TOC and nitrite/TOC consumptions given in Table 4.3 are similar to those observed when 3:1 diluted 101-SY simulant (EDTA as the organic source) was used as feed.

In the limited number of tests conducted using formate, citrate, or acetate as the organic sources, no clear distinction can be made as to whether nitrate or nitrite is preferentially consumed. Both nitrate and nitrite do appear to be involved in the destruction of the organics to some extent.

The relative destruction efficiencies of the various organics tested are illustrated in Figure 4.2. Of the organic species tested, acetate is by far the most difficult organic species to destroy under HTP test conditions. Citrate is the next most difficult organic species to destroy, followed by oxalate, EDTA, HEDTA/EDTA (2:1 molar ratio), and formate. It was slightly more difficult to destroy the EDTA in the filtered simulant than in the unfiltered simulant. The reason is unknown; however, it has been speculated that the solids may play a catalytic role to enhance organic destruction.

Runs 3 through 5 and Runs 31 through 35 are the lower-temperature HTP/heat and digest bridging tests that were conducted in FY 1995. The majority of the testing and temperatures evaluated were conducted using undiluted 101-SY simulant (Runs 31 through 35), primarily because 1) current heat and digest testing is being conducted using undiluted 101-SY actual waste, and 2) if heat and digest is

Table 4.2. HTP Batch Run Conditions

Run #	Hold Temperature (°C)	Hold Pressure (psig)	Hold Time (minutes)
3:1 Diluted 101-SY Simulant, EDTA as Organic Source			
1	226	1400	60
2	250	2940	60
3 ^(a)	249	1320	300
4	250	1820	300
5	255	2060	300
6	297	2500	60
7 ^(a)	301	1300	60
8	325	2680	60
9 ^(a)	343	1830	60
10 ^(b)	350	3320	15
11 ^(b)	350	2940	60
12 ^(b)	352	3150	60
3:1 Diluted 101-SY Simulant (Supernatant), EDTA as Organic Source			
13	325	2720	60
14	349	2870	15
15	351	3010	60
16	356	3210	60
1:1 Diluted 101-SY Simulant, EDTA as Organic Source			
17	325	2650	60
3:1 Diluted 101-SY Simulant, HEDTA/EDTA (2:1 mole ratio) as Organic Source			
18	306	2840	60
19	325	2820	60
20	355	3220	60
3:1 Diluted 101-SY Simulant, Formate as Organic Source			
21	328	3000	60
22 ^(b)	353	3260	60
3:1 Diluted 101-SY Simulant, Citrate as Organic Source			
23	325	2910	60
24 ^(b)	353	2930	60
3:1 Diluted 101-SY Simulant, Acetate as Organic Source			
25 ^(b)	303	2690	60
26 ^(b)	350	2210	60
27 ^(b)	350	3040	60
28 ^(b)	350	2930	240
29 ^(b)	411	4720	60

Table 4.2. (contd)

Run #	Hold Temperature (°C)	Hold Pressure (psig)	Hold Time (minutes)
3:1 Diluted 101-SY Simulant, Oxalate as Organic Source			
30	324	2980	60
Undiluted 101-SY Simulant, HTP/Heat and Digest Bridging Tests EDTA as Organic Source			
31 ^(a)	173	1100	8640
32 ^(a)	198	1170	2880
33	205	1510	2880
34	246	1500	225
35 ^(a)	250	1460	300
(a) Microautoclave used to conduct testing. (b) Batch tests conducted in FY 1993.			

Table 4.3. Total Organic Carbon, Nitrate, and Nitrite Consumption from Batch HTP Testing

Run #	Total Organic Carbon (mg/kg)		Nitrate (mg/kg)		Nitrite (mg/kg)		Nitrate Destroyed/ Total Organic Carbon Destroyed (mol/mol)	Nitrite Destroyed/ Total Organic Carbon Destroyed (mol/mol)
	Feed	Prod.	Feed	Prod.	Feed	Prod.		
3:1 Diluted 101-SY Simulant, EDTA as Organic Source								
1	5150	6950	33000	41000	38000	46000	---	---
2	5260	4380	39800	39600	38600	35900	0.04	0.80
3	4410	2740	30300	26000	31600	24100	0.49	1.2
4	4980	2860	41800	46600	36300	30100	0	0.76
5	5750	3070	45300	45500	39600	29400	0	0.99
6	4600	2470	39400	43700	30800	27900	0	0.36
7	4410	1130	30300	29500	31552	18966	0.04	1.0
8	5220	1020	48200	38800	41600	27700	0.43	0.87
9	4410	550	30300	26600	31600	20300	0.18	0.76
10	4770	1050	40700	36200	32800	23900	0.23	0.62
11	4820	270	40900	36600	33000	20200	0.18	0.74
12	4820	270	41900	37700	32800	20200	0.18	0.72
3:1 Diluted 101-SY Simulant (Supernatant), EDTA as Organic Source								
13	5610	1580	45300	46200	40300	28500	0	0.76
14	5610	1730	45300	45700	40300	28500	0	0.79
15	5610	1330	45300	42500	40300	26600	0.13	0.84
16	5200	840	45600	40100	40700	22200	0.24	1.11

Table 4.3. (contd)

Run #	Total Organic Carbon (mg/kg)		Nitrate (mg/kg)		Nitrite (mg/kg)		Nitrate Destroyed/ Total Organic Carbon Destroyed (mol/mol)	Nitrite Destroyed/ Total Organic Carbon Destroyed (mol/mol)
	Feed	Prod.	Feed	Prod.	Feed	Prod.		
1:1 Diluted 101-SY Simulant, EDTA as Organic Source								
17	9580	3540	70200	55700	60300	52100	0.47	0.35
3:1 Diluted 101-SY Simulant, HEDTA/EDTA (2:1 mole ratio) as Organic Source								
18	4830	1860	41900	37200	35900	22500	0.31	1.18
19	4830	570	40800	40800	36700	23300	0.0	0.82
20	4830	270	40800	37200	36700	22300	0.15	0.82
3:1 Diluted 101-SY Simulant, Formate as Organic Source								
21	5120	110	37900	31000	32500	20300	0.27	0.63
22	6770	460	39200	38300	33300	21100	0.03	0.50
3:1 Diluted 101-SY Simulant, Citrate as Organic Source								
23	7120	3760	44900	43900	41600	34200	0.06	0.58
24	5870	2500	43800	37400	34400	30800	0.37	0.28
3:1 Diluted 101-SY Simulant, Acetate as Organic Source								
25	5780	6190	39900	39100	32700	29600	--	--
26	5780	4740	39100	36100	36100	33400	0.56	0.68
27	5780	5120	39500	36200	34400	27300	1.03	2.8
28	5390	600	40600	25700	32200	30100	0.60	0.11
29	5390	120	40600	9600	32200	38400	1.13	--
3:1 Diluted 101-SY Simulant, Oxalate as Organic Source								
30	9840	4150	NR	NR	NR	NR	NR	NR
Undiluted 101-SY Simulant, HTP/Heat and Digest Bridging Tests EDTA as Organic Source								
31	14400	7930	117143	115294	117100	87100	0.06	1.2
32	14400	5600	117143	97222	117100	94400	0.43	0.67
33	14600	7560	150000	93125	103800	84400	1.51	0.72
34	17800	12300	121875	106875	104400	100600	0.52	0.18
35	14400	2740	117143	44222	117100	60000	1.21	1.27

implemented, the current plans are to treat the waste as-is, in-tank (i.e., undiluted). These tests were conducted to determine if HTP organic destruction and strontium removal (discussed in Section 4.4.2) results could be extrapolated with any degree of accuracy to heat and digest conditions.

Based on previous HTP batch testing results and assumed first order rate dependence on TOC and nitrite (Orth et al. 1993), the run conditions (i.e., hold time for a given temperature) for the low-temperature bridging tests were chosen such that between approximately 40% and 80% TOC destruction would be expected. The predicted and actual TOC destructions (taken from the data in Table 4.3) are given in Table 4.4 for the individual runs.

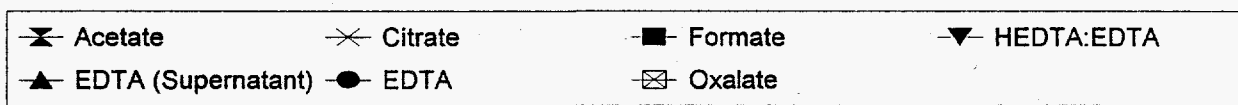
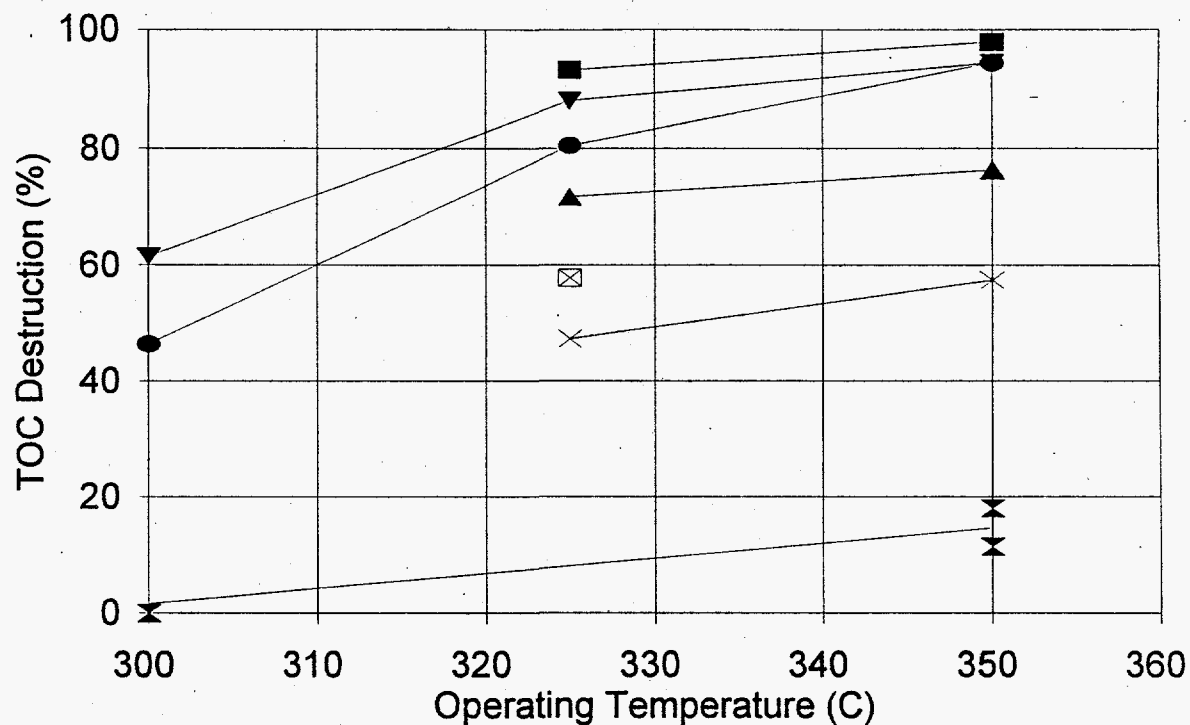


Figure 4.2. Relative HTP Organic Destruction Efficiencies for EDTA, HEDTA/EDTA, Formate, Citrate, Acetate, and Oxalate (1-hr batch tests, using 3:1 diluted 101-SY simulant).

Table 4.4. Predicted and Actual TOC Destruction for Low-Temperature Bridging Tests

Run #	Run Temperature (°C)	Time (minutes)	Predicted TOC Destruction (%)	Actual TOC Destruction (%)
3	249	300	40	38
4	250	300	40	43
5	255	300	50	45
31	173	8640	60	45
32	198	2880	70	61
33	205	2880	76	48
34	246	225	60	31
35	250	300	80	81

As can be seen from the comparison, all but two of the runs (Runs 33 and 34) gave TOC destructions comparable to those that would be expected, based on previous HTP batch tests. The TOC destructions for Runs 33 and 34 were significantly lower than what was estimated, but the reason is still unclear.

As compared with Runs 1 through 17, the moles nitrate consumption/moles TOC destruction ratios were higher for all of the undiluted simulant, low-temperature runs with the exception of Run 31. The moles nitrite consumed/moles TOC destroyed were approximately what was expected (based on Runs 1 through 17) for all of the runs with the exception of Run 34, which was significantly lower.

Overall, the test results obtained at the bridging temperatures were in fair agreement with what would be expected from the tests conducted at typical HTP conditions. This provides further confidence in applying the global kinetics that were obtained at typical HTP conditions (Orth et al. 1993) to heat and digest processing.

4.4.2 Removal of Strontium from Simulant Supernatant via HTP Treatment

The effect of organic destruction via HTP on the fate of strontium in the simulant supernatant is given in Table 4.5. In all cases, samples of the liquid feed and product were passed through 0.45- μm filters, and the resulting filtrate was analyzed for strontium.

As a result of the $\text{Sr}(\text{NO}_3)_2$ added to the simulant (Table 4.1), approximately 170 ppb strontium were present in the 3:1 diluted 101-SY simulant. However, in some cases (e.g., 3:1 diluted 101-SY simulant, HEDTA/EDTA, and citrate as organic sources, Table 4.5), significant amounts of strontium were introduced into the simulant as an impurity in the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ that was added (Table 4.1). Therefore, the approximate value of 170 ppb total strontium represents the minimum total strontium concentration initially present in the simulants.

The first set of data given in Table 4.5 is for 3:1 diluted 101-SY simulant containing EDTA as the organic source. As shown, the TOC destruction ranges from 0% to 94%, and the strontium removal from solution ranges from 45% to greater than 99%. TOC destruction of approximately 50% or greater leads to a decrease in supernatant strontium concentration of $\geq 94\%$.

The second set of data given in Table 4.5 is for 3:1 diluted 101-SY simulant supernatant (i.e., simulant was filtered prior to HTP treatment) containing EDTA as the organic source. In these tests, the simulant was passed through a 0.45- μm filter, and the filtrate was used as feed for HTP treatment. In this set of tests, the TOC destruction levels were between 72% and 76%, and 94% to $>99\%$ of the strontium was removed from solution. Comparison of the first two data sets in Table 4.4 indicates that filtration of the feed material prior to HTP treatment has little or no effect on strontium removal.

A 2:1 molar ratio of HEDTA/EDTA was the organic source used to obtain the next set of data presented in Table 4.5. For the conditions tested, $>99\%$ of the strontium was removed from solution by treatment with HTP. In the tests, TOC destruction levels ranged from 62% to 94%.

Table 4.5. Autogenous HTP TOC Destruction/Strontium Removal Results^(a)

Batch Test Conditions (temp, hold time)	TOC Destruction (%)	Initial Sr in Feed Supernatant (ppb)	Final Sr in Product Supernatant (ppb)	Sr Removed From Supernatant (%)
3:1 Diluted 101-SY Simulant, EDTA as Organic Source				
225°C, 1 hour ^(b)	0	220	98	56
250°C, 1 hour ^(b)	17	220	120	45
249°C, 5 hours	38	130	<4	>97
250°C, 5 hours	43	390	30	93
250°C, 5 hours	47	370	20	94
297°C, 1 hour	46	300	<2	>99
301°C, 1 hour ^(b)	74	130	<4	>97
325°C, 1 hour	81	380	9	98
343°C, 1 hour ^(b)	88	130	<4	>97
350°C, 0.25 hour	79	320	6, <2	98, >99
350°C, 1 hour	94	300	18	94
350°C, 1 hour	94	250, 240	<3, <2	>99, >99
3:1 Diluted 101-SY Simulant (Supernatant), EDTA as Organic Source				
325°C, 1 hour	72	370 ^(c)	<2	>99
349°C, 0.25 hour	69	370	<7	98
351°C, 1 hour	76	370	21	94
3:1 Diluted 101-SY Simulant, HEDTA/EDTA (2:1 MOL:MOL) as Organic Source				
306°C, 1 hour	62	820 ^(c)	6 ^(b)	99
325°C, 1 hour	88	820	<8	>99
355°C, 1 hour	94	820	<8	>99
3:1 Diluted 101-SY Simulant, Formate as Organic Source				
328°C, 1 hour	93	51	30	42
353°C, 1 hour	98	16	<3	>83
3:1 Diluted 101-SY Simulant, Citrate as Organic Source				
325°C, 1 hour	47	770 ^(c)	19	98
352°C, 1 hour	57	770	<8	>99
3:1 Diluted 101-SY Simulant, Acetate as Organic Source				
303°C, 1 hour	0	3 ^(c)	<2	>21
350°C, 1 hour	15	3	8	--
351°C, 4 hours	89	3	8	--
411°C, 1 hour	98	3	7	--

Table 4.5. (contd)

Batch Test Conditions (temp, hold time)	TOC Destruction (%)	Initial Sr in Feed Supernatant (ppb)	Final Sr in Product Supernatant (ppb)	Sr Removed From Supernatant (%)
Undiluted 101-SY Simulant, HTP/Heat and Digest Bridging Tests EDTA as Organic Source				
173°C, 144 hours ^(b)	45	290	210	29
198°C, 48 hours ^(b)	61	290	<13	>96
205°C, 48 hours ^(b)	48	790	280	65
246°C, 3.75 hours ^(b)	31	790	.960	--
250°C, 5 hours ^(b)	81	290	77	73
<p>(a) All strontium analyses conducted via graphite furnace atomic absorption with Zeeman correction unless noted otherwise. In some cases significant amounts of strontium were introduced into the simulant as an impurity in the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ that was added. In all cases, a minimum of 170 ppb strontium was added as $\text{Sr}(\text{NO}_3)_2$.</p> <p>(b) Strontium analyses conducted via inductively coupled plasma/mass spectroscopy.</p> <p>(c) One composite feed sample taken for that simulant.</p>				

Formate was the organic source used to obtain the next set of data given in Table 4.5. Formate does not complex strontium effectively in comparison with some of the other organic compounds evaluated. The strontium remaining in solution varied between <3 ppb and 30 ppb (i.e., 42% to >83% strontium removal) after greater than 90% TOC destruction.

The fifth set of data given in Table 4.5 is for 3:1 diluted 101-SY simulant with citrate as the organic source. Citrate effectively complexed strontium in the feed, but was very susceptible to destruction/defunctionalization. Greater than 97% strontium removal was achieved at TOC destruction levels below 60%.

The sixth set of data given in Table 4.5 is for 3:1 diluted 101-SY simulant containing acetate as the organic source. Strontium is not complexed well by acetate, as illustrated by the very low initial strontium concentrations in the feed supernatant. As was shown in Figure 4.2, acetate is by far the most difficult organic to destroy. However, from a complexant destruction perspective, it is unnecessary to destroy acetate.

The last set of data given in Table 4.5 is for the lower-temperature HTP/heat and digest bridging tests that were conducted with undiluted 101-SY simulant (EDTA as the organic source). As was observed in previous tests, where EDTA was the organic source, TOC destruction leads to strontium removal from solution. The results do indicate, however, that a higher TOC destruction may be required for the undiluted simulant as compared with the 3:1 diluted simulant. For example, in the undiluted case (treatment at 246°C and 3.75 hr), 31.2% TOC destruction led to no strontium removal from solution, while at similar conditions (249°C and 5 hr) and comparable TOC destruction (38%) for 3:1 diluted simulant (EDTA as the organic source), >96.7% of the strontium was removed from solution. For the undiluted simulant, low-temperature tests, as the TOC destruction approached 50% (and greater), significant amounts of strontium were removed from solution.

In addition to strontium, the effect of TOC destruction on other bulk metals was examined in this testing. As expected, calcium and nickel, both existing as divalent cations in the supernatant, behaved similarly to strontium. For example, in the presence of EDTA (3:1 diluted 101-SY simulant), the calcium concentration was approximately 92 mg/kg, and the nickel concentration was approximately 29 mg/kg in the filtered supernatant prior to HTP treatment. After HTP treatment of this feedstock (i.e., $\geq 50\%$ TOC destruction), the resulting calcium and nickel concentrations in the filtered supernatants were < 6 mg/kg and < 2 mg/kg, respectively. As expected, acetate and formate did not complex either nickel or calcium to an appreciable extent. Calcium and nickel concentrations were < 6 mg/kg in filtered 3:1 diluted 101-SY simulant feeds containing either acetate or formate as the organic sources.

Chromium concentrations in solution tended to increase upon HTP treatment. In the presence of EDTA, chromium concentrations in solution were approximately 120 mg/kg prior to treatment, and typically > 1000 mg/kg after HTP treatment of 3:1 diluted 101-SY simulant. In the runs conducted using filtered 101-SY simulant as feed (EDTA as the organic source), no change in chromium concentration in solution was noted. Initial chromium concentrations in filtered 3:1 diluted 101-SY simulant solutions containing either acetate or formate tended to be lower than when EDTA was present as the organic source. Chromium concentrations in these solutions were approximately 24 mg/kg; however, upon HTP treatment, the chromium concentrations in solution were typically > 1000 mg/kg. The increase in chromium concentration upon HTP treatment is likely due to the oxidation of Cr (III) to Cr (VI). The change in solution color from a greenish-brown, before treatment, to a yellowish color, after treatment, supports this hypothesis.

The same general trends discussed above, relating TOC destruction to strontium removal via HTP, were also observed in WAO testing (see Section 5.3.2).

4.5 Direction of Future Work

It is recommended that batch HTP testing be conducted with simulants and actual wastes, other than 101-SY, and with a variety of organic components (Campbell et al. 1994). The data obtained from these tests will be used to 1) optimize test conditions with actual waste so that testing costs can be minimized, 2) compare simulant results with similar testing performed using actual waste matrices, 3) determine the degree of TOC destruction for a variety of organics, and 4) further develop a relationship between TOC destruction for a variety of organics and strontium and TRU removal (or TRU surrogates).

Additional HTP (simulant and actual waste) tests should also be conducted at temperatures somewhat lower than typical HTP testing conditions (i.e., a temperature range of 150°C to 250°C). These data would be used primarily to support ongoing heat and digest work.

5.0. Batch WAO Testing with Simulant

Wet air oxidation has been successfully used by a wide variety of commercial industries since its initial development in the 1940s. Although originally applied to resource recovery (e.g., recovery of soda from spent pulp liquors), during the past 20 years WAO has been used to treat a wide variety of manufacturing and other process waste streams. More recently, WAO is receiving attention as an effective treatment for an increasing variety of environmental control, resource recovery, and energy-related issues.

The most frequent application of this type of hydrothermal processing technology has been for waste treatment. Examples of successful commercial applications are listed below:

- treating spent caustic from gas scrubbing, reducing the chemical oxygen demand (COD) and sulfide content by 95%, and eliminating the need for otherwise expensive landfill disposal of the liquid wastes
- conditioning wastewater plant sludge by oxidizing and solubilizing organics, which then breaks up the gel-like structure of the sludge and greatly increases its dewaterability
- treating coke oven gas scrubbing liquors from foundry and steel-making processes, with generation and recovery of ammonium sulfate and sulfuric acid as valuable byproducts
- treating black liquors from alkaline soda pulping operations, demonstrating high recovery of heat liberated during exothermic oxidation of organics, and recovery of valuable pulping chemicals
- treating sludges and wastewaters contaminated with highly toxic organics, cyanides, etc., with greater than 99% destruction of the toxics.

A variety of other high-strength industrial waste streams have been successfully treated with WAO. These waste streams include scrubbing liquors from styrene monomer-propylene oxide production, wastewaters from synthetic rubber and caprolactum manufacturing, sulfidic spent caustic from refineries, oil field spent caustic from sour gas cleanup, pesticide wastewaters, and solvent still bottoms. Operating results reported by the U.S. Environmental Protection Agency and others have shown destructions approaching or exceeding 99% for many substances, e.g., cyanides, phenols, sulfides, chlorinated hydrocarbons, pesticides, scrubbing liquors, and other regulated wastes.

Zimpro is prominent in the commercial deployment of hydrothermal processing technology. Their particular approach to WAO is currently being used to treat a variety of industrial and municipal wastewater streams worldwide. Zimpro's capabilities range from bench-scale treatability studies through pilot-plant testing to full-scale fabrication, installation, and startup support. Zimpro has provided WAO units to such industries as ethylene production plants throughout the United States and overseas for converting caustic waste liquors into nonhazardous effluents. In some cases, Zimpro has prefabricated these treatment systems as skid-mounted units capable of treating up to 20 gpm. Typically, hazardous organics are either converted to simpler biodegradable compounds or oxidized completely to CO₂ and water, depending on the desired degree of oxidation. For high degrees of

oxidation, organic or inorganic sulfur is converted to sulfate. Organic nitrogen is converted to ammonia. The halogens of halogenated organics are converted to inorganic halides.

Under subcontract to PNL, Zimpro conducted a series of batch-type, laboratory-scale WAO tests to evaluate the destruction of organic compounds and ferrocyanide. The primary focus of the batch WAO test runs was to determine the effects of temperature on destruction of organic compounds and ferrocyanide. Phase behavior (i.e., solids formation) and off-gas composition information was collected during the runs. A separate set of tests were performed to evaluate potential materials of construction for WAO and HTP processing equipment. The corrosion evaluation was performed with five variations of the 101-SY simulant composition.

5.1 Objectives

In FY 1993, the two primary treatment objectives of the batch WAO tests were 1) reduction of the TOC in the tank waste simulant to 1556 ppm after the simulant was concentrated/diluted to 5 M Na and 2) reduction of the cyanide complexed with iron compounds and other cyanide species to less than 2.5% by weight of the residual solid material. These objectives were dictated by IPM to resolve Hanford tank waste safety issues.

In FY 1994, another objective was identified: the destruction of TOC to enhance the removal of radioactive constituents such as strontium and TRU. Thus, treated and untreated samples from the FY 1993 batch WAO tests were analyzed for strontium.

5.2 Test Approach

During FY 1993, 37 batch tests (15 tests in duplicate, and 7 additional tests) were conducted in 500-mL and 750-mL autoclave reactors with five simulant compositions (variations of SY1-SIM-93A). The recipe used by Zimpro was identical to that used for PNL's HTP testing (see Table 4.1). The simulants contained one of the following: EDTA, acetate, formate, or potassium ferrocyanide. The organic compounds were added to produce a feed simulant that contained approximately 6000 mg/L TOC when diluted to 3:1. Potassium ferrocyanide was added to give a cyanide concentration of 2200 mg/L in the simulant. Each simulant composition was evaluated at three or four operating temperatures between 260°C and 325°C. Most of this testing involved the addition of air to the reactors; however, one set of tests was performed without air addition to compare against PNL's HTP test results. Table 5.1 is a detailed test matrix that shows simulant composition, dilution factors, and test temperatures for the batch reactor tests.

For each batch test, measured quantities of simulant were placed in reactors at ambient temperatures. Next, the reactors were sealed and charged to predetermined pressures with air or an inert gas. For the WAO runs, the quantity of air charged to the reactors was such that excess oxygen would be present in the reactors even at 100% TOC destruction. After the reactors were charged, they were placed in a heat-jacketed rocker assembly that was heated to the desired test temperature and controlled at that temperature for a period of 1 hr. At the end of the hold period, the reactors were cooled and depressurized. The volume of the generated noncondensable off-gas was measured and recorded. Concentrations of the following species in the off-gas were determined by GC: O₂, N₂, H₂, CO, CO₂, N₂O, NO_x, and CH₄. The liquid feed and treated simulant were analyzed for cations, anions, COD, TOC, TSS, total solids (TS), pH, and NH₃.

Table 5.1. WAO Test Matrix

Run No.	Stock Simulant	Dilution Factor	Test Temperature (°C)	Charge Gas
1	SY1-SIM-93A/EDTA	3:1	260	Air
2	SY1-SIM-93A/EDTA	3:1	280	Air
3	SY1-SIM-93A/EDTA	3:1	300	Air
4	SY1-SIM-93A/Acetate	3:1	260	Air
5	SY1-SIM-93A/Acetate	3:1	280	Air
6	SY1-SIM-93A/Acetate	3:1	300	Air
7	SY1-SIM-93A/Formate	3:1	260	Air
8	SY1-SIM-93A/Formate	3:1	280	Air
9	SY1-SIM-93A/Formate	3:1	300	Air
10	SY1-SIM-93A/EDTA	3:1	260	N ₂
11	SY1-SIM-93A/EDTA	3:1	280	N ₂
12	SY1-SIM-93A/EDTA	3:1	300	N ₂
13	SY1-SIM-93A/Ferrocyanide	3:1	260	Air
14	SY1-SIM-93A/Ferrocyanide	3:1	280	Air
15	SY1-SIM-93A/Ferrocyanide	3:1	300	Air
16	SY1-SIM-93A/EDTA	1:1	260	Air
17	SY1-SIM-93A/EDTA	1:1	280	Air
18	SY1-SIM-93A/EDTA	1:1	300	Air
19	Duplicate of Run 1	3:1		
20	Duplicate of Run 2	3:1		
21	Duplicate of Run 3	3:1		
22	Duplicate of Run 4	3:1		
23	Duplicate of Run 5	3:1		
24	Duplicate of Run 6	3:1		
25	Duplicate of Run 7	3:1		
26	Duplicate of Run 8	3:1		
27	Duplicate of Run 9	3:1		
28	SY1-SIM-93A/EDTA	3:1	280	He
29	SY1-SIM-93A/EDTA	3:1	300	He
30	SY1-SIM-93A/EDTA	3:1	325	He
31	Duplicate of Run 13	3:1		
32	Duplicate of Run 14	3:1		
33	Duplicate of Run 15	3:1		
34	Duplicate of Run 16	3:1		
35	Duplicate of Run 17	3:1		
36	Duplicate of Run 18	3:1		
37	SIM-SY1-93A/Acetate	3:1	320	Air

In conjunction with the batch testing, five sets of materials-of-construction evaluation tests were conducted at the conditions expected in a WAO system. Additionally, one set of corrosion evaluation tests was conducted under HTP conditions. For these tests, Zimpro evaluated commercially available coupons fabricated from a variety of corrosion-resistant materials. Metal certifications were obtained for each set of corrosion test specimens that included mechanical properties and chemical analyses. A standard finish was required for all of the coupons. Before exposure, the coupons were cleaned, weighed, and examined for manufacturing defects. The coupons were mounted on an insulated rod that was fastened to the inside of an autoclave head. For the corrosion testing, the coupons were exposed to five variants of the 101-SY simulant material. During the tests, the reactors containing the electrically isolated coupons were charged with fresh simulant every 24 hr. After exposure, the coupons were cleaned, reweighed, and examined visually and microscopically for evidence of corrosion.

5.3 Results and Discussion

5.3.1 Batch WAO Screening Tests

As noted in Section 5.1, the treatment objective for the batch WAO testing was to reduce the TOC to less than 1556 ppm when the simulant is concentrated or diluted to 5 M Na to meet LLW requirements. Test results showed that this reduction could be achieved at 280°C with a reaction time of 1 hr for the baseline simulant composition (i.e., 101-SY, 3:1 diluted, with EDTA). For the simulant containing formate as the source of organic, this objective was achieved at 260°C. Consistent with findings at both PNL and LANL (Dell'Orco et al. 1993; Foy et al. 1993), Zimpro's WAO testing showed that TOC reduction in simulant containing acetate is more difficult than any of the other organics tested. Even at a temperature of 320°C and a residence time of 1 hr, the TOC destruction target was not achieved with WAO for the simulant containing acetate. However, as shown in Section 4.4.2, acetate does not complex strontium, and its presence is not expected to adversely impact strontium and TRU removal processes. In all WAO runs conducted with ferrocyanide in the simulant, the cyanide content was reduced by over 99%. Therefore, the target ferrocyanide destruction level can be achieved with WAO at temperatures below 260°C.

To ensure Zimpro's run procedures and simulant makeup were consistent and comparable with those used by PNL, a set of runs were conducted without oxygen addition (i.e., HTP). Overall, the extent of TOC destruction and the analytical results from the feed and product were consistent with the results obtained from PNL's HTP testing. Evidence of the similarity of the PNL and Zimpro test results is provided in Figure 5.1, which shows PNL and Zimpro data on TOC destruction as a function of temperature for HTP. All data shown in this figure were collected from runs with 1-hr hold times at the target temperatures. Figure 5.1 also provides a comparison between WAO and HTP with 101-SY 3:1 diluted simulant containing EDTA as the source of organic. This figure shows that under HTP conditions, at a temperature of 280°C, less than 40% of the TOC is destroyed. In comparison, at 280°C, more than 98% of the TOC was destroyed using WAO. The limited data in this figure indicate that use of WAO can achieve TOC destruction equivalent to HTP at temperatures that are approximately 70°C lower. In the temperature range of interest (260°C to 360°C), a 70°C process operating temperature decrease can significantly reduce the required operating pressure since it is largely determined by the vapor pressure of water. For example, at 350°C, the vapor pressure of water is approximately 2400 psi; whereas at 280°C, the vapor pressure of water is only about 930 psi. This illustrates the tremendous difference in required operating pressure that results from even a

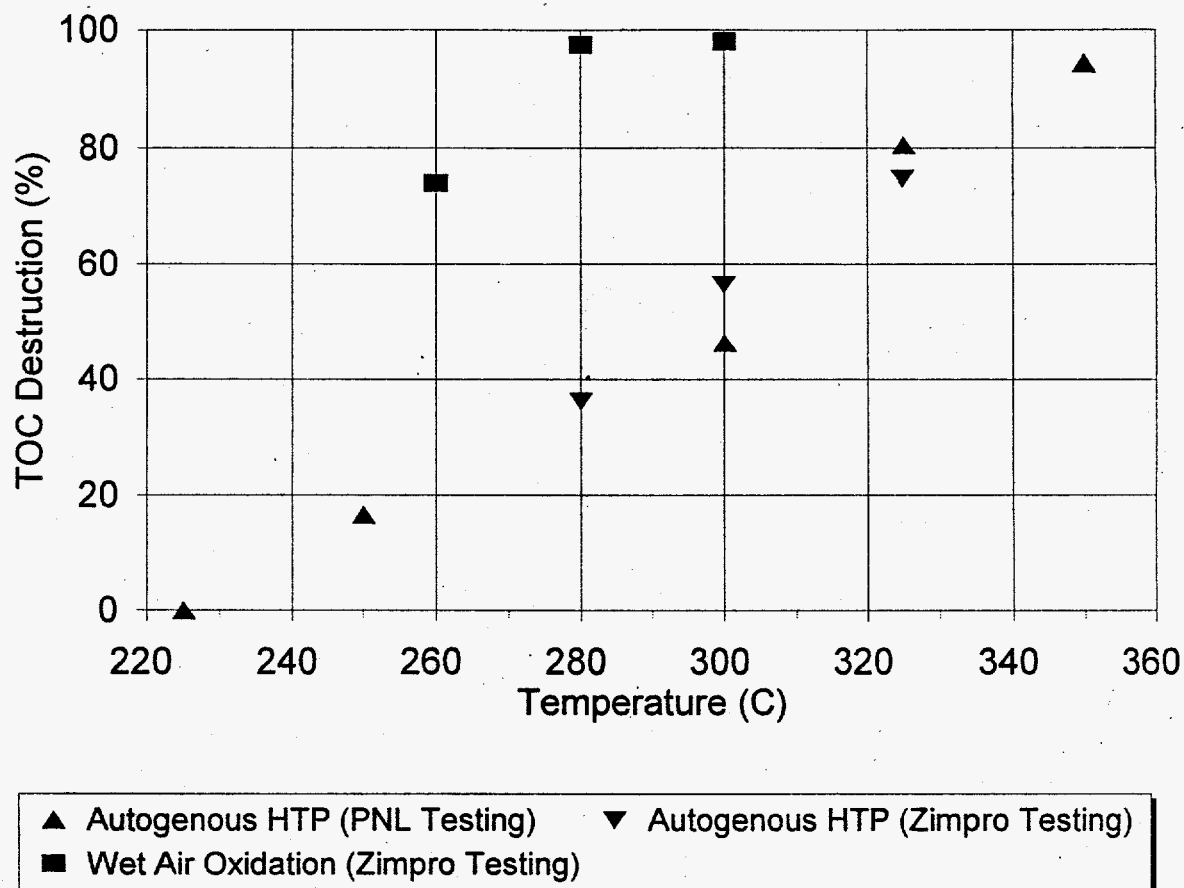


Figure 5.1. Relative TOC Destruction During HTP and WAO Batch Testing (1-hr hold time, 101-SY EDTA 3:1 diluted)

moderate decrease in operating temperature. At lower operating pressures, standard off-the-shelf equipment with proven operating records can be used for construction of full-scale systems.

Figure 5.2 provides the relationship between TOC destruction and temperature for 3:1 diluted 101-SY simulant containing acetate as the source of organic for tests conducted with 1-hr hold times. Under HTP conditions, negligible TOC destruction occurs at a temperature of 300°C, while for WAO, at this temperature, TOC destruction of approximately 25% was observed. Through qualitative analyses of the limited data in this figure, it can be seen that, as was seen with EDTA, WAO achieves TOC destruction equivalent to HTP at temperatures approximately 70°C lower.

WAO and HTP tests were also conducted with 101-SY (3:1 diluted) simulant containing formate as the source of organic carbon. At the conditions tested for both HTP (325°C and 350°C) and WAO (260°C to 300°C), the TOC destruction was always greater than 95%.

Analytical results from the WAO testing show that very little (within analytical error) nitrite is oxidized. This is a significant result because nitrite has the potential to consume much more oxygen

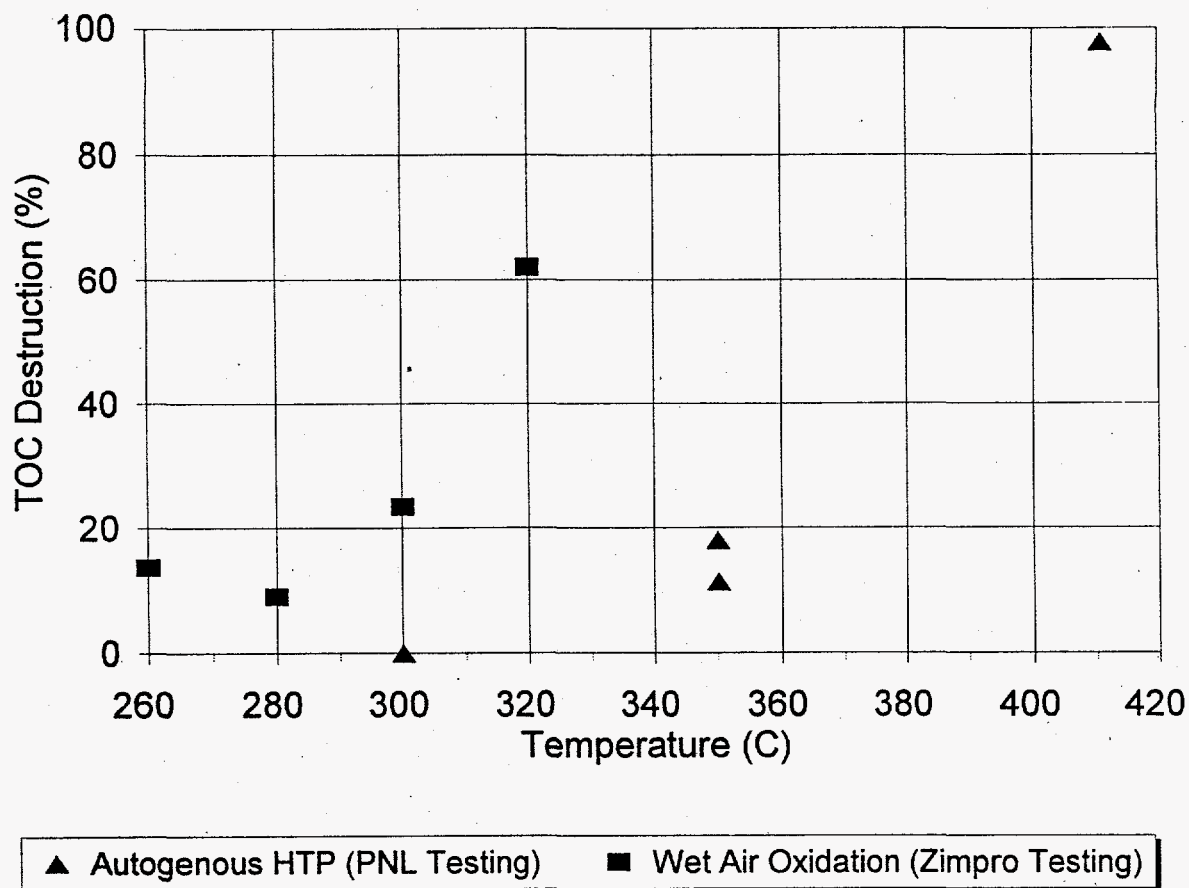


Figure 5.2. Relative TOC Destruction During HTP and WAO Batch Testing (1-hr hold time, 101-SY Acetate 3:1 diluted)

than the organic constituents in the tank waste. For both electrochemical destruction and ozonation, nitrite is typically oxidized prior to organic destruction. For ozonation, this results in a much greater ozone requirement. For electrochemical destruction of tank waste, the oxidation of nitrite to nitrate consumes significant quantities of power, and the current efficiency for organic destruction is therefore only about 20%. One other favorable factor in not oxidizing nitrite with WAO is that the presence of the nitrite inhibits the corrosion rate of the carbon steel tanks which contain the tank waste. Analytical results also showed that little or no nitrite and nitrate were consumed, indicating that most of the TOC oxidation was caused by oxygen under the conditions tested.

While conducting the WAO testing, Zimpro staff observed that the color of the simulant changed from green (for feed) to yellow (for product) [this color change is consistent with observations made during HTP and WAO testing at PNL]. It was hypothesized that this color change resulted from insoluble Cr(III) being oxidized to soluble Cr(VI). Analytical test results confirmed that more than 90% of the chromium was being oxidized. Since Cr(III) may impact the waste loading for high-level glass, oxidation and solubilization of the chromium is desirable. The soluble Cr(VI) can be separated from the sludge and processed with the LLW stream.

Off-gas analyses for WAO testing showed that only trace quantities of N_2O and NO_x were created when processing 3:1 diluted simulant. In the WAO testing with 1:1 diluted simulant containing EDTA as the organic source, measurable, but small, quantities ($<1\%$) of N_2O were formed. The ratio of moles of hydrogen generated per mole of EDTA destroyed via WAO is similar to that obtained for HTP. However, because of the nitrogen present in air, with WAO, the hydrogen is effectively diluted to concentrations below the lower flammability limit (LFL), making the WAO process off-gas safer to handle.

Measurements of total and suspended solids were performed on treated and untreated simulant. Zimpro's measurements of suspended solids in the 3:1 diluted feeds (EDTA, acetate, and formate) varied from 0.5% to about 1%. Suspended solids in the WAO-treated simulant varied from less than 0.1% to about 3%. For the HTP runs conducted by Zimpro, the suspended solids concentration in the treated product was 0.6%. With the formate feed, the suspended solids in the product were always less than in the feed. For both EDTA- and acetate-containing simulant, the suspended solids in the product were about two to three times higher than in the feed. PNL has conducted extensive suspended solids analyses on both feed and product from HTP and WAO testing with 101-SY (3:1 diluted) simulant. These analyses show that both the feed and product contain between 1% and 2.5% suspended solids with no clear trend regarding the generation of solids (i.e., it cannot be stated with confidence that there is a net generation or destruction of suspended solids attributable to WAO or HTP).

While disassembling the autoclave reactors, Zimpro staff examined the interior of the reactors for evidence of solid scale formation. No evidence of scale formation was found in any of the 37 autoclave runs.

5.3.2 Removal of Strontium from Simulant Supernatant via WAO Treatment

The relationship between strontium removal and TOC destruction via the Zimpro WAO and HTP testing is given in Table 5.2. The TOC analyses were performed by Zimpro; the strontium analyses were performed by PNL with ICP-MS using archived samples. The strontium removal results from the WAO and HTP testing conducted by Zimpro using EDTA, formate, and acetate as the organic sources are consistent with those shown in Table 4.5 from PNL's HTP testing.

Table 5.2. Wet Air Oxidation TOC Destruction/Strontium Results^(a)

Batch Test Conditions (temp, hold time)	TOC Destruction (%)	Initial Sr in Feed Supernatant (ppb)	Final Sr in Product Supernatant (ppb)	Sr Removed From Supernatant (%)
3:1 Diluted 101-SY Simulant, EDTA as Organic Source				
260°C, 1 hour	77	190 ^(b)	19	90
	74	190	6	97
280°C, 1 hour	98	190	--	--
	98	190	6	97
282°C, 1 hour ^(c)	96	1310	<4	>97
300°C, 1 hour	98	190	16	91
	98	190	4	98

Table 5.2. (contd)

Batch Test Conditions (temp, hold time)	TOC Destruction (%)	Initial Sr in Feed Supernatant (ppb)	Final Sr in Product Supernatant (ppb)	Sr Removed From Supernatant (%)
3:1 Diluted 101-SY Simulant, Formate as Organic Source				
260°C, 1 hour	80	4 ^(b)	7	--
	98	4	3	--
280°C, 1 hour	70	4	14	--
	97	4	3	--
300°C, 1 hour	99	4	9	--
	99	4	4	--
3:1 Diluted 101-SY Simulant, Acetate as Organic Source				
260°C, 1 hour	19	6 ^(b)	3	--
	9	6	3	--
280°C, 1 hour	10	6	3	--
	9	6	2	--
300°C, 1 hour	0	6	2	--
	23	6	3	--
3:1 Diluted 101-SY Simulant, Ferrocyanide as Organic Source				
260°C, 1 hour	32	6 ^(a)	7	--
	43	6	6	--
300°C, 1 hour	>98	6	--	--
	95	6	5	--
1:1 Diluted 101-SY Simulant, EDTA as Organic Source				
260°C, 1 hour	72	160 ^(b)	11	93
	76	160	14	91
280°C, 1 hour	87	160	10	94
	92	160	--	--
300°C, 1 hour	98	160	--	--
	98	160	11	93
3:1 Diluted 101-SY Simulant, EDTA as Organic Source (no air addition, He cover gas)				
280°C, 1 hour	36	190 ^(b)	9	95
300°C, 1 hour	56	190	5	98
325°C, 1 hour	75	190	6	97
<p>(a) WAO and HTP testing and TOC analyses conducted by Zimpro unless noted otherwise; strontium analyses conducted by PNL via inductively coupled plasma/mass spectroscopy. Strontium added to the simulant as $\text{Sr}(\text{NO}_3)_2 = 170$ ppb; additional strontium may be introduced as an impurity in the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ that was added to the simulant.</p> <p>(b) One composite feed sample taken for that simulant.</p> <p>(c) WAO test conducted by PNL, using the microautoclave described in Section 3.3.</p>				

The first set of data given in Table 5.2 was obtained under WAO conditions, using 3:1 diluted 101-SY simulant (EDTA as the organic source) as the feed. For TOC destructions between 74% and 98%, between 90% and 98% of the initial strontium was removed from solution.

The formate, acetate, and ferrocyanide results presented in Table 5.2 indicate that these compounds do not complex strontium to an appreciable extent. The formate and acetate findings are consistent with those reported in Table 4.5. The fifth set of data given in Table 5.2 was obtained under WAO conditions, using 1:1 diluted 101-SY simulant (EDTA as the organic source) as the feed. For TOC destructions between 72% and 98%, between 91% and 94% of the initial strontium was removed from solution.

The last set of data given in Table 5.2 was obtained under HTP conditions, using 3:1 diluted 101-SY simulant (EDTA as the organic source) as the feed. The results obtained here are consistent with those reported in Table 4.5. For TOC destructions between 36% and 75%, greater than 95% of the initial strontium was removed from solution. These data suggest that as low as 36% TOC destruction allows for 95% strontium removal from solution.

Based on the data both in Table 4.5 and Table 5.2, it appears strontium decomplexation is correlated to TOC destruction/complexant defunctionalization. Relatively low TOC destruction levels ($\leq 50\%$) correspond to removal of significant amounts of strontium ($\geq 90\%$). Whether the destruction/defunctionalization is accomplished by HTP or by WAO makes little or no difference.

5.3.3 Materials-of-Construction Evaluation

Zimpro performed materials-of-construction corrosion testing under WAO conditions with coupons fabricated from a variety of corrosion-resistant materials. The results of this preliminary corrosion evaluation support that 316L, 304L, or Inconel 600 would be acceptable materials of construction. From the corrosion tests, the general corrosion rates for these materials were less than 5.5 MPY in each test. Furthermore, the coupons constructed of these materials showed no evidence of localized or intergranular stress corrosion.

Although this materials-of-construction evaluation indicated that 316L and 304L stainless steel and Inconel 600 had acceptable general corrosion rates and gave no evidence of localized corrosion, long-term materials-of-construction evaluations are recommended prior to the construction of a full-scale WAO or HTP system.

5.4 Direction of Future Work

Batch WAO tests should be conducted with simulants and actual wastes, other than 101-SY, and with a variety of organic components (Campbell et al. 1994). The WAO tests should be conducted primarily at typical WAO operating temperatures so that the data can be applied to a continuous WAO system. However, some testing should also be conducted at temperatures slightly lower than those used under typical WAO conditions (i.e., a temperature range of 150°C to 250°C) to determine whether air addition enhances the heat and digest process.

6.0 Continuous WAO Testing with Simulant

Under HTP conditions, significant quantities of hydrogen gas and nitrous oxide are present in the off-gas (Orth et al. 1993). The off-gases from the runs conducted during FY 1993 typically contained from 27 to 53 mol% H_2 , 33 to 56 mol% N_2O , and 9 to 17 mol% N_2 . In FY 1994 an off-gas safety analysis was conducted to evaluate the potential concern regarding such high hydrogen and nitrous oxide levels in the off-gas. The analysis, and a key literature source (Cashdollar et al. 1992), showed that nitrous oxide/hydrogen mixtures are as flammable, if not more so, than air/hydrogen mixtures. The analysis also indicated that the nitrous oxide/hydrogen levels present in the off-gas from HTP were well within this flammable (and possibly the detonable) range. The complete HTP off-gas safety analysis is included here as Appendix A.

Two potential solutions to the off-gas concern were to 1) add an inert gas upstream of the reactor or 2) add air (e.g., WAO) upstream of the reactor. In both cases, the hydrogen content of the off-gas would be diluted to below the lower flammability limit by either an inert gas, such as argon, or by the nitrogen in the incoming air. In WAO batch tests conducted in FY 1993 by Zimpro for PNL, using 101-SY simulant as the feed (see Section 5.0), the highest hydrogen gas composition observed in the off-gas was approximately 3%. In addition, no nitrous oxide gas was detected. From these WAO tests and HTP batch tests, it was also observed that similar organic destruction levels could be obtained when operating the WAO process at roughly 70°C lower than HTP.

6.1 Objectives

The principal objectives of the continuous WAO bench-scale tests conducted in FY 1994 were to 1) evaluate the merits of WAO on a continuous processing basis for the destruction of organics in Hanford tank waste; 2) evaluate the off-gas produced from WAO; 3) evaluate the chemistry of the WAO process; and 4) compare continuous WAO testing results with continuous HTP testing results obtained in FY 1993.

6.2 Equipment/Facility Description

The continuous WAO tests were conducted using the same continuous reactor system (CRS) as was used in FY 1993 to conduct the HTP tests (Orth et al. 1993; Schmidt et al. 1993). A modification was made to the system to allow for air injection at the base of the reactor. This modification involved incorporating an air injection system. A simplified schematic of the modified CRS system is given in Figure 6.1. The feed used in the testing was the 3:1 diluted 101-SY simulant, using Na_4EDTA as the organic source, described in Table 4.1.

The modified CRS includes a 1-L tubular reactor, a feeding system, an air injection system, a product recovery system, and a data acquisition and control system. In its present configuration, the modified CRS is capable of operation at pressures between 1000 and 2000 psig and temperatures up to approximately 300°C. The pressure and temperature are currently limited by the pressure rating of the air injection system.

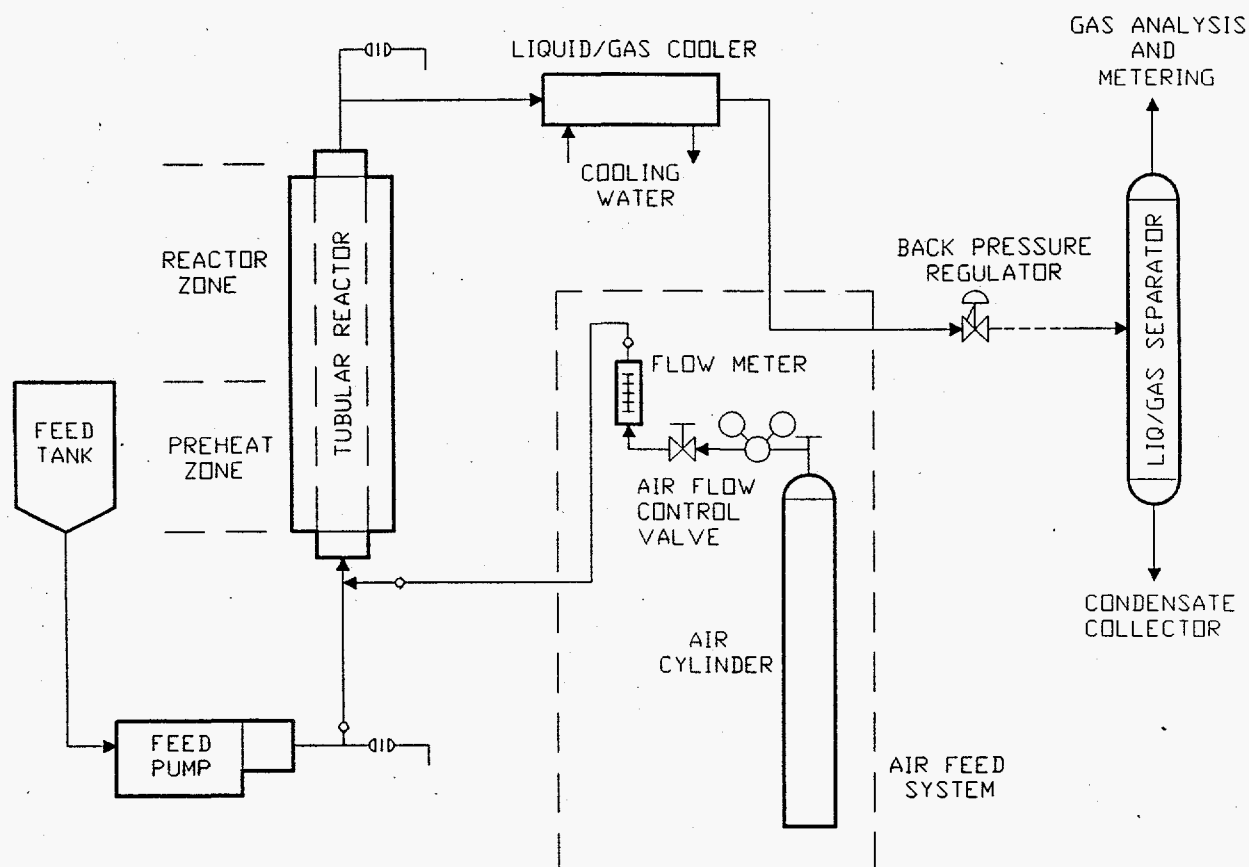


Figure 6.1. Schematic Diagram of the Bench-Scale Wet Air Oxidation Continuous Reactor System

The air delivery system consisted of a 2200-psig air cylinder, with coarse adjustment valves, and fine adjustment valves downstream of the cylinder to maintain the specified air flow to the system. The air flow rate to the system was monitored by an armored flow meter upstream of the reactor and with the use of a wet test meter downstream of the reactor. The air was injected into the simulant feed through a small-diameter tube at the bottom of the tubular flow reactor.

Feed was injected into the reactor with a high-pressure Milton Roy pump capable of delivering 1/2 to 3 liters per hour at pressures from 1000 to 4500 psig. The tubular reactor was packed with stainless steel diagonals to provide good heat transfer and the target void space to achieve the specified residence times in the reactor. For the WAO test runs, the effective void volume within the reactor was approximately 125 mL. The liquid feed flow rates, air flow rates, void space available in the reactor, and the operating temperatures and pressures translated into liquid residence times within the reactor (at temperature) of between approximately 3 and 9 min.

The reactor and the majority of the ancillary equipment under pressure are contained inside a 1/4-in. steel barricade. Temperature, pressure, and feed rate indicators, controllers, and alarms are located outside the barricade.

6.3 Results and Discussion

6.3.1 Experimental Design

Thirteen different WAO test conditions were evaluated. For each test condition evaluated, the system was allowed to come to steady-state, and operation under steady-state condition was maintained for at least 2 hr. All data reported were obtained during steady-state operation.

The test conditions ranged from approximately 260°C to 300°C and 1500 to 2000 psig, with liquid residence times (at temperature) from approximately 3 to 9 min. Air flow rates ranged from approximately 30 to 80 standard liters per hour. The targeted and actual test conditions are given in Table 6.1. In all tests, 3:1 diluted 101-SY simulant containing EDTA as the organic source was used as feed to the system. In addition, in all tests except for Test 10, the majority of the solids were removed from the 101-SY simulant by passing it through a Whatman (medium) filter. The filtering was done because the current Case Beta flowsheet calls for solids removal prior to organic destruction. The test matrix in Table 6.1 was designed to evaluate the effects of residence time, operating temperature, operating pressure, and air flow rate on TOC destruction.

Table 6.1. Bench-Scale Continuous Wet Air Oxidation Target and Actual Test Conditions

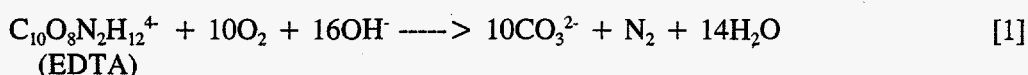
Test	Temperature (°C)	Pressure (psig)	Liquid Flow (L/hr, stp ^(a))	Air Flow (L/hr, stp ^(a))
1	260 (265) ^(b)	1500 (1560)	0.5 (0.47)	34 (62)
2	260 (271)	1500 (1590)	0.75 (0.82)	51 (80)
3	260 (255)	1500 (1540)	1.0 (1.1)	68 (83)
4	280 (280)	1500 (1530)	0.5 (0.52)	34 (44)
5	280 (285)	1500 (1550)	0.75 (0.73)	51 (66)
6	280 (279)	1500 (1580)	1.0 (1.1)	68 (75)
7	300 (307)	1500 (1520)	0.5 (0.49)	34 (34)
8	300 (303)	1500 (1540)	0.75 (0.73)	51 (54)
9	300 (307)	1500 (1570)	1.0 (1.1)	68 (72)
10 ^(c)	300 (300)	1500 (1500)	0.5 (0.57)	34 (34)
11	300 (300)	1500 (1520)	0.5 (0.49)	50 (62)
12	300 (300)	1800 (1710)	0.5 (0.49)	34 (34)
13 ^(d)	300 (304)	1500 (1540)	0.5 (0.49)	82 (72)

(a) Stp = standard temperature (25°) and pressure (1 atmosphere).
 (b) Targeted operating conditions given first; actual operating conditions given second in parentheses.
 (c) Unfiltered 3:1 diluted 101-SY simulant was used in this test. In all other tests, 3:1 diluted 101-SY simulant was filtered through Whatman filter paper to remove the bulk of the solids.
 (d) More EDTA was added to the filtered feed, raising the theoretical TOC concentration of the feed from approximately 5,000 mg/kg to approximately 12,000 mg/kg.

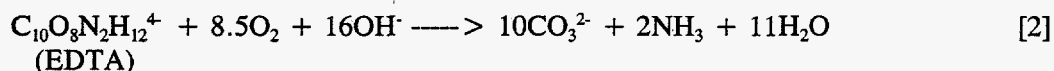
The first nine test conditions generated temperature/residence time data for the development of a kinetic expression for WAO destruction of EDTA. Test 10 was conducted using unfiltered (3:1 diluted) 101-SY simulant to determine whether the presence of solids affected the chemistry or operational stability of the system. No effects on operational stability (i.e., plugging) were observed during this test. Test 11 was conducted to determine the effects of increased air flow on TOC destruction, and Test 12 was conducted to determine the effects of increased system pressure on TOC destruction.

The final test (Test 13) presented a "worst case" scenario for complexant concentrate Hanford waste with respect to initial TOC and strontium concentrations. The TOC content is similar to that of Tank AN-107 (3:1 diluted), and the strontium concentration is somewhat higher than measured in Tank AN-102 (3:1 diluted).

The targeted air flow rates given in Table 6.1 (with the exception of Test 11) were equivalent to approximately 20% excess air, based on the EDTA in the simulant, and by assuming the following reaction:



It was also probable that some or all of the organic nitrogen would be converted to ammonia rather than, or in addition to, nitrogen gas. The following reaction can be written for the conversion of organic nitrogen to ammonia:



If Reaction [2] holds, the targeted air flows presented in Table 6.1 (with the exception of Test 11) would be equivalent to 43% excess air. Both of these reactions assume oxygen is only consumed by oxidation of organic. It is likely that some oxygen is also consumed through the oxidation of inorganic species, such as Cr(III).

A 5000-mg/kg TOC concentration (12,000 mg/kg TOC for Test 13) in the feed was assumed, and a feed density of 1.16 g/mL was used to calculate the required air. For designing the testing matrix, 20% excess air at 100% TOC destruction (based on Reaction [1]) was used to ensure that appreciable amounts of hydrogen gas would not be produced and that oxygen was not the limiting reactant. Perry's Chemical Engineers' Handbook (Perry 1963) suggests that up to approximately 18% excess air is required to obtain complete combustion in air/liquid fuel systems. Reaction [1] assumes that 1) all of the organic nitrogen is converted to nitrogen gas; 2) oxygen is consumed only via Reaction [1]; and 3) in the presence of oxygen, the nitrates and nitrites do not play a significant role in destroying the EDTA at the temperatures and pH studied.

The results obtained from the testing indicated that the assumptions made above were reasonable. The results indicated that Reaction [2] rather than Reaction [1] appeared to most accurately describe the global chemistry.

In all runs, except for Tests 1 and 2, the targeted and actual operating conditions were in fair agreement with one another. In Tests 1 and 2, the actual air flow rates were approximately two times higher than the targeted air flow rates. This was due to problems with the wet test meter during these tests.

For the actual conditions given in Table 6.1, the approximate liquid residence times within the reactor at the desired operating temperature are shown below:

Test #	Liquid Residence Times (minutes)
1	9.3
2	5.1
3	3.8
4	8.5
5	5.6
6	3.8
7	8.7
8	5.5
9	3.4
10	7.5
11	8.0
12	9.0
13	7.7

These liquid residence times were estimated by substituting measured parameters into an empirical equation (Pexidr and Charpentier 1975) for calculating gas holdup in packed bubble columns. The empirical equation was developed from experiments using Raschig-rings as packing in columns with void spaces ranging from 61 % to 97 %.

In PNL testing, the reactor was packed with 3/16-in. stainless steel diagonals, resulting in a 30 % void space. Decreased void space typically results in increased gas holdup; therefore, the liquid residence times given above are most likely conservative (i.e., high). The gas holdups resulting from these calculations ranged from 20 % to 30 %. It should also be noted that the empirical equation for gas holdup was developed from testing at near-ambient pressures. The WAO testing was conducted at elevated pressures, which decreases the density difference between the gas bubbles and liquid in the reactor. Since the density difference is the driving force for the gas velocity, at elevated pressures, it is expected that the gas holdup will be higher than predicted by the empirical equation.

6.3.2 Experimental Results

The off-gas analyses for the different test conditions are given in Table 6.2. As can be seen, the hydrogen gas levels never exceeded 2.5 % in the off-gas. In addition, nitrous oxide levels in the off-gas

Table 6.2. Off-Gas Analyses from Wet Air Oxidation

Test	H ₂ (mol%)	O ₂ (mol%)	N ₂ (mol%)	N ₂ O (mol%)	Other(mol%)
1	0.36	17.2	82.2	<0.1	CH ₄ = 0.23
2	0.74	16.4	82.6	<0.1	CH ₄ = 0.21
3	0.98	16.4	82.7	<0.1	--
4	1.37	13.7	84.8	<0.1	CH ₄ = 0.17
5	0.90	14.7	84.2	<0.1	CH ₄ = 0.19
6	1.04	13.0	85.8	<0.1	CH ₄ = 0.17
7	2.38	11.2	86.3	<0.1	CO ₂ = 0.07
8	2.22	11.9	85.7	<0.1	CH ₄ = 0.12
9	2.34	12.2	85.5	<0.1	---
10	1.70	10.1	87.9	<0.1	CH ₄ = 0.24
11	1.19	15.3	83.5	<0.1	CH ₄ = 0.07
12	1.40	12.1	86.3	<0.1	CH ₄ = 0.17
13	0.74	11.6	87.3	0.15	CH ₄ = 0.19

were less than 0.1% in all cases, with the exception of Test 13 which had a higher organic concentration. In this test the nitrous oxide concentration in the off-gas was 0.15%.

On the average, the air injected to the system consisted of $21.7 \pm 0.7\%$ oxygen and $78.2 \pm 0.8\%$ nitrogen. As would be expected, the oxygen levels in the steady-state product off-gas were lower than in the injection gas (see Table 6.2).

Liquid feed and liquid product pH values, ammonia levels, and TOC concentrations are given in Table 6.3 for the 13 test conditions. In all of the tests, a definite decrease in pH was measured. In all runs, except for the last condition tested, the product pH was on the order of 0.2 to 1 pH unit lower than the feed. This decrease in pH suggests that OH⁻ is consumed as TOC is destroyed. FY 1993 testing showed that direct measurement of OH⁻ in this matrix is extremely difficult; therefore pH is relied upon as only a qualitative measurement of OH⁻ consumption. In the first 12 tests, the product was yellow and contained minimal solids, in contrast to the feed, which was green.

In the final test (i.e., higher initial TOC), the pH of the product was approximately 10.5. The product from this test was gelatinous and cloudy. This was possibly due to Al(OH)₃ precipitating from solution at the lower pH. NaOH was added to some of the samples of product collected from the run. When sufficient NaOH was added to raise the pH to approximately 12.5, the product lost its gelatinous nature, and appeared (visually) to be similar to products from previous runs.

The ammonia concentration in the liquid product samples was measured, and the results are also given in Table 6.3. Liquid product ammonia levels were on the order of 680 to 1260 ppm for all runs, with the exception of the last one listed. During this last run, the liquid product ammonia level was

Table 6.3. Liquid Analyses from Wet Air Oxidation

Test	Liquid Feed			Liquid Product		
	pH	Ammonia (mg/kg)	TOC (mg/kg)	pH	Ammonia (mg/kg)	TOC (mg/kg)
1	13.6	< 50	4860	13.3	1090	1600
2	13.6	< 50	4860	13.3	1050	1820
3	13.7	< 50	4740	13.4	680	2290
4	13.6	< 50	4450	13.3	1040	1360
5	13.6	< 50	4450	13.3	920	1390
6	13.7	< 50	5560	13.3	1130	1830
7	13.9	< 50	4330	13.1	1260	380
8	14.0	< 50	3970	13.4	930	830
9	14.0	< 50	4340	13.4	980	1030
10	13.7	< 50	4420	12.6	1100	620
11	13.9	< 50	4330	13.1	1260	380
12	13.4	< 50	4190	12.6	1060	320
13	13.3	< 50	8730	10.6	2070	330

approximately 2000 ppm. According to Reaction [2], approximately 1400 mg/kg ammonia would be produced upon the conversion of 5000 mg/kg TOC to carbonate. Thus, the ammonia levels measured during the testing correspond well with that predicted by Reaction [2] (discussed further in Section 6.3.4). This suggests that Reaction [2] may predominate over Reaction [1]. It is not feasible to determine the amount of nitrogen gas produced from these tests since the quantity of nitrogen in the injection air is much greater than any that would be produced via Reaction [1].

6.3.3 Comparison of WAO with HTP

The TOC analyses (Table 6.3) show that TOC destructions ranging from approximately 52% to >90% were achieved during the WAO runs. As expected, TOC destruction increased with both operating temperature and residence time. Under the conditions tested, TOC destruction does not appear to have been significantly affected by increased operating pressure (Test 11 versus Test 9), increased air flow rate (Test 12 versus Test 9), or processing of unfiltered versus filtered simulant (Test 10 versus Test 9). The TOC results indicate that at approximately 280°C and a liquid residence time approximately 6 to 9 min (i.e., Tests 4 and 5), TOC destruction of approximately 70% can be achieved. This degree of TOC destruction is comparable to the 1556 ppm (i.e., based on 5500 ppm original TOC) limit originally set by IPM to satisfy LLW requirements. By comparison, in HTP runs conducted in FY 1993, operation at approximately 350°C and a residence time of approximately 8 min were required to achieve 70% TOC destruction (Orth et al. 1993).

This comparison of WAO versus HTP processing of the 101-SY simulant containing EDTA as the organic source is further illustrated in Figures 6.2 and 6.3. The HTP and WAO data presented here

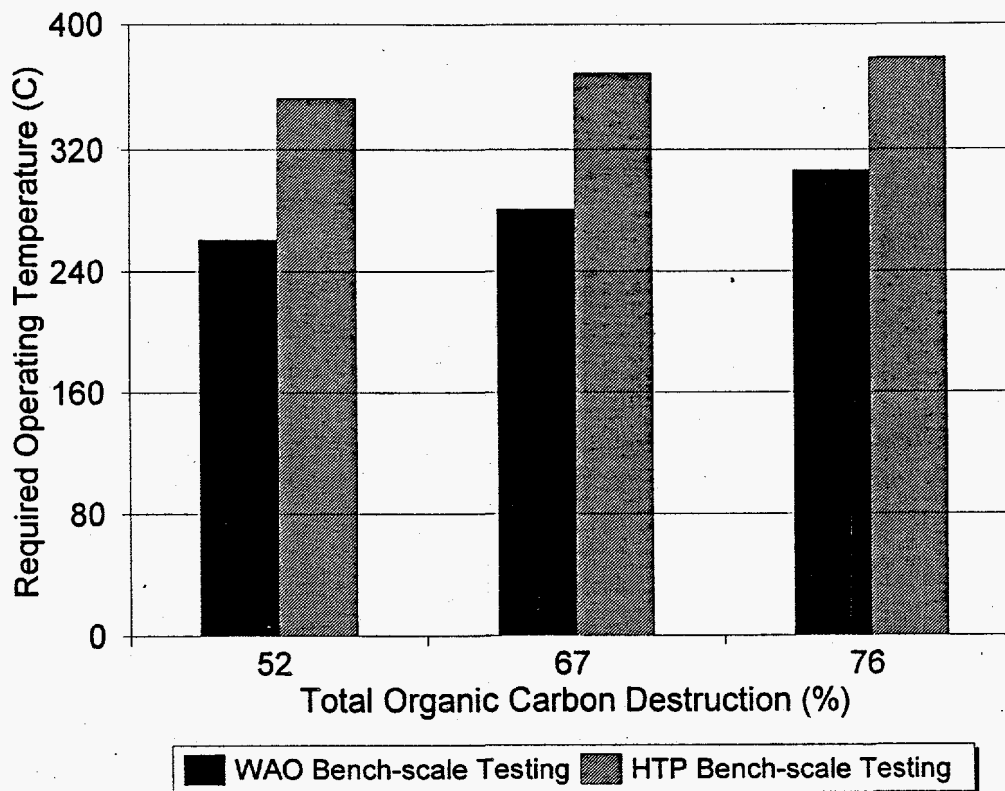


Figure 6.2. Required WAO and HTP Operating Temperature for Destruction of EDTA in 101-SY Simulant (residence time = 4 min)

were obtained from bench-scale continuous testing. The required HTP conditions to achieve the TOC destructions given in Figures 6.2 and 6.3 were obtained from a plot of predicted residence time versus operating temperature from the FY 1993 HTP testing (Orth et al. 1993). In all cases, WAO can be operated at substantially reduced temperatures (i.e., 77°C lower on average) as compared with autogenous HTP to achieve similar TOC destructions. This is in good agreement with batch testing (i.e., 70°C lower with WAO than HTP). Operation at lower temperatures also provides the opportunity to operate a system at lower pressures because of the reduced vapor pressure of water.

6.3.4 WAO Chemistry and Kinetic Evaluation

Molar ratios of hydrogen gas production/TOC destruction, ammonia production/TOC destruction, and oxygen gas consumption/TOC destruction are given in Table 6.4 for the WAO conditions tested. The data are presented in this way to facilitate an evaluation of the global chemistry of WAO destruction of EDTA.

The average oxygen consumption of 0.89 ± 0.10 mol/mol TOC destroyed, given in Table 6.4, corresponds well with both Reaction [1] (O_2 :TOC mole ratio = 1) and Reaction [2] (O_2 :TOC mole ratio = 0.85), which were previously proposed. Because of the small variability in the data, the oxygen data alone, do not allow for the determination of which reaction, if either, may predominate.

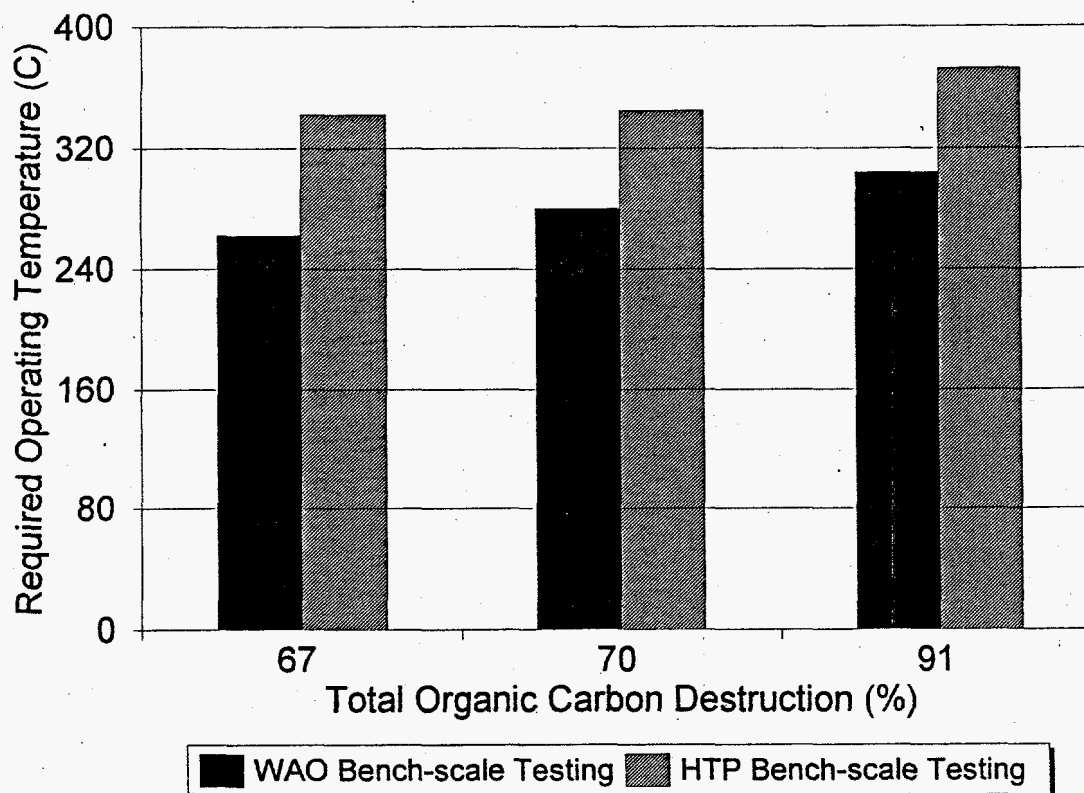


Figure 6.3. Required WAO and HTP Operating Temperature for Destruction of EDTA in 101-SY Simulant (residence time = 9 min)

The average hydrogen gas production of 0.12 ± 0.05 mol/mol TOC destroyed, given in Table 6.4, indicates that near-complete conversion of organic hydrogen to water per Reactions [1] and/or [2] is being accomplished. A similar calculation was made for comparison with the FY 1993 HTP runs that were conducted using 101-SY simulant and EDTA as the organic source (Orth et al. 1993; Schmidt et al. 1993). Based on 30 data points, under HTP conditions, approximately 0.14 ± 0.06 mol hydrogen gas were produced/mole TOC destroyed. This comparison shows that in both HTP and WAO processing, essentially identical quantities of hydrogen gas are being produced per mole of TOC destroyed. This also indicates that the much lower hydrogen concentrations in the off-gas from WAO processing can be attributed directly to the dilution from nitrogen gas present in the injection air.

The average ammonia production of 0.21 ± 0.02 mol/mol TOC destroyed, given in Table 6.4, indicates that nearly all of the organic nitrogen is being converted to ammonia. These data also suggest that Reaction [2] predominates over Reaction [1]. The ratio of moles ammonia produced per mole TOC destroyed is 0.2 for Reaction [2].

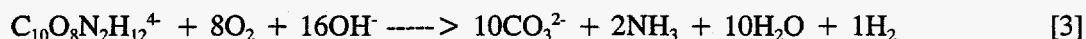
It was shown in Table 6.3 that the pH decreased upon TOC destruction under WAO conditions. However, based on the difficulties encountered in measuring for OH^- in the FY 1993 HTP testing using the 101-SY matrix, and the uncertainty in the values that were obtained, no attempt was made to determine OH^- consumption on a more quantitative basis for these tests.

Table 6.4. Mole Ratios of Oxygen Consumption, Hydrogen, and Ammonia Production to TOC Destroyed

Test	O ₂ Consumed/TOC Destroyed (mol/mol)	H ₂ Produced/TOC Destroyed (mol/mol)	NH ₃ Produced/TOC Destroyed (mol/mol)
1	0.91	0.06	0.23
2	0.83	0.10	0.24
3	0.84	0.12	0.20
4	1.03	0.15	0.24
5	0.98	0.10	0.21
6	0.76	0.08	0.21
7	0.80	0.16	0.22
8	1.10	0.20	0.21
9	0.88	0.17	0.21
10	0.79	0.10	0.20
11	0.89	0.15	0.23
12	0.76	0.10	0.19
13	0.89	0.05	0.17
Average	0.89 ± 0.10	0.12 ± 0.05	0.21 ± 0.02

Nitrate and nitrite concentrations are not reported here. However, in the FY 1993 WAO batch tests conducted by Zimpro for PNL, nitrate and nitrite levels in the feed and products from WAO testing were similar, indicating that these two components play little or no role under the WAO conditions tested (260°C to 325°C).

Based on the data presented in Table 6.4, in particular, the ammonia data, and based on observations made by Zimpro during the WAO batch tests, the global reaction chemistry for the WAO destruction of EDTA in 101-SY simulant can be fairly well represented by



This reaction is very similar to Reaction [2], which was previously proposed.

An Arrhenius plot of the WAO data is given in Figure 6.4. In this plot, the reaction is assumed to be first order with respect to TOC, and zero order with respect to oxygen. The assumption of zero order with respect to oxygen is supported by the observations that TOC destruction was not measurably affected by increasing the air flow rate or increasing the reactor pressure. As can be seen from the plot, a considerable amount of dispersion exists in the data. This may be due in part to rate dependence other than first order with respect to TOC, and zero order with respect to oxygen. It could also be an artifact of random scatter in the data. An activation energy of 11.4 kcal, and a pre-exponential

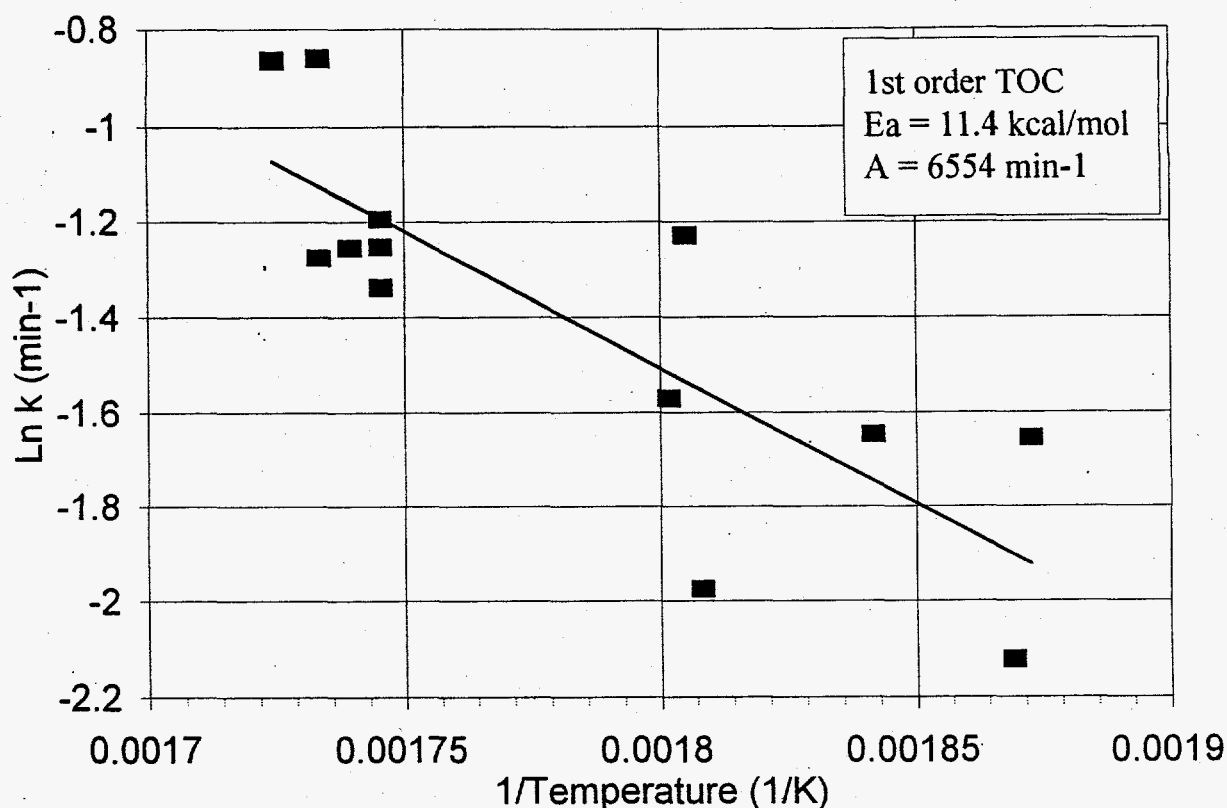


Figure 6.4. Arrhenius Plot of Wet Air Oxidation Runs

of 6554 min^{-1} were determined from the Arrhenius plot. The calculated activation energy of approximately 11.4 kcal/mol is relatively low (for these types of reactions). In comparison, an activation energy of approximately 24.4 kcal/mol for TOC destruction was obtained from the FY 1993 HTP testing of 101-SY simulant with EDTA as the organic source (Orth et al. 1993). The relatively low activation energy obtained from the WAO continuous tests indicates that mass transfer limitations are contributing to the global reaction rate for the destruction of TOC (Smith 1981). This is not uncommon of gas-liquid systems such as WAO systems.

From the Arrhenius plot, the assumption of first order with respect to TOC, and zero order with respect to oxygen, and operation in a tubular flow reactor (ideal plug flow), the following expression can be used to estimate WAO destruction of TOC in 3:1 diluted 101-SY simulant (EDTA as the organic source):

$$\ln [C_{\text{TOC},f}/C_{\text{TOC},i}] = -(6554 \text{ min}^{-1})e^{[(-11,400 \text{ cal/mol})/((1.987 \text{ cal/mol K}) \cdot T)]}t \quad [4]$$

where

- $C_{\text{TOC},f}$ = final TOC concentration (mmol/kg), (mg/kg), etc. (must have same units as $C_{\text{TOC},i}$)
- $C_{\text{TOC},i}$ = initial TOC concentration (mmol/kg), (mg/kg), etc. (must have same units as $C_{\text{TOC},f}$)
- T = temperature (K)
- t = residence time (min)

It should be realized that the expression given above (Equation 4) includes some apparent mass transfer limitations; therefore, if mass transfer limitations are eliminated, Equation [4] will underestimate TOC destruction. On the other hand, if another system has greater mass transfer limitations than the bench-scale system used here, Equation [4] will overestimate TOC destruction.

The stoichiometry given in Reaction [3] can also be used along with Equation [4] to estimate the consumption of oxygen and production of ammonia and hydrogen gas. The consumption of hydroxide can also be estimated, although that exact stoichiometry has not been verified through experimental OH⁻ measurement. However, it was observed that pH decreased with TOC destruction, indicating the hydroxide was being consumed. The production of carbonate can also be estimated using Reaction [3]. From Reaction [3], the following expressions can be obtained for oxygen and hydroxide consumption, and ammonia, hydrogen, and carbonate production:

$$(C_{\text{O}_2,i} - C_{\text{O}_2,f}) = 0.8*(C_{\text{TOC},i} - C_{\text{TOC},f}) \quad [5]$$

$$C_{\text{H}_2,f} = 0.1*(C_{\text{TOC},i} - C_{\text{TOC},f}) \quad [6]$$

$$(C_{\text{NH}_3,f} - C_{\text{NH}_3,i}) = 0.2*(C_{\text{TOC},i} - C_{\text{TOC},f}) \quad [7]$$

$$(C_{\text{OH}^-,i} - C_{\text{OH}^-,f}) = 1.6*(C_{\text{TOC},i} - C_{\text{TOC},f}) \quad [8]$$

$$(C_{\text{CO}_3,f} - C_{\text{CO}_3,i}) = (C_{\text{TOC},i} - C_{\text{TOC},f}) \quad [9]$$

where

- $C_{\text{TOC},i}$ = initial TOC concentration (mmol/kg liquid feed)
- $C_{\text{TOC},f}$ = final TOC concentration (mmol/kg liquid feed)
- $C_{\text{O}_2,i}$ = initial oxygen/liquid feed (mmol/kg liquid feed)
- $C_{\text{O}_2,f}$ = final oxygen/liquid feed (mmol/kg liquid feed)
- $C_{\text{H}_2,f}$ = final hydrogen/liquid feed (mmol/kg liquid feed)
- $C_{\text{NH}_3,i}$ = initial ammonia/liquid feed (mmol/kg liquid feed)
- $C_{\text{NH}_3,f}$ = final ammonia/liquid feed (mmol/kg liquid feed)
- $C_{\text{OH}^-,i}$ = initial hydroxide/liquid feed (mmol/kg liquid feed)
- $C_{\text{OH}^-,f}$ = final hydroxide/liquid feed (mmol/kg liquid feed)
- $C_{\text{CO}_3,i}$ = initial carbonate/liquid feed (mmol/kg liquid feed)
- $C_{\text{CO}_3,f}$ = final carbonate/liquid product (mmol/kg liquid feed)

The definitions given above are based on kg liquid feed; however, if we assume that kg liquid feed \approx kg liquid product, then the two can be used interchangeably. Based on the experiments conducted using 101-SY simulant, this is a valid assumption, since relatively small amounts of the feed material are in the off-gas.

These expressions can either be substituted for $C_{\text{TOC},f}$ in Equation [4], or Equation [4] can be solved to obtain $C_{\text{TOC},f}$ for a given time and temperature, and then $C_{\text{TOC},i}$ and $C_{\text{TOC},f}$ can be substituted into Equations [5] through [9] to obtain the consumption or production of the given components.

The actual and predicted values using Equations [4] through [7] for TOC destruction, oxygen consumption, and hydrogen gas and ammonia production are given in Table 6.5 for the 13 WAO bench-scale test conditions. As can be seen, the predicted values are in fairly good agreement with the actual values.

6.4 Direction of Future Work

The results of testing conducted by PNL and Zimpro show that through the addition of air, the required system operating conditions can be significantly reduced. The progression in the PNL HTP program strategy towards air injection has minimal impact in terms of the system design and components. The same bench-scale equipment used for HTP is currently being used for the WAO testing. Modifications to the equipment have also been minimal; i.e., an air injection port has been added at the base of the reactor.

Table 6.5. Predicted and Actual TOC Destruction, Oxygen Consumption, and Ammonia and Hydrogen Gas Production for Continuous WAO Destruction of EDTA in 101-SY Simulant

Test	TOC Destruction (%)		O ₂ Consumption (mmol/kg feed)		NH ₃ Production (mmol/kg product)		H ₂ Production (mmol/kg feed)	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	67	75	246	243	64	61	16	30
2	63	59	212	191	62	48	24	24
3	52	43	171	135	40	34	25	17
4	70	83	266	247	61	62	38	31
5	69	71	249	212	54	53	26	26
6	67	56	238	206	66	52	24	26
7	91	94	262	272	74	68	53	34
8	79	82	289	218	55	55	53	27
9	76	69	244	199	58	50	48	25
10	86	90	251	265	65	66	32	33
11	91	91	292	263	74	66	50	33
12	92	94	246	261	62	65	32	33
13	96	92	624	534	122	134	34	67

It is recommended that future efforts include both bench-scale and pilot-scale testing to support the design of a large-scale WAO system. HTP testing at temperatures lower than typical HTP conditions should be conducted to obtain additional kinetic data to support ongoing heat and digest work.

Continuous WAO and HTP testing with simulant should be conducted to further develop kinetic expressions (with a variety of organic-chelating species) and to investigate the overall operability of the process. The effects of feed dilution, temperature, pressure, and organic source should be evaluated. Also, with respect to WAO, process upsets; component reliability; and the ability to stop and restart the system while maintaining process integrity need to be examined, as well as the effectiveness and need for off-gas scrubbing (i.e., caustic scrubbing of the off-gas). To promote synergism, the WAO testing should be conducted in collaboration with Zimpro, and the use of alternative reactor designs to enhance mixing/mass transfer should be evaluated.

It is recommended that pilot-scale WAO testing be conducted to provide proof of principle and the scalability of a continuous WAO process for the destruction of chelating organics. Pilot-scale testing can be conducted at PNL with an existing test system using Hanford tank waste simulant at a feed rate of approximately 10 L/hr. These tests, along with the continuous WAO testing results, would be used to provide material balance, operation, and kinetic data to be used in the design of a WAO continuous process.

To provide further verification that the commercial WAO process is appropriate and applicable to the pretreatment of Hanford tank waste, additional pilot-scale WAO testing should be conducted at Zimpro's facilities. In the past, Zimpro has designed and operated numerous commercial WAO systems for various industrial applications. Under subcontract to PNL, Zimpro would perform continuous pilot-scale runs. The objectives of the pilot-scale testing are to demonstrate the feasibility of processing simulant tank waste on a large scale, to support considerations on design of a large-scale treatment process, to obtain kinetic data, to obtain sufficient processing data to develop a heat and material balance, and to obtain a measure of plant corrosion behavior. For the pilot-scale testing, Zimpro would log 200 hr of continuous processing at a feed rate in the range of 2 to 6 L/min (0.5 to 1.5 gpm). Zimpro has estimated that 6-1/2 months would be required to complete the pilot-scale testing and report the results.

Future plans should also include design and installation of a continuous bench-scale/pilot-scale WAO system for testing with actual waste, and bench-scale testing using actual waste. Design efforts for a large-scale WAO system would continue. It is anticipated that a large-scale WAO processing facility could be constructed and deployed within a time frame of 2 to 4 years.

7.0 References

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Appendix A

Determination of Off-Gas Compositions and Safe Operating Conditions for Continuous Bench-Scale Testing with 101-SY Simulant

Determination of Off-Gas Compositions and Safe Operating Conditions for Continuous Bench-Scale Testing with 101-SY Simulant

Summary

Potential safety concerns recognized by PNL personnel regarding off-gases generated by treatment of the 101-SY simulant led to a study on the flammability of hydrogen gas/nitrous oxide gas mixtures. This report contains information from pertinent references as well as supporting calculations for the bench-scale continuous reactor system (CRS) that is located in the Chemical Process Development Laboratory (CPDL) at PNL.

Experimental results indicate that the nitrous oxide gas is formed by the decomposition of the nitrates and nitrites in the waste. According to one of the references cited (Cashdollar et al. 1992), in some instances, the off-gas from the CRS contains sufficient amounts of nitrous oxide and hydrogen that the possibility of ignition or possibly even detonation exists. Both of these occurrences would require an ignition source.

According to the calculations contained in this report, the most serious situation arises when the reaction gas/liquid mixture is cooled just outside the reactor. At these conditions, assuming no heat absorption from the liquid water, unsafe operating conditions would exist, and a detonation could possibly take place. The situation may also be serious downstream of the back-pressure regulator, when the pressure is released and the liquid and vapor are separated in the gas-liquid separator; at this point the liquid water would presumably play no role in absorbing heat. Once the gases were vented, a problem would no longer exist because the flow rate of reactor gases (typically 4 liter/hour) is very small compared with the vent exhaust rate.

Calculations were also made (upstream of the gas-liquid separator), assuming that liquid water would be capable of absorbing the heat generated by the reaction of N_2O and H_2 . When this assumption was made, it was observed that the temperature increase was minimal (and in fact would not be seen in the actual system). It is a risky assumption that the liquid water could absorb the heat fast enough, however, especially if a detonation occurred.

A potential solution to the off-gas problem would be to inject an inert dilution gas (e.g., argon) upstream of the reactor, so that the off-gases were diluted throughout the entire reactor system. In our development studies, argon rather than nitrogen would be preferred as the dilution gas because it is desirable to monitor the generation of nitrogen as an off-gas product.

Another potential solution, which may be more practical, is to inject air into the system, upstream of the reactor (i.e., wet air oxidation). The nitrogen in the air would not only act as a dilution gas, but the oxygen in the air would significantly enhance the reaction kinetics for the destruction of organics. In FY 1993, Zimpro was contracted by PNL to conduct batch wet air oxidation testing on 101-SY simulant. These tests were conducted at temperatures between 280°C and 325°C and at 3000 psig. In

these tests, the required reaction temperature was on the order of 70°C lower to obtain the same organic destruction levels as compared with autogenous destruction. The highest hydrogen concentration in the off-gas was less than 4%, and no N₂O was detected in any of the runs. The oxygen content varied, depending on the amount of air injected into the system. The off-gas typically contained between 85% and 95% N₂ in the off-gas.

Overpressure calculations were conducted assuming worst-case scenarios: 1) complete reaction of hydrogen and nitrous oxide within the continuous reactor system, 2) release of 36,000 psi from the reactor into the CPDL, 3) assuming CPDL is not ventilated (whereas it is). Overpressures of 0.5 psi and 1.25 were calculated by two different methods. At these overpressures, flying glass could result, and some small flying missiles in the barricade could also result. However, this is well below eardrum or lung damage (these take place at overpressures greater than 2.5 psi). Although under worst-case scenarios, only minimal damage could result from failure of the bench-scale CRS in CPDL, significant damage could result as the process is scaled up. Therefore, these concerns must be recognized on the broader scale.

Introduction

Potential safety concerns recognized by PNL personnel regarding off-gases generated by treatment of the 101-SY simulant motivated a study to look into the flammability of hydrogen gas/nitrous oxide gas mixtures. The most comprehensive related data found was contained in a document prepared by the Pittsburgh Research Center, Bureau of Mines for Westinghouse Hanford Company (Cashdollar et al. 1992). In these studies, it was shown that nitrous oxide/hydrogen gas mixtures are as reactive, if not more reactive, than air/hydrogen mixtures. The lower flammability limit (LFL) for hydrogen gas in air is approximately 3%, while for hydrogen in nitrous oxide it was found to be 3%, using a low energy spark, and even lower (i.e., <1%), using a 5000 J ignitor (i.e., energy comparable to that of two books of matches, all ignited at once). In an experiment conducted with 50% hydrogen and 50% nitrous oxide, and a spark ignition source, it was reported that detonation of the gas mixture had most likely taken place.

In the report it was also noted that the LFL for a hydrogen gas/nitrous oxide gas mixture is considerably higher when argon or nitrogen gases are used as diluents. In these cases, the LFL is approximately 10% hydrogen/10% nitrous oxide/80% argon or 14% hydrogen/14% nitrous oxide/72% nitrogen.

Argon is used as a cover gas in batch hydrothermal tests conducted at the Chemical Process Development Laboratory (CPDL) at PNL, using 101-SY simulant. The reactor is initially pressurized with argon so that when the hold temperature is achieved, a reactor pressure of 3000 psig is attained. In all tests conducted to date, the highest hydrogen gas composition was 3.6% with 1.5% nitrous oxide, 2.9% nitrogen, and 92% argon (i.e., below the LFL in the presence of argon as reported by Cashdollar et al. 1992). This was in a run conducted with undiluted 101-SY simulant. Typical off-gas compositions are 2% hydrogen, 2% nitrous oxide, 3% nitrogen, and 93% argon for 3X diluted 101-SY simulant. These nitrous oxide/hydrogen levels are again below the reported LFL in the presence of argon. In these tests, EDTA, citrate, acetate, formate, and 2:1 mole ratios of HEDTA:EDTA have been used. The total organic carbon (TOC) concentration in the 3X diluted 101-SY simulant runs were approximately 4500 to 5000 ppm. Regardless of the organic component added to the waste, nitrous oxide has been identified as an off-gas product. This suggests that the nitrous oxide is being formed primarily from the decomposition of the nitrates and nitrites in the waste as opposed to the nitrogen in the organic compounds (i.e., present in EDTA and HEDTA). Supporting calculations have been conducted to assure that safe operating conditions do exist. An addendum (Attachment 1) was made to the batch test system Standard Operating Procedures (SOP), and batch testing has subsequently resumed.

In continuous tests, however, the off-gas can contain much higher concentrations of hydrogen and nitrous oxide because a diluent gas has not been used in the past. The off-gas concentration can be as high as 45% in either hydrogen or nitrous oxide with the majority of the remaining gas being nitrogen. The data presented by Cashdollar et al. (1992) and the calculations presented in this document show that these high hydrogen/nitrous oxide concentrations in the off-gas are a definite concern. The calculations show that the greatest concern is when the temperature in the system is decreased after the solution exits the reactor, dropping water vapor out, and essentially drying out the gas. Also of concern is when the gas is separated from the liquid in the gas-liquid separator.

Possible solutions to the off-gas problem are proposed in this document. One possibility is to introduce enough argon gas upstream of the reactor, so that the hydrogen and/or nitrous oxide concentrations do not exceed 3% anywhere in the reactor or in the off-gas. Introduction of argon gas after the reactor, or after the pressure let-down system, prior to the gas-liquid separator may still lead to potentially unsafe conditions. Argon gas is being considered rather than nitrogen gas, so that we can track the formation of nitrogen in the off-gas.

Another more practical, alternative is to inject air into the system, upstream of the reactor (i.e., wet air oxidation). The nitrogen in the air would not only act as a dilution gas, but the oxygen in the air would significantly enhance the reaction kinetics for the destruction of organics. In FY 1993, Zimpro was contracted by PNL to conduct batch wet air oxidation testing on 101-SY simulant. In these tests, the required reaction temperature was on the order of 65°C lower to obtain the same organic destruction levels as compared with no air injection (i.e., autogenous destruction). The highest hydrogen concentration in the off-gas was less than 4%, and no N₂O was detected in any of the runs. The oxygen content varied, depending on the amount of air injected into the system. The off-gas typically contained between 85% and 95% N₂ in the off-gas.

Experimentally determined off-gas concentrations and calculations are given in the following sections for the continuous reactor system (CRS) located at the CPDL. Calculations were conducted at different points in the reactor system. Calculation 1 was conducted within the reactor; Calculation 2 was conducted after the reactor (still at high pressure); and Calculation 3 was conducted in the gas-liquid separator (at atmospheric pressure). These were all "worst-case" calculations, assuming liquid water would not absorb heat released by a reaction. Calculations 4 and 5 were conducted within the reactor and downstream of the reactor (at pressure), assuming water could absorb heat from a reaction. Calculations 6 and 7 were conducted within the reactor and downstream of the reactor, assuming an argon cover gas is used. In addition to the calculations conducted within the reactor system, a calculation was conducted (Calculation 8) to determine the overpressure that would result in the CPDL, assuming failure of the high-pressure reactor system. These calculations showed that under worst-case conditions, only minor damage to CPDL may occur. These calculations were conducted assuming no ventilation in CPDL, which is not the actual case. This report gives the eight calculations along with conclusions discussed separately for each calculation.

Experimental Results

Table A.1 contains experimental results that were obtained from the runs conducted using the CRS. Typical test conditions are temperature = 300 to 350°C, and pressure = 3000 psig. The total high-pressure system volume is approximately 300 ml (assuming a packed reactor) and 1000 ml (assuming an unpacked reactor). Experiments were conducted using both packed and unpacked tubular reactors. For reference, a diagram of the CRS is given in Figure A.1.

Table A.1. CRS Experimental Results

Temperature (°C)	Residence Time (min.)	Gas Composition (vol %) H ₂ /N ₂ O/N ₂	Gas/Liquid Ratio (vol./vol.) ¹	%TOC Destruction ²
101-SY simulant diluted 3:1 (v:v) with water (EDTA as organic)				
301	4	53/34/13	0.1	10
300	4	56/34/10	0.04	9
301	6	54/36/6	0.1	8
305	7	38/51/11	0.6	24
305	8	37/55/8	0.9	25
302	9	44/46/10	0.4	21
302	11	35/55/10	0.6	23
325	4	42/51/7	1.0	29
326	7	34/53/13	2.1	47
333 ³	9	31/47/21	1.7	36
319	11	10/56/39	---	59
320	12	53/35/10	---	54
342	5	32/51/17	2.2	55
347 ³	8	31/48/21	3.0	54
345	9	22/63/14	---	83
345	10	10/58/32	1.6	
350	3	40/48/12	2.2	49
353	3	46/45/9	3.2	55
350	4	41/48/11	1.9	51
351	5	37/48/15	2.6	60
350	5	35/48/17	2.2	65
350	6	31/55/14	3.0	67
351	6	27/65/8	3.2	68
353 ³	8	28/52/20	3.8	64
354 ³	8	23/59/18	4.8	82

Table A.1. (contd)

Temperature (°C)	Residence Time (min.)	Gas Composition (vol %) H ₂ /N ₂ O/N ₂	Gas/Liquid Ratio (vol./vol.) ¹	%TOC Destruction ²
351	13	15/37/48	3.3	85
356 ⁴	48	15/16/68	4.8	66
368	2	40/49/11	2.7	42
363	3	36/51/13	3.1	50
365	3	35/50/15	2.1	53
365	3	33/52/15	2.6	61
360	6	27/60/13	3.4	75
361 ³	8	24/55/21	4.5	80
367 ⁴	71	22/28/49	6.4	75
378	3	55/34/11	2.7	88
375 ⁴	32	19/53/26	4.3	84
<ol style="list-style-type: none"> 1 The gas/liquid volumetric ratios are given for standard conditions (25°C, 1 atm). 2 Beginning TOC concentration = approx. 5000 ppm unless noted otherwise; all runs conducted in a packed tubular reactor unless noted otherwise. 3 These runs were conducted in an unpacked tubular reactor so that residence time could be increased, larger temperature gradients (i.e., 10-15°C) between the wall and centerline in this configuration as compared to the packed tubular reactor. 4 These runs were conducted in a CSTR reactor; the given temperatures are questionable due to very large temperature gradients from the top to bottom of the reactor (i.e., 70°C). 				

Safety Implications from the Experimental Results

The highest H₂/N₂O gas composition = 42/51 vol%. It appears that as residence time is increased in the reactor and/or conversion increases, the hydrogen concentration decreases significantly. This is especially evident in the CSTR runs that are reported in the table.

From Cashdollar et al. (1992), the lower flammability limit for 1:1 H₂:N₂O in nitrogen is 14% H₂, 14% N₂O, and 72% nitrogen. In one test reported in by Cashdollar et al. (1992), apparent detonation of a 50% N₂O - 50% H₂ gas mixture occurred. No data were reported in the range from 20% H₂ to 50% H₂, making it impossible to determine where detonation takes place. Although, in all cases, some nitrogen appears in the off-gas from the continuous runs, some of the runs approach the "detonable" region. From the results presented by Cashdollar et al. (1992) and from our experimental results to date, it appears that the off-gas from the HTP testing in the CRS is in the flammable and possibly close to the detonable range in some cases.

BENCH SCALE FLOW DIAGRAM

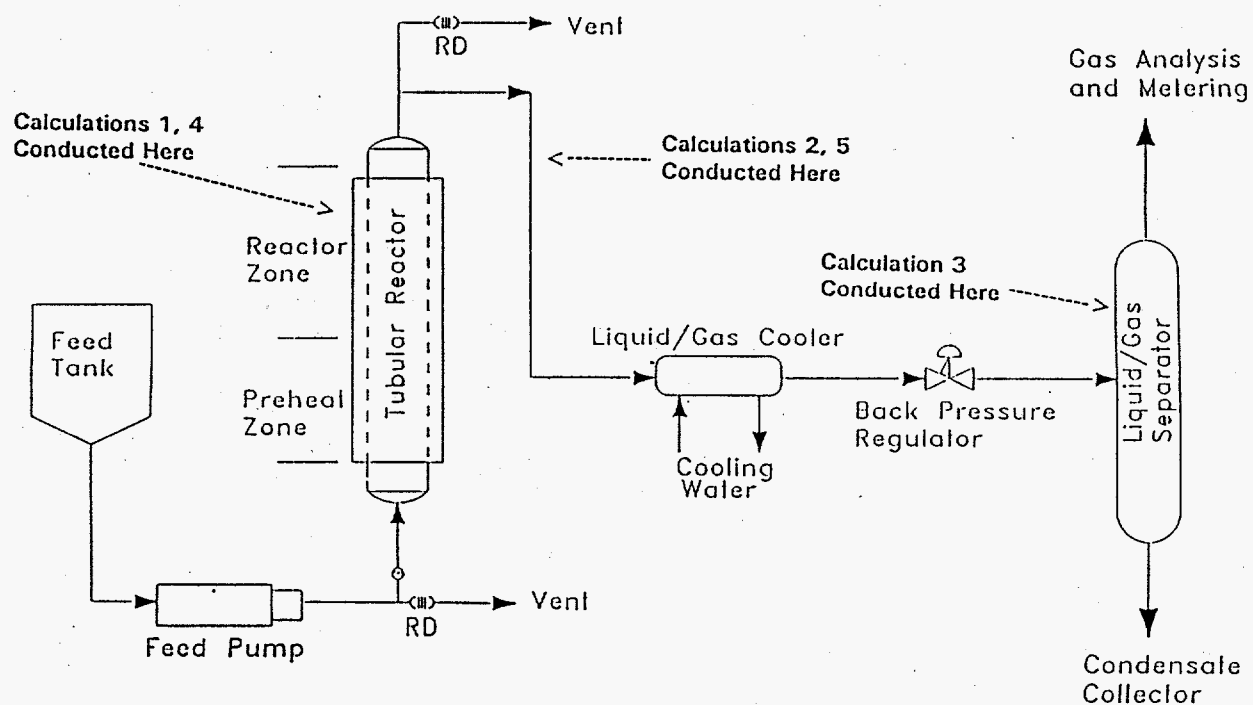


Figure A.1. Schematic of Continuous Reactor System (CRS)

Within the reactor, a large percentage (i.e., approximately 75%) of the gas is due to water vapor. Most likely, the highest concern for ignition or detonation of the off-gas is where it becomes "dry" after the feed leaves the reactor and cools. The calculations in the following sections focused on determining the major areas of concern within the reactor system. In all of the calculations, enthalpies were used rather than internal energies. The use of internal energies for gases would be more accurate; however, the use of enthalpies gives us a reasonable approximation of the magnitude of energy released in the reactions.

Continuous Reactor System Calculations

Calculations 1 through 5 are discussed individually in this section.

Calculation #1: Reactor at Temperature (350°C)

Problem Statement: Determine the gas composition in the reactor and the maximum temperature rise if all of the gas in the reactor ignites.

- Assumptions:**
- 1) Final reactor temp. = 350°C, final reactor pressure = 3000 psia.
 - 2) 1000 ml reactor, filled with 1000 ml solution + gas.
 - 3) vapor pressure simulant = vapor pressure of water = 2322 psia (Himmelblau 1982).
 - 4) density of simulant at 350°C and 3000 psia = density of water at 350°C and 3000 psia = 0.61 g/ml (Thermodynamic Properties of Steam). Density of simulant = density of water at 20°C = 1 g/ml.
 - 5) Ideal gas law and Dalton's law are suitable.
 - 6) Dry gas composition = 45% H₂, 45% N₂O, 10% N₂.
 - 7) 4 liters dry gas produced/liter feed (standard conditions) = 0.00292 moles dry gas/mole feed (assuming feed = liquid water).
 - 8) Liquid water will not absorb any heat.
 - 9) Most reactor contents (volumetric basis) can be assumed to be liquid.
 - 10) The molar ratio of dry gas/liquid in the reactor is the same as that given at standard conditions (i.e., in assumption #6, above).
 - 11) All of the gas present in the reactor reacts at once. In reality, it is unlikely that all of the gas in the reactor could be ignited at the same time.

The assumptions made above will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{water vapor}} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$3000 \text{ psia} = 2322 \text{ psia} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$678 \text{ psia} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$n_{\text{dry gas}} = (0.00292 \text{ moles dry gas produced/mole water}) * (1000 \text{ ml water}) * (0.61 \text{ g water/liter}) / (18 \text{ g water/mole})$$

$$n_{\text{dry gas}} = 0.0990 \text{ moles}$$

Therefore from assumption 6 and moles dry gas:

$$H_2 = 0.45 * 0.0990 \text{ moles} = 0.0445 \text{ moles}$$

$$N_2O = 0.45 * 0.0990 \text{ moles} = 0.0445 \text{ moles}$$

$$N_2 = 0.10 * 0.0990 \text{ moles} = 0.0099 \text{ moles}$$

volume dry gas =

$$V_{\text{dry gas}} = (0.099 \text{ moles}) * (0.082 \text{ liter atm/K mole}) * (623K) / (204 \text{ atm}) \quad [\text{Eqn 2}]$$

$$V_{\text{dry gas}} = 25 \text{ ml}$$

Now using:

$$(P_{\text{water vapor}} / P_{\text{dry gas}}) * n_{\text{dry gas}} = n_{\text{water vapor}} \quad [\text{Eqn 3}]$$

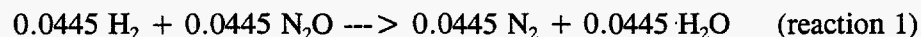
$$(2322 \text{ psia} / 678 \text{ psia}) * 0.099 \text{ moles dry gas} = \underline{0.339 \text{ moles water vapor}}$$

Therefore total initial gas composition is:

Water Vapor	0.339 moles	77.5%
H ₂	0.0445 moles	10.1%
N ₂ O	0.0445 moles	10.1%
N ₂	<u>0.0099 moles</u>	<u>2.3%</u>
TOTAL	0.438 moles	<u>100%</u>

From the detonation limit triangle (Attachment 2), 60% steam or more along with any combination of air and hydrogen gas is below the lower flammability limit. These data are for air and not for N₂O, and Cashdollar et al. (1992) showed that N₂O/H₂ mixtures are more reactive than air/H₂ mixtures.

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N_2O and H_2 under these conditions:



$$H_{\text{reaction, 25C}} = H_{f, \text{products}} - H_{f, \text{reactants}} \quad [\text{Eqn 4}]$$

$$H_{f, H_2} = 0 \text{ KJ/mol,}$$

$$H_{f, N_2O} = 82 \text{ KJ/mol,}$$

$$H_{f, N_2} = 0 \text{ KJ/mol,}$$

$$H_{f, H_2O} = -286 \text{ KJ/mol (Himmelblau 1982)}$$

$$H_{\text{reaction, 25C}} = \underset{(H_2O)}{-286 \text{ KJ/mol}} - \underset{(N_2O)}{(82 \text{ KJ/mol})} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol}) * 0.0445 \text{ mol} = \underline{-16.4 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H_2O_v	0.339 moles	0.384 moles
H_2	0.0445 moles	0 moles
N_2O	0.0445 moles	0 moles
N_2	0.0099 moles	0.054 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$C_p(H_2O_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$C_p(N_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$C_p(N_2O) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$C_p(H_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, Tf}} - H_{\text{reactants, To}}$$

$$\text{products} \rightarrow = [0.384 * (33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \quad [\text{Eqn 9a}]$$

$$+ 0.054 * (29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)]$$

$$\text{reactants} \rightarrow - [0.339*(33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \quad [\text{Eqn 9b}]$$

$$+ 0.0099*(29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)]$$

$$+ 0.0445*(38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4)$$

$$+ 0.0445*(29T_o + 3.9 \times 10^{-5}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)]$$

from $T_o = 623\text{K}$ to $T_f = ?$.

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \quad [\text{Eqn 10}]$$

from previous calculation, using equation [4] above $H_{\text{reaction, 25C}} = -16.4 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 9.7 KJ

therefore from equation [10]; $H_{\text{prod, Tf}} = 9.7 \text{ KJ} - (-16.4 \text{ KJ}) = \underline{26.1 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod, Tf}} = 26.1 \text{ KJ}$

1480K gives: $H_{\text{prod}} = 26.1 \text{ KJ}$

1480K (1207°C) corresponds to 26.1 KJ. This is worst case (assuming no heat losses, no absorption of heat by water, all gas reacts at once and assuming the reaction will go to completion). The corresponding pressure would increase to (assuming constant volume):

$$(3000 \text{ psia}) * (1480\text{K}) / (623\text{K}) = 7127 \text{ psia}; \text{ pressure increase of } 4127 \text{ psia.}$$

Conclusions from Calculation #1:

From the detonation limit triangle (Attachment 2), 60% steam or more along with any combination of air and hydrogen gas is below the lower flammability limit. These data are for air, not for N_2O , and Cashdollar et al. (1992) showed that $\text{N}_2\text{O}/\text{H}_2$ mixtures are more reactive than air/ H_2 mixtures.

According to the calculations, a significant increase in pressure could result. For a detonation, this pressure increase could most likely be realized because it would be so sudden that the back-pressure regulator, located downstream in the reactor system would not react fast enough to allow release of pressure. It is very unlikely, however, according to the detonation triangle that this gas mixture is near the detonation limit or even near the LFL.

Calculation #2: Gas and Liquid Exiting the Reactor is at 130°C

Problem Statement: Determine the gas composition after the gas and liquid exit the reactor and the maximum temperature rise if all of the gas in the entire high-pressure reactor system ignites.

- Assumptions:**
- 1) Exit reactor temp. = 130°C, final reactor pressure = 3000 psia.
 - 2) 1 liter high-pressure reactor system, filled with liquid + gas; includes reactor and all lines up to the pressure let-down system, assuming everything in the system is at 130°C.
 - 3) vapor pressure simulant = vapor pressure of water = 40 psia (Himmelblau 1982).
 - 4) density of simulant at 130°C and 3000 psia = density of water at 130°C and 3000 psia = 1 g/ml (Thermodynamic Properties of Steam). Density of simulant = density of water at 20°C = 1 g/ml.
 - 5) Ideal gas law and Dalton's law are suitable.
 - 6) Dry gas composition = 45% H₂, 45% N₂O, 10% N₂.
 - 7) 4 liters gas produced/liter feed (standard conditions).
= 0.00292 moles dry gas/mole feed (assuming feed = liquid water).
 - 8) Liquid water will not absorb any heat.
 - 9) Most reactor system contents (volumetric basis) can be assumed to be liquid.
 - 10) The molar ratio of dry gas/liquid in the high-pressure reactor system is the same as that given at standard conditions (i.e., in assumption #6, above).
 - 11) All of the gas present in the high-pressure reactor system reacts at once. In reality, it is unlikely that all of the gas in the reactor could be ignited at the same time.

The assumptions made above will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{water vapor}} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$3000 \text{ psia} = 40 \text{ psia} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$2960 \text{ psia} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$n_{\text{dry gas}} = (0.00292 \text{ moles dry gas produced/mole water}) * (1000 \text{ ml water}) * (1 \text{ g water/liter}) / (18 \text{ g water/mole})$$

$$n_{\text{dry gas}} = 0.162 \text{ moles}$$

Therefore from assumption 6 and moles dry gas:

$$\begin{aligned} \text{H}_2 &= 0.45 \cdot 0.162 \text{ moles} = 0.073 \text{ moles} \\ \text{N}_2\text{O} &= 0.45 \cdot 0.162 \text{ moles} = 0.073 \text{ moles} \\ \text{N}_2 &= 0.10 \cdot 0.162 \text{ moles} = 0.0162 \text{ moles} \end{aligned}$$

volume dry gas =

$$V_{\text{dry gas}} = (0.162 \text{ moles}) \cdot (0.082 \text{ liter atm/K mole}) \cdot (623\text{K}) / (204 \text{ atm}) \quad [\text{Eqn 2}]$$

$$V_{\text{dry gas}} = 41 \text{ ml}$$

Now using:

$$(P_{\text{water vapor}} / P_{\text{dry gas}}) \cdot n_{\text{dry gas}} = n_{\text{water vapor}} \quad [\text{Eqn 3}]$$

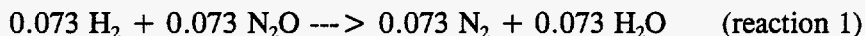
$$(40 \text{ psia} / 2960 \text{ psia}) \cdot 0.162 \text{ moles dry gas} = \underline{0.0022 \text{ moles water vapor}}$$

Therefore total initial gas composition is:

Water Vapor	0.0022 moles	1.3 %
H ₂	0.073 moles	44.4 %
N ₂ O	0.073 moles	44.4 %
N ₂	<u>0.0162 moles</u>	<u>9.9 %</u>
TOTAL	0.1644 moles	<u>100 %</u>

This gas composition could very well be in or very near to the detonable range according to Cashdollar et al. (1992) and from the detonation limit triangle (Attachment 2).

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N₂O and H₂ under these conditions:



$$H_{\text{reaction, 25C}} = H_{\text{f, products}} - H_{\text{f, reactants}} \quad [\text{Eqn 4}]$$

$$H_{\text{f, H}_2} = 0 \text{ KJ/mol,}$$

$$H_{\text{f, N}_2\text{O}} = 82 \text{ KJ/mol,}$$

$$H_{\text{f, N}_2} = 0 \text{ KJ/mol,}$$

$$H_{\text{f, H}_2\text{O}} = -286 \text{ KJ/mol (Himmelblau 1982)}$$

$$H_{\text{reaction, 25C}} = \underset{(\text{H}_2\text{O})}{-286 \text{ KJ/mol}} - \underset{(\text{N}_2\text{O})}{(82 \text{ KJ/mol})} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol}) \cdot 0.073 \text{ mol} = \underline{-26.9 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H ₂ O _v	0.0022 moles	0.0752 moles
H ₂	0.073 moles	0 moles
N ₂ O	0.073 moles	0 moles
N ₂	0.0162 moles	0.0892 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$C_p(\text{H}_2\text{O}_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$C_p(\text{N}_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$C_p(\text{N}_2\text{O}) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$C_p(\text{H}_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, Tf}} - H_{\text{reactants, To}}$$

$$\begin{aligned} \text{products -->} &= [0.0752*(33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \\ &+ 0.0892*(29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)] \end{aligned} \quad [\text{Eqn 9a}]$$

reactants -->

$$- [0.0022*(33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \quad [\text{Eqn 9b}]$$

$$+ 0.0162*(29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)]$$

$$+ 0.073*(38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4)$$

$$+ 0.073*(29T_o + 3.9 \times 10^{-5}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)]$$

from T_o = 403K to T_f = ?.

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \quad [\text{Eqn 10}]$$

from previous calculation, using equation [4] above $H_{\text{reaction}, 25^{\circ}\text{C}} = -26.9 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 2.2 KJ

therefore from equation [10]; $H_{\text{prod}, T_f} = 2.2 \text{ KJ} - (-26.9 \text{ KJ}) = \underline{29.1 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod}, T_f} = 29.1 \text{ KJ}$

1500K gives: $H_{\text{prod}} = 9.1 \text{ KJ}$ (highest the numbers used can be applied to)

The temperature increase is $\gg 1500\text{K}$. The high temperature increase indicates unsafe operating conditions exist.

Conclusions From Calculation #2:

The temperature increase is $\gg 1500\text{K}$. The high temperature increase indicates unsafe operating conditions exist. In addition, the gas composition is very close to the detonation range according to Cashdollar et al. (1992) and detonation triangle (Attachment 2). According to Cashdollar et al. (1992), the pressure increase within the reactor would be > 12 times the original pressure (Figure 20 in Cashdollar et al.). If we are operating at 3000 psig, this corresponds to a final pressure of at least 36,000 psig.

Calculation #3: Gas and Liquid is at 25°C in the Gas-Liquid Separator

Problem Statement: Determine the gas composition after the gas and liquid exit the reactor and the maximum temperature rise if all of the gas in the entire high-pressure reactor system ignites.

- Assumptions:**
- 1) Gas-Liquid Separator temp. = 25°C , pressure = 1 atm
 - 2) Gas-liquid Separator filled with 200 dry ml gas.
 - 3) No water vapor in the gas phase (i.e., the gas is completely dry).
 - 4) Ideal gas law and Dalton's law are suitable.
 - 5) Dry gas composition = 45% H_2 , 45% N_2O , 10% N_2 .
 - 6) Liquid water will not absorb any heat.
 - 7) All of the gas present in the gas-liquid separator reacts at once. This is probably more likely than in the reactor or any place prior to the gas-liquid separator because the gas and liquid are separated from one another in the gas-liquid separator.

The assumptions made above will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$1 \text{ atm} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$\text{ideal gas law: } PV = nRT \quad [\text{Eqn 2}]$$

$$P = 1 \text{ atm}$$

$$V_{\text{dry gas}} = 200 \text{ ml}$$

$$R = 0.082 \text{ liter atm/K mol}$$

$$T = 25^\circ\text{C} = 298 \text{ K}$$

$$\begin{aligned} \text{Solving for } n &= [(1 \text{ atm}) * (0.2 \text{ liters})] / \\ &\quad [(0.082 \text{ liter atm/K mol}) * (298 \text{ K})] \\ &= \underline{0.008 \text{ moles dry gas}} \end{aligned}$$

Therefore from assumption 5 and moles dry gas:

$$\begin{aligned} \text{H}_2 &= 0.45 * 0.008 \text{ moles} = 0.0036 \text{ moles} \\ \text{N}_2\text{O} &= 0.45 * 0.008 \text{ moles} = 0.0036 \text{ moles} \\ \text{N}_2 &= 0.10 * 0.008 \text{ moles} = 0.0008 \text{ moles} \end{aligned}$$

Therefore total initial gas composition is:

H ₂	0.0036 moles	45%
N ₂ O	0.0036 moles	45%
N ₂	<u>0.0008 moles</u>	<u>10%</u>
TOTAL	0.008 moles	<u>100%</u>

This gas composition could very well be in or very near to the detonable range according to Cashdollar et al. (1992) and from the detonation limit triangle (Attachment 2).

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N₂O and H₂ under these conditions:



$$H_{\text{reaction, 25C}} = H_{\text{f, products}} - H_{\text{f, reactants}} \quad [\text{Eqn 4}]$$

$$\begin{aligned}
H_{f, H_2} &= 0 \text{ KJ/mol,} \\
H_{f, N_2O} &= 82 \text{ KJ/mol,} \\
H_{f, N_2} &= 0 \text{ KJ/mol,} \\
H_{f, H_2O} &= -286 \text{ KJ/mol (Himmelblau 1982)}
\end{aligned}$$

$$H_{\text{reaction, 25C}} = \frac{-286 \text{ KJ/mol}}{(H_2O)} - \frac{(82 \text{ KJ/mol})}{(N_2O)} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol}) * 0.0036 \text{ mol} = \underline{-1.3 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H ₂ O _v	0.0 moles	0.0036 moles
H ₂	0.0036 moles	0 moles
N ₂ O	0.0036 moles	0 moles
N ₂	0.0008 moles	0.0044 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$Cp(H_2O_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$Cp(N_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$Cp(N_2O) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$Cp(H_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, Tf}} - H_{\text{reactants, To}}$$

$$\begin{aligned}
\text{products} \rightarrow &= [0.0036 * (33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \\
&+ 0.0044 * (29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)] \quad [\text{Eqn 9a}]
\end{aligned}$$

$$\begin{aligned}
\text{reactants} \rightarrow &- [0.0 * (33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \\
&+ 0.0008 * (29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)] \\
&+ 0.0036 * (38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4) \\
&+ 0.0036 * (29T_o + 3.9 \times 10^{-5}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)] \quad [\text{Eqn 9b}]
\end{aligned}$$

from T_o = 298K to T_f = ?.

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \quad [\text{Eqn 10}]$$

from previous calculation, using equation [4] above $H_{\text{reaction, 25C}} = -1.3 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 0.079 KJ

therefore from equation [10]; $H_{\text{prod, Tf}} = 0.079 \text{ KJ} - (-1.3 \text{ KJ}) = \underline{1.4 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod, Tf}} = 1.4 \text{ KJ}$

1500K gives: $H_{\text{prod}} = 0.4 \text{ KJ}$ (highest the numbers used can be applied to)

The temperature increase is $> > 1500\text{K}$. The high temperature increase indicates unsafe operating conditions exist.

Conclusions from Calculation #3:

The temperature increase is $> > 1500\text{K}$. The high temperature increase indicates unsafe operating conditions exist. In addition, the gas composition is very close to the detonation range according to Cashdollar et al. (1992) and detonation triangle (Attachment 2). According to Cashdollar et al. (1992, Figure 20), the pressure increase within the reactor would be > 12 times the original pressure.

One thing to note here as compared to Calculation #2 is that, even if the pressure were to increase 20 times above the original pressure, the resulting pressure would only be 20 atmospheres, as opposed to on the order of 2000 to 4000 atmospheres if this were to happen on the high-pressure side. The pressure rating of the gas-liquid separator is 400 psig (27 atm) at 298°C . It is difficult to say whether the shock wave from a potential detonation, or the temperature increase due to the ignition would cause the gas-liquid separator to fail.

Calculation #4: Reactor at Temperature (350°C); Liquid Water Capable of Absorbing Heat of Reaction

Problem Statement: Determine the gas composition in the reactor and the maximum temperature rise if all of the gas in the reactor ignites.

Assumptions: 1) Final reactor temp. = 350°C , final reactor pressure = 3000 psia.

2) 1000 ml reactor, filled with 1000 ml solution + gas.

3) Vapor pressure simulant = vapor pressure of water = 2322 psia (Himmelblau 1982).

4) Density of simulant at 350°C and 3000 psia = density of water at 350°C and 3000 psia = 0.61 g/ml (Thermodynamic Properties of Steam). Density of simulant = density of water at 20°C = 1 g/ml .

- 5) Ideal gas law and Dalton's law are suitable.
- 6) Dry gas composition = 45% H₂, 45% N₂O, 10% N₂.
- 7) 4 liters gas produced/liter feed (standard conditions).
= 0.00292 moles dry gas/mole feed (assuming feed = liquid water).
- 8) Liquid water will absorb heat (used heat capacity of water vapor).
- 9) Most reactor contents (volumetric basis) can be assumed to be liquid.
- 10) The molar ratio of dry gas/liquid in the reactor is the same as that given at standard conditions (i.e., in assumption #6, above).
- 11) All of the gas present in the reactor reacts at once. In reality, it is unlikely that all of the gas in the reactor could be ignited at the same time.

The assumptions made above (with the exception of assumption 8) will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{water vapor}} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$3000 \text{ psia} = 2322 \text{ psia} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$678 \text{ psia} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$n_{\text{dry gas}} = (0.00292 \text{ moles dry gas produced/mole water}) * (1000 \text{ ml water}) * (0.61 \text{ g water/liter}) / (18 \text{ g water/mole})$$

$$n_{\text{dry gas}} = 0.0990 \text{ moles}$$

Therefore from assumption 6 and moles dry gas:

$$\begin{aligned} \text{H}_2 &= 0.45 * 0.0990 \text{ moles} = 0.0445 \text{ moles} \\ \text{N}_2\text{O} &= 0.45 * 0.0990 \text{ moles} = 0.0445 \text{ moles} \\ \text{N}_2 &= 0.10 * 0.0990 \text{ moles} = 0.0099 \text{ moles} \end{aligned}$$

volume dry gas =

$$V_{\text{dry gas}} = (0.099 \text{ moles}) * (0.082 \text{ liter atm/K mole}) * (623\text{K}) / (204 \text{ atm}) \quad [\text{Eqn 2}]$$

$$V_{\text{dry gas}} = 25 \text{ ml}$$

Now using:

$$(P_{\text{water vapor}}/P_{\text{dry gas}})*n_{\text{dry gas}} = n_{\text{water vapor}} \quad [\text{Eqn 3}]$$

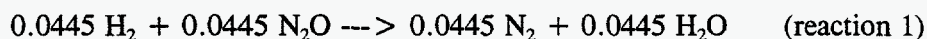
$$(2322 \text{ psia}/678 \text{ psia})*0.099 \text{ moles dry gas} = \underline{0.339 \text{ moles water vapor}}$$

Therefore total initial gas composition is:

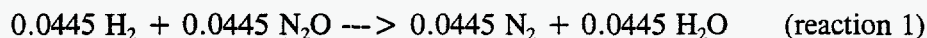
Water Vapor	0.339 moles	77.5%
H ₂	0.0445 moles	10.1%
N ₂ O	0.0445 moles	10.1%
N ₂	<u>0.0099 moles</u>	<u>2.3%</u>
TOTAL	0.438 moles	<u>100%</u>

From the detonation limit triangle (Attachment 2), 60% steam or more along with any combination of air and hydrogen gas is below the lower flammability limit. These data are for air and not for N₂O, and Cashdollar et al. (1992) showed that N₂O/H₂ mixtures are more reactive than air/H₂ mixtures.

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N₂O and H₂ under these conditions:



$$\text{moles liquid water} = (1 \text{ liter})*(610\text{g/liter})/(18 \text{ g/mol}) = 34 \text{ moles}$$



$$H_{\text{reaction, 25C}} = H_{\text{f, products}} - H_{\text{f, reactants}} \quad [\text{Eqn 4}]$$

$$H_{\text{f, H}_2} = 0 \text{ KJ/mol,}$$

$$H_{\text{f, N}_2\text{O}} = 82 \text{ KJ/mol,}$$

$$H_{\text{f, N}_2} = 0 \text{ KJ/mol,}$$

$$H_{\text{f, H}_2\text{O}} = -286 \text{ KJ/mol (Himmelblau 1982)}$$

$$H_{\text{reaction, 25C}} = \underset{(\text{H}_2\text{O})}{-286 \text{ KJ/mol}} - \underset{(\text{N}_2\text{O})}{(82 \text{ KJ/mol})} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol})*0.0445 \text{ mol} = \underline{-16.4 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H ₂ O _v	0.339 moles	0.384 moles
H ₂	0.0445 moles	0 moles
N ₂ O	0.0445 moles	0 moles
N ₂	0.0099 moles	0.0544 moles
H ₂ O _l	34 moles	34 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$C_p(\text{H}_2\text{O}_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$C_p(\text{N}_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$C_p(\text{N}_2\text{O}) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$C_p(\text{H}_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, Tf}} - H_{\text{reactants, To}}$$

$$\begin{aligned} \text{products} \rightarrow &= [34.384 \cdot (33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \\ &+ 0.0544 \cdot (29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)] \end{aligned} \quad [\text{Eqn 9a}]$$

$$\begin{aligned} \text{reactants} \rightarrow &- [34.339 \cdot (33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \\ &+ 0.0099 \cdot (29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)] \\ &+ 0.0445 \cdot (38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4) \\ &+ 0.0445 \cdot (29T_o + 3.9 \times 10^{-5}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)] \end{aligned} \quad [\text{Eqn 9b}]$$

from $T_o = 623\text{K}$ to $T_f = ?$.

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \quad [\text{Eqn 10}]$$

from previous calculation, using equation [4] above $H_{\text{reaction, 25C}} = -16.4 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 781.4 KJ

therefore from equation [10]; $H_{\text{prod}, T_f} = 781.4 \text{ KJ} - (-16.4 \text{ KJ}) = \underline{797.8 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod}, T_f} = 797.8 \text{ KJ}$

635 gives: $H_{\text{prod}} = 797.8 \text{ KJ}$

635K (362°C) corresponds to 797.8 KJ. This is worst case (assuming no heat losses, all gas reacts at once, and the reaction will go to completion). However, heat absorption by liquid water is assumed. The corresponding pressure would increase to (assuming constant volume):

$(3000 \text{ psia}) \cdot (635\text{K}) / (623\text{K}) = 3058 \text{ psia}$; pressure increase of 58 psia.

Conclusions from Calculation #4:

If liquid water were capable of absorbing the heat, safe operating conditions would exist. It is questionable, however, if liquid water could absorb the heat fast enough, especially in the case of a detonation.

Calculation #5: Gas and Liquid Exiting the Reactor is at 130°C; Liquid Water is Capable of Absorbing Heat of Reaction

Problem Statement: Determine the gas composition after the gas and liquid exit the reactor and the maximum temperature rise if all of the gas in the entire high-pressure reactor system ignites.

- Assumptions:**
- 1) Exit reactor temp. = 130°C, final reactor pressure = 3000 psia.
 - 2) 1 liter reactor system, filled with liquid + gas.
 - 3) vapor pressure simulant = vapor pressure of water = 40 psia (Himmelblau 1982).
 - 4) density of simulant at 130°C and 3000 psia = density of water at 130°C and 3000 psia = 1 g/ml (Thermodynamic Properties of Steam). Density of simulant = density of water at 20°C = 1 g/ml.
 - 5) Ideal gas law and Dalton's law are suitable.
 - 6) Dry gas composition = 45% H_2 , 45% N_2O , 10% N_2 .
 - 7) 4 liters gas produced/liter feed (standard conditions).
= 0.00292 moles dry gas/mole feed (assuming feed = liquid water).
 - 8) Liquid water will absorb heat (use heat capacity of water vapor).
 - 9) Most reactor system contents (volumetric basis) can be assumed to be liquid.

10) The molar ratio of dry gas/liquid in the high-pressure reactor system is the same as that given at standard conditions (i.e., in assumption #6, above).

11) All of the gas present in the high-pressure reactor system reacts at once. In reality, it is unlikely that all of the gas in the reactor could be ignited at the same time.

The assumptions made above (with the exception of assumption 8) will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{water vapor}} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$3000 \text{ psia} = 40 \text{ psia} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$2960 \text{ psia} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$n_{\text{dry gas}} = (0.00292 \text{ moles dry gas produced/mole water}) * (1000 \text{ ml water}) * (1 \text{ g water/liter}) / (18 \text{ g water/mole})$$

$$n_{\text{dry gas}} = 0.162 \text{ moles}$$

Therefore from assumption 6 and moles dry gas:

$$\text{H}_2 = 0.45 * 0.162 \text{ moles} = 0.073 \text{ moles}$$

$$\text{N}_2\text{O} = 0.45 * 0.162 \text{ moles} = 0.073 \text{ moles}$$

$$\text{N}_2 = 0.10 * 0.162 \text{ moles} = 0.0162 \text{ moles}$$

volume dry gas =

$$V_{\text{dry gas}} = (0.162 \text{ moles}) * (0.082 \text{ liter atm/K mole}) * (623\text{K}) / (204 \text{ atm}) \quad [\text{Eqn 2}]$$

$$V_{\text{dry gas}} = 41 \text{ ml}$$

Now using:

$$(P_{\text{water vapor}} / P_{\text{dry gas}}) * n_{\text{dry gas}} = n_{\text{water vapor}} \quad [\text{Eqn 3}]$$

$$(40 \text{ psia} / 2960 \text{ psia}) * 0.162 \text{ moles dry gas} = 0.0022 \text{ moles water vapor}$$

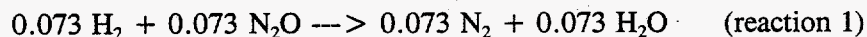
Therefore total initial gas composition is:

Water Vapor	0.0022 moles	1.3%
H ₂	0.073 moles	44.4%
N ₂ O	0.073 moles	44.4%
N ₂	<u>0.0162 moles</u>	<u>9.9%</u>
TOTAL	0.1644 moles	<u>100%</u>

This gas composition could very well be in or very near to the detonable range according to Cashdollar et al. (1992) and from the detonation limit triangle (Attachment 2).

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N₂O and H₂ under these conditions:

$$\text{moles liquid water} = (1 \text{ liters}) * (1000 \text{ g/liter}) / (18 \text{ g/mol}) = 56 \text{ moles}$$



$$H_{\text{reaction, 25C}} = H_{\text{f, products}} - H_{\text{f, reactants}} \quad [\text{Eqn 4}]$$

$$H_{\text{f, H}_2} = 0 \text{ KJ/mol,}$$

$$H_{\text{f, N}_2\text{O}} = 82 \text{ KJ/mol,}$$

$$H_{\text{f, N}_2} = 0 \text{ KJ/mol,}$$

$$H_{\text{f, H}_2\text{O}} = -286 \text{ KJ/mol (Himmelblau 1982)}$$

$$H_{\text{reaction, 25C}} = \underset{(\text{H}_2\text{O})}{-286 \text{ KJ/mol}} - \underset{(\text{N}_2\text{O})}{(82 \text{ KJ/mol})} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol}) * 0.073 \text{ mol} = \underline{-26.9 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H ₂ O _v	0.0022 moles	0.0752 moles
H ₂	0.073 moles	0 moles
N ₂ O	0.073 moles	0 moles
N ₂	0.0162 moles	0.0892 moles
H ₂ O _l	56 moles	56 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$C_p(H_2O_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$C_p(N_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$C_p(N_2O) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$C_p(H_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, Tf}} - H_{\text{reactants, Tb}}$$

$$\begin{aligned} \text{products} \rightarrow &= [56.075 \cdot (33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \\ &+ 0.0892 \cdot (29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)] \end{aligned} \quad [\text{Eqn 9a}]$$

$$\begin{aligned} \text{reactants} \rightarrow &- [56.002 \cdot (33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \\ &+ 0.0162 \cdot (29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)] \\ &+ 0.073 \cdot (38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4) \\ &+ 0.073 \cdot (29T_o + 3.9 \times 10^{-5}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)] \end{aligned} \quad [\text{Eqn 9b}]$$

from $T_o = 403\text{K}$ to $T_f = ?$.

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \quad [\text{Eqn 10}]$$

from previous calculation, using equation [4] above $H_{\text{reaction, 25C}} = -26.9 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 797.9 KJ

therefore from equation [10]; $H_{\text{prod, Tf}} = 797.9 \text{ KJ} - (-26.9 \text{ KJ}) = \underline{824.8 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod, Tf}} = 824.8 \text{ KJ}$

416K gives: $H_{\text{prod}} = 825.1 \text{ KJ}$. This is worst case (assuming no heat losses, all of the gas will react at once, and the reaction will go to completion). However, heat absorption by liquid water is assumed.

The corresponding pressure would increase to (assuming constant volume):

$$(3000 \text{ psia}) \cdot (416\text{K}) / (403\text{K}) = 3097 \text{ psia; pressure increase of } 97 \text{ psia.}$$

Conclusions from Calculation #5

If liquid water were capable of absorbing the heat, safe operating conditions would exist. It is questionable, however, if liquid water could absorb the heat fast enough, especially as close as we are to the detonable gas range.

Overall Conclusions from Calculations #1-5

According to the above calculations, the most serious situation arises when the reaction gas/liquid mixture is cooled just outside the reactor. At these conditions, assuming no heat absorbance from the liquid water, unsafe operating conditions would exist, and a detonation could even possibly take place. The situation may also be serious downstream of the back-pressure regulator, when the pressure is released and the liquid and vapor are separated (and gases accumulated to the greatest extent of approximately 100-200 ml) in the gas-liquid separator; at this point the liquid water would play no role in absorbing heat. Once the gases were vented, a problem would no longer exist because the flow rate of reactor gases (typically 4 liter/hour) is very small compared to the vent exhaust rate.

It should be noted that the dry gas/liquid ratio when the system is under pressure is only approximately 0.025, or 2.5% of the total volume in the system under pressure. Furthermore, the mole% of dry gas to liquid is approximately 0.29%. These numbers are relatively low; however, the close proximity of the gas mixture to the apparent detonation limit bring uncertainty into drawing the conclusion that no definite hazard exists, and makes it nearly impossible to determine the impact of detonation on the rest of the system. Once the fluid passes the back-pressure regulator into the gas/liquid separator, the dry gas/liquid ratio is 4 L gas/L liquid.

Also, as mentioned previously, the most likely places for ignition or detonation to take place would be downstream of the reactor, and also downstream of the back-pressure regulator (in the gas-liquid separator). The gas can accumulate to approximately 200 ml in the gas-liquid separator. This amount of gas could lead to energy release of approximately 1.3 KJ. According to Figure 20 in Cashdollar et al. (1992), this could lead to a pressure increase > 12 times the original pressure. Even if it were 20 times, the resulting pressure would be only 20 atm. Again, the possibility that the mixture is detonable complicates the issue as to whether this is an hazardous situation. At 20 atm, however, the gas would not be able to go back into the reactor because the reactor pressure is much greater than this, and thus one could expect that the explosion could be confined to a small area (i.e., the gas-liquid separator). If the gases did escape from the gas-liquid separator, and into the room or out the vent, the gases would almost immediately become too dilute to further ignite. The pressure rating of the gas-liquid separator is 400 psi (27 atm) at 298°C. It is difficult to say if the shock wave from a detonation, or the temperature rise due to ignition would cause the gas-liquid separator to fail.

In Calculations 4 and 5, it was assumed that liquid water would be capable of absorbing the heat generated by the reaction of N_2O and H_2 . When this assumption was made, it was observed that the temperature increase was minimal. It again is a risky assumption that the liquid water could absorb the heat fast enough, however, especially if a detonation occurred.

Potential Solutions to the Problem

Calculations 6 and 7 are discussed below.

Use of an Inert Cover Gas

A potential solution to the problem would be to inject dilution gas (e.g., argon) upstream of the reactor so that the off-gases are diluted throughout the entire reactor system. According to Cashdollar et al. (1992), the lower flammability limit for 1:1 $H_2:N_2O$ in argon is 10% H_2 , 10% N_2O , and 80% argon. Tests were also done in nitrogen, and it was found that nitrogen is even a better cover gas; LFL = 14% H_2 , 14% N_2O , and 72% N_2 .

For tracking nitrogen being produced it would be advantageous to use argon as the cover gas. To be well below the LFL, on the order of 40 liters argon/liter liquid feed would be required. This would give (worst case) 4.5% H_2 , 4.5% N_2O , 1% N_2 , and 90% Ar in the off-gas and anywhere in the system. Calculations 6 and 7 were done using the above dilution of argon gas. These are the same as Calculations 1 and 2, except argon gas is added.

At 40 liters argon/liter of feed at atmospheric conditions, the liquid to argon ratios in the reactor (assuming 350°C and 3000 psig) would be:

$$V_2 = (P_1 * V_1 * T_2) / (P_2 * T_1)$$

$$P_1 = 1 \text{ atm}$$

$$V_1 = 40 \text{ liters}$$

$$T_1 = 623K$$

$$P_2 = 204 \text{ atm}$$

$$T_2 = 298K$$

$$V_2 = (1 \text{ atm}) * (40 \text{ liters}) * (623K) / (204 \text{ atm}) / (298K)$$

$$V_2 = 0.4 \text{ liters}$$

assume density liquid at 204 atm, 350°C = density of water = 0.61 g/l

$$V_{\text{liq, reactor}} = (1 \text{ liter}) * (1 \text{ g/ml}) / (0.61 \text{ g/l}) = 1.64 \text{ liters}$$

Therefore, the gas liquid ratio in reactor = 0.4 liters/1.64 liters = 0.24. Thus, although our liquid residence time would be impacted somewhat, it is not extreme. Several years ago, a gas compressor was used in the CRS when the water-gas shift reaction was being studied. We are currently looking into what it would take to set the compressor up again, and what flow rates it can handle.

Calculation #6: Reactor at Temperature (350°C); Argon Added as Cover Gas

Problem Statement: Determine the gas composition in the reactor and the maximum temperature rise if all of the gas in the reactor ignites.

- Assumptions:**
- 1) Final reactor temp. = 350°C, final reactor pressure = 3000 psia.
 - 2) 1000 ml reactor, filled with 1000 ml solution + gas.
 - 3) Vapor pressure simulant = vapor pressure of water = 2322 psia (Himmelblau 1982).
 - 4) Density of simulant at 350°C and 3000 psia = density of water at 350°C and 3000 psia = 0.61 g/ml (Thermodynamic Properties of Steam). Density of simulant = density of water at 20°C = 1 g/ml.
 - 5) Ideal gas law and Dalton's law are suitable.
 - 6) Dry gas composition = 4.5% H₂, 4.5% N₂O, 1.0% N₂, 90% Ar.
 - 7) 40 liters dry gas produced/liter feed (standard conditions) = 0.0292 moles dry gas/mole feed (assuming feed = liquid water).
 - 8) Liquid water will not absorb any heat.
 - 9) Most reactor contents (volumetric basis) can be assumed to be liquid.
 - 10) The molar ratio of dry gas/liquid in the reactor is the same as that given at standard conditions (i.e., in assumption #6, above).
 - 11) All of the gas present in the reactor reacts at once. In reality, it is unlikely that all of the gas in the reactor could be ignited at the same time.
 - 12) The heat capacity of Ar is the same as N₂ (N₂ heat capacities are used for Ar in the calculations).

Many of the assumptions made above will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{water vapor}} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$3000 \text{ psia} = 2322 \text{ psia} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$678 \text{ psia} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$n_{\text{dry gas}} = (0.0292 \text{ moles dry gas produced/mole water}) * (1000 \text{ ml water}) * (0.61 \text{ g water/liter}) / (18 \text{ g water/mole})$$

$$n_{\text{dry gas}} = 0.990 \text{ moles}$$

Therefore from assumption 6 and moles dry gas:

$$\text{H}_2 = 0.045 * 0.99 \text{ moles} = 0.0445 \text{ moles}$$

$$\text{N}_2\text{O} = 0.045 * 0.99 \text{ moles} = 0.0445 \text{ moles}$$

$$\text{N}_2 = 0.01 * 0.99 \text{ moles} = 0.0099 \text{ moles}$$

$$\text{Ar} = 0.9 * 0.99 \text{ moles} = 0.89 \text{ moles}$$

volume dry gas =

$$V_{\text{dry gas}} = (0.99 \text{ moles}) * (0.082 \text{ liter atm/K mole}) * (623\text{K}) / (204 \text{ atm}) \quad [\text{Eqn 2}]$$

$$V_{\text{dry gas}} = 250 \text{ ml}$$

Therefore, assumption 9 is not quite accurate in this case; this will only impact the heat of reaction; i.e., it will be much higher in this case than in the actual case because the amount of gas will be higher than in a 1 liter (total) system. However, the corresponding temperature and pressure increases will be accurate because the remaining constituents are higher in concentration to the same magnitude as the reactants.

Now using:

$$(P_{\text{water vapor}} / P_{\text{dry gas}}) * n_{\text{dry gas}} = n_{\text{water vapor}} \quad [\text{Eqn 3}]$$

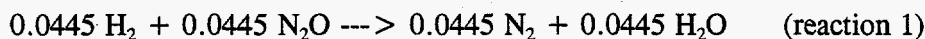
$$(2322 \text{ psia} / 678 \text{ psia}) * 0.99 \text{ moles dry gas} = \underline{3.39 \text{ moles water vapor}}$$

Therefore total initial gas composition is:

Water Vapor	3.39 moles	77.4%
H ₂	0.0445 moles	1.0%
N ₂ O	0.0445 moles	1.0%
N ₂	0.0099 moles	0.2%
Ar	<u>0.89 moles</u>	<u>20.4%</u>
TOTAL	4.38 moles	<u>100%</u>

From the detonation limit triangle (Attachment 2), 60% steam or more along with any combination of air and hydrogen gas is below the lower flammability limit. These data are for air and not for N₂O, and Cashdollar et al. (1992) showed that N₂O/H₂ mixtures are more reactive than air/H₂ mixtures.

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N_2O and H_2 under these conditions:



$$H_{\text{reaction, 25C}} = H_{f, \text{products}} - H_{f, \text{reactants}} \quad [\text{Eqn 4}]$$

$$H_{f, H_2} = 0 \text{ KJ/mol,}$$

$$H_{f, N_2O} = 82 \text{ KJ/mol,}$$

$$H_{f, N_2} = 0 \text{ KJ/mol,}$$

$$H_{f, H_2O} = -286 \text{ KJ/mol (Himmelblau 1982)}$$

$$H_{\text{reaction, 25C}} = \underset{(H_2O)}{-286 \text{ KJ/mol}} - \underset{(N_2O)}{(82 \text{ KJ/mol})} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol}) * 0.0445 \text{ mol} = \underline{-16.4 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H_2O_v	3.39 moles	3.43 moles
H_2	0.0445 moles	0 moles
N_2O	0.0445 moles	0 moles
N_2	0.0099 moles	0.054 moles
Ar	0.89 moles	0.89 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$C_p(H_2O_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$C_p(N_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$C_p(N_2O) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$C_p(H_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, } T_f} - H_{\text{reactants, } T_o}$$

$$\text{products} \rightarrow = [3.43 * (33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \quad [\text{Eqn 9a}]$$

$$+ 0.944 * (29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)]$$

$$\begin{aligned}
 \text{reactants} \rightarrow & - [3.39*(33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \\
 & + 0.9*(29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)] \quad [\text{Eqn 9b}] \\
 & + 0.0445*(38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4) \\
 & + 0.0445*(29T_o + 3.9 \times 10^{-5}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)] \quad [9b]
 \end{aligned}$$

from $T_o = 623\text{K}$ to $T_f = ?$.

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \quad [\text{Eqn 10}]$$

from previous calculation, using equation [4] above $H_{\text{reaction, 25C}} = -16.4 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 95.7 KJ

therefore from equation [10]; $H_{\text{prod, Tf}} = 95.7 \text{ KJ} - (-16.4 \text{ KJ}) = \underline{112.1 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod, Tf}} = 112.1 \text{ KJ}$

720K gives: $H_{\text{prod}} = 112.1 \text{ KJ}$

720K (447°C) corresponds to 112.1 KJ. This is worst case (assuming no heat losses, no absorption of heat by water, all gas reacts at once, and the reaction will go to completion). The corresponding pressure would increase to (assuming constant volume):

$(3000 \text{ psia}) * (720\text{K}) / (623\text{K}) = 3467 \text{ psia}$; pressure increase of 467 psia.

Conclusions from Calculation #6

From the detonation limit triangle (Attachment 2), 60% steam or more along with any combination of air and hydrogen gas is below the lower flammability limit. These data are for air and not for N_2O , and Cashdollar et al. (1992) showed that $\text{N}_2\text{O}/\text{H}_2$ mixtures are somewhat more reactive than air/ H_2 mixtures. Cashdollar et al. (1992) showed that the LFL for H_2 in argon gas was 10%. The gas mixture used above, even in the absence of water vapor contains less than 10% H_2 (i.e., contains 4.5% H_2).

According to the calculations, an increase in pressure could result. However, the pressure rating for the system is 4000 psig and 400°C. The potential safety hazards would be minimal under these conditions.

Calculation #7: Gas and Liquid Exiting the Reactor is at 130°C; Argon Added as Dilution Gas

Problem Statement: Determine the gas composition after the gas and liquid exit the reactor and the maximum temperature rise if all of the gas in the entire high-pressure reactor system ignites.

- Assumptions:**
- 1) Exit reactor temp. = 130°C, final reactor pressure = 3000 psia.
 - 2) 1 liter high-pressure reactor system, filled with liquid + gas; includes reactor and all lines up to the pressure let-down system, assuming everything in the system is at 130°C.
 - 3) Vapor pressure simulant = vapor pressure of water = 40 psia (Himmelblau 1982).
 - 4) Density of simulant at 130°C and 3000 psia = density of water at 130°C and 3000 psia = 1 g/ml (Thermodynamic Properties of Steam). Density of simulant = density of water at 20°C = 1 g/ml.
 - 5) Ideal gas law and Dalton's law are suitable.
 - 6) Dry gas composition = 4.5% H₂, 4.5% N₂O, 1.0% N₂, 90% Ar.
 - 7) 40 liters gas produced/liter feed (standard conditions).
= 0.0292 moles dry gas/mole feed (assuming feed = liquid water).
 - 8) Liquid water will not absorb any heat.
 - 9) Most reactor system contents can be assumed to be liquid
 - 10) The molar ratio of dry gas/liquid in the high-pressure reactor system is the same as that given at standard conditions (i.e., in assumption #6, above).
 - 11) All of the gas present in the high-pressure reactor system reacts at once. In reality, it is unlikely that all of the gas in the reactor could be ignited at the same time.
 - 12) The heat capacity of Ar is the same as N₂ (N₂ heat capacities are used for Ar in the calculations).

Many of the assumptions made above will lead to conservative (worst case) situations.

$$P_{\text{total}} = P_{\text{water vapor}} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}} \quad [\text{Eqn 1}]$$

$$3000 \text{ psia} = 40 \text{ psia} + P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$2960 \text{ psia} = P_{\text{Nitrogen}} + P_{\text{Nitrous oxide}} + P_{\text{Hydrogen}}$$

$$n_{\text{dry gas}} = (0.0292 \text{ moles dry gas produced/mole water}) * (1000 \text{ ml water}) * (1 \text{ g water/liter}) / (18 \text{ g water/mole})$$

$$n_{\text{dry gas}} = 1.62 \text{ moles}$$

Therefore from assumption 6 and moles dry gas:

$$H_2 = 0.045 * 1.62 \text{ moles} = 0.073 \text{ moles}$$

$$N_2O = 0.045 * 1.62 \text{ moles} = 0.073 \text{ moles}$$

$$N_2 = 0.010 * 1.62 \text{ moles} = 0.0162 \text{ moles}$$

$$Ar = 0.90 * 1.62 \text{ moles} = 1.46 \text{ moles}$$

volume dry gas =

$$V_{\text{dry gas}} = (1.62 \text{ moles}) * (0.082 \text{ liter atm/K mole}) * (623K) / (204 \text{ atm}) \quad [\text{Eqn 2}]$$

$$V_{\text{dry gas}} = 410 \text{ ml}$$

Therefore, assumption 9 is not quite accurate in this case; this will only impact the heat of reaction; i.e., it will be much higher in this case than in the actual case because the amount of gas will be higher than in a 1 liter (total) system. However, the corresponding temperature and pressure increases will be accurate because the remaining constituents are higher in concentration to the same magnitude as the reactants.

Now using:

$$(P_{\text{water vapor}} / P_{\text{dry gas}}) * n_{\text{dry gas}} = n_{\text{water vapor}} \quad [\text{Eqn 3}]$$

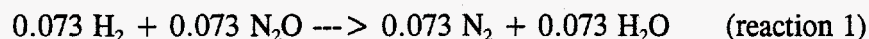
$$(40 \text{ psia} / 2960 \text{ psia}) * 1.62 \text{ moles dry gas} = \underline{0.022 \text{ moles water vapor}}$$

Therefore total initial gas composition is:

Water Vapor	0.022 moles	1.3%
H ₂	0.073 moles	4.4%
N ₂ O	0.073 moles	4.4%
N ₂	0.0162 moles	1.0%
Ar	<u>1.46 moles</u>	<u>88.9%</u>
TOTAL	1.644 moles	<u>100%</u>

This gas composition is below the LFL for H₂ in argon gas according to Cashdollar et al. (1992).

As another check we can calculate the adiabatic flame temperature, assuming complete reaction of N_2O and H_2 under these conditions:



$$H_{\text{reaction, 25C}} = H_{f, \text{products}} - H_{f, \text{reactants}} \quad [\text{Eqn 4}]$$

$$H_{f, H_2} = 0 \text{ KJ/mol,}$$

$$H_{f, N_2O} = 82 \text{ KJ/mol,}$$

$$H_{f, N_2} = 0 \text{ KJ/mol,}$$

$$H_{f, H_2O} = -286 \text{ KJ/mol (Himmelblau 1982)}$$

$$H_{\text{reaction, 25C}} = \frac{-286 \text{ KJ/mol}}{(H_2O)} - \frac{(82 \text{ KJ/mol})}{(N_2O)} = -368 \text{ KJ/mol}$$

$$(-368 \text{ KJ/mol}) * 0.073 \text{ mol} = \underline{-26.9 \text{ KJ}}$$

From reaction 1 and the total initial gas compositions, calculate final gas compositions:

	<u>Initial</u>	<u>Final</u>
H_2O_v	0.022 moles	0.095 moles
H_2	0.073 moles	0 moles
N_2O	0.073 moles	0 moles
N_2	0.0162 moles	0.0892 moles
Ar	1.46 moles	1.46 moles

Heat capacities of gases (Himmelblau 1982), J/mol K:

$$Cp(H_2O_v) = 33.5 + 6.9 \times 10^{-3}T + 7.6 \times 10^{-6}T^2 - 3.6 \times 10^{-9}T^3 \quad [\text{Eqn 5}]$$

$$Cp(N_2) = 29 + 2.2 \times 10^{-3}T + 5.7 \times 10^{-6}T^2 - 2.9 \times 10^{-9}T^3 \quad [\text{Eqn 6}]$$

$$Cp(N_2O) = 38 + 4.2 \times 10^{-3}T - 2.7 \times 10^{-5}T^2 + 10.6 \times 10^{-9}T^3 \quad [\text{Eqn 7}]$$

$$Cp(H_2) = 29 + 7.7 \times 10^{-5}T + 3.3 \times 10^{-6}T^2 - 8.7 \times 10^{-10}T^3 \quad [\text{Eqn 8}]$$

Integrate and get:

$$H_{\text{prod, Tf}} - H_{\text{reactants, To}}$$

$$\text{products} \rightarrow = [0.095 * (33.5T_f + 3.5 \times 10^{-3}T_f^2 + 2.5 \times 10^{-6}T_f^3 - 0.9 \times 10^{-9}T_f^4) \quad [\text{Eqn 9a}]$$

$$+ 1.55 * (29T_f + 1.1 \times 10^{-3}T_f^2 + 1.9 \times 10^{-6}T_f^3 - 7.3 \times 10^{-10}T_f^4)]$$

$$\begin{aligned}
\text{reactants} \rightarrow & - [0.022*(33.5T_o + 3.5 \times 10^{-3}T_o^2 + 2.5 \times 10^{-6}T_o^3 - 0.9 \times 10^{-9}T_o^4) \\
& + 1.48*(29T_o + 1.1 \times 10^{-3}T_o^2 + 1.9 \times 10^{-6}T_o^3 - 7.3 \times 10^{-10}T_o^4)] \\
& + 0.073*(38T_o + 2.1 \times 10^{-3}T_o^2 - 0.9 \times 10^{-5}T_o^3 + 2.7 \times 10^{-9}T_o^4) \\
& + 0.073*(29T_o + 3.9 \times 10^{-3}T_o^2 + 1.1 \times 10^{-6}T_o^3 - 2.2 \times 10^{-10}T_o^4)] \\
\text{from } T_o = 403\text{K to } T_f = ?
\end{aligned}
\tag{Eqn 9b}$$

$$H_{\text{prod, Tf}} = H_{\text{reactant, To}} - H_{\text{reaction, 25C}} \quad (\text{Himmelblau 1982}) \tag{Eqn 10}$$

from previous calculation, using equation [4] above $H_{\text{reaction, 25C}} = -29.9 \text{ KJ}$

also from equation [9b], $H_{\text{reactants}}$ can be calculated to be 20.0 KJ

therefore from equation [10]; $H_{\text{prod, Tf}} = 20.0 \text{ KJ} - (-26.9 \text{ KJ}) = \underline{46.9 \text{ KJ}}$

now iterate on T_f in equation [9a] to get $H_{\text{prod, Tf}} = 46.9 \text{ KJ}$

905K gives: $H_{\text{prod}} = 46.9 \text{ KJ}$

905K (632°C) corresponds to 46.9 KJ. This is worst case (assuming no heat losses, no absorption of heat by water, all gas reacts at once, and the reaction will go to completion). The corresponding pressure would increase to (assuming constant volume):

$(3000 \text{ psia}) * (905\text{K}) / (403\text{K}) = 6737 \text{ psia}$; pressure increase of 3737 psia.

Conclusions from Calculation #7

Cashdollar et al. (1992) showed that the LFL for H_2 in argon gas was 10%. The gas mixture used above, even in the absence of water vapor contains less than 10% H_2 (i.e., contains 4.5% H_2).

According to the calculations, a significant increase in pressure could result. The pressure rating for the system is 4000 psig and 400°C. However, in light of the actual data from Cashdollar et al. (1992), it is very unlikely that such an ignition could take place.

Use of Air as the "Cover Gas"

Another alternative, which may be more practical, is to inject air into the system, upstream of the reactor (i.e., wet air oxidation or addition of hydrogen peroxide to the feed). The nitrogen in the air would not only act as a dilution gas, but the oxygen in the air would significantly enhance the reaction kinetics for the destruction of organics. In FY 1993, Zimpro was contracted by PNL to conduct batch wet air oxidation testing on 101-SY simulant. In these tests, the required reaction temperature was on the order of 65°C lower to obtain the same organic destruction levels as compared to no air injection

(i.e., autogenous destruction). The highest hydrogen concentration in the off-gas was less than 4%, and no N_2O was detected in any of the runs. The oxygen content varied, depending on the amount of air injected into the system. The off-gas typically contained between 85% and 95% N_2 in the off-gas.

Gas Venting Calculations

According to a paper written by C.V. Moore (1967), "The Design of Barricades for Hazardous Pressure Systems," the overpressure for structural evaluation can be calculated by:

$$P = 5.75 \cdot V_p / V_c \cdot E_v$$

where:

P = effective static overpressure (psi)

V_p = volume of pressure vessel (in.^3)

V_c = volume of chamber into which fluid is released on explosion of pressure vessel (ft.^3)

E_v = energy released due to isentropic expansion of fluid or chemical reaction (if present) per unitvolume of pressure vessel ($\text{BTU}/\text{in.}^3$)

Calculation #8: The 1-Liter Pressure Vessel Ruptures at 36,000 psi.

Problem Statement: Determine the resulting overpressure and hydrogen concentration in CPDL.

Assumptions: 1) No ventilation exists in CPDL.

2) CPDL dimensions = 25'(W) x 25'(L) x 10'(H) = 6250 ft.^3

3) system pressure = 36,000 psi prior to rupture (corresponds to approximate highest pressure increase, calculation 2, > 12X pressure increase, i.e., from 3000 to 36000 psi).

4) pressurized system volume = 1 liter = 61 in.^3

5) hydrogen gas = 0.073 moles in reactor (i.e., from Calculation 2, worst case).

6) assume isentropic expansion of material in reactor, and that all is in gas phase.

7) ideal gas law applies.

The assumptions made above are very conservative (i.e., worst case). Assumption 1 in particular is very conservative. The actual ventilation rate in CPDL is 2750 scfm, and the barricades that contain the CRS are designed such that the air inflow through the openings in the barricades is > 85 ft/min.

$$P = 5.75 \cdot V_p / V_c \cdot E_v$$

$$V_p = 61 \text{ in}^3$$

$$V_c = 6250 \text{ ft}^3$$

Isentropic expansion of gases (Pohto et al. 1981, Eshbach 1975):

$$E = [P_1 V_1 / (n-1)] * [(P_2/P_1)^{(n-1)/n} - 1]$$

$$P_1 = \text{initial vessel pressure (lb}_f\text{/ft}^2\text{)} = (36,000 \text{ lb}_f\text{/in}^2) * 144 \text{ in}^2\text{/ft}^2 = 5.2 \times 10^6 \text{ lb}_f\text{/ft}^2$$

$$V_1 = \text{vessel volume (ft}^3\text{)} = (1 \text{ liter}) / (28.3 \text{ liter/ft}^3) = 0.035 \text{ ft}^3$$

$$n = C_p/C_v = 1.4 \text{ (approximately for diatomic gases) (Pohto et al. 1981)}$$

$$P_2 = \text{final pressure (assume atmospheric)} = 14.7 \text{ lb}_f\text{/in}^2 * 144 \text{ in}^2\text{/ft}^2 = 2112 \text{ lb}_f\text{/ft}^2$$

therefore:

$$E = [5.2 \times 10^6 \text{ lb}_f\text{/ft}^2 * 0.035 \text{ ft}^3 / (1.4-1)] * [(2112 \text{ lb}_f\text{/ft}^2 / 5.2 \times 10^6 \text{ lb}_f\text{/ft}^2)^{(1.4-1)/1.4} - 1]$$

$$E = 4.1 \times 10^5 \text{ ft-lb}^f = 527 \text{ BTU}$$

therefore:

$$E_v = 527 \text{ BTU} / 61 \text{ in}^3 = 8.6 \text{ BTU/in}^3$$

therefore:

$$P(\text{psi}) = 5.75 * (61 \text{ in}^3) / (6250 \text{ ft}^3) * (8.6 \text{ BTU/in}^3) =$$

$P(\text{psi}) = 0.5 \text{ psi}$ = overpressure in CPDL due to failure of high-pressure reactor, assuming no ventilation.

total moles air in CPDL:

$$n = PV/RT$$

$$R = 0.082 \text{ liter atm/mol K}$$

$$T = 298 \text{ K}$$

$$P = 1 \text{ atm}$$

$$V = 6250 \text{ ft}^3 = 177,000 \text{ liters}$$

$$n = (1 \text{ atm}) * (177,000 \text{ liters}) / (0.082 \text{ liter atm/mol K}) / (298 \text{ K}) =$$

$$n = 7243 \text{ moles}$$

$$\text{mole\% hydrogen gas in CPDL upon release from pressure vessel} = \\ (0.073 \text{ moles} / 7243 \text{ moles}) * 100 = 0.001$$

Conclusions from Calculation #8

An overpressure of 0.5 psi is relatively small. According to Wells (1980), flying glass could result, and some small flying missiles in the barricade could also result. However, this is well below eardrum or lung damage (these take place at overpressures greater than 2.5 psi). The damage from rupture of the 1 liter autoclave in CPDL at 20,000 psi was previously calculated (Baker 1984), and it was found that an overpressure of 0.7 psi would result. These calculations were conducted using a relationship from Pohto et al. (1981). When using this relationship, and the values stated in our problem (i.e., 36,000 psi), an overpressure of 1.25 is calculated (see calculation below). Thus, different values are obtained depending on which expression is used. However, in both cases, only limited damage would result from the overpressure. Both are well below values that would cause eardrum and lung damage (Wells 1980).

The hydrogen concentration, upon release from the reactor into CPDL is well below the LFL for hydrogen. It may be possible, however, that small pockets of hydrogen could form and ignite within the barricade. However, with the ventilation system in operation within the barricade, the hydrogen pockets would be displaced fairly rapidly. According to Baker (1984), the airflow through the barricades is approximately 100 scfm. At this airflow rate, the 1 entire air change-out in the barricade would take place in approximately 30 seconds.

Overpressure using the expression given by Pohto et al. (1981):

$$P = 7.6 * [(E/10^6)/V]^{0.72}$$

P = static pressure (bars)

V = containment volume = $[0.0283 \text{ m}^3/\text{ft}^3 \times \text{volume (ft}^3)] \text{ (m}^3)$

$V = 0.0283 \text{ m}^3/\text{ft}^3 * 6250 \text{ ft}^3 = 177 \text{ m}^3$

E = shock wave energy = $0.6 * [(1 \text{ lb TNT}) * (2 \times 10^6 \text{ joules/lb TNT})] \text{ (joules)}$

1 lb TNT = $1.43 \times 10^6 \text{ ft-lb}_f$ (Pohto et al. 1981)

lbs TNT = $4.1 \times 10^5 \text{ ft-lb}_f / (1.43 \times 10^6 \text{ ft-lb}_f/\text{lb TNT}) = 0.29 \text{ lbs}$

therefore:

$E = 0.6 * [(0.29 \text{ lbs TNT}) * (2 \times 10^6 \text{ joules/lb TNT})]$

$E = 3.5 \times 10^5 \text{ joules}$

therefore:

$P = 7.6 * [(3.5 \times 10^5 \text{ joules}/10^6)/177 \text{ m}^3]^{0.72}$

$P = 0.086 \text{ bars} = 1.25 \text{ psi}$

Appendix References

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Attachment 1: Batch Test Unit Addendum

MEMORANDUM

Date: February 14, 1994 Internal Distribution

To: D.C. Elliott/E.G. Baker M.R. Elmore
T.R. Hart

From: R.J. Orth *RJO* E.O. Jones
G.G. Neuenschwander
A.J. Schmidt
L.J. Sealock
A.H. Zacher

Subject: ADDENDUM TO BATCH REACTOR SYSTEM SOP-CPDL-1-90-1-Rev-2
IN CPDL FOR RUNS CONDUCTED WITH SIMULANT HANFORD TANK
WASTE

The product off-gases from the destruction of organics in SY-101 simulant are H_2 , N_2O , and N_2 . At certain concentrations H_2 and N_2O are flammable and potentially explosive. In the presence of argon (at $25^\circ C$), data shows that the lower flammability limit of H_2 and N_2O is 10 vol% for each of these gases (e.g., 10 vol% H_2 , 10 vol% N_2O , and 80 vol% Ar) [WHC-SD-WM-ES--219, 1992]. In batch tests conducted to date, using 3X diluted 101-SY simulant, H_2 values are typically 2 vol% and N_2O values are also 2%. Thus, we are operating well below the lower flammability limit for these two gases. To ensure that we operate below the flammability limits for these two gases, the following measures must be followed:

- 1) Make sure that no more than 300 ml (350 g) of simulant is added to the reactor.
- 2) Ensure that argon is the cover gas being used.
- 3) Take extra efforts to purge the batch reactor with argon gas prior to conducting the run.
- 4) Take extra efforts to ensure that no leak is detectable during the normal pre-run checks.
- 5) Add the following argon over-pressures for the given target temperatures below:

<u>Target Temperature</u>	<u>Initial Argon Over-pressure (at room temperature)</u>
300 $^\circ C$	875 psig
325 $^\circ C$	730 psig
350 $^\circ C$	480 psig

Subject: ADDENDUM TO BATCH REACTOR SYSTEM SOP-CPDL-1-90-1-Rev-2
IN CPDL FOR RUNS CONDUCTED WITH SIMULANT HANFORD TANK
WASTE

For these given target temperatures and initial argon over-pressures, the resulting pressure at the target temperature will be approximately 3000 psig. For other temperatures between 300 and 350°C, interpolation will give you an adequate initial argon over-pressure. For example, for a target temperature of 310°C, apply an argon over-pressure of approximately 820 psig.

The following step is in addition to steps in the Operating Procedures - Section 3.0:

- 6) After step #15 in Section 3.2 - Normal Operation Procedures, which states to "turn off all gas line valves", take a gas sample and inject on the GC to verify that argon is the cover gas being used. Follow the procedures under Section 3.3 - Sampling Operations.

By taking these special precautions, we will be assured that operation well below the lower flammability limits are being maintained.

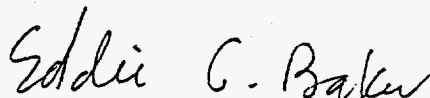
For operation above 350°C or for other SY-101 simulant dilutions, the chemist or engineer requesting the run should be consulted as to what argon over-pressure should be used.

Please sign off on the attached sheet prior to conducting batch testing with Hanford tank waste simulant.

CONCURRENCE:



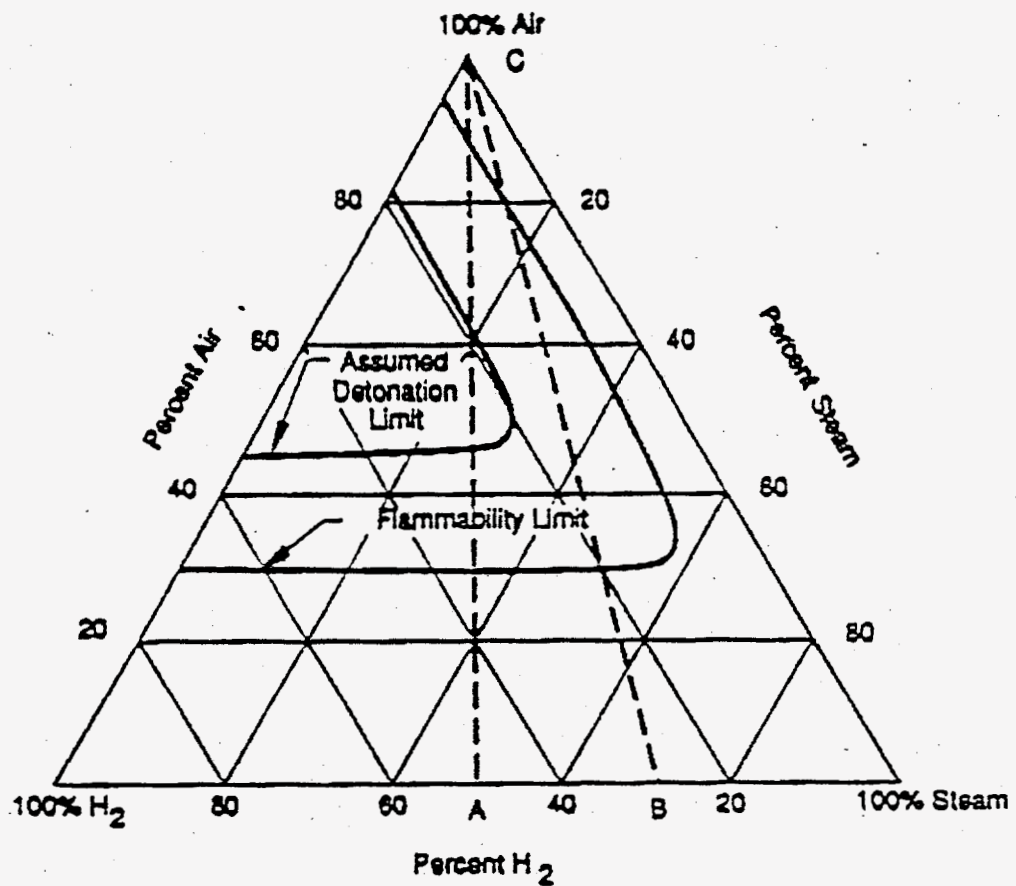
D.C. Elliott, Laboratory Monitor
Chemical Process Development Section



E.G. Baker, Manager
Chemical Process Development Section

2/18/94

Attachment 2: Detonation Triangle



ICPP-A-17589X
(7-91)

Figure 2.3-22. Denotation Limit

PS056-25.VP/ABM/OSA

2.3-79

Appendix B

Filtration Tests Using 101-SY Simulant

Filtration Tests Using 101-SY Simulant

Filtration tests were conducted recently to determine 1) what the filtering requirements are for removing strontium from solution after hydrothermal treatment, and 2) whether strontium exists as colloids in untreated or hydrothermally treated 101-SY simulants. An Amicon stirred ultrafiltration cell was used in the tests. The filtering was conducted in series, initially passing the solutions through a Whatman #4 filter (i.e., 20 to 25- μm pore size), then through a 0.45- μm filter, and finally through a 0.04- μm filter. The 0.04- μm filter was assumed to be small enough such that colloidal (strontium) if present would be retained. Thus, if colloidal strontium were present, a decrease in strontium concentration would be expected when comparing the filtrate from the 0.45- μm filtration step with the 0.04- μm filtration step. Untreated and hydrothermally treated 101-SY simulant (undiluted and 3:1 diluted) solutions were evaluated during this testing. EDTA was the organic carbon source in the simulants; the untreated, undiluted 101-SY simulant contained approximately $26,000 \pm 2600 \mu\text{g/L}$ total organic carbon, and the untreated, 3:1 diluted 101-SY simulant contained approximately $5775 \pm 580 \mu\text{g/L}$ total organic carbon.

The analytical results from this testing are given in Table B.1. The experimental uncertainties, given in Table B.1 for the strontium concentrations, were estimated by the analytical laboratory. The only sample that shows a possible slight decrease (i.e., very close to the estimated experimental error) in strontium concentration when comparing the filtrates from the 0.45- μm and 0.04- μm filtering steps is the undiluted, untreated 101-SY simulant sample. In all other cases, the strontium levels are essentially unchanged when comparing the filtrates from these two filtering steps. In fact, all of the other solutions, with the exception of one (undiluted 101-SY, 250°C, 1507 psig, 5 hr) showed no change in strontium concentration in the filtrates from all three filtering steps.

These results indicate that 1) minimal amounts of the strontium **may** exist as colloidal material in the undiluted, untreated 101-SY simulant; numerous repeat analyses would be required to establish a more certain experimental error to determine whether this observation is "real" or not, 2) there was no definitive evidence that strontium was present as colloids in treated undiluted 101-SY simulant, or untreated and treated 3:1 diluted 101-SY simulant, 3) the hydrothermal treatment does not appear to lead to the formation of (strontium) colloids, and 4) filtration, using a 0.45- μm filter (or even a Whatman #4 filter) is sufficient to remove insoluble strontium from solution.

Table B.1. Strontium Filtration Results

			Strontium Concentration ($\mu\text{g/L}$)		
Simulant Description	Hydrothermal Treatment Conditions ^(a)	Total Organic Carbon Destruction (%)	Whatman #4 Filtrate	0.45 μm Filtrate	0.04 μm Filtrate
Undiluted 101-SY	None	---	2250 \pm 225	2805 \pm 561	1695 \pm 339
Undiluted 101-SY	250°C, 1519 psig, 5 hour hold	32 ^(b)	2495 \pm 499	2270 \pm 454	2182 \pm 436
Undiluted 101-SY	200°C, 1507 psig, 48 hour hold	48	496 \pm 99	303 \pm 30	299 \pm 60
3:1 diluted 101-SY	None	---	352 \pm 35	379 \pm 38	381 \pm 38
3:1 diluted 101-SY	250°C, 2940 psig, 1 hour	17	170 \pm 17	171 \pm 17	152 \pm 15
3:1 diluted 101-SY	250°C, 1830 psig, 5 hours	43	< 10 40 \pm 30	< 10 18 \pm 2	< 10 13 \pm 5
<p>(a) The hydrothermal testing was conducted, using a 1-L batch reactor.</p> <p>(b) The % total organic destruction values given in the table are accurate to approximately $\pm 10\%$ of the reported value (e.g., 32\pm3).</p>					

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